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Use of alternative matrix materials and configurations for optimizing nitrogen removal in constructed wetlands

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Résumé

Les filtres plantés de roseaux (FPR) rencontrent un intérêt croissant depuis trois décennies en raison de leur bon potentiel épuratoire, leur faible coût d'exploitation ainsi que de l'image de "technologie verte" leur étant associée. Néanmoins, le secteur de l'assainissement étant un marché de plus en plus concurrentiel et, les normes de rejets devenant de plus en plus contraignantes, il est nécessaire de disposer d'une connaissance fine des processus afin de dispenser des solutions optimisées et spécifiques à chaque projet.

Le traitement de la pollution azotée est identifié comme étant le processus le plus limitant dans le cadre de l'épuration des effluents domestiques par FPR. Le suivi de ce paramètre a donc servi de fil conducteur, durant ces travaux de thèse, dans une perspective d'optimisation de leur conception et d'accroissement des performances épuratoires.

Un premier volet de l'étude s'est attaché à évaluer l'impact des conditions opératoires ainsi que des paramètres de dimensionnement sur le traitement de l'azote ammoniacal. Il a été effectué à travers un suivi de 20 mois sur 4 unités pilotes (2.25m²) de FPR à écoulement vertical plantés de roseaux. Chaque système présente des caractéristiques opératoires et de conception différentes afin de mettre en exergue leurs effets respectifs sur le traitement. Un premier filtre, conçu selon les règles de conception classique d'un FPR à écoulement vertical (40 cm de couche filtrante de gravier, charge hydraulique de 0.36 $m.jour^{-1}$), a servi de référence pour comparaison avec les autres unités expérimentales. Un second filtre est dédié à l'étude des effets de la hauteur de filtration. Il est constitué d'une couche filtrante de 100 cm de gravier, intégrant 5 systèmes de prélèvements intermédiaires, à différentes profondeurs du filtre, en vue d'établir un profil vertical de traitement de la pollution dissoute. Une troisième unité de filtration vise à évaluer l'intérêt d'un remplacement partiel du matériau de filtration (inerte) par un matériau réactif échangeur d'ions (zéolithe). Le dernier pilote évalue, quant à lui, l'impact d'une réduction de la surface de traitement par un accroissement simultané de la charge hydraulique (0.64 $cm.jour^{-1}$) et organique. Enfin, le filtre de conception classique a été dopé ponctuellement en matière organique dissoute et ammonium dans le but d'en identifier leurs effets respectifs.

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Conformément au fonctionnement classique du premier étage de FPR, chaque unité a fonctionné en alternant période d'alimentation (3.5 jours), en eau brute dégrillée, et période de repos (7 jours). Le suivi des installations a débuté après une période de fonctionnement de 5 mois afin de permettre un état stable de fonctionnement. Les prélèvements, réalisés sur la base de bilan 24-heures proportionnels au débit, ont été effectués lors des premiers et derniers jours de fonctionnement d'un cycle à l'aide de préleveurs automatiques réfrigérés. Chaque échantillon a été analysé en laboratoire, à l'aide de kits d'analyses rapides, pour la DCO totale et dissoute (DCO_{tot} et DCO_d, respectivement), l'ammonium et les nitrates ainsi que le calcium de carbonate. Des analyses de MES ainsi que des mesure de pH ont enfin également été réalisées.

Les résultats ont démontré l'impact positif d'un accroissement de hauteur de filtration (100cm) permettant une élimination de l'ammonium supérieure à 80% là où le dimensionnement classique (40cm) ne permet qu'un abattement de 62%. Une amélioration sensible a également été observée sur le paramètre de DCO_d. Néanmoins, la majorité des bactéries hétérotrophes et autotrophes sont implantées dans la couche de boue ainsi que la partie supérieure de la couche filtrante. Bien que l'accroissement de la profondeur de filtration augmente indéniablement les capacités de traitement, il convient d'en admettre la faible amélioration par unité de profondeur au-delà de 40 cm.

Par ailleurs, il a été identifié que l'augmentation de la charge hydraulique (de $0.36 m.jour^{-1}$ à $0.64 m.jour^{-1}$) provoque un flaquage rapide à la surface du filtre. Celui-ci empêchant la bonne réoxygénation du milieu, cette modification opérationnelle se traduit par de faibles performances d'élimination de l'ammonium (44%) et de la COD_d (44%). Il est toutefois intéressant de noter que, contrairement à la pollution dissoute, la pollution particulaire n'en est pas affectée.

L'adsorption de l'ammonium sur la matière organique représente un mécanisme majeur dans son traitement. Un abattement maximal de $15 gN.m^{-2}.j^{-1}$ a été observé pour des charges appliquées de $25 gN.m^{-2}.j^{-1}$. Un accroissement de la charge appliquée, au-delà de cette limite, entraîne une diminution importante des performances.

Enfin, l'ajout de zéolithe en fond de couche filtrante n'a quant à lui pas donné de résultats significativement meilleurs à un filtre classique. Ceci s'explique principalement par une masse insuffisante de zéolithe ainsi que des conditions opératoire inadaptées. Des études complémentaires sont nécessaires afin d'optimiser le process.

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Une seconde partie des travaux a porté sur l'évaluation du potentiel d'optimisation que représente la mise en œuvre de matériau échangeur d'ions (zéolithe) au sein de la couche de filtration. Une première série d'expérimentations, menées en laboratoire sur matériau vierge, a visé à caractériser plus précisément la capacité d'échange du matériau ainsi que l'effet des conditions opératoires (concentration initiale, présence d'autres espèces cationiques, charge hydraulique) et de conception (masse et mise en œuvre de la zéolithe). Une partie des expérimentations ont été conduites en conditions saturées tandis qu'un second volet a porté sur le fonctionnement en conditions librement drainé.

Deux colonnes, en plexiglass (h = 43 cm et ø = 5 cm), ont été évaluées en parallèle en conditions saturées à flux ascendant continu. La première colonne était intégralement remplie de gravier granitique concassé (2 – 6 mm) tandis que la seconde présentait de fines couches intermédiaires de zéolithe. La masse totale de zéolithe dans cette seconde colonne était d'environ 100g. Par ailleurs, des systèmes de prélèvements intermédiaires sont situés à différentes hauteurs au-dessus de chaque couche de zéolithe. Chaque colonne est alimentée en solution synthétique d'ammonium à 100 $mgN\text{-}NH_4.L^{-1}$ à l'aide d'une pompe péristatique dont le débit a été fixé à $0.1m.h^{-1}$ afin d'avoir un temps de séjour théorique de 104 minutes. Des prélèvements sont effectués en entrée et sortie de colonne ainsi qu'aux systèmes intermédiaire à l'aide d'une seringue. Après filtration à 0.45 µm, la concentration en ammonium est mesurée pour chaque échantillon.

Cette expérimentation a démontré que la zéolithe étudiée présente une certaine capacité d'adsorption. Cependant, le système n'est pas idéalement conçu et la concentration en ammonium augmente très rapidement jusqu'à totale saturation du système. La durée entre la percée et la saturation de la colonne est très longue et démontre que les conditions opératoires ne sont pas optimisées. Un débit plus lent permettrait probablement un meilleur contact entre le sorbant et le sorbat. Par ailleurs, une couche plus épaisse de zéolithe augmente considérablement les performances puisque cela permet d'accroître la masse de zéolithe et donc d'avoir une zone de transfert de masse plus importante.

Un nombre variable de colonnes (cf. paragraphe précédent) ont été étudiées à travers une succession d'expérimentations courtes visant à étudier les effets de divers paramètres de conception et fonctionnement sur des systèmes librement drainés. Chaque colonne était composée i) d'une couche de zéolithe prise entre ii) une fine couche de gravier en dessous et iii) une épaisse couche de diffusion supérieure en gravier concassé granitique (2 – 6 mm).

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Chaque colonne est alimentée avec une solution synthétique d'ammonium à 100 mgN-NH_4.L^{-1}. Les alimentations se font par bâchées de 2 cm toutes les 80 minutes. Chaque colonne étudiée présente une variante pour un paramètre de conception (masse de zéolithe, type de zéolithe) ou de fonctionnement (charge hydraulique, concentration en ammonium) afin d'en évaluer l'incidence sur le traitement.

Une première expérimentation, consistant à comparer les performances de deux clinoptilolites et une chabazite, a fait apparaître des performances légèrement meilleures avec cette dernière.

Le fonctionnement en conditions librement drainées fait apparaître de très bonnes capacités d'adsorption. Néanmoins, il semble que seule la fraction d'eau échangée à l'intérieur de la colonne entre deux bâchées consécutives réagisse effectivement avec la zéolite. La fraction de l'eau s'infiltrant rapidement au travers du filtre ne bénéficie pas d'un contact suffisant pour permettre une adsorption satisfaisante de l'ammonium. Il convient donc de privilégier de petites bâchées fréquentes à de rares grosses bâchées. Une étude, de l'impact de la fréquence de bâchées sur les performances, est nécessaire afin de déterminer l'optimum entre volume et fréquence d'alimentation.

Par ailleurs, l'accroissement de la masse de zéolithe permet également, en conditions librement drainé, d'atteindre de meilleures performances. Cela s'explique en partie par une augmentation du volume de pore "réactif" au sein duquel se déroule l'échange d'ions entre deux bâchées. Une masse de 30kg.EH^{-1}.$filtre^{-1}$ dans un filtre alimenté avec des bâchées de 2 cm permet d'atteindre des performances d'élimination supérieure à 90% pendant tout un cycle de fonctionnement. Néanmoins, quelle que soit la concentration d'ammonium en solution, les performances d'élimination diminuent au fur et à mesure de la saturation progressive des sites de fixation. Une régénération de la capacité d'échange est donc nécessaire vis-à-vis de la durabilité du process : un optimum est donc à trouver entre rétention et vitesse de nitrification.

Une dernière expérimentation, réalisée avec des matériaux issus de station en fonctionnement, a permis d'étudier l'efficacité de la régénération biologique de la capacité de sorption de la zéolithe. Sept colonnes, en PVC opaque (h = 60 cm, ø = 80 mm), sont remplies avec 40 cm de matériau filtrant. Une première colonne, remplie exclusivement de gravier provenant de station, a servi de référence pour l'estimation des phénomènes d'adsorption sur la matière organique ainsi que la nitrification. Six autres colonnes sont constituées d'une fine couche de gravier surmontée d'une couche de zéolithe (10 cm environ) et d'une épaisse couche de diffusion d'environ 30 cm de gravier de rivière (2 – 6 mm). Toutes les colonnes, sauf celle

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servant de témoin à la zéolithe, sont remplies avec des matériaux de stations. Les colonnes sont alimentées avec des effluents semi-synthétiques d'ammonium dont les compositions présentent des variations afin d'évaluer les effets liés à certains paramètres opérationnels (concentration en ammonium, présence d'autres espèces cationiques). Chaque colonne est alimentée, par 14 bâchées quotidiennes de 2 cm, pendant 3.5 jours puis est laissée au repos pendant 7 jours afin d'être le plus proche possible des conditions réelles d'utilisation. Un lessivage des matériaux, à l'eau distillée, a été effectué avant le début de l'étude afin d'éliminer les nitrates piégés dans le système. L'effluent est collecté en sortie de colonne dans un seau, préalablement acidifié afin de bloquer d'éventuelles réactions, puis analysé pour l'ammonium sur la base de bilan 24-heures ou 84-heures.

L'étude des performances à de fortes concentrations (2000 $mgN\text{-}NH_4.L^{-1}$) a démontré le fort potentiel d'échange de la zéolithe (19$mgN\text{-}NH_4.g^{-1}$). L'utilisation de zéolithe permet d'atteindre des performances d'abattement de l'ammonium supérieures à 80%, malgré la présence d'autres espèces telles que le sodium. Mais les performances chutent rapidement car le potentiel de régénération de sites d'échange étant très faible (0.12$mgN\text{-}NH_4.g^{-1}$) et une saturation progressive amène à une perte totale de sorption. Ceci peut partiellement s'expliquer par une difficulté de l'oxygène à traverser le biofilm et atteindre les particules de zéolithe, empêchant une nitrification optimale. Par ailleurs, vue la différence de taille des pores de la zéolithe (Å) et de celle des bactéries (µm), il est possible que la colonisation bactérienne soit limitée à la surface, empêchant une régénération des sites de la porosité. La zéolithe présente donc un potentiel important dans l'amélioration du traitement de l'ammonium. Néanmoins, des études complémentaires sont nécessaires en vue d'une exploitation durable.

Le troisième axe de cette étude, quant à lui, avait pour but de préciser les conditions opératoires permettant d'atteindre un traitement poussé des nitrates. Deux filtres à écoulement vertical (VFFs) (1.44m^2) saturés sur une profondeur de 85 cm et alimentés en eaux semi-synthétique ont été suivis pour les besoins de l'étude. L'effluent semi-synthétique a été préparé dans une cuve de stockage opaque avant chaque bâchée. Il est composé d'eau du clarificateur de la station d'épuration, sur laquelle sont implantés les pilotes, ainsi que de solution de nitrate de sodium et d'un cocktail de substrats organiques (glucose, glycine et glycérol). Chaque pilote reçoit quotidiennement 18 bâchées de 2 cm réparties de manière

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homogène à la surface du filtre par des rampes d'alimentations. Des prélèvements ont été effectués en sortie de système, par des préleveurs automatiques réfrigérés, en fonction du débit. L'effluent semi-synthétique a quant à lui été prélevé de manière ponctuelle avant une alimentation. Chaque échantillon est analysé en laboratoire, à l'aide de kits d'analyses rapides, pour la DCO_{tot}, DCO_d, $N\text{-}NH_4$, $N\text{-}NO_3$ et $CaCO_3$. L'analyse des concentrations en MES ainsi que des mesures de pH sont également effectuées. Des cannes de prélèvements, introduites horizontalement à différentes hauteurs, sont utilisées afin d'établir des profils verticaux de traitement. Les notions de temps de contact, de disponibilité en matière organique ainsi que de teneur en nitrate de l'effluent ont été abordées dans ces travaux.

Il a été vu que la disponibilité en matière organique facilement biodégradable est l'élément clé d'une dénitrification efficace. Tandis que l'absence de matière organique bio-accessible inhibe totalement la dénitrification, son accroissement se traduit par une augmentation des cinétiques de traitement ($29.2 gN.m^{-2}.j^{-1}$ observé pour un rapport DCO_{tot}:N de 6). Tenant compte des caractéristiques des effluents en sortie de premier étage de VFF, une limitation en carbone peut être anticipée et, par conséquent, des adaptations de conception sont à prévoir.

Par ailleurs, le temps de contact doit être considéré comme une seconde variable d'ajustement en fonction des objectifs de traitement puisque, en absence de limitation en carbone, près de 68% des nitrates sont éliminés pour un temps de contact de 0.3 jours (soit une concentration de sortie proche de $12 mgN.L^{-1}$) tandis qu'une augmentation du temps de contact jusqu'à 1 jour permet d'atteindre un abattement presque total (98%). En outre, l'accroissement de la charge appliquée en nitrate entraîne une augmentation de la cinétique de traitement permettant d'atteindre des rendements similaires à ceux obtenus pour des concentrations plus faibles et avec des ratios DCO_{tot}:N semblables. Il n'est par conséquent pas nécessaire de prévoir une augmentation significative du temps de contact, afin de garantir les performances de traitement lors du relargage post-période de repos, tant que la source en carbone n'est pas limitante.

Enfin, le développement d'un outil prédictif statistique d'aide au dimensionnement a été réalisé. Un tel modèle est capable de prendre en compte la variabilité du design et des caractéristiques de l'effluent mais présente actuellement un intervalle de prédiction trop important pour être utilisé tel quel.

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Samenvatting

Helofytenfilters (HFs) hebben de laatste drie decennia aan belang gewonnen omwille van hun goede zuiveringsefficiëntie, hun lage operationele kosten en hun milieuvriendelijk imago. De waterzuiveringssector is echter in toenemende mate competitief geworden en effluentnormen worden steeds strenger. Een optimaal ontwerp, aangepast aan de lokale omstandigheden, is daarom een noodzaak en vereist een zeer goede kennis van de mechanismen die bijdragen tot waterzuivering.

Stikstofverwijdering wordt aanzien als de belangrijkste limitatie bij zuivering van huishoudelijk afvalwater. Dit doctoraat focust dan ook op deze parameter, met als doelstelling te komen tot een beter ontwerp en betere zuiveringsefficiëntie van HFs.

Een eerste deel van dit werk werd uitgevoerd op 4 pilootschaal verticaal-doorstroomde HFs (VHFs), elk met een oppervlakte van 2,25m² en gevoed met ruw huishoudelijk afvalwater. Dit deel van het onderzoek had als doelstelling om het effect van een grotere filterdiepte te bepalen, evenals om de impact te bestuderen van een hogere hydraulische belasting en ammoniumbelasting. De resultaten bevestigen dat een grotere filterdiepte (100 cm) een positief effect heeft met een ammoniumverwijdering van meer dan 80% ten opzichte van een klassieke filterdiepte van 40 cm waar slechts 62% ammonium wordt verwijderd. Een toenemende hydraulische belasting (van 0,36m.d^{-1} tot 0,62m.d^{-1}) resulteert snel in stagnatie van water bovenop de filter. Dit verhindert het verversen van de zuurstofvoorraad binnen de VHF en resulteert op die manier in een lagere ammoniumverwijdering (44%). Tot slot werd ook vastgesteld dat sorptie van ammonium op de organische sliblaag bovenop de filter een belangrijke bijdrage levert. Een maximum verwijdering van 15gN.m^{-2}.d^{-1} werd bekomen bij een ammoniumbelasting van 25gN.m^{-2}.d^{-1}. Hogere ammoniumbelastingen zorgen voor een belangrijke daling in zuiveringsefficiëntie.

In een tweede luik werd gekeken welke voordelen het toevoegen van een reactief materiaal, zijnde zeoliet, aan het filtermateriaal oplevert. Een eerste groep experimenten werd op laboschaal uitgevoerd met als doel om de uitwisselingscapaciteit van vers zeoliet te bepalen en de impact daarvan op ontwerp (massa en wijze van toevoegen) en operationele (influent

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concentratie, invloed andere kationen, hydraulische condities) parameters. In een aanvullend experiment werd gewerkt met zeoliet afkomstig van een reeds in werking zijnde VHF, met als doel om het herstel van de uitwisselingscapaciteit te bestuderen via biologische mechanismen, in het bijzonder nitrificatie. De resultaten bevestigen de hoge efficiëntie van zeoliet om ammonium te verwijderen (tot 19mgN.g^{-1} onder de bestudeerde omstandigheden) maar tonen ook aan dat adsorptiecapaciteit beïnvloed wordt door de influent concentraties. Slechts 1,9mgN.g^{-1} adsorptie werd gemeten bij influentconcentraties typisch voor huishoudelijk afvalwater. Verder werd ook vastgesteld dat ammoniumverwijdering sterk afhangt van de kinetiek van verschillende processen. De contacttijd tussen de te adsorberen component en het adsorbens is een belangrijke parameter voor het optimaliseren van de adsorptie van ammonium. Een intermitterende belasting zorgt voor een lange contacttijd tussen opeenvolgende batches. Het verhogen van de batchfrequentie en terzelfdertijd verlagen van het batchvolume (2cm elke 80 minuten in plaats van 3cm elke 120 minuten) laat toe om het residueel watergehalte te verhogen en bijgevolg de fractie water die in het systeem opgeslagen wordt tussen twee verschillende voedingen. Het optimale compromis tussen beide criteria is nog voorwerp van verder onderzoek. Verder werd ook vastgesteld dat de implementatie van 30kg zeoliet.pe^{-1}.$filter^{-1}$ toelaat om, in de bestudeerde omstandigheden, verwijderings-efficiënties van meer dan 90% te bekomen gedurende een volledige operationele cyclus (3,5 dagen). Deze hoeveelheid wordt dan ook aangeraden voor verdere ontwerpen. Echter bleek ook dat biologische regeneratie zeer inefficiënt is (0,12mgN.g^{-1}) waardoor de zuiveringsefficiëntie snel zakt tot een niveau dat ook bij klassieke grind-gevulde systemen bekomen wordt.

Tot slot werd in het derde deel van dit werk gekeken naar de ideale omstandigheden om een hoge nitraatverwijdering te bekomen. Twee waterverzadigde VHFs (85cm saturatie) werden met dit doeleinde gemonitord, waarbij gekeken werd naar koolstoflimitatie, nitraatbelasting en contacttijd. De beschikbaarheid van makkelijk afbreekbaar koolstofverbindingen is een belangrijke parameter om hoge nitraatverwijdering te verkrijgen. Denitrificatie wordt duidelijk gelimiteerd door een gebrek aan makkelijk afbreekbaar koolstofverbindingen, maar de omzettingssnelheid stijgt tot 29,2 gN.m^{-2}.d^{-1} voor een CODtot:N verhouding van 6. Koolstoflimitatie is een te verwachten fenomeen gezien de samenstelling van het effluent van de eerste (niet-verzadigde) VHF (COD_{tot}:N $\approx$ 2.5). Een volledige denitrificatie is dus onmogelijk tenzij een extra interne of extra koolstofbron voorzien wordt.

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Contacttijd is een tweede belangrijke parameter die gebruikt kan worden om verwijdering te optimaliseren. Bijna 70% van alle nitraat werd verwijderd binnen de eerste 0,3 dagen contacttijd, op voorwaarde dat er geen koolstoflimitatie was, waardoor effluentconcentraties van 12mgN.L^{-1} werden bekomen. Een toename van de contacttijd met een factor 4 liet toe om nagenoeg volledige denitrificatie (98%) te bekomen. Bovendien werd vastgesteld dat hogere nitraatconcentraties in het influent zorgen voor een snellere proceskinetiek, bij eenzelfde COD_{tot}:N verhouding; een gelijkaardige verwijderingsefficiëntie kan dus bekomen worden bij kleinere contacttijd. Op die manier behoeft het denitrificeren van het uitgeloogde nitraat na een rustperiode geen lange hydraulische verblijftijd, op voorwaarde dat er geen koolstoflimitatie is. Tot slot werd ook een voorspellende statistische tool ontwikkeld om verdere ontwerpen te ondersteunen. Eenvoudige multi-lineaire modellen laten toe om de effecten van ontwerp en operationele parameters te beschrijven, maar de accuraatheid is momenteel nog te laag om deze modellen als betrouwbare ontwerptools te gebruiken.

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Abstract

Reed bed filters (RBFs) met an increasing interest over the past three decades because of their good treatment efficiency, their low operational cost as well as their eco-friendly image. Nevertheless, sanitation business becomes an increasingly competitive market whereas discharge regulations tend to more and more constraints. A better knowledge of the mechanisms involved in pollutant removal is strongly required in order to optimize the design in each particular case.

Nitrogen removal was identified as the main limit for domestic wastewater treatment. A particular attention was paid to this parameter, through these PhD works, with the aim to improve both design and treatment efficiency of RBFs.

A first part of this work was realized on 4 pilot-scale vertical flow filters (VFFs), of 2.25m² each, fed with raw domestic wastewater. This study aimed to assess the effect of filtration height as well as the impact of hydraulic and ammonium loads on ammonium removal efficiency. Results showed that increasing the filtration depth (to 100cm) positively affects treatment since more than 80% of ammonium removal is achieved whereas the classic design (40cm filtration depth) only reaches 62%. In other respects, increasing the hydraulic load (from 0.36m.d^{-1} to 0.64m.d^{-1}) quickly causes ponding, which hinders proper reoxygenation into the filter, and thus results in low ammonium removal efficiency (44%). Finally, ammonium removal by sorption onto the organic deposit was found to have an important influence on treatment efficiency. A maximum treatment capacity of 15gN.m^{-2}.d^{-1} has been observed for ammonium applied loads of 25gN.m^{-2}.d^{-1}. Any ammonium load beyond this limit results in important decreases of performance.

A second part of the study aimed to assess the advantage linked with the implementation of reactive material (i.e. zeolite) in the filtration layer. A first set of experiments was conducted in lab-scale conditions with clean zeolite in order to characterize the exchange capacity and assess the effects of design (mass and implementation of zeolite) and operational conditions (influent concentration, other cations, hydraulic conditions). Furthermore, a second experiment, using zeolite extracted from a full-scale treatment plant, was conducted with the aim to determine the ability to biologically restore exchange capacity through nitrification. The results confirm the high efficiency of zeolite to remove ammonium (up to 19mgN.g^{-1} in

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the studied conditions) but show that sorption capacity is influenced by influent concentration. Only 1.9mgN.g^{-1} of sorption has been observed with influent concentrations in the typical range of domestic wastewater. In other respects, ammonium removal strongly depends on the kinetics of various mechanisms. The contact time between adsorbent and adsorbate is a key parameter in order to optimize ammonium sorption. Pulse load operation allows providing long contact between consecutive batches. Increasing the batch frequency while reducing batch volume (2cm every 80min instead of 3cm every 120min) enables to increase the residual water content and thus improve the fraction of water which is stored within the system between feedings. The best compromise between both criteria should still be finely determined. Furthermore, the implementation of 30kg zeolite.pe^{-1}.bed^{-1} enables to reach, in the studied conditions, removal efficiencies higher than 90% during a full cycle of operation (3.5d) and thus appears as a good design in order to obtain high ammonium removal. Nevertheless, biological regeneration is quite inefficient (0.12mgN.g^{-1}) and treatment efficiency quickly dropped until reaching removal performances performed by a classic gravel-filled system.

Finally, the third part of this work aimed to determine the ideal conditions to achieve high nitrate removal. Two saturated VFFs (85cm of saturation) were monitored for this purpose. Carbon supply, nitrate load and contact time were studied. The availability of easily biodegradable carbon is the driving parameter in order to achieve high nitrate removal. While denitrification is inhibited by a lack of easily biodegradable organic matter, the process rate increases with carbon supply (29.2gN.m^{-2}.d^{-1} for COD_{tot}:N ratio set at 6). Carbon limitation may be expected considering the effluent characteristics from a first stage VFF (COD_{tot}:N ≈ 2.5). Full denitrification cannot thus be achieved unless design/operation modifications are made or an endogenous or exogenous carbon supply is provided. As well, contact time is a second key parameter which is available in order to optimize treatment efficiency. Almost 70% of nitrates are removed within the first 0.3d of contact, when no carbon limitation occurs, resulting in effluent concentrations of 12mgNO_3-N .L^{-1} in the studied conditions. Increasing the contact time by a factor just under 4 allows performing almost full denitrification (98%). Furthermore, increasing the influent nitrate concentration fasten process kinetics and thus allows to achieve similar performance than the ones observed with lower load at similar COD_{tot}:N ratio. Therefore, treating the first flush after a resting period does not require an important extension of retention time as long as there is no carbon limitation. Finally, a predictive statistical tool was developed with the aim to support design. Simple

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multicomponent linear models allow describing the effects of design parameters as well as operational conditions. Nevertheless, prediction accuracy remained poor and was still not suitable for design purposes.

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List of Acronyms

AOB: Ammonia Oxidizing Bacteria

BOD_5: 5-day Biological Oxygen Demand

CEC: Cationic Exchange Capacity

COD_d: Soluble Chemical Oxygen Demand

COD_{tot}: Total Chemical Oxygen Demand

HFF: Horizontal Flow Filter

HRT: Hydraulic Retention Time

MTZ: Mass Transfer Zone

NH_4-N: Ammonium nitrogen

NOB: Nitrite Oxidizing Bacteria

PBU: Primary Building Unit

pe: people equivalent

RTD: Retention Time Domain

SSF: SubSurface Flow filter

TKN: Total Kjeldahl Nitrogen

TN: Total Nitrogen

TSS: Total Suspended Solids

VFF: Vertical Flow Filter

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Introduction

The industrial revolution, and its poor attention to environmental issues, is over and, since a few decades, there is more awareness for a more responsible way of life. The question of wastewater management is a perfect illustration of the desire to control and improve the anthropogenic pressure on ecosystems in order to preserve our resources. Indeed, as an essential resource, water issues are a worldwide concern holding a central position in the political agenda.

The need to reduce our footprint on the environment has been translated in 1991 into the European urban wastewater treatment directive (91/271/CEE) to force communities to treat wastewater and comply with standards. For instance, minimal standards of discharge quality and treatment performances for small communities, producing less than 120 $kgBOD_5.d^{-1}$ (2000 people equivalent (pe)), are summarized in Table 1 for France and Belgium.

Table 1 Standards of effluent quality and treatment performances for small communities (≤ 120 $kgBOD_5/d$)

	France[a]		Belgium[b]	
Parameter	Maximum concentration in discharge effluent	Minimum removal performances	Maximum concentration in discharge effluent	Minimum mass removal performances
COD	200 $mg.L^{-1}$	60 %	125 $mg.L^{-1}$	90 %
BOD_5	35 $mg.L^{-1}$	60 %	25 $mg.L^{-1}$	75 %
TSS	None	50 %	35 $mg.L^{-1,c}$	70 %
TKN	None	None	None	None

[a] Official Journal of the French Republic, n°0190 August 19, 2015 p.14457 (Source: https://www.legifrance.gouv.fr/eli/arrete/2015/7/21/DEVL1429608A/jo/texte)

[b] VLAREM II, annex 5.3.1.c. Flemish Environmental Regulation. (Source: https://navigator.emis.vito.be/mijn-navigator?woId=10108)

[c] This value is given for treatment plants whose capacity ranges from 500 to 2000 pe. Effluent concentration lower than 60 $mg.L^{-1}$ is required for treatment plants smaller than 500 pe

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More recently the European Water Framework Directive (2000/60/CE) set out the ambitious goal of reaching "good ecological status" of water bodies in 2015. However, only 53% of European surface water bodies met the objective in due time (EEA, 2015) as it is shown in Figure 1 presenting European areas where water bodies have less than good ecological status.

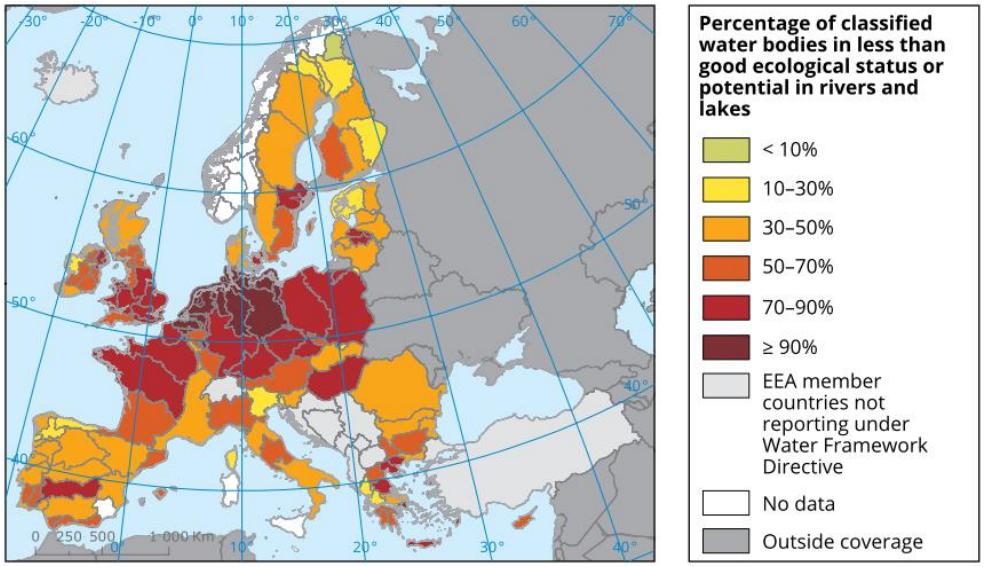

Figure 1 Percentage of classified water bodies in less than good ecological status or potential in rivers and lakes (Source: EEA, 2015)

A more detailed study shows that between 20% and 25% of European surface water bodies are subject to point source pollutions (see Figure 2) (EEA, 2015). Moreover, comparison with Figure 3, presenting the nitrate concentration in European rivers, suggests that a relationship exists between point source pollutions and nitrate levels in water bodies. That may be partly attributed to wastewater discharge as it was reported by European member states (European Commission, 2015).

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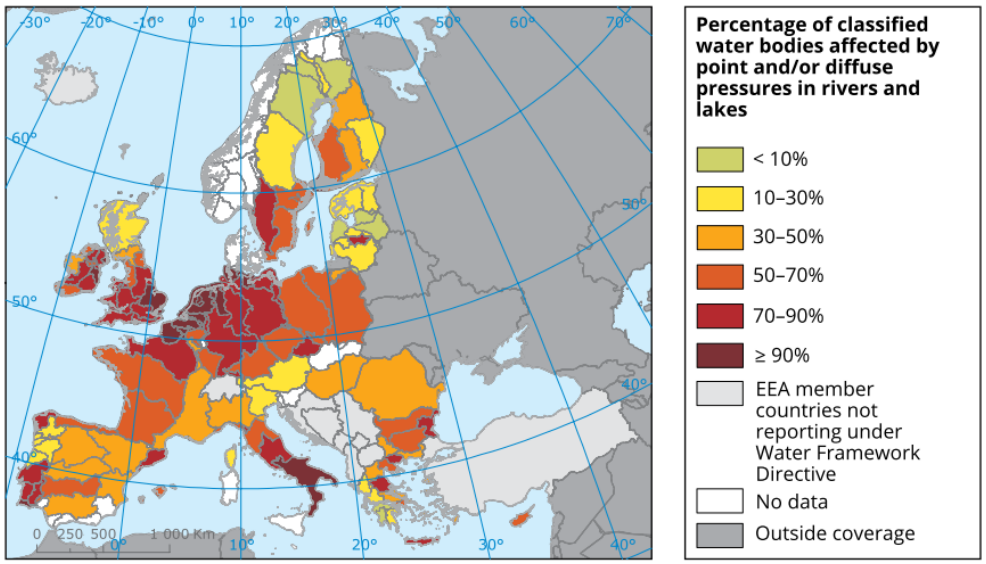

Figure 2 Percentage of classified drivers and lakes in Water Framework Directive river basin districts affected by pollution pressures (Source: EEA, 2015)

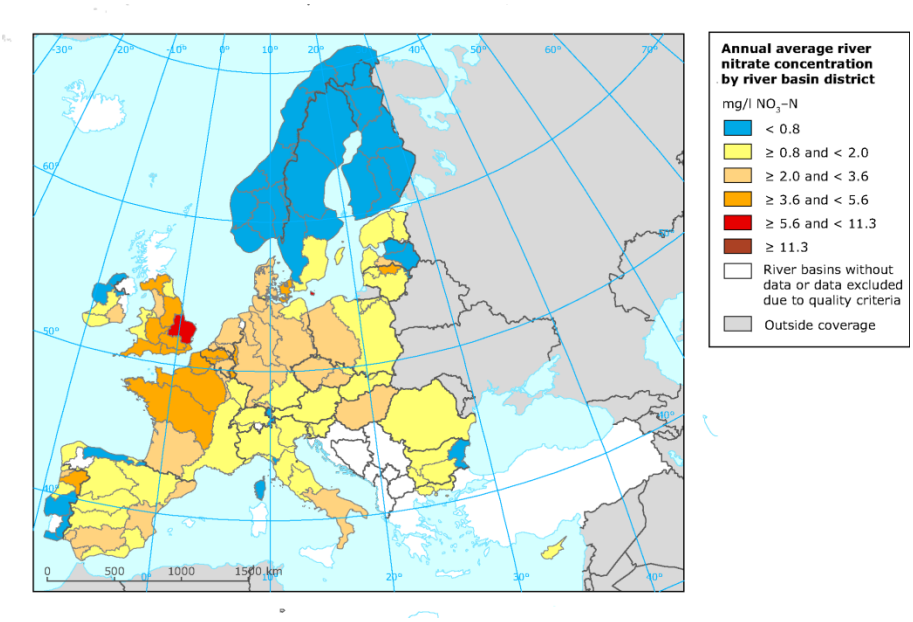

Figure 3 Annual average river nitrate concentration by river basin district (Source: EEA, 2015)

Small treatment plants are generally not subjected to strict regulation of total nitrogen (TN) discharge levels. However, these facilities may account for a large part of treatment plants and thus may significantly affect the integrity of water bodies. In France, for instance, more than 85% of treatment plants have a nominal capacity below 5000 pe, ensuring the treatment of more than 25% of the French domestic effluents (INSEE data).

Almost 20% of these treatment plants are constructed wetlands (CWs) while the rehabilitation of existing ponds and sand filters is a potential reservoir which may increase this number to

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50% of treatment plants smaller than 5000 pe (French environment ministry data). Nevertheless, total nitrogen (TN) removal is the more challenging process to manage in constructed wetlands. This treatment is indeed achieved through a series of processes which require fine settings in design and operation of constructed wetlands. Ammonium is first oxidized into nitrate during nitrification, under aerobic conditions in vertical flow filters, before being reduced into inert gaseous nitrogen, under anoxic conditions in saturated filters, through the denitrification process. Several treatment units, with different oxygen conditions, are thus necessary in order to fulfil the requirements for total nitrogen removal. Increasing the treatment footprint is a direct consequence which may be prohibitive in case of low surface availability or for large capacity treatment plants. In other respects, prolonged contact between influent and biomass is required in order to perform high ammonium removal under aerobic conditions. By knock-on effect, this operational constraint leads to enhanced removal of organic matter which is then not further available for denitrification resulting in nitrate accumulation. A compromise between nitrification and denitrification has therefore to be found in order to perform both processes, but with as a consequence incomplete TN removal.

Epur Nature (www.epurnature.fr) is a small enterprise (22 employees), of Syntea group (www.synteanature.com), which is specialized in water treatment with vegetated systems. As a historic national leader in the technology of treatment wetlands, Epur Nature is also a member of the international community Global Wetland Technology (www.globalwettech.com), composed of industrial specialists, allowing the positive emulation for the improvement of wetland technology. In other respects, Epur Nature is strongly involved in the promotion of wetlands and the improvement of their knowledge from almost two decades (1999). They dedicate around 5% of annual sales revenue to different projects of research in development which are carried out in partnership with various institutes. They have initiated, financed and hold the present research project (namely INNOPUR). Nowadays, they are owners of six national certificates and have their own experimental pilot platform and laboratory.

However, a tough economic context as well as the increasingly competitive sanitation market, related to the appearance of new players, force Epur Nature to considering new development strategies. Among the available strategies, we may point out (1) the positioning of wetland as complementary treatment in intensive systems (e.g. sludge management, co-treatment), (2) the implementation of wetland technology to different context (e.g. industrial influent, combined sewer overflows), (3) the attack on foreign markets and (4) the optimization of

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design in the aim to achieve high treatment efficiency with compact systems. Different approach may allow to reach high treatment efficiency with compact systems. On the one hand, intensified wetland systems (e.g. filled and drained systems, forced aeration systems) proved to be relevant for improving the treatment rate but also showed significant increase in energy consumption. On the other hand, recent studies (Silveira *et al.*, 2015; Troesch *et al.*, 2014; Millot *et al.*, 2015 (see appendix)) reported the positive effect of a partial bottom saturation in order to perform TN removal by a single stage vertical flow filter without increase in energy requirement. This last extensive alternative showed promising, but still insufficient, results to achieve almost full treatment in a single compact unit. Fine knowledge of relationships between the system characteristics (i.e. design and operational conditions) and the efficiency of each biological process, occurring within the system, is thus necessary to be competitive with other systems. This research thus aimed to highlight the key parameters, favoring efficient treatment, in order to provide applicable guidelines recommendations.

This study thus scopes three different axes:

1) A first part of the study has been focused on the optimization of treatment efficiency within the unsaturated layer. A specific attention has been paid to the removal of ammonium which is known to be the most limiting process in such system. Ammonium removal is related to intrinsic characteristics of influent (e.g. alkalinity, pH), which can not be controlled, but also relies on conditions which may be optimized by engineer. The objectives were therefore to determine the effects of different characteristics of design and operation in order to reach the most efficient treatment through a fine conception optimizing each removal processes. Three different questions were stated for this study:
    a) What is the maximum acceptable load of pollutant per surface unit?
    b) What is the effect of feeding frequency on the treatment efficiency?
    c) How improve contact between substrate and biomass?
        i) How much does the increase in contact between influent and biomass may be profitable to enhance the removal efficiency?
        ii) Is it possible to dissociate, in time, treatment and water flows by the implementation of reactive material (i.e. zeolite)?

    These questions have been evaluated for during an almost 2-year monitoring of four pilot-scale experimental units. Semi-industrial scale is usually more representative of the complex hydraulic behavior of VFFs than simple lab-scale systems. Moreover, the

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implementation of pilots on the site of a real municipal wastewater treatment plant was the opportunity to conduct a study in conditions close to reality. The systems have thus been fed with solution reproducing all characteristics of domestic effluent (i.e. daily variability, complex composition) and were subjects to the same weather conditions which may occurs in full-scale system (i.e. seasonal variations in temperature, rain events). The results were thus free of the bias which may result from laboratory experiments and which limit their application to real systems. These experimental tools were thus particularly well suited to the assessment of design parameters.

2) The second part of this study has aimed to determine the conditions which are required in order to perform full denitrification within the saturated layer of partially saturated filters. This system strongly depends on treatment performed in the upper unsaturated layer. Therefore, variability in influent characteristics may be expected (i.e. after a resting period or because of daily variations in characteristics of domestic influent). Moreover, adjusting the reactor volume is a key parameter in order to optimize costs of civil engineering. Therefore, the accurate knowledge of the effects of design and operational conditions is a prerequisite for the process optimization. Two questions were identified in order to determine the best conditions for an efficient removal of nitrate:
   a) What is the impact of organic carbon?
      i) What is the effect of COD:N ratio on denitrification efficiency and kinetic?
      ii) What is the impact of the biodegradability of organic carbon on denitrification efficiency?
   b) What is the optimal reactor volume?
      i) Does higher specific surface improve the removal rate for the same volume of reactor?
      ii) What is the effect of hydraulic retention time on denitrification efficiency?

   These different operational and design characteristics have been studied during a 7-months monitoring of two pilot-scale experimental units. As it was previously discussed pilot scale is suited well for the evaluation of system operating in conditions close to reality. Nevertheless, these experimental units had the particularity to combine both advantages from pilot scale and lab scale systems since they were fed with semi-synthetic wastewater. The feed solution was indeed prepared with effluent from tertiary clarifier of municipal treatment plant and a solution, prepared in our laboratory, containing nitrate and COD. The first component acted as a source of

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biomass and various substrates in solution which allowed to create a complex matrix which was representative of effluent from unsaturated layer. The second one allowed the setting of influent characteristics in order to assess a wide range of operational conditions (i.e. influent concentration of nitrate, COD:N ratios) in a short period.

3) Finally, a third step was conducted in laboratory in order to accurately study the sorption of ammonium onto zeolite. Although this material was assessed in a pilot-scale experimental unit, the use of zeolite in systems operating under free drainage conditions is very innovative. Therefore, that requires a large set of complementary experiments before the optimization of this process. To our knowledge this is the first study which goes as far in the assessment of zeolite use under unsatured conditions for the removal of ammonium. The implementation of zeolite in VFFs must address two distinct objectives. On the one hand, sorption process must be optimized within the system. On the other hand, sorption capacity has to be sustainable. For this purpose we had to face to several challenging questions in order to respect both constraints:
   a) What zeolite should be chose?
   b) What are the best hydraulic conditions:
      i) Does saturated conditions must be favored, with the related operational constraints (i.e. limitation in contact time), to free drainage?
      ii) Should we prefer more frequent small feedings to less frequent large feedings?
   c) What is the optimal amount of zeolite to perform high ammonium removal while keeping economic attractiveness?
   d) What are the effects of influent characteristics?
      i) What is the impact of ammonium concentration on treatment efficiency and sorption capacity?
      ii) What is the impact of other cations which may compete with ammonium in the sorption process?
   e) What is the ability of autotrophic bacteria to restore sorption capacity by nitrification process and what is the optimal sequence of operation (i.e. feeding and resting periods) in order to optimize the process?

All these questions were assessed in lab-scale experiments (i.e. batch and columns). The choice of lab-scale has been the direct consequence of two constraints. On the one hand, the large number of questions, and related experiments, would require the implementation of

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several different units dedicated to the assessment of a single condition. That was not technically feasible. On the other hand, lab-experiments enable a fine control of conditions (i.e. influent characteristics, easy management of operational conditions). While the operational variability was strength in previous parts of this study, it would become a weakness here. Lab-scale experiments were thus the perfect solution in order to easily tune each system in order to study the wide range of conditions which was necessary before further studies in semi-industrial systems.

After a preliminary literature section, this manuscript proposes an exhaustive description of experiments and discussions of each study on the basis of a compilation of five chapters which may be read as stand-alone research articles. Finally, a conclusion chapter provides a summary of studies' observations and several design recommendations for constructed wetlands.

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Chapter 1 Literature review

1.1 Treatment wetlands

The term treatment wetland refers to a wide range of designs, such as free water surface or subsurface flow filters (SSF), which mimic the natural capacity of self-purification which was observed in natural wetlands. The distinction between those different systems is mainly based on flow considerations (Fonder and Headley, 2013):

- Flow location: surface or subsurface
- Flow regime: saturated or unsaturated

The following section is focused on the different system of SSF.

1.1.1 Horizontal flow filters

Horizontal flow filter (HFF) is the most common wetland design worldwide. This saturated system is fed by pre-treated influent which horizontally flows from the inlet to the outlet (see Figure 4). The filter is filled with gravel material and planted with emergent vegetation (*Typha sp., Phragmites sp.*). Two gabion zones, at the inlet and the outlet, improve the water distribution into the system. The rules of such design are based on hydraulic restriction and an acceptable daily organic load of BOD_5 (Vymazal, 2005).

Vymazal (2009) reported load removal performances of up to 81%, 63% and 68% for BOD_5, COD and TSS respectively. Nevertheless, HFF only achieves low removal of total nitrogen (39% in Vymazal (2009)) because of its anoxic-anaerobic conditions which hinder the preliminary nitrification step.

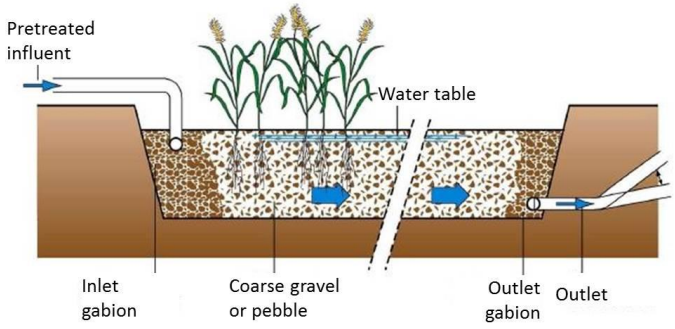

Figure 4 Schematic description of horizontal flow filter design (Source: Epuration des eaux usées domestiques par filtres plantés de macrophytes, Agence de l'eau RMC, june 2005)

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1.1.2 Vertical flow filters

Vertical flow filter (VFF) is the most popular design in Europe (Stefanakis and Tsihrintzis, 2009). The system is fed with settled wastewater from the surface in a sequential mode or continuously. This type of filter is filled with successive layers of material presenting an increasing granulometry from the surface to the bottom. A first layer of fine material ensures the filtration of suspended solids and the removal of dissolved pollutants whereas the bottom layer, filled with coarse material (i.e. pebble), enables to perform drainage of the system (see Figure 5). Finally, an intermediate layer of transition could be implemented in order to avoid migration of fine material to the bottom and also to improve the system oxygenation from the bottom of the filter.

VFFs achieve high performances to remove organic matter and ammoniacal nitrogen. Langergraber *et al.* (2010) reported performances over 99%, 96% and 99% with a single stage VFF for BOD_5, COD and NH_4-N respectively. However, such design is not suitable to perform total nitrogen removal because of the lack of anoxic conditions. For example Langergraber *et al.*, (2007) observed performances as low as 8% in total nitrogen removal with a single stage VFF.

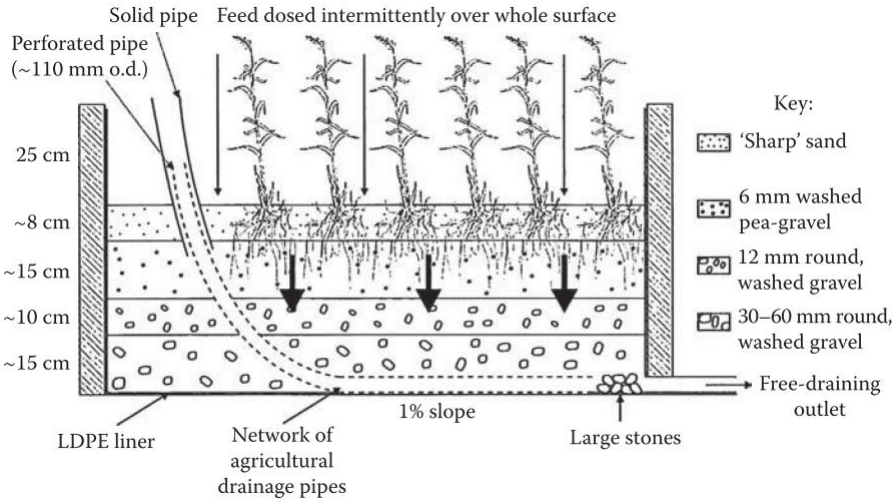

Figure 5 Schematic description of vertical flow filter design (Source: Kadlec & Wallace, 2009)

1.1.3 Description of the French design

The classical design of French constructed wetlands consists in the implementation of two successive stages of VFFs (see Figure 6a). The first stage, which is filled with gravel (see Figure 6b), is divided in three parallel beds of $0.4 m^2.pe^{-1}$ each (total treatment surface of

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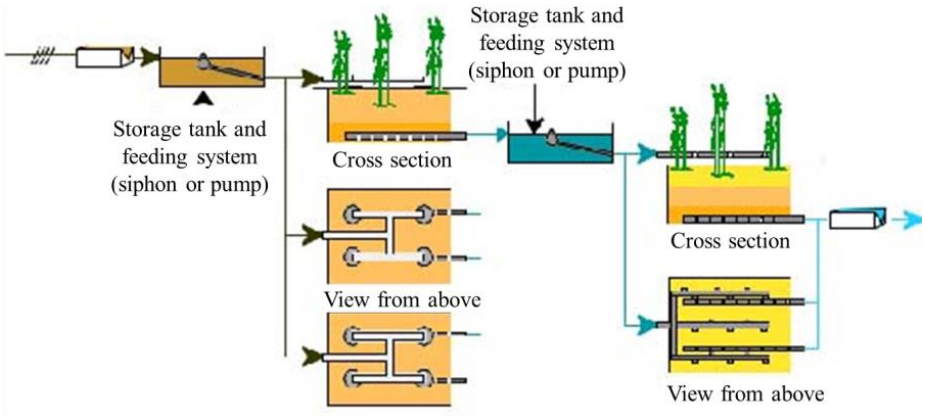
1.2m².pe^{-1}) operating in a sequential mode of feeding and resting periods (3.5 days and 7 days respectively). These units are fed, in pulse load operation, from the surface with raw screened wastewater. The design of the first stage is currently based on the daily load acceptance. Maximum loads of 300gCOD.m^{-2}.d^{-1}, 25 – 30gTKN.m^{-2}.d^{-1}, 150gTSS.m^{-2}.d^{-1} and 0.37m.d^{-1} on the filter in operation are used as design guidelines Molle *et al.* (2005). A high removal of suspended solids can be obtained at this stage. The accumulated sludge is mineralized and provides compost which in turn improves the filtration performances. A partial removal of TKN and COD is also observed at the outlet of the first stage although the second stage takes an important part in the treatment of dissolved pollutants. This second stage (0.8m².pe^{-1}) is composed of two parallel beds alternately operating for seven days and resting for seven days. These filters, which are filled with sand, are fed with effluent from the first stage units. Such design enables to reach high removal performances on TSS, COD and TKN, namely over 95%, 90% and 85% (Molle *et al.*, 2005).

a



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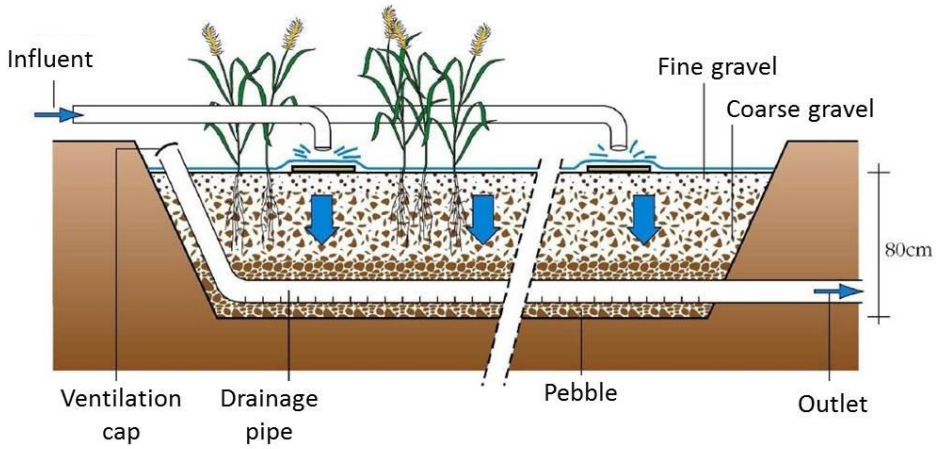

Figure 6 Schematic description of a classical two stage French system (Source: Irstea) **(a) and cross section of 1st stage of a French vertical flow filter (b)** (Source: Irstea)

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Table 2 shows performances from different studies dealing with the treatment of domestic wastewater with French system. Besides, sludge management is easier than other systems using settling tank as pre-treatment (compost recovery). Nevertheless, this system requires 2 to 2.5 $m^2.pe^{-1}$ of filter surface what could be problematic when land availability is limited. Moreover, the use of sand for the second stage faces the problem of local availability which can result in important additional costs. Consequently, system intensification is nowadays an important issue in order to optimize the design with regards to treatment objectives. The following section aims to present the most promising design alternatives.

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Table 2 Treatment performances with a two-stage French system (standard deviation is given between brackets). Note that n-value means the respective number of studied wastewater treatment plant for each study.

Source	COD			TSS			TKN		
	Inlet conc. ($mg.L^{-1}$)	Outlet conc. ($mg.L^{-1}$)	Removal perf. (%)	Inlet conc. ($mg.L^{-1}$)	Outlet conc. ($mg.L^{-1}$)	Removal perf. (%)	Inlet conc. ($mgN.L^{-1}$)	Outlet conc. ($mgN.L^{-1}$)	Removal perf. (%)
Molle *et al.* (2005) n = 72		66 (45.5)	91 (10.2)		14 (17.5)	95 (5)		13 (17.5)	85 (17.1)
Paing *et al.* (2015) n = 151	841 (310)	51 (21)	93 (4)	353 (207)	10 (10)	96 (4)	97 (27)	7 (7)	93 (7)
Troesch and Esser (2012) n = 70	651 (282)	50 (29)	92 (7)	242 (133)	8 (6)	97 (3)	56 (34)	7 (12)	90 (12)
Morvannou *et al.* (2015) n = 380		74 (168)	87 (14)		17 (64)	93 (9)		11 (13)	84 (17)
Boutin *et al.* (1997) n = 1	495	58	87.5	225	12	94.5	42.8	10.2	76

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1.1.4 Process improvement

Most of the studies dealing with system optimization focus on oxygen content in the filter, since it is one of the most limiting parameters in biological processes, while others assess the use of alternative media with high cation exchange capacity (CEC).

