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Hybrid constructed wetlands for the treatment of wastewater from a fertilizer manufacturing plant: microcosms and field scale experiments

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Abstract

Wastewater from a fertilizer manufacturing plant requires improvement prior to its environmental disposal. Ammonium is the critical contaminant to be removed. The aim of this study was to evaluate the feasibility of using free water surface wetlands (FWSWs), horizontal subsurface flow wetlands (HSSFWs), and their combination in hybrid wetlands (HWs) for the final treatment of wastewater with high ammonium concentration from a fertilizer manufacturing plant. Substrates and macrophytes were evaluated in microcosm experiments during three months. There were no significant differences in contaminant removal among HSSFWs with LECA or FWSWs planted with *Typha domingensis* or *Canna indica*. In a second stage, two configurations of pilot-scale HWs were constructed at the manufacturing facilities. Configuration A: HSSFW (A1)-FWSW (A2) and Configuration B: FWSW (B1)-HSSFW(B2) were evaluated during 12 months. There were no significant differences in contaminant removal (%) between the two configurations of HWs for COD (A:74.5±12.2/B: 81.5±9.4), ammonium (A: 59.5±17.5/B: 57.9±21.4), nitrite (A: 79.8±24.2/B: 80.6±16.8) and dissolved inorganic nitrogen (DIN) (A: 59.4±17.3/ B: 50.3±24.4). However, nitrate concentration (9.83 ± 3.11 mg N L^{-1}) was significantly lower after Configuration A than after Configuration B (18.8 ± 5.2 mg N L^{-1}). Comparing FWSWs and HSSFWs, they did not present significant differences in ammonium removal, while FWSWs presented the highest DIN removal. *T. domingensis* and *C. indica* in HSSFWs and *T. domingensis* in FWSWs tolerated wastewater conditions. *T. domingensis* presented the highest productivity. In further research, FWSWs in series planted with *T. domingensis* should be studied.

Keywords
Ammonium; Industrial wastewater; Removal efficiency; Free water surface wetlands; Horizontal subsurface wetlands

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1. INTRODUCTION

Over the last decades, the application of constructed wetlands (CWs) has expanded significantly from the traditional treatment of sewage to the treatment of various industrial effluents (Maine et al., 2009; 2013, 2017, Wu et al., 2014, 2015; Zhang et al., 2014; Arden and Ma, 2018). In Latin America, in countries such as Colombia, Peru, Mexico and Chile, this technology has been widely used for the depuration of municipal wastewater, university campuses, hotels, resorts, etc. However, CWs for industrial effluents are scarce in these countries. Although environmental conditions in Argentina are favourable, CWs are poorly implemented.

A nitrogen fertilizer manufacturing plant located in Buenos Aires, Argentina, requires an improvement of its wastewater treatment. There are two wastewater streams in the factory. Ammonium is the critical contaminant to be removed in an effluent stream. Currently, this effluent is treated in two stabilization ponds. The other effluent stream presents low ammonium concentration. Both effluent streams are discharged together in a channel, and final effluent concentrations meet regulations for discharge. Enhancing the treatment efficiency of the high ammonium concentration effluent, part of the other effluent stream could be reused, decreasing the final volume discharged. CWs are a good option for the final treatment of the high ammonium concentration effluent since a large land area is available at the manufacturing facilities.

Hybrid wetland (HW) systems have demonstrated to be efficient for ammonium removal (Adyel et al., 2017; Kadlec and Wallace, 2009; Vymazal, 2011; Vymazal and Kröpfelová, 2015). The most commonly used hybrid system configuration for ammonium removal is vertical flow wetland (VFW)-horizontal sub surface flow wetland (HSSFW), which has been used for the treatment of both sewage and industrial wastewaters (Kadlec and Wallace, 2009; Vymazal, 2011; Vymazal and Kröpfelová, 2015). Vymazal (2013) compared different configurations of hybrid systems operating all over the world. This author concluded that VFW-HSSFW hybrid systems are not more significantly efficient in ammonia removal than other configurations of hybrid systems. On the other hand, Wu et al. (2015) compared the different types of CWs, reporting that the energy operation and maintenance requirement increases as follows: Free water surface wetlands (FWSWs) < HSSFWs < VFWs < aerated systems, while land requirements increase inversely. As a consequence, FWSWs and HSSFWs need the least energy for operation and maintenance but the largest land area. In Argentina, large areas are generally available at manufacturing facilities while operation and maintenance costs are limiting factors. For these reasons, the use of FWSWs and HSSFWs was proposed as a suitable alternative for treatment of the plant effluents. Combinations of these types of CWs were used to treat different effluents such as commercial-scale shrimp aquaculture wastewater (Lin et al., 2005), landfill leachate (Kinsley et al., 2006), sewage (Yeh and Wu, 2009), fish product industry wastewater (Kantawanichkul et al., 2009), sewage from a picnic area (Canepel and Romagnolli, 2010), stormwater runoff (Adyel et al., 2017), among others. However, there is no information on CWs for the treatment of wastewater from fertilizer plants at a field scale. Our hypothesis was that a HW will be efficient for this effluent treatment and there will not be significant differences in contaminant removal efficiencies between the two configurations (HSSFW -FWSW and FWSW-HSSFW). The aim of this study was to evaluate the feasibility of using HWs and compare the performance of the two configurations (HSSFW -FWSW and FWSW-HSSFW) for the final treatment of wastewater with high ammonium concentrations, from a fertilizer manufacturing plant.

