KnE Materials Science
FibEnTech21
1st International FibEnTech Congress (FibEnTech21) New opportunities for fibrous materials in the ecological transition
Volume 2022

Research article

Phytoremediation of Boron From Wastewater in Vertical Flow Constructed Wetlands

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Abstract.
The aim of this work was to evaluate the possibility of boron removal from synthetic wastewater using a vertical constructed flow (VFCW) planted with *Vetiveria zizanioides*. Two boron concentrations were used (15 ± 1 and 30 ± 1 mg L^{-1}) and a hydraulic load (H_L) of 191 ± 10 L $m^{-2}d^{-1}$. The wastewater samples were taken and the flow rate in the inlet and outlet of the VFCW were measured. The levels of dissolved oxygen, electrical conductivity, pH and boron were determined in the wastewater. The concentrations of the essential elements and nutrients, namely total Kjeldhal nitrogen, phosphorus, calcium, magnesium, sodium and potassium in above growth biomass composition were measured. The results showed that: boron removal efficiencies depended on the boron concentration, so 60 ± 3% was obtained for the 15 mg L^{-1} concentration and 26 ± 2% for 30 mg L^{-1}; calcium, magnesium, potassium and sodium concentrations in the vegetal biomass decreased to the boron concentration of 30 mg L^{-1}, and boron may have interfered with *Vetiveria zizanioides* growth.

Keywords: biomass composition, boron removal, light expanded clay aggregates, *Vetiveria zizanioides*, vertical flow constructed wetland

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Published 10 August 2022

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the FibEnTech21 Conference Committee.

1. Introduction

Boron (B) is an inorganic, semi-metallic, water-soluble compound that causes environmental problems, especially in surface waters due to agricultural runoff, since its use is strongly associated with fertilizers and pesticides. The forms in which boron is present in wastewater are quite variable, and the some of the factors that control this are the pH of the water and the concentration of these compounds. That is, at high concentrations, greater than 50 mg L^{-1}, pH ≤ 10, boron is found essentially in the forms of triborate ($[B_3O_3(OH)_5]^{2-}$), tetraborate ($[B_4O_5(OH)_4]^{2-}$). However, at low concentrations (less than 4.8 mg L^{-1}), it is essentially found in the form of boric acid (H_3BO_3), borate ion ($[B(OH)_4]^-$) and boron oxide (B_2O_3) [1].The contamination of surface water and groundwater, derived from excess boron (B), can cause toxicity and chronic effects on crops and plants, and can also contaminate soil and/or sediment, as well as promote problems in the reproduction of some animal species and in humans [2]. Therefore, it is necessary to treat urban or industrial effluents in order to minimize/reduce the presence of this contaminant in water used for irrigation and drinking water production [3]. Effluent treatment is often carried out through electro-coagulation, ion exchange, adsorption, among others [4]. These technologies are known for their efficiency in removing some pollutants, such as heavy metals and organic matter, but are not suitable for boron removal [5, 6]. Vertical flow constructed wetland (VFCW), are environmentally sustainable technologies with characteristics and processes similar to natural wetlands and are used for wastewater treatment [7, 8, 9, 10]. These systems are designed and built with the objective of using the natural processes involving the plants, the substrate and their interaction with the microbial community present to treat effluents in a controlled manner. They have been used to treat various types of effluents, including urban wastewater, industrial wastewater, storm water, acid mine water, and to remove organic and inorganic pollutants, heavy metals, boron compounds, and many other pollutants [3].

This work aimed to study the possibility of using constructed wetlands planted with the *Vetiveria Zizanioides* to treat synthetic urban wastewater with high boron concentration and evaluate the effects of two different and increasing boron concentrations in above grow leaves biomass composition.