1.1.4.1 Recirculation of effluent

Recirculating part of the effluent is a simple optimization way enabling to enhance the contact between dissolved pollutants and biomass in the active layer (e.g. roots and first centimetres of the filter). Molle and Prost-Boucle (2012) observed slightly lower performance, of TSS and COD removal (87% and 82%, respectively) than a classical two-stage system ($2m^2.pe^{-1}$) by recirculating effluent on a single stage ($1.1 – 1.6m^2.pe^{-1}$) with a ratio of 100%, but nitrification was reduced to 37% (based on $N\text{-}NH_4$) in winter for hydraulic load above $0.7m.d^{-1}$ on the filter in operation.

Furthermore, the implementation of an extra pump increases the operational costs and the recirculation of effluent leads to higher hydraulic loads which must be taken into account.

1.1.4.2 Artificial aeration

Increasing the oxygen content in the filter by aeration from the bottom allows significant improvement of COD and TKN removal (Foladori *et al.*, 2013). Moreover, intermittent aeration allows to achieve total nitrogen removal by alternate aerobic and anoxic conditions which are necessary to perform both nitrification and denitrification, respectively.

Such system is highly efficient and competitive compared to conventional treatment systems. Austin and Nivala (2009) reported that the operation of a saturated aerated wetland requires only half of the power of an activated sludge plant in order to achieve similar performances.

However, this intensification of treatment wetlands increases the risk of clogging, due to high biomass growth and decay, and needs more maintenance (Wu *et al.*, 2014).

1.1.4.3 Tidal flow

Tidal flow filters appears as a compromise between operational costs and performance by lowering energy requirements by half compared to equivalent activated sludge process (size, performance (Wu *et al.*, 2011). This process consists in successive cycles of filling and draining periods. Organic matter is oxidised during the filling whilst ammonium is adsorbed onto the organic matter accumulated within the filter. Air is drawn into the filter and rapidly

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oxygenates the system during the drainage. Ammonium is further nitrified until the next cycle. Nitrates are released during subsequent flooding and are denitrified in presence of organic matter. Such system allows to treat total nitrogen by alternate steps of aerobic and anoxic conditions.

Performances depend on several parameters such as the schedule of filling and drainage periods, oxygen transfer through the media and substrate ability to fix ammonium.

Premature clogging can be expected because of high biomass development (Wu *et al.*, 2011).

1.1.4.4 Substrate selection

The use of material with high cation exchange capacity should improve ammonium removal. Ammonium is removed from wastewater during feeding periods and is further nitrified during resting periods. Several batch and column studies have shown the ability of zeolite to adsorb ammonium in solution (Alshameri *et al.*, 2014; Chmielewská, 2014; Erdoğan and Ülkü, 2011; Wen *et al.*, 2006) while only few works deal with the implementation of such material in vertical flow treatment wetlands (Fournel, 2012; Ruiz *et al.*, 2016). Although Stefanakis and Tsihrintzis (2012) did not observe significant improvement in treatment performances by the use of clinoptilolite, ion exchange appears as a credible and cost effective way of system optimization (Alshameri *et al.*, 2014). Table 3 proposes a comparison of treatment performance reached by first stage vertical flow filters with the different design optimizations presented here above.

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Table 3 Treatment performance of first stage vertical flow filers with different design optimization (standard deviation is given between brackets)

Sources	System	COD				TKN			
		Inlet conc. ($mg.L^{-1}$)	Load in ($g.m^{-2}.d^{-1}$)	Outlet conc. ($mg.L^{-1}$)	Removal perf. (%)	Inlet conc. ($mgN.L^{-1}$)	Load in ($gN.m^{-2}.d^{-1}$)	Outlet conc. ($mgN.L^{-1}$)	Removal perf. (%)
Morvannou *et al.* (2015)	Classical first stage	589	218[(1)]	126 (90)	77 (14)	66	24[(1)]	27 (19)	59 (21)
Molle and Prost-Boucle (2012)	Recirculated first stage (rec. rate: 100%)	736 (240)	300	73 (7)	92	63 (18)	25	19 (3)	82
Foladori *et al.* (2013)	Intermittent aeration	438 (88)	64	52 (17)	88	71 (10)	10	20 (7)	72
Stefanakis and Tsihrintzis (2012)	Use of zeolite	510 (69)	140	134 (76)	74 (13)	61 (9)	16	25 (9)	59 (13)

[(1)] values are estimated from average concentrations and mean hydraulic load ($0.37 m.d^{-1}$)

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1.2 Biological routes of nitrogen removal in constructed wetlands

Nitrogen in domestic wastewater is mainly present as organic and ammonium forms coming from human faeces (urea and protein). The total Kjeldhal nitrogen (TKN) is the sum of these species. A production of 15gTKN.pe^{-1}.d^{-1} is released into wastewater (Mercoiret *et al.*, 2010). As organic nitrogen is partly or totally ammonified, by heterotrophic bacteria in the sewer network, most of the nitrogen reaching a treatment plant is under ammonium form.

Several processes achieve the transformation or the ultimate removal of nitrogen in constructed wetlands (see Figure 7). Some of them are of low influence (such as ammonia volatilization, nitrogen fixation or plant uptake) while others play an important role in nitrogen treatment (nitrification, denitrification and adsorption) (Meng *et al.*, 2014). Finally, new processes such as Anammox are new specific fields of research. Nitrification and denitrification are known to be the main processes occurring in constructed wetlands. This section aims to briefly describe these processes and to highlight the factors influencing their efficiency.

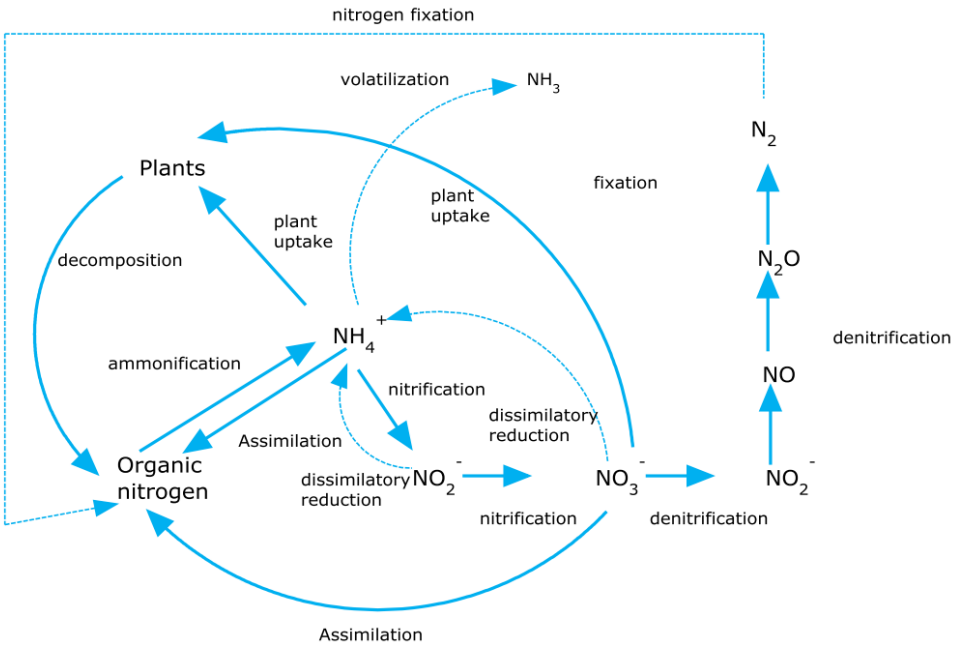

Figure 7 Major classical nitrogen removal routes in subsurface flow wetlands (Source: Saeed, 2012)

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1.2.1 Nitrification

1.2.1.1 Process description

Nitrification is the main process to remove ammonium from wastewater in constructed wetlands. This is also the preliminary step to achieve total nitrogen removal. Nitrification is a biological reaction transforming ammonium to nitrate under strictly aerobic conditions. This reaction is carried out in two successive steps by autotrophic bacteria:

The nitritation is the oxidation of ammonium into nitrite by ammonia oxidizing bacteria (AOB) such as *Nitrosomonas sp.*

$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+$ [Eq.1]

The nitratation produces nitrate from oxidation of nitrite by nitrite oxidizing bacteria (NOB) (e.g. *Nitrobacter sp.*)

$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$ [Eq.2]

This reaction uses oxygen as electron acceptor and carbonates as source of inorganic carbon. The total oxidation of 1g of NH_4-N consumes 4.18 g of oxygen (Chen *et al.*, 2006) and 4.31 g of HCO_3^- (Lee *et al.*, 2009). This reaction also produces 170 mg of biomass (stoichiometric estimation from [Eq. 3]) (Chen *et al.*, 2006), whose chemical formula is $C_5H_7O_2N$. Following equation sums up the global reaction of nitrification (Green *et al.*, 1998).

$NH_4^+ + 1.86\ O_2 + 1.98\ HCO_3^- \rightarrow 0.02\ C_5H_7O_2N + 1.04\ H_2O + 0.98\ NO_3^- + 1.88\ H_2CO_3$

[Eq.3]

1.2.1.2 Factors of influence

Based on a biological process, the oxidation of ammonium is affected by several parameters such as temperature, pH, organic matter, alkalinity, inhibitory compounds (Chen *et al.*, 2006 ; Lee *et al.*, 2009 ; Vymazal, 2007).

- Oxygen

The oxygen content is a controlling parameter of nitrification. Indeed, both successive reactions of nitritation and nitratation are oxygen dependent since this compound is consumed for bacterial respiration. Oxygen concentration higher than $1.5 mgO_2.L^{-1}$ is mandatory in order to perform nitrification (Liu *et al.*, 2013) and an almost total nitrification is achieved for

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oxygen availability over 4.2 – 4.5mgO_2/mgN-NH_4 (Saeed and Sun, 2012). Furthermore, NOB are more affected by oxygen limitation than AOM since oxygen saturation coefficients (K_s), according to Monod kinetic (see equation 4), are known to be 0.3 and 1.1 mgO_2.L^{-1} for nitritation and nitratation respectively (Jianlong and Ning, 2004). Low oxygen concentration may thus result in nitrite accumulation within the filter.

$$\mu_s = \mu_{max} \frac{s}{K_s + s} \qquad \text{[Eq.4]}$$

Where μ and μ_{max} are the specific growth rate and the maximum specific growth rate (d^{-1}) of the microorganism, respectively, s is the concentration (mg.L^{-1}) of the limiting substrate for growth and k_s is the half-saturation constant (mg.L^{-1}).

Since oxygen is consumed by both heterotrophic microorganisms and nitrifiers, its renewal in treatment facilities is of a major concern in order to avoid process limitation. This occurs by convection from the interface between the atmosphere and the biofilm surface in treatment wetlands. However the major mechanism of oxygen distribution in the system is diffusion. The gradient of oxygen partial pressure within the media is the driving force of such mechanism (Green *et al.*, 1998). The zero-order reaction model fits well with observation at high concentration of oxygen while half-order reaction model better describes the diffusion mechanism at lower concentration. The transition between both models depends on the fraction of support media which is covered by biofilm.

Passive or active aerations are often used in order to avoid oxygen limitation by increasing oxygen renewal of the treatment system. However, Green *et al.* (1998) observed that the distribution of oxygen is not uniform through the media in treatment wetlands and observed that oxygen content is higher in the immediate neighbourhood of aeration pipes than in furthest zones. Moreover, oxygen content decreases with depth in vertical flow filters.

- Alkalinity

Nitrification is a chemoautotrophic process. The oxidation of ammonium to nitrite is performed by strictly aerobic chemolithotrophic bacteria which consume CO_2 and bicarbonate, for the cell synthesis, and nitrogen to provide energy requirements (Lee *et al.*, 2009 ; Meng *et al.*, 2014). The second step of nitrification is executed by facultative chemolithotrophic bacteria which can use organic compounds as carbon sources. It is assumed that approximately 4.31 mgHCO_3^- is consumed per mg of ammonium nitrogen during its oxidation (Lee *et al.*, 2009). Alkalinity becomes rate limiting when calcium carbonate

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concentration ranges from 50 to 100mg.L^{-1} and strongly limits the process when concentration drops below 30mg.L^{-1} (Biesterfeld *et al.*, 2003). Zhang and Bishop (1996) proposed a ratio of alkalinity and dissolved oxygen of 5 above which nitrification is not affected while when this ratio drops below 3 the ammonium oxidation becomes limited.

- Organic matter

Competition between heterotrophic and autotrophic microorganisms for oxygen consumption leads to consider this parameter with attention. Indeed, heterotrophic metabolism is faster than the autotrophic one (Sun *et al.*, 1998). Consequently, an excessive amount of organic matter can highly disturb the oxidation of ammonium (Sun *et al.*, 2005).

The demand of oxygen can be summed up as follows (Molle *et al.*, 2005):

$$OD = COD + 4.57\ NH_4\text{-}N - 2.86\ NO_3\text{-}N \qquad [Eq.5]$$

Oxygen Demand (OD) and COD are expressed in $gO_2.m^{-2}.d^{-1}$ whereas units of ammonium and nitrate loads (NH_4-N and NO_3-N, respectively) are given in $gN.m^{-2}.d^{-1}$.

This characteristic directly impacts the growth of each community and contributes to the biofilm composition (Albuquerque *et al.*, 2009).

- pH

Microorganisms responsible for ammonium oxidation are sensitive to field conditions such as pH value. An optimum range of pH, between 6.6 and 8, is reported in literature. Hydrogen ions are toxic for microorganisms. It is supposed that this parameter can inhibit nitrification at pH equal to or below 5.7 (Biesterfeld *et al.*, 2003). This parameter impacts the growth rate of microorganisms and indirectly influences nitrification efficiency. Indeed, the enzyme responsible for nitrification seems to be activated or inactivated depending on the pH value.

- Temperature

An optimal range of temperature, comprised between 16.5 and 32°C has been reported by (Saeed and Sun, 2012). The efficiency of nitrification is increased by two to three times for every rise of 10°C in a range between 5 to 30°C (Jianlong and Ning, 2004).Temperature from 16.5 to 32°C is favourable to ammonium oxidation (Saeed and Sun, 2012) while low activities are observed at temperatures below 5°C or over 40°C (Hammer and Knight, 1994). For this reason, some variations between summer and winter performances can be expected (Ayaz *et al.*, 2012).

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In addition to biological considerations, temperature also affects mass transfer into the biofilm and the dissolved oxygen concentration (Zhu and Chen, 2002).

1.2.2 Denitrification

1.2.2.1 Process description

Denitrification is the main process ultimately removing nitrates in constructed wetlands (Hammer and Knight, 1994). This irreversible mechanism occurs under anoxic conditions at redox potentials ranging from +350 to +100mV (Kadlec and Wallace, 2009). This process, performed by heterotrophic facultative anaerobic microorganisms (whose main genera is *Pseudomonas sp.*), consumes organic matter and uses nitrate in their respiration mechanism. Nitrates are transformed by a four-step reaction (NO_3^- → NO_2^- → NO → N_2O → N_2) into gaseous inert nitrogen (Hamersley and Howes, 2002) which is released into the atmosphere. The reaction can be summed up as follow:

$$NO_3^- + 1.08\ CH_3OH + 0.24\ H_2CO_3 \rightarrow 0.056\ C_5H_7NO_2 + 0.47\ N_2 + 1.68\ H_2O + HCO_3^- \quad [Eq.7]$$

1.2.2.2 Factors of influence

- Oxygen content

Oxygen is one of the most controlling parameter of denitrification (Kjellin *et al.*, 2007) since nitrate competes with oxygen as electron acceptor in cell metabolism. Oxygen concentrations below 0.3 – 0.5 $mg.L^{-1}$ are required to perform nitrate reduction (Bertino, 2010). However, the limit in oxygen content is not clearly established. Hiscock *et al.* (1991) reported inhibition of denitrification at concentrations above 0.2 $mg.L^{-1}$ while other researchers did not observe limitation until 4.5 $mg.L^{-1}$. Since redox potential is closely connected with oxygen conditions (Ruano *et al.*, 2012), which is normally not present at redox potentials below +350mV (Seo and DeLaune, 2010), this parameter is useful in order to assess the potential to denitrify. Andalib *et al.* (2011) reported that denitrification occurs at redox conditions below -100mV while substantial amounts of nitrate and nitrite result in redox potential higher than -200mV.

- Organic matter

Denitrification is first and foremost an alternative way of organic matter degradation where organic carbon is used as electron donor. Therefore, the amount of available carbon (especially the easily biodegradable fraction) is a key factor of nitrate dissimilation. A theoretical requirement of 3.02g of organic matter is suggested by Kadlec and Wallace (2009)

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in order to reduce 1g $N\text{-}NO_3^-$. Low carbon availability leads to incomplete denitrification and nitrite accumulation (Ding *et al.*, 2012). Zhu *et al.* (2014) proposed an optimal C:N ratio of 5 whereas higher ratios do not significantly improve the denitrification performance. Strong correlation exists between denitrification potential and easily biodegradable organic matter (Her and Huang, 1995). Several studies have assessed the impact of adding different sources of carbon, such as glucose, acetate and plant material, resulting in improved performance (Hamersley and Howes, 2002; Kozub and Liehr, 1999; Leverenz *et al.*, 2010; Lu *et al.*, 2009). Although carbon supply proved to be beneficial for denitrification, the type of carbon source has its importance. A lower C:N ratio of easily biodegradable carbon than more complex compounds, such as aromatics, is required. Obviously, denitrification performances are better with easily assimilable carbon (Kjellin *et al.*, 2007).

Table 4 provides recommendations of exogenous carbon supply in order to perform full denitrification.

Table 4 Appropriate range of C/N ratio for nearly complete denitrification (Sources: Her *et al.*, 1995 and Degrémont, 1989**)**

Carbon source	Range substrate/N ratio (g/gNO_3-N)	BOD_5 supply (gO_2/g)
Methanol	2.7 – 2.7	1.0
Acetic acid	> 4	0.65
Glucose	> 5.0	0.6 – 0.8

Finally, high content of organic matter indirectly impacts the conditions of the system by consuming excess of oxygen for the oxidation of organic matter (Ding *et al.*, 2012; Nielsen *et al.*, 1990). Therefore, this parameter also enables to reach appropriate conditions for denitrification.

- Hydraulic retention time

Nitrate removal is limited by the kinetics of the denitrification process. Warneke *et al.* (2011) observed a linear decrease in nitrate concentration along the length (bed length of 176 m and samples spaced from 16 m each other) in a denitrifying horizontal flow filter whom retention time was estimated at 4.6d. This can be correlated with a longer retention time in the filter.

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Whatever the organic load, Ingersoll and Baker (1998) observed a drop in denitrification efficiency by increasing the hydraulic loading rate from 5 to 20 $cm.d^{-1}$. This decrease from 5 to 0.75 days of retention time led to worsen the removal performance of nitrate from 95% to 55%. Damaraju *et al.* (2015) also pointed out the impact of hydraulic retention time. They observed an improvement from 59.3% to more than 99% of nitrate removal by doubling the retention time from 4 to 8 hours in a bioreactor.

Molle *et al.* (2008) reported a good denitrification after 2 days of retention time in HFFs whereas Troesch *et al.* (2014) observed an almost complete nitrate removal in the saturated layer of VFFs after 1 day of contact time.

- pH

The optimal pH for denitrification activity ranges from 6 to 8, while the activity is slower at pH 5 and even absent below pH 4 (Vymazal, 2007).

- Temperature

Denitrification is temperature dependant since biomass growth is impacted by environmental conditions. It is reported that denitrification activity was detected only above 5°C in CWs (Meng *et al.*, 2014). Performances rise exponentially until 20 – 25°C where the reaction kinetics reach a threshold (Saeed and Sun, 2012). A doubling of removal rate is reported by Henze *et al.*, 2000 for an increase of temperature from 10°C to 20°C.

1.3 Physicochemical alternative for ammonium removal

Ammonium retention in the filter, thanks to specific material with chemical or physical sorption potential, is an interesting approach to make up for the low performances of ammonium removal by nitrification because of the kinetic limitations (see previously). Many materials, such as shale, fly ash, peat and zeolite, allow ammonium removal by entrapment onto the substrate. Among them, zeolite is the most studied.

1.3.1 Zeolite description

In 1756, the Swedish mineralogist Cronstedt observes for the first time a zeolite. Its name comes from greek "ζέω" (zeô) and "λίθος" (lithos) which significate "boil" and "stone" respectively. Indeed, zeolite seems to boil, when heated, because of a rapid loss of water.

Zeolite is a crystalline hydrated aluminosilicate of alkaline and alkaline-earth metals. Its general formula is $M_{x/n}[(AlO_2)_x(SiO_2)_y].zH_2O$. M is a metal (Na, K, Li and/or Ca, Mg, Ba,

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Sr); n is the cation charge; x, y and z depend on the type of zeolite[1]. The isomorphic substitution of silicium by aluminium leads to the formation of negative charges which are compensated by cations (Na^+, K^+, Ca^{2+}, Mg^{2+}). These cations are weakly bound and can be exchanged with other cations present in a water solution for example. This phenomenon calls an important notion, named "cationic exchange capacity" (CEC), which can be used as starting point in the assessment of material's ability for ammonium removal. The CEC is a theoretical value estimated from the amount of exchangeable cations in the material. The greater the substitution rate of silicium, the greater the need of cations for electrical neutrality.

The primary building unit (PBU) of its three dimensional framework is a tetrahedron formed by silicate (SiO_4^{4-}) and aluminate (AlO_4^{5-}) which are linked by shared oxygen atoms. The arrangement of these units reveals cages or a ring geometry which form a 3-D chain and layer of honey comb structures (some structure frameworks are shown in Figure 8). Consequently, zeolite is a porous material (internal porosity from 0.3 to 0.4) with an important specific surface area (up to $800 m^2.g^{-1}$). Moreover, the zeolite structure, fixed by its own geometry, exhibits small pore channels (ranging from 1Å to 20Å) which act as molecular sieves and confer a molecular selectivity (molecules which are small enough can penetrate into the channel and reach cavities where they will be sorbed). This particularity well explains the selectivity of zeolite for ammonium ions whose size is 2.86Å (Zhang and Bi, 2012). Examples of removal efficiency are given in Table 5.

a b c

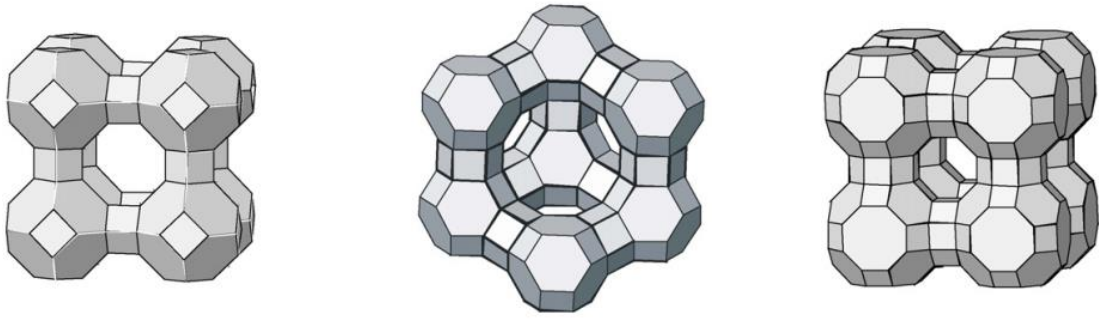

Figure 8 3D zeolite framework examples (zeolite A (a), zeolites X and Y (b) and zeolite Rho (c)). Note that the corner of each framework represent Si or Al which are linked by oxygen bridges (lines). (Source: Langmi and Mcgrady, 2007)

Numerous arrangements of PBUs and Si/Al ratios exist in nature and form different kinds of zeolites (more than 40) which are classified according to seven main families: Heulandite, Chabazite, Stilbite, Analcime, Gismondine, Natrolite and Harmotome. Moreover, synthetic

[1] y/x and z/x vary from 1 to 6 and 1 to 4 respectively (Wang and Peng, 2010)

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zeolite can be produced from natural materials which are rich in alumina and silica (clay for example) or with waste such as ash (Shoumkova, 2011).

Table 5 Example of adsorption capacity in different experimental conditions (batch)

Material	C_0 ($mgNH_4\text{-}N.L^{-1}$)	Solid:Liquid ratio (g:mL)	Exp. duration (h)	Particle size (mm)	Adsorption capacity ($mgNH_4\text{-}N.g^{-1)}$	Source
Chabazite	1500	1:80	336	0.15/0.21 (0.18)	32.2[a]	Leyva-Ramos *et al.*, 2010
Chabazite-Na	1500	1:80	336	0.15/0.21 (0.18)	37.2[a]	Leyva-Ramos *et al.*, 2010
Clinoptilolite	10	1:100	133.3	2/0.85	9.47[a]	Erdoğan and Ülkü (2011)
Clinoptilolite	400	1:100	48	0.83/1.7	10.53	Zhang and Bi (2012)

[a] maximum sorption capacities are determined from Langmuir isotherm model

1.3.2 Mechanisms of ammonium removal

One asset of zeolite, considering wastewater, is its high selectivity for ammonium molecule. Several authors assessed the selectivity ranking of different zeolites for water treatment. Barrer *et al.* (1969) proposed a range of selectivity of chabazite ($Tl^+ > K^+ > Ag^+ > Rb^+ > NH_4^+ > Pb^{2+} > Na^+ = Ba^{2+} > Sr^{2+} > Ca^{2+} > Li^+$) while others authors (Ames Jr., 1960) suggested another range of affinity for clinoptilolite ($Cs^+ > Rb^+ > NH_4^+ > Ba^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$). Besides the few differences in ranking, it appears that zeolite has less affinity with major cations present in wastewater, apart from potassium, than with ammonium. Several characteristics of the ions in solution lead to stronger or weaker exchange ability. Monovalent ions are more easily exchanged than polyvalent ones. That can probably be explained by the fact that it is easier to release one cation in order to fix another instead of two for one.

Because of its structure, zeolite acts as a molecular sieve through its small pores (macropores and micropores). Consequently, the hydrated radius is also a limiting factor for ion exchange. Only ions which are small enough can interact with internal sites (from 1Å to 20Å). The conception of synthetic zeolite can aim to adjust the selectivity of the material for a specific ion to exchange. The values of channel dimension of several zeolites are listed in Table 6a.

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Table 6 Channel dimension of different natural and synthetic zeolites (a) (Source: Shoumkova, 2011) and Table of ionic radii (b) (Source: Tansel, 2012)

a

Zeolite	Channel dimension (Å)
Chabazite	3.7 x 4.2
Clinoptilolite	3.9 x 5.4
Mordenite	2.9 x 5.7
NaX[1]	7.4
NaP1[1]	2.6
NaA[1]	4.2

[1] Synthetic zeolite

b

Ion	Unhydrated radius (Å)	Hydrated radius (Å)
Na^+	0.98 - 1.17	2.76 - 3.6
K^+	1.33 - 1.59	2.01 - 3.31
NH_4^+	1.48 - 1.61	3.31
Ca^{2+}	1.00 - 1.23	4.12 - 4.2
Mg^{2+}	0.57 - 0.72	3.00 - 4.7

Moreover ions with smaller hydration energy are easier to exchange. Table 6b summarizes the size of common cations in wastewater. These values show that calcium and magnesium are bigger than ammonium, potassium and sodium. This partly explains the higher selectivity of zeolite for the latter.

On the other hand, ammonium also exhibits an affinity ranking with some exchangeable cations. Indeed, Watanabe *et al.* (2003) observed that, in clinoptilolite, Na^+ is more exchanged than K^+, then Ca^{2+} and finally Mg^{2+}. Huang *et al.* (2010) noted a predominance of Na^+ to be exchanged with ammonium.

The intrinsic characteristics of zeolite also influence its reactivity. Thus, zeolite with high Al/Si ratio will be hydrophilic and present a good affinity for polar molecules while zeolites with low rate of substitution are hydrophobic and easily react with hydrocarbons. Moreover, ion exchange capacity increases with the increase of alkaline metals while the amount of earth alkalines does not impact the performances (Lebedynets *et al.*, 2004).

Basically this process is based on two mechanisms occurring in parallel: the ion exchange and the surface adsorption in pores of the structure, which are chemical and physical sorption processes respectively. Nevertheless, depending on the operational conditions (solid to liquid ratio), one of these mechanisms prevail over the other Ivanova *et al.* (2010).

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Ion exchange is considered as the main process allowing the removal of ammonium from water by zeolite (Wang and Peng, 2010). Sprynskyy *et al.* (2005b) underlined that the ion exchange process prevails when the concentration of cations to exchange in the liquid phase is equal or lesser than the amount of solid's exchangeable cations. The sorption process becomes more important when this ratio is exceeded.

The following section aims to describe both processes of ion exchange and surface adsorption.

1.3.2.1 Ion exchange

The ion exchange consists of the replacement of weakly bound cations on the zeolite by others which are present in the liquid phase. This process relies on the equilibrium between the amount of cations in solution and the amount in the solid phase. This is an isomorphic process which can be illustrated by the following equation:

$$Z_B \times A^{Z_A^+} + Z_A \times BL_{Z_B} \leftrightarrow Z_A \times B^{Z_B^+} + Z_B \times AL_{Z_A} \qquad \text{[Eq.9]}$$

A is a cation present in bulk solution and B is a cation weakly bonded to zeolite. Z_A^+ and Z_B^+ are the valence of the respective cations. L is a portion of zeolite framework holding a negative charge.

It is documented that the ion exchange process involves five steps (Cooney and Booker, 1999):

(1) Diffusion of the counterions through the film to the surface of the material: film diffusion
(2) Diffusion of the counterions within the solid: intraparticle diffusion
(3) Chemical reaction between the counterions and the ion exchange sites
(4) Diffusion of the removed ions within the solid
(5) Diffusion of the removed ions from the solid surface to the bulk solution

It is admitted that the slowest step controls the process and is the rate-limiting step. This process is mainly driven by the diffusion phenomenon. Two kinds of diffusion can be distinguished (see Figure 9):

Film diffusion (process ① in Figure 9a): an important amount of ammonium is present in solution, around the zeolite particle. This concentration can be considered as constant during

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water infiltration. A static layer of solution, which is called Nernst diffusion layer, is created around the particle. Ammonium and counter-ions diffuse through this liquid film according to the Fick's law which assumes that the diffusion flux is proportional to the concentration gradient. Therefore, the kinetics of diffusion are related with the external concentration of ammonium and the amount of ammonium in the diffusion film. Indeed, ammonium concentration will increase into the Nernst diffusion layer and a gradient of concentration will be established between itself and the solution. Consequently, the higher the solution concentration, the quicker the diffusion. The thickness of this film is known to be inversely proportional to flow velocity. The modelling of such process is further described in section 1.3.5.

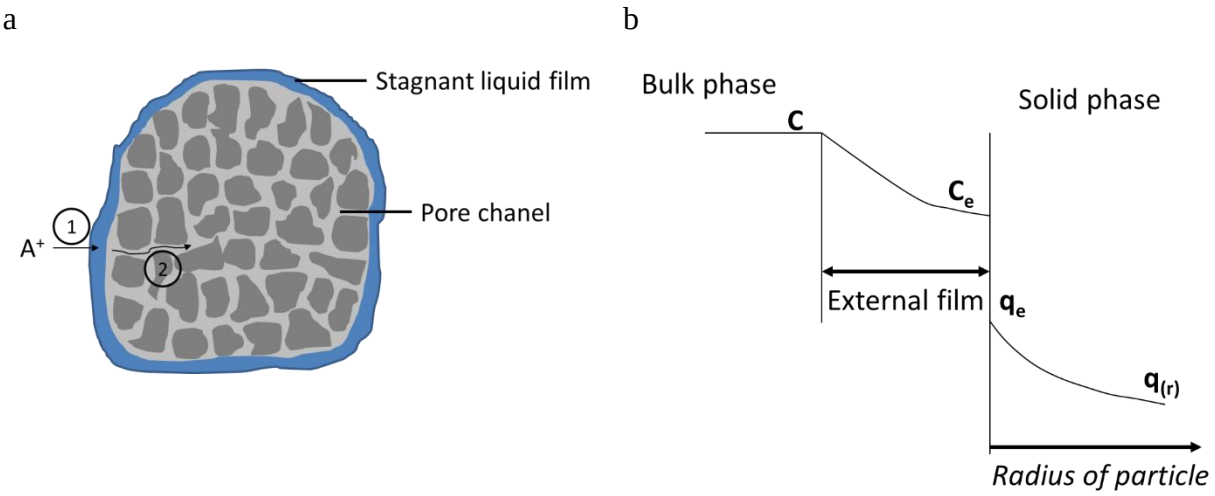

Figure 9 Description of ion exchange process' regulating mechanisms (a) and dynamic of ion concentration (b)

Particle diffusion (process ② in Figure 9a): this is the transport of ammonium and counter-ions within the porous structure of the particle (macro, meso and micropore structure). The pore diameter must also be considered since zeolite acts as a molecular sieve. The inner structure varies between zeolite types and confers variable selectivity for ammonium.

Film and intraparticle resistances are minimized when operational conditions are optimized. It results in thin external film and negligible steric resistance of the sorbate in the particle pores (Barros *et al.*, 2013).

1.3.2.2 Adsorption

The adsorption process is a surface interaction between molecules, which are present in the sorbate, and a solid material (sorbent). This phenomenon does not affect the solid structure

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and is a reversible process. Contrarywise to the ion exchange process, adsorption is not a stoichiometric process. This mechanism implies low energy bonding such as van der Waals forces, electrostatic interactions, Π-Π and hydrogen forces (Erdoğan and Ülkü, 2011).

1.3.3 Parameters influencing the process

❖ Inlet concentration

A key parameter of the sorption process is the difference between ion amount in solution and in solid phase. A higher ammonium concentration leads to increase the amount of adsorbed ammonium on the solid at equilibrium (q_e in $mg.g^{-1}$). Indeed, higher ammonium concentration in the liquid phase provides at larger driving force which enables the ion to reach and react with the internal structure of zeolite (Widiastuti *et al.*, 2011). Consequently, an improvement of sorption capacity is observed when the initial concentration of ammonium increases (Erdoğan and Ülkü, 2011). Nevertheless, the adsorbed mass of ammonium at equilibrium reaches a threshold (q_{max}) beyond a certain concentration. This value corresponds to the maximum adsorption capacity of the considered material, when all exchangeable ions have been removed.

Based on equilibrium between the amount of ammonium sorbed on the zeolite and the amount in solution this process is sensitive to variations in operating conditions. Thus, a drop in concentration can adversely affect the system by a shift in the mechanism which causes discharge of ammonium (Miladinovic and Weatherley, 2008).

Although equilibrium sorption capacity is positively affected by increasing sorbate concentration, Malekian *et al.* (2011) reported a lesser spontaneity of the ion exchange process for high concentrations of ammonium. Too much sorbate thus results in decreasing the equilibrium exchange capacity.

❖ Contact time

Increasing the contact time between sorbate and material improves the ion diffusion into the zeolite porosity and leads to better performances. However, gains are low considering performances improvement versus increase of contact time. Saltali *et al.* (2007) reported that most of adsorption was achieved after 15 – 30 minutes of reaction.

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❖ Particle size

Smaller particle sizes present higher surface areas. Consequently, decreasing the grain size leads to increase the fraction of active sites located at the surface of the material. The equilibrium capacity remains the same but a smaller part of this capacity is dependent of intra-particle diffusion (Erdoğan and Ülkü, 2011). This enables better performances for short contact time between effluent and solid. Several authors reported higher performances with the use of small particles compared to coarser ones (Hedström and Rastas Amofah, 2008; Wen *et al.*, 2006). This can be partly explained by an easier accessibility to internal structure of micropores with fine particles. This is confirmed by the observation from Sprynskyy *et al.* (2005a) which reveals an impact of size particle at higher flow rates while none at low flow rates. Therefore, we can conclude that smaller size of particles enables to facilitate the particle diffusion when contact time is limited.

However, the implementation of fine particles in water treatment systems leads to increase head losses (Hedström and Rastas Amofah, 2008). Therefore a compromise between retention time and particle size must be found.

❖ Other cations in solution

The presence of other cations can induce, to a certain extent, a decrease in ammonium removal through competition for exchange. A ranking in affinity of each cation with zeolite is established considering their sterical hindrance and load.

The practical adsorption capacity decreases when wastewater instead of ammonium solutions is filtered through the column: probably due to competition with other ions (Hedström and Rastas Amofah, 2008).

❖ pH

Ammonium uptake by zeolite is dependent on pH value. This parameter disturbs the process in two different ways. First of all, low pH is correlated with acidity and, consequently, presence of hydronium ions. A competition could exist between this ion and ammonium (Erdoğan and Ülkü, 2011). Another impact of pH is related to the two forms of ammonium (molecular and ionic forms). Indeed, the zeolite only allows the removal of the ionic form by ion exchange (Miladinovic and Weatherley, 2008). Beyond pH 9.2, the ammonia form (NH_3) predominates and leads to quick decrease in ammonium removal (Huang *et al.*, 2010). However, pH of wastewater is usually lower than this limit. The optimal pH of operation is

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not well established. Several studies deal with the impact of this parameter on ammonium adsorption by different types of zeolite. For example Saltali *et al.* (2007) reported an optimal pH range of operation between 4 and 8 with a maximum at 8 for a material composed of clinoptilolite, heulandite and mordenite. Leyva-Ramos *et al.* (2010) determined an optimal pH around 6 to perform ammonium removal by chabazite while Widiastuti *et al.* (2011) observed a maximum removal rate at pH 5 for a material containing clinoptilolite and mordenite. Nevertheless, all authors conclude that neutral pH is a suitable operational target.

Beyond its impact on process performances, the pH can also affect structural integrity of the material. For example, Huang *et al.* (2010) observed a partial dissolution of zeolite at pH above 9 while Sprynskyy *et al.* (2005b) reported an important decrease in performances after acidic treatment of zeolite because of structural alteration by aluminium removal from the material.

- Zeolite composition

Beyond the zeolite's substitution rate which determines its theoretical exchange capacity, its chemical composition is an important parameter to remove a specific ion. Every natural zeolite has individual properties due to their mineralogical and chemical composition (Ivanova *et al.*, 2010). Therefore individual assessment has to be carried out.

The cations of substitution are of a great concern for the process performances. Their type, their size and their place in the lattice, their ionic potential and the hydration energy determine the zeolite's properties (Ivanova *et al.*, 2010).

Zeolite mostly composed of sodium has been evaluated as the more efficient to treat ammonium (Hedström and Rastas Amofah, 2008). Leyva-Ramos *et al.* (2010) compared a natural chabazite and two homoionic pre-treated Na-chabazite and K-chabazite. An important improvement was recorded by the use of Na-chabazite (40%) while a drop in performances (37%) was noted for ammonium removal by K-chabazite. The study of ammonium adsorption on pre-treated Na- and K-chabazites in dynamic conditions also reveals a lag in the breakthrough for Na^+ substituted chabazite compared to the K-chabazite (Lahav and Green, 1998).

Moreover, the zeolite substitution rate is of a great importance in ammonium removal performances since aluminium ions provide the exchange sites. Leyva-Ramos *et al.* (2010) compared both chabazite and clinoptilolite exchange capacity. They observed a chabazite

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exchange capacity 43% higher than the clinoptilolite's one. The Si/Al ratio was directly linked with this observation.

❖ Amount of zeolite

The ion exchange process is based on equilibrium between the amount of cation adsorbed onto the zeolite and its amount in solution. Therefore, the increase of zeolite enables to increase the amount of cations adsorbed on the solid. Karadag *et al.* (2007) assessed several solid:liquid ratios from 0.2:50 to 1.5:50 (g:mL) at low ammonium concentration (20mgN.L^{-1}). Beyond 1:50 ratio, they did not observe further increase in removal performances. Ivanova *et al.* (2010) conducted similar experiment with clinoptilolite for concentrations on ammonium ranging from 60 to 800mgN.L^{-1} and solid:liquid ratio from 0.125:50 to 1.875:50. They found an impact of this ratio only for the low concentrations. Nevertheless, according to the current concentrations which are observed in wastewater, this parameter should be taken into account.

❖ Temperature

The impact of temperature is not well established. Whereas one of the positive arguments for ion exchange is its insensitivity to temperature conditions, some authors reported variations in performances for different temperatures. For example, Erdoğan and Ülkü (2011) observed a decrease in performances with increasing temperature. On the contrary, Karadag *et al.* (2007) did not observe any significant difference in performances by increasing the temperature from 30°C to 40°C.

❖ Organic matter

Zhang and Bi (2012) assessed the impact of humic acid (HA) on ammonium removal by Clinoptilolite. A decrease in performances was observed by adding HA at a concentration of 10mg.L^{-1}. The initial sorption rate dropped from 4.99 to 2.95 mg.g^{-1}.h^{-1}. Nevertheless, further increase in HA concentration does not significantly impact the process. This can be explained by adsorption of ammonium directly onto organic matter at the zeolite surface. However, the difference is not significant regarding q_{max}.

1.3.4 Industrial dynamic applications

Most of studies dealing with the sorption capacity of zeolite and describing the effects of operational conditions on the removal efficiency usually rely on static batch scale experiments (Huang *et al.*, 2010a; Erdoğan and Ülkü, 2011). They have suggested the high potential of removal of ionic substances, such as heavy metals and ammonium, by zeolite. This

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characteristic might find applications in various fields of treatment, such as drinking water, sanitation or treatment of complex influents (e.g. mining leakage), and has been extensively studied from several decades. However, although batch scale experiments allow the rapid assessment of material capacity and the relationships between performance and environmental and operational conditions (i.e. contact time, pH, temperature, substrate concentration, …), they only provide poor information on the real behavior of zeolite for specific industrial applications.

The switch from batch scale experiments to full size applications thus requires intermediate lab scale monitoring. Several column experiments (Malovanyy *et al.*, 2013; Nguyen and Tanner, 1998; Sprynskyy *et al.*, 2005a) reported high removal of ammonium under continuous feeding and saturated dynamic conditions while, marginally, others applications, such as supply of powder of zeolite in sequential batch reactors (Jung *et al.*, 2004) or use of zeolite under free drainage conditions (Stefanakis and Tsihrintzis, 2012a), showed variable successes. These studies pointed out that the effects of design and operational parameters were similar to the ones reported from batch scale experiments (e.g. contact time, influent concentration) (Note that Table 7 proposes a summary of these effects). The challenge for the use of zeolite for water treatment under dynamic conditions therefore relies on the optimization of settings for an efficient sorption. Besides the effect on ammonium concentration (Li *et al.*, 2011), several authors reported high removal during long operational periods (Chmielewská, 2014; Cooney and Booker, 1999; Miladinovic and Weatherley, 2008). Nevertheless they pointed out the strong limitation of contact time, between the sorbent and the sorbate (Nguyen and Tanner, 1998), which appears as the main limitation under dynamic conditions. Very low flow rate is thus required in order to optimize the sorption process what may be detrimental for industrial application. This constraint may be overstepped by the implementation of finer material which may enable to increase the external surface and thus improve the kinetic of sorption (Nguyen and Tanner, 1998). However, it must be remind that the implementation of fine material increases the risk of head losses and clogging.

Finally, restoration of sorption capacity, after complete exhaustion of the system, is another big issue. The usual method consists in chemical regeneration with highly alkaline concentrated brine which allow desorption of ammonium. A highly concentrated solution of ammonium is thus obtained and still must be treated. Furthermore, continuous operation requires the implementation of several parallel units in order to continue the treatment while exhausted systems are regenerated (Bochenek *et al.*, 2011). Although highly efficient, the

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constraining operation of such treatment systems thus mitigates the conclusion on industrial application of zeolite material.

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Table 7 Summary of the effect of operational parameters on sorption process

Reference	Scale	Material	Operational conditions	Variable	Observations and conclusions
Influent concentration					
Erdoğan and Ülkü, 2011	Batch	Clinoptilolite 0.85-2.00mm	solid:liquid ratio = 1g:100mL pH = 7 T = 25°C t = 132h	$[NH_4\text{-}N]$ = 10, 100 and 300mg.L^{-1}	q_e = 0.8[a], 7.1[a] and 9.0[a] mgN.g^{-1}, respectively ➲ Equilibrium capacity increases with influent concentration
Widiastuti *et al.*, 2011	Batch	Clinoptilolite	solid:liquid ratio = 1g:100mL t = 8h T = 25°C	$[NH_4\text{-}N]$ = 3.9 and 38.9mg.L^{-1}	q_e = 0.4[a] and 3.0[a] mgN.g^{-1}, respectively ➲ Equilibrium capacity increases with influent concentration
Contact time					
Huang *et al.*, 2010	Batch	Heulandite 0.2-0.3mm	solid:liquid ratio = 2.4g:100mL $[NH_4\text{-}N]$ = 62mg.L^{-1} pH = 8 T = 27°C	t = 0 – 5h	Performance of 67%[a], 80%[a] and 84%[a] after 0.25, 1 and 5h, respectively ➲ Positive effect of contact time ➲ Fast initial removal then slower removal
Ji *et al.*, 2007	saturated column	Clinoptilolite 0.42-0.97mm m = 1440g	$[NH_4\text{-}N]$ = 66mg.L^{-1}	Flow rates = 10, 40 and 70 mL.min^{-1}	$[NH_4\text{-}N]_{out}$ = 4.3 and 6.5mg.L^{-1}, respectively (after 7 BV[b]) ➲ Adverse effect of short contact time
Malovanyy *et al.*, 2013	Saturated column	Clinoptilolite 0.71-1.00mm 27.3g	$[NH_4\text{-}N]$ = 40mg.L^{-1}	Flow rates = 8.1 and 14.8mL.min^{-1}	$[NH_4\text{-}N]_{out}$ = 2mg.L^{-1} after 197 and 96BV, respectively ➲ Adverse effect of short contact time
Grain size					
Nguyen and Tanner, 1998	Saturated column	Mordenite 253g	$[NH_4\text{-}N]$ = 100mg.L^{-1} Flow rate = 7.8mL.min^{-1}	Grain size = 0.25-0.50 and 2.00-2.83mm	$[NH_4\text{-}N]_{out}$ = 2[a] and 48[a] mg.L^{-1} after 23BV, respectively ➲ Big grain are less efficient at fast flow rate since diffusion into grain is limited

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Reference	Scale	Material	Operational conditions	Variable	Observations and conclusions
Huang *et al.*, 2010	Batch	Heulandite	solid:liquid ratio = 2.4g:100mL $[NH_4\text{-}N] = 62mg.L^{-1}$ pH = 8 t = 0.25h T = 27°C	Grain size = 0.074-0.125 and 0.2-0.3mm	Performance of 67% and 81%, respectively, after 0.25h ➲ Initial sorption kinetic is faster with small particles
Ivanova *et al.*, 2010	Batch	Clinoptilolite	solid:liquid ratio = 1g:100mL $[NH_4\text{-}N] = 196.8mg.L^{-1}$ t = 5h T° = 25°C	Grain size = 1.00, 1.25, 1.60, 2.00mm	Slope of the linearized kinetic curve increases from 0.0187 to 0.0449 when particle size increases from 1 to 2mm q_e is similar for all particle size ➲ Kinetic is faster for small particles ➲ Capacity is similar whatever the size of particles
Other cations					
Huang *et al.*, 2010	Batch	Heulandite 0.2-0.3mm	solid:liquid ratio = 2.4g:100mL $[NH_4\text{-}N] = 62mg.L^{-1}$ pH = 8 t = 3h T = 27°C	$[K^+] = 0 – 250mg.L^{-1}$	Performance drops from 95%[a] to 83%[a] when $[K^+]$ increases from 0 to $250mg.L^{-1}$ ➲ Range of selectivity
Malekian *et al.*, 2011	Batch	Clinoptilolite 0.2-0.8mm	solid:liquid ratio = 1g:30mL $[NH_4\text{-}N] = 90mg.L^{-1}$ t = 2h T = 25°C	$[Na^+] = 690 – 6900mg.L^{-1}$	Performance drops from 89%[a] to 45%[a] when $[Na^+]$ increases from 690 to $6900mg.L^{-1}$ ➲ Range of selectivity
pH					
Widiastuti *et al.*, 2011	Batch	Clinoptilolite	solid:liquid ratio = 1g:100mL $[NH_4\text{-}N] = 38.9mg.L^{-1}$ t =8h T = 25°C	pH = 2 – 10	Performance of 10%[a], 50%[a] and 12%[a] at pH values of 2, 5 and 10, respectively ➲ Ionic form of ammonium prevails at pH < 9.25 ➲ Highly acidic pH degrade zeolite structure
Huang *et al.*, 2010	Batch	Heulandite 0.2-0.3mm	solid:liquid ratio = 2.4g:100mL $[NH_4\text{-}N] = 62mg.L^{-1}$ t = 1h T = 27°C	pH = 4 – 9	Performance of 81%[a], 83%[a] and 79%[a] at pH values of 4, 8 and 9, respectively ➲ Ionic form of ammonium prevails at pH < 9.25

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Reference	Scale	Material	Operational conditions	Variable	Observations and conclusions
Zeolite characteristics					
Chmielewská, 2014	Saturated column	Clinoptilolite 0.3-0.8mm	$[NH_4\text{-}N] = 2.5 mg.L^{-1}$ Flow rate = $150 mL.min^{-1}$	regeneration with 2% NaCl	Breakthrough after 28[a] and 50[a] BV for native and regenerated homo-ionic zeolite. ➲ Homo-ionic Na-form is more effective than native multi-species form
Ivanova *et al.*, 2010	Batch	Clinoptilolite 1.25mm	liquid:solid ratio = 1g:100mL $[NH_4\text{-}N] = 196.8 mg.L^{-1}$ t = 2h T = 25°C	Modification under homo-ionic form (Ca^{2+} or K^+)	q_e = 6.1[a], 3.8[a] and 7[a] $mgN.g^{-1}$ for native, Ca-enriched and K-enriched forms, respectively ➲Homo-ionic may improve capacity but it depends on the nature of exchangeable cation
Amount of zeolite					
Widiastuti *et al.*, 2011	Batch	Clinoptilolite	$[NH_4\text{-}N] = 3.9 mg.L^{-1}$ t =8h T = 25°C	solid:liquid ratio = 0.5g:100mL to 3g:100mL	q_e drops from 0.8[a] to 0.18[a] $mgN.g^{-1}$ when solid:liquid ratio increases from 0.5g:100mL to 3g:100mL ➲ For constant applied load q_e is lower but also does C_e: load per mass unit is lower
Ivanova *et al.*, 2010	Batch	Clinoptilolite 1.25mm	$[NH_4\text{-}N] = 196.8 mg.L^{-1}$ t = 2h T = 25°C	solid:liquid ratio = 0.25g:100mL to 3.75g:100mL	q_e drops from 9.6[a] to 5.9[a] $mgN.g^{-1}$ when solid:liquid ration increases from 0.25g:100mL to 3.75g:100mL ➲ For constant applied load q_e is lower but also does C_e: load per mass unit is lower
Temperature					
Saltali *et al.*, 2007	Batch	Clinoptilolite 0.075mm	solid:liquid ratio = 2g:100mL $[NH_4\text{-}N] = 46.7 mg.L^{-1}$ t = 0.5 pH = 8	T = 21 – 50°C	Performance decreases from 94%[a] to 92%[a] when temperature increases from 21 to 50°C ➲ Very low effect (temperature increases tendancy to desorb)
Erdoğan and Ülkü, 2011	Batch	Clinoptilolite 0.85-2.00mm	solid:liquid ratio = 1g:100mL pH = 7 T = 25°C t = 132h	T = 25 and 40°C	q_e decreases from 0.95[a] to 0.90[a] $mgN.g^{-1}$ when temperature increases from 25 to 40°C ➲ Suggest exothermic process which is favored at low temperature

[a] Graphically determined and [b] BV means Bed Volumes

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1.3.5 Modelling of sorption process

The composition of effluent over time depends on the sorbent characteristics, the effluent composition and the operational conditions (Barros *et al.*, 2013). Accurate modelling tools are therefore a suitable design support tool for engineers in order to assess effluent characteristics in relation to design and operational criteria.

Both equilibrium and kinetic knowledge are required for such predictive tools (Barros *et al.*, 2013). The following sections propose a non-exhaustive discussion of these models.

1.3.5.1 Equilibrium representation

The amount of adsorbed cations, at equilibrium, depends on the influent concentration. Several models, so called sorption isotherms, aim to represent the sorption process under static conditions. Such models characterize the equilibrium relationship between the amount of fixed ions onto zeolite and its equilibrium concentration in the solution after reaction. The equilibrium concentration at a given state of saturation of the material and the maximum sorption capacity for a considered zeolite can be predicted from these models. An example of sorption isotherm of ammonium onto zeolite is presented Figure 10.

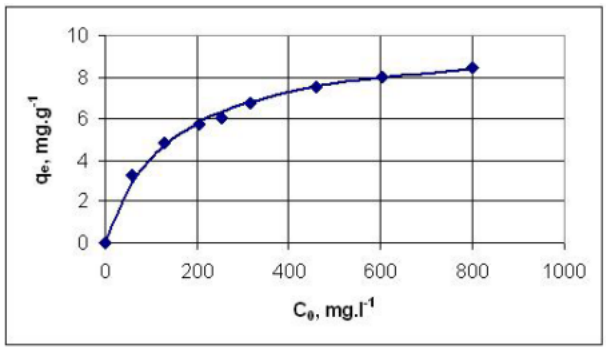

Figure 10 Adsorption isotherm of ammonium ion on a natural clinoptilolite (Source: Ivanova *et al.*, 2010)

The two most famous are the Freundlich and the Langmuir isotherm models. The first one assumes a heterogeneous surface with non-uniform distribution of independent and non-equivalent sorption sites. On the contrary, the Langmuir model is based on the assumption of a homogeneous monolayer adsorption within equivalent sorption sites. Numerous studies have been conducted with the conclusion that the Langmuir isotherm model is the most suitable in order to describe ammonium removal by zeolite (Wang and Peng, 2010;

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Shoumkova, 2011 ; Erdoğan and Ülkü, 2011 ; Malekian *et al.*, 2011) since it takes limitations, such as monolayer adsorption, into account.

The Langmuir model equation is given below:

$$q_e = \frac{q_m.b.C_e}{(1+b.C_e)} \quad \text{[Eq.10]}$$

where q_m is the maximal monolayer adsorption capacity ($mg.g^{-1}$) and b is the coefficient of Langmuir isotherm ($L.mg^{-1}$).

The isotherm parameters can be graphically determined by linearization (Bolster and Homberger, 2007).

The determination of a separation factor R_L based on values from the Langmuir isotherm is of a particular interest. This parameter gives information about the ability to perform the adsorption. There are four possibilities: $R_L = 0$, $R_L = 1$, $R_L > 1$ or $R_L < 1$ (Irreversible, linear, unfavourable and favourable, respectively (Malekian *et al.*, 2011)).

$$R_L = \frac{1}{1+b.C_0} \quad \text{[Eq.11]}$$

Where C_0 is the initial concentration of exchangeable cations in $mg.L^{-1}$

Ivanova *et al*. (2010) reported values from 0.09 to 0.57 indicating a favourable mechanism of ammonium adsorption onto clinoptilolite.

