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Long-term investigations on ammonium removal with zeolite in compact vertical flow treatment wetlands under field conditions

Hernán Ruiz-Ocampo^{a,b,c}, Katharina Tondera^{IWA id^{d,*}}, Joëlle Paing^b, Pascal Molle^{IWA^d} and Florent Chazarenc^{IWA id^d}

^a Institut Mines Telecom Atlantique, GEPEA, UMR CNRS 6144, 4 rue Alfred Kastler, Nantes 44307, France

^b CREA Step, 49 route de la Borde, Beaumont Louestault 37370, France

^c Circular Economy Research Center, Ecole des Ponts, Business School, Marne-la-Vallée, France

^d INRAE, REVERSAAL, Villeurbanne F-69100, France

*Corresponding author. E-mail: katharina.tondera@inrae.fr

 KT, 0000-0002-8888-1919; FC, 0000-0001-6819-1884

ABSTRACT

The scope of this study was to investigate if using zeolite as a reactive material in a vertical-flow wetland under field conditions improves ammonium removal from domestic wastewater in the long term. The experimental setup consisted of two pilot-scale first stage French vertical flow treatment wetlands (2.3 m² surface area each), which were implemented under field scale conditions inside a wastewater treatment plant in the central region of France (L'Enclouire, 37360). The filters were operated during 27 months. A compact pilot containing Leca[®] as a main filtration layer (Ø 1–5 mm) was compared to a similar one filled with natural zeolite (Ø 2–5 mm). The pilots were fed according to regular feeding/resting periods (3½/7 days) and the nominal loading rate was of 300 g COD m⁻² d⁻¹ and 33 g·N·m⁻²·d⁻¹ during operation. In both pilots, results showed a removal efficiency of more than 90 and 85% for TSS and COD, respectively. They also showed an increased NH₄-N removal of 9% on average (total removal efficiency of 84%) with the use of zeolite compared to Leca[®]. The ion exchange capacity of zeolite seemed not to be affected after 27 months of experiments; however, the material was compacted and more friable after operation.

Key words: compact wetland, French Reed Bed, Leca[®]

HIGHLIGHTS

- A zeolite layer in a French Vertical-Flow Wetland improved the ammonium removal.
- Seasonal effects impacted the removal efficiency.
- Material compaction of the zeolite during the trial period needs to be further investigated.

1. INTRODUCTION

Nitrogen compounds are nutrients essential to all forms of life, but when present in substantial quantities in receiving water bodies such as lakes and rivers, they cause eutrophication, resulting in an excessive growth of algae and degradation of water quality. Municipal wastewater contains nitrogen compounds, originating mostly from urine. Legislation for the discharge of wastewater from small communities in France is becoming stricter in order to achieve a good water quality. French standards discard limits for small communities (<2,000 p.e.) are currently established for Biological Oxygen Demand (25 mg O₂·L⁻¹), Total Suspended Solids (35 mg TSS·L⁻¹) and Chemical Oxygen Demand (125 mg O₂·L⁻¹); however, local authorities frequently define stringent limits including Total Kjeldahl Nitrogen (<15 mg N·L⁻¹) (EPNAC 2015).

The use of Treatment Wetlands (TWs) is recognized as an alternative to conventional wastewater treatment especially suitable for small communities. Two-stage Vertical Flow Treatment Wetlands (VFTWs) treating raw wastewater known as 'French VFTWs' (Cross *et al.* 2021) are popular in France with more than 4,000 plants implemented for small communities (Martinez-Carvajal *et al.* 2019). The 'classical' French VFTW consisting of two treatment stages (2 m²·p.e.⁻¹) achieves more than 90% of ammonium removal.

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Over the last 10 years, a compact version of the French VFTW consisting of one single vertical flow bed (Prigent *et al.* 2013) has gained popularity as it requires a smaller footprint ($1.2 \text{ m}^2 \cdot \text{p.e.}^{-1}$). The compact system named Ecophyltre[®] developed by CREA Step (formerly OPURE), was designed using several layers composed by a mixture of gravel and expanded schist (Mayennite[®]). The use of expanded schist improves biological activity by favoring biofilm growth due to its porosity, which increases the overall treatment performances (Prigent *et al.* 2013; Paing *et al.* 2015).

