Use of shrimp shell for adsorption of metals present in surface runoff

Aline Schuck Rech, Julio Cesar Rech, Jakcemara Caprario, Fabiane Andressa Tasca, María Ángeles Lobo Recio and Alexandra Rodrigues Finotti

ABSTRACT

This research analyzes the use of natural shrimp shell and commercial chitin for biosorption of metal ions in surface runoff. Investigation of the use of these biosorbent materials in drainage systems becomes a management measure for two extremely important issues in Brazil, fish waste management and the surface runoff quality. Methodological procedures involved treatments with different amounts of unprocessed shrimp shell and commercial chitin (5 g and 10 g) for 200 mL of a compensatory drainage mechanism (infiltration swale). The contact time of biosorbent and runoff was 24 h and removal of metal ions Fe, Mn, Zn, Cu, Ni, Pb, and Cr was studied. Tests with unprocessed shrimp shell showed high concentrations of metallic ions (Pb, Ni, and Cu) causing contamination of the environment. However, the two biosorbents presented good removal of specific metallic ions (Fe, Mn, Zn, and Cr). These results indicate the need for a biosorbent pre-treatment prior to full-scale use. We indicate the need for a more detailed investigation of water quality in the environment used for shrimp farming. Tests with commercial chitin presented satisfactory results for two concentrations tested. Tests with 10 g of commercial chitin allowed removal of all tested metal ions (Fe, Mn, Zn, Cu, Ni, Pb, Cr) with removal percentage between 6.7% and 84.4%. This efficiency may be related to the chitin's composition (shrimp, crustaceans, and crab) and to the chemical process applied to the product prior to commercialization.

Key words | heavy metals, shrimp shell, surface runoff

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INTRODUCTION

Socioeconomic development has transformed preserved areas into large urban centers. This rapid development reflects the increase in surface runoff, resulting in environmental impacts such as erosion, silting, flooding and reduction of groundwater recharge. Besides that, surface runoff may be contaminated by anthropogenic contaminants, which reach various receiving waters such as streams, rivers, lakes, estuaries, and oceans. These problems combined with a lack of government planning result in degradation of surface and groundwater resources, as well as the destruction of soil biodiversity (Tassi *et al.* 2014; Schuck *et al.* 2015). In this way, this type of urban development proves to be inadequate for the conservation of water resources and stormwater management (SWM). It is being studied worldwide (Stephenson 2001).

Due to the multiple challenges posed by increasingly stringent and expensive environmental regulations, aging infrastructure, demographic changes, degraded rivers, climate change and flood protection, many cities around the world have faced complex problems with supply of drinking water, collection and treatment of sewage and stormwater (Tasca *et al.* 2018). Measures aimed at preserving, restoring and creating spaces to compensate for the effects of urbanization are of great relevance among researchers (Fletcher *et al.* 2015). Therefore, it is imperative to manage efficiently urban stormwater runoff in order to reduce urbanization impacts.

Several solutions for SWM are adopted and applied worldwide; depending on the region, the technique has different names. In this paper, the concept adopted is

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based on best management practices and stormwater control measures, which are used to reserve or treat urban runoff to reduce flooding, remove pollution, and provide other facilities, reducing impacts of urbanization on the hydrological cycle (Ellis *et al.* 2004). They consider stormwater as a resource and use water by water storage facilities for drainage.

A well-known example of these structures is the swale infiltration. Swales are shallow, open vegetated drains/channels/ditches that are designed to convey, filter and infiltrate stormwater runoff (Deletic & Fletcher 2005). Advantages include groundwater recharge, low stream flow augmentation, water quality enhancement, and reduction in total runoff volume (Abida & Sabourin 2006). On the other hand, these infiltration structures can lead to the accumulation of contaminated sediments because they receive surface runoff with concentrations of pollutants from the basin activities. Urban drainage flow is rich in heavy metals (e.g. Fe, Al, Zn, Cu, Cd, Ni and Pb), motor oil, fuel, polycyclic aromatic hydrocarbons, herbicides, and insecticides among many other toxic compounds, which influence surface and groundwater quality (Jia *et al.* 2003).