Although the Freundlich model and the Langmuir models are widely used in practice, several other numerical tools for prediction of performances exist. Among them the Redlich-Peterson and the Langmuir-Freundlich fit better with experimental data (Malekian *et al.*, 2011). Nevertheless they are less studied since they implement three parameters instead of two for both Langmuir and Freundlich models which makes them less convenient in practice.

It must be noticed that most studies are dealing with sorption isotherms obtained under batch tests. However, Kleinübing and Silva (2008) reported that dynamic equilibrium was different than static conditions. Dynamic column isotherms must thus be favored to static batch isotherms.

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1.3.5.2 Kinetic models

Several kinetic models were developed in order to correctly describe the controlling parameters in the adsorption process.

First order and second order models describe the dynamics of fluid concentration over time whereas pseudo-first order and pseudo-second order models are based on the dynamics of adsorbed load onto zeolite (Ho, 2006). These models are simple expressions of concentration in relation to a kinetic constant and lump all diffusion mechanism through one simple equation. Numerous studies (Arslan and Veli, 2012 ; Huang *et al.*, 2010a ; Kučić *et al.*, 2013) reported that pseudo-second order kinetics provide the best fitting with experimental data for ammonium sorption onto zeolite. Figure 11 shows fitting of pseudo-second order kinetic model with batch experimental data.

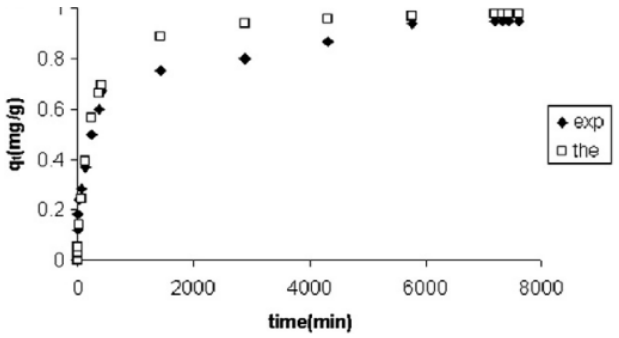

Figure 11 Comparison of experimental and theoretical data for pseudo-second order model (Source: Erdoğan and Ülkü, 2011**)**

However, under dynamic operational conditions, the sorption process is affected by film and intraparticle diffusion resistances as well as axial dispersion (Babu and Gupta, 2004). More complex mechanistic models, such as double resistance model, were developed in order to properly describe the relative effect of each mechanism. Several authors (Bochenek *et al.*, 2011 ; Lee and Kim, 2003 ; Ostroski *et al.*, 2014 ; Siahpoosh *et al.*, 2009) reported successful description of sorption process by mechanistic models.

Nevertheless, mechanistic models are mathematically complex (differential equation-based model) and require knowledge of various parameters. Empirical models (Bohart-Adams, Thomas or Yoon-Nelson models, for example (Trgo *et al.*, 2011)) were thus developed in order to properly describe dynamic systems with more simple numerical tools. Such models assume that film and intraparticle diffusions are negligible and that no dispersion phenomenon occurs within the column (Barros *et al.*, 2013). The Thomas model is one of the most widely used model and showed suitable application on description of sorption dynamics

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(Mahendra *et al.*, 2015 ; Zheng *et al.*, 2008). This model, based on Langmuir isotherm and second order reversible reaction kinetics, makes the assumption that no dispersion occurs within the system.

1.3.5.3 Breakthrough curve

Design and operational characteristics of sorption systems rely on the breakthrough curve (Babu and Gupta, 2004). This curve is based on equilibrium of sorption (isotherms) and transport mechanisms (kinetics) (Lee and Kim, 2003). This is a representation of effluent concentration dynamic during operation. Effluent concentration indeed varies over time but also according to location within the filtration bed. A mass transfer zone (MTZ), where most of removal is performed, is moving along the filtration depth as material is progressively saturated. Breakthrough (t_b in Figure 12) occurs when MTZ is close to the outlet and effluent concentration becomes higher than 5% of influent concentration. Saturation is reached when effluent concentration is higher than 95% of influent concentration (Barros *et al.*, 2013).

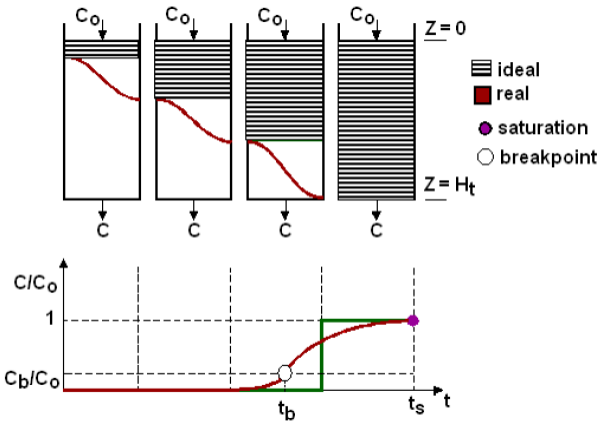

Figure 12 Description of MTZ dynamic and breakthrough curve (Source: Barros *et al.*, 2013)

Ideal operational conditions are characterized by a long period before breakthrough occurs and a short period between the breakthrough and total exhaustion of sorbent.

1.3.6 Regeneration

During operation, the zeolite exchange capacity progressively decreases until reaching a partial fouling which is characterised by breakthrough. The treatment thus becomes inefficient and material needs to be replaced or regenerated. Considering both costs of operation and costs of investment, the second pathway is usually the most appropriate ones. Several processes allow the restoration of exhausted systems, in different degrees of effectiveness, by the regeneration of saturated media.

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1.3.6.1 Chemical regeneration

Based on the equilibrium between the amount of a given cation, adsorbed onto the solid, and its concentration in the bulk solution, ammonium could theoretically be desorbed by washing the system with tap water. Hedström and Rastas Amofah (2008) assessed this way of regeneration for a fouled zeolite. They observed a weak regeneration (17% of total adsorbed nitrogen) after 48h. The use of chemicals seems thus more suitable for high rate regeneration over a short regeneration period.

The chemical regeneration process is probably the easier method to carry out. This method of regeneration consists in replacing the adsorbed ammonium by another cation. This is most often operated by washing the media with solution of sodium chloride at concentrations ranging from 0.1 to 0.6M. The cations are fixed onto zeolite and ammonium is released in the brine. Such operation can be conducted under both downflow and upflow conditions. The use of sodium is more suitable than calcium since calcium risks to be permanently adsorbed and thus decreases the exchange performances.

A parallel supply of sodium hydroxide enables to increase the pH and turn the ammonium into ammonia form. Therefore, regeneration with both NaCl and NaOH allows to sharply decrease brine requirements (up to 90%) (Hedström, 2001). Nevertheless, input of NaOH must be carried out with care in order to avoid zeolite attrition. Hedström (2001) reported the use of 20 bed volumes of brine (NaCl 2% and pH 11.5) to regenerate fouled zeolite.

1.3.6.2 Chemicobiological regeneration

Although highly efficient, the previously described process is probably unadvisable for biological treatment systems. Indeed, the high concentration of chloride ions and the alkaline pH of operation could jeopardize the biomass and cause a decrease in the overall biological process efficiency. Nevertheless, the chemical regeneration can be envisaged if a fast and efficient desorption is required. Miladinovic and Weatherley (2008) reported that some bacteria survived after alkaline regeneration. The surviving ones then performed better than before treatment. Consequently, a time-limited loss of performances can be expected but the remaining biomass will quickly recolonize the system.

Thus, when ammonium removal is the main purpose, its biological transformation appears as a more suitable mechanism with regards to the entire system. A solution of regenerant ($NaHCO_3$) is used for this process. Ammonium ions are released from the zeolite by exchange with sodium ions in solution. The ammonium is then nitrified in aerobic conditions. The

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carbonate serves as source of inorganic carbon for the nitrifiers and also acts to buffer the solution since hydrogen ions are produced during the ammonium oxidation.

The microorganisms are only able to nitrify the ammonium which is present in solution. Therefore, a first step of desorption of ammonium is needed before further nitrification (Lahav and Green, 1998):

$$Z - NH_4^+ + Na^+ \rightarrow Z - Na^+ + NH_4^+ \quad \text{[Eq. 12]}$$

The oxidation of ammonium cations to nitrate anions allows to use the same volume of regenerant during the bioregeneration process (Lahav and Green, 1998).

1.3.6.3 Biological regeneration

The process is based on the affinity between the adsorbed ion and the zeolite. It is believed that adsorbed ammonium can be nitrified by bacteria in aerobic conditions. Wen *et al.* (2006) recovered around 78% of the initial sorption capacity of fouled zeolite after 73 days of cultivation. The adsorption of ammonium onto zeolite lies in its positive load which fills the electronic gap caused by the substitution of silicium ions (Si^{4+}) by aluminium ions (Al^{3+}). When ammonium is biologically oxidized in nitrate by nitrification, this affinity ceases since nitrate is negatively loaded. Therefore, nitrogen is released during subsequent feeding of the material.

Beyond its impact on material regeneration, the biofilm can also improve the removal performances. Miladinovic and Weatherley (2008) reported that a larger volume of influent is treated before reaching breakthrough when nitrifying biomass is already established in the system. Furthermore, Wen *et al.* (2006) did not observe any differences in the equilibrium sorption capacity between a fresh and a colonized zeolite whereas they reported an improvement in the initial sorption rate by the seeded zeolite.

1.3.7 Enhancement of the process: modification of natural zeolite

Several methods of pre-treatment were assessed in order to increase the performance of ammonium removal by zeolite.

A pre-treatment with diluted acid solution enables to remove impurities, which block the pores and therefore increases the specific surface area of zeolite. However, this may also impact the sieving potential of the zeolite which could lead to decrease the ammonium selectivity. The use of solutions at low pH value causes a severe modification of structure by

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dealumination (Sprynskyy *et al.*, 2005a). Consequently the acid treatment leads to improve the sorption capacity but decreases the ion exchange capacity (Wang and Peng, 2010). This treatment is thus inappropriate for ammonium removal.

The most efficient modification of zeolite is the transformation into homoionic form. Wei *et al.* (2011) reported an improvement in sorption capacity after a NaCl pre-treatment of Clinoptilolite (5.232 and 7.586 $mg.g^{-1}$ for natural and modified zeolite respectively). Hedström (2001) reviewed similar behaviour for Na-forms of zeolite whereas other homoionic pre-treatment (Ca^{2+}, Mg^{2+}) showed slighter improvement.

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Part A Study of domestic wastewater treatment with a vertical flow filter

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Ammonium is a pollutant of major concern because of its adverse effect on aquatic organisms. The French department of Environment, Energy and Sea (2016) reported that ammonium concentration below 0.4 $mgNH_4\text{-}N.L^{-1}$ is required in order to fulfil the objective of good ecological status. However, domestic source of nitrogen pollution mainly consists in ammonium and organic nitrogen which will be quickly ammonified during transport in sewer network. Mercoiret (2010) reported an average nitrogen production of 15.5 $gTKN.pe^{-1}.d^{-1}$. Wastewater treatment plants are thus required to treat important loads of ammonium before discharging into environment.

Furthermore, the classic state of the art of CWs only allows to achieve partial pollutant removal with a single stage of VFFs. This is particularly true for ammonium removal which only reach performance of the order of 59% (Morvannou *et al.*, 2015) on the first treatment stage. The short contact time of influent with biomass as well as the limited sorption capacity, onto the organic matter accumulated within the system, may partly explain this low efficiency. The implementation of a second stage of VFF, leading to additional costs and technical constraints, becomes thus necessary in order to treat the remaining fraction of pollution.

In an increasingly competitive market and in tough economic conditions, a decrease in unnecessary construction costs is the main leverage parameter available for engineer. Although several studies reported the beneficial effects of process intensification (e.g. artificial aeration or tidal flow) on the optimization of treatment footprint, that also implies additional devices and energy requirements which make it not competitive. Epur Nature believes in the opportunity to optimize biological processes through the implementation of an ideal simple design, of a single stage VFF, based on accurate knowledge of relationships existing between both natural mechanisms and design and operational characteristics. In this purpose, the following section has been focused on the assessment of the effects of design characteristics on pollutant removal in a single stage treating domestic wastewater. The final objective was to provide design and operational recommendations to get the best process efficiency with simple VFFs treating domestic wastewater.

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Chapter 2 Pilot study of ammonium removal

This chapter is an extended version of the homonymic paper published in ecological engineering (Millot *et al.*, 2016, vol. 97). Most of these results were presented at Wetpol conference in York (2015).

Effects of design and operational parameters on ammonium removal by single-stage French vertical flow filters treating raw domestic wastewater

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Abstract

Four pilot-scale single-stage vertical flow filters (of 2.25m² each), treating raw domestic sewage, were studied over 20 months in order to assess the impact of different designs and operational conditions on treatment efficiency. One of them was designed and operated as a standard 1st stage "French" vertical flow constructed wetland unit. The other three pilots differed from the standard pilot with respect to the filtration depth, the loading rate or the partial replacement of gravel by zeolite (chabazite), respectively. The pilots were monitored by analysing 24-hour flow-weighted composite samples for TSS, COD_{tot}, COD_d, ammonium, nitrate and carbonate. All pilots showed a high ability to remove TSS and COD_{tot}, with average removal of 81% and 75%, respectively. Increasing the depth of the filtration layer from 40cm to 100cm allowed to significantly improve ammonium removal (81%), whereas the simultaneous increase in hydraulic and organic loads resulted in a deterioration of ammonium and COD_d removals (44% for both parameters). Using zeolite did not induce any observable improvements in ammonium removal under the conditions of the study.

Keywords : Ammonium, Vertical flow constructed wetland, Domestic wastewater, Design

2.1 Introduction

Constructed wetlands (CWs) for wastewater treatment met an increasing worldwide interest during the past three decades because of their performances, low investment and operational costs and their environmental friendly image. Moreover, this system is efficient to treat various kinds of effluents such as domestic wastewater, industrial wastewater or combined sewer overflows, etc. (Ávila *et al.*, 2013; Wu *et al.*, 2015; Meyer *et al.*, 2013).

The classical design of "French CW systems" treating raw domestic wastewater (Molle *et al.*, 2005) consists of two stages of vertical flow constructed wetlands (VFCWs) operating in a sequential mode of feeding and rest periods (3.5 days and 7 days, respectively). The first stage (1.2 m²/population equivalent), composed of three parallel filters filled with gravel, is fed by batches of raw screened wastewater. Most of the suspended solids and a part of the dissolved pollution (organic matter and ammonium) are removed at this stage. The second stage (0.8 m²/pe, divided in 2 parallel units), filled with sand, ensures a further treatment of dissolved pollution under aerobic conditions. This configuration allows high removal performances on COD_{tot}, TSS and TKN, namely over 90%, 95% and 85%, respectively (Morvannou *et al.*, 2015) and also easier sludge management than other conventional processes. Besides, "French

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systems" have a high tolerance to variation of hydraulic and organic loads (Molle *et al.*, 2006; Arias *et al.*, 2014).

TKN removal is dependent on various parameters such as wastewater composition, design considerations (media characteristics, design loads…) or external parameters (maintenance, climate). Proper design and optimal operation are needed in order to provide favourable conditions for nitrification. Molle *et al.* (2005) reported that a minimum surface area of 2 m²/p.e. was required in order to achieve full nitrification for a two-stage VFCW configuration. This may be a problem for larger units or when land availability is limited. Recirculation has been reported to improve TKN removal performance (Prigent *et al.*, 2011). Nevertheless, recirculation increases hydraulic loads and can thus negatively affect oxygen transfers. Prost-Boucle and Molle (2012) proposed to limit the hydraulic load to 0.7m/d on the filter in operation in order not to affect nitrification. Oxygen transfer can be increased by implementing passive or active aeration systems (e.g. tidal flow (Sun *et al.*, 2005) or forced bed aeration (Boog *et al.*, 2014; Foladori *et al.*, 2013; Nivala *et al.*, 2013)). However, such intensifications lead to additional operating costs (Austin and Nivala, 2009).

Current methods for design improvement appear to favour more complex and more intensified systems. The objective of the present study was to assess the extent of removal performance improvement by adapting design parameters without increasing energy consumption. Since nitrification is known to be highly sensitive to several operational conditions, such as oxygen transfer into the filter, hydraulic and organic loads or the feeding strategies, it was used as an indicator for design optimisation. Four pilot-scale French VFCWs were monitored over 20 months for this purpose. One of them was designed and operated as a standard 1st stage filter according to the French guidelines (Molle *et al.*, 2005) in order to serve as a reference. The design parameters tested were the filter depth (0.4m to 1.0m), the use of zeolite (chabazite) as filter media and the hydraulic and organic loading rates.

2.2 Materials and Methods

2.2.1 Experimental setup

Four vertical flow pilot filters of 2.25 m² each were monitored for 20 months, from March 2014 to October 2015 (see appendix II). One of them, denoted as Vertical Flow Standard (VFSt), was designed and operated as a standard 1st stage "French" VFCW unit. The other 3 pilots differed from the standard pilot with respect to the filtration depth (Vertical Flow

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Gravel^{+}, VFG^{+}), loading rate (Vertical Flow High Load, VFHL) or a partial replacement of gravel by zeolite (Vertical Flow Zeolite, VFZ), respectively.

The pilots were all composed, from bottom to the top, of a 15cm-deep drainage layer made of 16/22mm grain size cobbles and a filtration layer whose characteristics are given in Table 8. To avoid particulate migration from the filtration layer to the drainage layer in the VFHL pilot, a 10cm-deep transition layer (grain size 16/22mm) was implemented above the 15cm-deep drainage layer which was composed of 20-50mm cobbles as shown in Figure 13.

The pilots were operated outdoors on an experimental site located at the site of a domestic wastewater treatment plant (Jonquerettes, south east of France). This facility allowed us to assess the performance of VFCWs for the treatment of real raw domestic wastewater screened at 20mm under Mediterranean climate.

A sludge deposit layer was progressively formed at the surface of the filters by accumulation of filtered particles (up to a thickness of 3cm at the end of the monitoring period). The pilots were planted in September 2013 with one year old plantlets of *Phragmites australis* at a density of 6 plants.m^{-2}. According to French guidelines, the pilots were fed for 3.5 days and rested for 7 days. During the feeding periods, 18 batches of 2cm were applied daily (2 m^{3}.h^{-1}), except for the high load pilot VFHL where 32 batches a day were applied which was considered as the highest acceptable hydraulic load based on full-scale observations. The influent of the standard pilot (VFSt) was spiked in organic matter and ammonium, at the end of the study, in order to assess the effect of pollutant load at constant hydraulic load. The organic matter supply consisted in the addition of glucose, glycerol and glycine (50%, 35% and 15%, respectively) in distilled water. The addition of easily (glucose and glycerol) and slowly (glycine) biodegradable organic matter aimed to mimic the characteristics of domestic wastewater. Ammonium sulphate was used to increase the ammonium inlet concentration. The synthetic solution of organic matter and ammonium was added to the influent thanks to a peristaltic pump through a padding clamp located on the feeding pipe of VFSt. The peristaltic pump was activated whenever VFSt was dosed and was operated for 1 minute. Its flow rate was initially set in order to supply the required volume of synthetic solution in order to double the ammonium and organic loads. The monitoring started after a commissioning period of five months which was meant to allow for the establishment of microorganisms and reeds.

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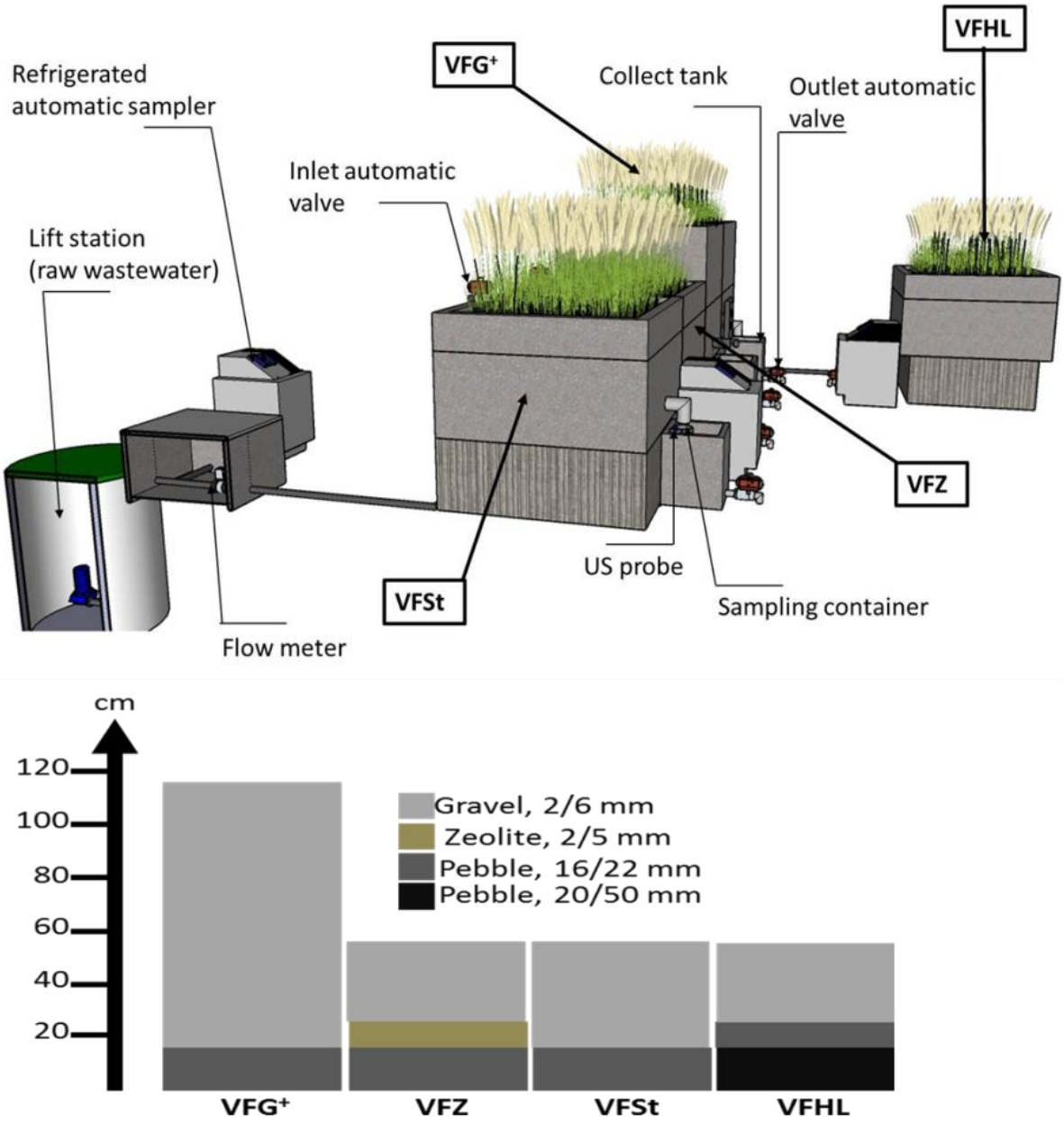

Figure 13 Experimental setup and design characteristics

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Table 8 Characteristics of the pilot design

Pilot units	Studied parameters	Filtration layer			Passive aeration location (cm) [1]/[3]	Hydraulic load ($m^3.m^{-2}.d^{-1}$) [2]	Organic load ($gCOD.m^{-2}.d^{-1}$) [2]
		Material	Depth (cm)	Sampling systems (cm)[1]			
Standard (VFSt)	Unit of reference	Gravel 2/6 mm	40	10 and 30	Bottom	0.36	234 (62)
Deep Filtration (VFG+)	Effect of filtration depth	Gravel 2/6 mm	100	10, 20, 40, 60, 80	Bottom, 30 and 60	0.36	240 (80)
High Load (VFHL)	Effect of hydraulic and organic loads	Gravel 2/6 mm	30	10, 20	Bottom and 30	0.64	536 (276)
Zeolite Chabazite (VFZ)	Effect of sorbent materials	Gravel 2/6 mm Zeolite 2/5 mm	30 + 10	10 and 40	Bottom	0.36	237 (71)

[1] Depth from the filter surface

[2] Loads are calculated for the filter in operation

[3]All drains are connected to the atmosphere, resulting in a passive aeration from the bottom on the length of the filter. The intermediate passive aeration systems consist of drilled pipes, with connection to the atmosphere, which are crosswise implemented in the filtration layer of the pilot.

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2.2.2 Preliminary validation of reference pilot

A preliminary step of validation of the reference unit was required to verify whether the treatment performance of the VFSt was in the range of those usually observed at full-scale 1st stages of a classical French VFCW. For that purpose, inlet and outlet concentrations of the VFSt were compared with a set of data collected from three full-scale treatment plants with the same design (part of data from Morvannou *et al.*, 2015). The inflow of each pilot was also compared in order to confirm that they received the same wastewater during the study so that their performance could be compared.

2.2.3 Experimental monitoring of the pilots

The inlet and outlet water concentrations were assessed for the first and the last day of the feeding periods using refrigerated samplers (Ponsel, ISCO 4700 and Hach, Bühler 2000). 24-hour flow-weighted composite samples were taken from the outlet while, for the inlet, 24-hour composite samples were obtained from one grab sample per batch. Intermediate 24-hour composite samples were taken from different depths (see Table 8) and analysed. Pore water was collected during infiltration by PVC gutters (9 cm and 30 cm of width and length, respectively), located at different depths within the filtration layer, and then stored into pre-acidified 25L polyethylene containers. Each pilot was evaluated for total and dissolved COD (COD_{tot} and COD_d, respectively), TSS, NH_4-N, NO_3-N and $CaCO_3$ using quick method tests (Hach).

Online measurements were also carried out for continuous monitoring of hydraulic and treatment performance dynamics. Inlet flows were determined using an electromagnetic flowmeter (Siemens, SITRANS MAG 5100W) whereas outlet flows were measured with ultrasonic probes (Pil, P43-F4V-2D1-D0-330E) by the rise of the level of effluent drained into a collecting tank. Nitrogen concentrations (NH_4-N and NO_3-N) were continuously monitored at the inlet and the outlet of each pilot at time intervals of 15 and 2 minutes, respectively, using ion selective electrodes (AN-ISE, Hach).

The monitored data were used to compare the performance of pilots. For this purpose, removal rates were calculated on mass basis considering the measured concentrations and the inlet volumetric flows.

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2.2.4 Statistical analysis

Experimental results were statistically analysed using R software. Kruskal Wallis tests were carried out on the full set of data, in order to validate that all pilots received the same influent, while Wilcoxon and Student tests were used for pair-wise comparison of each pilot with the reference unit. Significant difference was established at p-value ≤ 0.05.

2.3 Results and Discussions

2.3.1 Validation of control pilot VFSt

The treatment performance of VFSt was compared to full-scale classical French first stage filters (Morvannou *et al.*, 2015) with respect to TSS, COD_{tot} and ammonium as shown in Figure 14. The results of Wilcoxon statistical comparison between VFSt and full-scale VFCWs confirmed that the reference pilot VFSt of the study could be considered as a standard filter. Moreover the pollutant concentrations in the inlet (TKN/COD_{tot}, TSS/COD_{tot} and TKN/NH_4-N) were in the range of what was reported from a survey of almost 3000 treatment plants of small French communities (Mercoiret *et al.*, 2010).

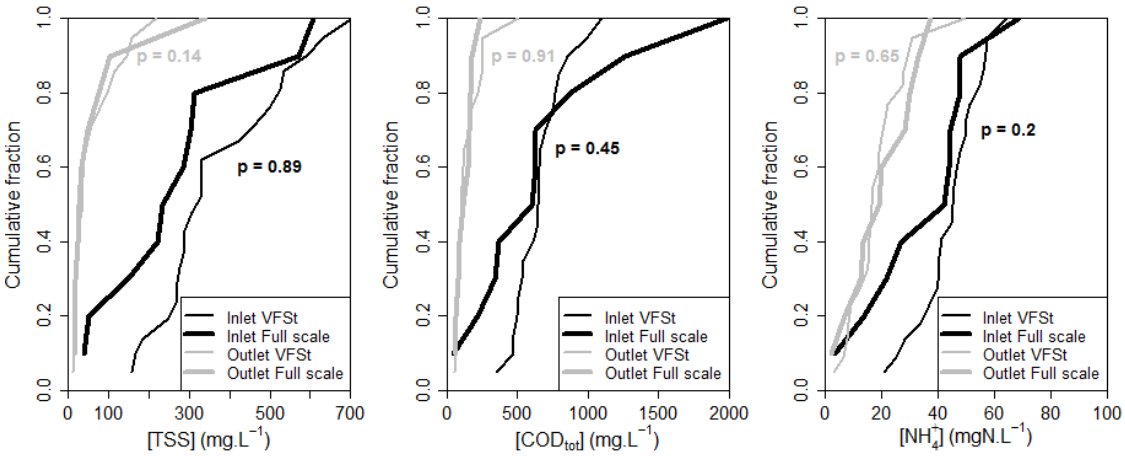

Figure 14 Influent and effluent composition of VFSt and Full scale treatment plants (depth of 40cm) (p-values are the outcome of a Wilcoxon test comparing data from pilot and full-scale systems)

Figure 15 shows the distribution of influent composition over the whole study without distinction between pilots. It can be observed that inlet composition during the study was similar for all pilots, as confirmed by the Kruskal Wallis test comparing average inlet concentrations of each pilot. It was therefore relevant to compare them with the VFSt filter. Nitrate concentrations however were significantly different. This can be explained by a few high values measured in the influent which modified the average value.

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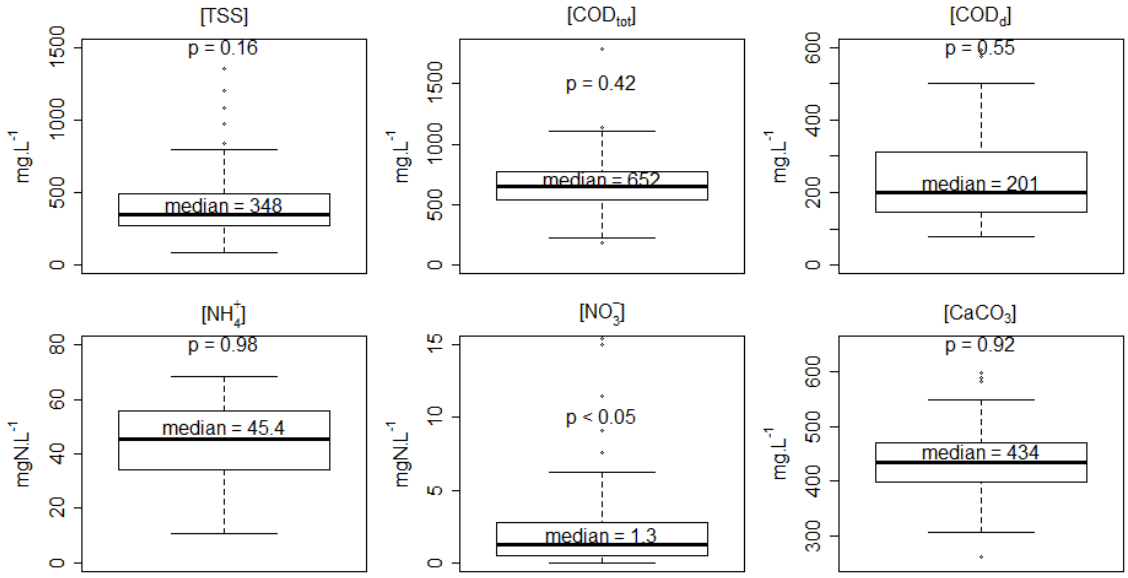

Figure 15 Influent wastewater composition during the study (note that one TSS outlier over 3000mg/L, one COD_{tot} outlier over 1500mgO_2/L, one COD_d outlier over 1000mgO_2/L and four NO_3^- outliers between 10 and 20mgN/L are not shown for visibility reasons). P-values are the outcome of a Kruskal Wallis test comparing data from pilot full dataset.

2.3.2 Influence of filtration depth

Increasing the filtration layer depth from 40cm to 100cm did not significantly improve TSS removal ($p = 0.09$). Median TSS removal efficiency was 92% and 91% for VFSt and VFG^+, respectively, falling within the range of removal rates usually observed for first stage filters in French VFCW system (Morvannou *et al.*, 2015, Paing and Voisin, 2005). Molle *et al.* (2005) and Paing and Voisin (2005) reported that TSS removal mostly occurred at the surface of the first stage filter. Figure 16a shows the effect of applied load on treatment efficiency. It can be seen that TSS removal was linear even for high loads. The lowest removal rates (especially for the VFSt at loads of $100 g.m^{-2}.d^{-1}$) were obtained within the first five months after the commissioning period when the sludge deposit layer was still very thin. TSS removal efficiencies were thereafter higher than 90%. This observation confirmed the positive effect of the thickness of sludge deposit layer on filtration performance (Molle *et al.*, 2005).

The effect of filtration depth on COD_{tot} removal was quite similar as for TSS (Figure 16b). This was mainly explained by the fact that most of COD_{tot} was under particulate form ($COD_d/COD_{tot} = 0.3$ in this study).

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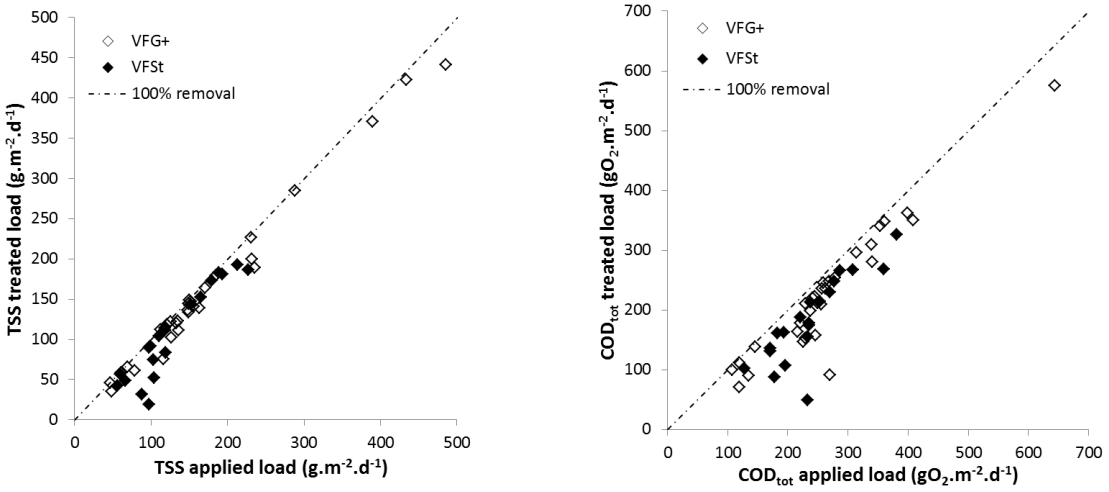

Figure 16 Treated TSS (a) and COD_{tot} (b) loads according to the applied TSS and COD_{tot} loads, respectively

Figure 17a showed that, within the range of COD_d loads applied in this study, the reference pilot VFSt performed similarly to the deep filter pilot VFG^+. COD_d removal was not statistically improved by increasing the filtration depth ($p = 0.06$) although a slightly better removal was observed for VFG^+ (59% and 66% for VFSt and VFG^+, respectively). Even though the implementation of a deeper filtration layer did not result in a statistically significant improvement of COD_d removal, it allowed a slight improvement of the outlet concentration (92.5 and 73.1 $mgCOD_d.L^{-1}$ on average for VFSt and VFG^+, respectively).

Around 60% of COD_d was degraded within the upper 20cm of the filter as shown by the depth profile presented in Figure 17b. The removal rate then strongly decreased up to 40cm-depth to become almost negligible with further depth. Morvannou *et al.* (2014) reported that the heterotrophic community was mainly located in the sludge deposit and the upper part of the filtration layer in French first stage VFCW. Their similar performance in COD_d removal was consistent with the distribution of heterotrophic bacteria of Morvannou *et al.* (2014). Olsson (2011) carried out a similar experiment with VFCWs filled with different media (gravel or sand) and fed with pre-treated wastewater. The depth profile of total organic carbon (TOC) in sand revealed 68% removal at 20cm-depth, which was very close to the COD_d profile observed in the present study. For gravel however, the profile was quite linear until 80 cm deep, suggesting that heterotrophic community can colonize deeper zones of filtration. This different depth profile with gravel may be explained by the fact that the gravels used in Olsson's work were coarser than in this study (4/8 mm and 2/6 mm, respectively) and the

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influent was pre-treated in a settling tank. In our study, the infiltration rate was thus probably lower. The similar depth profile between our study and the sand VFCW (1/3 mm) of Olsson shows the positive impact of sludge deposit on the hydraulics of the French systems (Molle *et al.*, 2006).

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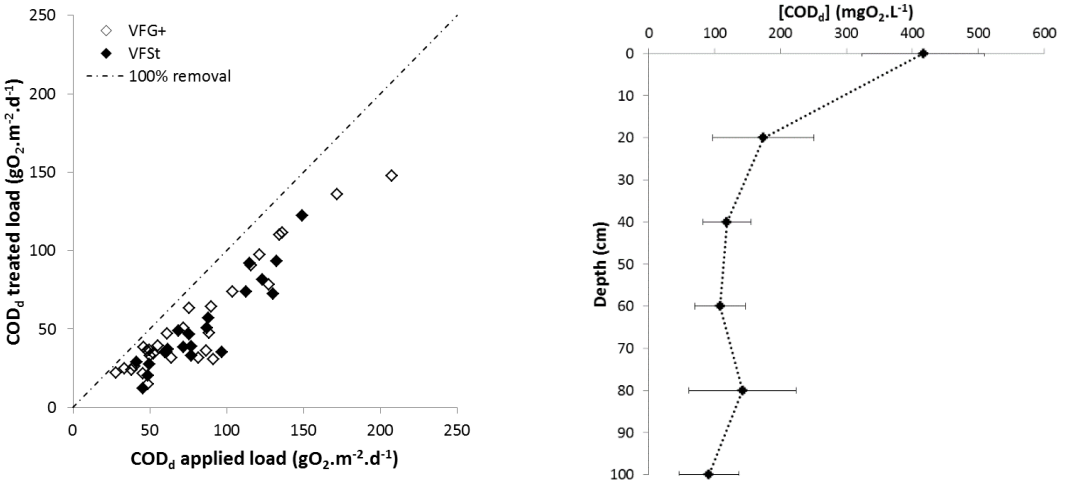

Figure 17 Treated COD_d loads according to COD_d the applied loads (a) and COD_d depth profile during feeding cycle for the VFG^+ pilot (Six 24-hour composite samples) (b)

As illustrated in Figure 18a, ammonium removal efficiency was significantly improved by increasing the filtration depth ($p = 0.01$). It increased from 62% in 40cm-deep reference pilot VFSt to 81% in 100cm-deep VFG^+. Ammonium removal was linear within the applied load between 5 and 25 $gNH_4\text{-}N.m^{-2}.d^{-1}$.

We also observed a significantly different consumption of alkalinity ($p = 0.04$) and production of nitrate ($p = 0.001$). While VFSt had a mean nitrate production of 10.1 $gN.m^{-2}.d^{-1}$ and removed 57.1 $g.m^{-2}.d^{-1}$ of alkalinity (in $CaCO_3$) on average, increasing the filtration depth from 40cm to 100cm improved the phenomena by almost 50% (14.1$gN.m^{-2}.d^{-1}$ and 75.9$g.m^{-2}.d^{-1}$ of nitrate production and alkalinity (in $CaCO_3$) removal, respectively). These observations, along with the results on ammonium removal discussed above, revealed that a deeper filtration layer enhanced the nitrification rate.

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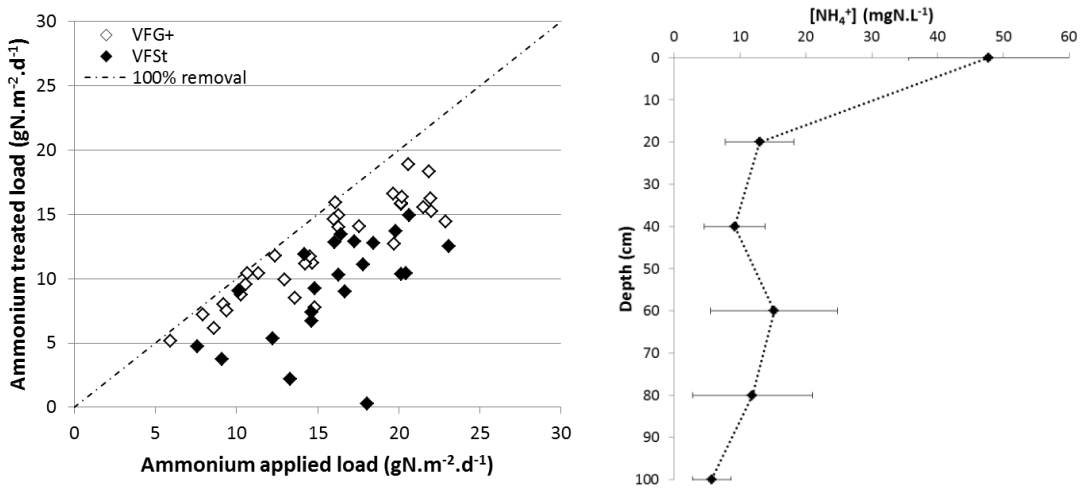

Figure 18 Ammonium treated loads according to the ammonium applied loads (a) and ammonium depth profile during feeding cycle for the VFG+ pilot (Six 24-hour composite samples) (b)

The depth profile of ammonium concentration (Figure 18b), carried out on six 24-hour composite samples in the last stages of operation, showed that the upper 40cm achieved about 75% of removed ammonium, while the overall performance was 87% at 100cm deep. These results are in accordance with previously published works. Thus, Torrens *et al.* (2009) observed a higher TKN removal when increasing the filtration depth of a sand VFCW (from 69% to 78% at 25 cm and 65 cm, respectively) and Molle *et al.* (2008) reported a negligible improvement of TKN removal when increasing the filtration depth of the first stage of a French system from 60cm to 80cm. These observations may be attributed to the fact that autotrophic bacteria are mainly located in the sludge deposit and the upper 30cm of the filtration layer as reported by Morvannou *et al.* (2014).

2.3.3 Effects of hydraulic and organic loads

Figure 19a presents the removal efficiency observed for TSS, COD_{tot}, COD_d and NH_4 in the reference (VFSt) and high load (VFHL) pilots. VFSt and VFHL showed a slight difference in their capacity to remove suspended solids (92% and 84%, respectively). Nevertheless, no significant effect of hydraulic load was observed by statistical analysis of their respective TSS outlet concentrations ($p = 0.12$). Higher ponding was observed in VFHL which may partly explain the slight difference of TSS removal. Hydrostatic pressure head is higher in VFHL and fine particles are thus less retained within the filter. It must be noted that analytical data

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were exploited in terms of concentrations since the pilots did not receive identical loads.

COD_d removal was significantly impacted ($p = 0.04$). It was reduced from 59% in VFSt to 44% in VFHL as shown in Figure 19a. This observation may be explained by the hydraulic changes induced by the increase of the loads. More frequent feedings resulted in an increase of ponding time, a decrease of water retention time (Molle *et al.*, 2006) and thus hindered oxygen renewal within the filter. This in turn was detrimental for aerobic microbial activity. The impact of hydraulic conditions is well described in Figure 19b which shows the COD_d removal in relation with loads. The removed load was lower with VFHL than with VFSt for similar applied organic loads. On the other hand the shape remained quite constant when organic load was extended to 250 $g.m^{-2}.d^{-1}$ (twice the initial organic load) for VFSt-HL (same hydraulic load). This observation suggested that oxygen availability and contact time were sufficient to perform COD_d removal as long as the hydraulic load remained lower than 0.36 $m.d^{-1}$. The hydraulic load was therefore the most limiting parameter to achieve high COD_d removal with a 1st stage VFF.

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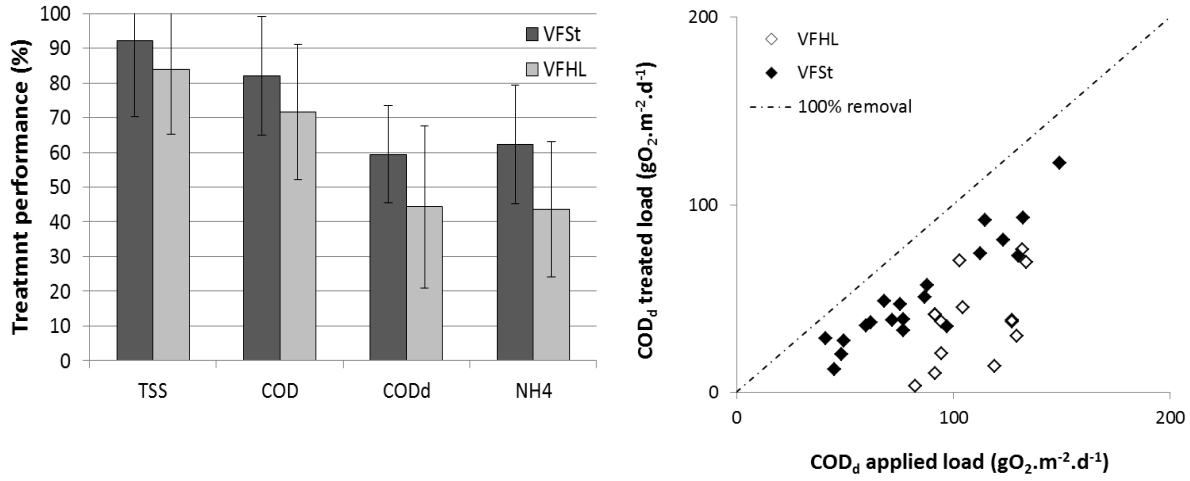

Figure 19 Treatment performance for global pollutants (a) and COD_d treated loads according to the COD_d applied loads (b) (Note that a selection in VFHL data was carried out in order to study treatment efficiency for similar organic loads but different hydraulic loads)

A significant reduction of ammonium removal ($p = 0.007$) occurred when increasing the hydraulic load from $0.36cm.d^{-1}$ to $0.64cm.d^{-1}$. Performance dropped from 62% to 44% for VFSt and VFHL, respectively (Figure 19a). Ammonium removal related to applied loads in VFSt and VFHL is shown in Figure 20a. For similar applied ammonium loads (between 5 and

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25 $gN.m^{-2}d^{-1}$), VFHL exhibited lower removal capacity than VFSt. This might be explained by the lower oxygen transfer capacity of the system and the lower water retention time due to shorter time between two consecutive batches.

Furthermore, Figure 20b showed the removal of ammonium by standard pilot, for normal and spiked operation conditions (VFSt and VFSt-HL, respectively), in relation with the applied load. Ammonium removal starts to decrease around 15 $gN.m^{-2}.d^{-1}$ which is coherent with results observed by Molle *et al.* (2008). This limit in ammonium removal may be explained by the saturation of ammonia adsorption sites onto organic matter. The limit of acceptable load might be slightly improved over time as long as sludge deposit increases.

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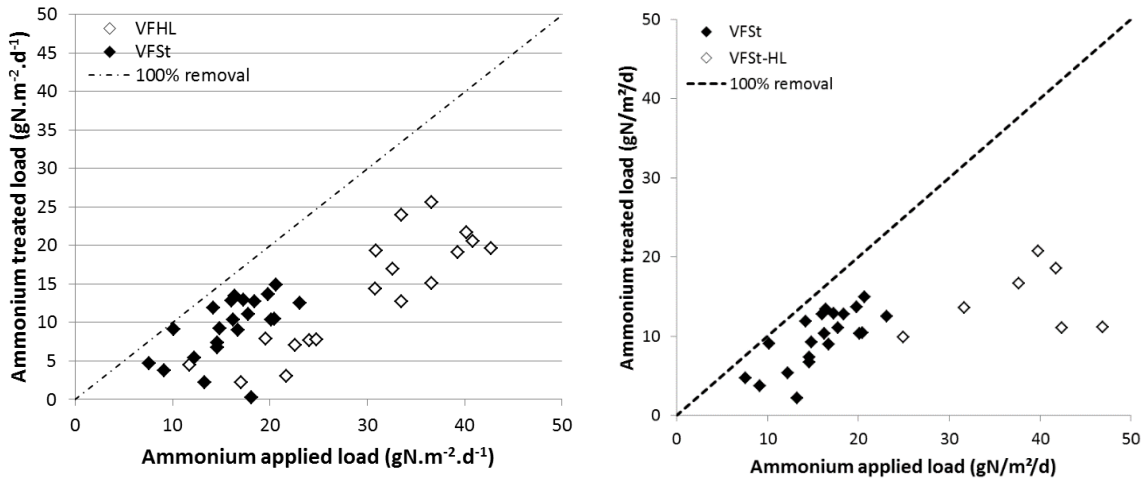

Figure 20 Ammonium treated loads according to the ammonium applied loads for pilots receiving the same average concentration of ammonium but operating under different hydraulic loads (VFHL: 0.64 $cm.d^{-1}$ and VFSt: 0.36 $cm.d^{-1}$) (a) and for pilots receiving different average concentration of ammonium (VFSt: 43.6 $mgN.L^{-1}$ and VFSt-HL: 103.7 $mgN.L^{-1}$) but operating under identic hydraulic loads (b).

2.3.4 Effect of the implementation of a sorbent material

The implementation of zeolite layer of 10cm at the bottom of the filtration layer did not result in a significant improvement of ammonium removal ($p = 0.29$) regardless of the applied load as shown in Figure 21a. VFSt and VFZ achieved 62% and 68% of ammonium removal, respectively. This observation was consistent with Stefanakis and Tsihrintzis (2009) who reported that no significant improvement occurred in TKN removal by using zeolite in VFCW.

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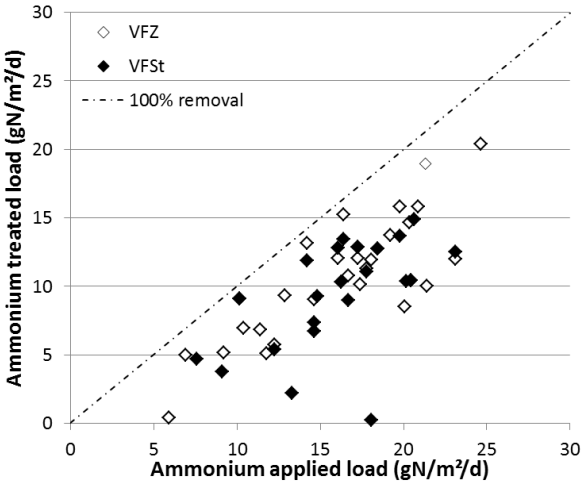

Figure 21 Ammonium treated loads in relation with the ammonium applied loads

Nonetheless the continuous monitoring of nitrogen for VFSt and VFZ (Figure 22a and b, respectively) showed that zeolite was not totally ineffective face to ammonium removal. First of all, the release of nitrate, in the early stage of feeding period, by VFZ is much higher than the release observed at the outlet of VFSt. This difference in nitrate production suggested that ammonium was stored in a higher extent into VFZ than VFSt during the feeding period. This observation supported the idea that ammonium was exchanged with zeolite medium. Furthermore the effluent ammonium concentration was initially low for VFSt (1st day of operation) whereas nitrate concentration decreased until reaching stable discharge level. This phenomenon may be attributed to the restoration of adsorption sites onto organic matter. Therefore ammonium was initially removed by nitrification and adsorption onto organic matter. Ammonium concentration then rose as the sorption sites were progressively saturated. Contrariwise to VFSt, ammonium concentration remained constant, for VFZ, over the whole period of feeding. This difference of ammonium dynamic may be related with a higher exchange potential of VFZ than VFSt due to zeolite implementation. Finally the ammonium concentration was less affected by inlet variation for VFZ than VFSt. The addition of zeolite seemed to allow more constant discharge level.

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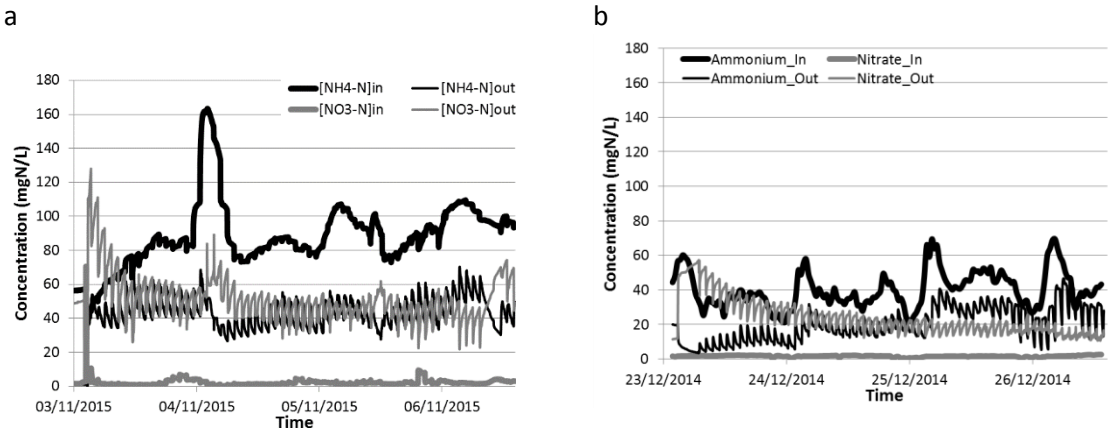

Figure 22 Nitrogen dynamic during a feeding cycle for VFZ (a) and VFSt (b)

Knowing the cationic exchange capacities of zeolite (Erdoğan and Ülkü, 2011; Malekian *et al.*, 2011; Huang *et al.*, 2010; Ivanova *et al.*, 2010), we can observe that adsorption process was not efficient with the design used for VFZ. Since regeneration of sorption sites was expected to occur through nitrification of ammonium during the resting period, the progressive fouling of the media may not fully explain this lack of efficiency. The alkalinity concentrations and the pH values measured in VFZ effluent were favourable for nitrification (284 mg/L and 7.5, respectively). However, Figure 23b shows that almost no ammonium removal occurred in the zeolite layer. Different possible explanations can be drawn as preferential flows, short water retention times as well as the low ammonia concentration at this stage (< 10 $mgN.L^{-1}$). Nevertheless, Lahav and Green (1998) reported outlet ammonium concentrations lower than 1 $mgN.L^{-1}$ with upflow mode columns fed at 40 $mgN.L^{-1}$. Such ammonium removal was possible by the implementation of large amount of chabazite (almost five times the amount in this study) with short contact time (2 minutes). It should be thus possible to improve the ammonium removal by increasing the zeolite fraction of the filtration layer.

It is also known from kinetic studies, carried out under static conditions for different contact times, that sorption increases with contact time until an equilibrium is reached (Huang *et al.*, 2010; Wen *et al.*, 2006). Therefore, limiting the outflow rate may be one possible option to improve the effect of zeolite by increasing contact time without adding more zeolite.

