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Pb removal from water by three types of biofilters

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ABSTRACT

Introduction: As aquatic organisms are directly affected by water quality, the use and evaluation of biofilters aiming at the previous removal of Pb guarantee the adequate water physicochemical parameters to the maintenance of the organisms of interest.
Objective: This note aims to report the results of a water pre-treatment testing three types of biofilters (river gravel and two types of seashell-based media: self-collected and commercial) to evaluate their ability to absorb and consequently remove the Pb from water.
M&M: Temperature and salinity were measured using Hg thermometers and a refractometer, respectively. Commercial colorimetric test kits were used to monitor pH and the toxic ammonia concentration. The Pb determination was performed by using GF AAS analytical technique.
Results: According to results, biofilters can significantly remove concentrations of Pb from the water column. The evaluated biofilters kept the water physical-chemical parameters stable. Results support the use of these biofilters to treat water before any experiment.
Conclusion: This report may subside future studies on the use of these biofilters in other activities, such as aquaculture and waste treatment, to maintain the physical-chemical water parameters well-controlled.
Statement of Novelty: The present study has tested in laboratory conditions, three types of biofilters (river gravel and two types of seashell-based media: self-collected and commercial) to evaluate their ability to absorb and consequently remove the Pb. This report may subside studies on the use of these biofilters in activities, such as aquaculture and waste treatment, to maintain the physical-chemical water parameters well-controlled, applying low-cost biomaterials.

Introduction

Biofilters are known as any type of filter with attached biomass on the filter-media that can favor the biodegradation of pollutants by micro-organisms [1]. They are extensively used in aquaculture to control ammonia and nitrite concentrations in ornamental aquaria, pounds, and recirculation aquaculture systems [2–5]. Regarding ammonia, the absence of active nitrification in aquaculture operations or aquaria increases ammonia levels. Ammonia can quickly achieve lethal concentrations and negatively affect aquatic organisms [4,6–8]. According to Kuhn [9], ammonia and nitrite are toxic to aquatic fauna at relatively low levels (e.g., acute toxicity between 3 and 6 mg L-1 for Pacific white shrimp - [10,11]). On the other hand, nitrate is the final step in the nitrification process and has much lower toxicity than ammonia and nitrite (e.g., chronic toxicity >200 mg/L for Pacific white shrimp; [9]).

Despite other chemical parameters, few studies have assessed the use of biofilters on removing specific contaminants from water (such as metals), considering the influence of water physical-chemical parameters [12]. Tessier and Campbell [13] have proposed that according to the environmental conditions, metals may be in a reactive form, which

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can determine their bioavailability. Also, the degree of retention of metals in substrates depends on different factors such as type and amount of organic matter, cation exchange capacity, and mineral formation [14]. According to Bordon et al. [15], non-treated residues of anthropic activities can release metals such as lead (Pb) into water bodies. Plus, the previous treatment of water is essential from laboratory studies to fisheries and aquaculture activities. As these organisms are directly affected by water quality, the use and evaluation of biofilters aiming at the previous removal of Pb guarantee the adequate water physicochemical parameters to the maintenance of aquatic organisms of interest.

Concluded in 2017, the project FAPESP n. 2014/01576-6 evaluated the effects of Pb exposure through feeding and contaminated water in the blue crab *C. danae*. Before performing the exposure assays reported by Bordon et al. [15,16], a pre-treatment was developed to remove the remained metals from water. Therefore, the present study aims to report the results of tests using three types of biofilters to evaluate their influence on the seawater physical-chemical parameters and their ability to absorb and consequently remove the Pb from water in laboratory conditions.

Methods

For this study, glass aquaria were applied. The following treatments were investigated, in triplicate: control (no filter), and three biofilters (gravel- G, natural self-collected - scS and commercial seashells - cS). The commercial seashells had a standardized size (size ≥ 2mm) and the self- collected shells were sieved to suit the same size as the commercial seashells.

