Journal of Environmental Science and Engineering A 6 (2017) 542-551
doi:10.17265/2162-5298/2017.11.002

DAVID PUBLISHING

Microcosm Study: Effect of Fe(II) Addition in Sawdust for Phosphorous Recovery from Eutrophic Aquatic Ecosystems

Glaucia Pantano, Francisco Wendel Batista de Aquino, Edenir Rodrigues Pereira-Filho, Antonio Aparecido Mozeto and Pedro Sergio Fadini

Chemistry Department, Federal University of São Carlos, São Carlos 13565-905, Brazil

Abstract: The recovery of phosphorus in eutrophic water bodies is important to ensure water and food security, phosphorus adsorption in sawdust can be promoted by Fe(III) oxide-hydroxides biofilms. The main objective of this study was to analyze the influence of iron addition in sawdust on phosphorus adsorption. The microcosm experiment was performed with water and sediment samples from a eutrophic reservoir located in Barra Bonita/SP. Three control flasks (without bags) and 18 others as treatments (with two bags filled with sawdust, with or without previous Fe(II) addition) were assembled. The addition of iron did not promote greater phosphorus adsorption, the sawdust without previous iron addition had a total phosphorus concentration of 49 $\mu g \cdot P \cdot g^{-1}$, while the sawdust with previous iron addition had 14.4 $\mu g \cdot P \cdot g^{-1}$. The use of sawdust for the remediation of eutrophic water bodies is interesting, especially considering the low-cost and possibility of reuse as fertilizer in agriculture.

Key words: Phosphorus, eutrophication, remediation, biosorbent, iron.

1. Introduction

Anthropogenic activity due to rapid urbanization has been putting water quality at risk and, consequently, endangering the aquatic life of different worldwide freshwater ecosystems. Several studies have evaluated water quality around the world and the contribution of phosphorus to eutrophication of aquatic ecosystems and groundwater contamination [1-5].

This problem in lakes and reservoirs may have negative effects on the economy and the environment. The main causes are the intensive use of phosphate fertilizers and the inadequate disposal of industrial and urban sewage in aquatic bodies. Eutrophication is a process of degradation of lakes and other natural water reservoirs generated mainly by excess nutrients, in particular phosphorus and nitrogen [6-10].

Corresponding author: Pedro Sergio Fadini, Ph.D., main research fields: emergent contaminants in water and biogeochemistry of mercury.

The behavior of phosphorous in aquatic ecosystems is often associated with sediments characteristics, this compartment can act as a sink or source of nutrients in relationship to the water column. Sediment that presents a reddish-brown color sometimes indicates possibly the presence of biogenic iron oxides, able to adsorb phosphorus, in a mechanism where adsorption is promoted by an Fe(III) oxide-hydroxides biofilm resulting from the oxidation of Fe(II) by iron-oxidizing bacteria of the genus *Leptothrix* [11, 12].

Despite the scenario of eutrophication in water bodies, there is great concern about the depletion of phosphate rock, which can affect global food security. Some studies suggest that phosphate deposits may be depleted in the next 20-30 years, other recent estimates suggest that there will be resources for the next 100 years [13, 14]. Phosphorus is an essential nutrient for plant growth and development, so its low availability in soil can restrict crop production. The overall maintenance of food production depends on the availability and accessibility of phosphorus [15-17].

The study of phosphorus recovery techniques in eutrophic aquatic ecosystems is very important considering water scarcity and food production. The use of sawdust for removal of this excess from eutrophic systems for further use as soil fertilizer is a possible solution to ensure water and food security [18-20].

In eutrophic water bodies, phosphorus can be recovered by several techniques, but none has the objective of reusing this essential nutrient for agriculture. These techniques involve the chemical treatment with aluminum or iron salts, injections of nitrate in sediment, injections of aluminum chloride into the sediment, aluminum hydroxide, zeolite/hydrous aluminum oxide and modified clay minerals [21-25].

In 2016, Brazil had 7.84 million hectares of planted forest area, of which 1.6 million ha were of the *Pinus* species [26]. Since the sawdust is generated in large volumes by timber industry as organic waste, its use is of low cost and easy access. The great advantage of this technique for phosphorus adsorption is the possible reuse of this element as a fertilizer in agriculture.

The phosphorus adsorption by sawdust is based on the formation of Fe(III) oxide-hydroxides, that have a high phosphorus adsorption capacity. These are compounds of biogenic origin and are formed in the water column and in the surface sediments by iron-oxidizing bacteria [9, 10].

This study aimed to verify if the addition of an Fe(II) salt in the sawdust can improve the phosphorus adsorption, since the Fe(III) oxide-hydroxides biofilm can adsorb phosphorus.

2. Materials and Methods

2.1 Study Site

Barra Bonita reservoir was built to produce hydroelectricity, however, over the years it has been used for several purposes, among them leisure, fish production, irrigation, navigation and urban water supply. The reservoir is located in Barra Bonita city, São Paulo state, with geographic coordinates (SE Brazil, 21°54’20’’-23°57’26’’ S; 46°39’27’’-48°34’52’’ W). The volume of reservoir is 3.62×10^9 m^3 with total area of 310 km^2 [27].