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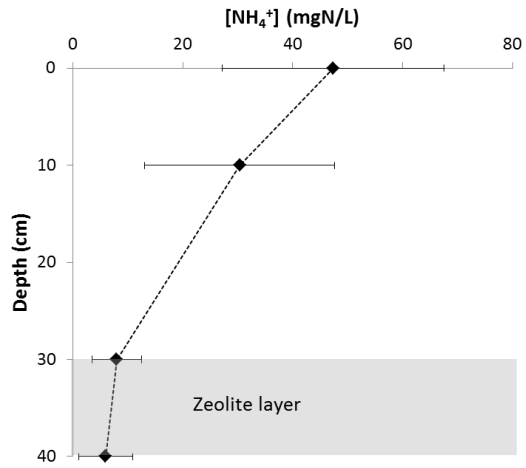

Figure 23 Depth profile of ammonium concentration during a feeding cycle (3 24-hour composite samples) Note that the systems were drained vertical flow filters which were therefore operated under unsaturated conditions.

2.4 Conclusion

This study aimed at identifying the leverage actions in order to reduce the treatment footprint of VFCW. The respective impact of design criteria and operation conditions on the ability of a 1st stage of VFCW to perform treatment of different pollutants (TSS, COD_d, ammonium), from raw domestic wastewater, were assessed for this purpose.

TSS removal was not affected by the studied modifications of design or operational parameters since it was mainly a surface mechanism. Therefore, reduction of the 1st stage surface would not result in a drop in particles treatment efficiency. Nevertheless, the decrease in surface of treatment (from 0.4 m²/p.e./bed to 0.25 m²/p.e./bed, respectively) would cause an increase in daily hydraulic load (from 0.36m.d^{-1} to 0.64m.d^{-1}) which showed significant adverse effects on COD_d and ammonium removal (from 59% to 44% and from 62% to 44%, respectively) because of the shorter contact time as well as lower oxygen renewal within the filter.

The lower removal of COD_d and ammonium observed when decreasing the surface of the 1st stage might be partly counterbalanced by the implementation of deeper filtration layer. Ammonium removal was actually raised from 62% to 81% and COD_d removal was improved from 59% to 66% when filtration depth increased from 40cm to 100cm. Nevertheless, the relation between gain of performance and depth of filtration was low, especially when the filtration layer was deeper than 60cm since the microbial community was mainly located in the upper part of the filtration layer. In addition, a deeper filtration layer enabled to maintain a

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more constant efficiency which might be valuable when fluctuation of performance is observed (i.e. when temperature variations, over year, are wide).

Furthermore, despite its theoretical ion exchange capacity, zeolite implementation in the filtration layer did not allow to reach the expected improvement of ammonium removal for the assessed characteristics of design and operation. Higher zeolite content might provide different conclusions but would result in prohibitive extra-costs (zeolite was almost 5 times more expensive than gravel). The implementation of such reactive material, as suitable alternative to intensification, should not be further considered unless the operation conditions allowed the optimal use of exchange capacity. Further studies are thus necessary to determine the best design and operational conditions for its efficient use.

In conclusion, it seems difficult to reach low discharge levels with a single stage of VFCW treating domestic wastewater. However, surface requirements may be reduced to 0.25 m^2/p.e./bed if a second stage ensures the final treatment of remaining pollution and if filtration depth is also used as an adjustment parameter.

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Part B Study of denitrification with saturated vertical flow filters

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Important production of nitrate is a direct consequence of the optimization of aerobic processes in 1st stage VFFs. Although nitrate has a smaller impact on aquatic ecosystems, it may contribute to the phenomenon of eutrophication of surface water bodies. The French department of Environment, Energy and Sea (2016) reported an objective of nitrate concentration below 11.3mgNO_3-N.L^{-1} in order to switch from medium to good ecological status in rivers. This concentration of nitrate may often be easily obtained, justifying the absence of clear discharge objectives on TN removal. Nevertheless, the flow rate of some receiving water courses may be insufficient for providing the required dilution of fluxes. Such phenomenon may be a consequence of variation in flow rate over year (especially during summer) but may also be related to additional diffusive pollution (most often from agricultural origin). Regulation in discharge of nitrate in the effluent of wastewater treatment plants thus becomes a powerful leverage for the management of nitrate in water bodies.

However, highly aerobic standard design of VFFs does not provide the anoxic conditions which are required for biological removal of nitrate. Less than 20% of TN removal is thus performed in such system (Prigent *et al.*, 2013). Usual extensive solution relies on the implementation of an additional anoxic system (e.g. HFF or pond) which will ensure the final treatment of nitrogen. Obviously, this solution presents several economical and technical disadvantages affecting the development of wetland's technology. An alternative design, commercialized as BiHofiltre® by Epur Nature, consists in the partial saturation of the bottom of VFFs. This modification enables to provide both aerobic and anoxic conditions in the same compact unit and thus allows the treatment of TN on a small treatment surface.

In other respects, literature dealing with nitrate removal in anoxic CWs (especially in HFFs) presents two main characteristics which may limit their extrapolation to the saturated layer of BiHofiltre®. First of all, studies mostly report results from systems operating as primary treatment stage. Contrariwise to the characteristics of effluent from an unsaturated layer, the loads of nitrate which should be removed is therefore quite low. No previous nitrification process has thus indeed been carried out whereas anoxic conditions do not allow high nitrification of ammonium. Moreover, the organic matter, which is necessary to perform denitrification process, is available in a large amount while high removal of COD has been already performed in the unsaturated layer of BiHofiltre®. The prediction of denitrification efficiency in the saturated layer, based on observations from these studies, is therefore unrealistic because of the large difference in characteristics of influents. Furthermore, the studied anoxic systems usually operate with very long hydraulic retention time (i.e. several

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days). The implementation of a vertical flow saturated layer does not allow such long retention time unless increasing the saturated depth in an unacceptable extent. A better knowledge of the kinetic of denitrification process is thus necessary in order to provide optimized recommendations for design.

The following part aims at identifying key parameters of an optimal denitrification process in a saturated vertical flow layer treating pre-treated domestic influent. Recommendations on the design's optimization of saturated layer of BiHofiltre® as well as prediction of expectable treatment performance were aimed in these studies. The development of a simple predictive numerical tool was also carried out in order to assist engineer for the optimization of design in regards with specific context.

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Chapter 3 Effects of design and operational conditions

This chapter has not been submitted yet. A lightened version is in the reflection stage for a research paper.

Effect of COD:N ratio and Hydraulic Retention Time on Nitrate Removal from Domestic Sewage in Saturated Vertical Flow Filter

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Abstract

Two saturated vertical flow filters (1.44m²), packed with 0.85m of filtration media of different specific surface (pebble and Biofill Type C®, respectively), were studied under different operational conditions (COD:N ratio and inlet concentration). The pilots were dosed in batch mode (18 batch.d^{-1}, 0.36m.d^{-1}), with semi-synthetic wastewater, in order to mimic the effluent from a 1st stage vertical flow filter. Influent and effluent were analyzed for COD_{tot}, ammonium, nitrate and TSS. Punctual analyses at intermediate depths were also carried out in order to assess the effect of retention time. Denitrification was limited by carbon availability for COD_{tot}:N of 3 and lower whereas high carbon supply (COD_{tot}:N = 6) allowed almost full denitrification. The COD_{tot}:N ratio also impacted the denitrification kinetics which dropped with ratio. Higher inlet nitrate concentrations caused an increase of denitrification rate resulting in similar treatment performance. Denitrification was affected by retention time but full denitrification may be achieved at retention times as short as one day. Finally, both pilots performed similarly, suggesting that specific surface of the media was not a suitable criterion of process optimization.

Keywords: Denitrification, Domestic wastewater, Saturated vertical flow filter

3.1 Introduction

The French design of constructed wetlands (CW) has shown, for almost 30 years, its good capacity to perform high TSS, COD and TKN removal (up to 95%, 90% and 85%, respectively) (Morvannou *et al.*, 2015; Troesch and Esser, 2012; Molle *et al.*, 2005). This system, treating raw domestic sewage, consists of two stages of vertical flow filters (VFFs), composed by 3 and 2 parallel units (0.4m²/p.e. each one), for the first and second stage respectively, operating in a sequential mode of operation and rest periods (3.5/7d and 7/7d, respectively). Although the French design enables good nitrification, only low TN removal is achieved (less than 20% (Prigent *et al.*, 2013)) because of its highly oxygenated conditions. Therefore, the nitrate concentration can be high in the discharged wastewater of French CWs, especially in the first flush consecutive to the start of a new feeding period.

Denitrification is assumed to be the main process performing nitrate removal in CWs (Saeed and Sun, 2011a). This strictly anoxic process, carried out by facultative anaerobic bacteria (Song *et al.*, 2011), is an alternative route of organic matter oxidation which reduces nitrate to inert nitrogen gas. Nitrate serves as electron acceptor in this respiration process. The oxygen

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content is thus the first controlling factor of denitrification. Aerobic microbial metabolism is preferred, and nitrate removal drops dramatically, when oxygen concentration is higher than $3.7 mgO_2.L^{-1}$ (Warneke *et al.*, 2011). Higher concentrations of oxygen lead to incomplete denitrification and nitrite accumulation which is toxic for plant and soil microorganisms (Lu *et al.*, 2009). Furthermore, denitrification efficiency is also affected by numerous field conditions and water characteristics (e.g. pH, temperature, nitrate and organic matter availability).

The addition of an anoxic filter is necessary to obtain efficient removal of total nitrogen by French VFFs. The implementation of a horizontal flow unit between both stages of VFFs is usually done when regulation in nitrate discharge is mandatory. Such design adjustment results in an increasing treatment footprint and in process intensification due to recirculation of effluent from the 2nd stage VFFs to the inlet of the horizontal flow filter. Current design optimization focuses on reducing the treatment footprint through the implementation of hybrid systems which stack an unsaturated filtration layer onto a vertical flow saturated drainage compartment (Troesch *et al.*, 2014). Nevertheless, characteristics of 1st stage effluent might be unfavourable for optimal denitrification in the subsequent anoxic reactors especially due to the high removal of COD performed by this stage.

This study aimed to assess the effect of different criteria of design and operation on the denitrification capacity of a saturated drainage layer of VFF treating the effluent from the first stage of a French system. The objectives were defined as: (i) to determine the optimal COD_{tot}:N ratio to obtain full denitrification, (ii) to assess the impact of the inlet concentration of nitrate, (iii) to improve the design of saturated drainage layer (i.e. media type, depth of filtration).

3.2 Materials and Methods

3.2.1 Experimental setup

Two pilot-scale unplanted saturated vertical flow filters, located in Jonquerettes (South east of France) on the site of the municipal wastewater treatment plant, were studied for 7 months from March to September 2015 (see appendix II).

Each pilot, of 1.44m², was left unplanted to mimic the saturated layer of a partially saturated filter. Pilots were packed with 0.85m of a different inert material (pebbles or plastic media (Biofill Type C®), respectively) in order to assess the effect of medium specific surface (see

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characteristics in Table 9) on the denitrification process. Water table was set few millimeters below the surface in order to limit light effects.

Table 9 Pilot characteristics

Pilot	Media				
	Type	Size (mm)	Porosity (%)	Bulk density ($kg.m^{-3}$)	Specific surface ($m^2.m^{-3}$)
Saturated Vertical Flow Pebble (SVFP)	Pebble	20/50	44	≈ 1900	≈ 100
Saturated Vertical Flow Biomedia (SVFB)	Biofill Type C®	25	84	127	> 460

Pilots were continuously operated during the studied period and were fed in a batch mode (18 $batch.d^{-1}$, $0.36m.d^{-1}$, batch flow rate of 1.2 $m.h^{-1}$) in order to mimic the outlet of a 1st stage vertical flow filter. Each system was fed from the surface by two 1m-long parallel feeding pipes (PVC, ø32mm), located at 0.3m from the pilot edge and perforated by two series of 3 holes (ø6mm), equally distributed along with the length and with an angle of 45° to the vertical axis, in order to ensure an homogeneous distribution of influent. A single central drain (PVC, ø110mm), connected to the regulation system of saturation level, collected the effluent. Intermediate sampling ports, distributed along the filtration depth (5, 20, 35, 50, 65, 80cm depth), aimed to assess the effect of retention time. These systems consisted of PVC pipes (ø20mm), horizontally introduced into the filter (40cm from pilot edge), ending in manual valves. Figure 24 presents an overview of the experimental setup.

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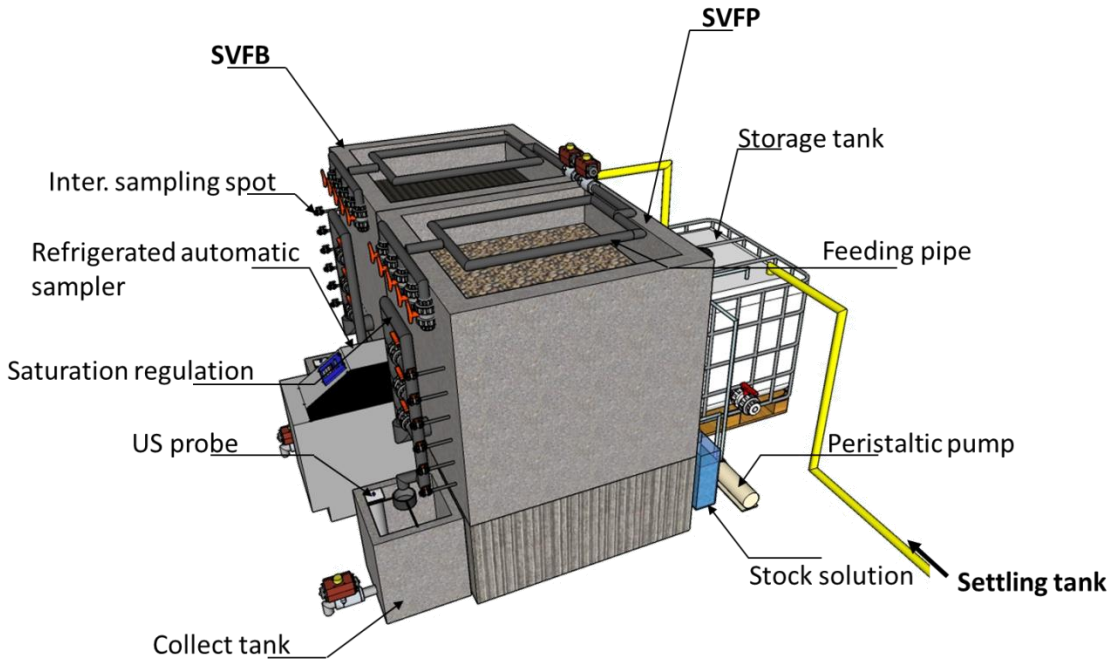

Figure 24 Experimental setup

The pilots were fed with semi-synthetic wastewater in order to obtain the controlled conditions which were required for the study objectives. The feed solution was prepared with effluent from the tertiary clarifier of the wastewater treatment plant and spiked with concentrated stock solutions of nitrate (sodium nitrate) and COD. The organic matter was supplied as a mix of glucose and glycerol which are easily biodegradable, and glycine (slowly biodegradable). Glycerol, glucose and glycine accounted for 55%, 25% and 20% of the stock solution's COD supply, respectively. The stock solutions were supplied by a peristaltic pump which time of operation and flowrate were initially set to fulfil the targeted influent characteristics. The required batch volume was prepared 15 minutes before feeding, in order to avoid modification of influent characteristics by biological processes, and stored in a $1m^3$ PEHD tank. The storage tank was covered with a Mylar® layer reflecting light in order to prevent algae growth. The feed solution was homogenized 5 minutes before the feeding by a drainage pump in reverse flow mode; then was applied successively to the pilots with a pump (MC&DWP400, MacAllister).

After a commissioning period of 2 months meant to allow biomass growth, 4 different influent characteristics were studied in order to assess the effect of nitrate concentration (40 and $80mgN.L^{-1}$) as well as the impact of COD_{tot}:N ratio (6, 3 and 1) on the denitrification process. It must be noted that the semi-synthetic influent was prepared from a real treated wastewater. The supply of nitrate and organic carbon was regulated by temporization in a

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programmable logic control. Variations of characteristics of treated wastewater thus had direct effect on characteristics of semi-synthetic influent. Although the objective was to provide the most constant characteristics of influent as possible, these conditions of operation did not avoid slight variations. Nevertheless, the variations in concentration of nitrate, observed between the first 3 phases of the study, were assumed not to affect the comparison. In other words, a fraction of residual organic carbon, mostly under inert or slowly biodegradable forms, was observed in treated wastewater ($[COD_{tot}] = 33.8 \pm 7.8$ $mgO_2.L^{-1}$). Nitrate concentration has thus been slightly increased ($[NO_3^-] = 52.0 \pm 10.0$) for the third phase of this study (COD_{tot}:N = 1) in order to allow the addition of a sufficient amount of biodegradable organic carbon.

3.2.2 Water analysis

The outlet water composition was assessed every weekday on 24h flow composite samples collected by an automatic single bottle refrigerated sampler (SIGMA SD 900, Hach). The inlet composition was assessed via daily grab samples (collected from the storage tank) as a preliminary comparison of grab and 24-hour composite samples had indicated a quite constant nitrate concentration over 24h. 24-hour composite samples were also punctually collected at intermediate depths into pre-acidified polyethylene 10L containers.

Each pilot was evaluated for NO_3^-, NH_4^+, Alkalinity (in $CaCO_3$) and total COD (COD_{tot}), using quick test methods (LCK339, 303, 362 and LCI400; Hach), as well as for TSS by mean of method EN 872:2005 and pH (C1010, CONSORT).

Online monitoring of hydraulics, redox potential and nitrogen pollutants' dynamics was also carried out. The inflow and outflow were measured by water level fluctuation, in the storage tank with a pressure head sensor (Siemens, SITRANS P 7MF1570), and by ultrasonic probe (Pil, P43-F4V-2D1-D0-330E) in the effluent collecting tank. Ammonium and nitrate concentrations as well as redox and temperature were measured at the outlet, at time intervals of 2 minutes by ion selective electrodes (AN-ISE, Hach) and differential ORP sensors (pHD-S sc ORP, platina electrode, Ag/AgCl reference, Hach), respectively.

3.2.3 Tracer test

A tracer experiment was carried out with fluorescein, at the end of the study, in order to characterize the hydraulic dynamics in the filter. Outlet grab samples were collected by a refrigerated automatic sampler (ISCO 4700, PONSEL), at time intervals of 80 minutes (batch

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frequency). Each sample was analysed for absorbance, in the laboratory, at 496 nm with a spectrometer (Helios Epsilon, Thermo Scientific). The concentration of fluorescein was then calculated by means of a calibration equation (y = 0.1497x, R^2 = 0.995) obtained from an initial calibration experiment (0 – 4 $mg.L^{-1}$, Pilot effluent).

The tracer experiment provided information on the residence time distribution (see Eq.[13]) as well as the average retention time (Eq.[14]).

$$E(t) = \frac{C(t)}{\int_0^\infty C(t).dt} \qquad \text{Eq.[13]}$$

$$\tau = \int_0^\infty t.E(t).dt \qquad \text{Eq.[14]}$$

3.2.4 Statistical analysis

Statistical analysis of experimental results was conducted using R software. Pair-wise Mann-Whitney tests were performed for the comparison of both saturated pilots. Significant differences were established for p-values ≤ 0.05.

3.3 Results and Discussion

Figure 25 presents influent and effluent concentrations of nitrate and COD_{tot}, for SVFP, during the study while Table 10 summarizes influent and effluent characteristics. Almost constant concentration of nitrate was applied to the system during the 3 first periods of the study whereas the concentration of COD_{tot} gradually decreased from 249.5 to 70$mg.L^{-1}$. Although feeding solution was prepared in identical conditions, variation in COD_{tot} concentration was observed between samples amongst the same phase of the study. This variability might be explained by the use of effluent from the treatment plant whose characteristics may vary (influent characteristics, aeration process).

In other respects, the effluent concentration of nitrate was negatively correlated with carbon supply and thus increased between successive periods. Almost full denitrification was achieved when COD_{tot} was supplied in a large quantity suggesting that carbon availability was thus the main limit in the studied conditions.

Furthermore, COD_{tot} was still present in significant concentration whatever the initial conditions suggesting that part of organic matter was not available for biological process. An average concentration of COD_{tot} of 33.8$mg.L^{-1}$ was measured in the clarifier's effluent which was in the range of values measured in the pilot's effluent during the 2nd and the 3rd phases of

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the study (38.2 and 35.6mg.L^{-1}, respectively). It may thus be suppose that this organic supply was mostly composed of inert COD_{tot} and, therefore, cannot be consumed during denitrification. Consequently, this value was removed from samples' COD_{tot} data in order to assess only the effect of biodegradable fraction. However, effluent concentration was higher than the inert COD for the 1st and the 4th phases of the study. Although it may be assumed that COD_{tot} removal was probably limited by nitrate availability during the 1st phase another explaination is required for the last one. Slowly biodegradable COD_{tot} (i.e. glycine) accounted for 20% of the carbon supply by the stock solution (i.e. 31mg.L^{-1} for the 4th phase). Supposedly, only part of the slowly biodegradable fraction was removed by denitrification (42%) while another part was remaining in the effluent.

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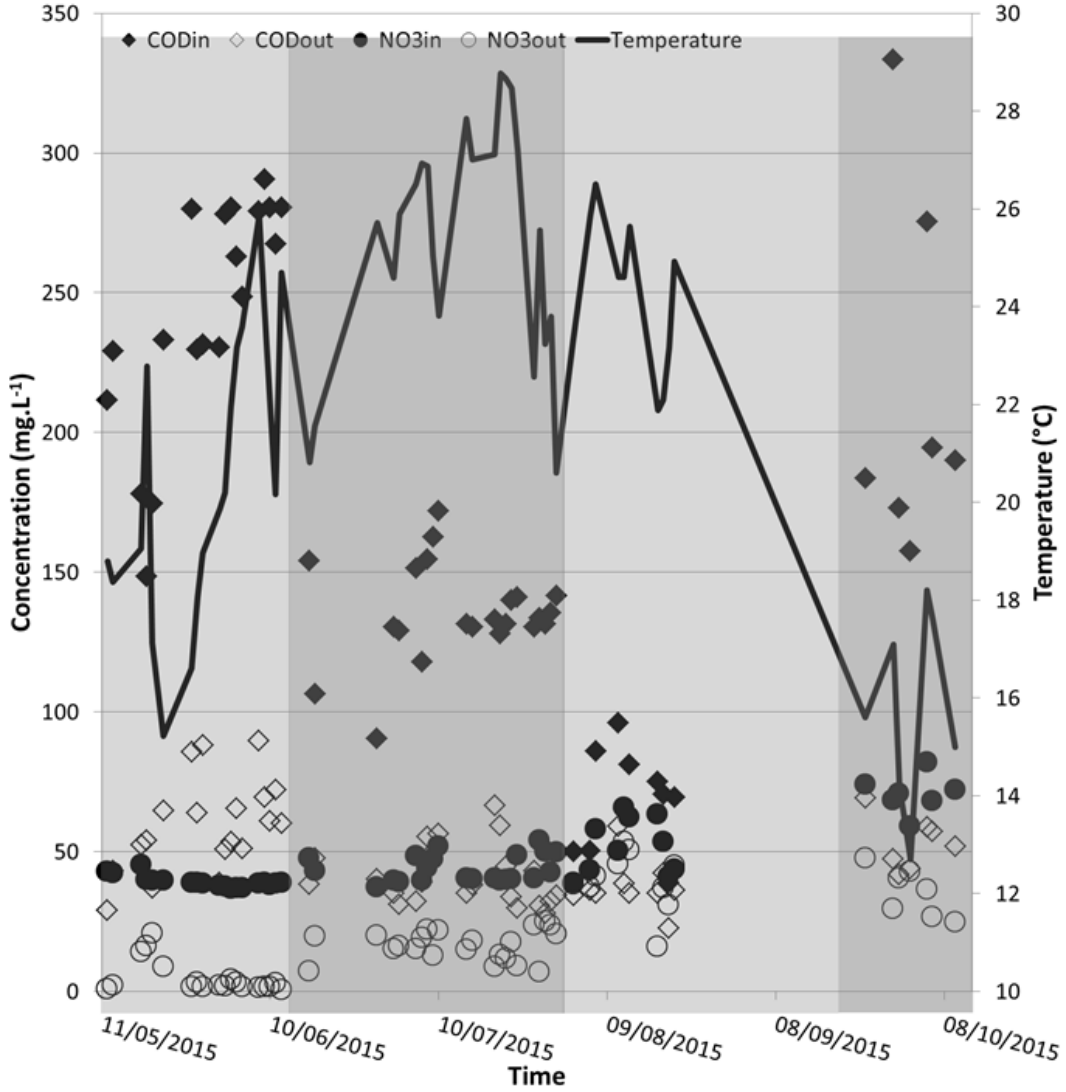

	Phase I	Phase II	Phase III	Phase IV
$[NO_3\text{-}N]_{out}$ ($mg.L^{-1}$)	2.1 ± 5.9	16.9 ± 5.5	39.8 ± 10.7	36.4 ± 8.6
$[COD_{tot}]_{out}$ ($mg.L^{-1}$)	60.2 ±16.9	38.2 ± 10.7	35.6 ± 9.1	51.8 ± 9.1
Consumption ($mgCOD.mgN^{-1}$)	5.4 ± 1.0	3.6 ± 0.9	2.9 ± 2.2	4.9 ± 1.7

Figure 25 Influent and effluent substrates concentration (namely, COD_{tot} and NO_3-N) of SVFP (left axis) and air temperature (right axis) during the study. Note that mean outlet concentrations as well as the consumption of COD for denitrification are reported below the plot.

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Table 10 Water composition and performance for SVFP and SVFB operating under different COD_{tot}:N ratios

Phase	SVFP			SVFB		
	Inlet ($mg.L^{-1}$)	Outlet ($mg.L^{-1}$)	Performance (%)	Inlet ($mg.L^{-1}$)	Outlet ($mg.L^{-1}$)	Performance (%)
Ratio 6	**(n = 19)**			**(n = 13)**		
TSS	46.2 ± 28.9	10.9 ± 9.9	76	34.9 ± 30.5	5.0 ± 11.3	86
COD_{tot}	249.5 ± 41.5	60.2 ± 16.9	76	231.5 ± 45.9	54.5 ± 9.5	76
NH_4-N	13.4 ± 6.1	12.9 ± 5.2	4	8.2 ± 7.4	11.1 ± 5.3	< 0
NO_3-N	38.8 ± 2.2	2.1 ± 5.9	95	38.9 ± 2.1	4.8 ± 7.2	88
Alkalinity (in $CaCO_3$)	328.5 ± 38.8	441.0 ± 45.8	< 0	322.5 ± 45.5	403.5 ± 58.1	< 0
pH	7.5 ± 0.1	8.2 ± 0.1	-	7.6 ± 0.1	8.2 ± 0.1	-
Ratio 3	**(n = 22)**			**(n = 20)**		
TSS	45.6 ± 36.3	5.7 ± 7.4	88	42.9 ± 16.7	4.0 ± 2.1	91
COD_{tot}	132.3 ± 17.6	38.2 ± 10.7	71	132.3 ± 20.3	35.3 ± 11.8	73
NH_4-N	2.7 ± 0.9	0.6 ± 2.1	78	2.5 ± 0.9	0.8 ± 4.1	70
NO_3-N	41.6 ± 4.9	16.9 ± 5.5	59	41.6 ± 5.6	13.6 ± 5.2	67
Alkalinity (in $CaCO_3$)	310.8 ± 36.8	455.8 ± 72.0	< 0	310.8 ± 28.6	410.5 ± 45.7	< 0
pH	7.3 ± 0.2	8.2 ± 0.1	-	7.3 ± 0.2	8.2 ± 0.0	-

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Phase	SVFP			SVFB		
	Inlet ($mg.L^{-1}$)	Outlet ($mg.L^{-1}$)	Performance (%)	Inlet ($mg.L^{-1}$)	Outlet ($mg.L^{-1}$)	Performance (%)
Ratio 1	**(n = 10)**			**(n = 11)**		
TSS	24.9 ± 7.8	2.4 ± 8.0	91	21.5 ± 8.3	3.4 ± 3.7	84
COD_{tot}	70.0 ± 17.8	35.6 ± 9.1	49	65.2 ± 14.7	31.4 ± 8.5	52
NH_4-N	4.4 ± 0.8	0.2 ± 0.1	96	4.2 ± 0.8	0.4 ± 0.6	92
NO_3-N	52.0 ± 10.0	39.8 ± 10.7	24	51.6 ± 10.0	38.8 ± 10.1	25
Alkalinity (in $CaCO_3$)	316.0 ± 33.1	360.4 ± 44.5	< 0	312.0 ± 27.4	365.5 ± 36.9	< 0
pH	7.5 ± 0.1	8.2 ± 0.1	-	7.5 ± 0.1	8.2 ± 0.0	-
Ratio 3bis	**(n = 7)**			**(n = 9)**		
TSS	50.8 ± 29.6	9.2 ± 5.5	82	50.8 ± 27.7	4.0 ± 4.6	92
COD_{tot}	190.0 ± 67	51.8 ± 9.1	73	190.0 ± 56.9	31.5 ± 5.9	83
NH_4-N	11.9 ± 4.6	1.8 ± 2.6	85	10.8 ± 4.3	0.3 ± 2.7	97
NO_3-N	70.8 ± 7.1	36.4 ± 8.6	49	72.2 ± 6.7	38.5 ± 4.9	47
Alkalinity (in $CaCO_3$)	342.5 ± 67.3	489.0 ± 90.6	< 0	342.5 ± 66.8	490.0 ± 87.5	< 0
pH	7.4 ± 0.2	8.0 ± 0.2	-	7.4 ± 0.1	8.1 ± 0.1	-

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3.3.1 Effect of influent COD_{tot}:N ratio

Figure 26 shows the removal performance of nitrate and COD_{tot} of both saturated pilots. Nitrate removal was high at ratio 6 (88% and 92% on average for SVFB and SVFP, respectively) but dropped to 20% when decreasing COD_{tot}:N to 1. On the other hand, removal of COD_{tot} was quite constant between ratio 6 and 3 (around 75%) but decreased to 45% for the lowest COD_{tot}:N ratio.

a b

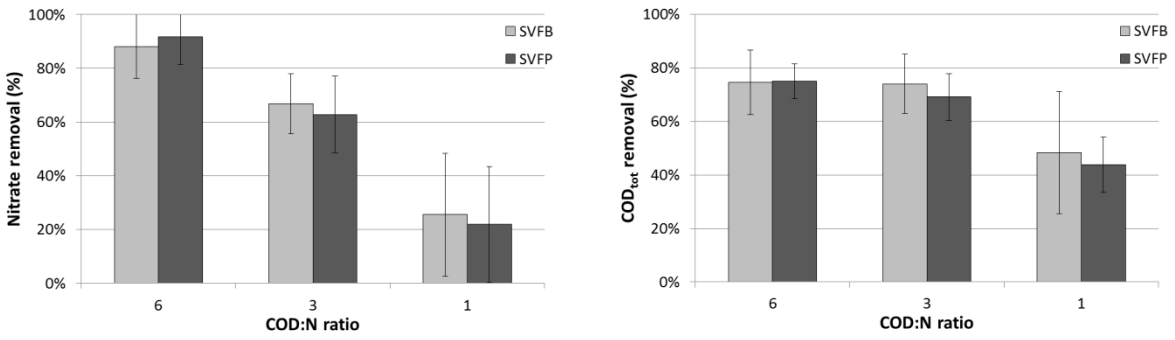

Figure 26 Nitrate (a) and COD_{tot} (b) mean removal for both pilots as affected by COD:N ratio

The nitrate removal rate which was observed at the highest COD_{tot}:N ratio may be explained by the influent composition (see Table 10). COD_{tot} was available in a large amount and almost 80% of COD_{tot} supply was easily biodegradable while 20% was slowly biodegradable. The organic supply was thus a major limitation in denitrification (Ding *et al.*, 2012; Lu *et al.*, 2009) occurring for COD_{tot}:N ratio close to 3 or lower. This observation is in accordance with Ye and Li (2009) who reported that the reduction of 1 gNO_3-N implies the oxidation of 2.86gBOD_5.

The low removal performances observed at low ratio (COD_{tot}:N = 1) should be interpreted with care since part of the influent COD_{tot} was supplied by the clarifier effluent whose COD_{tot} concentration was significative (33.8 ± 7.8mg.L^{-1}) and which is mainly slowly biodegradable. As such, the slowly biodegradable COD fraction was higher at low COD_{tot}:N ratios. In order to face to this uncontrolled COD_{tot} supply, nitrate concentration was kept slightly higher at ratio 1 (52mgN.L^{-1}) than at the other feeding ratios operating at 40 mgNO_3-N.L^{-1} (see Table 10). The observed performance at low ratio also suggested the complete removal of easily biodegradable COD_{tot}. The availability of easily biodegradable COD_{tot} was thus a limiting

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parameter for the denitrification process and significantly affected nitrate removal ($p = 0.04$ for both pilots). Not only the availability of COD_{tot} but also its composition (COD/BOD_5) should thus be considered with attention for denitrification purposes. If COD_{tot} was completely biodegradable, an optimal COD_{tot}:N ratio between 6 and 3 might allow a full denitrification. This is consistent with Zhu *et al.* (2014) who reported an optimal COD_{tot}:N ratio of 5 or Ding *et al.*, (2012) who observed an improvement, up to 100%, in nitrate removal when increasing the COD_{tot}:N ratio ratio from 1 to 9. Therefore, in regards with the relationship between denitrification and degradability of organic matter, it would be advisable to focus on BOD_5 instead of COD_{tot} when it is possible.

Nevertheless, systems such as the French design of CW, which implement an aerobic treatment before the anoxic zone, perform nitrification and consume the organic matter in the first stage. This carbon source is thus no longer available to achieve a high denitrification rate (Saeed and Sun, 2011). Morvannou *et al.* (2015) and Molle *et al.* (2005) reported COD_{tot} and NO_3^--N concentrations of 130 and 40 $mg.L^{-1}$, respectively, in effluent from a French 1st stage of VFFs. Assuming an inert COD concentration at $30mg.L^{-1}$, the COD_{tot}:N ratio in the anoxic zone was around 2.5 suggesting that carbon availability may limit denitrification process. Several studies (Ding *et al.*, 2012; Zhao *et al.*, 2011; Lu *et al.*, 2009; Rustige and Nolde, 2007) reported the positive impact of carbon addition on denitrification performances. That being said, the type of carbon supply is also an important parameter since labile carbon (e.g. glucose, methanol, acetate) is more easily available for microorganisms than molecules with higher molecular weights (Meng *et al.*, 2014; Kjellin *et al.*, 2007). Other authors (Warneke *et al.*, 2011; Leverenz *et al.*, 2010; Schipper *et al.*, 2010) reported good nitrate removal by systems filled with organic media such as woodchips. The roots decomposition and the accumulation of organic matter within the macroporosity, with maturation of the 1st stage of VFFs, might result in a release of COD acting, like woodchips material, as an additional passive source of carbon. Further studies on the kinetic of COD release as well as the lability of organic matter might be interesting in order to properly assess the potential effect of such COD supply. In other respects, nitrogen concentration varies widely during day in domestic effluent and, therefore, also the denitrification's COD demand. Better knowledge of the denitrification kinetic and the effects of influent characteristics (nitrate concentration, COD_{tot}:N ratio) is thus required in order provide optimal retention time and adapt the exogenous carbon supply depending on the conditions.

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3.3.2 Effect of filtration medium

Figure 26, presenting nitrate and COD_{tot} removal by SVFP and SVFB at different COD_{tot}:N ratios, shows similar performance for both pilot units. The Mann-Whitney tests confirmed that, irrespective of the applied COD_{tot}:N ratio, increasing medium specific surface (from 100 to 460 $m^2.m^{-3}$) did not result in better removal efficiency (all p-values > 0.10).

Moreover, the Biofill Type C® porosity was twice the pebble porosity. Theoretical retention time should thus be higher in SVFB than SVFP since both pilots had the same reactor volume and were fed with identical daily hydraulic loads. Therefore, this consideration suggests that the areal removal rate, at the highest COD_{tot}:N, was lower with Biofill Type C® than with pebble (25.6$mgN.m^{-2}_{Biofill}.d^{-1}$ and 153$mgN.m^{-2}_{pebble}.d^{-1}$, respectively).

Two operational conditions might explain this rather unexpected observation. Firstly, Biofill Type C® media were designed for fluidized reactors such as moving bed biofilm reactors, which allow the efficient use of its specific surface. In the present study, the media were bulk packed in the reactor and therefore contacting each other, resulting in a decrease of the usable surface. Secondly, its use under fluidized conditions causes collisions between individual carriers, resulting in biofilm management (biomass detachment). In the present case, biofilm growth was not controlled, resulting in partial pore clogging (see Figure 27).



Figure 27 Biofilm growth on Biofill Type C®

3.3.3 Effect of retention time

As previously discussed, both pilots performed similarly in terms of COD_{tot} and nitrate removal. Consequently, the following sections focus on SVFP which is more representative of classic saturated VFFs than SVFB.

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Assuming that hydraulic behavior in the pilot was comparable to plug flow reactor (PFR), theoretical hydraulic retention time (HRT) was estimated, with regards to design characteristics (see Table 9) and operational conditions, at 1 day. Slightly longer HRT was determined from tracer experiment (1.18d). However some reserves may be expressed on the reliability of the results as it is suggested by the recovery rate higher than 1. This inaccuracy may be partly attributed to flow measurement uncertainty as well as to interactions between tracer and the matrix during flow infiltration. Nevertheless, the results of tracer recovery in relation to experiment duration, presented in Figure 28, showed that effluent tracer concentration increased almost immediately, probably because of side effects, while a tail was observed at the end suggesting the presence of stagnant zones. Consequently, the effect of retention time, based on the assumption of PFR, has to be taken with care.

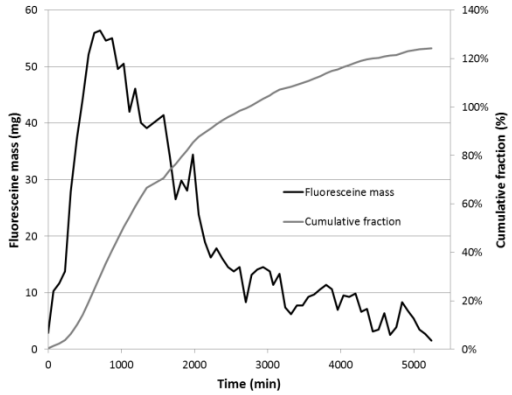

Figure 28 SVFP fluorescein release dynamics

Nitrate and COD_{tot} effluent concentrations, in relation to theoretical retention time, are presented in Figure 29 for 3 different COD_{tot}:N ratios but same nitrate concentration (C_{in}=40mgN.L^{-1}). Both nitrate and COD_{tot} treatment performance follow a logarithmic shape and reach a plateau after a retention time depending on ratio conditions. The actual calculated COD_{tot}:N ratio at each retention time is reported next to its respective dot. These ratios decreased during treatment suggesting that the consumption of organic matter was higher than nitrogen in denitrification process which was consistent with Ye and Li (2009) who proposed a theoretical consumption of 2.86mgBOD_5.mgNO_3-N^{-1}.

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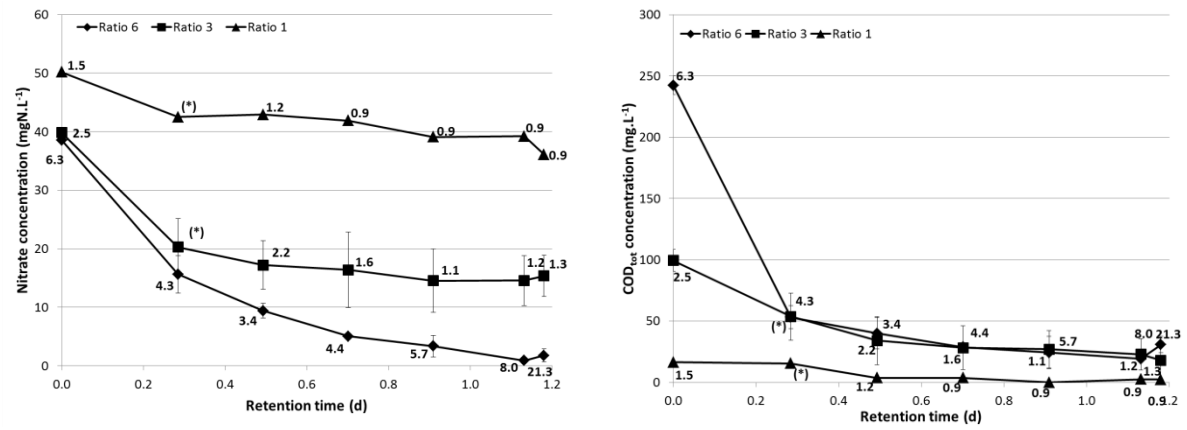

Figure 29 Nitrate (a) and COD_{tot} (b) SVFP outlet concentration in relation to retention time for different COD_{tot}:N ratio (C_{in} = 40mgNO_3-N.L^{-1}). Note that COD_{tot}:N ratios are presented for each retention time in front of each data (* means that the ratio cannot be determined).

Nitrate removal continuously increased with retention time, for high COD_{tot}:N ratio (i.e. 6), and reached almost full denitrification after 1.18d. Removal dynamics showed that the process rate was fast until 0.3d (29.2gN.m^{-2}.d^{-1}) then decreased for longer retention time (6.3gN.m^{-2}.d^{-1}). In other respects, the instantaneous COD_{tot}:N ratios increased after 0.5d, and became higher than the influent ratio after 1.1d, while nitrate was almost negligible. This observation suggested that complete denitrification may be carried out after 1d of contact but also that COD_{tot} was present in excess in the influent. A tertiary unit of treatment might be thus required in order to reach standards for COD_{tot} discharge in environment.

The monitoring of nitrate removal at ratio 3 and 1 showed a nearly constant performance (57% and 15%, respectively) after 0.5d while the instantaneous ratios reached a threshold which may be explained by denitrification shutdown. The plateau was indeed concomitant with the observation of very low concentration of COD_{tot}, whereas nitrate concentration remained quite high, for the lower influent ratio suggesting that carbon availability became a limiting factor. Uncertainty in the estimation of the correction factor of inert COD may probably explain that final COD_{tot} concentration for medium ratio was not close to zero.

Another explanation might also rely on the COD_{tot} composition since 20% of carbon supply was slowly biodegradable (i.e. glycine). A very slight decrease may be observed for both substrates, at ratio 3, after 0.5d of retention. It was tricky to determine if this trend was related

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with the analysis uncertainty or if very low removal occurred. However, it might be supposed that slowly biodegradable may be consumed for denitrification but, at so low kinetic rate, that it was negligible for the studied retention times. Stein *et al.* (2006) evaluated the effect of incubation time from 1 to 20 days. A first high drop in COD concentration was observed during the first day, then the concentration slowly decreased until reaching a background concentration after 20d. Their study thus suggested that part of the slowly biodegradable COD may be removed by increasing the contact time but also that part of COD cannot be removed. Based on these observations and, considering the economical and engineering criteria, increase the retention time with the aim of using slowly biodegradable COD_{tot} for denitrification purposes seem inappropriate. It would be better to supply additional carbon source in order to increase the COD_{tot}:N ratio.

Finally, the comparison of initial slope of each curve showed that the kinetics were affected by COD_{tot}:N ratio. Whereas initial removal rate was quite similar between ratios 6 and 3 (29.2gN.m^{-2}.d^{-1} and 24.9gN.m^{-2}.d^{-1}, respectively), in the upper 20cm of the system (i.e. HRT=0.28d), this value dropped at 9.8gN.m^{-2}.d^{-1} for the lower ratio. The kinetic therefore seems to be strongly affected if carbon availability is initially low. The optimization of retention time without consideration of COD_{tot}:N ratio is therefore inappropriate. Furthermore removal rates were lower in the zone between 20cm and 50cm (4.5gN.m^{-2}.d^{-1} and 3.4gN.m^{-2}.d^{-1}). It would be interesting to monitor the profile of redox potential along filtration depth in order to assess the effect of filtration depth on the system conditions.

3.3.4 Effect of influent nitrate concentration

Figure 30 presents nitrate concentration, in relation to retention time, for 2 influents with similar COD_{tot}:N ratio (3) but different nitrate concentrations (41.6 or 70.8 mgN.L^{-1}, respectively). Both curves showed a similar logarithmic shape reaching a threshold after 0.7d. The denitrification process was limited by carbon availability in both cases since the characteristics of carbon supply were the same.

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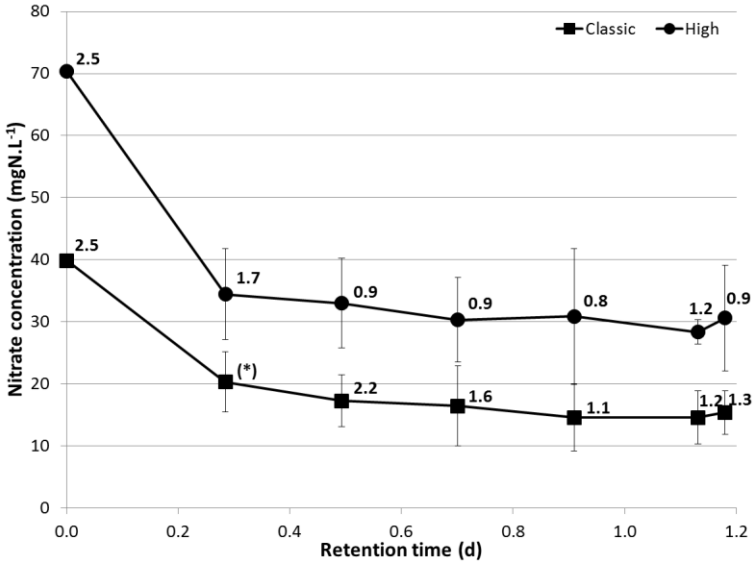

Figure 30 Nitrate removal, for different inlet nitrate concentrations (C_{in} = 41.6 and 70.8mgN.L^{-1}, respectively), by SVFP in relation with retention time

Thus, increasing the nitrate load did not affect removal efficiency if COD_{tot}:N ratio still high. Moreover, an equal treatment of the doubled load was achieved for a similar retention time. This observation suggests that the denitrification removal rate is mainly dependent on applied concentration (9.5 and 15.2gN.m^{-2}.d^{-1} for influent concentration of 41.6 and 70.8mgN.L^{-1}, respectively). This is consistent with Lu *et al.* (2009) or Sirivedhin and Gray (2006) who also observed that nitrate concentration affected the denitrification rates. Higher nitrate concentration in the influent led to the establishment of robust and active denitrifying biomass which enables better removal rates (Lee *et al.*, 2009).

The optimization of retention time must therefore be carried out considering the influent concentration and not only the applied load. Further study of increasing nitrate concentrations is thus required with the aim to determine the relationship between removal rate and inlet concentration.

3.4 Conclusion

This study aimed to assess the effects of various design and operational criteria on the denitrification process.

The main limitation was related to the carbon supply. First of all, only the easily biodegradable fraction of organic matter should be considered for an optimized design of a denitrification bed. Consequently, BOD_5, instead of COD_{tot}, is more suited for design purpose since it provides information of the usable organic carbon whereas COD_{tot} sums up all

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fractions of organic matter. Moreover, the hardly biodegradable fraction of COD_{tot} may vary widely depending on local context which would result in flawed use of design guidelines based on such parameter.

A denitrification bed cannot perform full nitrate removal if the inlet COD_{tot}:N ratio is lower than 3. Since effluent from the 1st stage of VFFs generally has low COD_{tot} concentration, an additional carbon supply should be considered. The implementation of carbon-rich filtration media can provide the required organic matter but no information on their life span is available and risk of clogging is expected. On the other hand, a direct supply of a carbon-rich solution (e.g. methanol) into the saturated zone by a dosing pump is easy to manage, but investment and operational costs will increase (organic substrate, pumps). Finally, another alternative might rely on design optimization of the first stage VFFs in order to limit the heterotrophic removal of COD_{tot}. The first 20cm of first stage VFFs is the more active zone of filtration layer considering the removal of organic matter. A thinner filtration layer might be a solution in order to increase the COD_{tot} concentration in effluent. In other respects, reduction of the treatment surface may also result in lower performance on COD_{tot} removal. In both cases, high ammonium removal cannot be achieved on the first stage. Nitrification must thus be carried out on a 2nd stage VFF whose effluent must be recirculated ahead from the denitrification unit. Carbon would thus be supplied from the 1st stage whereas nitrate would be provided by the 2nd stage. These design optimizations might allow to achieve good TN removal without needs of exogenous carbon source. Reduction in treatment footprint might also be expected.

In other respects, retention time must be considered as an adjustment variable of performance level. A short retention time (1d) enables to achieve almost full denitrification if easily degradable organic matter supply is in excess, since denitrification rate is fast ($29.2 gN.m^{-2}.d^{-1}$), while slightly longer retention times must be considered for COD_{tot}:N ratios close to 3 as denitrification rate decreases. The first stage of VFFs achieves high COD_{tot} removal and the carbon supply may limit the process kinetic as well as the efficiency due to carbon limitation. Accurate estimation of carbon content at the outlet of the first stage is thus a prerequisite in order to set optimal design in relation with influent characteristics. A long retention time is pointless since it does not allow to efficiently oxidize the slowly biodegradable COD_{tot} fraction.

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Finally, the inlet concentration does not affect the design since denitrification rate increases with inlet concentration. Nevertheless, the effect concentrations exceeding 80 $mgN.L^{-1}$ was not assessed but may need to be studied as nitrate release in the early stage of a feeding cycle of a 1st stage of VFF frequently reaches higher concentrations. Further study of the impact of nitrate concentration must be conducted in order to assess the effect of this first flush and thus adjust retention time if necessary.

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Chapter 4 Numerical tools for prediction of nitrate removal

This chapter has not been submitted for publication. Further data processes, based on a large heterogenous dataset, is required before reaching the objective of a simple accurate predictive tool.

Prediction of Nitrate Removal by Saturated Vertical Flow Filter: Which appropriate Simple Numerical Tool for Design engineering?

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Abstract

Two simple "black-box" models (linear model and PkC model, respectively) were studied in the purpose of design assistance for denitrifying constructed wetlands. A saturated vertical flow filter was monitored over 4 months, under different conditions (inlet $[NO_3^-]$, COD_{tot}:N ratios), and was analyzed, for different retention times, in COD_{tot} and nitrates. Linear model provided good prediction for low nitrate concentrations and high COD_{tot}:N ratio but was less effective for higher inlet concentrations and short contact time. PkC model was not able to correctly describe substrate limitations since it was based on 1st order kinetic. The implementation of individual sub-models in a metamodel improved its effectiveness. Such modification of PkC model performed good prediction of nitrate and COD_{tot} concentrations for long retention time whatever the COD_{tot}:N ratio.

Keywords: *Denitrification, PkC model, Statistical model, Saturated vertical flow constructed wetland*

4.1 Introduction

The fate of nitrogen present in wastewater met a growing attention because of its negative impact on aquatic ecosystems (e.g. toxicity of unionized ammonia and eutrophication). The classical French design of constructed wetlands (CWs), composed of two successive stages of vertical flow filters (VFFs), is highly efficient to treat TKN (Morvannou *et al.*, 2015) but is quite ineffective to remove total nitrogen (Langergraber *et al.*, 2008) from wastewater because of its highly aerated conditions. The implementation of an intermediate horizontal flow filter (HFF) is thus necessary, in order to provide anoxic conditions, when nitrate removal is required. That results in higher energy consumption (recirculation of effluent from last VFF to HFF) and significant increase of treatment surface which may be problematic if land availability is limited.

For this reason, partly saturated VFFs, such as Biho-Filter®, were recently studied (Prigent *et al.*, 2013; Troesch *et al.*, 2014; Silveira *et al.* 2015) in order to provide both aerobic and anoxic conditions into a single filter.

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While HFF design was initially based on simple rules of thumb (Rousseau *et al.*, 2004; Stein *et al.*, 2006), such as maximum loading rates (Stein *et al.*, 2006), nowadays designers most frequently adopt their design from the prediction of outlet concentrations by first-order kinetic models (von Sperling and de Paoli, 2013) or by regression equations.

Input – output (I/O) monitoring is the most widespread method of wetland investigation (Rousseau *et al.*, 2004). The derivation of a simple empirical relationship between I/O datasets is thus an obvious solution (Kumar and Zhao, 2011) and many of them were proposed in literature. Nevertheless, such simple black-box model lumping all processes into a simple equation provides a good representation of a given system but is not necessarily valid for different systems.

First-order kinetic models describe the exponential decrease in concentration over time until reaching zero (Saeed and Sun, 2011b). However it is unrealistic to assume reaching close-to-zero concentration in wetlands for some substrates such as COD because of the presence of a recalcitrant fraction. Several authors (Nivala, 2012; Stein *et al.*, 2006; von Sperling and de Paoli, 2013) implemented with success a background concentration (C^*) in order to fix this inaccuracy of the model. First-order k-C^* kinetic model is usually associated in the published studies with a plug flow description of hydraulic dynamics. This approach is not consistent with the actual hydraulic dynamics in VFFs, and generates inaccuracy (Sun and Saeed, 2009). An alternative approach, for a better description of residence time within the system, relies on the assumption of series of ideal stirred tank reactors. This method, namely P-k-C^* first-order model, give more accurate results (von Sperling and de Paoli, 2013). Furthermore, first-order kinetic model shows another limit in the ability to describe denitrification process (Saeed and Sun, 2011). Ojeda *et al.* (2008) successfully described, with first-order kinetic model, the complex relationships between the processes regulating the dynamic of substrates. Multiplicative inhibition terms and saturation terms for electron acceptor were implemented in order to properly represent the whole complexity of the system. However, general approach on first-order kinetic models usually relies on the assessment of a single substrate assuming that the others are under optimal conditions (excess or absence). This is somehow an oversimplification which may hinder proper description of complex processes, such as denitrification, based on the synergy of multiple substrates and conditions. Moreover, in its usual formulation, first-order kinetic models also assume that removal rate does not depend on substrate availability. Multiple Monod-kinetic model is a suitable alternative to overcome these limitations. It allows considering the effect of each substrate of interest, for a given

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biological process, and switching from zero to first-order kinetic according to substrate availability through the implementation of multiplicative half saturation constants of limiting substrates and maximum pollutant removal rates.

The simple models described here above do not represent the real complexity of CWs and are generally only able to represent the outlet concentration of a single parameter for a specific design and a given operational condition. However, CWs are complex systems and the current objective is to develop models considering the hydrodynamic as well as the numerous processes (biological, physico-chemical), occurring in such systems, at the same time (Meyer *et al.*, 2015). These models generally consist in several submodels describing substrate cycles (Monod-type kinetic processes, adsorption mechanisms, biofilm diffusion), hydraulic (network of ideal reactors or more complex representations) and other processes such as oxygen transfer or plant uptake (Rousseau *et al.*, 2004). Only few models were developed up to now (Kumar and Zhao, 2011) and none of them are yet usable for design purpose (Meyer *et al.*, 2015). This is mostly explained by the complexity of such models which use a lot of state variables and parameters. The monitoring of various parameters (field conditions, weather conditions, influent characteristics) as well as the calibration of many kinetic parameters is thus required and is currently a major limit in the establishment of mechanistic models. As mechanistic models are too complex for design purpose (Meyer *et al.*, 2015), accurate simple predictive models can be useful for engineers in order to validate the suitability of proper wetland design. Even if simplified models cannot perfectly describe the complex mechanisms occurring in CWs (Saeed and Sun, 2011), this study aimed to assess two different simple models (regression model and first-order model) to define in which extent they are able to predict nitrate concentration at the outlet of a saturated vertical flow filter. Special attention was paid to COD_{tot}:N ratio as well as residence time since the denitrification process is highly dependent of both parameters.

