REVIEW ARTICLE

CRUSTACEAN WASTE SHELLS AS ADSORPTION MATERIALS FOR HEAVY METALS IN AN AQUEOUS SOLUTION

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ABSTRACT

Laguna de Bay is one of the country's major lakes, providing a third of the fish consumed by Metro Manila's 16 million residents. It also provides support for agriculture, industry, and hydropower generation, as well as providing a welcome respite for many Filipinos. However, because of the lake's importance, it is threatened by a variety of issues, including pollution. Heavy metals such as mercury and lead are present in high concentrations in the lake. And these heavy metals may persist in fish, water, air and the human body. As a result, an adsorption technique for heavy metal removal in an aqueous solution was investigated. As an adsorbent, the produced chitosan from crustacean waste shells was employed. The study's parameters were contact time, adsorbent quantity, and pH. Results showed that 0.5 g of chitosan has a higher absorption rate of 99% in 500 mg/L solutions compared to 1.0 g of chitosan with an adsorption rate of 98%. In terms of contact time, 60 minutes showed almost 100% adsorption rate while 120 minutes was 98%. With increasing pH, the amount of metal adsorption rises. This developed chitosan from crustacean waste shells indicates high capacity as adsorbent materials for heavy metals. As a result, it appears to be a viable material for water treatment.

KEYWORDS

Adsorption, crustacean waste shells (chitosan), heavy metals

1. INTRODUCTION

The most popular crustaceans are shrimp and crabs. However, the seafood industry's shell waste is becoming a rising problem, posing substantial environmental and health risks. Empty seashells are usually discarded as rubbish since they have no value to people. Empty shells are tossed everywhere, adding to the massive amounts of solid waste in the environment. According to R.A. 9003, also known as the "Ecological Solid Waste Management Act of 2000," National research and development initiatives for improved solid waste management and resource conservation techniques, more effective institutional structures, and indigenous and enhanced trash reduction, collection, separation, and recovery shall be promoted by the State's policy. In the Philippines, most of the crustacean waste is used as fertilizers. However, there were studies that some crustacean shells could be an effective biosorption of heavy metals in surface water. The use of Philippine mud crab (*Scylla serrata*) and mussel (*Perna viridis*) shells for lead and chromium adsorption is successful, according to (Adornado, 2018). She discovered that these crustaceans have chitin, which permits the metal to be removed from solutions, during her research.

The non-toxic qualities of crustacean shells make them a good bio sorbent. Both chitin and chitosan may be acetylated to produce metal complexes, and both are organic compounds. (Cabanban, 2018). The findings of highly deacetylated chitosan as an excellent low-cost heavy metal adsorbent material for water removal were reported in the Asian

Journal of Physical and Chemical Sciences on March 7, 2018. The potential of biological materials to acquire heavy metals from wastewater via physical pathways is known as bio-sorption (Kumari, 2017). Heavy metals, usually referred to as trace metals, are among the most persistent contaminants found in wastewater. High levels of heavy metals discharged into water bodies have a variety of environmental and health consequences (Oghenerobor, 2014). Lead, which is considered a natural poison, is one of the most dangerous metal ions. The main sources of lead pollution include factories, metal recycling, lead-acid batteries, and pipelines (Wani et al., 2015).

Its ingestion can harm the human body's reproductive, renal, hematopoietic, and central neurological systems (Assi, 2016). There are many heavy metal wastewater treatment methods have been developed so far, including chemical precipitation, ferrite method, ion exchange, membrane separation, electrochemical method, and adsorption. Adsorption is one of these approaches that is frequently used in the treatment of heavy metals due to its ease of use, high efficiency, and low cost. The key to heavy metal wastewater treatment by adsorption is the performance of the adsorbent (Liu, 2018; Khan et al., 2011). Metal ions can be entirely removed from industrial effluents using biopolymers. Cellulose, chitin, chitosan, lignin, alginate, and carrageen are among the biopolymers in this category. Recently, cellulose and chitosan have been proposed as suitable absorbents to replace activated carbon in the process of removing contaminants from wastewater (Olivera et al., 2016).