The Barra Bonita reservoir was selected considering that this region receives water coming from two areas, the metropolitan region of São Paulo and the metropolitan region of Campinas, via the Tietê river basin and all, have serious sanitation problems. The trophic state of the Barra Bonita reservoir has been reported in several studies [28-31].

2.2 Sample Collection

A Van Dorn bottle was used to collect water samples from the sediment-water column interface and surface sediment samples were collected with a stainless steel Birge-Ekman grab sampler. In the laboratory, the interstitial water was extracted from the sediment by a centrifugation procedure described by Mozeto, A. A., et al. [32]. Water quality parameters such as pH, redox potential, turbidity, DO (Dissolved Oxygen) and conductivity in water samples were determined using a multi-parameter probe (YSI 6820 V2-2).

2.3 Bags with Sawdust

The polyester bags (7 × 6 cm) filled with 10 g of dry biosorbent were immersed in the water column in the 18 treatment microcosms. The sawdust used as biosorbent was obtained from *Pinus* species trees.

2.4 Microcosm Experiments

The experiments were conducted in 5 L glass jars that were assembled with water and sediment, both collected at the study site. The microcosm flasks were filled with 1 kg of sediment and 4 L of water. After 12 hours of stabilization, the bags with biosorbent were placed in the treatment microcosms 4 cm above the surface of the sediment. The control (water and sediment without bags) and treatment (water and sediment with bags) microcosms were stored at 22 ± 2 °C in a temperature-controlled room.

Experiments were conducted up to 240 days. Among the 21 flasks, three were used as controls (disassembled only at the end of the experiment), nine served as treatment microcosms, containing bags with iron previously added in the sawdust and nine as treatment microcosms, with bags filled with sawdust without iron addition. In the experiments using previous addition of iron to the sawdust, the spiked amount was 10 $mg \cdot Fe \cdot g^{-1}$ sawdust. In this procedure, after the iron solution addition, the sawdust was dried before being placed inside the bags.

2.5 Physicochemical Parameters

In the laboratory, the pH and redox potential were measured by a Digimed DM-2P pH meter. A YSI oximeter was used to measure dissolved oxygen. Turbidity was evaluated using a HACH-2100P portable turbidimeter.

2.6 Water Chemical Analyses

The RSP (Reactive Soluble Phosphorus), sulfate and Fe(II) were determined in the water samples, before analysis the water samples were filtered through cellulose acetate membranes, 0.45 μm porosity. In the analysis of reactive soluble phosphorus the ascorbic acid method described by APHA was used, allowing a LOQ (Limit of Quantification) of 2.4 $ug \cdot L^{-1}$. Sulfate concentration was determined by the turbidity method, using a HACH DR 2010 spectrophotometer, and the LOQ was 8.9 $mg \cdot L^{-1}$. The phenantroline method was used for determination of the Fe(II) concentration, for which the LOQ was 0.011 $mg \cdot L^{-1}$ [33].

2.7 Sediment Granulometric and Chemical Analyses

Granulometric analysis was conducted according to ABNT recommendations [34]. The total carbon, total nitrogen and total sulfur were measured using a Fisons EA1108 Elemental Analyzer. Total phosphorus was determined using the method described by Andersen, J. M. [35]. The LOQ of total P was 1.7 $mg \cdot kg^{-1}$.

Cadmium, chromium, copper, iron, nickel and zinc metals were determined according to the USEPA 3050B method [36]. The concentrations were detected by Plasma emission spectrometry (ICP OES) using an iCAP 6000 instrument (Thermo Fischer Scientific, Waltham, MA, USA). The LOQs were: Cd—0.36, Cr—1.77, Cu—0.14, Fe—13.50, Ni—0.40, Pb—1.79 and Zn—0.37 $mg \cdot kg^{-1}$ (dry weight).

2.8 Sawdust Chemical Analyses

Total phosphorus concentration was determined after the persulfate digestion method using the ascorbic acid method, with an LOQ of 4.4 $\mu g \cdot g^{-1}$ [33]. The metals were determined according to the 3050B method [36], and LOQs were Cd—0.36, Cr—1.77, Cu—0.14, Fe—13.50, Ni—0.40, Pb—1.79 and Zn—0.37 $mg \cdot kg^{-1}$ (dry weight).

2.9 Statistical Analysis

ANOVA (Analysis of Variance) was used to find significant differences among the means and to determine whether the treatment influenced in any response variables.

3. Results and Discussion

3.1 Physicochemical Parameters Determined in Field

Parameters determined for water samples are presented in Table 1.

Table 1 Parameters determined *in situ* in water collected at Barra Bonita reservoir.

Parameters	Water
Depth (m)	21.0
pH	6.5
E_H (mV)	-185
Conductivity ($\mu S \cdot cm^{-1}$)	291
Dissolved oxygen ($mg \cdot L^{-1}$)	0.14
Turbidity (NTU)	39
Temperature (°C)	27.0

Table 2 Parameters in sediment collected at Barra Bonita reservoir.