2. MATERIALS AND METHODS

2.1. Microcosm experiment: HSSFWs and FWSWs

Substrates and macrophytes were evaluated. Twenty-seven batch reactors simulating microcosm-scale HSSFWs (0.1 m^2, height: 0.45 m) and FWSWs (0.1 m^2, height: 0.60 m) were arranged in a greenhouse. HSSFWs were filled with 0.35 m of river gravel (particle size: 20-30 mm) or light expanded clay aggregates (LECA 10-20 mm) up to a height of 0.4 m. They were planted with *Canna indica* (Indian shot) or *Typha domingensis* (Cattail). FWSWs were filled with 0.25 m of soil and planted with *T. domingensis* or *C. indica*. Water level was 0.3 m. Unplanted HSSFWs and FWSWs were also arranged. Treatments were arranged in triplicate.

Before the experiment, macrophytes were acclimatized for two months with diluted treated wastewater (1:4). Then, during the experiment, wetlands were fed with real treated wastewater from the fertilizer manufacturing plant. Influent was loaded and after 7 days, reactors were drained. Evapotranspiration was compensated to maintain the water level every day. Twelve sampling s were done during the three-month experimental period. pH, ammonium and nitrate were measured in the wastewater before and after the treatment (APHA, 2012).

2.2. Field Experiment: Pilot-scale HWs

HWs were constructed in the facilities of a fertilizer factory located in the Campana Industrial Complex, Buenos Aires province, Argentina (34° 10´ 17´´ S; 59° 00´ 32´´W). The mean daily effluent flux is 50 m^3/h. In this area, mean annual temperature and mean annual rainfall are 16.4 ° C and 989 mm, respectively). Two configurations of HWs were evaluated as follows A: HSSFW (A1)-FWSW (A2) and B: FWSW (B1)-HSSFW (B2) (Fig. 1). HSSFs were 8 m long and 3 m wide, and FWSWs were 6 m long and 3 m wide. They were waterproofed with a PVC membrane. HSSFWs were filled with LECA up to a height of 0.65 m. FWSs were filled with soil up to a height of 0.5 m and the water level was set to 0.4 m. FWSWs and HSSFWs were planted with three plants by m^2 (4/5 of wetland surface was planted with *T. domingensis* and 1/5 with *C. indica*).

The acclimatization period lasted 6 months. During this period, wetlands were fed with wastewater after pond treatment, diluted 1:4 during 3 months and 1:2 during the following 3 months. After acclimatization, the experimental period lasted 12 months. Wetlands were fed with wastewater after pond treatment. Wastewater was pumped from the adjacent stabilization pond. Both HWs operated in a continuous flow regime with a flow rate of 1000 L day^{-1} in each configuration. Hydraulic residence time was 7 days in each wetland (14 days by each configuration). Along this period, 11 samplings were carried out, collecting influent and effluent in each wetland. pH, ammonium, nitrate, nitrite, alkalinity and chemical oxygen demand (COD) were determined as described in APHA (2012). Dissolved inorganic nitrogen (DIN) was estimated as the sum of NH_4^+-N + NO_3^--N + NO_2^--N.