Paing *et al.* (2015) evaluated the removal efficiencies for 24 compact systems operated with domestic wastewater at a hydraulic load of $<0.6 \text{ m} \cdot \text{d}^{-1}$ and a plant age >6 months. The ammonium-nitrogen inflow concentrations of $63 \pm 29 \text{ mg NH}_4\text{-N} \cdot \text{L}^{-1}$ were reduced to $14 \pm 29 \text{ mg NH}_4\text{-N} \cdot \text{L}^{-1}$ on average, representing an overall removal efficiency of 77%. Furthermore, Morvannou *et al.* (2014) verified that 22% of the TKN load applied to a mature full-scale French VFTW remained in the effluent, 44% were nitrified, and 32% adsorbed onto the organic matter retained on the filter surface and in the inorganic filter material. Thus, the ammonium retention within the systems can still be improved. One way of increasing the adsorption further is by using zeolite as filtration material in TWs due to its ion exchange capacity (Wen *et al.* 2012; Araya *et al.* 2016).

The use of zeolite in a single horizontal flow wetland with artificial aeration increased the $\text{NH}_4\text{-N}$ removal efficiency between 25 and 60% compared to conventional materials (Araya *et al.* 2016). In an experiment lasting ten months, Gisvold *et al.* (2000) found a continuous biological regeneration of the $\text{NH}_4\text{-N}$ sorption capacity of zeolite in a filter column charged with wastewater with strongly fluctuating inflow concentrations.

While these investigations remained on laboratory scale and over the duration of one growth period in maximum, we hypothesized that the use of zeolite improves the $\text{NH}_4\text{-N}$ removal in a single stage French VFTW in comparison to other filter materials also under field conditions and in the long term. The main goal was to quantify how filtration media and hydraulic conditions as well as seasonal effects impact $\text{NH}_4\text{-N}$ removal using single stage TWs. Finally, zeolite adsorption capacity was compared at the beginning of the trials and after 27 months of monitoring to evaluate the effect of aging.

2. MATERIALS AND METHODS

2.1. Experimental setup

The pilots were implemented in a full-scale wastewater treatment plant located in Beaumont-la-Ronce, France, in order to perform the study under field-scale conditions. The pilot design was adapted from an Ecophyltre[®] configuration (Prigent *et al.* 2013) with an overall footprint of $1.2 \text{ m}^2 \cdot \text{p.e.}^{-1}$. Each pilot had a surface of 2.3 m^2 with different filling materials (Figure 1): one with zeolite (filter Z10), one with another specific material available on the market (light expanded clay aggregate Leca[®], filter L30).

The study lasted 27 months, and organic and hydraulic loads were regularly increased. A commissioning period (Month M0 -M3) was established at a COD value of $78 \text{ gO}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, then during the intermediate period (Month M3 - M12), the load was increased up to $195 \text{ gO}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ in October 2014 and finally during the nominal period (Month M12 - M27), the COD load was increased to $300 \text{ gO}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ in the operating filter. This feeding strategy was chosen to allow good establishment of both microbial activity and plants. Seasons were defined as cold when temperatures were lower than $10 \text{ }^\circ\text{C}$, above that as warm. The data presented in this study concern the period of monitoring (Month M3 - M27).

Filters were fed during 3.5 days and a resting period of 7 days was established according to French VFTW standard strategies (Molle *et al.* 2005). Filters were fed with fresh raw domestic wastewater that was pumped from the inlet of the

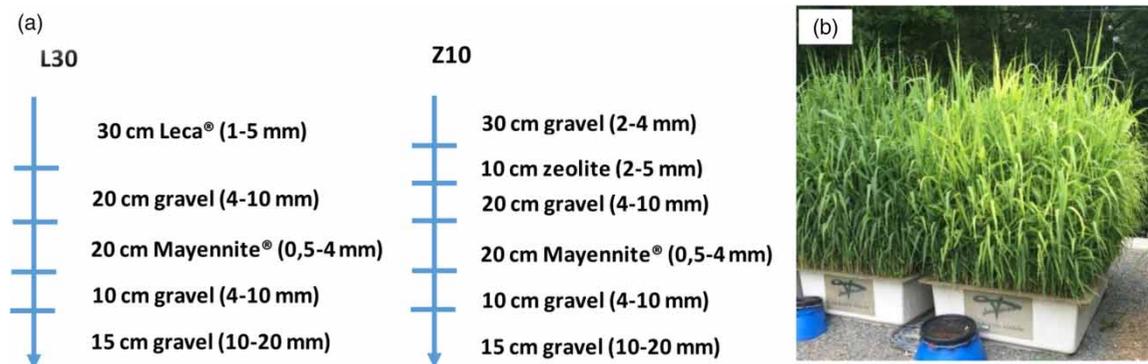


Figure 1 | (a) Filter layering with particle sizes of the two pilot setups; (b) photo of the experimental pilots.

wastewater treatment plant. The volume of each batch was 69 L (3 cm per batch on top of the filter surface) and its frequency was modified from three to 10 per day during the different phases.