4.2 Material and method

4.2.1 Experimental setup

A pilot-scale saturated VFF, located on the municipal wastewater treatment plant site of Jonquerettes (France), was monitored over 5 months from May to September 2015 (see appendix II).

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The pilot structure, consisting of a concrete tank (L = 1.2m, W = 1.2m, H = 1.0m), was filled with 0.85 m of river pebble (20/50mm).

Six sampling devices were distributed along the depth profile (5, 20, 35, 50, 65 and 80 depth-cm, respectively). These devices were composed of horizontal PVC pipes (ø20mm) which were introduced in the filter (40cm), through the wall of the pilot, and ending with manual valves.

The filter was fed from the surface by 2 parallel feeding pipes (PVC, ø32mm, 1 m-long) spaced 60cm from each other and 30cm from the edge of pilot. Each pipe was perforated by 2 lines of 3 holes (ø6mm), fairly distributed along the length and making a 45° angle with the vertical axis, in order to ensure homogeneous water repartition. Figure 31 proposes an overall description of the pilot.

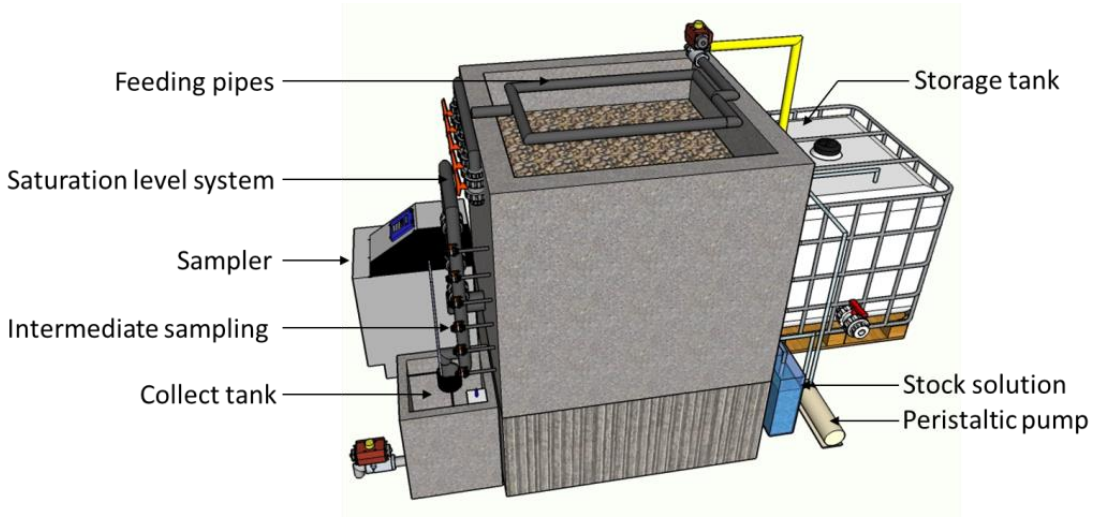

Figure 31 Experimental setup

The pilot was operated each day in intermittent batch-fed mode (18 batches, 0.36 $m.d^{-1}$) with a flow feeding of 1.2$m.h^{-1}$ approximatively. Semi-synthetic wastewater was used, for the study, in order to control the nitrate and total COD (COD_{tot}) concentrations. The feeding solution was composed of effluent from the tertiary settling tank of the wastewater treatment plant which was spiked with stock solutions containing nitrate ($NaNO_3$) or organic matter, respectively. Glycerol, glucose and glycine accounted for 55%, 25% and 20% of the stock solution's COD supply, respectively. The concentration of COD_{tot} and nitrate of the stock solutions was adapted throughout the study in order to assess 3 different COD_{tot}:N ratios (6, 3 and 1 respectively) as well as the effect of influent nitrate concentration. It must be noted that the semi-synthetic influent was prepared with a real treated wastewater. The supply of nitrate

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and organic carbon was regulated by temporization in a programmable logic control. Variations of characteristics of treated wastewater thus had direct effect on characteristics of semi-synthetic influent. Although the objective was to provide the most constant characteristics of influent as possible, these conditions of operation did not avoid slight variations. Nevertheless, the variations in concentration of nitrate, observed between the first 3 periods of the study, were assumed not to affect the comparison. In other words, a fraction of residual organic carbon, mostly under inert or slowly biodegradable forms, was observed in treated wastewater ($[COD_{tot}]$ = 33.8 ± 7.8 $mgO_2.L^{-1}$). Nitrate concentration has thus been slightly increased ($[NO_3^-]$ = 52.0 ± 10.0) for the third phase of this study (COD_{tot}:N = 1) in order to allow the addition of a sufficient amount of biodegradable organic carbon. The influent characteristics are listed in Table 11. The feeding solution was stored in a $1m^3$ plastic tank covered by a Mylar® layer in order to prevent algae growth and limit temperature variation. The required volume of solution for a single batch was prepared 15 minutes before each feeding in order to avoid the occurrence of biological reactions which may modify the influent characteristics over time. The stock solutions were added by a peristaltic pump. The stored solution was stirred during 5 minutes before feeding, in order to ensure homogenization of the influent, and then was applied to the system by a drainage pump.

Table 11 Influent characteristics during the study

Phase	Duration (d)	$[COD_{tot}]$ $mg.L^{-1}$	$[NO_3^-]$ $mgN.L^{-1}$	COD_{tot}:N ratio	n
I	38	249 ± 41.5	38.8 ± 2.2	6.8 ± 1.3	19
II	33	132.3 ± 17.6	41.6 ± 4.9	3.3 ± 0.3	22
III	19	70.0 ± 17.8	52.0 ± 10.0	1.4 ± 0.3	10
IV	17	190.0 ± 67.0	70.8 ± 7.1	2.7 ± 1	7

4.2.2 Sampling and Water analysis

24-hour flow composite samples were collected at the outlet by a refrigerated sampler (SIGMA SD 900, Hach) while grab samples of the storage tank were used (the influent characteristics remained constant over one day). Intermediate 24-hour continuous sampling

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were also punctually collected, for depth assessment purpose, in polyethylene containers previously added with sulphuric acid in order to inhibit biological reaction.

The influent and effluent compositions were evaluated every weekday for COD_{tot}, nitrate, ammonium and carbonate, with Hach quick test methods (LCI400, LCK339, LCK303, LCK362). TSS and pH were also measured, according to method EN 872:2005 by filtration on 0.45µm cellulosic filters and with CONSORT (C1010) sensor, respectively.

4.2.3 Online monitoring

Online monitoring of the hydraulic dynamics was carried out by measuring the water level variation in the storage tank (pressure head sensor, Siemens SITRANS P 7MF1570) and in a tank collecting the effluent (ultrasonic probe, Pil, P43-F4V-2D1-D0-330E).

Ammonium and nitrate dynamics were also monitored at the outlet of the pilot, at time interval of 2 minutes, with ion selective probes (AN-ISE, Hach).

4.2.4 Tracer test

A tracer experiment was carried out with fluorescein, at the end of the study, in order to characterize the hydraulic dynamics inside the filter. Outlet grab samples were collected by a refrigerated automatic sampler (ISCO 4700, PONSEL), at time intervals of 80 minutes (batch frequency). Each sample was analysed in the laboratory for absorbance, at 496nm with a spectrometer (Helios Epsilon, Thermo Scientific). The concentration of fluorescein was then calculated by means of a calibration equation ($y = 0.1497x$, $R^2 = 0.995$) obtained from an initial calibration experiment (0 – 4 $mg.L^{-1}$, Pilot effluent).

The tracer experiment allowed to calculate the residence time distribution (see Eq.[15]) as well as the average retention time (Eq.[16]).

$$E(t) = \frac{C(t)}{\int_0^\infty C(t).dt} \qquad \text{Eq.[15]}$$

$$\tau = \int_0^\infty t.E(t).dt \qquad \text{Eq.[16]}$$

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4.2.5 Model approach

❖ Characterisation of hydraulic dynamics

Hydraulic characterisation of the system is a prerequisite to advance in modelling since hydraulic and removal processes are closely related (Marsili-Libelli and Checchi, 2005). Chazarenc *et al.* (2003) reported that pulse tracer test is one of the best method for the assessment of CWs' flow paths.

Plug flow model is inadequate to describe hydraulic behavior in CWs (Kadlec and Wallace, 2009). Chazarenc *et al.* (2003) suggested that CWs may be theoretically considered as a succession of CSTR in series. The number of tanks in series (NTIS) can be graphically determined from residence time distributions (RTDs) for different N-values (Eq.[17]). The N-value was chosen in order to optimize the fitting of E_N and experimental RTD.

$$E_N = \frac{N}{\tau} \times \left(\frac{N \times t}{\tau}\right)^{(N-1)} \times \frac{e^{-N \times t/\tau}}{(N-1)!} \qquad \text{Eq.[17]}$$

This flow representation was used for the first-order model. Nevertheless, it is important to keep in mind that it is a simple representation of more complex hydraulic phenomena. This model may lead in a poor data fitting even if large number of tank in series is used (Marsili-Libelli and Checchi, 2005).

❖ Model 1: Regression model

Multivariate linear modelling (statistical model) was carried out in order to obtain a simple equation ($y = \alpha + \beta_1.x_1 + \beta_2.x_2 + \ldots + \beta_n.x_n$) (Dong *et al.*, 2012) linking design and operational criteria with outlet concentration. This regression model was developed with R-studio software using the experimental data set.

First, the establishment of a training dataset, which was used for model development, and a validation dataset was necessary. Ten samples of the full dataset were randomly selected and excluded in order to further assess the model quality. The remaining samples were used to develop the model.

Based on experimental observations, independent explanatory variables were selected, among the different studied criteria, in order to predict the concentration (Dong *et al.*, 2012). A preliminary assessment of these variables was conducted in order to evaluate the risk of multi-

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collinearity (Lacombe *et al.*, 2014). The less relevant variable was excluded when multi-collinearity was detected.

The model was based on polynomial regression (2nd order) which was supplemented with additional interaction between variables since the influence of a variable may be modified by changing the settings of other variables (Ni *et al.*, 2013). The linear relationship was validated if R-squarred value was greater than 0.5 (Hijosa-Valsero *et al.*, 2011). The simpler the structure, the greater the statistical model (Crawley, 2005). The principle of parsimony (as little explanatory variables as possible, preferring linear than curve models, limit interaction terms) was followed in order to fulfil this recommendation. The model was thus developed following backward step-wise method (Dong *et al.*, 2012; Crawley, 2005). First, the most complex model expression (maximal model) was evaluated for prediction. Explanatory variable was considered to be significantly different than zero if its p-value, from t-student test, was lower than 0.05 (Lacombe *et al.*, 2014). The less significant parameter of the model (higher p-value) was then excluded from the model expression. The new model was in turn assessed. The final expression was obtained when each parameter was significantly relevant for prediction (minimal adequate model). The simplification step aims at removing non-significant interactions terms, non-significant quadratic terms as well as non-significant explanatory variables (Crawley, 2005).

The minimal adequate model was then assessed graphically. The homoscedasticity (homogeneity of residuals) must be respected in order to validate that no pattern are related with concentrations. The residuals distribution against concentrations must thus be randomly distributed around zero (Babatunde *et al.*, 2011) and the standardized residuals must be normally distributed. Moreover, the observation of the Cook's distance allow to identify and remove outliers which have abnormal influence on the parameter estimation (Lacombe *et al.*, 2014). If values with high leverage were identified, they were excluded from the data set and the model calibration was started over. The confidence interval (accuracy of the model to explain the entertainment data set) and the prediction interval (accuracy of the model to explain new data) were assessed.

The minimal adequate model was finally validated on the validation data set (obtained from the same experiment but which was not used for model calibration). The predicted data were plotted against observations in order to assess the model accuracy.

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Nitrate removal depends on the COD_{tot} availability. Inert COD_{tot} may remain in solution (background concentration) but is not available for denitrification process. The COD_{tot} data (inlet and outlet) were corrected by the subtraction of an arbitrary correction factor (33.75 $mg.L^{-1}$), corresponding to the average clarifier outlet's concentration, in order to allow capturing the COD_{tot} limitation effect by the regression and thus improve reliability of the nitrate model. The regression of COD_{tot} was conducted with the raw data set since it was believed that the limitation may be integrated in the intercept parameter.

❖ Model 2: first-order kinetic model

The PkC^* model is based on the assumption of first-order reaction kinetics in a series of CSTR. The first-order removal rate can be determined as follows (Kadlec and Wallace, 2009):

$$k_v = \left[\left(\frac{C_{out}-C^*}{C_{in}-C^*}\right)^{-1/P} - 1\right] \times \frac{P}{\tau} \qquad \text{Eq.[18]}$$

Where k_v is the modified first-order volumetric rate constant (d^{-1}), C_{in}, C_{out} and C^* are the inlet, outlet and background substrate concentrations ($mgN.L^{-1}$). C^*_{NO3} was set to 0 according to Kadlec and Wallace (2009) recommendations while C^*_{COD} was estimated through the fitting-step. τ is the retention time (d) and P is the apparent number of tank in series (TIS) which is related with two parameters. The first one (N) is the actual number of tank in series which is graphically determined from experimental data of RTD. The second parameter (n) is the k-value distribution breadth and is related with the type of studied substrate. Indeed some analysis procedure, such as the removal of COD_{tot}, lump several substrates whose individual biodegradation kinetic may be different (Kadlec and Wallace, 2009) and water composition thus vary over weathering. The k_v parameter is thus a modified first-order summarizing the different substrate in a single kinetic parameter in order to simplified the model. A detailed explaination of theory is available in Kadlec and Wallace (2009).

The effect of temperature is modelled via an Arrhenius-type equation (Rousseau *et al.*, 2004):

$$k_{V,T} = k_{V,20} \times \theta^{(T-20)} \qquad \text{Eq.[19]}$$

The model was developed for nitrate and COD, respectively, to minimize the sum of squared errors (SSE) and the mean absolute error (MAE) (Hauduc *et al.*, 2011) between predicted and experimental data of vertical profiles (which were more appropriate than simple I/O calibration (Kadlec, 2000)) with the solver tool of Excel™ software. The fitting of PkC^*

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model on experimental data from different locations along the filtration height requires accurate knowledge of their respective HRTs. The NTIS determined from tracer experiment was small (N = 2) and was thus inadequate for the estimation of HRT for each intermediate sampling spots. For convenience, HRTs were thus estimated, for each intermediate sampling depth, making the assumption that water behaved, within the pilot, similarly to a PFR.

A regression equation of first-order rate constants was determined for each pollutant and was implemented in a metamodel which was developed with R software. This metamodel was a calculation loop (time step = 1% of residence time) which simultaneously considered both nitrate and COD parameters. The model adjusted the concentrations and the constant rates at each time step and then returned the results. The calculation was stopped at the end of the loop or as soon as substrate limitation occurred. This metamodel was finally validated on the routine I/O samples.

4.3 Results and discussion

Influent nitrate concentration was remained almost constant during the three first phases of the study ($[NO_3\text{-}N]_{in}$ = 43.7 ± 7.1 $mg.L^{-1}$) while COD_{tot} supply was gradually decreased in order to assess the effect of COD_{tot}:N ratio on the efficiency of nitrate removal. Figure 32 presents the nitrate concentration in the effluent in relation to the COD_{tot}:N ratio during the study. The effluent concentration of nitrate increased exponentially when ratio decreased. In other respects, COD_{tot} concentration remained quite constant ($[COD_{tot}]_{out}$ = 47.9 ± 15.5 $mg.L^{-1}$) whatever the ratio and was in the range of the values observed in the effluent from the treatment plant's clarifier (33.8 ± 7.8 $mg.L^{-1}$). It was thus believed that the remaining fraction of COD_{tot} was mainly hardly biodegradable and was not available for denitrification for the studied retention times.

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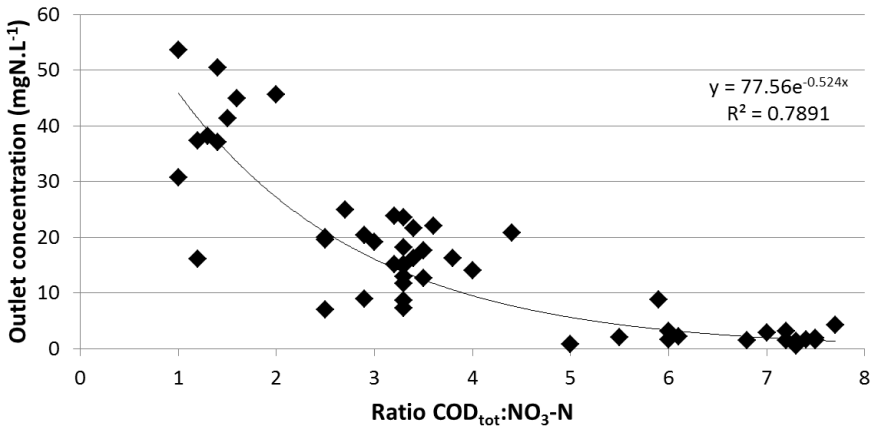

Figure 32 Effluent nitrate concentration in relation to the COD_{tot}:NO_3-N ratio (C_{in} = 40 mgN.L^{-1}, HRT = 1.18 d)

The evolution of effluent nitrate concentration in relation to COD_{tot}:N ratio showed that complete nitrate removal might be perform for ratio higher than 5 whereas a limitation occurred for ratios lower than 4. This observation was in accordance with Zhu *et al.* (2014) who reported that denitrification optimal efficiency was reached for ratios higher than 5.

4.3.1 Statistical model

Multicomponent linear models propose simple mathematical equations linking the outlet concentration of a single pollutant with few design and operational parameters which are easily available for engineers in the early stage of the design process (shown in Table 12).

Table 12 Regression equation and their adjusted R coefficient for prediction of COD and nitrate effluent concentration. Note that concentrations are given in mg.L^{-1} and HRT in days. HRT was a theoretical value of mean residence time. $^{(.)}$, $^{(*)}$, $^{(**)}$ and $^{(***)}$ describe p-value which are ≤ 0.1, 0.05, 0.01 and 0.001, respectively.

Predicted parameter	Regression equation	R_{adj}^2
$[COD_{tot}]_{out}$ (mg.L^{-1})	$293.04^{(***)} - 4.67^{(*)}[NO_3\text{-}N]_{in} - 263.59^{(***)}HRT - 1.50^{(*)}[COD_{tot}]_{in} + 36.57HRT^{2(*)} + 3.91^{(*)}[NO_3\text{-}N]_{in}*HRT + 0.04^{(*)}[NO_3\text{-}N]_{in}*[COD_{tot}]_{in} + 1.36^{(*)}[COD_{tot}]_{in}*HRT - 0.03^{(*)}[NO_3\text{-}N]_{in}*[COD_{tot}]_{in}*HRT$	0.50
$[NO_3^-]_{out}$ (mgN.L^{-1})	$5.69^{(.)} + 0.83^{(***)}[NO_3\text{-}N]_{in} - 0.11^{(***)}[COD_{tot}]_{in} - 8.62^{(***)}HRT$	0.80

Figure 33 shows, for each sample of the training dataset, the relationship between observed and predicted value (black dots) while the upper and lower bounds of prediction interval, at 90% level, was presented by blue and red dots. A perfect model would result in an optimal samples distribution along a straight line and with a thin prediction interval.

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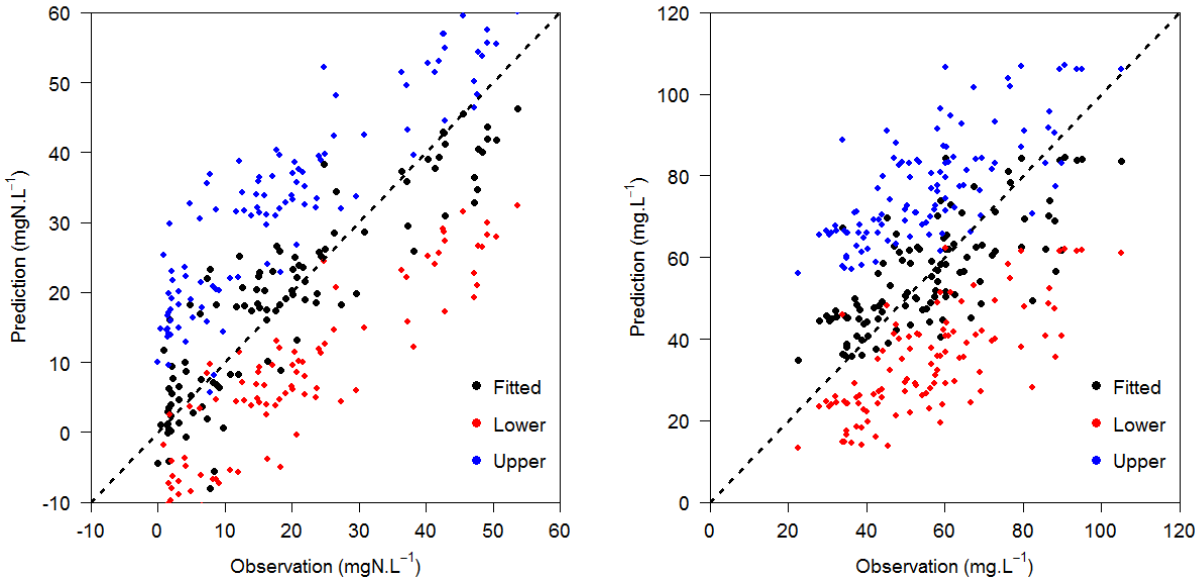

Figure 33 Predicted nitrate (a) and COD_{tot} (b) concentrations and their 90% prediction interval in relation to their respective observed value (black dots are the data whereas blue and red dots are the upper and lower bounds of prediction interval, respectively)

Although adjusted regression coefficients were low (R_{adj}^2=0.50 and 0.80 for COD_{tot} and nitrate, respectively), samples were homogeneously distributed close to the line. This observation suggested that the model was efficient to explain the full set of training data. That was partly explained by sensitivity analysis (Residuals vs Leverage and Cook's distance) which did not reveal differences in sample weight, suggesting equivalent impact of each data point on the regression process. Moreover, R_{adj}^2 were higher than or equal to 0.5 suggesting that these variables showed linear relationship with the studied independent variables.

Furthermore, the wide prediction interval (±13.7mgN.L^{-1} and ±21.6mg.L^{-1} for nitrate and COD_{tot}, respectively) pointed out that model robustness was weak. Table 13 summarizes the effluent mean concentrations (HRT=1.18d) for the different studied inlet conditions. Standard deviations showed important variability in outputs, throughout the study, which might affect the regression and thus explain the low prediction accuracy. Additional data would decrease the impact of such variability.

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Table 13 Outlet concentration of COD_{tot} and nitrates for retention time of 1.18d

Phase	Duration (d)	Inlet characteristics		$[COD_{tot}]_{out}$ ($mg.L^{-1}$)	$[NO_3\text{-}N]_{out}$ ($mg.L^{-1}$)	n
		$[NO_3\text{-}N]$ ($mg.L^{-1}$)	COD:N			
I		38.8 ± 2.2	6	57.9 ± 16.5	2.4 ± 1.9	17
II		41.6 ± 4.9	3	42.9 ± 11.1	15.5 ± 6.4	22
III		52.0 ± 10.0	1	31.0 ± 7.4	35.4 ± 4.1	10
IV		70.8 ± 7.1	3	55.8 ± 10.0	35.2 ± 9.6	7

Figure 34 presents the prediction of the validation samples, by linear models, in relation with their respective observations. The trend was correctly described for both substrates but the accuracy in prediction was quite poor in some cases. The model of nitrate tended to slightly overestimate the effluent concentration whereas, at the opposite, effluent COD concentration was generally underestimated.

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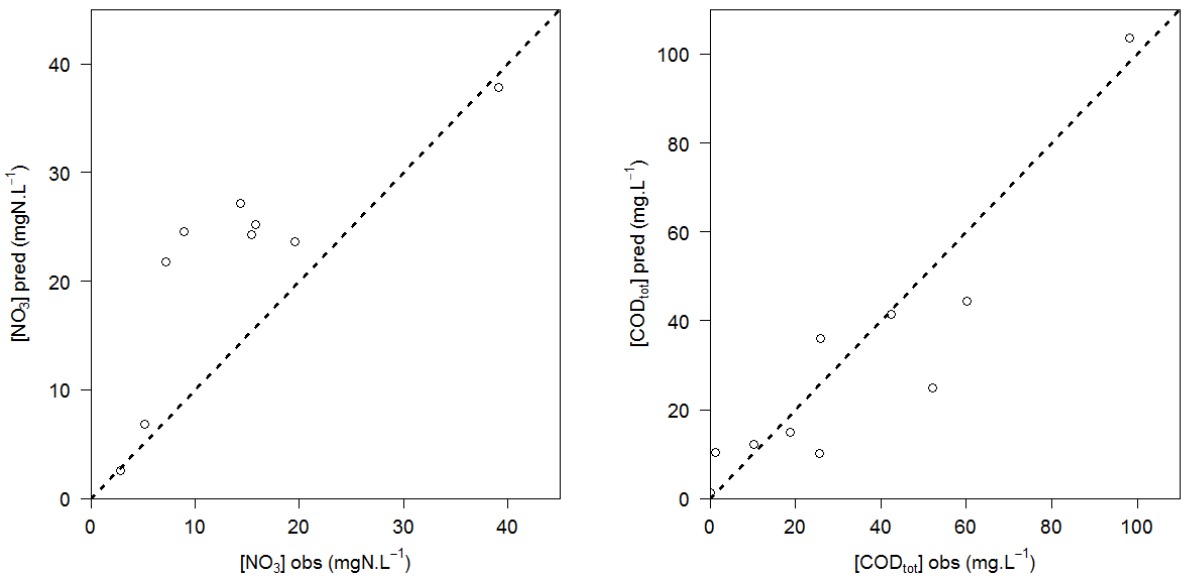

Figure 34 Predictions of outlet nitrate (a) and COD_{tot} (b) concentration in regards with their respective observations for the validation dataset.

The models were able to properly describe the effect of substrate concentration and of HRT for the studied conditions. However, although the models were suitable to provide an

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estimation of the expected outlet concentration, they were not sufficiently accurate to be used as design tools. The low accuracy may be partly explained by high variability in outputs for similar initial conditions suggesting that other processes may occur and that additional independent variables should be taken into account. The actual model was thus unable to capture the whole complexity of nitrate removal. The acquisition of supplementary data as well as the implementation of extended parameters (temperature, nitrite and ammonium concentration for example) may allow to improve the prediction of such output variability.

Furthermore, design and operational conditions were unevenly presented in the training data set what may affect their relative effect on linear regression. Intermediate retention times or high nitrate concentration, for instance, were under-represented whereas outlet samples, for influent nitrate concentration of 40mgN.L^{-1}, accounted for more than 66% of the data. More even representation of each condition, by important sampling (Monte Carlo sampling, latin hypercube), might allow to improve the fitting of the regression with experimental data. However, the experimental data set was not large enough to proceed for such data process.

4.3.2 First-order kinetic model

The experimental residence time distribution in pilot, determined from tracer test experiment, is presented in Figure 35. The figure also shows the effect of the number of tank-in-series (N: 2 – 4) with the aim to determine the best N-value to represent the experimental pilot hydraulic behavior. The description with 2 tank-in-series provided the best fitting with experimental data. This value was far from the average value of 11 TIS presented in Kadlec and Wallace (2009) for saturated filters (horizontal subsurface flow filters (HSSFs)) suggesting that the hydraulic behavior within the pilot was closer to CSTR than PFR. P-parameter was set at 2 in the model since this parameter was not used as adjustment variable in the model. This simplification was consistent considering the poor absolute effect of P on the model as well as the values reported by Nivala (2012) for BOD_5 and TN in HSSFs (P = 2 and 3, respectively). Furthermore, the recovery rate of tracer was higher than supply (124%) suggesting uncertainty in the results. This overestimation of tracer recovery may be partly explained by a bias in sampling. Effluent was indeed taken from a small sampling reservoir (2L) placed below the outlet and whose water volume was renewed by overflows. Nevertheless, the volume was probably not perfectly renewed and a dilution phenomenon might occur, resulting thus in the tail observed at the end of the tracer experiment. It might thus be supposed that the tracer concentration was overestimated in the latter times of experiment.

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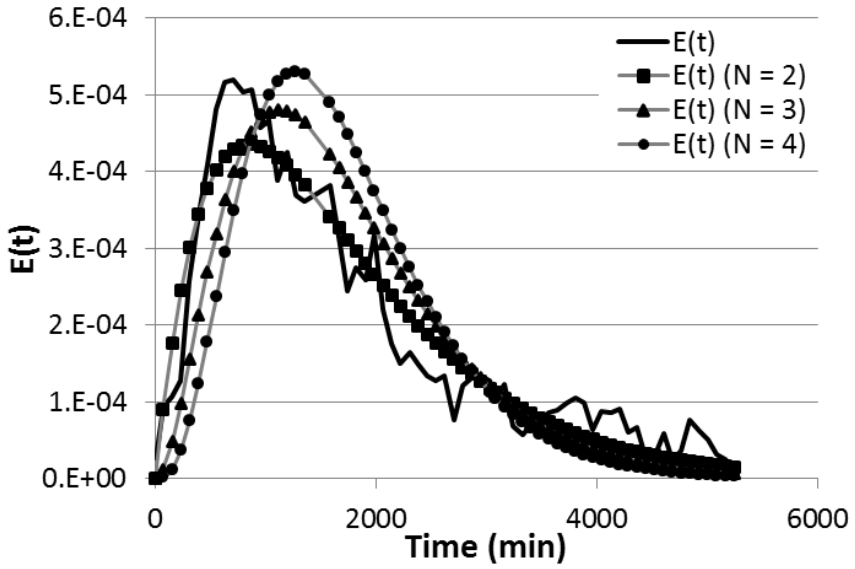

Figure 35 Residence time distribution function for different N-values

A decrease in ammonium concentration was observed between influent and effluent. Nitrification process was thus assumed to occur in the upper zone of the filter, resulting in nitrate production in the system. Consequently, a correction of influent nitrate concentration was thus applied taking into account the nitrate production based on ammonia decrease. Making the assumption that nitrification was the single route of ammonium removal, this correction was estimated by the difference of inlet and outlet ammonium concentration.

Furthermore, it was not possible to adjust model parameters on the full set of profile data without distinction between COD_{tot}:N ratios or between pollutants (COD_{tot} and nitrate). The value of SSE after optimization of the first-order rate constant remained very high and the reliability of prediction (results not shown) was very poor. The model adjustment was then carried out for each pollutant at the different ratios. Each fitting was based on the mean concentration profiles, for each pollutant and ratio, in relation to residence time in the system.

Figure 36 shows the evolution of pollutant concentrations in relation to retention time for the COD_{tot}:N ratio of 6. The predicted concentrations fitted well with the observed concentrations except for low retention time. This observation may be explained by the location of the first sampling point which was placed close to the surface. Non-homogeneous repartition of influent as well as dead volume might cause inaccuracy of this measurement.

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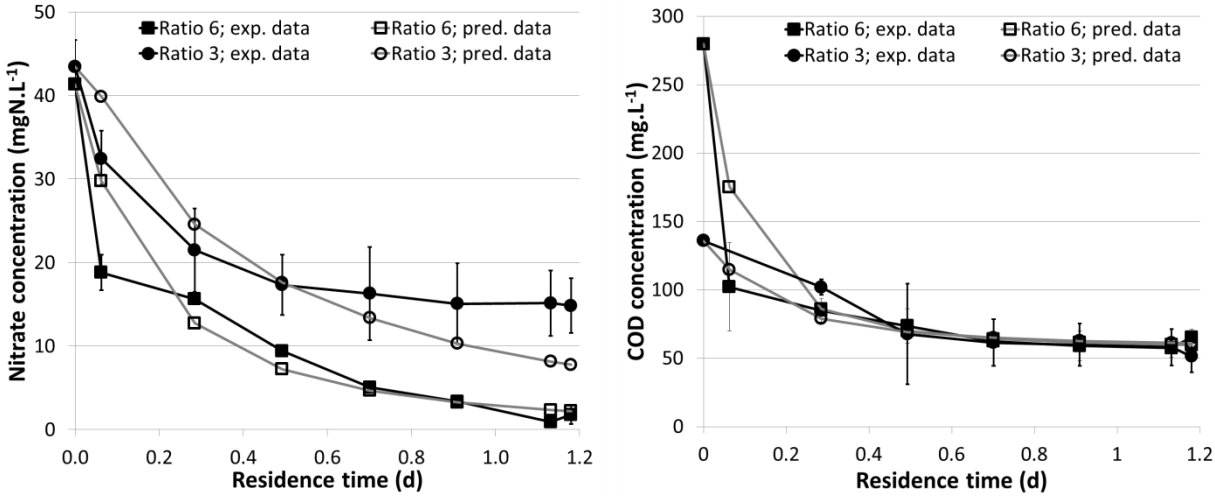

Figure 36 Experimental and predicted values of nitrate (a) and COD (b) concentrations against residence time at COD:N = 6 and 3

The model parameters are listed in Table 14. A ratio of 2.18 was observed comparing COD and nitrate first-order rate constants. The adjusted background concentration of COD (56.4mg.L^{-1}) was high in comparison with the value (14mg.L^{-1}) used by von Sperling and de Paoli (2013) (tertiary treatment unit, domestic influent). On the other hand, Stein *et al.* (2006) (synthetic influent with sucrose and meat proteins simulating secondary effluent) reported a C^*_{COD} ranging from 53 mg.L^{-1} to 230mg.L^{-1} for unplanted saturated vertical flow columns. This wide range of value was also underlined by Kadlec and Wallace (2009) who explained that this parameter is largely affected by the type and the status of the wetlands and influent. The type of influent may probably also affect this parameter. The background concentration varied widely during this study. For instance values from 28mg.L^{-1} to 67mg.L^{-1} where observed during the 3rd phase of the study ([NO_3-N] = 40 mg.L^{-1}, COD_{tot}:N = 3). This large variation underlined the tricky aspect of an accurate estimation of the C^*-parameter. Invalid estimation of C^*_{COD} would result in bad accuracy of the model since the lowest attainable concentration directly depends on it (see equation 18).

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Table 14 Adjusted rate constant

	k_V (d^{-1})	C^* (mg/L)	SSE	MAE
Ratio 6				
Nitrate	5.64	0	0.2	1.2
COD_{tot}	12.28	56.4	0.01	2.8
Ratio 3				
Nitrate	2.32	0	0.1	3.4
COD_{tot}	6.47	57.7	0.1	6.8

Figure 52 presents the predictions and observations of pollutant concentrations in relation to retention time for the COD_{tot}:N ratio of 3. The first-order rate constants were almost twice lower than for COD_{tot}:N ratio 6. The nitrate observations and predictions showed similar shape for short retention time (≤ 0.5d) but then diverged for longer retention time.

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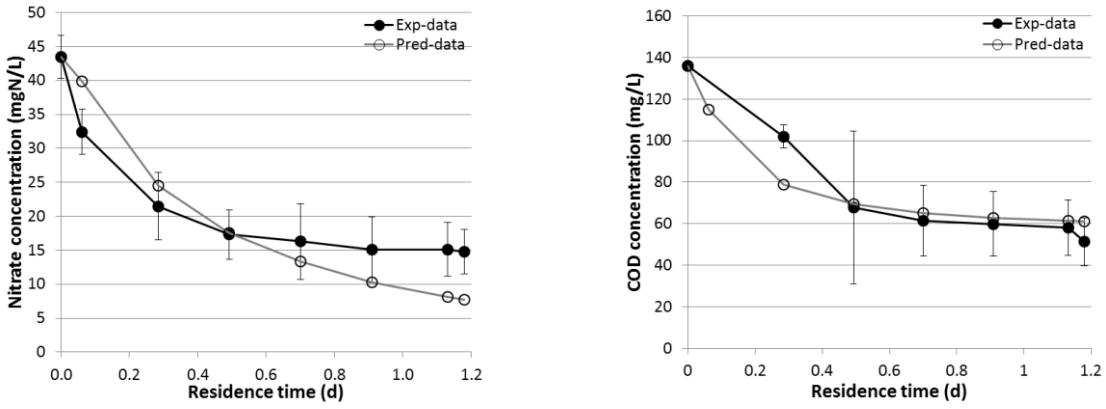

Figure 37 Experimental and predicted nitrate (a) and COD_{tot} (b) concentration against residence time at COD_{tot}:N = 3

A closer look at the COD_{tot} profile revealed that background concentration was reached at 0.5d. This observation suggested that COD_{tot} limitation was related with the zone of nitrate model inaccuracy. This is consistent with the characteristics of the denitrification process which requires supply of organic matter to remove nitrate. Since classic representation of

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PkC* model only considers a single substrate, the limitation of another one could not be considered.

Figure 38 presents the validation of the metamodel on I/O routine dataset. Nitrate predictions showed similar variations than the observation for the different ratios. Nevertheless, some predictions diverged strongly from their respective observations. This may be related with the strong variability which was observed in outlet concentrations for identical operational conditions. The model was not able to consider other parameters which might modify the efficiency (temperature, rainfall, variation in COD_{tot} characteristics). Predictions of COD_{tot} concentration were strongly affected by the background concentration. Indeed, the operational conditions resulted in COD_{tot} limitation in most of the cases. Consequently, the model efficiency could not be correctly assessed on the validation dataset. Moreover, the C^* parameter is a constraint for a generalized use of this model. Shepherd *et al.* (2001) proposed a retardation factor which causes the removal rate to lower over detention time instead of considering a background concentration. This method assumed that the kinetics of organic matter oxidation were initially rapid (when easily biodegradable COD is available) then decreased with time (as slowly biodegradable COD becomes predominant). This method could be a good alternative to the implementation of residual concentration.

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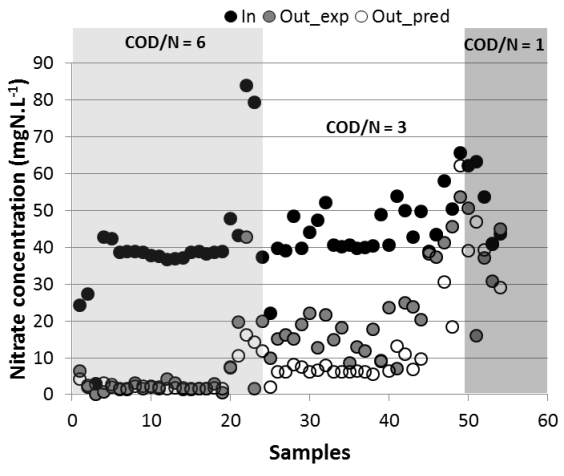

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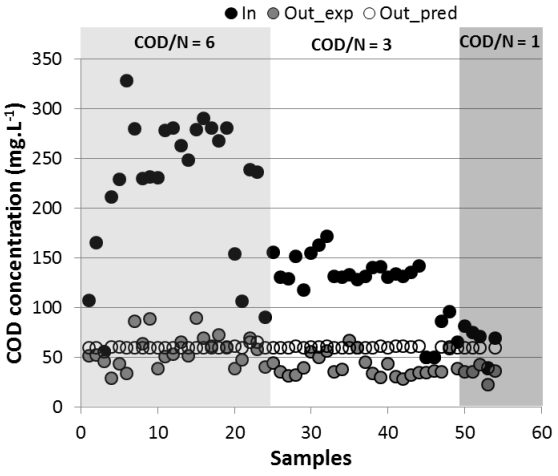

Figure 38 Nitrate (a) and COD (b) measured and predicted concentrations for residence time of 1.18d

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4.4 Conclusion

The present study aimed to assess the potential of simple predictive models with the purpose of design assistance. Both statistical and first-order models were developed as substitutes for abacus and enabled prediction of outlet concentrations with few parameters. The results showed positive ability to provide an estimation of the outlet concentration for both COD_{tot} and nitrate. Nevertheless, the prediction accuracy was not acceptable for design purpose.

Furthermore, both models were strongly dependent on the range of assessed conditions and required numerous data. Wide confidence intervals were observed suggesting the need of complementary training data. Moreover, model validation was conducted with a dataset from the studied system (same design and operational conditions). A second step of validation with data from a different system is therefore necessary in order to check their robustness.

To conclude, statistical models seem to be more efficient to capture the overall complexity of CWs (design, operational conditions and removal processes) than first-order kinetic models. This first method thus appears as a promising alternative tool provided that the training data set is sufficiently wide and dense as well as the variables are sufficiently numerous in order to perform an accurate “learning phase”.

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Part C Study of ammonium removal by adsorption onto zeolite

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The consecutive study of nitrification and denitrification has highlighted that high treatment efficiency, in unsaturated layer, is incompatible with full denitrification in the saturated one. Design optimizations, which have been determined in order to achieve high rate of nitrification, indeed has also a positive effect on the removal of organic carbon which is therefore not further available for denitrification process. An antagonism is thus inherent in the mechanisms involved in total nitrogen treatment.

In other respects, zeolite material has shown interesting capacity of ammonium sorption thanks to its high cationic exchange capacity and its strong affinity for ammonium. The implementation of such material within the filtration layer might thus be the perfect solution which allows to dissociate the fate of ammonium and organic carbon in unsaturated system. A new design of filter would thus allow to reach high ammonium removal while achieving low oxidation of organic carbon. The ammonium removal would then have all the required time to be nitrified between batches or during the resting period. And, finally, the nitrate produced during nitrification process should be released from zeolite, because of the repulsion between anions and zeolite, and then denitrified in the saturated layer with sufficient availability of organic carbon. This alternative thus may theoretically provide all requirements for an optimal treatment in a single compact system.

However, most of studies dealing with ammonium removal with zeolite has been conducted under static conditions whereas the remaining assessed this process in saturated dynamic conditions. The extrapolation of these results to the specific conditions of operation of VFFs thus show an important limit related to their significantly different contact characteristics. The study of sorption efficiency should thus be studied in order to assess the potential of ammonium removal within systems operating under free drainage conditions. For this purpose, the effect of operational conditions as well as the impact of design characteristics has to be determined in order to optimize process while remaining economically competitive. Furthermore, the regeneration of sorption capacity is usually carried out by backwashing with highly concentrated cationic solution. The capacity of biological restoration of exchange sites is currently not well documented and a specific focus has to be addressed to this process. The following part thus aimed at determining the best way to perform efficient and sustainable ammonium removal in VFFs by the implementation of zeolite material.

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Chapter 5 The use of zeolite for ammonium removal

This chapter is a synthesis of all the results from experiments conducted on clean material. No part of this chapter was submitted for publication. This work can be valued through different publications.

Ammonium removal by zeolite filtration layer in vertical flow filter: a study of medium potential

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Abstract

This study aimed at improving ammonium removal from wastewater by the use of natural zeolite. Column scale experiments were conducted under various operation modes and design characteristics in order to determine the parameters which affect ammonium removal as well as to provide design recommendations. The columns consisted of plexiglass pipes of 5cm inner diameter and 43cm height, fed with synthetic ammonium solutions. Ammonium adsorption under static conditions was shown to be a two-step process, suggesting that it was regulated by different mechanisms which may be incompatible with standard operational conditions, and which hinder an optimal use of exchange capacity. The column that was operated under saturated upflow conditions only achieved low removal performance and the breakthrough occurred almost immediately. This pointed out that contact time is a key parameter for the adsorption process, that must be optimized in order to reach high efficiency. Better removal efficiency was obtained with systems fed in pulse-load mode and operating under free drainage conditions, since part of the influent was stored within the pore volume between consecutive feedings. Consequently, increasing the batch hydraulic load from 2cm to 3cm resulted in a drop of performance from 78% to 61%, suggesting that the lower the batch hydraulic load, the better the performance. Increasing the amount of zeolite was another leverage parameter in order to reach low ammonium concentration. The implementation of $30kg.pe^{-1}.filter^{-1}$ should enable to obtain ammonium removal above 90% during a full feeding cycle. Nevertheless, after a high initial removal, the system performance quickly decreased and a regeneration of sorption sites must be scheduled in the operation program of such system, leading to an increase of both capex and opex costs.

Keywords : Adsorption, Ammonium, Vertical columns, Zeolite, Constructed wetlands

5.1 Introduction

Treatment wetlands met an increasing interest over the past decades due to their good performances as well as their low initial and operational costs and their eco-friendly image. In France, the so-called “French design” is composed by two stages of vertical flow filters (VFFs) (1.2 m²/p.e. and 0.8 m²/p.e., respectively) divided in 3 and 2 parallel beds, respectively, operating alternately according to a sequential mode of feeding and resting

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periods (3.5 / 7d and 3.5 / 3.5d, respectively for the 1st and 2nd stage) (Molle *et al.*, 2005). The first stage, filled with coarse gravel as filtration medium, achieves good performance for TSS and COD_{tot} removal (83 and 77%, respectively (Morvannou *et al.*, 2015)) but performs quite low on TKN removal (59%). Ammonium removal mostly relies on nitrification (Ahn, 2006) which is performed under aerobic conditions following a two-step mechanism of ammonium and nitrite oxidation (Chen *et al.*, 2006). This process is slower than heterotrophic respiration and is therefore limited by the short retention time within the first stage unit. Moreover, competition for oxygen availability between heterotrophic and autotrophic bacteria may also limit the efficiency of nitrification. The need for a second stage is thus mainly related with the requirement of further treatment of ammonium. This results in increasing the treatment surface by 40% which may be detrimental when land availability is limited or for large treatment plants. Alternative designs and operational conditions allowing acceptable treatment by a single-stage treatment unit have thus been actively studied in the past years. The current promising solutions, such as forced aeration (Foladori *et al.*, 2013) or recirculation (Prost-Boucle and Molle, 2012), leads to complexification and increase the operational cost of such system. The implementation of reactive material, such as zeolite, might be another simple and cost effective alternative.

Zeolite is a porous alumino-silicate composed of a 3D honeycomb framework of tetrahedral silicate and aluminate linked by water molecules (Karadag *et al.*, 2007). The substitution of Si^{4+} by Al^{3+} ions causes negative charges which are compensated by weakly bounded (Widiastuti *et al.*, 2011) exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+} or K^{+}) (Erdoğan and Ülkü, 2011). The cation exchange capacity (CEC) of zeolite has been largely studied in various applications (drinking water (Li *et al.*, 2011), wastewater (Cooney *et al.*, 1999), industrial water (Arslan and Veli, 2012)) for different purposes (ammonium removal (Huang *et al.*, 2010), heavy metals treatment (Kleinübing and Silva, 2008)) and showed high potential of cation removal (from 2.16 to 4.54 $meq.g^{-1}$ (Shoumkova, 2011)). Furthermore the molecular selectivity and the high affinity of zeolite for ammonium (Lebedynets *et al.* 2004; Saltali *et al.*, 2007) as well as its large availability (Shoumkova, 2011) make this material a propitious solution for ammonium removal in VFFs.

Nevertheless, most studies dealing with ammonium adsorption onto zeolite were carried out under batch (Ivanova *et al.*, 2010; Leyva-Ramos *et al.*, 2010) or saturated conditions (Sprynskyy *et al.*, 2005; Demir *et al.*, 2002), optimizing thus the contact between solution and zeolite unlike VFFs whose drainage conditions are not controlled. Furthermore, operational

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conditions (i.e. ammonium influent concentration, contact time) or design parameters (i.e. mass of zeolite, type of zeolite) may affect removal efficiency. In this study ammonium removal by zeolite was investigated for various design and operational conditions. A preliminary characterization of zeolite was conducted, followed by a study of ammonium removal under optimized conditions. Design and water characteristics were finally assessed under hydraulic conditions close to reality.

5.2 Materials and Methods

5.2.1 Zeolite characterization

A preliminary characterization of 3 different zeolites was conducted in order to assess their theoretical ability to remove ammonium. Supplier datasheets allowed to derive a theoretical CEC from the substitution rate, but also provided information concerning their exchangeable cations what is useful in order to estimate their affinity with ammonium.

DRX analysis was conducted, by the refractometry laboratory of the Claude Bernard University (Lyon), in order to confirm the supplier information about mineral composition. The estimation of chabazite content, in the supplied medium, was carried out by the method of reference intensity ratio which consisted to compare one or several peaks of a given mineral with a known reference (Chipera and Bish, 1995).

Finally, the specific surface of chabazite was characterized by Brunauer, Emmet and Teller method (BET) (see equation 1) through the monitoring of thermic conductivity variation of a gas containing nitrogen (adsorbate) and helium (transport) in a range of increasing partial pressure. Ladavos *et al.* (2012) provide an interesting description of the method theory.

$$S_{BET} = \frac{(\sigma \times V_s \times N_0)}{V_m} \qquad \text{Eq. [1]}$$

Where S_{BET} is the specific surface ($m^2.g^{-1}$), σ is the volume f one molecule of adsorbat (16.2Å for nitrogen), N_0 is the Avogadro number ($6.023x10^{23}$ molecules.$mole^{-1}$), V_s is the volume adsorbed per mass unit at a given pressure and V_m is the molar volume of gas (22.4L.$mole^{-1}$).

Mesoporous and microporous volumes and mean diameters were determined by Barret, Joyner and Halenda method (BJH) and Horvath and Kawazoe method (HK), respectively (Note that HK method provides knowledge on the total porous volume. Difference between

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HK and BJH enables to assess the microporosity). Groen *et al.* (2003) is an interesting reference for further information on this topic.

5.2.2 Static experiment

A static batch experiment was conducted in order to assess the exchange kinetics as well as the equilibrium concentration for an influent concentration of 100mgNH_4-N.L^{-1}. Tested media were chabazite (grain size of 2 – 5mm) and crushed granitic gravel (grain size of 2 – 6mm), the latter being the standard medium in VFFs.

The ammonium solution was prepared with $(NH_4)_2SO_4$ (>99% purity grade, Fisher Chemical) dissolved in distilled water. The batch tests were carried out in 100mL glass sealed bottles containing 80mL of solution and 1g of medium (gravel or chabazite, respectively). The system was continuously stirred, by bar magnet, under slow rotation speed in order to avoid material destruction.

The effect of contact time was assessed through monitoring of ammonium concentration (quick test method, LCK 303, Hach) at variable time-step intervals. This experiment was conducted over 28h until reaching almost constant equilibrium value. Note that equilibrium was assumed to be reached when the difference between two consecutive analysis was lower than 1% per hour.

5.2.3 Saturated upflow experiment

Ammonium exchange was assessed under dynamic conditions while optimizing contact between influent and zeolite.

The experiment was carried out under saturated upflow conditions with 2 plexiglass columns (h = 43cm, ø = 5 cm). Intermediate sampling spots, made of flexible pipe (ø = 0.5cm) starting in the column center and ending outside the column in a manual valve, were distributed along the column height (at 10, 20, 30 and 36.5cm, respectively). A standard column was filled exclusively with 43cm-heigth of crushed granitic gravel (grain size 2/6mm) while the other was filled with the same granitic gravel and zeolite (chabazite, grain size 2/5mm). Zeolite was implemented in 5 thin layers (each less than 2cm height) separated by gravel layers (details are presented in Figure 39). Each zeolite layer was introduced between 2 consecutive sampling spots, thus allowing to assess the effect of zeolite mass on ammonium removal. Note that the two last layers of zeolite were located nearby. Uncertainty, due to the syringe sampling, at the fourth sampling spot led to remove these data from the discussion. The

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medium were initially dried at ambient temperature in order to accurately determine their respective mass without modifying zeolite structure (the water present in zeolite structure was not removed).

Columns were initially fed, for 2 hours, with distilled water in order to reach steady state hydraulic conditions. Then they were continuously fed with synthetic influent, from the bottom, by a peristaltic pump (Masterflex). The hydraulic loading rate was set at $0.1 m.h^{-1}$ for a theoretical residence time of 104 minutes in the system. The synthetic solution was prepared by dissolving $(NH_4)_2SO_4$ (>99% purity grade, Fisher Chemical) in distilled water and stored in a 15L polyethylene tank. The required volume was prepared daily. The feed solution was continuously stirred with an aquarium pump (NJ600, New Jet) in order to keep the solution homogeneous.

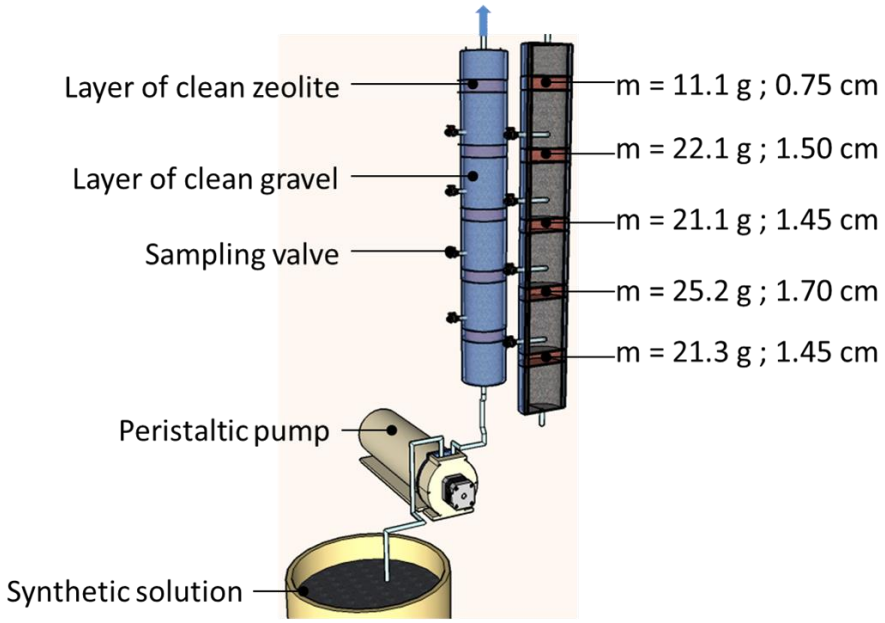

Figure 39 Experimental setup of saturated upflow operation mode

Grab samples were punctually taken, at variable time-step intervals, from the inlet, outlet and intermediate spots and analyzed for ammonium concentration by quick test method (LCK 302 and 303, Hach). Intermediate depths were sampled, by 100mL plastic syringe, from the top to the bottom in order to avoid flow perturbation. These samples were filtered before analysis on cellulose 0.45µm filters (Fisherbrand). Data of the zeolite column were corrected from ammonium adsorption onto gravel with data from the reference column (i.e. gravel)

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beforehand data process. The adsorption onto gravel was prorated based on the mass of zeolite content within the zeolite column.