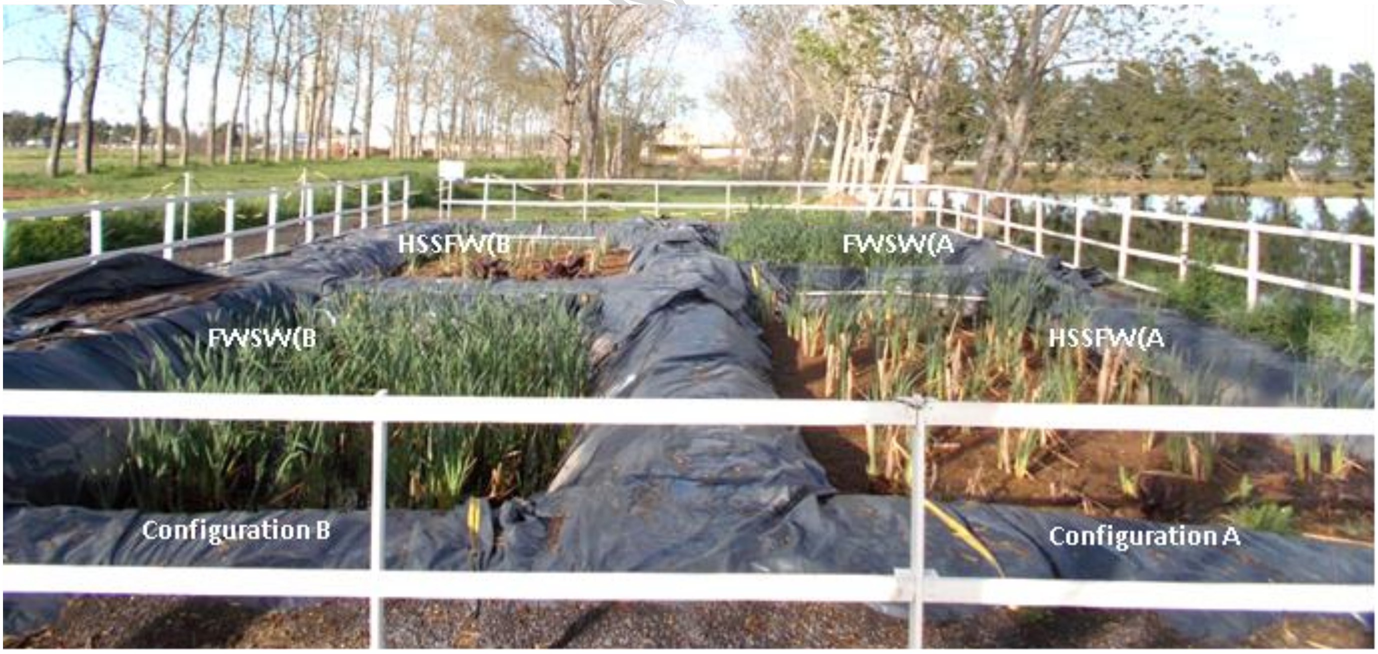

Figure 1. Picture of the two studied configurations after the six month of acclimatization period. Configuration A: HSSFW(A1)-FWSW(A2), and Configuration B: FWSW(B1)-HSSFW(B2).

2.3. Statistical analysis

In the microcosm experiment, analysis of variance (ANOVA) was used to determine significant differences in contaminant removal efficiencies among treatments considering each wastewater addition along time as a completely randomized block. The normality of residuals was analyzed graphically. Homogeneity of variances was checked applying Bartlett's test. Duncan's test was used to differentiate means where appropriate. In the field experiment, paired tests were used to corroborate statistical differences between the influent and effluent contaminant concentrations in water. A level of $p < 0.05$ was used in all comparisons. Statgraphics Plus 5.0 software was used to perform statistical analysis.

3. RESULTS AND DISCUSSION

3.1. Microcosm experiment: HSSFWs and FWSWs

Chemical composition of the wastewater used in the experiment ranged between pH: pH: 8.1-9.0; conductivity = 1.587-3.040 µS cm^{-1}; NH$_4^+$-N= 129.0-136.4 mg L^{-1}; NO$_3^-$-N= 1.8-2.0 mg L^{-1}; NO$_2^-$-N= 1.8-2.0 mg L^{-1}; alkalinity= 407.3-871.5 mg CaCO$_3$ L^{-1}, COD= 96.2-254 mg O$_2$ L^{-1}, BOD= 33.2-127 mg O$_2$ L^{-1}.

Ammonium removal reached efficiencies above 80 % in all planted wetlands. Effluents after treatment in HSSFWs with river gravel showed a significantly higher ammonium concentration range than those treated in HSSFWs with LECA (Table 1), in agreement with the lowest macrophyte growth. River gravel did not allow a suitable root system development. The best performances were obtained with the HSSFWs with LECA planted with *C. indica* or *T. domingensis.* Macrophytes tolerated treatment after a proper acclimatization in the HSSFWs with LECA, which proved to be a suitable substrate for root development. Ammonium removal may be directly correlated with the depth of penetration of macrophyte roots into the substrate (Crites et al., 2006).