Parameters	Sediment
E_H (mV)	-160
pH	6.5
Water content (%)	78
Granulometric analysis (%)	66% clay; 17% silt

The water column presented a slightly acid pH (pH = 6.5) and a negative redox potential value, thus reducer characteristics. The high conductivity and low dissolved oxygen concentration is an indicative of sewage discharge into the reservoir. The high turbidity value was an expected result, because at collection time there was a green film present over a large part of the aquatic surface denoting the trophic state of the reservoir. Blooms of *Microcystis sp*. were described by Tundisi, J. G., et al. [30]. This serious environmental problem has also already been reported by CETESB (Environmental Sanitation Technology Company) [29]. Parameters determined for sediment samples are presented in Table 2.

The pH value of the sediment sample was slightly acid (pH = 6.5) and the negative redox potential value show reducing conditions. Clay and fine sand compose the predominant sediment thus providing a 78% water retention capacity.

3.2 Physicochemical Parameters in the Microcosms

The redox potential and pH values were determined in sediment, interstitial water and water column. Dissolved oxygen and turbidity were measured in the water column. Turbidity and dissolved oxygen concentration values are presented in Fig. 1.

The turbidity in the treatment microcosms containing iron in the sawdust was significantly higher ($p < 0.05$) than without iron addition, probably due to iron sulfide formation. This hypothesis is reinforced by the presence of a black precipitate in the water column. In this case, it is worth mentioning that even when the sulfate concentration is high, part of it can be reduced to sulfide, generating the aforementioned precipitate.

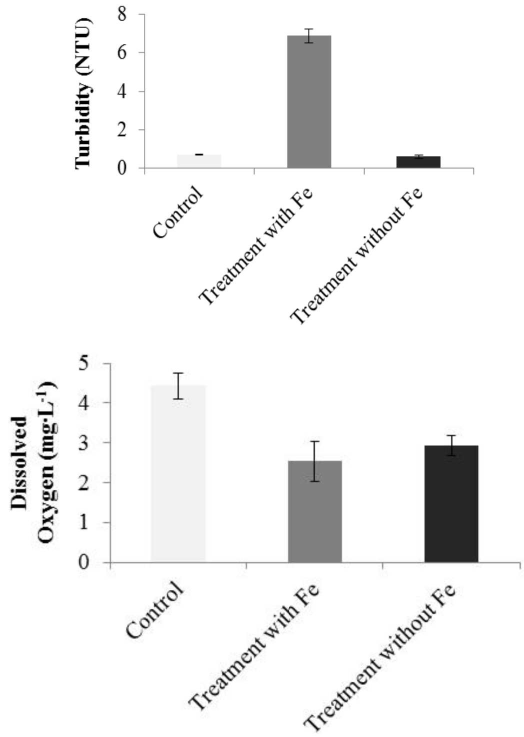

Fig. 1 Turbidity values and dissolved oxygen concentration in the water column.

Dissolved oxygen concentrations in treatment microcosms were significantly lower ($p < 0.05$) compared to the control microcosm as a consequence of the oxidation of the organic matter present in the bags filled with sawdust placed in the treatment microcosm.

Redox potential values for the water column, interstitial water and sediment are presented in Fig. 2.

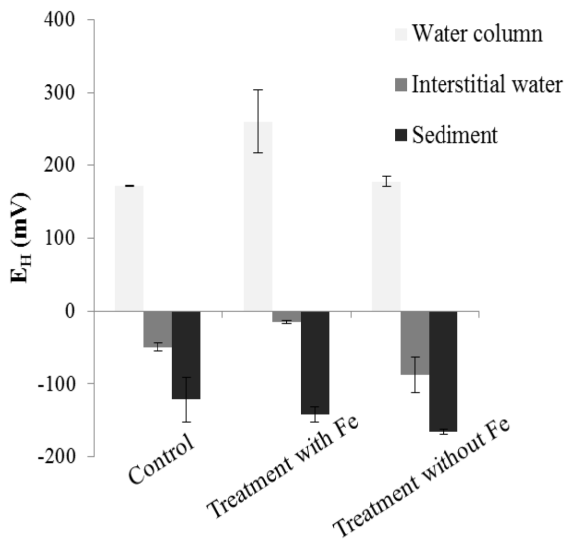

Fig. 2 Redox potential values in water column, interstitial water and sediment.

Only the redox potential values determined in the water column of the treatment with iron addition is significantly higher ($p < 0.05$) than the control, and the same was observed in relationship to interstitial water. The redox potential values for the sediment did not vary significantly ($p < 0.05$) with treatment. Throughout the microcosm experiments the reducer characteristics and the field anoxic conditions were maintained.

The pH values for the water column, interstitial water and sediment are presented in Fig. 3.

The pH values of the water column ranged from 6.09 to 6.14 for the control microcosm, from 4.84 to 5.36 for the treatment microcosm with previous iron addition and 5.40 to 6.21 for the treatment microcosm without iron. Only the sawdust with iron experiment was significantly ($p < 0.05$) lower than the control.