Contamination from infiltration is probably the most common subterranean contamination mechanism, especially when groundwater levels are high, and when the soil layer is thin and soil permeability is high (Stigter & Dill 2000; Eckhardt *et al.* 2009; Kaliraj *et al.* 2015). In this way, searching for a treatment that removes organic and inorganic pollutants from surface runoff has become of interest to many managers worldwide. Numerous studies have tested biosorbent materials for removing these pollutants. Biosorption is the process of removing compounds, metal ions or other materials using an inactive (non-living) sorbent of biological origin, by means of tensile forces between removed material and biosorbent (Núñez-Gómez *et al.* 2017).

Among the materials investigated for inorganics removal, the biosorbents exhibit the best characteristics of affinity, capacity and selectivity with target metals. Biosorbents are natural, abundant, non-toxic and inexpensive materials (Franco 2004; Velásquez 2006). Traditional adsorbents used for the removal of metallic ions are considered high investment (Pontoni & Fabbricino 2012), making necessary the search for new alternatives that are financially viable. In addition to the characteristics mentioned above, researchers highlight the need to apply environmental sustainability in these processes, such as waste management and reuse at the local level (Arulvek *et al.* 2016). In this sense, different adsorbents to remove the metal ions present in the agricultural residues, wastewater, and surface runoff were tested: cassava waste (Abia *et al.* 2003); peanut shell (Dubey & Gopal 2006); orange waste (Perez-Marin *et al.* 2007); corn cob (Igwe & Abia 2007); rice husk (Krishnani *et al.* 2008); canola waste (Amouei *et al.* 2013); peel of melon seeds (Giwa *et al.* 2013); sweet potato peel (Asuquo & Martin 2016); grape pomace (Nayak *et al.* 2016), and commercial chitin (Núñez-Gómez *et al.* 2017).

Among these adsorbents, commercial chitin and chitosan are highlighted in this study. Chitin and chitosan are examples of biosorbents. Chitin is a hard, white, crystalline, nitrogen-containing polysaccharide present in exoskeletons of many crustaceans and insect arthropod mollusks. On the other hand, commercial chitin is a biopolymer resulting from the processing of shrimp, crab and lobster waste. After processing, the material presents low content of metal and calcium carbonate, allowing the neutralization of the pH. Chitosan is derived from the deacetylation process of chitin, and consists mainly of exoskeletons of crustaceans. According to Núñez-Gómez *et al.* (2017), they are an excellent adsorbent of metal ions, especially under high-strength conditions and are capable of removing elements such as aluminum, arsenic, chromium, copper, iron, manganese, nickel and zinc from the aqueous solution.

The use of natural shrimp shell was studied for effluents with acid pH and high concentrations of metals and metalloids, presenting satisfactory results (Gamage & Shahidi 2007; Núñez-Gómez *et al.* 2016, 2017). Núñez-Gómez *et al.* (2017) used commercial chitin for the removal of metallic ions (Ni, Pb, Zn, Fe, Al, Cr, Mn, Mg) present in mine waters and obtained satisfactory results for most of them. The researchers used 9.36 g/L of shrimp shells at a stirring speed of 188 rpm. However, Gamage & Shahidi (2007) used chitosan derived from crab for the removal of metallic ions present in industrial wastewater. The results were satisfactory for Hg, Fe, Ni, Pb, Cu, and Zn. It is important to emphasize the importance of laboratory analysis, and pretreatment of biosensors before the application in real scale is considered.

Despite the good results found in the initial research, the use of inorganic shrimp and commercial chitin as biosorbents for removal of metallic ions in surface runoff is new worldwide. Consolidation of these surveys can direct the use of these adsorbents in compensatory drainage mechanisms for remediation of pollutants. Aiming to contribute to and increase the consolidation in these surveys, this paper studied the biosorption using shrimp shells (without the head) and commercial chitin for the removal of metallic ions present in surface runoff from an infiltration swale in a district of the state of Santa Catarina, in the south of Brazil. To investigate the efficiencies of these biosorbents, different treatments were performed in the laboratory. There is an abundance of these materials in the coast of this state due to the fishing activity, as well as a large number of infiltration structures in this district (Caprario *et al.* 2019). In this way, the use of biosorbents in compensatory drainage structures becomes an investigative and promising field.