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Chitosan's functional groups, such as hydroxyl and amino, make it even more appealing as an adsorbent for metal contaminants and insecticides (Dehaghi et al., 2014). Chitin, after cellulose, is the second most abundant biopolymer found in nature (Yeul, 2013). The efficacy of the natural materials chitin and oyster shell powder (OSP) to remove saxitoxin (STX) from water was examined (Melegari, 2012). Adsorption reactors containing 200 mg of adsorbents and known STX concentrations in pH 5.0 or 7.0 solutions were made and incubated at 25°C with an orbital shaker spinning at 200 RPM. The adsorption isotherms were studied after 48 hours, and the results revealed a decrease in STX concentrations in a variety of solutions (2–16g/L). Within the concentration levels tested (> 50% over 18 hours), chitin and OSP were found to be effective adsorbents with a high capacity for removing STX from aqueous solutions. As contact time increased, the rate of STX removal for both adsorbents dropped. pH influenced the adsorption equilibrium, according to the data.

In an aqueous media, clam shell remains, and sewage sludge were combined to form excellent phosphate removal adsorbents (Souza et al., 2018). The adsorbents were described before and after adsorption testing, and the adsorption equilibrium and kinetics were investigated. Phosphate removal was obtained in samples prepared with 0.1 X 1.0, where X corresponds to sewage sludge/clam shell mass (Mishra, 2014). A study was conducted to determine how to make chitosan from shrimp shells. Chitosan, a natural biopolymer comprised of a linear polysaccharide containing a (1–4)-linked 2-amino 2-deoxy bD glucopyranose, was created via deacetylation of chitin, one of the essential structural elements that forms the exoskeleton of crustacean shrimps. Using an atomic absorption spectrophotometer, the heavy metal removal efficiency of produced chitosan was measured. Fe (II), Cr (IV), Cu (II), and Zn (II), were found to be successful at removing metal ions from industrial effluent using chitosan.

The study investigates the possibility of employing crab shell chitosan as a low-cost biosorbent for heavy metal removal from aqueous solutions in an adsorption filtering system (Rana, 2009). Chitosan was created by treating chitin with a strong alkali solution under reflux conditions, and chitin was removed from crab shells before being decalcified and deproteinized. The heavy metal concentration was determined using a spectrometric (AA and UV) technique. According to the findings, produced chitosan had superior removal performance for Mn, Cd, and Zn, while removal efficiency for Co, Ni, and Fe was satisfactory, but it had the least performance for Pb and Cr. Studies mentioned above shown that a developed chitosan from crustacean waste shells has high potentials of removing metals from wastewater. However, the researcher did not find any literature that used both shrimp and crab to developed as chitosan. That is why the present study investigated the high capability of using both shrimp and crab as developed chitosan as adsorbent material in removing lead in an aqueous solution. This data will be beneficial for future system design applications in the treatment of real waste effluents.

2. OBJECTIVES OF THE STUDY

The general objective of this study is to determine the ability of crustacean waste shells produced as chitosan as an adsorption material for heavy metals such as lead (Pb) in an aqueous solution. Its goal is to determine the impact of contact time, adsorbent amount, and pH level on the adsorption process of chitosan.

3. MATERIALS AND METHODS

This experimental study was conducted last March to September 2020 in LSPU Research Laboratory Los Baños, Laguna. Adsorbent were made from the crustacean waste shells of shrimps and crabs. These were obtained from the different seafood restaurant in the first district of Laguna, Philippines. The shells were washed thoroughly and dried under the heat of the sun for 12 hours. The development of chitosan was adopted with some modification (Islam et al., 2014). At 100 degrees Celsius for 5-6 hours, a 1.25 gram of Chitin was added to 50 ml of 40% NaOH. After draining NaOH, the chitin was washed multiple times with cool potable water before being dried in the oven for 8 hours. The final step was to pulverize the product and package it as chitosan. Laboratory test was conducted for the water that undergone treatment with the crustacean shells. The change on the value of the dependent variable was assessed. There were at least 3 trials to ensure the validity of the result. Water samples was tested for pH before and after adsorption process using pH meter. While adsorption of the lead (Pb) was tested using Atomic Adsorption Spectrophotometer- 300 (SPAA-300).