Table 1. pH, NH$_4^+$ and NO$_3^-$ concentrations (Min.-Max, n= 12) in the influent and after the treatments, and mean NH$_4^+$ and NO$_3^-$removal during the experiment. Different letters represent statistically significant differences among treatments.

Treatments	pH	NH$_4^+$-N (mg N L^{-1})	NH$_4^+$ Removal (%)	NO$_3^-$-N (mg N L^{-1})	NO$_3^-$Removal (%)
INFLUENT	8.1-9.0	129.0-136.4	--	1.8-2.0	
AFTER TREATMENT					
HSSFW-River gravel					
T. domingensis	7.4-7.5	23.2-27.1	80.9 a	2.3-3.5	-20.9 a
C. indica	7.4-7.5	23.8-26.3	81.8 a	2.1-3.2	-16.7 a
Unplanted	7.8-7.9	31.0-34.5	75.7 b	11.3-12.6	-526 b
HSSFW-LECA					
T. domingensis	7.0-7.1	12.7 -16.4	89.5 c	2.6-2.8	-40.9 c
C. indica	7.0-7.1	12.0-16.2	91.0 c	2.5-2.7	-37.3 c
Unplanted	7.7-7.8	28.5-31.7 ^{a}	77.3 b	12.0-13.6	-557 b
FWSW					
T. domingensis	7.0-7.1	13.4-16.7	88.3 c	1.9-2.3	-5.5 d
C. indica	6.6-6.9	15.3-17.0	87.6 c	1.8-2.1	-2.3 d
Unplanted	7.5-7.7	31.6-35.4	55.6 d	2.0-2.2	-9.9 e

After the treatments, the effluents from unplanted HSSFWs presented higher concentrations of ammonium and nitrate than the effluents from planted ones (Table 1). It is likely that nitrification-denitrification processes were favoured by the presence of macrophytes. Plant root system generates aerobic microzones where nitrification is probably favoured (Crites et al., 2006). Plants also favoured the denitrification process because of the greater availability of carbon from the root exudates and dead plant detritus (Crites et al., 2006; Lee et al., 2009). By the other hand, it is also known that plants uptake ammonium and nitrate (Kadlec and Wallace, 2009). However, ammonium removal did not present significant differences in the microcosms planted with the different species in our experiment. On the other hand, there were no significant differences in ammonium removal between HSSFWs with LECA and FWSWs planted with *C. indica* or *T. domingensis* (Table 1). *T. domingensis* showed the highest productivity and it grows naturally at the factory facilities. *C. indica* has high aerial part biomass to accumulate nutrients, with the advantage of being an ornamental species. Considering the results of this microcosm experiment, HSSFWs with LECA and FWSWs planted with *T. domingensis* or *C. indica* were chosen to be used in the following field experiment.

3.2. Field Experiment: Pilot-scale HWs

Chemical composition of the wastewater used in the experiment ranged between pH= 8.1-8.9; conductivity= 1.490-3.040 µS cm^{-1}; NH_4^+-N= 94.4-233.5 mg N L^{-1}; NO_3^--N= 5.49-36.6 mg L^{-1}; NO_2^--N= 0.59-8.01 mg L^{-1}, Alkalinity= 463.3-777.9 mg $CaCO_3$L^{-1}, COD= 96.2-254.3 mg O_2 L^{-1}, BOD= 33.2-126.9 mg O_2 L^{-1}.

During the acclimatization period, the growth of *C. indica* was not favoured by the flood conditions of the FWSWs and disappeared. At the beginning of the experimental period, *T. domingensis* covered 80% of FWSWs surface, while in HSSFWs *T. domingensis* and *C. indica* reached a cover of 60% and 5%, respectively.

During 12-month experiment, plants were exposed to ammonium concentrations between 94.4-233.5 mg N L^{-1}. *T. domingensis* tolerated effluents conditions in the FWSWs, covering 80-100 % of the wetland surface during the study period (Fig. 2) Macrophytes also showed tolerance to effluent conditions in HSSFWs, *T. domingensis* covered 55-70 % and *C. indica* covered 5-10 % of the wetland surface. According to Clarke and Baldwin (2002), toxic ammonium concentration for several wetland plants is above 200 mg L^{-1} N. However, in our experiment plants tolerated ammonium concentrations higher than 200 mg L^{-1} N, showing no symptoms of phytotoxicity.

Figure 2. Plant growth at the end of study (left: HSSFW, right: FWSW).