MATERIALS AND METHODS

In this work, the surface flow of an infiltration swale was analyzed for quantification of metallic ions. The infiltration structure is located in the Campeche District, in the Florianópolis city, southern Brazil (Figure 1). According to the climatic classification of Köppen, this region has a Cfa climate (temperate humid with hot summer) and the annual precipitation varies from 1,400 to 1,600 mm presenting an average of 160 rainy days per year. This region faces many problems in its stormwater management, especially conflicts of land use. There is an unconfined aquifer (Campeche) susceptible to surface runoff contamination and illegally disposed household effluents. To intensify this problem, there are deficiencies in the drainage system (pipes) and lack of sewage collection and treatment in this district. Therefore, a good understanding of the operation and design of the swale is necessary to fulfill its purpose. Although it has been used to control runoff for almost 15 years, there are few studies on its qualitative–quantitative functioning.

Urban Stormwater and Compensatory Techniques Laboratory (LAUTEC), linked to the Federal University of Santa Catarina (UFSC), have begun monitoring this swale since 2014. The parameters monitored are related to the quality of surface water, groundwater and soil. Preliminary results from Pacheco (2015) demonstrated the presence of high concentrations of Cd, Cu, Pb and Cr in the runoff, demonstrating the potential for contamination of the soil and, possibly, groundwater. Based on this scenario, we searched for alternatives that could be implanted within the compensatory technique, in order to retain metals from the surface runoff. As a requirement for the choice of the alternative, the non-alteration of the structure-function, the non-aggravation of the potential contamination, and the low cost of application, searching for regional materials, were considered. In a literature review on the removal of heavy metals with the use of biosorbents, two alternative materials were determined for laboratory study: shrimp shell (without the head and organic matter) and commercial chitin.

The materials selected for laboratory study meet the requirements that incorporate the concept of sustainability

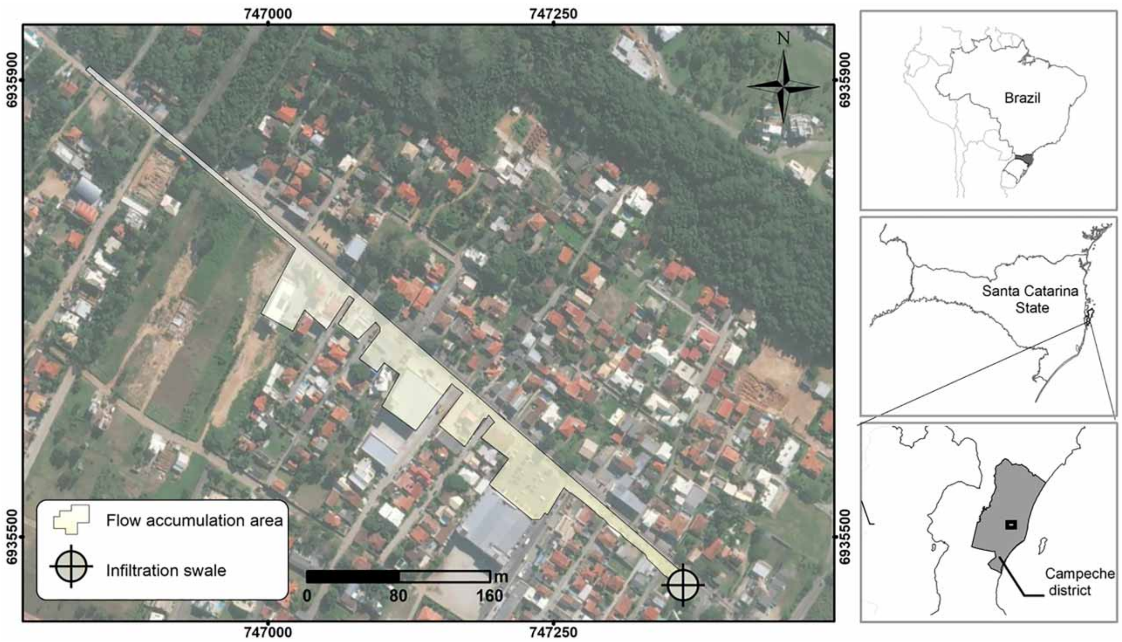

Figure 1 | Infiltration swale location.