2. Methods

2.1. Characteristics of experimental set-up

The experimental work was carried out by 24 weeks in a pilot-scale VFCW with an area of 0.24 m^2 and a depth of 0.70 m filled with light expanded clay aggregates (Leca® NR 10/20) and planted with *Vetiveria zizanioides*. Batches of 125 dm^3 of boric acid (H_3BO_3) in aqueous solution were homogenized by one submersible pumps and VFCWs were fed through a network of equidistant sprinklers. The medium was not saturated due to effluent drainage type and substrate material used, allowing the oxygen diffusion into the beds. The affluent was prepared using H_3BO_3 as a boron source, with a variable concentration. The VFCW was fed with synthetic wastewater, prepared by mixing tap water with KNO_3, Na_2HPO_4, CH_4N_2O, KH_2PO_4, $CaCl_2$, $MgCl_2$, $FeSO_4$ and $C_2H_2NaO_2$ prepared according to Almeida et al. [11].

2.2. Experimental conditions

It was used two different and increasing boron concentrations (15 ± 1 and 30 ± 1 mg L^{-1}) and the flow rate to the VFCW was kept constant, with and hydraulic load (H_L) of 191 ± 10 L $m^{-2}d^{-1}$, as described in Table 1.

2.3. Sampling collection and analysis

The system was monitored at all times during the testing period, from Monday to Friday, around 10 a.m. At the beginning of each test, a value was set for the feed flow rate, depending on the hydraulic load (H_L) with which it was intended to work. The measurements of flow rate, at the influent and effluent of the VFCW, were performed manually, in a valve placed at the inlet of the VFCW and in the liquid outlet siphon, with the aid of a stopwatch. The samples were analyzed for pH, electrical conductivity (EC), redox potential (Eh), dissolved oxygen (DO). To determine the remaining parameters, when it was not possible to analyze them immediately, aliquots were stored and conserved at -20°C for short periods of time, as indicated in *Standard Methods of Analysis* [12].

Visual observation of the system was done in order to detect possible toxicity effects on the plants (tissue). Plant growth was through marking and measurements at the beginning of the trial. The leaf biomass was also sampled for subsequent determination of nitrogen, moisture, chlorophylls (a, b, total) and carotenoids. The mineral and nutrient composition was also determined, namely the calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), phosphorus (P) and nitrogen (N) content according to Horneck & Miller [13].

TABLE 1: Operational condition applied to the VFCW. Values are means ± standard deviation (SD), ($n \geq 10$).

Exp	**H_L** (L $m^{-2}d^{-1}$)	**[B]** (mg L^{-1})
1	191 ± 10	30 ± 1
2		15 ± 1

3. Data analysis

Results were statistically verified using software the software "Statistica 12 '"(StatSoft Inc. USA) was used. Differences in wastewater quality between influent and effluent of the VFCW bed were tested using ANOVA at the significance level of $p < .05$, Post-hoc (a posteriori) Tukey's test was used to determine differences between means of specific variables. All results were presented as means ± standard deviation calculated for n ≥ 10.

4. Results and discussion

Boron removal efficiency up to 60 ± 3% was obtained for a concentration of 15 mg L^{-1}. It can be observed that when the boron concentration increased, the capacity of VFCW to boron removal decreased (Fig 1). Ye et al. [10], in wetland microcosms were obtained B removal efficiency of the 30% to a boron concentration of the 46.5 ± 1.4 mg L^{-1}. Where Gross et al. [14], reported 50% removal for VFCW systems in Israel with an initial concentration of 0.3 ± 0.03 mg L^{-1}. Furthermore, studies from Turkey showed that VFCW systems planted with *T.latifolia* and *P.australis* removed 32% of boron in the effluent at a concentration >1 mg L^{-1} [1]. Rees et al. [15], revealed that B was transported to leaves and stems after being taken up by below-ground parts (roots/rhizomes) in the plants. These findings support the fact that B is transported from roots to stems and leaves into the xylem with the stream of transpiration water. Thus, harvesting could be a viable option for removing of B from CWs when B is efficiently stored into the aboveground biomass.