2.2. Experimental monitoring

2.2.1. Hydraulic performances

Two tracer tests were performed on each pilot during the study to evaluate the impact of pilot composition and ageing on the hydraulic behavior. The first one was done at the beginning of the nominal load period (Month M12) and the second one was performed at the end of monitoring (Month M24). A precise amount of fluorescein tracer was injected during the first seconds of a batch flow directly into the distribution pipe (1 L of a solution of 500 mg·L⁻¹). Tracer outlet concentrations were measured with a fluorimeter (G-GUN) during four intermittent batches in one-minute time steps along with the outflow using a tipping bucket.

The mass recovered at the outlet was 16–60% of the total mass injected. Thus, to calculate the hydraulic retention time (HRT), the final mass obtained was used as the initial mass injected.

2.2.2. Treatment performances

Samples during a complete batch were collected at inlet and outlet of each pilot twice per month after one complete batch drainage during the 3rd day of feeding. Analysis was done the same day using MERCK measurements kits. Parameters analyzed were Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), Total Nitrogen (TN), ammonium-nitrogen (NH₄-N), nitrate-nitrogen (NO₃-N) and nitrite-nitrogen (NO₂-N). Three series of samples were also analyzed during nominal load period by an external laboratory to validate measurement accuracy.

2.2.3. Isotherms

The capacity of zeolite to remove ammonium before and after 27 months in the mesocosm TWs was investigated in series of isotherm batch experiments (adapted from ASTM D4646-87 2001). For both trials, a series of 6 glass bottles containing 250 mL of a synthetic solution prepared with deionized water and different initial NH₄-N concentrations (0, 50, 100, 150, 200, 250 mg N·L⁻¹) was mixed with 10 g of zeolite and placed on an agitation table at 125 rpm under controlled temperature conditions (20 °C) during 7 days. For the zeolite sample after treatment, the total zeolite layer was removed from the pilot, the material mixed homogeneously, and a subsample taken. The residual NH₄-N concentrations were measured after filtration using 0.45 μm filters.

The ammonium removal capacity (Q_e) expressed in mg N/g zeolite was calculated from Equation (1), where V is the volume of the solution (L), M the mass of zeolite (g), C_{in} the initial NH₄-N concentration (mg N·L⁻¹) and C the residual NH₄-N concentration of the solution after 7 days of reaction (mg N·L⁻¹).

$$Q_e = \frac{(C_{in} - C)V}{M} \quad (1)$$

2.2.4. Statistical analysis

Variance test was used for statistical analysis to evaluate the normal distribution of the samples. Student's t-test was employed to determine if there were significant differences between the pilots. Statistical tests were considered significant at $p \leq 0.05$.

3. RESULTS

3.1. Hydraulic performances

The retention time distribution curves (RTD-curves) for L30 and Z10 pilots are shown in Figure 2. Normalized RTD-curves represent the ratio of outlet tracer concentration (C_i) to inlet tracer concentration (C_o) as a function of time.

The L30 curve in Month M12 showed a rapid tracer response at the outlet, and a wide shape during the first batch event with a multi-peak curve showing fluctuations until the second batch event. During the second batch event, the concentrations dropped drastically down, subsequently remaining constant and a non-decreasing long tail appears.

The Z10 curve showed a different pattern. The first peak appears 6 min later than the one observed for L30. Fluctuations were not observed and the curve showed a wider shape followed by an exponential decrease until the next batch. During the second batch event, a small peak appeared and then the curve decreased continuously becoming long-tailed during the next

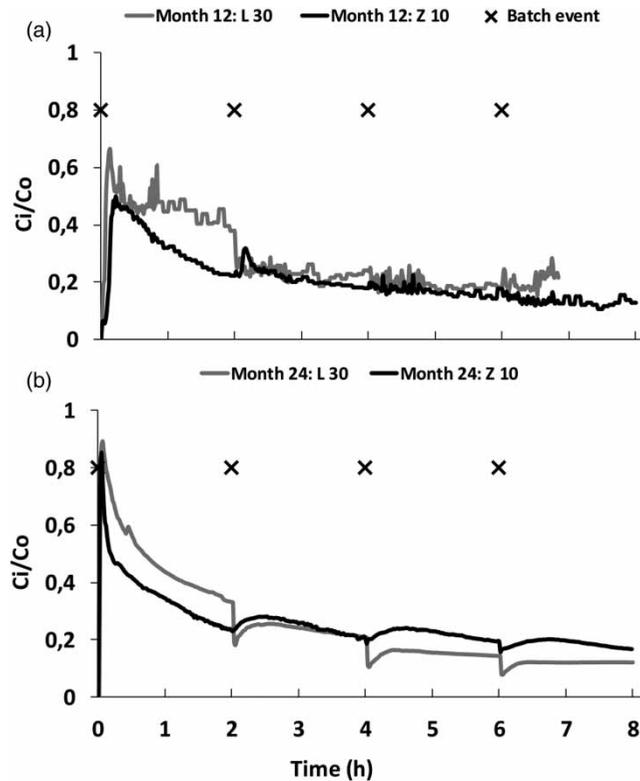


Figure 2 | Retention Time Distribution curves for both pilots: (a) Tracer 1 injected in Month M12 of operation; (b) Tracer 2 injected in Month M24.

batches until the end of the experiment. The mean HRT is similar for both pilots with values of 2.5 and 2.7 hours for L30 and Z10, respectively (Table 1).