The aquaria size was 29.5cm x 11.5 cm x 19.5 cm. Each substrate was placed at the bottom of each aquarium. The substrate occupied the volume of 1 L, and the aquaria were filled with 3 L of water artificially salinized (sal. 30ppm), with constant aeration. Aliquots of a Pb standard solution (Perkin Elmer) were added to the salinized water to achieve the final concentration ([Pb]=0.5 μg ml^{-1}). Temperature and salinity were measured using Hg thermometers and a refractometer, respectively. Commercial colorimetric test kits were used to monitor pH (SERA) and toxic ammonia concentrations (Labcon). Experiments were performed in static conditions without any water exchange neither recirculation. After contamination, water samples were collected after 30 min (T0); 6 (T6), 12(T12), 30(T30), 36 (T36), and 48 (T48) h, considering the exposure times proposed by aforementioned project FAPESP. Water parameters were measured in triplicate according to “Standard Methods” [17].

The Pb concentration was determined in triplicate by a Graphite Furnace Atomic Absorption Spectrometer (GF AAS) Perkin Elmer, model Analyst 800. The limit of detection (LD) was calculated by according to INMETRO [18]. The validation of methodology was performed by evaluating the Pb recovery of a 0.5 μg ml^{-1} spiked solution (Recovery= 0.46±0.03 μg ml^{-1}).

Table 1
Physical-chemical parameters regarding the tested biofilters (gravel- G, natural self-collected - scS and commercial seashells – cS).

		pH	Temp.°C	Tox.Ammon(ppm)	Sal (ppm)	Pb (μg ml^{-1})
G	mean	7.6	26.3	0.012	28.6	0.02
	Max	8.6	28	0.055	29	0.13
	Min	7.3	26	0.004	27	<LD
scS	mean	7.8	24	0.007	27.6	<LD
	Max	8.6	26	0.046	28	<LD
	Min	7.3	22	0	27	<LD
cS	mean	7.9	24.3	0.006	28.9	0.02
	Max	8.4	26	0.032	29	0.09
	Min	7.6	24	0	28	<LD
C	mean	8	22	0.008	29.1	0.36
	Max	8.9	22	0.038	30	0.41
	Min	7.8	22	0	28	0.33

LD -limit of detection = 0.004 μg g^{-1}.

Results and discussion

Water physical-chemical parameters related to each treatment are presented in Table 1.

The pH range was between 7.3 and 8.9. The temperature was higher in the river gravel aquarium but remained stable in all treatments (general average 29±1°C). Salinity did not vary during the experiment (Table 1). The ammonia concentration considerably decreased in T6 for all treatments. This reduction could be justified by the action of nitrifying bacteria that transform ammonia (NH_3) in less toxic compounds such as nitrite (NO_2) [19]. However, a recent review reaffirmed that the removal of ammonia, nitrite and nitrate nitrogen in conventional biological filters requires longer times for being activated naturally, as bacterial biomass yield in treatment systems increases extremely low [20]. Thus, the obtained results do not support that ammonia decreased due to a stable biofilm. The Pb concentration observed in the control treatment was around 100% of the expected concentration (Fig. 1). The Pb concentration dropped to 0 in all biofilter treatments, probably due to adsorption. Regarding seashells, Tudor et al. [21], Egerić et al. [22] and Mahendra et al. [23] reported the importance of surface area and the presence of the organic matrix of biominerals in the water removal process. As these commercial shellfish are composed mainly by crustaceans and mollusks carapaces, the chitin presented in crustaceans carapaces can link to Pb and remove it from water. Mollusk shells can be used as a

