Effect of *Spathiphyllum blandum* on the removal of ibuprofen and conventional pollutants from polluted river water, in fully saturated constructed wetlands at mesocosm level

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ABSTRACT

In this study, the effect of *Spathiphyllum blandum* on the removal of ibuprofen (IB) and conventional pollutants such as chemical oxygen demand (COD), total nitrogen (TN), ammonium (NH_4^+-N), total phosphorus (TP), and total suspended solids (TSS) is reported; this, through its use as an emergent vegetation in fully saturated (FS) constructed wetlands (CWs) at mesocosm level treating polluted river water. With the exception of TP and COD, it was found that for TN (12%), NH_4^+-N (11%), TSS (19%), and IB (23%), the removals in systems with vegetation were superior to systems without vegetation ($p < 0.05$). These findings demonstrate the importance of the species *S. blandum*, in particular, for the removal of ibuprofen, which is an anti-inflammatory drug commonly found in effluents of wastewater treatment plants. Thus, the results obtained provide information that can be used for the design of future efficient large-scale systems using a new ornamental species, mainly under tropical climatic conditions.

Key words | developing countries, polluted rivers, ornamental plants, tropical climate, wastewater treatment

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INTRODUCTION

The use of pharmaceutical products in large quantities and their improper disposal have led them to be found in rivers, lakes, seas, wetlands, and groundwater (Quesada-Peñate *et al.* 2009; Veras *et al.* 2019). In the last decade, interest in removing pharmaceutical compounds from wastewater has increased, mainly non-steroidal anti-inflammatory drugs due to their ability to negatively affect aquatic ecosystems. Ibuprofen is one of the most commonly prescribed anti-inflammatory agents found in effluents from wastewater treatment plants in concentrations between 10 ng.L^{-1} and 169 μg.L^{-1} and is the third most manufactured drug in the world with more than 15,000

doi: 10.2166/wh.2020.232

tons per year produced (Ghauch *et al.* 2012). On the other hand, the high costs of construction and implementation of technologies that have proven efficient for the removal of this type of compound, such as advanced oxidation, UV radiation, membrane biofilm reactors, etc., (Zhang *et al.* 2017) are expensive to solve this problem, in particular for developing countries. Fortunately, recent studies with CWs for the treatment of different types of wastewater have shown that it is feasible to eliminate drugs such as carbamazepine (Tejeda *et al.* 2017), acetaminophen, diclofenac, ibuprofen (Ávila *et al.* 2013), etc., with this technology. However, it is still necessary to study the influence of design parameters and CW components such as the filter medium and vegetation, in addition to the impact of environmental factors (Li *et al.* 2014). Moreover, very few studies have been carried out in tropical conditions where there is a great biodiversity. Recent studies include that performed by de Oliveira *et al.* (2019), who evaluated in Brazil, the removal of ibuprofen and caffeine in mesocosm-scale CWs planted with *Heliconia rostrata* and *Eichhornia crassipes* and obtained removal efficiencies >80% for both pharmaceuticals; that carried out by Zhang *et al.* (2018) in a subtropical climate in the south of China, for the removal of acidic pharmaceuticals (ibuprofen, gemfibrozil, naproxen, ketoprofen, and diclofenac) in subsurface flow CWs planted with *Canna indica* L., finding that the macrophytes favored the removal of ibuprofen and gemfibrozil; and that conducted by Lancheros *et al.* (2019), who evaluated the removal of ibuprofen and naproxen in horizontal subsurface flow CWs planted with *Cyperus ligularis* in the tropical climate of Colombia. On the other hand, within the wide range of tropical ornamental vegetation, it has been found that the *Sphathiphylum* family adapts easily to the flood conditions that prevail in CWs. Zamora *et al.* (2019) reported the use of *Sphathiphylum wallissi* in subsurface flow CWs for phosphorus and organic matter from community wastewater. For this reason, it is worth evaluating *S. blandum*, a species that grows faster than *S. wallissi* in the vicinity of natural aquatic bodies in rural areas in southeastern Mexico (Díaz-Jiménez *et al.* 2015; Villaseñor 2016). Therefore, the aim of this study was to evaluate the effect of *S. blandum* on the removal of ibuprofen and conventional contaminants such as chemical oxygen demand (COD), total nitrogen (TN), ammonium (NH_4^+-N), total phosphorus (TP), total suspended solids (TSS), in fully saturated (FS) CWs at mesocosm level from polluted river water; this river receives discharges of untreated municipal wastewater.