5.2.4 Vertical free drainage experiment

Five design and operational parameters were assessed in order to better characterize the effect of zeolite implementation as filtration medium in vertical flow filters (see Table 15). First, the effect of the design of zeolite layer was studied. Two different modes of implementation (zeolite layer or mix of zeolite and gravel) were compared in order to determine which configuration allowed the optimal use of exchange capacity. Moreover, the effect of batch hydraulic load and batch frequency was assessed. Two systems fed with the same daily hydraulic load but at different doses (2 or 3cm, respectively) and at different batch frequencies (80 or 120 minutes, respectively) were assessed. Furthermore, the effect of zeolite mass on outlet concentration was studied (from 10 to 40$kg_{zeolite}.PE^{-1}.filter^{-1}$) while the effect of influent concentration was assessed through a fourth experiment. Finally, 3 different zeolites (1 chabazite and 2 clinoptilolites from Spain and Turkey) were compared in order to determine the best type of zeolite for ammonium sorption purposes. Only ammonium sorption was studied through these experiments since they were conducted on clean material and with distilled water spiked in ammonium.

These experiments were also conducted with plexiglass columns (h = 43cm, ø = 5cm) operating under free drainage conditions, with the exception of the experiments with varying influent concentrations, which were done with bigger columns of 20cm inner diameter. Each column was filled, from the bottom to the top, according to the following design. A thin layer of crushed granitic gravel (grain size 2/6mm) was introduced at the bottom of the system in order to avoid zeolite release. The zeolite layer (grain size 2/5mm) was placed between this first layer and another thick layer of gravel aiming to achieve optimal distribution of influent before reaching the zeolite compartment.

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Table 15 Summary of unsaturated experimental conditions

Experiment	Zeolite			Columns	Operation			
	Type	Mass (g)	Design (separate layers of gravel and zeolite or mixed)		Batch hydraulic load (cm)	Frequency (batch.d^{-1})	Feeding (min)	Run duration (d)
Design assessment	Chabazite	100	Layered or Mixed	2	3	18	2	2
Batch load assessment	Chabazite	100	Layered	2	2 or 3	18 or 12	1 or 2	1
Mass assessment	Chabazite	From 50 to 200	Layered	4	2	18	1	10
Zeolite comparison	Chabazite, Clinoptilolite	100	Layered	3	2	18	1	2
Concentration assessment	Chabazite	2360	Layered	3	2	18	3	3.5

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The columns were fed, in batch mode, by a peristaltic pump (Masterflex) with synthetic solution from a single central feeding pipe located close to the surface (the synthetic solution was prepared as previously described in section for saturated conditions). The inflow rate was set to 1.2m.h^{-1} and the feeding regulation was managed by a digital timer which triggered the pump to simulate batch operation at constant time-interval. Figure 40 presents an overall description of the experimental setup for free drainage conditions.

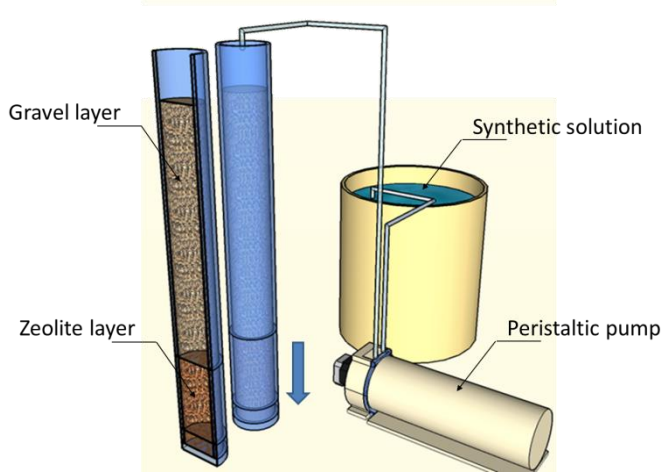

Figure 40 Experimental setup of free drainage operation mode

Grab inlet samples and batch outlet samples were taken at variable time intervals and were then analyzed for ammonium concentration with quick test methods (LCK 302 and 303, Hach). The effect of gravel on the removal efficiency was estimated as described for saturated conditions.

5.3 Results and Discussion

5.3.1 Zeolite characterization

The XRD patterns of 3 different zeolite-rich minerals are shown in Figure 41. The high intensity peaks at 2θ close to 9.5°, 20.5° and 31° are characteristics for chabazite (Leyva-Ramos *et al.*, 2010) while clinoptilolite was confirmed by peaks at 2θ close to 10°, 22° and 30° (Erdoğan and Ülkü, 2011). Each medium was thus confirmed to contain zeolite. Since chabazite was the main mineral studied in this study, the relative intensity method was used to verify the purity grade as given by the supplier. A zeolite content of 57% was estimated from this method, which was slightly lower than the supplied characteristics (65 ± 5%).

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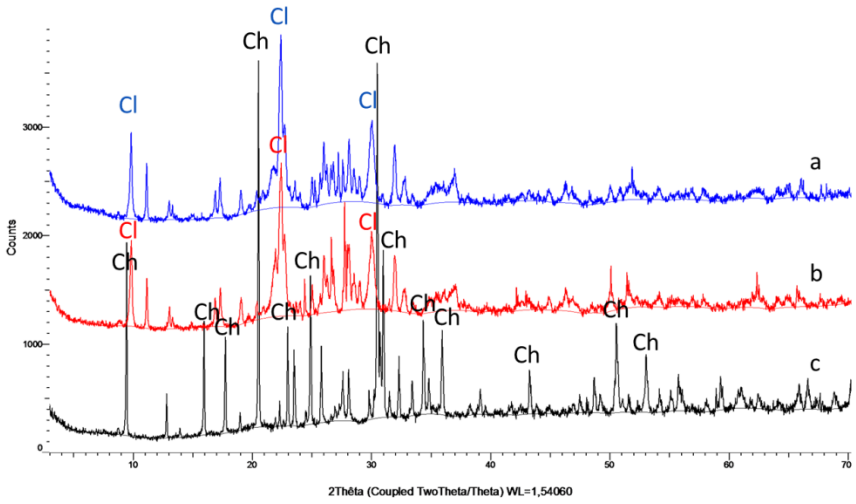

Figure 41 XRD patterns of Turkish clinoptilolite (a), Spanish clinoptilolite (b) and Italian chabazite (c)

The chemical composition of each mineral, given in Table 16, highlighted that Ca^{2+} and K^{+} were the main exchangeable cations while Na^{+} was present to a smaller extent. Sarioglu (2005) reported that the best form of clinoptilolite for ammonium removal was the Na-rich clinoptilolite whereas Lahav and Green (1998) observed higher selectivity of chabazite for K^{+} and Ca^{2+} than NH_4^{+}. These considerations suggested that the studied materials were not optimized for ammonium removal. Chemical modifications by, for instance, thermal treatment (Ivanova *et al.*, 2010) or selection of exchangeable ions (Leyva-Ramos *et al.*, 2010, Demir *et al.*, 2002), may be carried out in order to improve ammonium removal. Nevertheless, it would result in extra-costs which are not acceptable in this context.

Although the selected zeolites appeared suboptimal for ammonium removal, further analysis showed that each zeolite had a high cation exchange capacity ranging from 1.2 to 2.1 $meq.g^{-1}$ (Table 17). Ammonium removal was thus expected with the use of these natural zeolites.

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Table 16 Chemical composition of studied zeolites (data from suppliers)

Chemicals	Chabazite	Spanish Clinoptilolite	Turkish Clinoptilolite
SiO_2	52.0 ± 4 %	68.15 %	66 – 69 %
Al_2O_3	17.0 ± 2 %	12.3 %	11 – 12 %
TiO_2	0.5 ± 0.1 %	0.2 %	< 0.1 %
Fe_2O_3	3.6 ± 0.5 %	1.3 %	1 – 1.7 %
P_2O_5	0.3 ± 0.05 %	-	-
MnO	0.2 ± 0.05 %	-	-
MgO	2.0 %	-	1 %
CaO	5.7 ± 0.7 %	3.95 %	2 %
Na_2O	0.6 ± 0.2 %	0.75 %	0.5 %
K_2O	6.1 ± 0.6 %	2.8 %	3 – 3.5 %
H_2O	12.0 ± 2 %	-	12 – 14 %
BaO	-	-	< 0.1 %
SrO	-	-	< 0.1 %

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Table 17 Physical and mineralogical characteristics of studied zeolites (data from suppliers)

Parameter	Zeolite		
	Chabazite	Spanish Clinoptilolite	Turkish Clinoptilolite
Mineralogical composition	Chabazite (60±5 %) phillipsite K-feldspar biotite pyroxene volcanic glass	Clino. (82 – 86 %) feldspar illite cristobalite traces of quartz	Clino. (80 – 90 %) mica clay
Apparent density ($g.cm^{-3}$)	0.7 – 0.9	0.58 – 0.84	0.7 – 1.0[a]
Apparent porosity (%)	N.D.	24 – 32	35 – 40
Specific surface area ($m^2.g^{-1}$)	365[b]	30 – 50	40.79
CEC ($meq.g^{-1}$)	2.1 ± 0.1	1.2 – 1.5	1.8

[a] value is for bulk density. [b] value from analysis in the laboratory of the Research institute of catalysis and environment of Lyon (IRCE-Lyon)

5.3.2 Static conditions

The kinetics of ammonium adsorption onto zeolite and gravel are presented in Figure 42 Kinetics of ammonium removal by chabazite. While no ammonium removal was observed in presence of gravel, the dynamic of ammonium removal, onto zeolite, followed a logarithmic shape with a rapid initial adsorption phase, then a second step with slower uptake after approximately 6h. The initial fast adsorption may be explained by the full availability of unoccupied exchange sites (Huang *et al.*, 2010). The decrease in removal may be correlated with progressive exhaustion of surface sites whereas remaining sites were located in the porous structure of zeolite (Lebedynets *et al.*, 2004). This observation was in accordance with Erdoğan and Ülkü (2011) who reported, from batch experiments, that the adsorption process was initially driven by the external mass transfer, by diffusion through the external film

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surrounding the medium, while intra-particle diffusion was the limiting mechanism during the second step of the adsorption process.

In other respects, sorption kinetic strongly decreases after 8h of operation and the adsorbed load tends to stabilize. Furthermore, the system reached a plateau, close to $4mgNH_4\text{-}N.g^{-1}_{zeolite}$ (i.e. $0.29meq.g_{zeolite}^{-1}$), which may be considered as the maximum uptake capacity under the studied conditions. This adsorption limit was very lower than the CEC given by the suppliers. Several authors (Sarioglu, 2005; Malekian *et al.*, 2011; Widiastuti *et al.*, 2011) reported that the sorption capacity was affected by numerous parameters such as the concentration of cations in solution or the zeolite loading. A survey of ammonium adsorption onto zeolite is presented in Table 18.

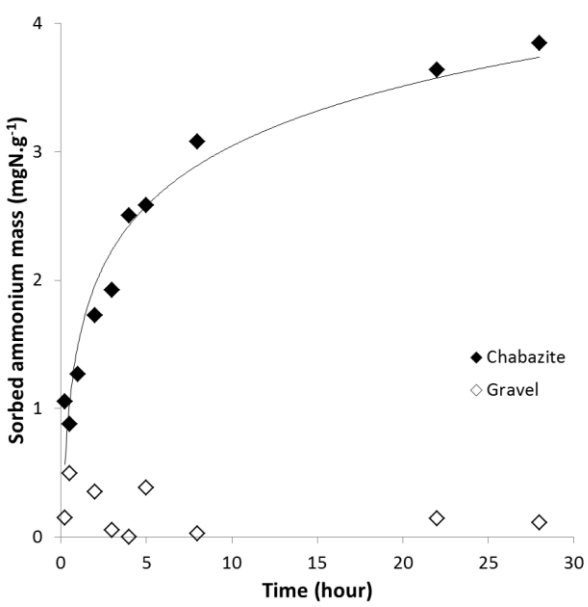

Figure 42 Kinetics of ammonium removal by chabazite

Considering the use of zeolite for ammonium removal in VFFs, these observations highlighted two main aspects of adsorption which must be considered. On the one hand, the ammonium concentration in domestic wastewater is typically below or equal to the studied concentration. The theoretical CEC is thus an inaccurate design parameter. On the second hand, the fast infiltration of water through the system would result in a short contact time between influent and zeolite and may hinder an optimal use of the uptake capacity of zeolite. The study of ammonium removal under dynamic conditions is thus required in order to draw useful conclusions on the potential of zeolite implementation in VFFs.

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Table 18 Survey of ammonium removal by zeolite in batch conditions

Zeolite	Grain size (mm)	$[NH_4^+]$ ($mgN.L^{-1}$)	solid : liquid (g : mL)	q_e ($mgN.g^{-1}$)	Study
Clinoptilolite	0.85 – 2	100	1 : 100	7.2[a]	(Erdoğan and Ülkü, 2011)
Clinoptilolite	1.25[b]	60	1 : 100	3.1[a]	(Ivanova*et al.*, 2010)
Chabazite	N.C.	6000	5 : 100	20	(Montégut *et al.*, 2016)
Chabazite	<0.074	400[c]	1 : 100	12.9	(Torracca *et al.*, 1998)
Chabazite	0.15 – 0.21	1500	1:80	32.2	(Leyva-Ramos *et al.*, 2010)
Clinoptilolite	0.3 – 0.6	100	2 : 100	3.8	(Karadag *et al.*, 2007)
Clinoptilolite	0.16 – 0.315	100	1 : 100	6.8	(Lebedynets *et al.*, 2004)

[a] is graphically determined

[b] is the mean diameter

[c] note that solution contained both Na^+ and NH_4^+ in same concentration (i.e. 0.1N)

5.3.3 Saturated conditions

Figure 43 shows the breakthrough curves of ammonium at different sampling depths (i.e. different mass of zeolite) during the experiment. Breakthrough was assumed to occur when the ratio of outlet to inlet ammonium concentrations (C_t and C_0, respectively) was higher than 0.05 whereas the system was considered to be exhausted when C_t/C_0 was higher than 0.95 (Mahendra *et al.*, 2015). The ratio followed a logarithmic shape before reaching a plateau

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after approximately 75h for the different sampling locations. Initial ratios were different in the early stages of operation, but then show similar values at the end of the study when the system was completely exhausted. Contrariwise to the sigmoid curve characterizing an efficient process (Miladinovic and Weatherley, 2008), the observed curve suggested that breakthrough occurred almost immediately while total exhaustion was reached after relatively longer period. Considering a normal, full-scale VFF feeding period (3.5d and a production of $15gNH_4\text{-}N.pe^{-1}.d^{-1}$), the outlet concentration would be close to $60mgNH_4\text{-}N.L^{-1}$ at the end of the period (i.e. 13.5h in this experiment) which is not acceptable for treatment objectives.

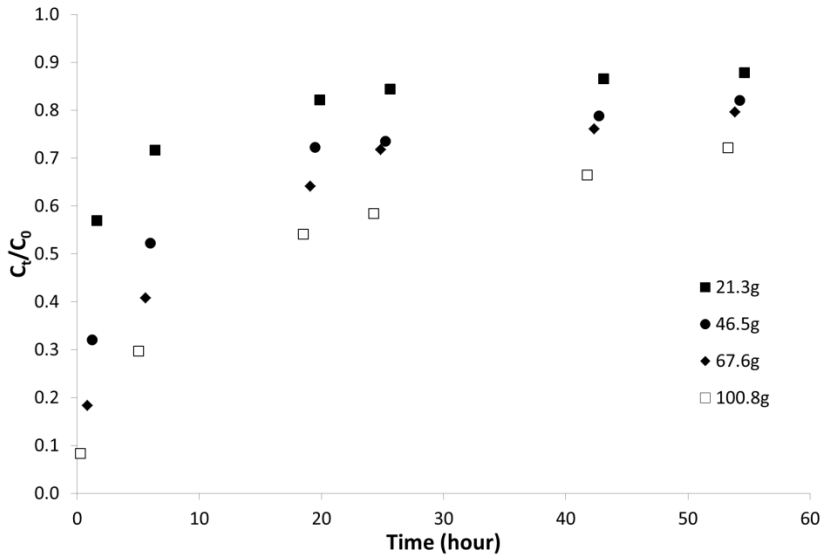

Figure 43 Breakthrough curves of ammonium for different masses of zeolite

The studied zeolite mainly contained K^+ ions which have strong affinity with chabazite. The higher affinity of chabazite for potassium than ammonium may result in faster breakthrough (Lahav and Green, 1998). The zeolite form should thus be considered as a criterion of design. Pre-conditioning the zeolite (Na-form) may also be an alternative in order to foster the ion exchange (Leyva-Ramos *et al.*, 2010).

In addition, the experimental flow rate may also partly explain the fast breakthrough since adsorption onto zeolite is mainly driven by intra-particle diffusion when surface sites are occupied. Nguyen and Tanner (1998) compared the ammonium removal efficiency ($[NH_4^+]$ = $100mgN.L^{-1}$) of two mordenite columns operating at different retention times (0.32h and 17.8h, respectively). Whereas breakthrough occurred almost immediately for the first system, they reported outlet ammonium concentration lower than $1.2mgN.L^{-1}$ for the second system

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after even 40 bed volumes. This observation suggested that a lower flow rate may decrease the influence of diffusion limitation and thus improve the medium efficiency. A theoretical contact time within the zeolite layer was estimated at 16.6 minutes (i.e. 0.28h) during the present study. Considering a treatment surface of $0.4 m^2.pe^{-1}.bed^{-1}$, a volume of $150 L.d^{-1}.pe^{-1}$ and an identical height of zeolite (i.e. 7cm), such design could allow a maximum retention time of 1.8h (more than 6-fold longer than during this experiment). Almost 60% of ammonium was removed by the system during the first 13.5h of operation (the applied and adsorbed loads were 14.0 and $8.2 mgNH_4\text{-}N.g^{-1}$, respectively) while $3.9 mgNH_4\text{-}N.g^{-1}$ was adsorbed from the 13th to the 53rd hour of this experiment. If a longer retention time indeed improves the removal efficiency (by fresh, clean zeolite), up to 87% of removal might be expected considering the observed sorption capacity.

Furthermore, a smaller grain size might also enhance the treatment efficiency by increasing the amount of surface sites which are easily available. Hedström and Rastas Amofah (2008) studied ammonium adsorption onto different grain sizes of clinoptilolite (4/8 mm and 7/15mm, respectively) and observed higher initial outlet concentrations with the coarse zeolite. Erdoğan and Ülkü (2011) indeed reported that the equilibrium concentration remained constant whatever the grain size but pointed out that the process was faster with fine medium.

Finally, ammonium removal increased with column height. This observation underlined that the higher the mass of zeolite, the better the performance. The increase in zeolite content had thus a dual role. On the one hand, the adsorption process relies on the equilibrium between the solution concentration and the adsorbed load. Influent ammonium concentration decreased along with the infiltration through zeolite medium. The equilibrium load was therefore lower in the most remote zeolite layers than in the layers nearby the inlet. On the other hand, dynamic conditions resulted in short contact time between influent and zeolite. Increasing the medium mass thus resulted in longer contact between ammonium and zeolite and counteracted the kinetic limitation.

Figure 44 presents the adsorbed load of ammonium in the different layers of zeolite. The adsorbed loads increased logarithmically in each layer. Nevertheless, the uptake rate varied widely depending on the location. Although each layer had a similar content of zeolite (22.4 ± 1.9g, except the outlet layer which only contained 11.1g) the amount of ammonium exchanged with zeolite was lower in remote than closer locations to the inlet. This observation may be explained by the decrease in ammonium concentration along with the filtration height.

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Therefore each layer was dosed at different concentrations resulting in different uptake rates. Longer monitoring after total exhaustion of the first layer might show an increase in the adsorbed load in the subsequent compartment as the applied concentration raises.

Furthermore, the study of adsorbed load by the first layer of zeolite suggested that the equilibrium concentration in zeolite under dynamic conditions was higher than found in the batch experiment (9 versus 4mgN.$g^{-1}_{zeolite}$, respectively). That may be partly explained by the difference in treated volumes during both experiments. Indeed, the liquid:solid ratio was very different between both experiments. Moreover, the ammonium concentration of influent was constant over the full column experiment while a decrease was observed in batch conditions. A limitation in ammonium availability thus occurred under static conditions.

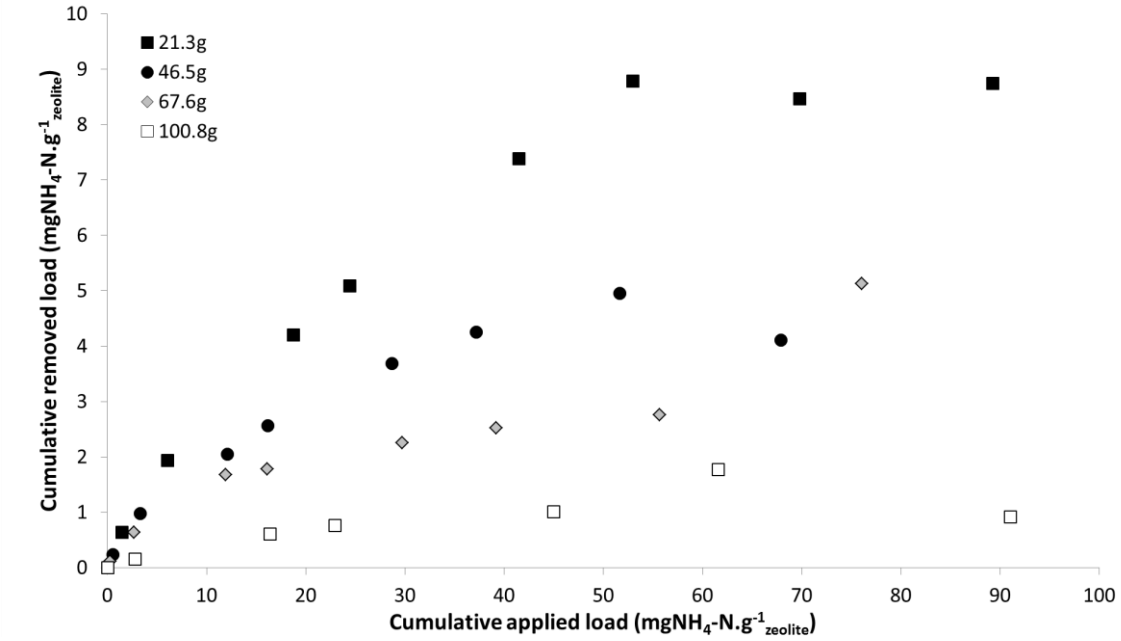

Figure 44 Cumulative adsorbed ammonium load in relation to the cumulative applied load of each layer

5.3.4 Free drainage

The previous sections highlighted that the adsorption process is affected by design and operational parameters. The assessment of ammonium removal under hydraulic conditions close to VFFs operation was thus a necessary and the logical next step. The following section summarizes results from several short experiments focusing on the effect of different design and operational parameters on ammonium removal by free drainage vertical flow columns.

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5.3.4.1 Effect of the zeolite type

Theoretical cationic exchange capacity may vary widely depending on the type of zeolite (from 2.16 to 4.54 meq.g^{-1}) (Shoumkova, 2011). Nevertheless, CEC is not the unique parameter to take into account since the affinity for ammonium also varies between zeolite species. Preliminary assessment of zeolite efficiency is thus required, when aiming at optimizing the sorption capacity, since its implementation results in extra-costs in comparison with conventional gravel medium use.

To this purpose, 3 different zeolites (2 clinoptilolites and 1 chabazite) were compared in order to determine the best medium. Figure 45 presents the ammonium concentration, at the outlet of the 3 columns, in relation to the total applied load during the 2 first days of a feeding period. Although each column reached high performance (≥ 75%) throughout the whole period, the chabazite column performed slightly better than the clinoptilolite ones, especially in the early stages of operation. The higher CEC of chabazite (see Table 17) may partly explain this observation.

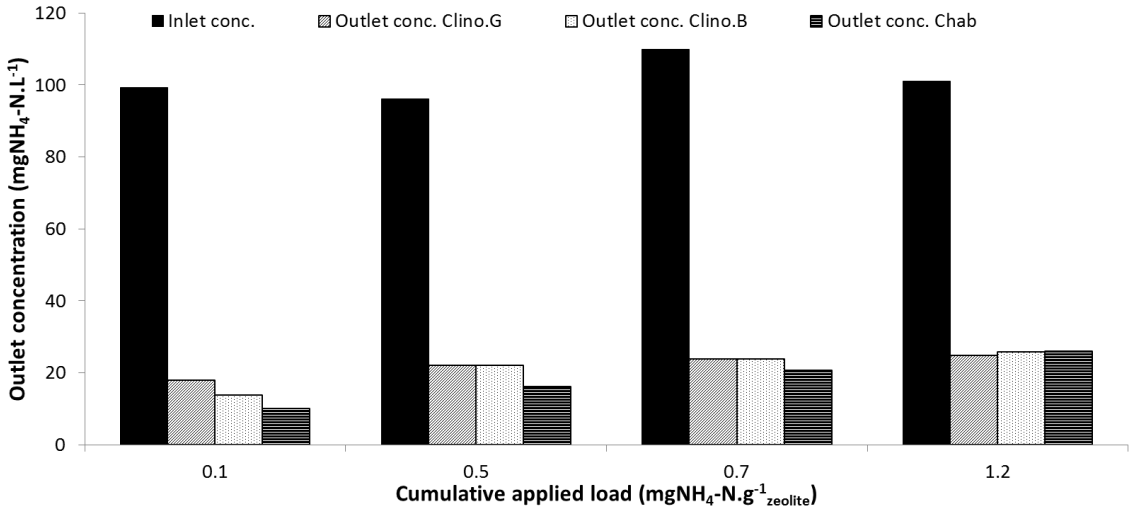

Figure 45 Evolution of ammonium concentration in relation to the cumulative applied load of ammonium during a 2-days period of operation

Furthermore, the ammonium concentration of effluent from the chabazite column increased during the experiment, from 10 to 26mgN.L^{-1}. This observation suggests that treatment efficiency may vary strongly during a whole feeding period. Consequently, the design must be based on the final efficiency in order to respect discharge levels during the full feeding period. That may result in an important increase in the required mass of zeolite. It might thus be

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advisable to consider the opportunity of shorter feeding periods, by increasing the number of beds in the first stage or by a faster rotation in beds' operation for example, in order to minimize such limit.

5.3.4.2 Effect of zeolite implementation

The study of ammonium removal under saturated dynamic conditions pointed out that contact time between influent and zeolite was a limiting parameter in the adsorption process. The implementation of a thin compact reactive layer of zeolite may result in non-optimized contact between both solid and liquid phases. The distribution of zeolite into a thicker layer composed by a mix of gravel and zeolite was expected to provide an optimized contact for adsorption. Figure 46 shows the adsorbed load in relation to the applied load of ammonium for two columns with a different design of the zeolite compartment (compact and mix, respectively). For both systems, the adsorbed load increased linearly with the applied load following the same slope. Moreover, the higher the applied load the more the plot diverged from the full removal dotted line. These observations suggest that both columns performed similarly and therefore the mix of zeolite and gravel instead of a compact zeolite layer did not improve the sorption process.

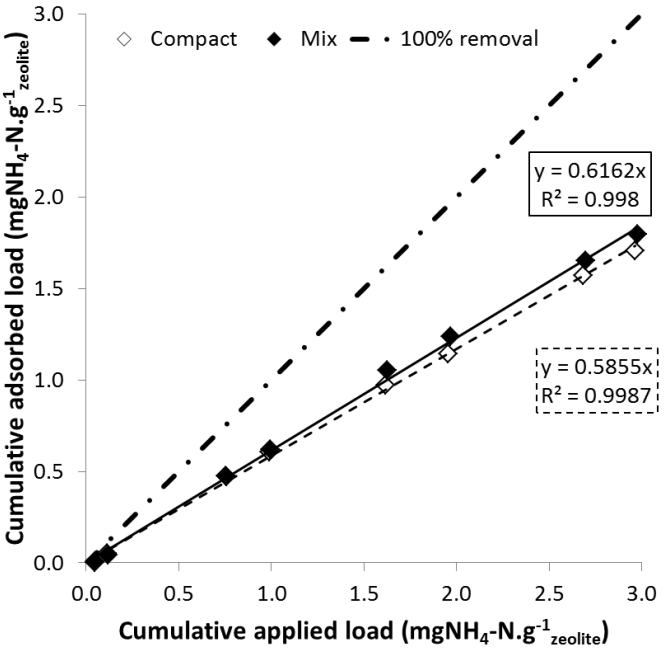

Figure 46 Ammonium cumulative adsorbed load in relation to the ammonium cumulative applied load (from the 1st to the 37th batch) for two different designs of the zeolite layer

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This phenomenon may be partly explained by the presence of a gravel top layer which allowed the efficient distribution of influent throughout the whole treatment surface before reaching the reactive layer and thus enabled an optimal contact between influent and zeolite.

5.3.4.3 Effect of the zeolite mass

The experiment under saturated conditions suggested that a higher zeolite content allowed reaching higher removal efficiency as previously observed by several authors (Arslan and Veli, 2012; Huang *et al.*, 2010; Ivanova *et al.*, 2010; Saltali *et al.*, 2007). Establishing the optimal amount of zeolite to use, in order to fulfill both high treatment standards and economic requirements, is thus necessary for design guidelines.

Figure 47 presents the adsorbed mass of ammonium depending on the total load of ammonium applied to 4 similar systems operating in identical conditions but containing increasing masses of zeolite. Each column showed a power relationship between the applied and the adsorbed load of ammonium. Removal rates were close to the 100% removal efficiency (dotted straight line) for low adsorbed mass then diverged when increasing the applied load. This decrease in removal efficiency may be partly explained by progressive exhaustion of surface sites, which are easily available for substrate. However, the equilibrium saturation state of zeolite was not reached yet since adsorbed load still increased, even at a lower rate. Erdoğan and Ülkü (2011) reported, from batch experiment, that ammonium sorption is controlled by successive mechanisms. Ammonium removal is first limited by external film transfer and diffusion into the macropore structure of the adsorbent. These processes are fast while the two last sorption steps (i.e. diffusion into the meso and microporous structure) are slower. Variations in the kinetic of mechanisms may also partly explain the lower ammonium removal at the end of the experiment. The adsorption process was thus affected to a higher extent by the contact time resulting in lower efficiency.

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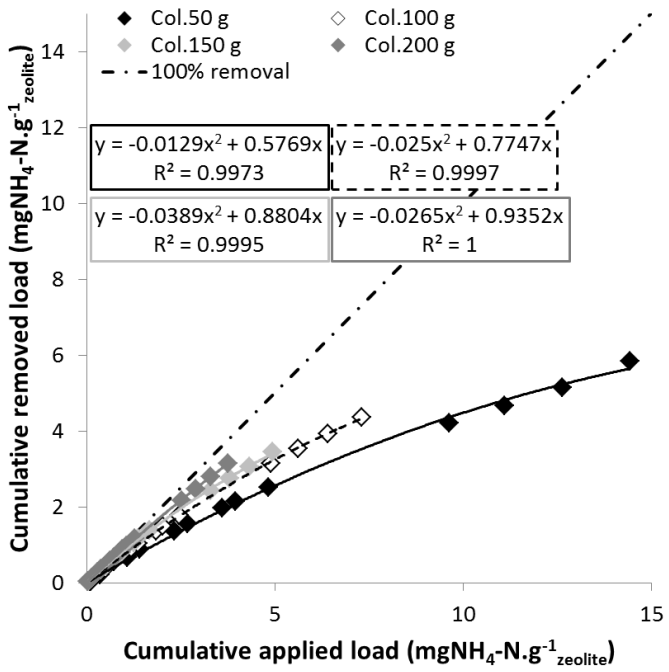

Figure 47 Adsorbed mass in relation to the cumulative applied load of ammonium for 4 different increasing masses of zeolite.

Furthermore, the comparison of these curves shows that the higher the amount of zeolite, the better the efficiency. On the one hand, increasing the mass of zeolite, for an identical applied load of ammonium, allowed to reduce the applied load per mass unit. Since performance dropped when applied load increased, the implementation of more zeolite allowed to remain in the optimal conditions for an efficient sorption process. Nevertheless, it may be expected that, after longer time of operation, the curve of the column filled with the highest mass of zeolite (200 mg) will show a similar shape than the one with the lower amount of zeolite (50 mg) since saturation of surface sites will occur.

However, comparison of these columns shows that their adsorption capacity varied for a similar applied load per mass unit (2mgN.g^{-1} for an applied load of 3.6mgN.g^{-1} and 3.15mgN.g^{-1} for an applied load of 3.8mgN.g^{-1}, for the column filled with 50 and 200mg, respectively). That may be partly explained by the hydraulic behavior of vertical filters. During infiltration, in pulse-load operation, part of the influent quickly flowed through the system by macropores while part of the influent was stored between batches inside the pore volume. A higher depth of zeolite did not result in diminished the preferential pathways (filtration height remained constant in the column) but provided higher reactive volume. Since the adsorption process was partly limited by short contact time, it is believed that most of the

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removal was carried out on the fraction stored in the pore volume between successive batches. This assumption was partly confirmed by the comparison with results from the study in saturated conditions. For instance, the column filled with 100g of zeolite adsorbed 3.14mgN.g^{-1} whereas, for similar zeolite mass, the saturated system performed a removal of 2.38mgN.g^{-1} for respective applied loads of 4.9 and 5mgN.g^{-1}. The contact time was a priori longer in the saturated system but the feeding frequency resulted in longer contact for the fraction within the pore volume. The higher adsorption rate observed for the unsaturated column thus suggests that the longer contact time of the stored volume enabled to perform better than under saturated conditions.

Consequently, increasing the amount of zeolite did not only enable to limit the relative applied load but also provided a design which allowed optimizing the use of exchange capacity. A deeper zeolite layer thus enabled to reach better overall removal efficiency. Furthermore, the study of identic systems receiving the same daily hydraulic load but operating with different batch load and feeding frequency might provide valuable information in order to determine the optimal contact time and thus optimize the fraction of water stored in the pore volume.

5.3.4.4 Effect of batch hydraulic load

The contact time between influent and zeolite was pointed out as strongly affecting the removal efficiency. The batch hydraulic load was related to the frequency of daily pulse-loading and thus with the contact time. Longer intervals between feeding were reported to provide a better infiltration rate because of increased drying between batches (Molle *et al.*, 2006). Figure 48 shows the adsorbed load, in relation to the applied load, for two identical systems receiving the same daily hydraulic load but operating at different batch hydraulic load (2 and 3cm, respectively). Both systems had a linear dynamic, during the studied period, but the slopes were quite different. The performance of the column fed at 2cm/batch was initially close to the 100% removal efficiency then quickly diverged. On the other hand, the column operating at 3cm/batch showed a similar shape but was already far from optimal removal as soon as the experiment began. This observation suggested that the higher the batch hydraulic load, the worse the performance.

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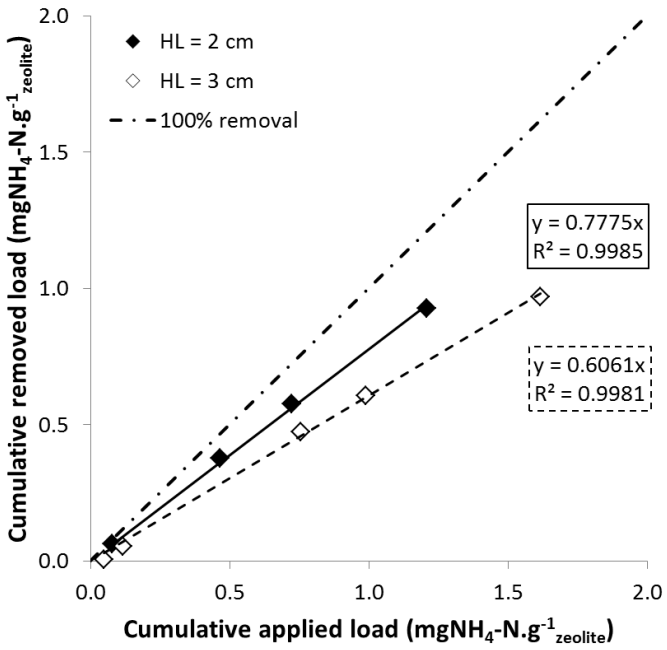

Figure 48 Adsorption capacity in relation to the cumulative load of ammonium for 2 different batch hydraulic loads

This observation may be explained by the higher fraction of influent which quickly flowed through the system with a short retention time (Molle *et al.*, 2006) when using higher batch loads. Most of the treatment is expected to occur during inter-batch periods on the water stored in the pore volume. Since this volume was constant whereas the feeding frequency was different for each system, the faction of daily volume, stored in the pore volume, was lower when the batch load increased. This is consistent with Molle *et al.* (2006) who reported that shorter feeding frequency and lower batch load allowed to increase the volume of residual water with the filter. This suggests that numerous small batches may optimize the hydraulic dynamic of the filter and thus improve the treatment efficiency in reactive beds since less water is expected to pass directly to the outlet.

5.3.4.5 Effect of influent concentration

Several authors (Erdoğan and Ülkü, 2011; Karadag *et al.*, 2007; Lebedynets *et al.*, 2004) reported that influent concentration had a strong impact on equilibrium exchange capacity of zeolite. In other respects, inlet ammonium concentration may vary strongly depending on local context (mean concentration of 55 mgN.L^{-1}, ranging from 12 to 98 mgN.L^{-1} (Mercoiret *et al.*, 2010) in communities smaller than 2,000 p.e. in France). Moreover, influent characteristics fluctuate, according to a diurnal cycle, showing a high peak of ammonium

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concentration around 8:00 a.m. whereas almost no ammonium was observed between 2:00 and 6:00 a.m. (Almeida *et al.*, 1999). It was thus necessary to characterize the system's capacity in relation to the operational conditions in order to optimize the zeolite implementation depending on local context.

Figure 49 presents the adsorption dynamics in relation to the applied load of ammonium for 3 identical columns receiving different inlet ammonium concentrations. The values were initially close to the 100% removal line but then progressively diverged when cumulative applied load was higher than $0.3 mgN.g^{-1}$. Almost all initial values from the 3 different systems were situated on the same line, suggesting that the sorption process was not directly affected by the applied concentration, for low saturation state, but was rather related to the applied load of ammonium for the studied conditions. However, this observation is not consistent with the results from studies under static (Arslan and Veli, 2012; Karadag *et al.*, 2007; Demir *et al.*, 2002) and saturated dynamic conditions (Mahendra *et al.*, 2015) which reported variations in kinetic constants of the ion exchange processes depending on the influent concentration.

The shape of the column fed at $60 mgN.L^{-1}$ diverged from the "shared curve" when the applied load was higher than $0.4 mgN.g^{-1}$. This observation suggested that sorption dynamics became concentration-dependent over a certain applied load. Nonetheless, both columns fed at 60 and $100 mgN.L^{-1}$ showed similar removal efficiency over the experiment which was not consistent with expectations based on results from static experiments (Alshameri *et al.*, 2014). A tracer test might have provided information on the presence of hypothetical dead volumes in the column fed at $60 mgN.L^{-1}$. It was thus not possible to conclude on the absolute effect of influent concentration under unsaturated dynamic conditions. Although concentration did not seem to be the key parameter in removal efficiency, the effect of such operational parameter must be further studied, especially until reaching the equilibrium saturation state, in order to confirm this observation.

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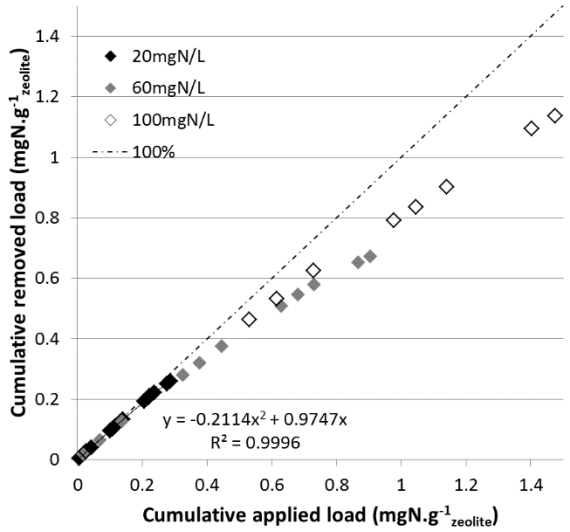

Figure 49 Adsorption capacity in relation to the ammonium applied load for varying inflow ammonium concentrations

5.4 Conclusions

This study was carried out in order to assess the potential of ammonium removal, from water, by zeolitic materials. The scope of this work was to determine the feasibility of zeolite implementation in VFFs in order to improve the ammonium treatment and thus reduce the footprint of such system.

Although material characterization suggested high removal capacity (i.e. high CEC up to 2.1 meq.g^{-1}), the actual efficiency, with regards to operational conditions, remained far below expectations. This confirms that supplier datasheets may be helpful for medium choice but are definitely not the only critical design criterion.

Optimization of the adsorption process under dynamic conditions was a challenging objective since numerous operational parameters may affect the treatment.

Although saturated conditions were assumed to provide an optimal contact between sorbate and sorbent, the system did not allow reaching the expected low outlet concentration and the system was quickly exhausted. The studied operational conditions (i.e. 16.6 minutes contact time with the reactive layer) were thus not adapted for efficient removal of ammonium, but a longer retention time might improve treatment performance. Nevertheless, a maximum contact time of 1.8h could be achieved in full-scale VFFs with the studied design (7cm of zeolite height). This retention time must be assessed in order to conclude on the operation

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under saturated conditions. In other respects, the saturated mode is incompatible with the operational characteristics of VFFs. The implementation of a bottom zeolite layer operating in tidal flow mode (alternation of saturated and unsaturated periods) may enable to optimize the adsorption process in VFFs but would result in operational extra-costs.

Despite a theoretical poor contact between sorbent and sorbate, systems operating under free drainage conditions showed good removal efficiency. It was assumed that this may be attributed to the storage of part of the influent within the inter-particle pore volume between consecutive feedings, which therefore ensured long contact time between influent and zeolite. The optimal batch hydraulic load should thus be a compromise between the fraction of water stored within pore volume and the contact time (feeding frequency).

Furthermore, increasing the filtration depth of zeolite is another alternative to improve the removal efficiency. Besides the increase in the "reactive" pore volume, higher amount of zeolite allowed to reduce the applied load of ammonium per mass unit of material resulting in a slower saturation of surface sites. Adsorption kinetic was thus optimized since adsorption onto surface sites is believed to be easier and faster than onto internal sites. The implementation of $30 kg.pe^{-1}.bed^{-1}$ allowed to achieve ammonium removal above 90% over a full feeding cycle, suggesting promising results for its use in wastewater treatment.

Although zeolite achieved high ammonium removal, a fast decrease in efficiency was observed after few days of operation. Using synthetic water solution, no biological activity allowed nitrification of adsorbed ammonia and consequently no regeneration of adsorption sites occurred. This system must therefore be further studied with semi-synthetic wastewater, or with material previously colonized by biofilm, in the aim at assessing the biological regeneration mechanism (regeneration kinetic and regeneration rate, evolution of sorption capacity, etc.).

To conclude, zeolite has valuable properties for wastewater treatment but the current operational characteristics of VFFs must probably be slightly modified in order to allow the optimal use of sorption capacity. Moreover the implementation of $30 kg.pe^{-1}.bed^{-1}$ may result in significant increase in initial costs and the comparison with other optimization of design must be carried out. Finally, the restoration of exchange capacity has to be scheduled and the potential of biological regeneration is not still perfectly controlled. The assessment of alternative designs and operation modes must be carried out before its implementation in full scale treatment plants.

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Chapter 6 The use of zeolite in vertical flow filters

This chapter was submitted to the IWA special issue in water science and technology. Furthermore, these results were presented in Gdańsk at the ICWS conference on wetlands.

Natural chabazite as filtration medium for ammonium removal optimization in vertical flow filters: a column experiment

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Abstract

An ion exchange process was assessed with the purpose of improving ammonium removal by vertical flow filters (VFFs). Six column scale VFFs, filled with gravel and zeolite (depth of 30cm and 10cm, respectively), were compared with a standard column with a 40cm-deep filtration layer of gravel. To mimic real conditions, columns were fed for 3.5 days with semi-synthetic wastewater (14 batches per day of 2 cm-load every 100 minutes), then rested for 7 days. Each column, filled with zeolite, had different inlet characteristics in order to study the effects of several operational parameters initially pointed out as affecting the ion exchange process. Two columns were dedicated to assess the impact of ammonium concentration ($100 mgNH_4\text{-}N.L^{-1}$ versus $2000 mgNH_4\text{-}N.L^{-1}$) on exchange capacity and performance dynamics. The effect of competition of ammonium with other cations, on removal efficiency and saturation rate, was studied at three different concentrations of sodium ($0 mg.L^{-1}$, $85 mg.L^{-1}$ and $300 mg.L^{-1}$, respectively). Finally, regeneration of exchange capacity by nitrification, as well as the effects of such restoration, on treatment efficiency was studied. Although zeolite showed promising exchange capacity in the early stages of column operation (> 80%), treatment performance quickly declined, until reaching a similar removal efficiency as the standard (60%), suggesting an insufficient regeneration of exchange sites. Moreover the influent concentration strongly affected the ion exchange capacity, the latter one being quite low for the range of ammonium concentrations usually observed in domestic wastewater. The sodium supply did not result in performance reductions for the studied conditions.

6.1 Introduction

Nitrogen pollution in domestic wastewater is mostly observed as organic nitrogen and ammonium (Mercoiret *et al.*, 2010) and is predominantly associated to human excrements (urea) (Almeida *et al.*, 1999). Because of the high toxicity of its unionized form, for aquatic organisms (Kadlec and Wallace, 2009), particular attention has to be paid to ammonium removal in wastewater treatment.

The main process of ammonium removal in wastewater management, namely nitrification, relies on the two-step biological oxidation of ammonium to nitrite and then nitrate under strictly aerobic conditions by autotrophic bacteria (Ahn, 2006; Vymazal, 2007).

The classic French design of treatment wetlands consists in the implementation of two successive stages of vertical flow filters (VFFs), composed by 3 and 2 parallel units

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(0.4m²/p.e./filter), respectively, operating in a sequential mode of feeding and resting periods (3.5 / 7 days and 3.5 / 3.5 days, respectively) (Molle *et al.*, 2005). The first stage, filled with gravel, achieves high removal performance of TSS and COD (83% and 77% on average, respectively) but only performs partial nitrification (59%) (Morvannou *et al.*, 2015). The low removal of ammonium is explained by the short contact time between influent and biomass (Sun *et al.*, 2003) as well as the competition between heterotrophic and autotrophic bacteria to consume oxygen for organic matter and ammonium oxidation processes (Ling and Chen, 2005; Chen *et al.*, 2006). A second stage is therefore needed to achieve near-complete nitrification.

Zeolite material is a porous alumina-silicate medium in which the substitution of silica by aluminium results in negative charges which are compensated by weakly bonded cations (Na^+, K^+, Ca^{2+} or Mg^{2+}) (Erdoğan and Ülkü, 2011) resulting in a high potential for cation exchange (Wang and Peng, 2010). Moreover, zeolite structure consists of a network of small pore channels (ranging 3Å to 8Å) acting as molecular sieve (Hedström, 2001). Several authors reported high selectivity of zeolite for ammonium (Ivanova *et al.*, 2010; Leyva-Ramos *et al.*, 2010; Widiastuti *et al.*, 2011).

The implementation of zeolite as filtration medium in VFFs might thus allow to overcome the non-optimal nitrification in the first stage of a French treatment wetland system. Indeed, it is assumed that ammonium in solution will be fixed onto zeolite, during the feeding period, and will be then further nitrified, during the resting period, before being released as nitrate (nitrate repulsion with negative charges) in the subsequent feeding period. The high nitrate release, consecutive to almost full ammonium removal during previous feeding period, observed by Fournel (2012) in VFFs containing zeolite material indeed suggested the potential of biological regeneration of exchange capacity in such system.

Although theory suggests a high potential of ammonium removal by zeolite, several factors such as the inlet ammonium concentration or the presence of other cations, may affect the process (Huang *et al.*, 2010). Moreover, the potential of regeneration of exchange sites as well as the impact of biofilm are still not completely known. This study aimed to assess these different aspects through the monitoring of 7 columns operating in various conditions. The final goal of the present article is to conclude on the potential of optimization of ammonium removal by the use of zeolite as well as to provide recommendations for further operation.

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6.2 Materials and Methods

6.2.1 Columns design

Seven columns were studied for this experiment. Six columns were filled with materials originating from a full scale treatment wetland while another was filled with clean materials (column 6). They consisted of an opaque PVC pipe of 12.5cm diameter and 60cm depth. Six columns were filled, from the bottom to the top, by a thin layer of gravel (2/6mm), a 10 cm zeolite layer (2/5mm, 613g) and finally a 30cm gravel layer (2/6mm, 4 345g on average). The bottom thin layer of gravel avoided release of zeolite while the top thick layer of gravel allowed an optimal distribution of influent before reaching the zeolite layer. The seventh column was filled with a 40cm homogeneous layer of gravel. This last column acted as a reference for the study. A description of the experimental setup is proposed in Figure 50.

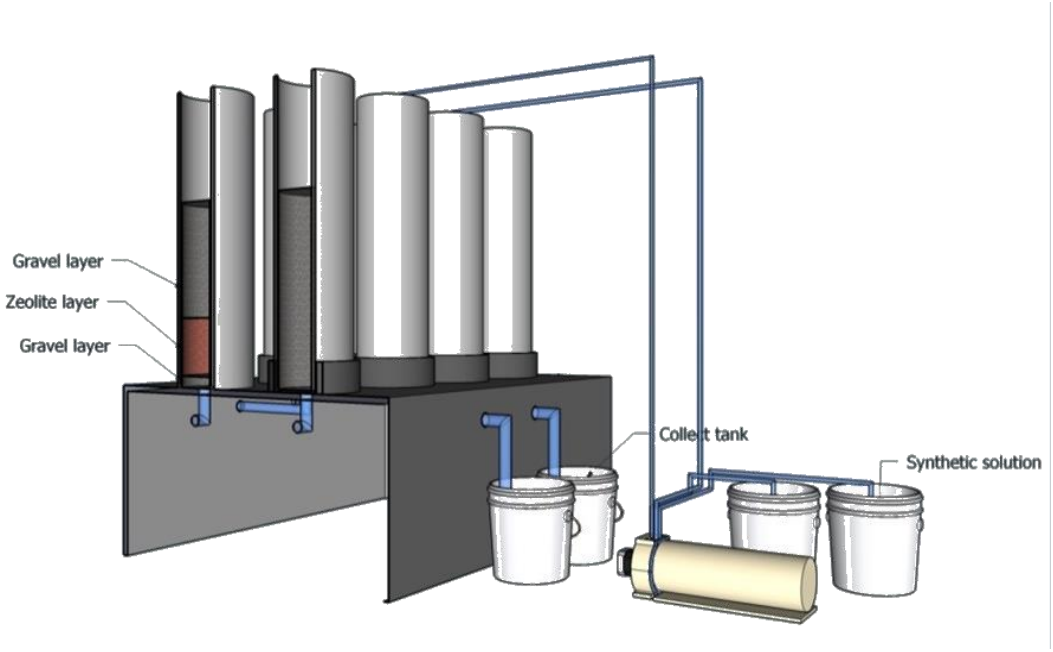

Figure 50 Schematic description of the experiment

6.2.2 Operation description

Zeolite and gravel media, sampled in treatment plant, were washed with distilled water before starting the experiment. That allowed to release the nitrogen which was already stored in the system. Each column was dosed 6 times a day with distilled water (8cm/batch) until ammonium and nitrate concentrations reached close-to-zero value.

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To mimic real conditions, columns were fed during 3.5 days and then rested for 7 days. This cycle of operation was repeated 10 times during the experiment. The columns were dosed 14 times a day at a hydraulic load of 2cm ($28cm.d^{-1}$). The batch frequency was set at 100 minutes with a digital timer while the flow rates of the peristaltic pumps were adjusted at targeted values of $0.4m.h^{-1}$.

The columns were fed from the surface, by a single feeding pipe (smooth PVC, diameter 8mm) located in a central position, with semi-synthetic wastewater. The effluent was then collected in individual 15L polyethylene buckets which were spiked in sulphuric acid in order to inhibit biological processes (pH ≈ 2). Each feed solution was prepared by spiking a volume of treated wastewater (water from the tertiary clarifier of an activated sludge treatment plant) with pre-determined volumes of the required concentrated stock solutions (namely, ammonium, sodium and allylthiourea solutions) as shown in Table 19. Note that allylthiourea (ATU) is a well-known nitrification inhibitor (Hall, 1984). This reagent inhibits ammonium oxidation by chelating the copper of the ammonia monoxygenase active sites (Krustok *et al.*, 2016). It was added to solutions when nitrification inhibition was required by the experiment objectives. The stock solutions were prepared with ammonium sulphate, sodium carbonate and allylthiourea to reach $75gNH_4\text{-}N.L^{-1}$, $75gNa.L^{-1}$ and $10gATU.L^{-1}$ in distilled water, respectively. Inhibition of nitrification process was required by the experimental objectives of certain columns. ATU was therefore supplied in this purpose. First of all, columns 2 and 6 (namely Z_used-reference and Z_clean-reference, respectively) have been compared in order to assess the effect of maturation, such as the presence of biofilm or the impact of previous sorption – restoration cycles, on the sorption efficiency. It was thus necessary to inhibit nitrification process in these columns in order to focus on sorption process. On the other hand, an accurate characterization of the processes occurring within the gravel layer was necessary for a proper assessment of the nitrogen dynamic within the zeolite layer. Addition of ATU during the second period of operation of column 7 (namely G_reference) enabled to assess the fraction of ammonium which was removed by adsorption onto the organic matter which is fixed on gravel. Assuming that both processes of nitrification and adsorption occurred during the first period, it was possible to determine their respective removal rate by making the difference between the ammonium removal rates of each period.

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Table 19 Influent and objectives description of studied columns

Column	Name	Influent characteristics			Objectives	Method
		$[NH_4^+]$ ($mgN.L^{-1}$)	$[Na^+]$ ($mg.L^{-1}$)	[ATU] ($mg.L^{-1}$)		
1	Z_low-ammonium	100	0	0	1) Effect of zeolite implementation 2) Effect of ammonium concentration 3) Effect of other cations 4) Potential of regeneration	1) Comparison of columns 1 and 7 2) Comparison of columns 1 and 3 3) Comparison of columns 1, 4 and 5 4) Evaluation of performance dynamics
2	Z_used-reference	100	0	20	**Reference of used zeolite layer** 5) Evolution of exchange capacity (used medium) 6) Effect of thin biofilm on ammonium diffusion	5) Comparison of columns 2 and 6 6) Comparison of columns 2 and 6
3	Z_high-ammonium	2 000	0	0	2) Effect of ammonium concentration	2) Comparison of columns 1 and 3
4	Z_low-cations	100	85	0	3) Effect of other cations	3) Comparison of columns 1, 4 and 5
5	Z_high-cations	100	300	0	3) Effect of other cations	3) Comparison of columns 1, 4 and 5
6	Z_clean-reference	100	0	20	**Reference of clean zeolite layer** 5) Evolution of exchange capacity (fresh medium)	5) Comparison of columns 2 and 6
7	G_reference	100	0	0 / 20*	**Reference of gravel layer**	

* ATU concentration was initially set to 0 then rose to 20$mg.L^{-1}$ in order to inhibit the process of nitrification.

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6.2.3 Analytical procedure

The columns were monitored by analysis of outlet water composition on 24-hour and 84-hour composite samples. Inlet grab samples were analysed periodically to verify the stability of the concentration of the feed solution. The applied and collected volumes were determined by weighing the storage and collection buckets, respectively.