COD concentrations decreased significantly after treatments (Fig. 3), reaching high COD removals. However, there were no significant differences between configurations (A: 74.5 ± 12.2 % and B: 81.5 ± 9.4 %) (Table 2). These results agree with the findings reported by Vymazal (2013), who reported that there were no significant differences in COD removal rates among different HW configurations. Comparing COD removal of each type of single CW, there were not significant differences neither between A1 and B1 for the first stage nor for A2 and B2 for the second stage.

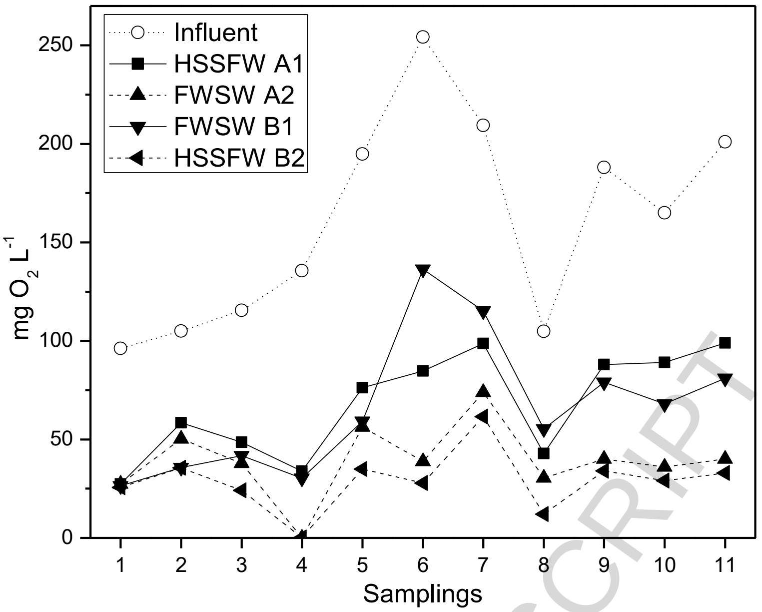

Figure 3. COD (mg O_2 L^{-1}) measured in each sampling in the influent and in the effluent after each stage of the studied configurations. Dot lines indicate concentrations after the first stage and solid lines represent final concentrations.

Ammonium concentration in the influent was high and variable along the experiment (Fig. 4). Ammonium concentration decreased not only its mean value but also its variability after the treatments. There were no significant differences in ammonium removal between the configurations studied (A: 59.5 ± 17.5 % and B: 57.9 ± 21.4%, Table 2). Comparing ammonium concentrations after the first stage (A1 and B1) there were no significant differences, suggesting that both FWSWs and HSSFWs could be used for the first stage of this treatment.

Table 2. Contaminant removal (%, mean±standard deviations) obtained in each stage (considering influent and effluent concentrations in each stage) and Configuration A and Configuration B Removals (considering the concentrations of the influent in the first stage and effluent of the second stage of each configuration).

Parameter	HSSFW(A1)	FWSW(A2)	**Config. A**	FWSW(B1)	HSSFW(B2)	**Config. B**
COD	58.0±9.9	*40.4 ±28.0*	**74.5±12.2**	*60.4±10.9*	56.1±32.3	**81.5±9.4**
NH_4^+-N	36.0±12.5	*38.3±17.9*	**59.5±17.5**	*40.2±16.3*	32.9±21.4	**57.9±21.4**
NO_3^--N	-129.5±112.8	*66.6±27.3*	**38.6±44.9**	*23.7±51.1*	-101,0±153,8	**-62.7±128.9**
NO_2^--N	81.9±21.1	*6,6±73,9*	**79.8±24.2**	*67.9±29.7*	27.8±60.4	**80.6±16.8**
DIN	27.4±12.3	*44.5±19.3*	**59.4±17.3**	*40.8±14.9*	18.0±32.9	**50.3±24.4**

Nitrification and plant uptake are reported as the main mechanisms for ammonium removal in CWs (Reddy and D'angelo, 1997; Spieles and Mitsch, 2000). Plant roots release oxygen creating aerobic microzones in the plant rhizosphere where nitrification occurs (Coban et al., 2015; Kadlec and Wallace, 2009; Lee et al., 2009), and also provide surface areas for nitrifying bacteria growth (Stottmeister et al., 2003). It is likely that nitrification also occurs in the top layer of the water column (Coban et al., 2015). Besides, when the nitrification reaction occurs alkalinity decreases. In our study, wastewater alkalinity decreased not only in the first but also in the second stage of both HWs (initial: 463.3-777.9 mg $CaCO_3$ L^{-1}, after treatment: Config. A: 181.3-400.9 mg $CaCO_3$ L^{-1} and Config. B: 160.3-404.7 mg $CaCO_3$ L^{-1}). According to Ahn (2006), an alkalinity of 7.07 mg $CaCO_3$ /mg of oxidized NH_4^+-N is required for nitrification. Estimating the ratio mg $CaCO_3$ consumed/mg of oxidized NH_4^+-N in our experiment, it seems that nitrification accounted for approximately 50 % of ammonium decreased. Nitrification rates also decline quickly when pH is lower than 7.0 (Ahn, 2006). Alkaline pH of the wastewater studied probably favour not only nitrification but also ammonium volatilization as NH_3 in FWSW (Maine et al., 2007). Regarding plant uptake, ammonium preference by macrophytes increases in environments where this nutrient concentration is high (Garnett et al., 2001).