The pH values in interstitial water were significantly lower (p <0.05) than the control only for the treatment with iron in the experiment. The pH values in sediments that do not contain iron previously added to sawdust were significantly higher ($p < 0.05$) than the control microcosm.

3.3 Sulfate, Fe(II) and Reactive Soluble Phosphorus in the Water Column and Interstitial Water

Sulfate concentration in the water column and interstitial water are presented in Fig. 4.

In the water column of the control microcosm, the sulfate concentration was significantly lower ($p < 0.05$) than the values observed in the treatment with previous iron addition, indicating the existence of intense reducing conditions, favoring the sulfide formation. No significant differences ($p < 0.05$) were observed between the control and treatment microcosms without previous iron addition. In the interstitial water the same behavior is observed, however, the sulfate concentration is lower compared to the water column due to reduced sediment conditions.

Fe(II) concentration values are presented in Fig. 5.

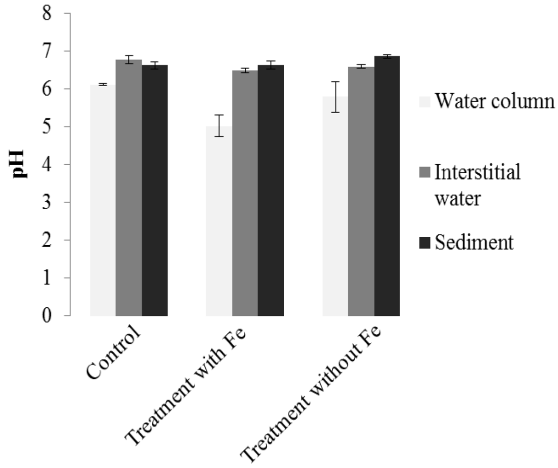

Fig. 3 pH values in water column, interstitial water and sediment.

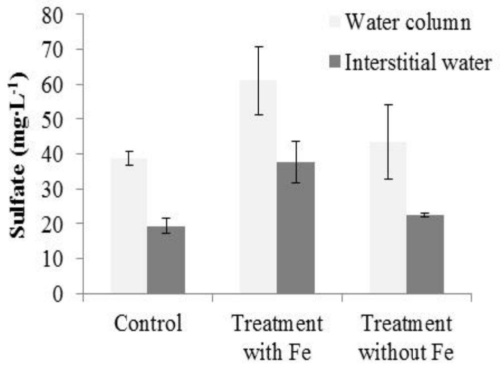

Fig. 4 Sulfate concentrations in water column and interstitial water.

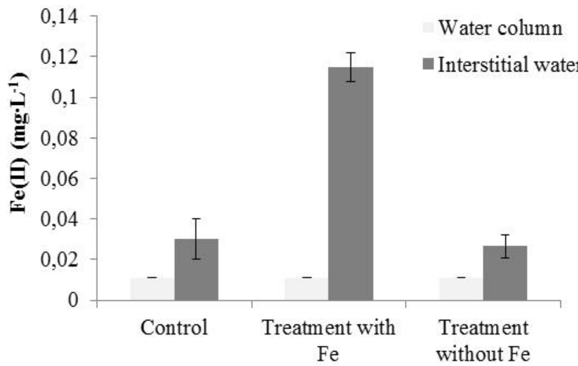

Fig. 5 Fe(II) concentration in water column and interstitial water.

In the water column, the Fe(II) values are lower than the LOQ determined by the method (0.02 $mg \cdot L^{-1}$) and there is no significant difference ($p < 0.05$) between the control and treatment microcosms. Fe(II) probably was oxidized to Fe(III), which is important for phosphorus adsorption, once that phosphorus

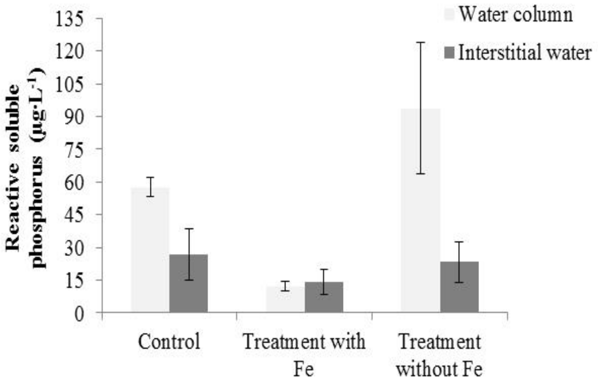

Fig. 6 Reactive soluble phosphorus concentrations in water column and interstitial water.

adsorption is promoted by an Fe(III) oxide-hydroxides biofilm resulting from the oxidation of Fe(II) [9].

The treatment with the sawdust containing iron caused a significant increase ($p < 0.05$) in Fe(II) concentration in the interstitial water, and the higher concentration of iron, compared to the values in the water column is justified by the high amount of iron present in the sediments.

The reactive soluble phosphorus concentration in the water column and interstitial water are presented in Fig. 6.