RTD-curves in Month M24 showed a narrow peak at the beginning of the first batch in both pilots followed by an exponential concentration decrease. L30 showed higher concentration values between both pilots. The multi-peak curve of L30 disappeared, replaced by a single peak. RTD-curve for Z10 showed a sharper peak compared to Tracer 1 (Figure 2).

During the following batches, concentration decreased progressively in L30 and a long tail was formed until the end of the experiment. In the case of Z10, the concentration showed a small increase after the batches and the tracer left the pilot slower than in L30. The mean HRT is lower in L30 and remains constant in Z10 with values of 1.7 and 2.6 hours, respectively (Table 1).

3.2. Treatment performances

3.2.1. Inlet wastewater characteristics

Table 2 shows the comparison between inlet values of this study and the survey study for small communities in France (Mercoiret 2010). There was not much difference between loading phases or seasons' values, except for the cold seasons during intermediate load.

Table 1 | Tracer test results for both pilots after 12 and 27 months of operation: Percolation time (t_p) and mean Hydraulic Retention Time (mean HRT)

		Tracer 1: Month 12		Tracer 2: Month 27	
		t_p (h)	Mean HRT (h)	t_p (h)	Mean HRT (h)
L30	Mean	$0,5 \pm 0,01$	2,5	$0,4 \pm 0,02$	1,7
Z10	Mean	$0,6 \pm 0,02$	2,7	$0,4 \pm 0,03$	2,6

Table 2 | Domestic wastewater in French small communities compared to inlet characteristics of our study under both load conditions and by seasons

Concentration mg·L ⁻¹	Mercoiret (2010)			Months 3–12: intermediate load (195 g COD·m ⁻² ·L ⁻¹)		Months 12–27: nominal load (300 g COD m ⁻² ·L ⁻¹)	
	Lower limit	Mean	Upper limit	Warm (n=9)	Cold (n=3)	Warm (n=18)	Cold (n=6)
	TSS	53	288	696	455 ± 148	845 ± 436	359 ± 74
COD	122	646	1,341	942 ± 237	2,133 ± 367	918 ± 133	965 ± 237
BOD ₅	39	265	57	–	–	500 ± 120	–
TKN	14	67.3	123.1	111.9 ± 34.8	111.8 ± 13	107.4 ± 18.9	99.4 ± 13.9
NH ₄ -N	12	54.9	98.3	82.1 ± 18.4	86.7 ± 11.6	91.8 ± 16.6	74.7 ± 10.1

3.2.1.1. TSS and COD. The outlet monitoring during intermediate (Months M3-M12) and nominal (Months M12-M27) loading periods are shown in Figure 3. TSS outlet concentrations were not significantly different between both pilots during nominal loading ($p=0.055$). The mean outlet TSS and COD concentrations were clearly lower than those of the inlet. A decrease of TSS removal over time during nominal load operations was observed (Figure 3(a)); however, the average solids removal of the filters was efficient with more than 88% for both pilots when considering the entire monitoring period (Months M3-M27).

COD removal was also good, as expected; outlet concentrations were significantly different between the filters during nominal load operations ($p=0.03$). Outlet concentrations were below the French discard limit (125 mg·L⁻¹) almost constantly during Months M3-M12 in Z10. When the load was increased (Month M12-M27), outlet concentrations showed fluctuations in both filters with some values exceeding the discard limit (Figure 3(b)). Figure 3(b) shows that COD concentrations fluctuated in both pilots, probably because of fast filtration, allowing wastewater to reach the outlet quickly. The mean COD removal efficiencies achieved were 86 and 89% for L30 and Z10, respectively, when considering both periods.

3.2.1.2. TKN, NH₄-N and NO₃-N. The outlet monitoring during the intermediate (Months M3-M12) and nominal (Months M12-M27) loading period are shown in Figure 3. The mean TKN removal was 75 and 81% for L30 and Z10, respectively, during Months M12-M27. Outlet concentrations for TKN were significantly different between both filters during nominal load operations ($p<0.05$).