and management of fishing waste at the local level. Initially, both shrimp shell and commercial chitin were processed and tested in the laboratory. They went through two treatments, one with distilled water and another with runoff of an intense vehicular traffic area.

Shrimp shell and commercial chitin

The procedure used for natural shrimp shells preparation was based on the methodology described by Núñez-Gómez *et al.* (2017). First, the shrimp shells (without the head) were thoroughly washed for removal of the organic matter. The shrimp shells were dried for 72 hours at 100 °C and stored at 50 °C until tests were performed. Shrimp shells were obtained from an animal food processing industry located in Laguna, 130 km from the Campeche district. The city sells shrimp for the entire state and, in the case of a high demand for biosorbents, the industry can supply the demand. The thermal procedure applied for commercial chitin was the same as for shrimp shell. Commercial chitin was purchased from a crustacean carapace industry located in northeastern Brazil because it was the only company with processed raw material available for commercialization. Shrimp shells were ground to maintain homogeneity in size. The size of shrimp shells and commercial chitin flakes varied from 0.1 to 1 cm.

Surface runoff

The tested effluent was collected in the summer of 2017, a period characterized by high intensity rainfall. After collection, the sample was preserved cooled (±10 °C) and sent to the laboratory for biosorption and quantification of metallic ions. This area is characterized by intense road flow, mixed construction uses (residential, commercial and industrial), absence of sewage collection networks, a partial drainage network and numerous infiltration structures. According to Pacheco (2015), the flow provided from this area presents considerable parcels of metallic ions, making the underground environment extremely fragile and prone to contamination. In addition, some maintenance is done in this infiltration swale (removal of excess sand, vegetation, and urban solid waste).

Laboratory tests

This research investigated the removal of metallic ions present in the surface runoff using two biosorbents, commercial chitin and unprocessed shrimp shell. These biosorbents were used to remove the following metallic ions: Cr, Pb, Ni, Cu, Zn, Fe and Mn. The surface runoff has a considerable amount of metallic ions (Pacheco 2015). The surface runoff was collected and the concentrations of metallic ions were analyzed. This experiment was called the 'standard test' in this paper. The results obtained in the standard test (surface runoff) were compared with the results obtained with biosorbents in the removal of metallic ions. The tests with 200 mL of surface runoff and 200 mL of distilled water, when applied on commercial chitin and shrimp shell, were denominated as 'treatments'.

In preliminary tests, metallic ions were found in biosorbents. In this procedure, in the treatment A, distilled water was used. In the treatment B, 200 mL of surface runoff was used to verify the sorption capacity of each biosorbent. The treatments were applied in proportions of 5 g and 10 g of each biosorbent. All samples remained in a volumetric flask for 24 hours on a low-speed stirring table (0–100 rpm). Triplicates were performed for all analyses. The procedures performed in this research are summarized in Figure 2.

To aid understanding of the experimental procedures performed in this study, the treatments A and B are detailed in Table 1.

The calibration of the pH meter was performed through an electrode potentiometer before and after each treatment with the biosorbents. In all experiments of surface runoff/biosorbent or distilled water/biosorbent, the contact time was 24 h and the temperature was monitored by a liquid thermometer (22 °C ± 2). A shaker table (Cientec model CT-145) with stirring speed of 0 to 100% or 100 rpm was used. The filtration of the sample was performed in cellulose acetate membranes with 0.45 μm porosity. For monitoring possible changes in intrinsic conditions, a blank was tested (no liquid sample of biosorbent). An aliquot was separated to analyze the concentration of metallic ions. The concentration of the metals of each sample was measured by an SM 3111B atomic/flame absorption method.