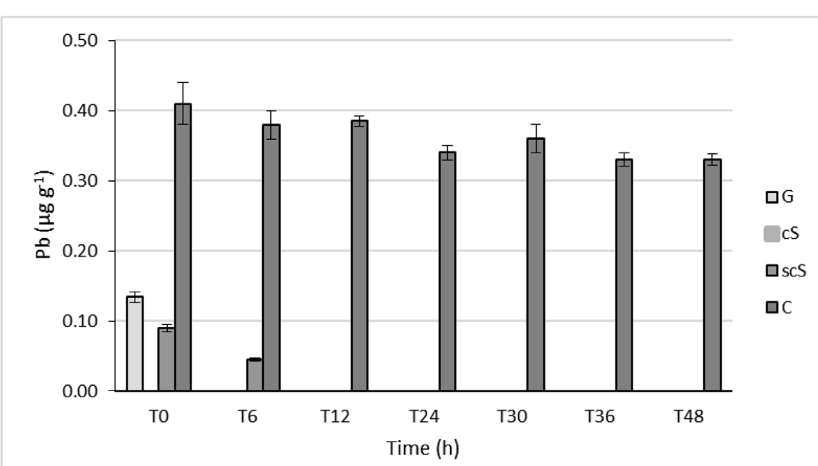

Fig. 1. Pb concentration (mean±SD, n=3) during the experiment. (C: control; scS: self-collected shells; cS: commercial shells; G: river gravel).

calcium carbonate substitute to facilitate various specific chemical reactions that may require an alkaline environment, or simply for pH control. Plus, seashells are porous and enable entrapment of particles. As the pH remained slightly alkaline, the commercial and self-collected biofilter could control the toxic ammonia form (ionized chemical species).

Few previous have assessed the Pb removal using similar biofilters. Lee et al. [24] reported that 99 % of Pb were removed in 2h after contact with a powder of Portunus trituberculatus carapaces, corroborating with Lee et al. [25]. Lee et al. [24] also observed that the initial pH of the solution (pH = 3) influences the removal of Pb and that there is no decrease in Pb removal in the presence of other metals in the solution (Cd^{+2}, Cu^{+2}, Fe^{+2} and Zn^{+2}). An et al. [26] confirmed that carapaces of Chinonecetes opilio presented the best metal removal rates, according to the removal order: Cd> Pb> Cr≥Cu. Kim et al. [27] reported that the presence of Cd^{+2} e Cr^{+3} in solution interfered in Pb^{+2} removal using the carapaces of C. opilio. Kim et al. [28] reported that there is an influence in Pb^{+2} removal when carapaces of C. opilio are previously treated with acid or alkaline reagents. Vijayaraghavan et al. [29] confirmed that Portunus sanguinolentus carapaces triturated until the size of 0.767mm could efficiently remove Cu and Co in initial concentrations and pH of 2000mg L^{-1} e 6, respectively. These authors reported that the removal rate was fast, and a major part of removal was completed in 2 h. For gravel biofilter, no information was found about Pb removal. This study is a novelty since gravel, natural self-collected and commercial seashells were applied as biofilters (and not just powders or fragments of crustacean carapaces).

Conclusion

According to results, biofilters can greatly remove Pb from the water column. The evaluated biofilters kept the water physical-chemical parameters stable, compared to treatments with no addition of biofilter. Our results support the use of these biofilters to pre-treatment of water before applied in exposure assays, guaranteeing the water quality. As the quality of water is essential in laboratory studies, the obtained results can encourage further studies for the removal of residual metals from freshwater and seawater contaminated by closed mining activities or mining tailings. Additionally, this report may subside future studies on the use of these biofilters in other activities, such as aquaculture and waste treatment, to maintain the physical-chemical water parameters well-controlled.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Isabella C. Bordon: Methodology, Data curation. **Bruno G. Campos:** Methodology, Data curation. **Caio A. Miyai:** Methodology, Data curation. **José Roberto Machado Cunha da Silva:** Data curation, Writing – review & editing. **Marycel E.B. Cotrim:** Writing – review & editing. **Deborah I.T. Favaro:** Writing – review & editing. **Denis M.S. Abessa:** Supervision, Conceptualization, Formal analysis.

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