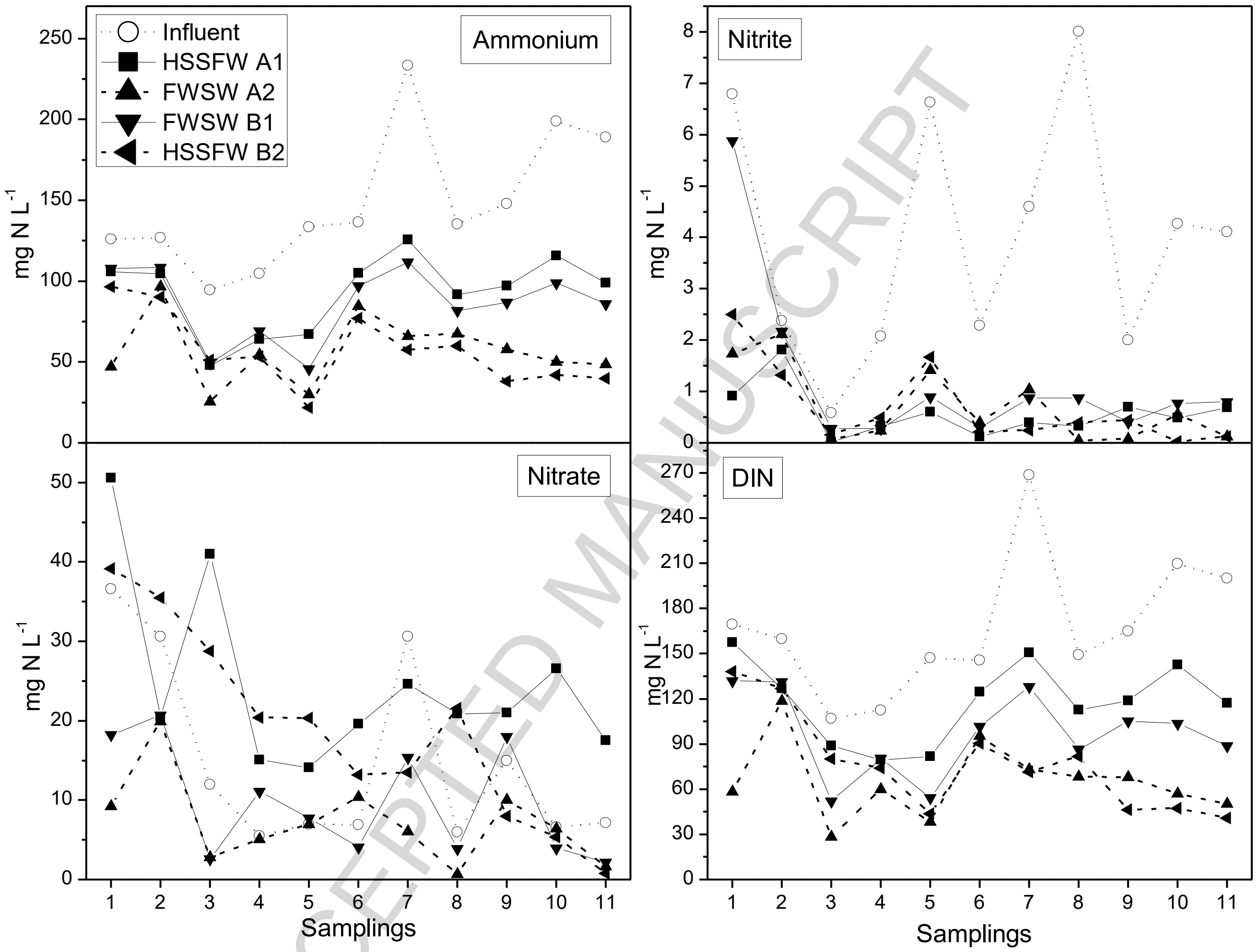

Figure 4. Concentrations of ammonium, nitrite, nitrate and DIN measured in each sampling in the influent and in the effluent after each stage of the studied configurations. Dot lines indicate concentrations after the first stage and solid lines represent final concentrations.