Ammonium and nitrate concentrations were analysed by spectrometry with quick test methods (LCK 303, LCK 339 and 340; Hach).

6.3 Results and discussion

6.3.1 Study of the gravel layer

Column 7 provided knowledge on the removal processes occurring in the top gravel layer of columns filled with gravel and zeolite. That allowed to determine the actual load applied to each zeolite layer.

Figure 51 shows cumulative loads of ammonium and nitrate which were respectively removed and produced over the whole studied period. Two distinct trends, in relation to ATU supply, were visible. Ammonium removal was initially fast and constant (16.1gN.m^{-2}.d^{-1} on average), being close to the rate reported by Morvannou *et al.* (2012), then dropped to 2.8gN.m^{-2}.d^{-1} when ATU was added to the feed solution. Treatment efficiency thus decreased from 64%, which was in the range of values observed at first stages of French VFFs (Morvannou *et al.*, 2015; Paing and Voisin, 2005), to 7% on average when column 7 was fed with ATU. Moreover ammonium removal and nitrate production were closely related as evidenced by the parallel evolution of both sets of data during operation without ATU supply.

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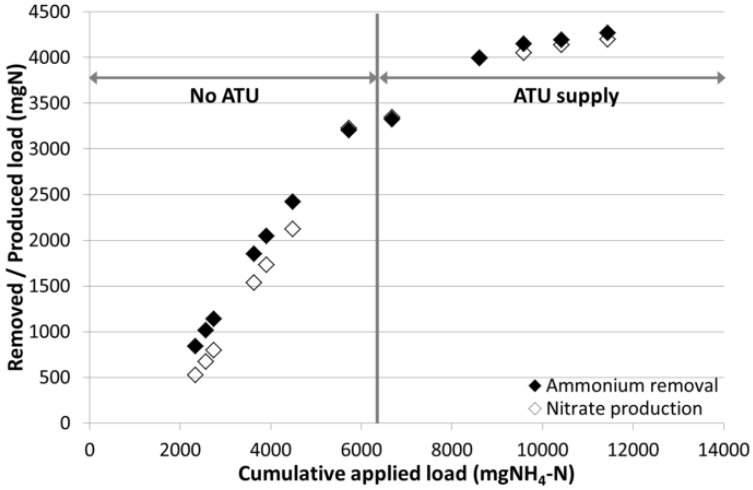

Figure 51 Cumulative removed load of ammonium and produced load of nitrate with regards to the cumulative load of ammonium applied to column 7 (the 6 first data were obtained on 24-hour composite samples while others were 84-hour composite samples)

These observations confirmed that, on the one hand, nitrification was the main mechanism of ammonium removal in the system while, on the other hand, another process, most probably adsorption onto organic matter fixed on gravel, enabled to remove a small amount of ammonium even when nitrification was inhibited.

The constant removal of ammonium during the first period of the experiment suggested that no oxygen limitation occurred during feeding periods. That could be partly explained by the absence of ponding which generally limits the oxygen renewal in VFFs (Molle *et al.*, 2006) as well as by the low content of COD in the feed solution, which in addition was assumed to be mostly slowly biodegradable COD ($69.2 mg.L^{-1}$). Oxygen was thus almost exclusively available for autotrophic bacteria and the nitrification rate was therefore probably slightly overestimated. The ammonium removal and the nitrate production were quite similar during the first period of operation (without ATU supply), suggesting that near-complete nitrification of removed ammonium was achieved.

Nitrification, within the gravel column, should be completely inhibited when the influent is spiked with ATU. Consequently, nitrogen dynamics would provide useful information. First, the nitrate release, observed during the first cycle with ATU, is the result of nitrification during the resting period. It should thus allow to determine the nitrification kinetic during resting period. Furthermore, kinetic of direct nitrification could also be assessed from this knowledge. The difference between the load of nitrate produced during a cycle without ATU

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and the load of nitrate released after the first cycle with ATU can indeed be considered as the direct nitrification. Secondly, the ammonium removal observed during the first cycle with ATU can not be related to nitrification (process inhibition). The ammonium dynamic during this first cycle should thus provide information on the capacity of sorption onto organic matter which is fixed on gravel. The sorption capacity is expected to be fouled after the first cycle of operation with ATU. Its restoration would not occur since nitrification is inhibited. The production of nitrate and the removal of ammonium should thus drop to zero for the second cycle with ATU. Nevertheless, ammonium removal did not drop to zero, after the first cycle with ATU, and nitrate was still produced, in small amounts, suggesting that nitrification process enabled the regeneration of all or part of the sorption sites of organic matter. The low rate of nitrate production suggested that nitrification was only partially inhibited. This small production of nitrate may be explained by a short persistence of ATU in the environment. Since column rested for 7 days between consecutive feeding cycles, partial nitrification might occur after some days of resting, leading to the production of nitrate and the restoration of fixation sites on organic matter. Moreover, the question of the effectiveness of nitrification inhibition by ATU may also be arised. The results thus suggest a bias, with no clear explanation, which hinders a clear conclusion on the different mechanisms. It is interesting to note that treatment efficiency may slightly increase over time, in full scale treatment plants, as organic deposit, and consequently adsorption sites, will increase.

6.3.2 Study of the zeolite layer

Ammonium removal occurred in the top layer of gravel as shown in the previous section. The estimation of the actual ammonium load, reaching the zeolite layer, was thus necessary in order to properly describe the process of ion exchange.

An ammonium removal rate of 35.9µgNH_4-N.g_{gravel}^{-1}.d^{-1} was initially determined from the ammonium areal removal rate observed in column 7 during the operation without ATU supply. The load of ammonium applied to the system was thus corrected, taking into account the mass of gravel in the top layer as well as the period of operation for each sample, in order to determine the load of ammonium reaching the zeolite layer.

Difference between loads of ammonium at the inlet and the outlet of the zeolite layer is caused by both nitrification and sorption processes. The effect of nitrification, occurring in the zeolite layer, was estimated in order to accurately determine the fraction of ammonium removal resulting of sorption process. Since gravel and zeolite have similar grain size,

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assumption was made that the ammonium removal rate determined for gravel may be extrapolated to zeolite. Difference between the load of ammonium which was removed, in the zeolite layer, and the removal which is assumed to be related with nitrification thus allows to determine the load of ammonium which was removed by sorption process. It must be noted that removal rate on gravel was expressed in $\mu gNH_4\text{-}N.g^{-1}_{gravel}$. A factor of correction based on bulk density (i.e. $\rho_{gravel} = 1.6 ton.m^{-3}$ and $\rho_{zeolite} = 0.75 ton.m^{-3}$) was thus required in order to convert the removal rate in $\mu gNH_4\text{-}N.g^{-1}_{zeolite}$.

6.3.2.1 Impact of zeolite layer on the removal of ammonium

The effect of zeolite implementation on ammonium removal by a 40cm-deep filtration layer was assessed through the comparison of column 7 (gravel, $100 mgNH_4\text{-}N.L^{-1}$) and column 1 (mix gravel and zeolite, $100 mgNH_4\text{-}N.L^{-1}$).

Figure 52 showed treatment performance of column 1 during the study, depending on the cumulative applied load of ammonium. Initial efficiency was higher than 80% then decreased logarithmically until levelling off close to 60%. The plateau was already reached after 3 feeding periods. This observation confirmed the positive effect of zeolite implementation on ammonium removal but also suggested that the life span of the ion exchange process was limited.

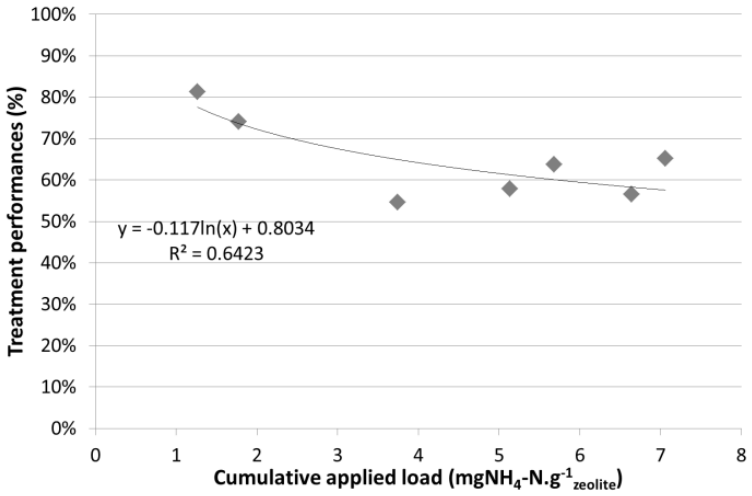

Figure 52 Ammonium removal efficiency of column 1 in relation to the cumulative applied load of ammonium (84-hour composite samples)

The ammonium removal by two systems (column 6 and 2) filled with clean or used zeolite (from which the fixed ammonium was previously washed out), respectively, and operating in

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identical conditions was similar (see Figure 53). That suggested that exchange capacity remained quite constant over time if the ammonium was properly removed from the system between subsequent cycles and that a performance decrease was not related to an intrinsic modification in zeolite CEC.

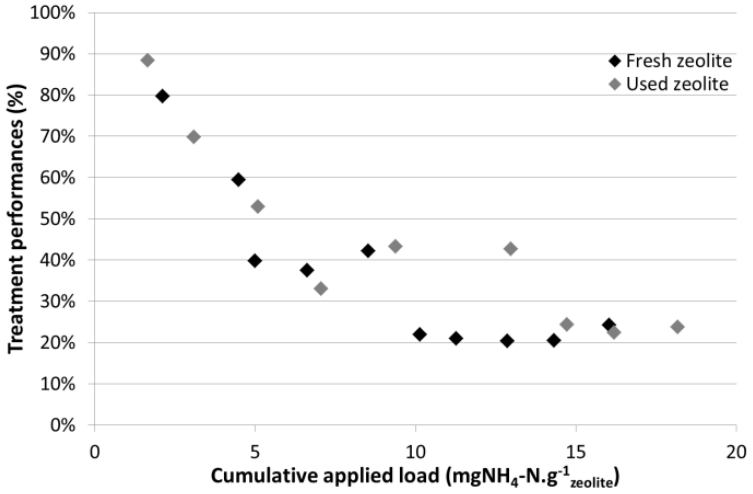

Figure 53 Ammonium removal by fresh and restored zeolite VS ammonium applied load

The use of zeolite in the filtration layer mainly relied on the assumption of biological regeneration of exchange capacity (Jung *et al.*, 2004), by nitrification of ammonium, during the resting period. Nevertheless the results showed in Figure 52 suggested that, in the early stages of operation, ion exchange and nitrification processes both occurred. The system exchange capacity was then progressively saturated. Finally, nitrification was the single process performing ammonium removal in the last times of the study.

Moreover, the design which was assessed in this study did not allow to reach low ammonium concentrations in the effluent. A higher content of zeolite in the filtration layer might improve the outlet concentration (Arslan and Veli, 2012).

The dynamics of ammonium removal and nitrate production of column 1 during the first day of a feeding cycle were shown in Figure 54. The black and white bars showed the nitrogen cumulative loads during the batch monitoring of column 1 (ammonium removal and nitrate production, respectively). The regeneration, corresponding to dark grey bars, was estimated as the difference between the nitrate production and the ammonium removal. These 3 parameters presented the nitrogen dynamic as well as the zeolite exchange potential in the system. On the other hand light grey bars described, on a batch scale, the ammonium removal. This last parameter provided an insight on the dynamic of ammonium removal. Nitrate production was

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initially high, and was more intense than ammonium removal. On the other hand, ammonium removal remained quite constant over the monitoring period although nitrate release decreased after eight batches. Furthermore, the trend of the regeneration process became negative after eight batches. Such observation suggested that part of the ammonium, which was previously exchanged with zeolite, was nitrified during the rest period and was released at the beginning of the subsequent feeding period thus restoring some exchange sites. Longer monitoring might show progressive decrease in ammonium removal as the free exchange sites were saturated. Indeed the mean removal performance was slightly higher in the first times of feeding cycle.

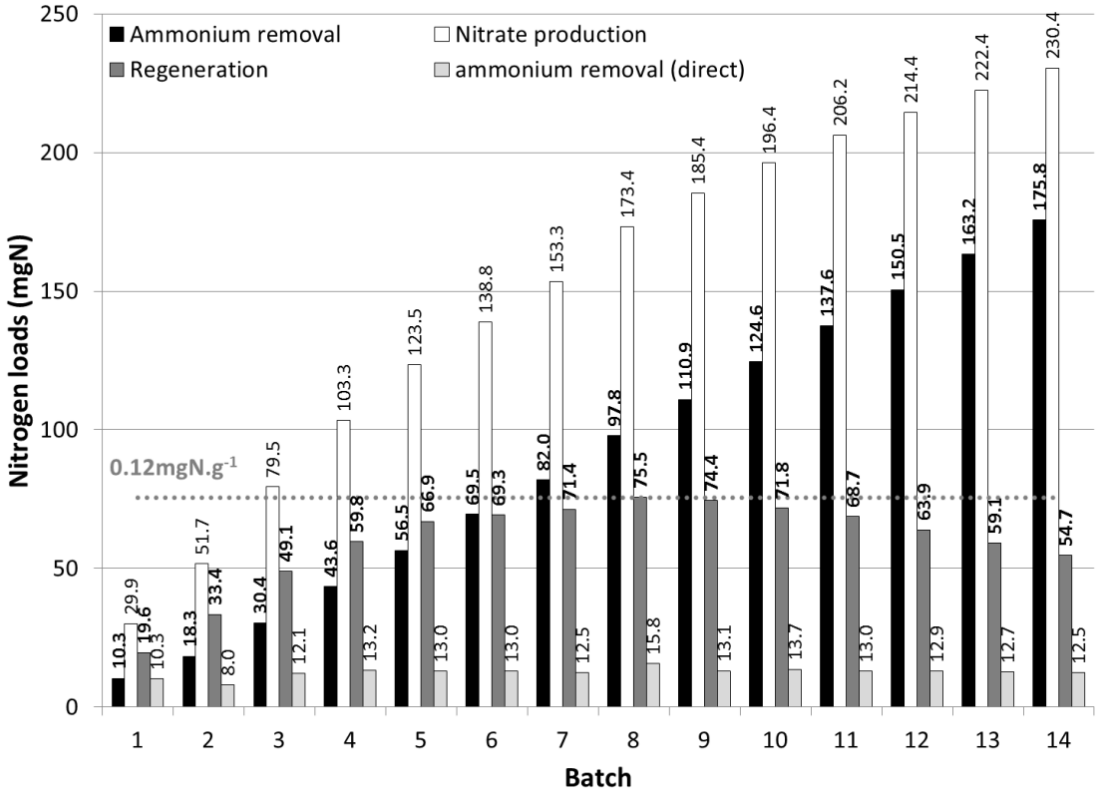

Figure 54 Mass balance of the first day of feeding cycle (end of the study, cycle 10) of column 1

A maximum regeneration rate was measured at 0.12mgNH_4-N.$g^{-1}_{zeolite}$ after the eighth batch of the feeding period. This low regeneration rate may be explained by the incapacity of autotrophic bacteria to ensure full nitrification of the exchanged ammonium. The porous structure of zeolite enabled to obtain an important exchange surface. Nevertheless the size of pore channels, which acts as molecular sieve, was probably too small considering the size of bacteria. Therefore growth of bacteria might be restricted to the grain surface where

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regeneration occurred. Ammonium oxidizing bacteria could therefore not achieve the nitrification of ammonium which diffused into the zeolite pores.

The zeolite exchange capacity was thus quickly saturated and the impact of the ion exchange process became negligible after a few cycles of operation. The use of a finer zeolite could probably improve the treatment performances as well as the life span of the exchange capacity since the fraction of surface sites should be higher (Erdoğan and Ülkü, 2011; Huang *et al.*, 2010). Moreover the decrease in grain size would also improve the exchange rate by reducing the intra-particle diffusion limitation (Wen *et al.*, 2006). The nitrification of ammonium would therefore be improved by an easier access for autotrophic bacteria. Fournel (2012) reported high ammonium removal and no exhaustion of exchange capacity by the use of fine zeolite (0/2mm) for sewer overflow treatment.

6.3.2.2 Effect of initial ammonium concentration

Figure 55a showed the removal efficiency of full system in column 3, fed with a high ammonium concentration (2000mgNH_4-N.L^{-1}), in relation to the cumulative applied load of ammonium. Treatment performance evolved according to a similar logarithmic shape as column 1 (100mgNH_4-N.L^{-1}), shown in Figure 52, from 65% to close to 0%.

Figure 55b described the dynamics of ammonium and nitrate loads which were respectively removed and produced, by the zeolite layer, during the monitoring. Ammonium removal was very high in the early stages of operation (9mgNH_4-N.$g^{-1}_{zeolite}$ for the first day of operation) but then quickly dropped. In other respects, nitrate production was low and remained in the same range of values during the study.

These observations suggested that a high rate of ion exchange may be obtained with concentrated solutions. Nevertheless they also confirmed the inefficiency of bacteria to fully restore the exchange capacity by nitrification of fixed ammonium.

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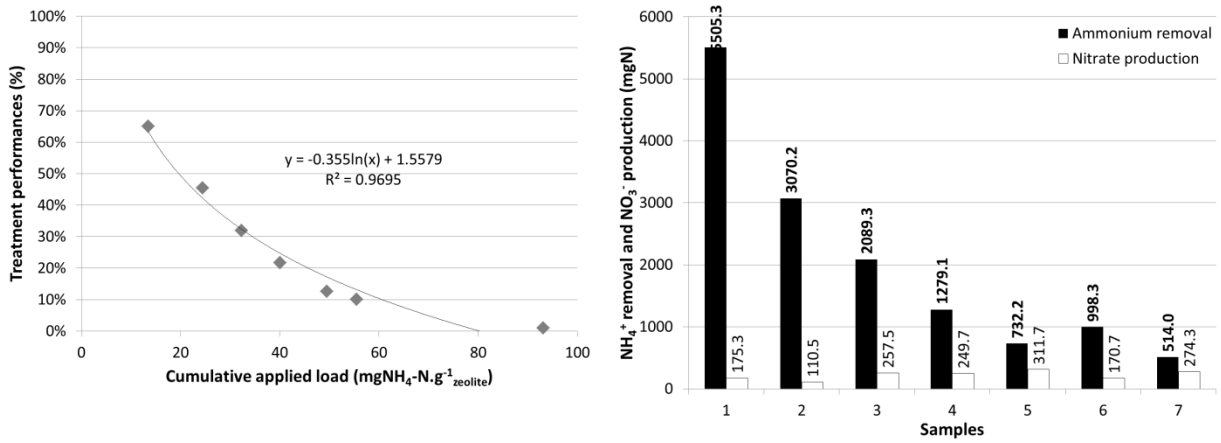

Figure 55 Ammonium removal, by the system, in relation to applied load of ammonium (a) and nitrogen mass balance, of the zeolite layer (b), for 24-hour composite samples in column 3

The amount of ammonium exchanged with zeolite in columns 1 and 3 (Figure 56a and b, respectively) increased according to a logarithmic trend until reaching a threshold. Final concentrations in zeolite varied widely depending on the inlet concentration. A maximum concentration close to 19mgNH_4-N.g^{-1} was estimated in the column fed with an influent concentration of 2000mgNH_4-N.L^{-1} while only 1.9mgNH_4-N.g^{-1} was stored in the zeolite operated with an influent concentration of 100mgNH_4-N.L^{-1}. Such observation was in accordance with the results, in column and batch conditions, of ammonium removal by zeolite (Arslan and Veli, 2012; Demir *et al.*, 2002; Karadag *et al.*, 2007) which showed that solid-phase concentration increased with influent concentration due to the establishment of an equilibrium between the concentration in the solid phase and in solution.

Although the studied chabazite had a theoretical cation exchange capacity (CEC) of 2meq.g^{-1} (i.e. 28mgNH_4-N.g^{-1}, data given by supplier), the final ammonium adsorption in zeolite varied widely depending on the inlet concentration.

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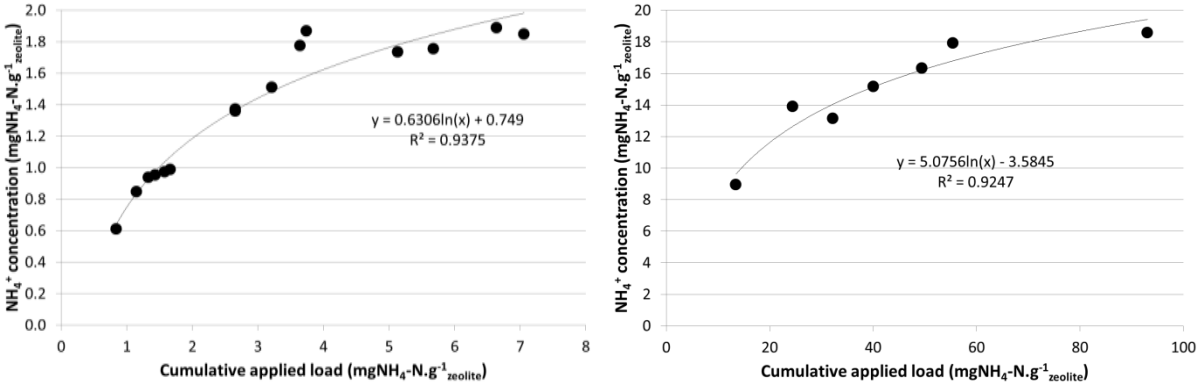

Figure 56 Ammonium concentration in solid phase regarding to the cumulative applied load for columns treating ammonium influent concentration of 100mgNH_4-N.L^{-1} (a) and 2000mgNH_4-N.L^{-1} (b)

The ammonium concentrations generally observed in domestic wastewater may not allow an optimal use of the CEC of zeolite. A preliminary estimation of the equilibrium concentration is therefore advisable before the implementation of zeolite in a treatment wetland. On the other hand the use of zeolite for treatment of highly concentrated solutions, such as swine manure, might probably improve the fraction of usable exchange sites.

6.3.2.3 Effect of another cation in solution

Several authors reported the competition which may exist between species if several types of cations are in solution (Huang *et al.*, 2010; Lei *et al.*, 2008). In a coastal context or during winter, when deicing is necessary, important concentrations of sodium might be observed in domestic wastewater. Its impact was assessed by comparing the ammonium concentration in zeolite for three different systems fed with the same ammonium concentration (100mgNH_4-N.L^{-1}) but with different concentrations of sodium (0, 85 and 300mgNa.L^{-1}).

Ammonium removal, in relation to the cumulative applied load of ammonium, was detailed in terms of performances and exchange capacity for the three sodium concentrations in Figure 57a and b. The three columns showed the same logarithmic decrease in performance from more than 90% to close to 60% while their dynamics of exchange capacity had similar shapes. The comparison of these three systems suggested that the process of ammonium exchange was not affected by the presence of sodium under the studied conditions.

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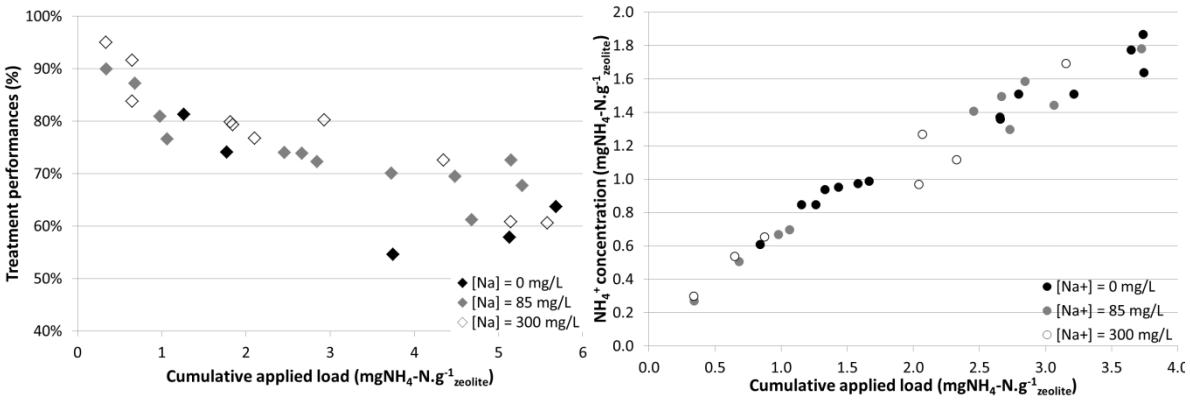

Figure 57 Treatment performances (a) and ammonium concentration in zeolite (b) in relation to the applied load of ammonium in columns 1, 5 and 6

Although the presence of sodium did not modify the ion exchange capacity, higher concentrations of sodium might cause a modification in the ion exchange equilibrium between ammonium and sodium (Jung *et al.*, 2004) and thus lead to ammonium release. This is an interesting phenomenon which could be suitable for exchange site restoration between subsequent cycles of operation. Lahav and Green (1997) performed desorption of ammonium, by backwash of the system with a Na-rich solution, followed by nitrification in a dedicated tank. That resulted in intensification of the process (Na supply with pumps, implementation of a nitrification tank) but allowed to sustainably remove the ammonium.

6.4 Conclusions

This study aimed to determine the benefit of zeolite implementation as filtration material in vertical flow filters in order to optimize ammonium removal.

Zeolite showed a real potential for ion exchange which enabled to improve the ammonium removal from 60% to 80% by the system treating an influent concentration of 100mgNH_4-$N.L^{-1}$. Nevertheless, the solid-liquid equilibrium did not allow the full use of the available exchange capacity and an important amount of zeolite, meaning excessive costs, must be implemented in order to reach a close-to-zero ammonium concentration in the effluent.

This medium might probably be more interesting for the treatment of concentrated influents such as swine manure, of which the high concentration would allow a nearly complete use of the CEC.

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Although zeolite showed clear capacity to remove ammonium through ion exchange process, the regeneration of the exchange capacity was not effective and the material was quickly saturated, leading to a severe drop in performance. This exhaustion of exchange capacity was believed to be related with the incapacity of autotrophic bacteria for accessing to the ammonium, entrapped inside the pores, because of their size which hindered their establishment in the pore channels. The use of finer zeolite might probably improve the efficiency of biological regeneration by increasing the amount of surface exchange sites.

Finally the presence in solution of sodium did not affect the treatment performance, under the studied conditions. It seems that zeolite had higher selectivity for ammonium than sodium. Nevertheless, sodium carbonate could be used in a two-step chemical and biological regeneration consisting in ammonium release followed by nitrification in a dedicated tank at the end of the feeding period. Such method would enable to restore the exchange capacity and improve the ammonium removal but also result in significant additional costs. The feasibility of this method must be thoroughly assessed before its implementation in a full scale treatment plant.

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Conclusions and perspectives

Treatment wetlands met a growing interest over the past three decades because of their good treatment efficiency and eco-friendly image as well as their low initial and operational costs. Nevertheless, they can suffer unsatisfactory performance on total nitrogen removal when targeting to limit their footprint, especially for large capacity treatment plants. Furthermore, sanitation became a highly competitive market and is hindered by current design guidelines of CWs which rely on experience, mostly gathered from trial and error methods. Better knowledge of treatment mechanisms as well as the relative effect of design and operational parameters on performances is thus highly required in order to rationalize the system for better TN removal with reduced treatment footprint.

For this purpose, this study was divided in three distinct research axes which were each dedicated to the assessment of a particular process of nitrogen removal. A first part attempted to assess, through pilot scale experiments, the treatment efficiency of a 1st stage vertical flow filter (VFF), treating raw domestic wastewater, under different design and operational characteristics (i.e. filtration depth, treatment surface as well as hydraulic and organic loads). Particular attention was paid to nitrification performance. Although treatment processes have been, already, widely described in literature, this study aimed at characterizing the effects of system's modifications on treatment efficiency. Relationships between such modifications and the filter's conditions were then established in order to propose recommendations for engineer support. In a second time, this study focused on denitrification process in saturated vertical flow filters. Only few works were specifically dedicated to the study of denitrification in constructed wetlands and, most of them, were based on unrealistic designs (long retention times) or influent characteristics (low nitrate concentration). Consequently, pilot scale experiments were conducted with different design characteristics (i.e. retention time, filling media) and under various influent characteristics (i.e. nitrate and COD_{tot} concentration). Driving parameters of denitrification process were identified from this study in order to propose operation and design guidelines. Finally, nitrification kinetic may be an obstacle to achieve full nitrification. The implementation of reactive media (i.e. zeolite), able to adsorb ammonium, might be an interesting solution. Based on this statement, the last part of this work was devoted to the assessment of zeolite as an alternative material for high ammonium removal. A first set of experiments was carried out, in column scale experiments for different

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design (i.e. mass of zeolite, type of zeolite) and operational conditions (i.e. feeding frequency, influent concentration), in order to improve the knowledge of sorption process under dynamic conditions. A second experiment, conducted under column scale conditions, was conducted in order to assess biological restauration of exchange capacity by nitrification. This experiment aimed to validate the use of zeolite as filtration medium in VFFs and optimize the cycle of operation in order to perform full regeneration of sorption sites.

This work allowed thus to consider TN removal as a whole and provided suitable information on requirements for an efficient TN removal with CWs. This section is built around the three axes developed in this work.

- Treatment of raw screened domestic influent with 1st stage VFF

The effect of filtration height, treatment surface as well as pollutant load were assessed through pilot monitoring.

VFFs achieve TSS removal efficiency higher than 90%. **Particles removal is a surface mechanism which is neither affected by filtration depth nor hydraulic load** (resulting from surface reduction). No particular attention in design must therefore be paid with regards to this parameter. Furthermore, sludge accumulation, at the filter's surface, improves treatment. A maturation period of almost one year is necessary before reaching steady-state performance. It must be noted that decreasing the treatment surface would lead to faster accumulation of solids which might reduce the period of maturation but also might result in increasing the risk of short term clogging and thus reducing the expected life span of such system.

The first 40cm of filtration is the most active zone of filtration while further increase of filtration depth (up to 100cm) does not significantly improve COD_d treatment performance ($p = 0.06$). Such behavior suggests a limited bacterial activity which might be explained by a lower biomass density in deeper filtration zone. Nevertheless, a slightly lower effluent concentration is obtained by increasing the height of filtration material (92.5 and 73.1mg.L^{-1} at 40cm and 100cm, respectively), suggesting that heterotrophic bacteria may colonize the deeper zone as well. A lower microbial activity in deeper zone (> 40cm) than in the upper zone might also be explained by limited substrate availability. Higher influent concentration might show different concentration profile. This design modification may thus be useful if

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discharge levels are low or if influent concentration is high. Moreover, increasing filtration depth may also make effluent characteristics more constant.

In other respects, the increase of hydraulic load from 0.36m.d^{-1} to 0.64m.d^{-1} (consequence of a treatment surface reduction from 0.4m².pe^{-1}.filter^{-1} to 0.25m².pe^{-1}.filter^{-1}) induces shorter feeding frequency and causes longer periods of ponding. This design and operation modifications result in a loss of performance in COD_d removal. This drop in treatment efficiency may be explained by limitation in oxygen renewal, due to hydraulic conditions (Forquet *et al.*, 2009), resulting in oxygen depletion within the filtration layer.

Furthermore, increasing the organic load does not affect treatment efficiency as long as oxygen renewal occurs properly.

➔ *A particular attention must be paid on the relationship between oxygen renewal rate (by convection) and oxygen demand from pollutants and microbial kinetics in order to optimize the treatment area and avoid oxygen limitations.*

Ammonium removal in VFFs is mainly achieved through the nitrification process. Inorganic carbon availability must thus be considered in the early stage of design since this process is carried out by autotrophic microorganisms. A consumption of 5.5 ± 4.3g$CaCO_3$.gN^{-1} was observed during the experiments. **Alkalinity supply should be foreseen when influent concentrations are below 250 – 300 mg$CaCO_3$.L^{-1}**.

Nitrification is a slower process than heterotrophic respiration and thus requires longer contact time between influent and biomass. Adsorption of ammonium onto organic matter, prior to nitrification, enables to extend the retention period of ammonium within the system. However, sorption capacity is not extendable and the ammonium removal reached **a threshold (15gN.m^{-2}.d^{-1}) from which nitrification performances start to decrease**.

Moreover, as an aerobic process, nitrification also depends on oxygen availability and is affected by the ability to renew oxygen content within the filter. Increasing the hydraulic load causes long periods of ponding which hinder nitrification of adsorbed ammonium and thus result in fast saturation of sorption sites. **Ammonium removal efficiency drops**, from 62% to 44%, **when increasing the hydraulic load** from 0.36 to 0.64m.d^{-1}.

➔ *It might be interesting to assess to which extent full ammonium removal may be obtained by decreasing the hydraulic load on a single stage VFF. A special attention must be paid to*

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the effect of organic matter, fixed on the media, on ammonium removal by adsorption (sorption capacity). Moreover, nitrification rates must be studied in order to assess the capacity to restore sorption sites between successive feeding and thus maintain a sufficient sorption capacity over a whole feeding period.

Furthermore, the vertical profile of ammonium concentration shows that most of the treatment occurs in the upper part of the filter (40cm) since nitrifying bacteria are mainly located in the sludge deposit and the first 30cm of filtration layer. Nevertheless, **slight improvement of ammonium removal is observed by further increase in filtration depth**. Although gains in efficiency in relation with filtration depth are low, treatment efficiency rises from 62% to 81% when filtration height was set at 100cm instead of the usual 40cm.

➔ *Additional treatment profiles are however required in order to provide a fine relationship between effluent concentration and filtration depth.*

➔ *Moreover the effect of filtration depth might be masked by the low ammonium concentration at 40cm-depth. The assessment of higher ammonium concentrations would also provide valuable information on the effect of filtration depth.*

Based on these observations, the following recommendations may be provided in order to achieve high treatment efficiency with a single stage unsaturated VFF:

- Avoid as much as possible ponding periods which hinder proper oxygen renewal within the filter. To this purpose, **treatment surface must not be smaller than 0.4m².pe^{-1}.filter^{-1}** with the current state of knowledge.
- Filtration height has positive effects on removal of dissolved pollutants. **40cm-depth filtration layer should be sufficient to fulfil treatment requirements on COD treatment** (effluent concentration $\leq$ 200 mg.L^{-1} and treatment efficiency $\geq$ 60%) with a single stage VFF. Further increase in filtration depth could be envisioned if more stringent objectives of treatment are required on ammonium.
- Although treatment efficiency is not limited by organic load, as long as no oxygen limitation occurs in the studied conditions, **applied load must be considered in order to not exceed 15gN.m^{-2}.d^{-1}**.

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- Denitrification in a saturated vertical flow filter

Several design criteria (hydraulic retention time and specific surface of filtration medium) and effluent characteristics (carbon availability and nitrate load) were assessed in order to identify the best conditions for high performance of denitrification with saturated VFFs.

The denitrification process concerns the anoxic oxidation of organic matter using nitrate as electron acceptor. The availability of **easily biodegradable carbon** is thus the main limitation for high denitrification rates. Nitrate removal was not limited by carbon availability as long as **COD_{tot}:N influent ratio is higher or equal than 5**. Inert and slowly biodegradable carbon is not available for denitrification, at the studied retention time. Knowledge on the biodegradability of organic sources is therefore required in order to assess the risk of carbon limitation. Furthermore, it must be noted that a **background concentration of inert COD_{tot},** unavailable for denitrification, should be expected in domestic wastewater. A preliminary assessment of inert fraction should thus be carried out in order to determine the amount of organic matter which is available for denitrification.

➔ *Carbon limitation may be expected after a 1st stage VFF treating domestic wastewater (COD_{tot}:N ratio around 2.5 – 3). Although addition of exogenous carbon enables to improve denitrification efficiency, it also results in extra-costs due to the implementation of dedicated devices as well as the consumption of reagents.* ***Passive release of organic matter by a carbon-rich filtration medium*** *is another interesting way of improvement. The study of carbon supply (quantity, kinetics and life span) as well as the structural evolution of such material is necessary before its use in saturated filters.*

Hydraulic retention time is another adjustment variable in order to reach low nitrate concentrations. Most of the treatment occurs in the upper zone of saturation and almost **63% of treatment is achieved for a retention time of 0.3d**, when carbon availability is not limited. For longer contact times, the kinetic decreases, from 29.2 to 6.3$gN.m^{-2}.d^{-1}$, probably because substrate becomes less accessible for the biomass. **Full denitrification may be achieved with a retention time of 1d** (i.e. **80cm of saturation**) if carbon supply is sufficient.

Alternative filtration medium (i.e. Biofill type C®), with higher specific surface and porosity, enables longer retention time. However, a similar reactor volume is required in order to reach a similar efficiency as a conventional medium (i.e. pebbles). That may be explained by inappropriate implementation which hinders the proper use of medium characteristics

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(medium arrangement does not provide such high specific surface). Longer retention time thus clearly not guarantees higher treatment efficiency if biomass density is not increased at the same time.

➔ *The current design of partially saturated systems, with partial saturation, usually implements separated saturated zones for each of the 3 filters constituting the first stage of VFFs. Saturated denitrifying VFFs do not require resting periods. The use of a shared single saturated layer (see* Figure 58*) would significantly reduce the total volume of saturation and therefore earth-moving costs. However, such design modification requires homogenous influent distribution in the saturated layer in order to ensure sufficient contact within denitrifying compartment.*

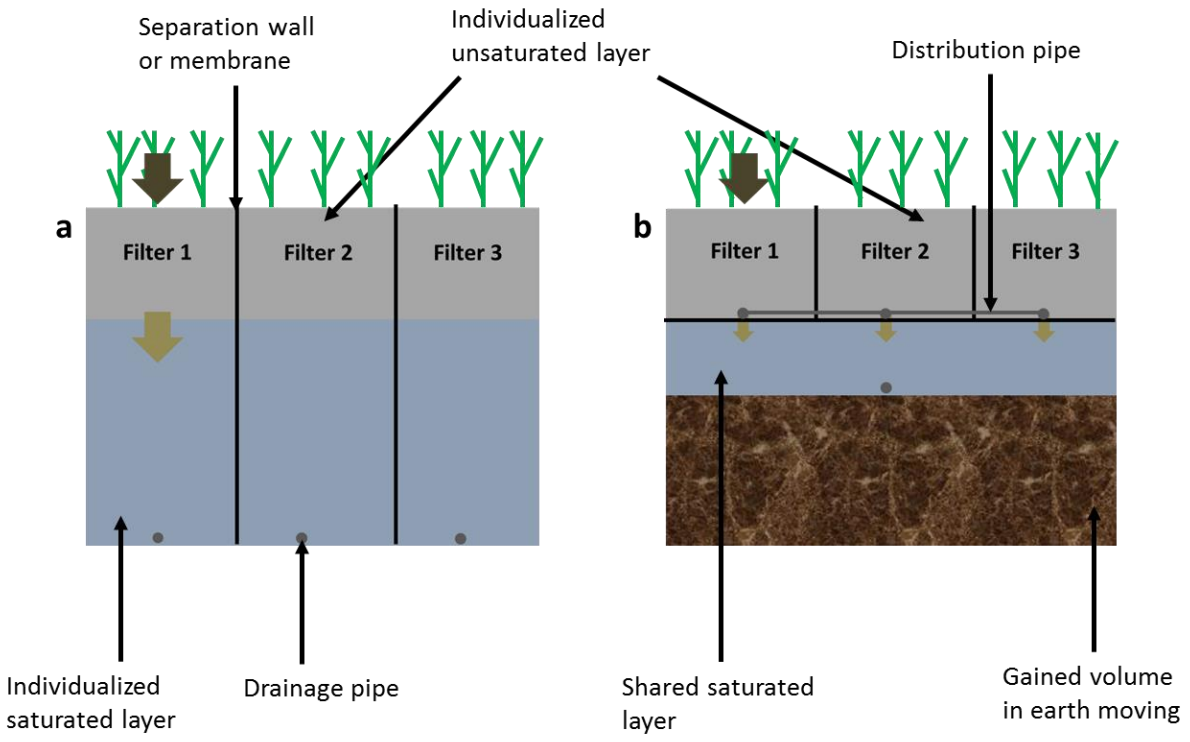

Figure 58 Schematic description of usual design (a) and proposed design (b) of partially saturated filters

➔ *Denitrification depends on ORP conditions. Increasing the saturated reactor volume may result in ORP variation and lead to inappropriate conditions which may also partly explain the decrease in denitrification kinetics. Further study might be valuable in order to identify the best ORP conditions, for denitrification, and characterize conditions in relation to saturation depth.*

First stage VFFs are usually fed for 3.5d then rest for 7d. Such operation enables sludge mineralization, oxygen renewal within the filter as well as nitrification of adsorbed

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ammonium. High concentrations of nitrate may thus be observed in the first flush, after a resting period, when nitrate is released. However, denitrification rate increases with input (9.5 and 15.2gNO_3-N.m^{-2}.d^{-1} for influent concentrations of 40 and 80mgNO_3-N.L^{-1}, respectively). A significant increase in retention time is thus not necessary as long as carbon availability is not limiting.

➔ *The effect of nitrate concentration on process kinetics might be helpful in order to optimize design with regards to influent characteristics.*

- Modeling as a simple and accurate tool for design assistance

Design of treatment wetlands mainly relies on experience and field observations. The development of predictive models, available for engineers, with the purpose of design assistance would thus be useful. Such model must be as simple as possible and must provide accurate prediction with limited amount of effluent characteristics and design parameters. Simple mathematical predictions are possible with statistical models which may be easily compiled through excel file or R-script. However, prediction accuracy depends on the quality and the amount of training data as well as the range of studied conditions.

➔ *Further experiments are therefore required in order to properly characterize the outputs for various conditions of design and operation.*

➔ *A second step should then focus on the effect of climate conditions such as rainfalls or temperature in order to improve predictions.*

- Zeolite: a solution to the dilemma between nitrification and carbon availability

Engineers have to face an inextricable problem when full TN removal is the objective. Indeed, full nitrification requires long contact, between influent and biomass, which also results in an important consumption of organic matter which is not further available for denitrification. A compromise between nitrification and denitrification has usually to be made and part of the nitrogen therefore still remains in the effluent.

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Because of its composition, zeolite theoretically appears as a realistic solution in order to improve nitrification efficiency. A shallow filtration layer of zeolite would allow to store a high amount of ammonium within the filter, through an ion exchange process, while removal of organic matter would be minimized ensuring sufficient carbon supply for denitrification. Trapped ammonium would then be nitrified during the rest period before being released under nitrate form during the next feeding period. This system would therefore provide a suitable and reliable solution in order to obtain high TN removal with simple constructed wetlands.

Zeolite implementation in the filtration layer has indeed a positive effect on ammonium removal by VFFs. For instance, partial replacement of gravel by zeolite (40cm of filtration layer, 10cm of zeolite) enables to increase the performance from 60% to more than 80% for an influent concentration of 100mgNH_4-N.L^{-1}.

Nevertheless, exchange capacity may vary among different types of zeolite while each medium has its own affinity for ammonium. Chabazite is slightly more efficient than clinoptilolite for ammonium removal. Moreover, the chemical composition may also impact efficiency. **Na-rich chabazite is the most appropriate medium for ammonium treatment in VFFs**.

Furthermore, the real adsorption capacity depends on operational conditions and is usually lower than the theoretical CEC which is determined from the substitution rate (Si^{4+} by Al^{3+}). **This parameter is thus not suitable for design purposes**.

The adsorption process is affected by the ability of ions and counter-ions to diffuse through the surrounding surface film and into the porous structure (film diffusion and intra-particle diffusion, respectively). The exchange process is thus limited by their respective kinetics and **removal efficiency therefore depends on contact time between sorbent and sorbate**. Unsaturated VFFs, fed under pulse load operation, perform better (higher exchange rates) than saturated VFFs fed under slow continuous upflow mode (0.1m.h^{-1}) in the studied conditions. Part of influent is indeed stored within the pore volume between consecutive loads therefore optimizing the contact between adsorbent and adsorbate. However, the study of different batch volumes shows that the fraction of influent which quickly flows through the system is not properly treated. The batch volume should thus be as small as possible, while keeping sufficient contact time, in order to optimize the fraction trapped in the system.

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➔ *The* ***best performance was reached with free drained VFFs loaded every 80 minutes with 2cm of water****. The best compromise between batch volume and feeding frequency must be determined through additional experiments.*

Moreover, the adsorption process relies on equilibrium between solid and liquid phases. Adsorption capacity is therefore affected by influent concentration. Although high exchange capacity ($19mgNH_4\text{-}N.g^{-1}$) is reached with high ammonium concentration ($2000mgNH_4\text{-}N.L^{-1}$), lower adsorption is observed when concentration decreases. A maximum of $1.9mgNH_4\text{-}N.g^{-1}$, at an influent concentration of $100mgNH_4\text{-}N.L^{-1}$, is trapped within zeolite suggesting that **exchange capacity is limited for domestic wastewater whose ammonium concentration ranges from 20 to $100mgNH_4\text{-}N.L^{-1}$**. However, it must be noted that zeolite behaves similarly for the full range of concentrations which is usually reported in domestic wastewater. Removal efficiency is more affected by zeolite's saturation rate than the influent concentration for this range of concentration. The efficiency progressively decreases as the saturation rate increases.

➔ *More concentrated influent, such as piggery manure or fish farm effluent, might allow to use the full potential of exchange capacity.*

Nonetheless, increasing the mass of zeolite may allow to counter the effect of ammonium concentration in order to reach high removal efficiency. Indeed, deeper layer of zeolite allows increasing the mass transfer zone. Lower ammonium concentration, requiring lower equilibrium sorption rates, can thus be reached thanks to this extra-amount of reactive material. Moreover, a deeper layer of zeolite also increases the “reactive pore volume”, within which ammonium is removed from stored fraction of water between consecutive flushes. Therefore the contact between adsorbent and adsorbate is optimized. The implementation of $30kg_{zeolite}.pe^{-1}.filter^{-1}$ in the filtration layer is deemed satisfactory since it allows treatment efficiency higher than 90% during a full cycle of operation and remains economically attractive.

However, these promising results are currently ruined by insufficient regeneration capacity ($0.12mgNH_4\text{-}N.g^{-1}$). Exhaustion of sorption sites quickly occurs until reaching treatment efficiency close to the ones reported from gravel filters. Incapacity of oxygen to diffuse through the biofilm surrounding zeolite particles may explain part of this inefficient regeneration. Moreover, zeolite pore size is smaller than bacteria dimensions (angstrom and

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micrometer, respectively) which may hinder nitrifying biomass to colonize the internal porous structure resulting in ammonium accumulation within the system.

➔ *Further experiments must be conducted in order to identify the limitations for proper biological restoration otherwise zeolite implementation will remain unsatisfactory. The use of finer media may increase the density of surface sites, easily accessible for biomass, and thus improve the capacity of biological regeneration. Nevertheless it would also result in clogging issues. Deeper investigation is therefore necessary before its implementation in full-scale treatment plants.*

- Design and operation recommendations:

Based on the present work and with the purpose of reaching high TN removal with a single partially saturated VFF, the following subsection aims to propose recommendations of design and operation.

First of all, it must be remind that biological removal of nitrogen relies on two successive processes, namely nitrification and denitrification, occurring in the unsaturated layer and the saturated layer, respectively. The efficiency of each process depends on various field conditions and operational characteristics which have to be optimized. The design of partially saturated VFF has thus to fulfil each requirement in order to achieve full removal of TN.

- Nitrification
  - Availability of oxygen
  - Contact with biomass
- Denitrification
  - Absence of oxygen
  - Availability of easily biodegradable organic carbon
  - Contact with biomass

❖ **Optimization of ammonium removal in the unsaturated layer**

- <u>Optimization of contact</u>
  - Depth of filtration layer

The implementation of a deep filtration layer of gravel may be a simple and cost effective solution in order to improve ammonium removal. However, it also results in higher COD_{tot} removal. The addition of exogenous carbon could thus be required in order to perform further

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complete denitrification in the saturated layer. Furthermore, **filtration layer deeper than 60 – 80cm is not advisable** since gains in treatment are negligible.

- Implementation of zeolite

Although increasing the filtration depth enables to improve nitrification it also results in high removal of COD_{tot}. A thin **filtration layer of 20 – 30cm** must therefore be preferred in order to guarantee a sufficient amount of COD_d (150 – 180mg.L^{-1}) in the saturated layer. It must be noted that such design might increase the risks of preferential flows which may result in decreasing treatment efficiency.

The **implementation of zeolite (20 – 30kg.pe^{-1}.$filter^{-1}$)** in the bottom part of the filtration layer allows the retention of ammonium (more than 80% during a feeding cycle), by sorption process, within the unsaturated layer. This process extends the contact time between the substrate and the biomass in order to optimize nitrification. However, only partial biological regeneration of the sorption capacity is achieved in the current state of knowledge. This incomplete restoration of sorption capacity leads to progressive exhaustion of the exchange potential and hinders the good sustainability of the system. Furthermore, the sorption rate depends on influent concentration. The zeolite layer might thus be located in the upper part of the filtration layer in order to optimize the sorption rate since the ammonium concentration is higher in the surface vicinity than at 20cm. However, thick and heterogeneous biofilm might colonize zeolite media and could hinder proper oxygen diffusion through the biofilm, resulting in weak nitrification efficiency. Modification in the duration of feeding and resting periods might thus be necessary in order to optimize the restoration of sorption capacity.

- Optimization of oxygen availability

Treatment surface lower than 0.4m^2.pe^{-1}.$filter^{-1}$ leads to increase the frequency of feedings. It is believed that more frequent loadings results in resistance to oxygen renewal and thus causes limitations in nitrification. Such modification of design and operation should thus be avoid when using gravel as filtration material. However, **frequent small loadings** have positive effect on the overall dynamic of pollutants when using zeolite. They indeed could be favored in order to optimize ammonium adsorption while reducing oxygen transfer and thus increasing the effluent COD concentration (Note that the best compromise must be determined).

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❖ **Optimization of nitrate removal in the saturated layer**

- Optimization of the availability of organic carbon

Full denitrification can be reached in the saturated layer when carbon is available in a sufficient amount. An optimal COD_{tot}:NO_3-N ratio was found at 5. A carbon supply must be foreseen if the ratio is lower than 5 in the effluent from the unsaturated layer. Supply of exogenous organic carbon is the easiest solution but will result in additional cost of reagents and devices. A second solution may consist in the implementation of C-rich material providing carbon supply by slow passive diffusion. Nevertheless, although promising results were described in literature, preliminary studies on the dynamic of carbon release and the evolution of material structure are required.

- Optimization of the retention time

A retention time of **1d** is sufficient in order to perform full denitrification in the range of nitrate concentrations which is usually observed at the outlet of unsaturated VFFs. A **single shared saturation layer of 30cm-depth** may be used for the 3 parallel filters in order to reduce the saturation depth and thus minimize earth-moving.

To conclude, we can propose two distinct designs for the optimization of TN removal in single partially saturated VFF. First, a "classic" design whom recommendations can be directly implemented by engineer. Secondly, a "next generation" design is proposed. Further additional experiments are necessary before its optimization but such design seems to be able to promote high TN removal with very compact and simple systems (i.e. none energy nor reagent supply).

"Classic" design

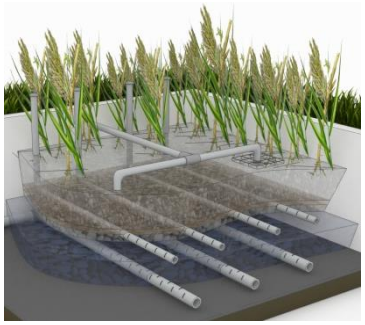
Unsaturated layer

- 60 – 80cm of gravel
- 0.36cm.d^{-1}
- 2cm per batch

Saturated layer

- 1d of retention time
- Carbon supply (e.g. acetate)

Partially saturated filter



"Next generation" design

Unsaturated layer

- 30cm
- 20 – 30$kg_{zeolite}$.pe^{-1}.$filter^{-1}$
- > 0.36cm.d^{-1}
- < 2cm per batch

Saturated layer

- 1d of retention time
- Organic material

Figure 59 Summary of different ways of design optimization

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Appendix I:
Can a single stage hybrid constructed wetland achieve good total nitrogen removal?

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INTRODUCTION

Constructed wetlands (CWs) have emerged as a suitable and reliable process to treat domestic wastewater. The French design consists in two stages of vertical flow filters (VFFs) totalling 2 m²/pe of filtering area and are respectively composed by three and two parallel filters operating in a sequential mode of feeding and resting periods. Filters of the first stage (1.2 m²/p.e.) are filled with gravel and are fed by batch from the surface with screened raw wastewater. Most of suspended solids and part of dissolved pollution are removed from this stage. The second stage sand-filled filters (0.8 m²/p.e.) enable further removal of dissolved parameters. This configuration enables to achieve high performances of SS, COD and TKN removal, namely over 95%, 90% and 85% respectively (Troesch & Esser, 2012; Molle et al., 2005).

However, this highly aerobic treatment suitable for nitrification is ineffective when a total nitrogen removal is required because of the lack of anoxic conditions. The implementation of a third saturated unit, between both stages of VFFs, is therefore necessary for denitrification. This leads to an increased global footprint area (up to 3 - 5m²/p.e.).

Considering this constraint and also that the high performances observed with such design are not systematically needed, the question arises if a single stage could be used, ensuring both nitrification and denitrification with a lower required area. The implementation of a two-layered saturated / unsaturated stacked filter providing both oxygen conditions seems an interesting issue. This kind of filter is proposed by Epur Nature as BiHo-Filter®. The upper unsaturated part is designed according to the same guidelines as first French CW stage. Filtration of suspended solids and oxidation of organic matter and ammonium occur under aerobic conditions in this layer enhanced by an intermediate aeration network. On the other hand, the saturated layer below has anoxic conditions which are appropriate to remove nitrate

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and remaining organic matter through denitrification process. Moreover, this saturated zone also acts as a settlement tank and thus improves the removal of TSS.

Few data are yet available and therefore numerous questions still remain concerning its ability to achieve stringent standards and its long term behaviour. This article aims to assess the ability of BiHo-Filter to remove total nitrogen and to point out the design parameters which must be considered in order to optimize the treatment.

MATERIAL AND METHODS

Experimental setup:

Two vertical flow pilots of 2.25m² each were monitored during nine months, from March to December 2014. The experimental site is located at a wastewater treatment plant (Jonquerettes, France) allowing the use of real raw domestic wastewater screened at 20 mm. The pilots were planted in September 2013 with one year old plants of Phragmites australis at a density of 6 shoots/m². As performances are impacted by filter maturation, a 5 months commissioning period was introduced before any monitoring to reach a stable state. According to French guidelines, pilots operated for 3.5 days and rested for 7 days. They were dosed eighteen times a day by batches of 2cm. The characteristics of the pilots are summarized in Table 20.

Table 20 Pilot description

Pilot units	Filtration layer	Saturated layer	Aeration layer	Hydraulic load	Organic load (CODt)
Standard (VFSt)	Gravel 2/6 mm 40 cm	None	No	0.36m/d	241.4 (40.0) g/m²/d
BiHo-Filter® (BiHo)	Gravel 2/6 mm 50 cm	Pebble 16/22 mm 25 cm	Yes	0.36m/d	248.2 (114.2) g/m²/d

Continuous monitoring:

During the experiments, online measurements were done to have a better insight in hydraulic and treatment performance dynamics. Inflow was determined by an electromagnetic flowmeter (Siemens) whereas outflows were measured with ultrasonic probes (Pil) by the level of effluent drained into a collection tank. Inlet and outlet ammonium and nitrate concentration were measured continuously with ion selective probes (AN-ISE, Hach Lange).