MATERIALS AND METHODS

The experimental units of FS CWs at mesocosm level consisted of ten cylindrical plastic units adapted as 20 L subsurface wetlands. These units were established outdoors and each unit was filled with tezontle (diameter between 1 and 1.8 cm); five units were planted with *S. blandum* and five units remained without vegetation, as control systems. The wastewater used for the study was collected every 8 days from a branch of the Sordo River (that receives municipal wastewaters from the city of Xalapa, Veracruz, Mexico) and pumped into a 500 L storage tank into which ibuprofen was added at a concentration of 50 $\mu g.L^{-1}$. Ibuprofen was obtained from the drug Motrin®-infantile in a concentration of 2 g.100 mL^{-1}. Additionally, it was found that in the river, the concentration of ibuprofen was in the range of 8 to 11 $\mu g.L^{-1}$ before the addition of ibuprofen for this study; afterwards, the final concentration of ibuprofen was around 60 $\mu g.L^{-1}$.

The experimental units operated at a continuous flow of 5.3 L/d. The monitoring of the systems began 30 days after the FS CWs were installed and lasted eight months, from March to October 2018. For the measurement of contaminants such as COD, TSS, NH_4^+-N, TN, and TP, samples were taken every 15 days at the input and outputs of the systems; while for the quantification of ibuprofen, samples were taken every 30 days. Conventional pollutants were measured using standard methods (APHA-AWWA & WEF 2005). Ibuprofen was quantified according to Cervantes *et al.* (2017) in a Waters Acquity UPLC H-Class coupled to a Xevo TQD (triple quadrupole) mass spectrophotometer equipped with an electrospray ionization source (EIS). Prior to the UPLC analysis, water samples were filtered through filter paper to remove suspended solids. Then, the analyte was extracted with dichloromethane, concentrated to dryness with a rotary evaporator at 35 °C and reconstituted by using 1 mL of ethanol. Each resuspension was filtered through a 0.2 μm PTFE filter. The recovery rate was 95.7 ± 1.8%. A Waters column (Symmetry C18), 50 mm long, 2.1 mm internal diameter and 1.7 μm in particle size was used. The mobile phase was formic acid at 0.01% in water, and formic acid at 0.01% in methanol, the flow rate was 0.3 mL/min. The limit of detection was 1 $\mu g.L^{-1}$.

The results were analyzed in SPSS® Statistics 19. A variance analysis was performed to find statistical differences ($p \leq 0.05$) between the influent and effluents of the systems. Prior to statistical analysis, all data were analyzed to determine their normality and statistical distribution. The homogeneity of the variance was tested using the Levene test.

RESULTS AND DISCUSSION

Plant development

During this study, under the average climatic conditions of 21 °C and 82% relative humidity, the *S. blandum* reached a height between 76 and 98 cm. This growth was 2.1% higher than in its natural habitat during a similar period (Chízmar-Fernández 2009). On the other hand, light intensity during the study averaged 805.81 lux, which falls in the intensity ranges for tropical zones (500 to 2,100 lux) (Sandoval-Herazo *et al.* 2018).

Removal of conventional pollutants

It can be seen from Table 1 that the removal of COD in mesocosms planted with *S. blandum* and without vegetation were, on average, 72.29% and 66.40%, respectively. Statistically, there was no significant difference ($p > 0.05$) in the removal of COD between these mesocosms; similar to that reported by Albalawneh *et al.* (2016) when evaluating vegetated and unvegetated systems. Regarding phosphorus, there was also no significant difference ($p > 0.05$).

However, the presence of *S. blandum* increased the removal ($p < 0.05$) of TSS, NH_4^+-N, and TN by 18%, 11%, and 13%, respectively (Figure 1) in comparison to the unvegetated system.

Table 1 | Average concentrations of water quality parameters (±standard deviation, $n = 80$) at the influent and effluents, as well as removal efficiencies in the FS CWs, during the period of experimentation

Parameters	*S. blandum*	Control
COD		
Influent concentration ($mg.L^{-1}$)	318.13 ± 102.47	
Effluent concentration ($mg.L^{-1}$)	88.13 ± 63.30	106.88 ± 73.68
Removal efficiency (%)	72.29	66.40
TSS		
Influent concentration ($mg.L^{-1}$)	695.63 ± 24.12	
Effluent concentration ($mg.L^{-1}$)	337.50 ± 49.79	459.38 ± 32.46
Removal efficiency (%)	51.48	33.96
NH_4^+-N		
Influent concentration ($mg.L^{-1}$)	22.88 ± 2.70	
Effluent concentration ($mg.L^{-1}$)	12.25 ± 3.49	14.63 ± 3.62
Removal efficiency (%)	46.46	36.05
TN		
Influent concentration ($mg.L^{-1}$)	103.75 ± 6.41	
Effluent concentration ($mg.L^{-1}$)	53.38 ± 5.34	63.75 ± 7.03
Removal efficiency (%)	48.54	38.55
TP		
Influent concentration ($mg.L^{-1}$)	11.21 ± 2.89	
Effluent concentration ($mg.L^{-1}$)	4.08 ± 1.29	4.15 ± 1.09
Removal efficiency (%)	63.60	62.97