RESULTS AND DISCUSSION

Adsorption with shrimp shell and commercial chitin

First, results were obtained from the test with shrimp shell and distilled water. These results indicate that high concentrations of Pb, Ni, and Cu are present in the shrimp shell (treatment A). This initial concentration of Pb, Ni, and Cu directly affected the subsequent adsorption results of

Figure 2 | Procedures used in this research: surface runoff pattern; white test for biosorbents and treatments with shrimp shell and commercial chitin.

Table 1 | Analyses performed in the laboratory using natural shrimp shells and commercial chitin

Test	Material								Standard runoff
	Shrimp shells				Commercial chitin				
Quantity (g)	5	5	10	10	5	5	10	10	–
Treatment	A	B	A	B	A	B	A	B	B

Except for standard test (runoff), all tests were performed under the conditions of 24 hours of contact time and low agitation (0–100 rpm). In all tests the Cr, Pb, Ni, Cu, Zn, Fe, and Mn metals were analyzed.
Treatment A: 200 mL of distilled water; treatment B: 200 mL of runoff.

treatment B, procedures using 5 g of shrimp shell. In the treatment B, with an addition of 5 g of shrimp shell in surface runoff, there was an increase of 138% for Pb and 58% for Ni in the liquid medium. Cu presented opposite results, there was a reduction of 1.80% of this metal ion in the treatment. These negative results (Pb and Ni) evidenced the presence of the excess of these chemicals in the biosorbent; that is, biosorbents were not efficient in the removal and increased the concentration of these metallic ions in the solution.

After the treatments A and B (5 g of shrimp shell/distilled waters and shrimp shell/surface runoff), similar treatments were performed for 10 g of this biosorbent to verify the removal of metallic ions. The increased biosorbent amounts in the liquid-base were used with the objective of verifying the efficiency of the material tested. The results of the white tests showed the initial presence of Ni and Cu in the biosorbent. However, the values of Ni and Cu were lower than those for treatment A with 5 g of biosorbent in previous tests. The presence of these ions resulted in the contamination of the sample by 15% for Ni and 2% by Cu (results treatment B). Pb did not present alteration in this treatment, in contradiction to the treatments with 5 g. A possible justification for this change is related to filtration failures, and residues of biosorbents in the liquid sample may alter the results. The suggestion for new tests is to perform double filtration. These initial concentrations of metal ions in the biosorbents directly influenced surface water tests, reducing the potential for removal of biosorbents. These chemical elements present in the biosorbent indicate contamination of the shrimp cultivation site. There is a need for analysis and specific observations of the activities developed around the area of crustacean breeding. These metallic ions are derived from different sources: urban waters, industrial activities, and sanitary sewage.

However, the unprocessed shrimp shell presented satisfactory results in the removal of some metal ions. The best biosorption results were obtained for Fe (62.8%) and Cr (55.6%) in the test with 5 g of material. The tests with 10 g of fresh shrimp shell showed satisfactory results for Fe (63.4%) and Cr (62.2%). The results of the 5 g and 10 g treatments are shown in Table 2. The most satisfactory results are with 10 g of shrimp shell. In this way, greater amounts of biosorbent material allow better efficiencies.

The pH of the runoff increased from 6.03 to 7.45 with the addition of the shrimp shells. This increase is justified because this fresh biosorbent contains calcium and chitin, leaving the sample alkaline. An increase in the pH was also recorded in Núñez-Gómez *et al.* (2017). The two quantities of shrimp shells tested with the surface runoff presented variations of removal of metal ions and selectivity. In the research, the pH was close to neutral. Gamage & Shahidi (2007) highlight that chitin and chitosan are abundant in nature and are excellent chelators for some kinds of metal ions, especially for Hg(II), Fe(II), Ni(II), Pb(II), Cu(II), and Zn(II) of industrial effluents but at pH 7.0.