NH₄-N values throughout the experiments followed a similar trend compared to TKN and significant differences were found between both pilots during the nominal load period ($p<0.05$). Outlet concentration remained higher in L30 and more fluctuations were observed than in Z10. Outlet concentration for L30 decreased during Months M21-M27 and values lower than 15 mg·L⁻¹ were observed. Outlet values in Z10 were also lower than 15 mg·L⁻¹ almost all the time (Figure 3(d)).

NO₃-N outlet concentrations followed the same trend in both filters and mean concentration values were 43.7 and 45.5 mg·L⁻¹ for L30 and Z10, respectively, considering intermediate (Months M3-M12) and nominal load (Months M12-M27) periods (Figure 3(e)).

3.2.2. Effect of load on TKN and NH₄-N

The TKN and NH₄-N evolution and load increase had different effects on the pilots. The actual TKN loads applied varied from 10 to 40 g·N·m⁻²·d⁻¹. When intermediate loads were applied (Months M3-M12), L30 outlet concentrations were higher than the French discard limit (TKN=15 mg·L⁻¹) through almost all the investigation period. Those for Z10 were lower than for L30 and values under 15 mg·L⁻¹ were reached during Months M9-M12.

When the load was increased, the average TKN removal increased as well from 66 to 74% for L30. Z10 outlet concentrations showed some exceeding values from Month 18 on and high TKN values were also observed during Months M21-M27 in both filters. Mean outlet concentrations were lower than 30 and 20 mg·L⁻¹ for L30 and Z10, respectively (Table 3).

For NH₄-N, when the load was increased, the average removal efficiency increased to 77% in L30 and up to 84% in Z10. Z10 outlet concentrations were usually lower than 15 mg NH₄-N·L⁻¹ and L30 outlet values were lower than 15 mg NH₄-N·L⁻¹ at the end of monitoring (Figure 3(d)).

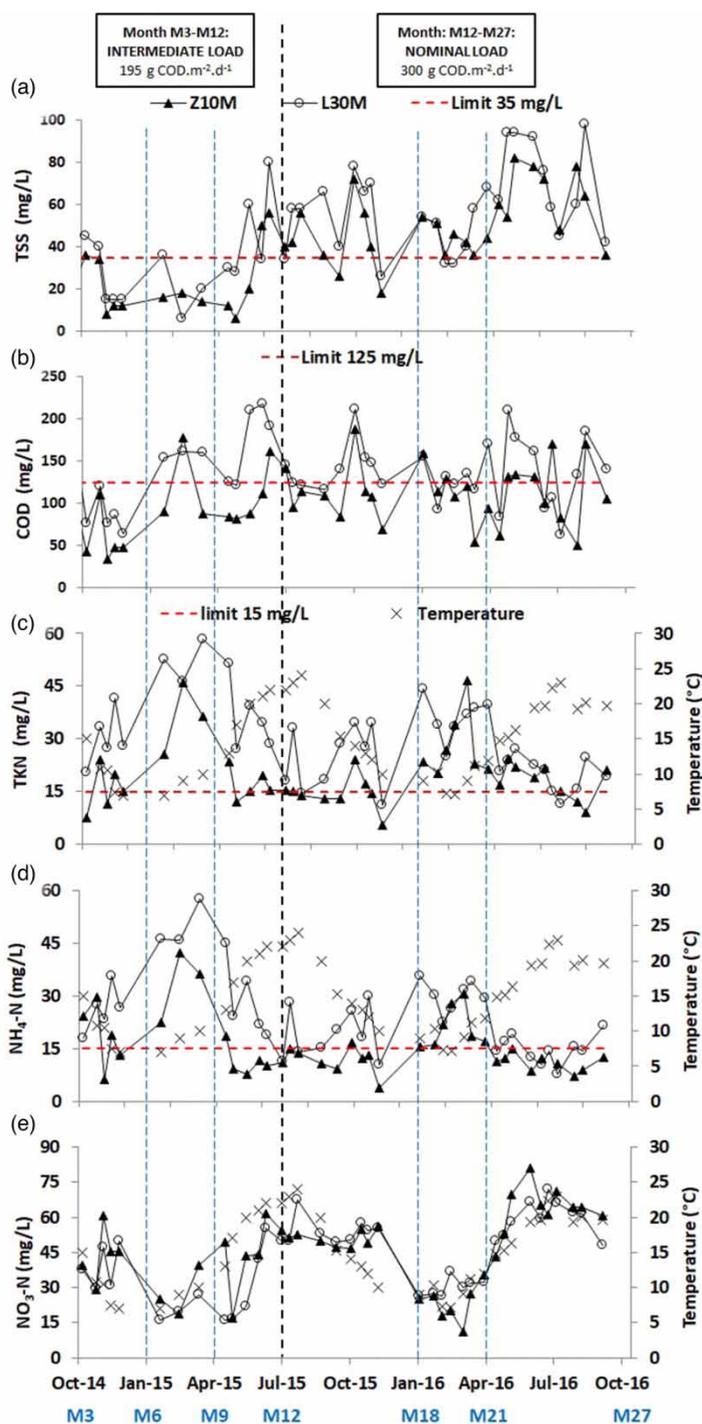


Figure 3 | Overall monitoring at the outlet of the filters (Months M3-M27) (left y axis) and air temperature (right y axis); the dashed line in M12 separates the intermediate load period (M3-M12) from the nominal load period (M12-M27).