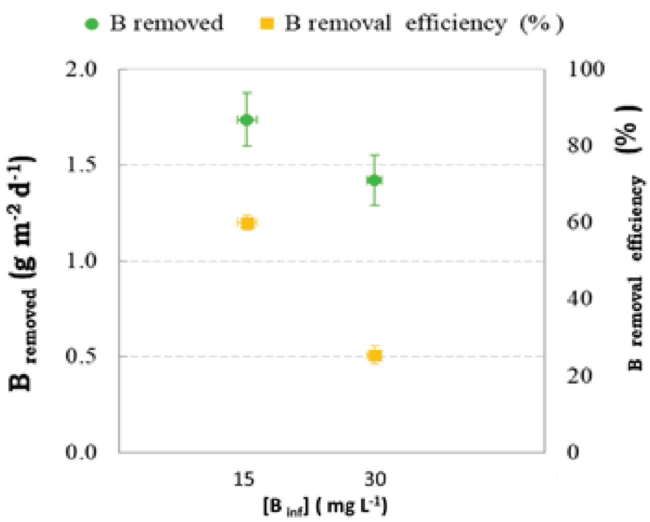

Figure 1: Boron mass load removed and removal efficiencies.

Boron may interfere with the physiological structure of plants or the microorganisms present in the VFCW. When boron concentration was the highest the plants stop growth and leaves chlorosis was observed (Fig. 2).

Dissolved oxygen (DO) and pH (Fig. 3) in effluent were decreased with significantly differences in trial that was done with lower boron concentration (15 mg L^{-1}) or lower

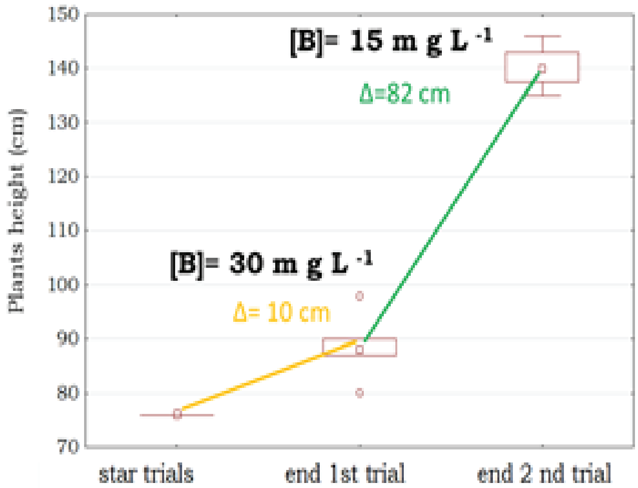

Figure 2: Plants leaf growth during the experimental trials.

boron probably due to the boron phytoremediation processes that can consume oxygen. The pH decreased in effluent because boron removal mechanisms can produce H^+ so pH decreased. The redox potential (Eh) (Fig. 3), like the dissolved oxygen concentration, is a parameter to measure or evaluate the possible occurrence of oxidation-reduction reactions, namely, how degradation or reactions involving oxidation state changes of the boron compounds have occurred.