There was contamination of the sample with Pb, Ni, and Cu, and removal of Fe, Mn, Zn, and Cr ions. The concentrations of metals in the shrimp shell became a warning for the use of alternative materials without pretreatment as metallic biosorbents. Annually, numerous studies are carried out using local biosorbents found in abundance, trying to use them in the removal of pollutants, but without adequate techniques and processes, these biosorbents can transfer pollutants to the environment.

After treatments with unprocessed shrimp shell, the potential of metal ions removal with commercial chitin was investigated. This biosorbent results from the chemical treatment of crustacean shells (residues from the fishing activity) and commercialized for numerous industrial applications. The procedures applied with this biosorbent are the same as those applied to shrimp shell.

White tests were performed for 5 g and 10 g commercial chitin. The results of the tests with commercial chitin (5 g) were satisfactory for Cr (82.4%), Cu (82.2%), Zn (76.2%), Fe (83.5%), and Mn (92.9%)). The exception is Ni; this metal ion contaminated the sample by 18%. Tests with 10 g of commercial chitin allowed the removal of all tested metal ions. It was noted that this biosorbent, commercial chitin, increased the pH from 6.3 to 8.10, whereas using shrimp shell the pH went from 6.3 to 7.45. The commercial test results are shown in Table 3.

The use of commercial chitin as adsorbent achieved satisfactory results. The results of treatment B (10 g) achieved effective removal for all tested metal ions: Cr (79.4%), Pb (6.7%), Ni (37.9%), Cu (84.4%), Zn (64.6%), Fe (64.5%), and Mn (81.3%). These results may be related to the processing of crustacean shells in the commercial chitin processing industry. The chemicals used to remove the organic matter

Table 2 | Results of laboratory tests using natural shrimp shells in treatments A and B (metal concentrations in mg/L)

Measured parameter	5 g shrimp shells			10 g shrimp shells			Standard runoff
	A	B	Removal (%)	A	B	Removal (%)	B
Cr	0.003	0.016	55.60	0.004	0.014	62.20	0.033
Pb	0.020	0.081	−138.20*	0.126	0.130	7.10	0.014
Ni	0.050	0.103	−58.50*	0.093	0.125	−15.70*	0.015
Cu	0.136	0.167	1.80	0.234	0.274	−2.20*	0.034
Zn	0.190	0.248	22.50	0.359	0.432	11.70	0.130
Fe	0.421	2.161	62.80	0.789	2.262	63.40	5.390
Mn	0.158	0.162	34.40	0.199	0.245	14.90	0.089
pH initial	–	6.03	–	–	6.03	–	6.03
pH final	–	7.41	–	–	7.450	–	–

*Negative results indicate that the adsorbent contaminated the sample.

Table 3 | Results of laboratory tests using commercial chitin in treatments A and B (metal concentrations in mg/L)

	5 g commercial chitin			10 g commercial chitin			Standard runoff
Measured parameter	A	B	Removal (%)	A	B	Removal (%)	B
Cr	0.001	0.006	82.4	0.001	0.007	79.4	0.033
Pb	0.011	0.025	0.0	0.001	0.014	6.7	0.014
Ni	0.021	0.103	−18.1*	0.014	0.018	37.9	0.015
Cu	0.011	0.008	82.2	0.011	0.007	84.4	0.034
Zn	0.021	0.036	76.2	0.031	0.057	64.6	0.130
Fe	0.316	0.944	83.5	0.812	2.204	64.5	5.390
Mn	0.052	0.010	92.9	0.045	0.025	81.3	0.089
pH initial	–	6.03	–	–	6.03	–	6.03
pH final	–	7.88	–	–	8.10	–	–

*Negative results indicate that the adsorbent contaminated the sample.

present in the shells are possibly removing the metal ions identified in shrimp shell.