Another mechanism that may also account for ammonium decrease is anammox (anaerobic ammonium oxidation) (Gajewska and Ambroch, 2011; Strous et al., 2002; Vymazal, 2007; Wu et al., 2014; Zhai et al., 2016). Considering the mosaic of aerobic and anaerobic zones as well as the usually low dissolved oxygen concentration, CWs are assumed to offer favourable conditions not only for nitrification but also for anammox (Zhu et al., 2010). However, Coban et al. (2015) reported that although anammox bacteria were detected, anammox activity was absent and therefore this process appeared to be of a low importance in N transformation in their studied HSSFW. In our study nitrite concentrations decreased significantly after treatments (Fig. 4). Nitrite concentrations decreased mainly in the first stage in both configurations. High nitrite removals suggest that nitrite was rapidly transformed into nitrate during nitrification. However, anammox process could also occur. Sediments in FWSWs tend to be anaerobic just below the water-sediment interface, inducing anammox activity (Wallace and Austin, 2008). In HSSFWs, the limited oxygen conditions and effective removal of ammonium and COD observed in our experiment favoured the anammox process, in agreement with reports by Gajewska and Ambroch (2011). Comparing nitrite concentrations after treatments with the configurations studied, there were no significant differences (79.8 ± 24.2 % and 80.6 ± 16.8 % for Configuration A and B, respectively) (Table 2). Lin et al. (2005) also reported high removal efficiencies for nitrite (83-94%) and ammonium (64-66%) in a HW consisting of FWSW-HSSFW.

Nitrate concentrations presented a high variability along the study (Fig. 4). Mean nitrate concentrations after Configuration A (9.83 ± 3.11 mg N L^{-1}) were significantly lower than after Configuration B (18.8 ± 5.2 mg N L^{-1}). In Configuration B, nitrate concentrations increased during the second stage after the treatment in the HSSFW(B2), causing negative removal values (Table 2). Regarding the first stage, nitrate concentrations were also significantly higher after the HSSFW(A1) treatment (24.7 ± 11.3 mg N L^{-1}) than those after FWSW(B1) treatment (7.21 ± 5.31 mg N L^{-1}). These facts probably suggest that even when nitrification occurred, denitrification was inefficient in HSSFWs. Anoxic conditions should favour denitrification in HSSFWs, oxygen concentration ranged between 0.5-1.1 mg O_2 L^{-1} during the experiment. However, the wastewater studied presented a low C/N ratio (0.33-0.41); therefore, wetlands should provide the organic carbon source for denitrification. In HSSFWs, LECA did not provide a carbon source, while the substrate of the FWSWs contained organic matter. In addition, in FWSWs much more organic matter from plant detritus is released to water than in HSSFWs, in consequence there is much more carbon available for denitrification. According Kadlec and Wallace (2009), in the absence of a carbon source, denitrification is inhibited. Crites et al. (2006) proposed that FWSWs can be more effective for nitrate removal than the HSSFWs because of the greater availability of carbon source from the plant detritus.

The final goal of the treatment is the decrease of DIN that reflects the removal of all inorganic N forms. There were no significant differences in DIN removal between configurations (A: 59.4 ± 17.3% and B: 50.3 ± 24.4%) (Table 2). Comparing the first stage of both configurations, FWSW(B1) showed a significantly higher removal of DIN than the HSSFW(A1) (Table 2). The same can be seen in the second stage; FWSW(A2) presented a better performance in DIN removal than HSSFW(B2). Ammonium removals were not significantly different between FWSWs and HSSFWs. However, nitrate increased in HSSFWs, as it was explained. In further research, FWSWs in series planted with *T. domingensis* will be studied. In Argentina, FWSWs are of special interest due to their low cost, easy operation and maintenance, and the usual large availability of land around manufacturing plants. Vymazal (2013) concluded that HWs with FWSWs remove significantly more total nitrogen compared with other types of HWs.

4. CONCLUSIONS

T. domingensis tolerated wastewater conditions and presented the highest productivity in both HSSFWs and FWSWs

Both HWs studied configurations were efficient for the treatment of an effluent with high ammonium concentration, not presenting differences in COD, ammonium, nitrite and DIN removal. However, HSSFW-FWSW showed a significantly higher nitrate removal than FWSW-HSSFW.