Removal of ibuprofen in FS CWs

The average concentration of ibuprofen in the polluted river water evaluated in this study was 9 $\mu g.L^{-1}$; this value is in agreement with Ghauch *et al.* (2012), who reported that ibuprofen has been found in wastewater at concentrations between 10 ng L^{-1} and 169 $\mu g.L^{-1}$. Regarding ibuprofen removal, it was higher in vegetated systems ($p < 0.05$) (71%) in comparison to non-vegetated systems (52%). These values are higher than the 44% reported by Březinova *et al.* (2018) carried out in a temperate climate, which could be due to the fact that this study was carried out in a tropical climate and higher temperatures favored the removal of the drug. However, they are inferior to what was found by Zhang *et al.* (2017) (between 68% and 83%) in a tropical climate, probably because the authors performed the study with lower concentrations, i.e., between 11.5 $\mu g.L^{-1}$ and 48.5 $\mu g.L^{-1}$.

On the other hand, the difference between vegetated and unvegetated systems can be explained by the fact that the plant rhizosphere acts as a microcosm in which recalcitrant chemical compounds such as ibuprofen are degraded

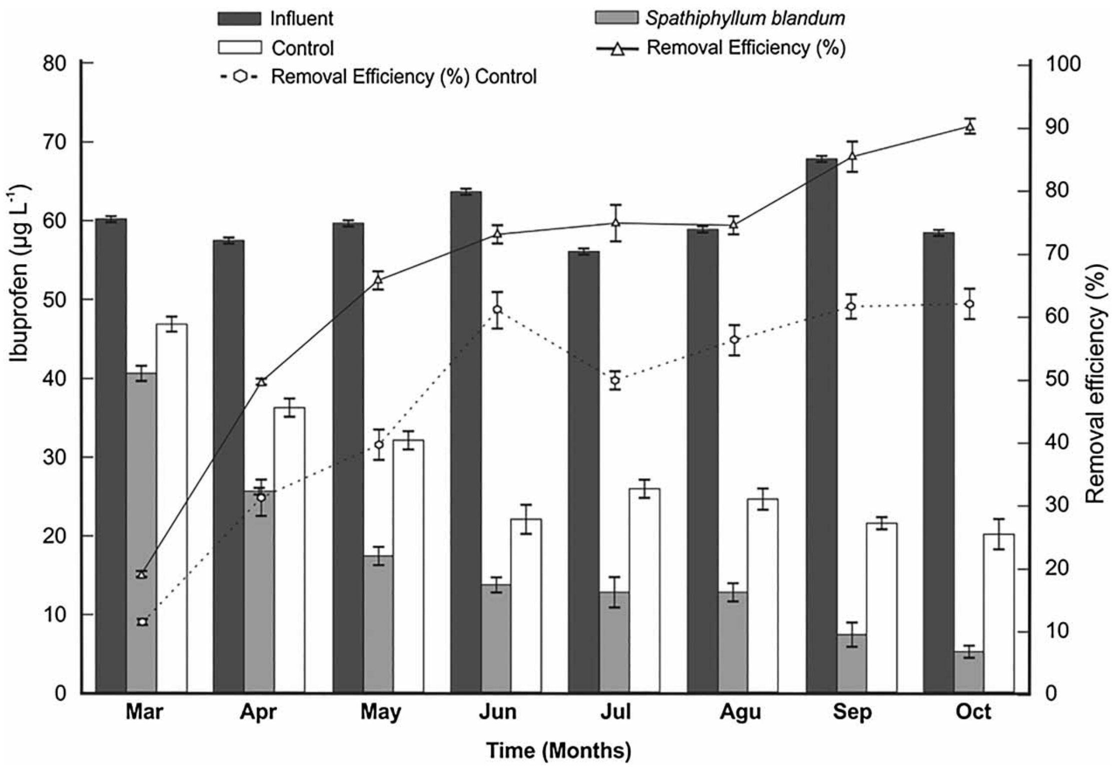

Figure 1 | Concentrations and removal of ibuprofen in the FS CWs during the study.

(Lancheros *et al.* 2019). Biodegradation and biotransformation in wetlands occur mainly in the rhizomes; additionally, the exudates released in the radical zones of plants intensify microbial activity and can improve the bioavailability of pharmaceuticals in these systems. In general, it has been found that the presence of vegetation in CWs improves drug elimination (Truu *et al.* 2015). Furthermore, according to Verlicchi *et al.* (2012), the removal of ibuprofen is greater in aerobic conditions, since aerobic microorganisms favor the removal of this compound.

CONCLUSIONS

In general, ibuprofen removal was moderately high in the FS CWs. In addition, the presence of *S. blandum* increased the removal of ibuprofen in FS CWs over unplanted systems by 19%; it also increased the removal of TSS, NH_4^+-N, and TN. Such results indicate that the presence of the plants probably generated aerobic micro zones that improved the elimination of the drug.

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First received 13 November 2019; accepted in revised form 29 January 2020. Available online 12 March 2020