According to Antonino (2007), the main chitin sources are the exoskeletons of several crustaceans such as crabs and shrimp. Chitin is strongly related to proteins, inorganic material, pigments, and lipids. The process of cleaning consists in removing the impurities and there is still no standard process, but a pre-treatment of demineralization, deproteinization, deodorization, and drying is necessary. These are the main stages of the removal of the organic material (tissue portions) and other materials that can accompany the residue that take place during treatment. In the case of larger dimensions (different), it is necessary to grind the material to obtain lower particle size. The demineralization phase is used to reduce the content of raw material matter. Deproteinization reduces protein nitrogen and the demineralized raw material has a higher content of sodium hydroxide solution than is found without a stirred tank. In the deodorization process, sodium hypochlorite solution is added to the tank in which the raw material is deproteinated in order to reduce the smell from the material and remove the pigments. The final step is drying at 80 °C for 4 hours (Moura *et al.* 2006).

The results of the removal of metallic ions with the shrimp shells and the commercial chitin are compared in Figure 3. The best removal results were obtained with a concentration of 10 g of commercial chitin (with a minimum removal of 6% for Pb and maximum removal of 81.3% for Mn. It was observed that the concentrations of Ni metal ions are considerably reduced with the use of chitin, unlike the tests presented with shrimp shell, which increased the concentration of this metal in the medium. With the addition of shrimp shells to remove metallic ions, the opposite process was observed for two specific ions, Ni and Pb. The shrimp shells have an accumulation of these ions; thus they contaminate the liquid medium.

The shrimp shells were acquired from an animal feed industry in Laguna. The industry receives the rejects from the processing of raw shrimp and other crustaceans. The monitoring carried out in this research, using only shell information, indicates that the breeding sites have a high concentration of Pb, Ni, and Cu in water, emphasizing the need for research on the quality of water in breeding sites and also on the quality of the meat consumed. According to information in the literature, there are several species of shrimp and, consequently, there are variations in their eating habits. Living in nature, especially in salt water, shrimps can be detritivores, scavengers, algivores, and filterers, and can show cannibalism and commensalism (Ribeiro *et al.* 2014). In captivity, for shrimp farming, the feed is based on balanced food, supplied differently for each stage of development. Natural feeding also occurs, based on plankton and nutrients entering tanks through water circulation (Ribeiro *et al.* 2014). By feeding in this way, shrimps become bioaccumulators of pollutants. This research identified an excess of Pb, Ni, and Cu concentration in shrimp shells. Santos & Jesus (2014) describes that these pollutants are linked to anthropogenic sources, the use of fertilizers rich in metals such as Pb and Ni, and domestic sewage rich in Cu. The comparison between the shrimp shell and the commercial chitin treatment is shown in Figure 3.

As an alternative for the removal of the metals found in the natural shrimp shells, treatment methods involving the process of demineralization and deproteinization are necessary. However, these methods require large amounts

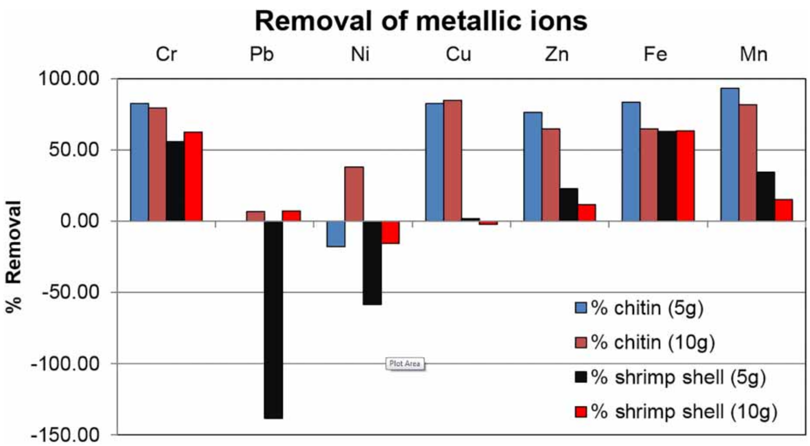

Figure 3 | Comparison between fresh shrimp shell and commercial chitin.

of acid and alkali (Barriada *et al.* 2007). Considering that the shrimp shell contains at most 20% chitin (Moret & Rubio 2003), in order to achieve the same results for the removal of metallic ions obtained by commercial chitin, larger amounts of the natural resource are required. Thus, opting for the methods of complete treatment of shrimp shell can make its use limited, given the fact that commercial chitin undergoes the same treatments with an associated low cost/price.