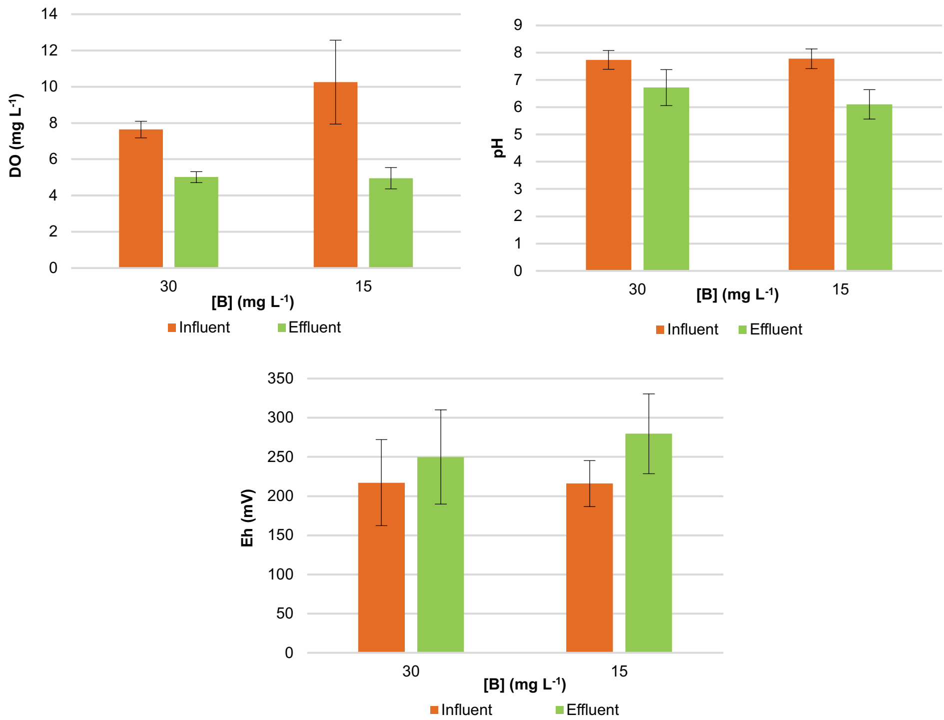

Figure 3: Values of DO, pH and Eh in the influent and effluent.

The micronutrients composition (calcium, magnesium, potassium and sodium in dry biomass (DB)) in vegetal biomass decreased when wastewater boron concentration increased (Table 2).

TABLE 2: Leaf biomass composition at beginning and the end of each trial.

Parameter (mg g^{-1} DB)	**Leaf biomass composition**		
	Start trials	**end**	
		1^{st} **trial** (30 mg L^{-1} B)	2^{nd} **trial** (15 mg L^{-1} B)
Ca^{2+}	13±1.5	12±4	21±4
Mg^{2+}	22±1	13±1	20±2
Na^{+}	11±4	36±1	45±3
K^{+}	33±41	33±6	68±4
TN	10±1	9±1	11±1
P	1.1±0.1	0.7±0.1	2.6±0.3

The Table 2 it is possible to observe a tendency for an increase, less significant in the test performed with the highest boron concentration (30 mg L^{-1} B). In the analysis of the previous results, boron causes more changes in the cations and nutrients (P and N) present in the leaf biomass of *Vetiveria zizanioides* (Table 2 and Fig. 4).

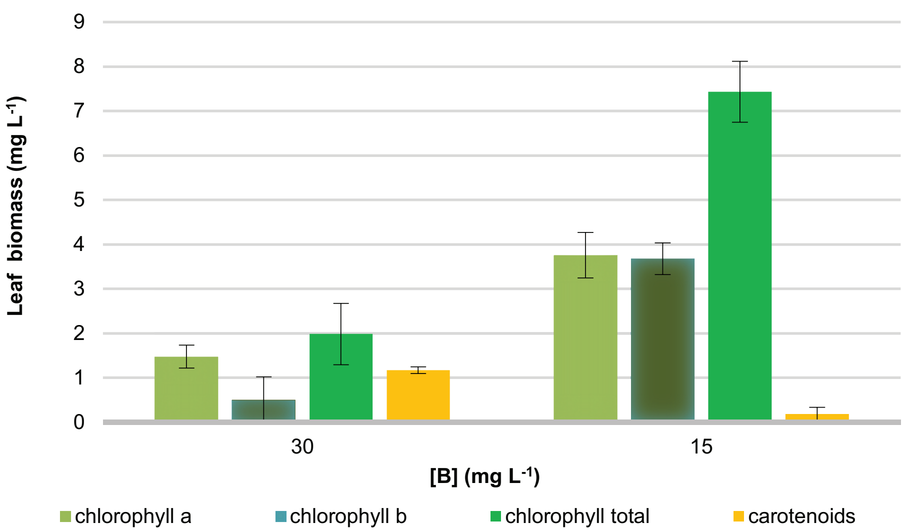

Figure 4: Concentration of chlorophylls a, b, total and carotenoids.

5. Conclusions

Through the analysis of Fig 1, it was found that boron removal occurred by phytoremediation. The main conclusions should be highlighted in this section. So, we can conclude that Boron removal efficiencies of 60% were obtained for the 15 mg L^{-1} concentration and 26% for 30 mg L^{-1}. Also, Boron may interfere with the *Vetiveria zizanioides* growth and with respectively physiological structure of plants.

6. Acknowledgments

The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds through the project UIDB/00195/2020 (FibEn-Tech).

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