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Redox potential and temperature were measured by pHD sc probes (Hach Lange). All data from these devices were stored by a SC1000 data logger (Hach Lange) at the inlet and the outlet at time intervals of 15 and 2 minutes respectively.

Water quality analysis:

The inlet and outlet water quality were assessed for each first and last day of the feeding periods by 24h composite samples using refrigerated samplers (Ponsel, ISCO 4700 and Hach Lange, Bühler 2000). Each pilot was evaluated for COD (total and dissolved), SS, NH4-N, NO3-N and Alkalinity (in $CaCO_3$) using quick method tests (Hach Lange).

Pilot hydraulic behaviour

Tracer tests were also conducted for each filter in order to assess the hydraulic residence time and potential preferential flows in each pilot. A fluorescein solution was consistently applied all along the first batch of a feeding cycle. The fluorescein concentration in the effluent was recorded with a fluorimeter (FL30, Albillia) at time interval of 1 minute.

Statistical analysis:

Experimental results were statistically analysed using R software. Mann Whitney tests were used for pair-wise comparison of pilots. Significant difference was established at p-value $\leq$ 0.05.

Results

Influent quality:

The influent composition was in the typical range of wastewater composition from rural communities in France (Troesch and Esser, 2012) (see Table 21). Nevertheless, quite high variations were noticed due to the combined sewer and the dilution occurring during storm events.

No significant differences were observed between the influent quality of each pilot during the study. Based on the Kruskal Wallis test, the differences observed in the performances of the pilots were therefore solely attributable to the influence of design parameters.

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Table 21 Water quality

Parameters	VFSt				BiHo			
	Inlet	Outlet	Perf. (%)	n	Inlet	Outlet	Perf. (%)	n
[TSS] mg/L	335.3 (129.7)	102.9 (72.0)	67.9 (23.0)	15	373.0 (185.3)	31.6 (23.0)	90.7 (7.7)	26
[CODt] mgO2/L	670.5 (166.8)	220.5 (126.4)	66.6 (18.8)	14	706.0 (309.9)	106.7 (51.2)	82.9 (8.6)	26
[CODd] mgO2/L	196.4 (47.7)	113.9 (66.5)	51.2 (11.8)	13	204.4 (59.5)	89.9 (36.8)	54.4 (17.6)	26
[TKN] mgN/L	65.4 (12.9)	34.7 (11.6)	46.2 (16.5)	13	63.9 (17.3)	30.9 (11.1)	48.8 (14.4)	23
[NH4+] mgN/L	50.0 (9.7)	24.9 (8.1)	49.6 (14.7)	13	49.2 (13.2)	22.2 (8)	52.1 (14.4)	23
[NO3-] mgN/L	1.3 (1.3)	24.3 (5.7)	-	23	2.0 (3.3)	17.2 (8.1)	-	11
[TN] mgN/L	67.3 (14.3)	54.7 (10.3)	21.9 (10.7)	8	65.9 (16.3)	48.1 (12.7)	27.9 (9.1)	22

Values in brackets are standard deviation

TKN removal:

Although Figure 60 shows slight improvement in nitrification (46.2% and 48.8% of TKN removal with VFSt and BiHo), no significant difference in TKN removal ($p = 0.2673$) was noticed between VFSt and BiHo. The unsaturated layer of BiHo has the same efficiency to remove kjeldhal nitrogen than a classic first stage of French system with the same filtration depth. Figure 60a perfectly illustrates the similar behaviour of both filters since values are distributed according to a homogeneous cloud of points. Nevertheless, this also highlights that they are less efficient than previously reported (Molle et al., 2008). Figure 60b shows several outliers. Two and one values lower than 20% are observable on BiHo and VFSt performances

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respectively. These values are the first values of the study. These low performances are probably linked with cold climate and the end of commissioning period. On the other hand, one and two data higher than 70% were noticed for BiHo and VFSt respectively. These analyses were done at the end of this study after a period of one month during which the operation was not perfectly managed. Longer rest period probably enables a total nitrification of sorbed ammonium and improves sorption of ammonium in subsequent feeding periods.

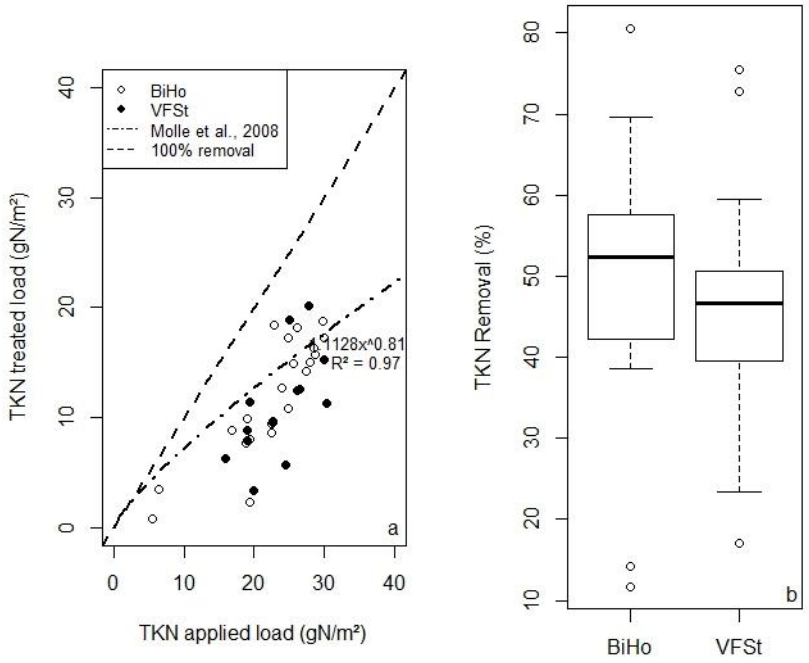

Figure 60 TKN removal, with (a) in loads (gN/m²) and (b) in performances (%)

Figure 61 shows nitrogen dynamics of pilots. Ammonium is efficiently removed over the first day by both filters. The treatment then deteriorates with time because of progressive saturation of sorption sites of organic matter. A partial depletion in oxygen in the filter could also be suspected leading to lower nitrification rates.

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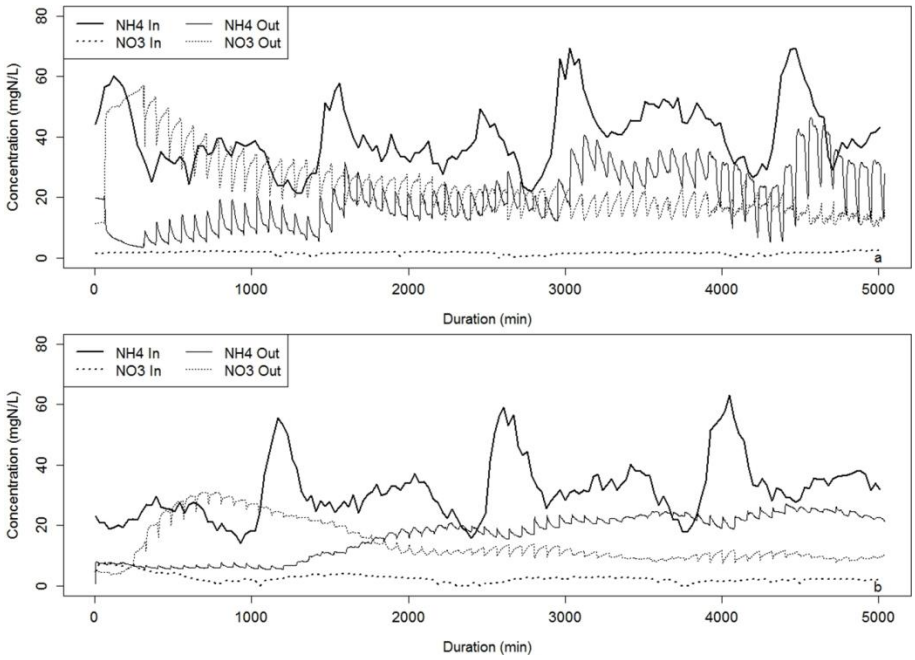

Figure 61 Nitrogen dynamics at the outlet of VFSt (a) and BiHo (b) during a feeding period

TSS removal:

The efficiency of TSS removal is highly improved (p = 4.671E-5) by the implementation of a saturated layer which acts as a settling tank (Figure 62b). Performances of 90.7% removal and a outlet water quality of 31.6mg/L were observed for BiHo.

Organic matter removal:

The treatment of organic matter is significantly improved (p = 9.37E-4) by the presence of the saturated layer (Figure 62a). However, we only noticed a slight non-significant improvement of CODd removal (p = 0.08078) which indicates that most of this improvement concerns non-soluble COD.

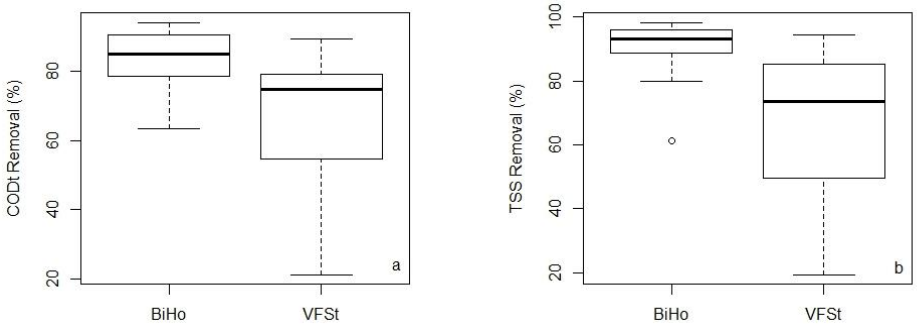

Figure 62 CODt (a) and TSS (b) removal performances

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Total nitrogen removal:

The implementation of a saturated layer slightly improves the treatment of total nitrogen as shown by removal performances (Table 21). However, important amount of nitrate remains at outlet of BiHo (17.2mgNO3-N/L) while CODt concentration is still high (106.7mg/L). This partial denitrification does not seem limited by reactive but rather by retention time of influent in the saturated layer.

Overall, the nitrate dynamic (Figure 61) shows a lower concentration at the outlet of BiHo than VFSt. Assuming that nitrification performances are similar on both filters, this confirms the ability of this first unit to remove TN. The delay in nitrate release and the lower amplitude in nitrate peaks at the outlet of BiHo also suggest a buffering potential of its saturated layer.

DISCUSSION

Higher ability of BiHo to remove TSS was noticed during this study. This is mainly explained by settling in the saturated layer. This suggests that an accumulation of sludge can be expected during operation which could lead to clogging of the system if no regular withdrawals are done.

The performances to remove CODt are also improved by BiHo. Part of this improvement is linked with SS removal and the denitrification process which occurs into the saturated layer (denitrification process needs 2.86gBOD5 to reduce 1g of nitrates). Nevertheless the incomplete denitrification observed on BiHo (TN removal < 30%) seems to be rather due to a low hydraulic residence time (<0.3d in theory) than the carbon availability (CODt/NO3-N > 6). Indeed, Troesch et al. (2014) reported better performances on TN removal (52%) on full scale BiHo-Filter® with a similar unsaturated layer depth but a deeper saturated zone (0.65m) allowing a longer retention time (1.09d).

Although a slight improvement on total nitrogen removal was observed an optimization way would consist in higher residence time in the saturated layer.

If we assume that (1) no nitrates are produced in the saturated layer, (2) 10% of total nitrogen is entrapped in sludge deposit by sorption phenomena and (3) only denitrification process removes TN into the filter, then for a mean performance of 82.5% of COD removal, 22.2% (26.8 of total removal) is linked with the denitrification process. A consumption of 57.8 gCODt/m².d happened in the saturated part of BiHo while 157.9gCODt/m².d equivalent to 60.7% (73.2 of total removal) occurs in the unsaturated layer. This is consistent with performances of a single stage treating raw wastewater (Molle et al., 2005) and considering that preferential flows were highlighted by tracer test on VFSt (results not show).

Nitrification process is also not total and some TKN is not oxidized. A deeper unsaturated layer or a recirculation could enable to achieve better nitrification. If the depth of filtration is increased, a particular attention must be paid to the concomitant improvement of organic

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matter oxidation in order to bring sufficient amount of COD (ratio COD/N-NO3) in the saturated layer to perform denitrification.

CONCLUSION

The results show that the implementation of a saturated layer at the bottom of vertical flow filters appears as an interesting way to improve global efficiencies of the "classical" French constructed wetland first stage and especially total nitrogen removal due to the saturated layer anoxic conditions. However, the incomplete denitrification could be improved by a deeper saturated layer with a longer HRT and should consequently improve the COD removal.

The saturated layer acts as a settling tank and strongly improves the removal of suspended solids. The sludge accumulation, at the bottom of filter, must be carefully managed in order to avoid premature clogging of this system.

Treatment of total nitrogen with a single stage of hybrid constructed wetland is a promising alternative to reduce global footprint of the plants but seems to have some limits for a global TN removal efficiency. Further studies, in particular dealing with the retention time linked to the carbon availability, have to be carried out in order to optimize this design.

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Appendix II:

Description of the experimental site of pilots

1) Introduction

An experimental site was designed and built with the aim to assess different issues related with domestic wastewater treatment by constructed wetlands. The present chapter proposes a split description of the different units in relation with the specific objectives of each section. This extra-chapter aims to propose a summary of the facility in order to provide an extensive overview of the pilot setup.

2) Experimental setup

2.1) Site description

The experimental site was located in the south east of France in Jonquerettes (20km from Avignon), a small rural community of 1300 inhabitants for whom viticulture is the main economic activity. The facility (see Figure 63), composed of 7 different pilot units, was established on the site of the municipal wastewater treatment plant, thus allowing the use of screened (20mm) real domestic wastewater. The average characteristics of wastewater during the study are listed in Table 22. Pollutant concentrations and ratios were in the range of mean composition of domestic influent, determined by a survey from 1999 to 2009 of almost 3000 treatment plants in French rural context (Mercoiret *et al.*, 2010).

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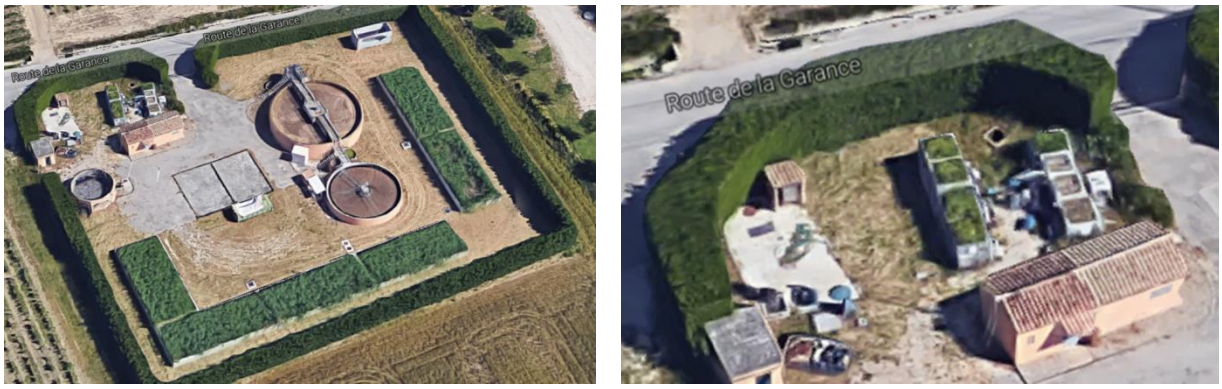

Figure 63 Birds-eye views of the wastewater treatment plant (a) and of the experimental setup (b) (Source: Google Maps)

Table 22 Domestic wastewater characteristics at the WWTP of Jonquerettes

[TSS] ($mg.L^{-1}$)	[COD_{tot}] ($mgO_2.L^{-1}$)	[COD_d] ($mgO_2.L^{-1}$)	[NH_4^+] ($mgN.L^{-1}$)	[NO_3^-] ($mgN.L^{-1}$)	[Alkalinity] ($mgCaCO_3.L^{-1}$)	pH
426.7	675.3	240.2	44.0	2.3	438.9	7.9
± 348.4	± 231.5	± 138.6	± 13.5	± 3.3	± 62.6	± 0.2
n = 97	*n = 97*	*n = 98*	*n = 104*	*n = 102*	*n = 90*	*n = 63*

The pilots were placed outdoors, allowing the study of domestic wastewater treatment under Mediterranean climate, meaning hot summer and mild winter. Figure 64 shows the temperature variations and rainfalls, recorded by the weather station from Saint-Saturnin-lès-Avignon (adjoining city), during the study. The average cumulative annual rainfall was 852.4mm.yr^{-1} but this value was strongly affected by two values which were particularly high in November 2014 and October 2015, respectively. Furthermore, temperature was positive during the whole period.

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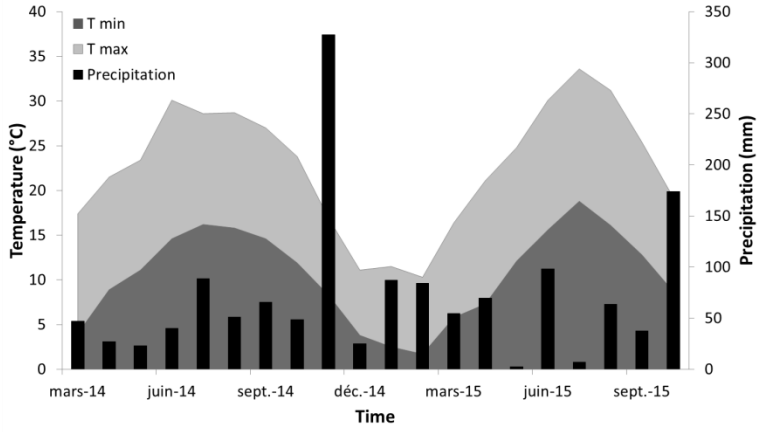

Figure 64 Climate variations during the study period

2.2) First stage vertical filters

High removal of TSS and COD_{tot} (83 and 77%, respectively (Morvannou *et al.*, 2015)) but only partial treatment of TKN (59%) are achieved on a first stage VFF (2m²/p.e.). The implementation of a second treatment stage, resulting in the increase of surface footprint, is thus required to improve TKN removal. Accurate knowledge of the effects of design and operational conditions on treatment efficiency is required to optimize the system.

Four pilot-scale vertical flow filters were designed and monitored in this purpose. The following section aims to describe the experimental setup.

2.2.1) Water supply

A submerged pump, introduced in the lift station of the wastewater treatment plant, ensured influent supply. The pump was connected to a common horizontal network, for the 4 pilots, on which vertical distribution branches led to each filter. Each branch was equipped with a motorized valve (referred as inlet valve) in order to allow the feeding of one filter at a time. These distribution pipes ended in an elbow oriented upwards in order to limit the scouring phenomenon.

An electromagnetic flowmeter, placed in a valve chamber close to the pumping station, controlled the input volumes and rotation frequency of the pump in order to maintain a feeding flowrate around $1m^3.m^{-2}$. A check valve was implemented upstream to the flowmeter in order to keep constant head in the network. Furthermore, a motorized valve, located in the valve chamber in downstream position to the flowmeter, allowed to drain the network between batches in case of freezing risks.

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2.2.2) Design

❖ Overall description

Each pilot (2.25m²) differed in terms of design but respected the same common basis which is described below. Figure 65 presents the overall description of the 1st stage vertical flow pilots.

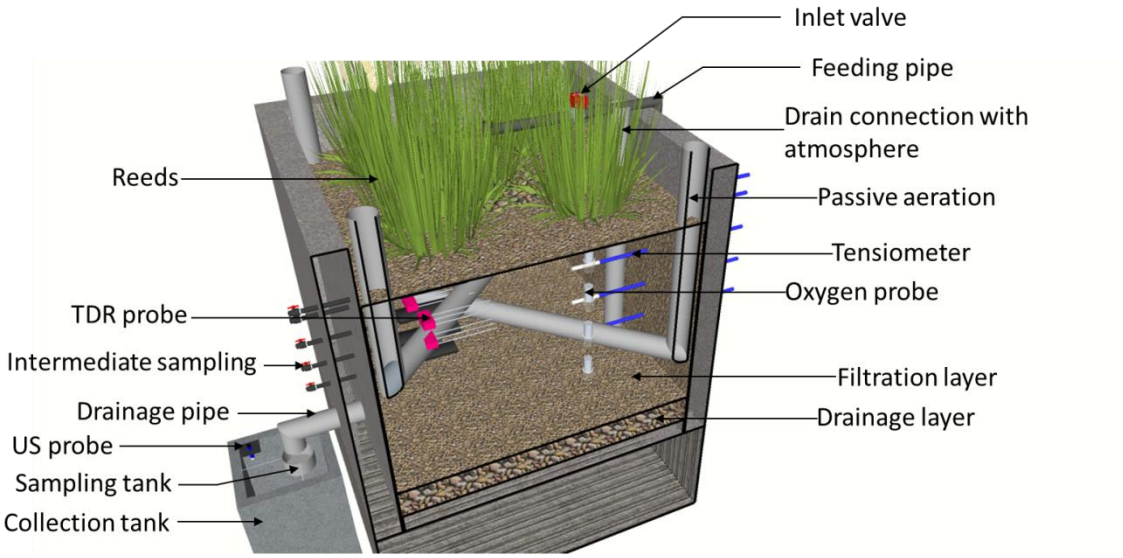

Figure 65 Schematic cross section of a 1st stage pilot unit

A layer of pebbles (grain size 16/22mm) was implemented at the bottom of each filter in order to facilitate effluent drainage. Note that the bottom structure was modified to obtain a 2% slope from the edges to the center ensuring an optimal collection of effluent by the single drainage pipe (PVC, ø110mm, 1 cm-width slots spaced at intervals 10cm). This drainage pipe was connected to the air in order to improve oxygen renewal into the filter during feeding periods. The filtration layer was composed of crushed granitic gravel (grain size 2/6mm) to prevent medium dissolution and thus avoid external carbonate supply which may interfere with the nitrification process. A thin 40cm diameter disc of pebbles was placed under the feeding pipe in order to limit the local scouring phenomenon which might result in preferential flows.

Passive aeration, consisting of the drainage pipe (PVC, ø90mm) connected to the air, was diagonally placed at the bottom of the filtration layer to enhance its oxygen renewal during operation. Such system provided an aeration surface of $80cm^2/m^{-2}$.

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Effluent was collected in a concrete tank (S = 0.16m², h = 0.5m) dedicated to outflow rate measurement. A normally closed motorized valve (referred as outlet valve) allowed elevation of the water table in the collecting tank during pilot drainage. Effluent flow rate was determined by measuring the water level elevation with an ultrasonic (US) probe (Pil, P43-F4V-2D1-D0-330E) during drainage. The valve was opened in order to empty the tank before each new batch. A perforated pipe was used to protect the US sensor from splashes while allowing water level elevation in the measurement system. A layout of the collecting system is shown in Figure 66.

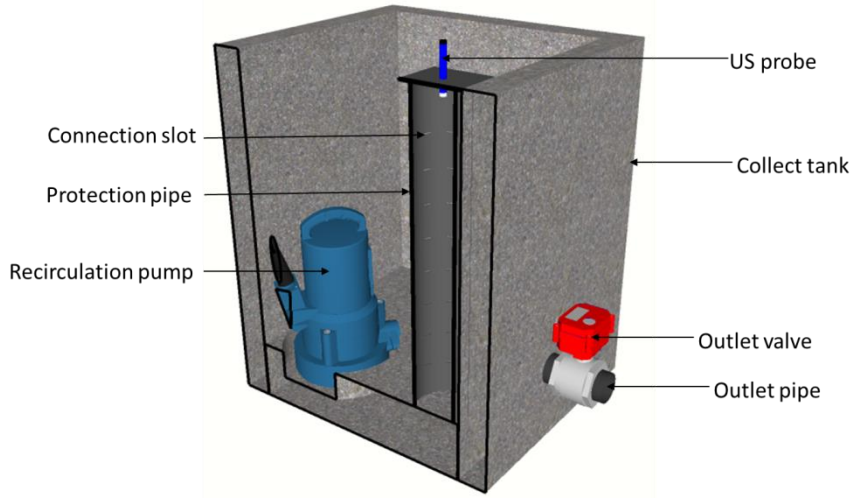

Figure 66 Description of collecting system

Pilots were planted in September 2013, with one year old plantlets of *Phragmites australis* at a density of 6 plants.m^{-2}.

❖ Pilot features

Each pilot design aimed at assessing the effect of a single parameter on treatment efficiency. Their respective features are listed in Table 23. Most of the current researches on treatment optimization are focused on oxygen management (i.e. artificial aeration (Foladori *et al.*, 2013) or tidal flow operation (Sun *et al.*, 2005)) or contact time improvement through partial recirculation of influent (Molle and Prost-Boucle, 2012), resulting in system intensification and increase of operation costs. This study aimed at enhancing VFFs performance through the optimization of classic design parameters in order to keep the system simple.

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A standard unit, designated as Vertical Filter Standard (VFSt), was designed following the classical design of a French 1st stage vertical flow filter (Molle *et al.*, 2005), though with some minor modifications in order to make it more compact. The filtration layer was 40-cm deep and was filled with 2/6 mm crushed granitic gravel. The transition layer, which is generally placed between the filtration layer and the drainage layer in order to avoid gravel migration, was removed while the drainage layer was filled with finer media than usual (grain size 16/22mm instead of 20/40mm) in order to respect the requirements of the Terzaghi rules. This filter was used as a reference, in this study, in the comparison to the other designs.

Different authors reported a positive impact of a deeper filtration layer on treatment efficiency (Prochaska and Zouboulis, 2009; Stefanakis & Tsihrintzis, 2009; Torrens *et al.*, 2009), mainly because of the resulting longer residence time in the system. The effect of filtration depth was assessed through monitoring of Vertical Filter Gravel^{+} (VFG^{+}) which was filled with 100cm of crushed granitic gravel. Two passive aeration pipes were introduced at 30 and 60cm from the surface respectively, in order to avoid oxygen limitation.

Reactive materials, especially zeolites, have shown high exchange capacity and strong selectivity towards ammonium (Erdoğan and Ülkü, 2011; Leyva-Ramos et al., 2010; Wang and Peng, 2010). The implementation of such materials in the filtration layer might thus be a solution to counterbalance the competition for oxygen between organic matter oxidation and nitrification during feeding periods. The addition of zeolite in the filtration layer was studied through the monitoring of Vertical Filter Zeolite (VFZ) pilot. A 10cm-deep layer of zeolite (i.e. 20kg$_{zeolite}$/p.e.) was placed below a thick layer of crushed granitic gravel (30cm). The implementation of the reactive medium at the bottom of the filtration layer aimed at optimizing contact with the influent. Moreover, since heterotrophic growth is mainly located in the upper region of the filtration layer (Morvannou *et al.*, 2014), this design enabled to select more for a nitrifying/autotrophic microbial population in the biofilm surrounding the zeolite medium. The mass of zeolite was decided on the basis of results from previous column experiments (Perez, 2012) and on technical-economic considerations.

Vertical flow filters showed good acceptance of hydraulic overloads (Molle *et al.*, 2006) but experience underpinned that routine hydraulic loads of 0.7m.d^{-1} should be considered as a limit for the 1st stage. Furthermore, Stefanakis and Tsihrintzis (2012) reported equal efficiency when increasing the hydraulic and organic load, from 0.26 to 0.44m.d^{-1} and from

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125 to 220gCOD.m^{-2}.d^{-1}, respectively, while (Boutin *et al.*, 2010) have observed high robustness in performance when organic and nitrogen loads punctually and quickly increased by a factor of 2-3. The current design of 1st stage French vertical flow filter has a surface requirement of 1.2m^2.PE^{-1} (0.4m^2.PE^{-1}.bed^{-1}) which may be problematic when land availability is limited or for high capacity treatment plants. Treatment performance was assessed for smaller treatment surfaces (0.75m^2.PE^{-1}) with Vertical Filter High Load (VFHL). Coarser drainage material (pebble 20/60mm) and a transition layer (pebble 16/22mm) were implemented in order to reduce risks of drainage limitation and to improve the oxygen renewal within the filter. Punctual concentration profiles were established by sampling the pore water at various intermediate depths (see Table 23), with dedicated collecting systems. PVC gutters, inserted into the filtration layer with a slope of 1-2%, collected pore water while PVC pipes (ending in a manual valve) allowed sampling at the edge of the filter. A description of the intermediate sampling system is presented in Figure 67.

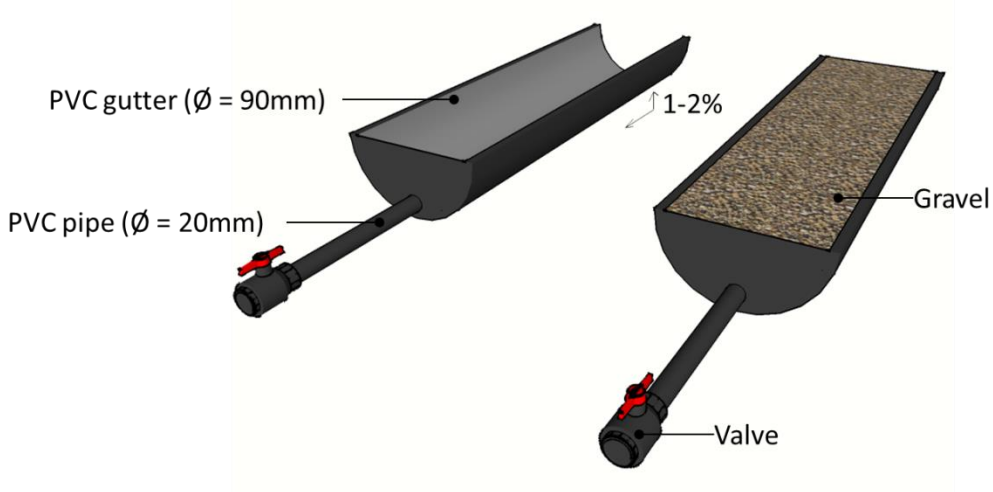

Figure 67 Layout of intermediate sampling systems

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Table 23 Pilots' design and operational characteristics

	Filtration layer				Drainage layer		Operational conditions	
Pilot	Material	Depth (cm)	Passive aeration depth (cm)	Sampling depth (cm)	Medium	Depth (cm)	Hydraulic load ($m.d^{-1}$)	Batch frequency (minutes)
VFSt	Gravel (2/6mm)	40	Bottom	10, 30	Fine pebble (16/22mm)	15	0.36	80
VFG^{+}	Gravel (2/6mm)	100	Bottom, 30 and 60	10, 20, 40, 60, 80	Fine pebble (16/22mm)	15	0.36	80
VFZ	Gravel (2/6mm) Zeolite (2/5mm)	30 10	Bottom	10, 30	Fine pebble (16/22mm)	15	0.36	80
VFHL[1]	Gravel (2/6mm)	30	Bottom and 30	10, 20	Large pebble (20/50mm)	15	0.64	45

[1] Note that a 15 cm-depth transition layer of fine pebble (16/22 mm) has been implemented between the filtration layer and the drainage layer

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2.2.3) Pilot operation

The experimental setup was completely controlled by a programmable logic control (PLC) system (S550, Sofrel) which was preset for the study needs. Each pilot has operated as a classic French 1st stage vertical flow filter, meaning alternation of feeding and resting periods (3.5 and 7d, respectively). The filters were fed in a sequential pulse-loading mode (2cm.batch^{-1}) every 80 minutes (excepting for VFHL which was loaded every 45 minutes). A feedback loop between inlet flowmeter, inlet valves and PLC allowed to control the applied volume as well as the fed pilot. VFSt and VFZ were fed simultaneously while VFHL and VFG^{+} feeding cycles started 3.5d and 7d later, respectively. This schedule of operation reduced the number of beds to monitor at the same time, thus optimizing the use of online probes and samplers which are described in sections 3 and 4.

A 5-month commissioning period was respected in order to allow biomass establishment.

2.3) Saturated vertical flow filters

Although vertical flow filters are highly efficient to perform the nitrification process, they cannot remove nitrate because of their highly aerated conditions. On the other hand, saturated constructed wetlands, such as horizontal flow filters, provide suitable oxygen conditions for the denitrification process. Although horizontal flow filters' performance is largely discussed in literature, most of those studies report global treatment efficiency but do not focus on denitrification specifically. Therefore, only few references are available with detailed information on denitrification. Thus, two saturated vertical flow filters were studied under different operation conditions in order improve the knowledge of key parameters such as retention time, organic matter availability or influent concentration. The following sections aim at describing their design and operation.

2.3.1) Water supply

Influent characteristics strongly affect the denitrification process (Ding *et al.*, 2012; (Sirivedhin and Gray, 2006). The saturated vertical flow filters were thus fed with semi-synthetic wastewater in order to assess different COD:N ratios and nitrate concentrations (see Table 24). The solution was prepared with wastewater from the settling tank, of the treatment plant, spiked with a concentrated stock solution of nitrate and organic matter. A shunt, with pneumatic valves, located on the outlet pipe allowed the supply of effluent from the settling

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tank. The stock solution, consisting of $NaNO_3$ and three different organic substrates dissolved into distilled water, was stored in a 10L polyethylene jerrycan. Organic matter supply was composed of a mix of glucose, glycerol and glycine (55, 25 and 20% of COD_d content, respectively) in order to mimic the characteristics of a 1st stage effluent. The feed solution was prepared and stored in a $1m^3$ polyethylene storage tank. The volume required for a single batch on both pilots was prepared 15 minutes before each new feeding. This operational characteristic was necessary since, because of the presence of denitrifying biomass in treated domestic wastewater, variations in effluent characteristics were expected if a single daily volume of semi-synthetic effluent had been prepared. The addition of stock solution was performed by a peristaltic pump, preset at a certain flow rate and operation time according to the targeted influent characteristics. The storage tank was insulated from light radiation by a thin layer of Mylar in order to prevent algae growth. Monitoring of water level elevation, by pressure head probe (SITRANS P 7MF1570, Siemens), inside the storage tank, was used to control the pneumatic valve of wastewater (settling tank) supply. Once the solution had been prepared, homogenization was ensured for 5 minutes, by a drainage pump (MC&DWP400, MacAllister). Finally, the pilots were consecutively fed by a similar drainage pump. The volume of feed solution was controlled by a feedback loop between the pressure head probe and the PLC. Note that saturated pilots may also be fed directly with effluent from 1st stage pilots. However, in order ensure the control on influent characteristic which was required by the aims of this study, only semi-synthetic influent was used.

Table 24 Influent characteristics

Period	1	2	3	4
$[NO_3^-]$ ($mgN.L^{-1}$)	40	40	40	80
COD:N	6	3	1	3

2.3.2)Design

Both units had the same design but differed in terms of filling medium. The denitrification beds had a treatment surface of 1.44m² and were filled by 85cm of medium. A first pilot was packed with pebbles (20/60mm) while the other was filled with a plastic medium (Biofill

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Type C®) characterized by a specific surface almost fivefold higher than the used pebbles. The features of both media are summarized in Table 25.

Table 25 Media characteristics

Medium	Bulk density ($kg.m^{-3}$)	Porosity (%)	Specific surface ($m^2.m^{-3}$)
Biofill Type C®	127	84	460
Pebbles (20/60mm)	1900	44	100

Figure 68 proposes an overall description of the saturated filters. A drilled floor (h = 85 mm), collecting the settled sludge, was implemented at the bottom in order to determine the solid accumulation and thus assess the risk of clogging. A trap was inserted through the edge of the filter in order to sample the sludge after emptying the system.

A central drainage pipe (PVC, ø90mm) was connected to the system of saturation level regulation. Denitrification occurs at redox potentials (ORP) lower than +400mV while sulfate reduction and methanization are predominant at ORPs below -100 and -200mV, respectively (Dušek *et al.*, 2008). Furthermore, several authors (Corbella *et al.*, 2014; Dušek *et al.*, 2008) reported a negative correlation between ORP and filter depth. Deep filters may foster low ORPs which are not suitable for optimal denitrification and may result in bad smelling. The system of water level regulation allowed to set the water table at 4 different depths (20, 40, 60 and 85cm, respectively), thanks to a series of intermediate horizontal branches controlled by manual valves, in order to assess the effect of redox conditions on the denitrification process. Finally, a last manual valve was implemented on the drainage pipe for maintenance purpose (flush valve).

Two 1m-long parallel feeding pipes (PVC, ø 32mm), spaced at 0.3m from the edge and 0.6m from each other, ensured water supply at the surface. Each pipe was drilled by 2 series of 3 holes (ø 6mm) equally distributed along with the length and making a 45° angle with the vertical axis in order to ensure homogeneous feeding of the pilot. Feeding was done with the semi-synthetic solution (see 3.2.1) or alternatively, a series of valves allowed feeding with effluent of 1st stage VFF pilots in order to study the system under real influent conditions.

Horizontal sampling pipes (ø20mm), ending in a manual valve, were horizontally introduced in the pilots at different depths (5, 20, 35, 50, 65 and 80cm from the surface, respectively) in

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order to determine a vertical profile of treatment. The sampling location was approximately 30cm from the filter edge. Assuming that the pilots behave as ideal plug flow reactors, this would result in an interesting relation between hydraulic retention time and treatment efficiency.

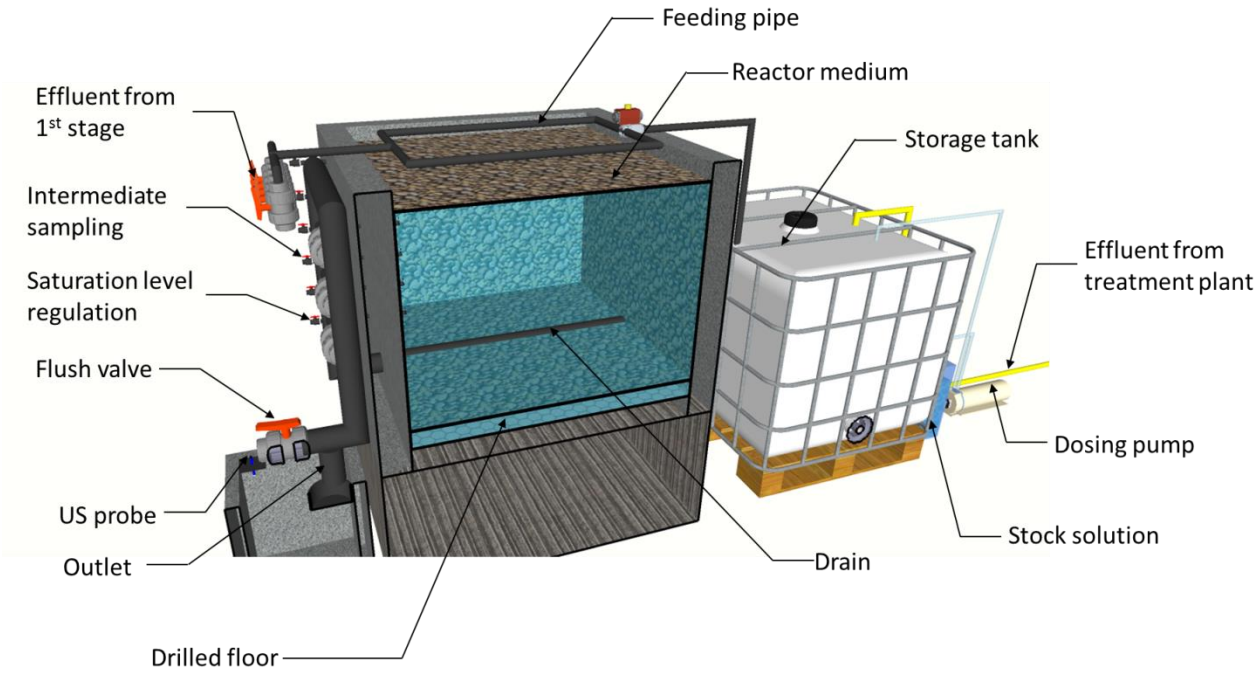

Figure 68 Schematic cross section of a saturated vertical pilot

2.3.3) Pilot operation

The pilots were constantly operated in a sequential pulse-load mode which aimed at reproducing the hydraulic load ($0.36 m.d^{-1}$) and the feeding frequency (time step of 80 minutes) of a French 1st stage VFF. Constant operation was applied in order to assess the feasibility of treatment of effluent from the 3 1st stage units by a single saturated filter.

A 2-month commissioning period of feeding with effluent from the different 1st stage pilots was conducted in order to allow biomass growth within the system.

2.4) Partially saturated filter

Several authors (Prigent *et al.*, 2013; Troesch *et al.*, 2014; Silveira *et al.*, 2015) reported enhanced denitrification efficiency by partly saturated 1st stage VFF. A similar system

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combining different oxygen conditions, in order to perform both nitrification and denitrification in a single stage of VFF, was thus studied.

2.4.1) Water supply

As first stage of treatment, this unit is fed with screened raw domestic wastewater. Water is supplied in the same manner as previously described in the section 0.

2.4.2) Design

This hybrid pilot, referred to as BiHofilter, combined both aerobic and anoxic conditions by the implementation of a partial saturation at the bottom of the filter. Figure 69 describes the design of the BiHofilter. A filtration layer filled with 50cm of crushed granitic gravel (grain size 2/6mm) was foreseen for aerobic treatment processes while a saturated drainage layer (45cm-deep) composed of pebbles (grain size 16/22) was foreseen for denitrification. An unsaturated transition layer (15cm-depth, pebbles) was implemented between both compartments.

A central passive aeration system, implemented within the transition layer and connected to the atmosphere, enhanced the oxygen renewal within the filtration layer but also acted as a second drain if necessary. Silveira *et al.* (2015) reported significant improvement of denitrification efficiency by increasing the saturation depth from 15 to 25cm. The level of saturation was thus adjustable, at 3 different depths (15, 30 and 45cm, respectively), by a similar regulation system as previously described in section 2.3.2.

Intermediate sampling spots were distributed throughout the filter depth in order to assess the treatment dynamics inside the system. Sampling devices of unsaturated and saturated compartments were described in previous sections.

The filter was planted with reeds with the same density as 1st stage pilots.

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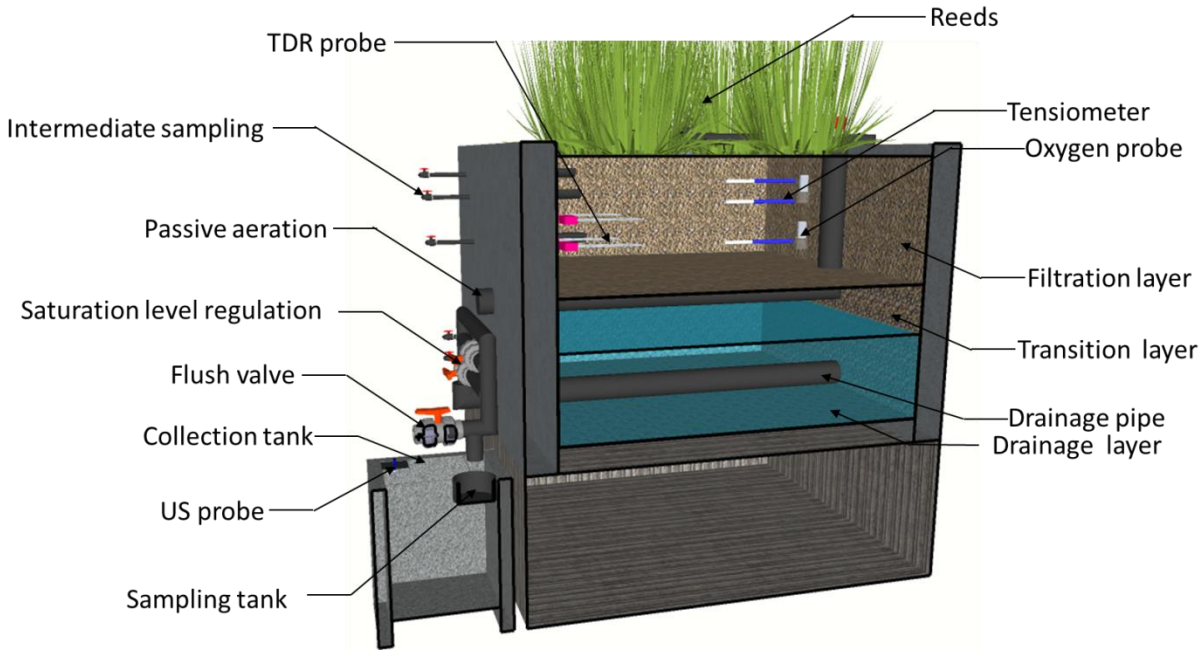

Figure 69 Schematic cross section of BiHofilter

2.4.3) Pilot operation

BiHofilter was operated as a classic 1st stage VFF (see section 2.2.3), for 3.5d then rests for 7d. The filter was pulse-loaded 18 times a day by batches of 2cm.

A 5-months commissioning period was respected to allow filter colonization by micro-organisms.

3) Continuous monitoring

3.1) Internal monitoring

Accurate characterization of hydraulic dynamics inside a vertical flow filter is a prerequisite for modelling purposes (Langergraber, 2008). Water content and infiltration-drainage mechanism were monitored by TDR probes (home-made probes, irstea) and tensiometers (UMS GmbH, T4e), respectively, at different depths and locations in the filtration layer.

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Table 26 Summary of probes location

Pilot	Depth from the surface (cm)		
	Oxygen probes	TDR probes	Tensiometers
VFG^{+}	5, 15, 40, 60, 80	80, 90	5, 15, 40, 80
VFZ	10, 25	10[a], 25[a]	10, 25
VFSt	30	15, 25, 35	35
VFHL	10, 25	10[a], 20[a]	10, 20
BiHo	None	20, 30, 40	30, 48

[a] 2 probes are located at the same depth but are horizontally spaced from 20 cm (1 probes is in a central position while the other is closer to the filter edge).

Furthermore, oxygen content within the filtration layer was identified to strongly affect treatment processes in VFFs. Oxygen sensors (SO120, apogee) were implemented at different depths in the filtration layer of 1st stage VFFs in order to study the oxygen dynamics during feeding and resting periods.

Each probe was logged by a CR1000 datalogger (Campbell scientific) at time step intervals of 1 minute.

3.2) Water monitoring

Influent and effluent were continuously monitored for nitrogen parameters (ammonium and nitrate), with ion selective probes (AN-ISE, Hach), as well for pH, redox and temperature (pHD sc sensor, Hach). The probes were introduced in the lift station (1st stage and hybrid pilots) or in the storage tank (saturated VFFs) for measuring influent characteristics whereas the effluent was monitored in a small sampling tank (1.6L), located below the outlet, in order to allow the permanent submersion of sensors while ensuring acceptable water renewal for accurate dynamic measurement. Influent and effluent characteristics were recorded by a SC1000 datalogger (Hach) at time step intervals of 15 and 2 minutes respectively. Probes and datalogger are shown in Figure 70.

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a b



Figure 70 Probes and sampling tank (a) and SC1000 datalogger (b)

These probes were calibrated twice a week. The experimental facility was equipped with 3 sets of probes for the continuous monitoring of all pilots (n = 7). Consequently, a rotation in the pilots' monitoring was carried out in relation to operation cycles as well as study objectives.

4) Water sampling and analysis

4.1) Sampling

4.1.1) 1st stage and hybrid pilots

Influent and effluent were sampled on the 1st and the 3rd day of operation in order to study the variations in treatment efficiency during a feeding cycle and also to assess the nitrate discharge after resting periods.

The influent was sampled once per batch, through a padding clamp located on the feeding line, by an automatic refrigerated sampler (ISCO 4700, Ponsel). A feedback loop between pump, inlet valves and PLC allowed to trigger the sampler when a feeding occurred on the preset pilot.

Effluent sampling was flow-regulated (every 5L) in order to produce representative samples. A feedback loop between the US probe and the PLC regulated the automatic refrigerated sampler (Bühler 2000, Hach) collecting effluent in a small sampling tank (1.2L) placed between the outlet and the collection tank. Such system allowed to collect instantaneous

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representative sample since dilution and biological reactions were expected in the collection tank where flow rate measure was carried out.

24-hour samples were punctually carried out for intermediate depths. The sealing valve was opened before starting sampling in order to purge the system of accumulated water and excess particles. Effluent directly flowed down, by a flexible pipe connected to the valve, to a pre-acidified 25L polyethylene jerrycan which ensured storage during the sampled period.

4.1.2) Saturated vertical flow filters

Samples were collected every day for these pilots since they constantly operated and the monitoring period was shorter than for 1st stage pilots.

A single grab influent sample was collected in the storage tank before the 9:00 a.m. feeding since the effluent characteristics were constant during the day. That was confirmed by preliminary comparison of grab samples and 24-hour samples of influent.

The effluent was sampled once per batch in the collect tank by an automatic refrigerated sampler (Sigma sd 900, Hach) in order to provide a 24-hour composite sample for analysis.

The sampling at intermediate depths was conducted in the same manner as described in the previous section. Nevertheless, the orifice of the valve was initially set in order to regulate the flow rate at values lower than 20L.d^{-1} (in order to avoid storage jerrycan overflow).

4.2) Analysis

Influent and effluent of each system were analyzed for total and dissolved COD (COD_{tot} and COD_d, respectively), NH_4-N, NO_3-N and calcium carbonate by quick test methods (LCK, Hach) with spectrometer (LASA 100, Hach). Note that all parameters, excepting COD_{tot}, were measured after filtration on 0.45µm cellulose filters. TSS was determined by filtration on 0.45µm cellulose filters while pH was measured with pH probe (C1010, CONSORT).

Note that intermediate samples were assessed on the same parameters excepting calcium carbonate, TSS and pH due to pre-acidification of samples which affected the results.

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March – July 2009	**Technician at Aquatiris (Le Rheu, France)** Project on the assessment of environmental and health risks linked with the use of constructed wetlands for non-collective sanitation purpose
March – September 2011	**Engineer at Irstea (Lyon, France)** Research project on combined sewer overflows and urban runoff treatment by vertical flow filters (SEGTEUP). *Promotor: Dr. Pascal Molle*

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February – September 2012	**Engineer at Irstea (Lyon, France)** Research project on treatment of domestic wastewater by vertical flow filters with partial bottom saturation (ATTENTIVE). *Promotor: Dr. Pascal Molle*
November 2012 – March 2016	**PhD position at Epurnature (Caumont sur Durance, France)** Research project on optimization of design and operational conditions for constructed wetlands treating domestic wastewater with a particular focus on nitrogen pollution (INNOPUR). *Promotors: Prof. dr. ir. Diederik P.L. Rousseau and Prof. dr. Rémy Gourdon*
August – December 2016	**Engineer at Irstea (Villeurbanne, France)** Research project assessing the use of microbial fuel cells as biosensor (CLOGGWATCH). *Promotor: Dr. Nicolas Forquet*

PUBLICATIONS

International journal publications with peer-review

Millot, Y., Troesch, S., Esser, D., Molle, P., Morvannou, A., Gourdon, R., Rousseau, D.P.L. Effect of design and operational parameters on ammonium removal by single-stage French vertical flow filters treating raw domestic wastewater. *Ecological Engineering*, **97** (12), 516-523.

Millot, Y., Troesch, S., Esser, D., Gourdon, R., Rousseau, D.P.L., Molle, P. Natural chabazite as filtration medium for ammonium removal optimization in vertical flow filters : a column experiment. *Water Science and Technology*, submitted to special issue IWA 2016.

Publications in international proceedings with peer-review

Millot, Y., Troesch, S., Esser, D., Molle, P., Gourdon, R., Rousseau, D.P.L. Design and operational improvements for high ammonium removal by one-stage vertical flow filters. *6th International Symposium on Wetland Pollutant Dynamics and Control*. 13th - 18th September 2015, York.

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Millot, Y., Troesch, S., Esser, D., Gourdon, R., Rousseau, D.P.L., Molle, P. Natural chabazite as filtration medium for ammonium removal optimization in vertical flow filters : a column experiment. *15th IWA International Conference on Wetland Systems for Water Pollution Control*. 4th – 9th September 2016, Gdańsk.

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ATTENDED SYMPOSIA, CONFERENCES AND WORKSHOPS

5th International Symposium on Wetland Pollutant Dynamics and Control. 13th – 17 October 2013, Nantes, France. Poster presentation.

20th National Symposium of Applied Biological Sciences. 30 January 2015, Louvain-la-Neuve. Oral presentation.

6th International Symposium on Wetland Pollutant Dynamics and Control. 13th - 18th September 2015, York. Oral presentation.

15th IWA International Conference on Wetland Systems for Water Pollution Control. 4th – 9th September 2016, Gdańsk. Oral presentation.

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THESE DE L'UNIVERSITE DE LYON OPEREE AU SEIN DE L'INSA LYON

NOM: MILLOT DATE de SOUTENANCE: 21 Mars 2017
Prénoms: Yoann

TITRE: Use of alternative matrix materials and configurations for optimizing nitrogen removal in constructed wetlands

NATURE: Doctorat Numéro d'ordre: 2017LYSEI021

Ecole doctorale : Chimie, Procédés, Environnement
Spécialité : Environnement

RESUME:
L'assainissement d'effluents résiduaires urbains par filtres plantés de roseaux rencontre, depuis plus de trois décennies, un engouement croissant en raison de ses remarquables performances de traitement ainsi que de considérations technico-économiques et écologiques. Néanmoins, des objectifs de traitement de plus en plus contraignants, ainsi qu'un marché de plus en plus concurrentiel, amènent la nécessité d'une meilleure connaissance des processus afin d'en optimiser la conception en fonction du contexte.
Une attention toute particulière a été portée au traitement de l'azote, au cours de cette étude, en raison de l'aspect particulièrement contraignant de son élimination. Ces travaux se sont articulés autour de trois axes principaux permettant l'évaluation des principaux mécanismes d'élimination de l'azote (nitrification, dénitrification et adsorption, respectivement).
Un premier volet, conduit sur unités pilotes alimentées en effluents domestiques réels, s'est attaché à identifier l'impact respectif de divers critères de dimensionnement et opérationnels (profondeur de filtration, surface de filtration, charges hydrauliques et organiques) afin de proposer des consignes de conception adaptées aux objectifs de traitement sur l'azote ammoniacal ainsi que la matière organique et la pollution particulaire.
Une seconde partie de l'étude, mené à échelle pilote à partir d'effluents semi-synthétiques, s'est quant à elle focalisée sur le processus de dénitrification afin de mettre en exergue les critères majeurs (composition des effluents, paramètres de conception et fonctionnement) pour l'atteinte de performances poussées sur le traitement des nitrates.
Enfin, un dernier axe de recherche, effectué en laboratoire en colonne, a visé à évaluer l'effet de l'adsorption d'ammonium sur matériaux filtrants réactifs (zéolithe) en vue d'optimiser par la suite le temps de rétention de cette espèce au regard des cinétiques de dégradation biologique.
Une synthèse des connaissances acquises au cours de cette étude a donné lieu à des conseils de conception ainsi qu'à des recommandations pour d'éventuelles études complémentaires.

MOTS-CLÉS: Nitrification, Dénitrification, Adsorption, Filtres plantés de roseaux, Effluents domestiques

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