The residence time of the biosorbent in the liquid medium and its contact surface (particle size) are extremely determinant in the sorption capacity of the chelator for the polluting agent (complexing agent), in this case, metallic ions. In this study, a relatively long residence time was adopted, being 24 h. With a residence time of 24 h, the results were considered satisfactory, mainly in relation to commercial chitin. Gamage & Shahidi (2007) investigated different residence times and contact times between adsorbent and metal ions, defined as type 1: 20 h (adsorbent particle size 350–500 μm), type 2: 10 h (350–1,000 μm) and type 3: 4 h (1,000 μm). All exposure times presented satisfactory results. However, the greatest adsorption of metallic ions was with the contact time of type 1: 20 h. The commercial chitin size used in this research is 0.1 to 1.0 cm, a particle size relatively larger than quoted by researchers. This particle size was adopted with the aim of applying the test to commercial chitin with its actual size of commercialization.

The commercial tests of chitin evidenced its great potential as biosorbent and also the possibility of application in one of the several compensatory structures of drainage existing in the District of Campeche. In this way, studies are suggested for the application of drainage mattresses as mechanisms to remove metallic ions. However, information on the adsorption capacity, the thickness of the mattress, the retention time and the degradation of biological material needs to be studied.

CONCLUSIONS

This research investigated the use of commercial chitin and unprocessed shrimp shell as biosorbents of metal ions in the runoff. It sought to jointly resolve two particularly environmentally sensitive issues in Brazil, waste management from fishing activity and surface runoff quality. In the Brazil coastal region, fishing activities have great economic importance due to the generation of jobs and food production. The correct handling of this waste is needed. An alternative evidenced is the use of these biosorbents in the removal of pollutants present in surface runoff. Surface runoff in urban areas has characteristics of the developed economic activities of the area, and for that reason it may present concentrations of metallic ions that are toxic to the environment.

Thinking about sustainability, this research addressed the innovation allied to waste management and the use of shrimp shell to remove metallic ions present in the surface runoff. Initial tests indicated high concentrations of metal ions in unprocessed shrimp shell, increasing the final concentrations in surface runoff, mainly for Pb and Ni. However, satisfactory results were found for Cr, Cu, Zn, Fe, and Mn.

Tests with commercial chitin showed better results in the adsorption of metals, probably due to the industrial processing of crustacean shells, the main source of raw material. The processing of the shells involves products for the bleaching of the residues; in this process there is the partial elimination of contaminants, especially the metallic ions. The use of commercial chitin also raised the pH; this factor can avoid the mobility of metallic ions in the soil.

In general, good metal ion removal results of commercial chitin suggest its application as a full-scale biosorbent, e.g. as a draining mattress in an infiltration swale. This application may indicate the effective functionality of this compensatory technique. However, natural shrimp shells cannot be used in metallic ions removal without a pre-treatment. The shrimp shell tested had excessive amounts of metal ions (Pb, Ni, and Cu), which resulted in the contamination of the sample, affecting the results of the treatments applied. Further research on water quality in shrimp breeding environments is needed, due to the shrimp's ability to absorb undesirable substances in the water. Shrimp (sea) crayfish may be receiving unwanted pollutants (domestic or industrial sewage), affecting raw material quality.

More repetitions with biosorbents are suggested for future tests. In this case, the use of commercial chitin showed the best results except for Pb and Ni. This low removal may be related to effective care during the treatments, as it is a determinant for results, mainly with the filtration process for biosorbent residues removal. We observed in this research that increasing the amount of biosorbent in effluent consequently increased the metallic ions removal. In this way, tests with larger quantities can also be investigated. Another measure that can be investigated is the contact time of biosorbent with effluent. Tests with a contact time of more than 24 hours can increase the effectiveness of biosorbent and identify maximum capacity of pollutant retention.

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