



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

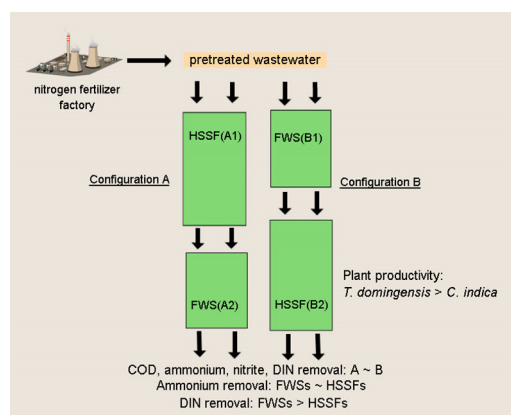
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## HIGHLIGHTS

- Wastewater from a fertilizer manufacturing plant requires final treatment.
- Two configurations of HWs (HSSF-FWSW and FWSW-HSSF) were compared.
- There were no significant differences in contaminant removal between configurations.
- There were no significant differences in  $\text{NH}_4^+$  removal between FWSWs and HSSFWs.
- FWSWs presented the highest DIN removal.

## GRAPHICAL ABSTRACT



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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: HSSF(A1)-FWS(A2) and Configuration B: FWS(B1)-HSSF(B2) were evaluated during 12 months. There were no significant differences in contaminant removal (%) between the two configurations of HWs for COD (A:  $74.5 \pm 12.2$ /B:  $81.5 \pm 9.4$ ), ammonium (A:  $59.5 \pm 17.5$ /B:  $57.9 \pm 21.4$ ), nitrite (A:  $79.8 \pm 24.2$ /B:  $80.6 \pm 16.8$ ) and dissolved inorganic nitrogen (DIN) (A:  $59.4 \pm 17.3$ /B:  $50.3 \pm 24.4$ ). However, nitrate concentration ( $9.83 \pm 3.11 \text{ mg N L}^{-1}$ ) was significantly lower after Configuration A than after Configuration B ( $18.8 \pm 5.2 \text{ mg N L}^{-1}$ ). 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.

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*T. domingensis* presented the highest productivity. In further research, FWSWs in series planted with *T. domingensis* should be studied.

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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 (HSSF), 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-HSSF 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) < HSSFs < VFWs < aerated systems, while land requirements increase inversely. As a consequence, FWSWs and HSSFs 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 HSSFs 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 Romagnoli, 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 (HSSF-FWSW and FWSW-HSSF). The aim of this study was to evaluate the feasibility of using HWs and compare the performance of the two configurations (HSSF-FWSW and FWSW-HSSF) for the final treatment of wastewater with high ammonium concentrations, from a fertilizer manufacturing plant.

## 2. Materials and methods

### 2.1. Microcosm experiment: HSSFs and FWSWs

Substrates and macrophytes were evaluated. Twenty-seven batch reactors simulating microcosm-scale HSSFs (0.1 m<sup>2</sup>, height: 0.45 m) and FWSWs (0.1 m<sup>2</sup>, height: 0.60 m) were arranged in a greenhouse. HSSFs 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 HSSFs 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 samplings 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<sup>3</sup>/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: HSSF(A1)-FWSW(A2) and B: FWSW(B1)-HSSF(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. HSSFs were filled with LECA up to a height of 0.65 m. FWSWs were filled with soil up to a height of 0.5 m and the water level was set to 0.4 m. FWSWs and HSSFs were planted with three plants by m<sup>2</sup> (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<sup>-1</sup> 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<sub>4</sub><sup>+</sup>-N + NO<sub>3</sub><sup>-</sup>-N + NO<sub>2</sub><sup>-</sup>-N.

### 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

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