Comparing the performance of each type of single CW, FWSWs and HSSFWs did not present significant differences in ammonium and COD removal, while FWSWs showed the highest DIN removal.

The treatment of the high ammonium concentration effluent was improved using the studied HWs. Ammonium concentrations in the effluent after HWs treatment decreased significantly, allowing a decrease in the final volume discharged and the reuse of part of the other effluent stream.

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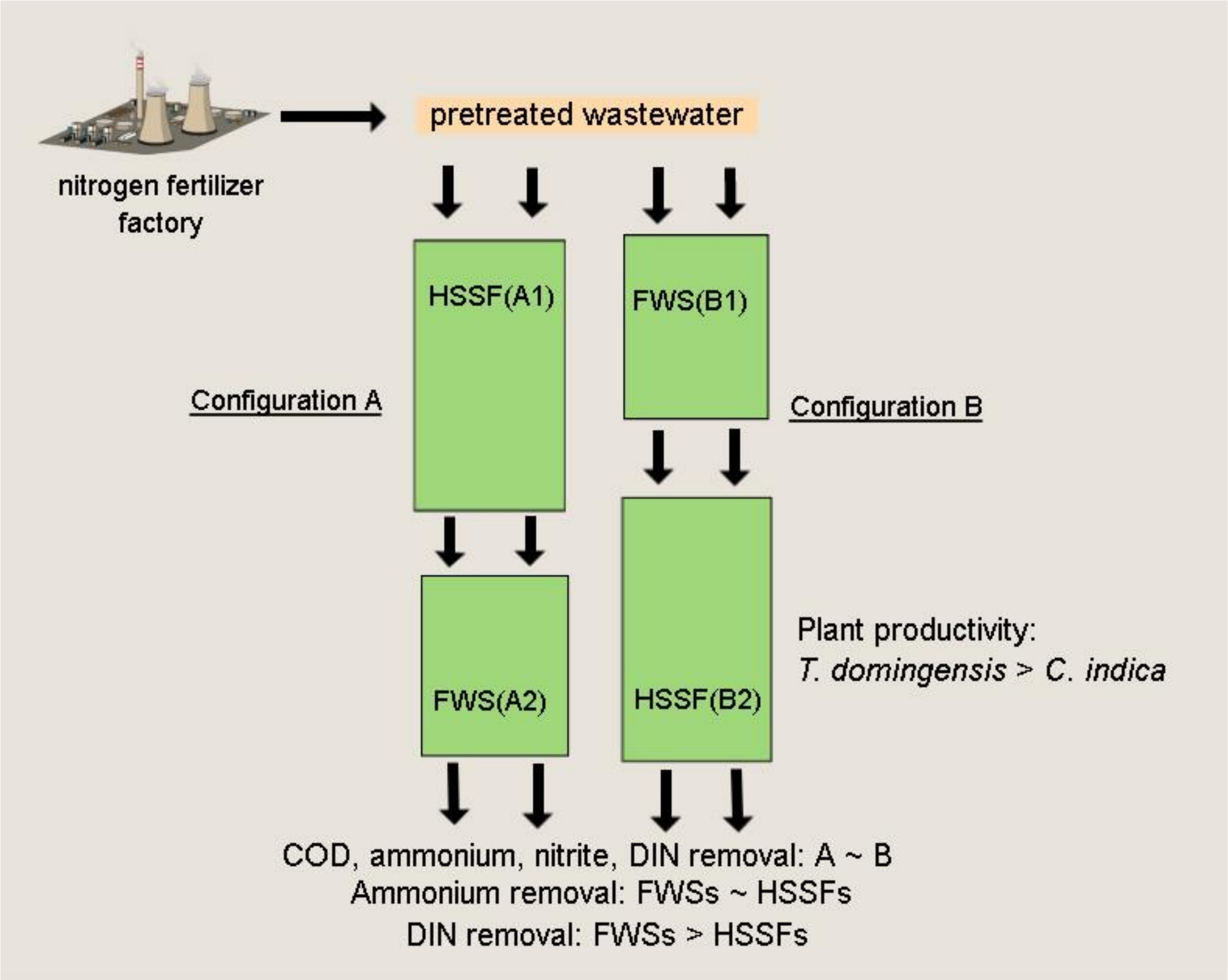
Graphical abstract



Highlights

Wastewater from a fertilizer manufacturing plant requires final treatment

Two configurations of HWs (HSSFW-FWSW and FWSW-HSSFW) were compared

There were no significant differences in contaminant removal between configurations

There were no significant differences in NH_4^+ removal between FWSWs and HSSFWs

FWSWs presented the highest DIN removal