A higher reactive soluble phosphorus concentration was found in the water column and in the interstitial water of the treatment microcosms without Fe, evidencing a greater internal flow in these microcosms.

Statistical analyzes showed that treatment with iron previously added to sawdust promoted significant changes ($p < 0.05$) in the concentration of RSP present in the water column. For the interstitial water samples, no significant change ($p < 0.05$) was provoked by the treatments.

3.4 Total Phosphorus and Metals in Sediment

Fig. 7 shows TP (Total Phosphorus) concentrations in sediment.

The high TP values found in the sediments of the reservoir evidenced the eutrophication of the reservoir studied. The total phosphorus concentration in the sediment was not significantly ($p < 0.05$) influenced by the proposed treatments.

Furthermore, even after the entire incubation period, the sediment continued to present a large phosphorus stock, thus evidencing that this environmental compartment could be a source of nutrients for the water column for a long time, even after the reduction of external nutrient sources.

Metal concentrations in sediment of the microcosm experiments are presented in Table 3.

The nickel, cadmium, chromium, lead, zinc and copper metals had concentration values that did not change significantly ($p < 0.05$), so these metal concentrations in the sediment are not influenced by the treatment proposed. In treatment microcosms, the concentrations vary between 45.11 and 47.42 mg·kg^{-1} for Ni; 1.42 and 1.44 mg·kg^{-1} for Cd; 35.75 and 35.81 mg·kg^{-1} for Cr; 15.86 and 15.97 mg·kg^{-1} for Pb; 0.018 and 0.044 mg·kg^{-1} for Zn and 49.92 and 50.23 mg·kg^{-1} for Cu.

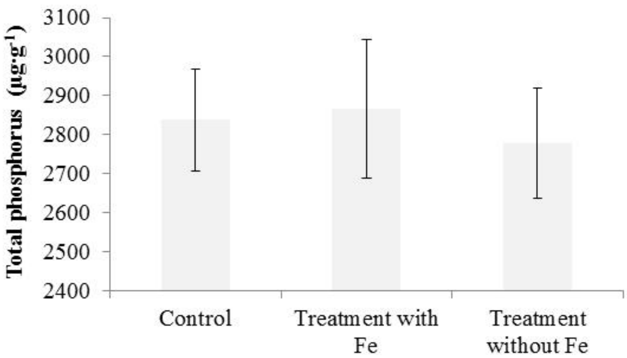

Fig. 7 Total phosphorus concentrations in sediment samples.

Table 3 Metal concentrations in sediment of microcosm experiments.

Metals (mg·kg^{-1} ± SD)	Control	Treatment with Fe	Treatment without Fe
Cd	1.47 ± 0.03	1.42 ± 0.04	1.44 ± 0.02
Cr	34.82 ± 0.96	35.75 ± 0.63	35.81 ± 0.40
Cu	51.06 ± 0.80	49.92 ± 0.46	50.23 ± 0.06
Ni	46.86 ± 1.19	47.11 ± 0.57	47.42 ± 0.03
Pb	15.61 ± 0.23	15.86 ± 0.08	15.97 ± 0.24
Zn	< 0.37	< 0.37	< 0.37
Fe	53.81 ± 2.24	52.46 ± 1.64	48.19 ± 2.01

SD: standard deviation standard deviation of replicates.

The concentrations of iron varied significantly, in treatment microcosms the concentrations vary between 48.19 and 52.46 mg·kg^{-1}. The concentrations in the treatment with previous iron addition were significantly higher ($p < 0.05$) than concentrations in the treatment microcosms without iron.

The metal concentrations determined in sediments were compared with the GVSQ (Guide Values of Sediment Quality) established by the CCME (Canadian Council of Ministers of the Environment) [37]. The TEL (Threshold Effect Level) is related to the minimal effect range within which adverse effects rarely occur, or are not expected. The concentrations above the PEL (Probable Effect Level) define the level above which adverse effects are expected to frequently occur. The TEL and PEL presented in Table 4 were used as the GVSQ.

Observing Table 3, cadmium and copper metal concentrations for control and treatment microcosms were above the TEL values, the high Cu concentrations can be related to the copper sulfate addition in the water column used to control cyanobacterial blooms.

The Ni metal concentration values in both microcosm experiments were above the PEL. Factories that manufacture stainless steel and other alloys, nickel-cadmium batteries and electrical equipment can be some probable sources of this metal [38]. Cr, Pb and Zn metals did not show concentrations higher than the threshold effect level and probable effect level values.

3.5 Metals and Phosphorus in Biosorbent

Metal concentrations determined in sawdust are presented in Table 5.

There is no legislation concerning the disposal of sawdust in soils, so the CONAMA No. 375/2006 was used to compare the results [39]. This is a Brazilian resolution, that defines criteria and procedures for agriculture use of sewage sludge generated in wastewater treatment plants, was used to evaluate the possibility of biosorbent application as a possible fertilizer.

Table 4 Values of TEL and PEL.

Metal	TEL	PEL
Pb	35	91.3
Ni	18	36
Cr	37.3	90
Cu	35.7	197
Zn	123	315
Cd	0.6	3.5

Table 5 Metal concentrations determined in sawdust.