3.2.3. Effect of temperature

$\text{NH}_4\text{-N}$ outlet concentrations varied in the different seasons during the two loading periods. During first measurements in Months M3-M6, some fluctuations were observed; in the cold seasons (Months M6-M9; Months M18-M21), when the temperature was lower than 10°C , the $\text{NH}_4\text{-N}$ outlet concentrations increased in both filters. In the warm season (Months M9-M12), the concentrations in the Z10 pilot seemed to reach stability and values lower than $15\text{ mg}\cdot\text{L}^{-1}$ were observed, whereas L30 values showed variations.

Table 3 | Average outlet concentrations and removal efficiencies for the two pilot systems during both periods and different seasons

	Months 3–12: intermediate load (195 g COD·m ⁻² ·L ⁻¹)				Months 12–27: nominal load (300 g COD·m ⁻² ·L ⁻¹)			
	L30 (mg·L ⁻¹)		Z10 (mg·L ⁻¹)		L30 (mg·L ⁻¹)		Z10 (mg·L ⁻¹)	
	Warm (n=9)	Cold (n=3)	Warm (n=9)	Cold (n=3)	Warm (n=18)	Cold (n=6)	Warm (n=18)	Cold (n=6)
TSS	41±20 ^a	21±15	32±19 ^{b,c}	17±1 ^{b,d}	64±21 ^{a,e}	44±11 ^c	51±18 ^c	44±8 ^d
COD	145±63	159±4 ^a	103±56	135±62	137±36	126±21 ^a	113±36	114±34
BOD ₅	–	–	–	–	64±24	–	51±22	–
TKN	33.2±9 ^{a,b,c}	52.3±6 ^{a,d}	16.4±5 ^b	36.0±10	23.1±8 ^{c,e,f}	35.4±6 ^{d,e}	16.5±5 ^{f,g}	29.0±10 ^g
NH ₄ -N	27.6±8 ^{a,b,c}	49.9±7 ^{a,d}	15.0±8 ^b	33.6±10	17.5±7 ^{c,e,f}	30.2±5 ^{d,f,g}	11.6±3 ^{e,h}	21.8±6 ^{g,h}
Removal efficiencies (%)								
TSS	90±6	96±4	92±6	98±1	82±5	88±5	87±6	89±3
COD	85±6	93±1	90±5	94±2	86±5	86±4	88±3	88±6
BOD ₅	–	–	–	–	87±4	–	89±6	–
TKN	70±3	53±9	85±4	68±6	79±5	64±4	84±5	71±9
NH ₄ -N	66±7	42±3	80±14	61±10	81±5	60±4	87±3	70±11

Concentrations followed by the same letter in one line are significantly different.

In Months M12-M18, performance improvements were observed in both pilots with temperature increase. NH₄-N outlet concentrations in Z10 remained under 15 mg·L⁻¹ almost all the time. However, in L30 more fluctuations were continuously observed. During the last warm season (Months M21-M27), concentrations remained mostly stable in Z10 while partially reaching values lower than 15 mg·L⁻¹ in L30 (Figure 3(d)).

NO₃-N concentration seemed to behave similarly in both filters. Lower values were found in cold seasons (Months M6-M9 and M18-M21), and an NO₃-N increase at the outlet was observed with higher temperatures (Months M3-M6, M9-M18, M21-M27). The highest concentrations were observed in the Z10 pilot during Months M21-M27 after the last cold season.

3.2.4. Regeneration of zeolite

Figure 4 showed isotherms and ion exchange-kinetics performed before (Month M0) and after (Month M27) operating the filters. The concentration of 100 mg NH₄-N·L⁻¹ for kinetic experiments was chosen to represent the concentrations of the domestic wastewater used in this study.

Isotherms (Figure 4(a)) showed a decrease in adsorption capacity of zeolite, before and after operation. The kinetics showed that zeolite was saturated faster in Month M27 than in Month M0 and the maximum retention capacity was lower in M27. A small difference was observed in total equilibrium capacity of the zeolite after 168 h (Figure 4(b)).