3.1 Adsorbent Dosage Studies

In each experiment, 500 mg/L lead solution were placed together with a

fixed mass of adsorbent chitosan (0.5 g and 1.0 g) at the optimum pH. Samples were obtained after 60 minutes and 120 minutes.

3.2 Adsorption Studies

The pH, and heavy metal lead (Pb) of the aqueous solution was tested to determine the effectivity of the crustacean's shells as adsorbent material. The following are the standard procedures for determining pH, and heavy metal such as lead (Pb):

a). Water samples was tested for pH before and after adsorption process using pH meter (EPA, 2010). Water quality analysis method). Water samples were tested for heavy metal such as lead using Atomic Adsorption Spectrophotometer- 300 (SPAA-300). After shaking the container of the sample, nitric acid will be added to 1 litre for acid digestion and filtered to 50 ml to detect the trace of metal using AAS technique.

4. RESULTS AND DISCUSSION

4.1 Effect of pH

With increasing pH, the amount of metal adsorption rises. At pH 4, the highest adsorption occurs. At a pH of 3.4, the least amount of adsorption occurs. This result was the same in the study of rate of adsorption increases as the pH value increase (Murrieta, 2014). At low pH, there was less adsorption competition between protonated amino groups, metal ions, and hydronium ions. Meanwhile, the pH rises due to a decrease in positive sites on the adsorbent's surface, which reduces their electrostatic repulsion with the iron ions.

Figure 1: Effect of pH on % adsorption of lead by crustacean waste shells, adsorbent dose= 0.5 g, contact time = 60 minutes.

4.2 Effect of contact time

Effect of contact time was observed on adsorption of lead (Pb), chitosan as adsorbent. Percent adsorptions increase at 60 minutes, after this it starts to decrease slowly at 120 minutes. Desta investigated how contact time affects metal adsorption (Desta, 2013). It was thought to be one of the most important aspects of the batch adsorption process. Within 60 minutes, the initial adsorption rate had rapidly increased, and the maximum removal efficiency had been achieved. However, there was no significant change in equilibrium concentration after increasing the contact period.

Figure 2: Effect of contact time on % adsorption of lead by crustacean waste shells, adsorbent dose= 0.5 g, contact time = 60 minutes and 120 minutes.

4.3 Effect of adsorbent dosage

The adsorbent doses vary from 0.5 and 1.0 g. Results showed that 0.5 g amount of chitosan percent of adsorption is higher compared to the percent adsorption of 1.0 g chitosan. This result was same in the study reported that when adsorbent dose increases it did not change the rate of removal (Rahmanifar, 2013). A dosage range of 0.5–1.5g, a 98 % of removal pesticide was found. This was attributable to the fact that with greater doses of sorbents 0.5 g, the active sites available on the nanocomposite were diminishing (Rahman, 2012; Marzuki, 2019). The surface area that was fully active increases as the composite dosage is increased (Ponce, 2017; Rana 2009).

Figure 3: Effect of the amount of adsorbent on % adsorption of lead by crustacean waste shells, adsorbent dose= 0.5 g and 1.0 g. contact time = 60 minutes

5. CONCLUSION

Conclusions are drawn from the above results and discussion:

1. Crustaceans waste shells developed as chitosan is a cheap and effective adsorbent for the adsorption of lead (Pb) from aqueous solution.
2. The maximum adsorption of lead (Pb) by chitosan was observed at pH 4, contact time 60 minutes, and adsorbent dose 0.5 gram at 500 mg/L lead solution.
3. This research supports the study that shrimp shells can remove heavy metals in an aqueous solution. Likewise, this present study contribute to the study that the use of waste crab shells to remove heavy metals such as Cr(VI) from aqueous systems is a cost-effective and environmentally friendly option. However, this study shown that the removal efficiency of this chitosan from crustacean waste shells of shrimp and crab (99%) is better than that of chitosan from shrimp shells only with a removal efficiency of 59.33%. Study found out that removal efficiency of lead from prepared chitosan of crab shells were not satisfactorily observed which is in contrast of what the present study was observed. Therefore, further studies are recommended using the combination of shrimp and crab prepared as chitosan in removing heavy metals in the real wastewater under real environment condition.

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