	In natura	With Fe	Without Fe	CONAMA No. 375/2006
	Concentrations (mg·kg^{-1} ± SD, dry weight)			
Cd	< 0.36	< 0.36	< 0.36	39
Cr	< 1.77	< 1.77	< 1.77	1,000
Cu	1.24 ± 0.07	1.57 ± 0.25	0.96 ± 0.23	1,500
Ni	0.77 ± 0.06	3.88 ± 1.38	1.20 ± 0.12	420
Pb	< 1.79	< 1.79	< 1.79	2,800
Zn	5.47 ± 0.78	11.67 ± 1.05	4.73 ± 0.53	300
Fe	157.31 ± 27.30	2.16 ±147	255.49 ± 47.14	-

SD: standard deviation of replicates.
In natura: sawdust that did not have contact with reservoir water.

Analyzing Table 5, cadmium, chromium and lead metals had concentrations lower than the LOQ values. Copper and nickel were determined in the biosorbent, but there was no significant difference ($p < 0.05$) between the adsorbed concentrations, so these metals are from *in natura* sawdust. However, it was possible to observe that for the Zn concentration there was a significant increase ($p < 0.05$) in the previous iron addition experiments, the concentrations of adsorbed zinc in the sawdust was 11.67 mg·kg^{-1}. The iron metal shows a significantly increasing concentration ($p < 0.05$) in both treatments.

All metals were at concentrations below the guide values established by the CONAMA legislation, so the sawdust can be used as a fertilizer without restriction in relation the analyzed metals.

Total phosphorus adsorbed in the biosorbent is presented in Fig. 8.

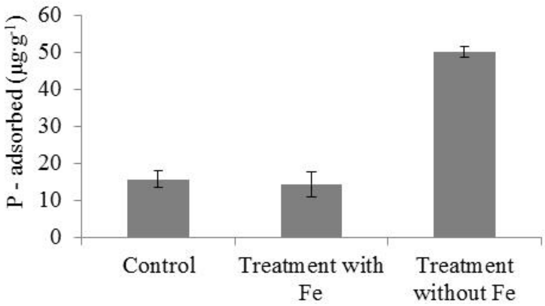

Fig. 8 Total phosphorus determined in the sawdust.

Upon analysis, it was possible to verify that the addition of iron in the sawdust did not promote higher phosphorus adsorption, since the sawdust without previous iron addition contained 49 $\mu g \cdot P \cdot g^{-1}$ in the period of 240 days. There was no significant difference ($p < 0.05$) between the control (15.8 $\mu g \cdot g^{-1}$) and the treatment (14.4 $\mu g \cdot g^{-1}$) containing sawdust with previously added iron.

Considering a mass balance where the maximum phosphorus absorbed by sawdust was 49 $\mu g \cdot P \cdot g^{-1}$, the total volume of the reservoir (3.6×10^{12} L), a mean concentration of 30 $\mu g \cdot P\text{-}PO_4^{3-} \cdot L^{-1}$ in the water column, Barra Bonita reservoir has a stock of 108 tons of phosphorus in the water column. Such a quantity would require the use of 2.2×10^6 tons of sawdust for the total removal of all the P present in the water column. The values do not show an immediate viability of this remediation technique, however, due to water scarcity and depletion of phosphate rock deposits, the use of sawdust can be considered through an increase in phosphorus adsorption.

Pantano, G., et al. [20] performed a similar study in Brazil, and the amount of phosphorus retained reached a maximum of 31.9 $ug \cdot g^{-1}$ at 159 days. It is possible that a longer exposure time of the biosorbent in the water column favors a higher phosphorus adsorption rate.

Takeda, I., et al. [19] were pioneers in phosphorus adsorption studies using sawdust, the adsorption varied between 146 and 251 $ug \cdot g^{-1}$ depending on the mass of adsorbent used in the bag.

In another study, Benyoucef, S. and Armani, M. [40] performed phosphorus adsorption experiments using sawdust in the laboratory with a synthetic solution. Several pre-treatments to the biosorbent performed by Benyoucef, S. [40] and collaborators were made which can hamper implementation of this technology on a large scale.

4. Conclusion

Experiments have shown that previous addition of iron is not necessary in the way of increased phosphorus adsorption in sawdust. This remark, coupled with the low-cost, sawdust abundance, non-adsorption of the studied toxic metals and mainly the possibility of reuse of the biosorbent in agriculture could be advantageous compared to other techniques for eutrophic environment remediation.

Acknowledgments

The authors thank the FAPESP (process 2016/00490-6) and Analitica/Thermo for ICP OES instrument.

References

[1] Hernández-Crespo, C., Gargallo, S., Benedito-Durá, V., Nácher-Rodríguez, B., Rodrigo-Alacreu, M. A., and Martín, M. 2017. "Performance of Surface and Subsurface Flow Constructed Wetlands Treating Eutrophic Waters." *Science of the Total Environment* 595: 584-93.