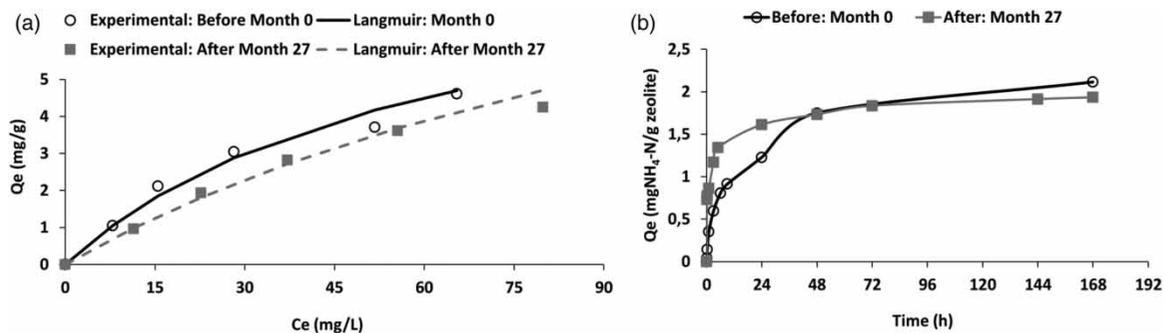


Figure 4 | (a) Isotherms of the NH₄-N adsorption capacity of zeolite before and after operations; (b) adsorption kinetics at 100 mg NH₄-N·L⁻¹ before and after operation.

4. DISCUSSION

4.1. Hydraulic performances

Tracer losses may have occurred due to organic matter adsorption within the filter media, but also because of photo degradation. Fluctuations observed in hydraulic behavior in tracer 1 (Month M12, [Figure 2\(a\)](#)) for L30 can be explained by the presence of different flow velocities in internal paths. The plateau of the first batch could be due to few exchanges between mobile and immobile water. The presence of a single peak in Z10 during Month M12 as well as in both RTD-curves during Month M24 ([Figure 2\(b\)](#)) seemed to represent a piston flow behavior with less exchanges and preferential paths.

Nevertheless, after the single peak at the beginning of Month M24, the outlet in L30 decreased just after the second batch while concentrations raised up in Z10, showing probably a faster flow rate in L30 compared to Z10. The wastewater might go through the filter via preferential path, while concentration increase after the second batch in Z10 suggests more interactions inside the filter. Several authors ([Fisher 1990](#); [Werner & Kadlec 1996](#)) highlighted that fast-moving parcels of water in wetland experience limited interactions with sediment, substrate and biota, ultimately leaving the wetland with limited chemical alteration and thus, affecting filters' performances.

Installation size effect could affect overall performances of the filter. Additionally, the presence of rodent holes was also observed in the filter.

4.2. Treatment performances

4.2.1. TSS and COD

Average TSS and COD removal efficiency higher than 93 and 88% ([Table 3](#)) observed in both pilots during Months M3-M12 can be explained by effective physical filtration of the systems and low loading rates. When loads were increased during Months M12-M27, higher outlet concentrations were observed. TSS outlet concentrations seemed as well to change with the season, with higher concentrations during summer. It is likely that higher organic matter mineralization in summer decreased filtration efficiency of the deposit layer as well as organic matter decay and release contributing to the TSS concentrations.

However, the TSS and COD mean removal was higher than 84 and 85% ([Table 3](#)) in both pilots during nominal load operation. The mean overall removal efficiency for both COD and TSS was in range with the results observed on average for first stage full-scale systems ([Paing *et al.* 2015](#)).

4.2.2. Effect of season and load on nitrogen removal

As $\text{NO}_3\text{-N}$ is a product of nitrification and temperatures below 15 °C in treatment wetlands have a limiting effect on nitrifying bacteria ([Kadlec & Reddy 2001](#)), the progressive increase in $\text{NH}_4\text{-N}$ outlet concentrations in winter results in a decrease of $\text{NO}_3\text{-N}$ ([Figure 3](#)). However, the additional adsorption capacity of the zeolite in Z10 acted as buffer and resulted in a lower outlet concentration even in the colder months ([Wen *et al.* 2012](#)).

$\text{NH}_4\text{-N}$ removal efficiency increased from the intermediate to nominal period with average values from 76 to 84% and from 61 to 76% for Z10 and L30, respectively. The highest $\text{NH}_4\text{-N}$ removal observed in warm periods using zeolite (Z10) ([Table 3](#)) was probably connected to higher hydraulic load. This allowed a better distribution of wastewater on top of the filter, increasing contact time, whereas the increase to nominal load in L30 seemed to enhance microbial activity within the porous material. This is in accordance with [Prigent *et al.* \(2013\)](#), who observed an increasing TKN removal over time with increasing maturity of the full-scale Ecophyltre® with a final value of 70% after two years of operation. [Langergraber *et al.* \(2010\)](#) as well observed that filter performances enhance with their maturity.