[2] Luo, L., Duan, N., Wang, X. C., Guo, W., and Ngo, H. H. 2017. "New Thermodynamic Entropy Calculation based Approach towards Quantifying the Impact of Eutrophication on Water Environment." *Science of the Total Environment* 603: 86-93.

[3] Nieminen, M., Sallantaus, T., Ukonmaanaho, L., Nieminen, T. M., and Sarkkola, S. 2017. "Nitrogen and Phosphorus Concentrations in Discharge From Drained Peatland Forests Are Increasing." *Science of the Total Environment* 609: 974-81.

[4] Peng, Y., Liu, L., Jiang, L., and Xiao, L. 2017. "The Roles of Cyanobacterial Bloom in Nitrogen Removal." *Science of the Total Environment* 609: 297-303.

[5] Schindler, D. W., Carpenter, S. R., Chapra, S. C., Hecky, R. E., and Orihel, D. M. 2016. "Reducing Phosphorus to Curb Lake Eutrophication is a Success." *Environmental Science and Technology* 50: 8923-9.

[6] Bai, X., Sun, J., Zhou, Y., Gu, L., Zhao, H., and Wang, J. 2017. "Variations of Different Dissolved and Particulate

Phosphorus Classes during an Algae Bloom in a Eutrophic Lake by 31P NMR Spectroscopy." *Chemosphere* 169: 577-85.

[7] Dai, W., Zhang, J., Tu, Q., Deng, Y., Qiu, Q., and Xiong, J. 2017. "Bacterioplankton Assembly and Interspecies Interaction Indicating Increasing Coastal Eutrophication." *Chemosphere* 177: 317-25.

[8] Oladosu, N. O., Abayomi, A. A., Olayinka, K. O., and Alo, B. I. 2017. "Wet Nitrogen and Phosphorus Deposition in the Eutrophication of the Lagos Lagoon, Nigeria." *Environment Science and Pollution Research* 24 (9): 8645-57.

[9] Emerson, D., and Weiss, J. V. 2004 "Bacterial Iron Oxidation in Circumneutral Freshwater Habitats: Findings from the Field and Laboratory." *Geomicrobiology Journal* 21 (6): 405-14.

[10] Takeda, I., and Fukushima, A. 2004. "Phosphorus Purification in a Paddy Field Watershed Using a Circular Irrigation System and the Role of Iron Compounds." *Water Research* 38 (19): 4065-74.

[11] Smil, V. 2000. "Phosphorus in the Environment: Natural Flows and Human Interferences." *Annual Review of Energy and the Environment* 25 (1): 53-88.

[12] Steen, I. 1998. "Phosphorus Availability in the 21st Century: Management of a Non-renewable Resource." *Phosphorus and Potassium* 217: 25-31.

[13] Iwaniec, D. M., Metson, G. S., and Cordell, D. 2016. "P-Futures: Towards Urban Food & Water Security through Collaborative Design an Impact." *Current Opinion Environmental Sustainability* 20: 1-7.

[14] Pantano, G., Grosseli, G. M., Mozeto, A. A., and Fadini, P. S. 2016. "Sustainability in Phosphorus Use: A Question of Water and Food Security." *Química Nova* 39: 732-40.

[15] Springer, N. P. 2017. "Physical, Technical and Economic Accessibility of Resources and Reserves Need to be Distinguished by Grade: Application to the Case of Phosphorus." *Science of the Total Environment* 577: 319-28.

[16] Cordell, D., and White, S. 2015. "Tracking Phosphorus Security: Indicators of Phosphorus Vulnerability in the Global Food System." *Food Security* 7: 337-50.

[17] Van Vuuren, D. P. P., Bouwman, A. F., and Beusen, A. H. W. 2010. "Phosphorus Demand for the 1970-2100 Period: A Scenario Analysis of Resource Depletion." *Global Environment Change* 20: 428-39.

[18] Ashley, K., Cordell, D., and Mavinic, D. 2011. "A Brief History of Phosphorus: From the Philosopher's Stone to Nutrient Recovery and Reuse." *Chemosphere* 84: 737-46.

[19] Takeda, I., Somura, H., and Mori, Y. 2010. "Recovery of Phosphorus from Water Bodies Using Iron-oxidizing Bacteria and Woody Biomass." *Ecological Engineering* 36: 1064-9.

[20] Pantano, G., Ferreira, J. S., Aquino, F. W. B., Pereira-Filho, E. R., Mozeto, A. A., and Fadini, P. S. 2017. "Biosorbent, a Promising Material for Remediation of Eutrophic Environments: Studies in Microcosm." *Environment Science and Pollution Research* 24: 2685-96.

[21] Cooke, G. D., Welch, E., Martin, A. B., Fulmer, D. G., Hyde, J. B., and Schrieve, G. D. 1993. "Effectiveness of Al, Ca and Fe Salts for Control of Internal Phosphorus Loading in Shallow and Deep Lakes." *Hydrobiologia* 253: 323-35.

[22] Epe, T. S., Finsterle, K., and Yasseri, S. 2017. "Nine Years of Phosphorus Management with Lanthanum Modified Bentonite (Phoslock) in a Eutrophic, Shallow Swimming Lake in Germany." *Lake and Reservoir Management* 33: 119-29.

[23] Fang, H., Cui, Z., He, G., Huang, L., Chen, M. 2017. "Phosphorus Adsorption onto Clay Minerals and Iron Oxide with Consideration of Heterogeneous Particle Morphology." *Science of the Total Environment* 605: 357-67.

[24] Li, Y. W., Fan, Y., Li, X. D., and Wu, D. Y. 2017. "Evaluation of Zeolite/Hydrous Aluminum Oxide as a Sediment Capping Agent to Reduce Nutrients Level in a Pond." *Ecological Engineering* 101: 170-8.

[25] Yamada, T. M., Sueitt, A. P. E., Beraldo, D. A. S., Botta, C. M. R., Fadini, P. S., Nascimento, M. R. L., et al. 2012. "Calcium Nitrate Addition to Control the Internal Load of Phosphorus from Sediments of a Tropical Eutrophic Reservoir: Microcosm Experiments." *Water Research* 46 (19): 6463-75.

[26] IBÁ—Indústria Brasileira de Árvores. 2016. "Relatório de Indicadores de Desempenho do Setor Nacional de Árvores Plantadas Referentes ao Ano de 2015." Accessed January 18, 2018. http://iba.org/pt/biblioteca-iba/publicacoes.

[27] AES—Eletropaulo. 2017. "Barra Bonita." Acessed November 17, 2017. http://www.aestiete.com.br/usinas/Paginas/Usinas.aspx.

[28] Abe, D. S., Sidagis-Galli, C., Matsumura-Tundisi, T., Tundisi, J. E. M., Grimberg, D. E., Medeiros, G. R., et al. 2009. "The Effect of Eutrophication on Greenhouse Gas Emissions in Three Reservoirs of the Middle Tietê River, Southeastern Brazil." *Internationale Vereinigung fur Theoretiche und Angewandte Limnologie: Verhandlunge.* 30 (6): 822-5.

[29] CETESB—Environmental Sanitation Technology Company. 2014. "Relatórios de Qualidade das Águas Interiores do Estado de São Paulo, 2014". Accessed August 16, 2017. http://www.cetesb.gov.br/agua/rios/publicacoes.asp.

[30] Tundisi, J. G., Matsumura-Tundisi, T., and Abe, D. S. 2008. "The Ecological Dynamics of Barra Bonita (Tietê River, SP, Brazil) Reservoir: Implications for Its Biodiversity." *Brazilian Journal of Biology* 68: 1079-98.

[31] Buzelli, G. M., and Cunha-Santino, M. B. 2013. "Análise e Diagnóstico da Qualidade da Água e Estado Trófico do Reservatório de Barra Bonita, SP." *Ambi-agua* 8 (1): 186-205.

[32] Mozeto, A. A., Umbuzeiro, G. A., and Jardim, W. F. 2006. *Métodos de Coleta, Análises Físico-químicas e Ensaios Biológicos e Ecotoxicológicos de Sedimentos de Água Doce*. São Carlos: Cubo Multimídia & Propaganda.

[33] APHA. 2017. *Standard Methods for the Examination of Water and Wastewater, 23rd ed.* Washington, DC: American Public Health Association.

[34] ABNT—Associação Brasileira de Normas Técnicas. 1982. "NBR 7181: Análise Granulométrica de Solos/Métodos de Ensaio." Rio de Janeiro.

[35] Andersen, J. M. 1976. "An Ignition Method for Determination of Total Phosphorus in Lake Sediments." *Water Reseaarch* 10: 329-31.

[36] EPA—Environmental Protection Agency. 1996. "Method 3050B—Acid Digestion of Sediments, Sluges and Soil." Accessed November 17, 2017. https://www.epa.gov/sites/production/files/2015-06/documents/epa-3050b.pdf.

[37] Canadian Council of Ministers of the Environment. 2003. "Canadian Sediment Quality Guidelines for the Protection of Aquatic Life." Acessed March 05, 2018. https://www.ccme.ca/en/resources/canadian_environmental_quality_guidelines/index.html.

[38] Mozeto, A. A., Yamada, T. M., De Morais, C. R., Nascimento, M. R. L., Fadini, P. S., Torres, R. J., et al. 2014. "Assessment of Organic and Inorganic Contaminants in Sediments of an Urban Tropical Eutrophic Reservoir." *Environment and Monitoring and Assessment* 186: 815-34.

[39] CONAMA—National Environment Council. 2006. "Define Critérios e Procedimentos, Para o Uso Agrícola de Lodos de Esgoto Gerados em Estações de Tratamento de Esgoto Sanitário e Seus Produtos Derivados, e dá Outras Providências." Accessed November 05, 2017. http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=506.

[40] Benyoucef, S., and Amrani, M. 2012. "Adsorptive Removal of Phosphate from Aqueous Solution by Chemically Modified Biosorbent." *Desalination and Water Treatment* 44: 306-13.