The effect of zeolite on nitrogen removal in this study was more apparent than reported in literature. [Stefanakis & Tsihrintzis \(2012\)](#) did not observe significant differences in VF filters with zeolite addition compared to others, most probably because of relative lower contact time between material and wastewater or the use of a too small quantity of material ([Millot *et al.* 2016](#)).

4.3. Regeneration of zeolite

After 27 months of operation, the zeolite was compacted and friable as smaller grain sizes <0.5 mm were observed ([Figure 5](#)). Migration of upper gravel material was also found in the core sample. Probably along with the friability of zeolite, some finer grain sizes could migrate to deeper layers and were replaced with upper gravel material.

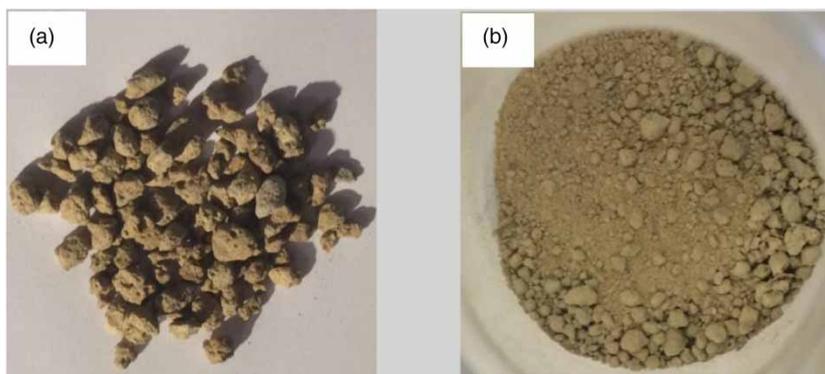


Figure 5 | Zeolite: (a) Before experiments, zeolite shows gravel structure; (b) after 27 months' operations, material is compacted and friable.

Isotherms and the ion exchange-kinetics performed before (Month M0) and after (Month M27) operations (Figure 4) showed a slight decrease on ammonium removal capacity of zeolite, but the differences observed were not significant; however, additional core samples would be necessary to perform statistical tests. The results are in line with the findings of Lahav & Green (2000). The authors performed batch experiments on the adsorption kinetics of virgin and biofilm covered zeolite (chabazite). They observed that the virgin chabazite reached 93% of the equilibrium rate already after 120 min while the biofilm-covered material reached 70% in the same time. However, no significant difference was observed when reaching the total equilibrium rate after 600 min.

The maximum adsorption capacity under process conditions could be estimated at approximately 1 mg/g as observed in zeolite after 27 months of operations (Figure 4). Since the hydraulic behavior is a piston flow and the contact time is short (few minutes), one can expect this maximum retention capacity to be a limit. Therefore, considering the average mass removal in L30 and Z10 (20 and 21.7 gNH₄-N·m⁻²·d⁻¹, respectively), ensuring higher contact time between the material and wastewater could enhance removal performances of the system to reach outflow levels lower than 15 mg NH₄-N. Pucher *et al.* (2017) showed in a compact TW model that using a larger zeolite layer reduces the outlet concentration (up to 10 mg NH₄-N·L⁻¹ for 20 cm zeolite). The higher removal efficiency of NH₄-N in Z10 up to 84% compared to L30 supports the hypothesis that zeolite enabled NH₄⁺ adsorption followed by regeneration via nitrification.

5. CONCLUSIONS

The long-term investigations of the NH₄-N adsorption capacity of two single stage vertical flow wetlands under field conditions showed that the removal efficiency was higher in a filter with a zeolite layer of 10 cm over all operating phases than in a filter with light expanded clay aggregate Leca[®]. Seasonal variations affect filter performances. Lower NH₄-N effluent concentrations were observed during warm periods, and NH₄-N outlet concentrations increased progressively in the zeolite filter during winter since the overall efficiency of zeolite is limited by reduction in nitrification leading to a larger saturation of the adsorption sites.

The hydraulic behavior also plays an important role and preferential flow paths could affect the contact time and the efficiency in a zeolite filter. Additionally, a homogenous distribution on the filter surface should improve the use of all available material for adsorption process by avoiding hydraulic failures.

Further, the use of a larger zeolite layer could not only improve the removal and the reliability of the system, but also help to retain more NH₄-N in cold seasons. Finally, the evolution of the zeolite structure over time needs to be further investigated in the TWs as after 27 months, a considerable breakdown of the material structure was observed.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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