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Use of ground crawfish shells for the removal of chromium in solution ☆

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ABSTRACT

Crawfish shells are an abundant waste product that has the potential to remediate contaminated bodies of water. This study demonstrates that ground crawfish shell could be used as an effective biosorbent material for the treatment of chromium in contaminated aqueous solutions. Phase I experiments determined that the adsorption was completed within 2 h. For the time periods examined it could be concluded that the maximum chromium adsorption occurs within the first 2 h. Phase II experiments demonstrated that chromium adsorption increased with sample volume and concentration, however the efficiency decreased with increasing sample volume for the relative high concentrations of chromium. Phase III experiments showed that chitin is a major constituent for biosorption of chromium and likely other metals in crustacean species including crawfish. Salinity experiments showed that salt (sodium chloride) at the 30 ppt (parts per thousand) concentrations does not affect the crawfish shell ability to adsorb chromium. The pH was the most important factor for chromium adsorption by the crawfish powder. Chromium adsorption increased with increasing pH. The presence of lead ions did not significantly interfere with the adsorption of chromium ions onto the crawfish shell powder for the relatively high concentrations examined. However, for relatively low concentrations the chromium adsorption was somewhat suppressed by the lead ions.

1. Introduction

The surface of the earth is approximately 70% water (oceans, lakes and rivers) and is most often the last stop for metal ions originating from a variety of sources including industrial (accidental or poorly enforced environmental laws) and anthropogenic (fires, volcano eruptions and other weather related phenomena). The need to remove metal ions from these aqueous solutions is obvious due to their (negative) impact on seafood and ultimately on the intake of this source of food for many of the world's population. The most common or conventional means of removing metals from aqueous solutions include chemical precipitation, evaporation, ion exchange, cementation, electrolysis and reverse osmosis. However, these techniques can be inefficient and frequently not cost-effective. In the last two decades or so, a new technique of biosorption has been proposed and investigated to remove but also recover many metals including chromium [1]. The removal of metals ions from an aqueous solution through binding to various biomasses has been referred to as biosorption.

Several materials have been proposed for biosorption including, algae, oysters, bacteria, yeast and various plants [1]. One group that has shown promise is crustaceans in particular crab (crabshells) [2]. One further potential material in this group is crawfish (*Procambarus clarkii*), in particular crawfish shells. Several projects on absorption of metals by live crawfish showed its potential for absorption of selected metals [3–5]. In southwest Louisiana approximately 120 million lbs of crawfish were collected during the 2010 season, typically January to June (latest figures available). A grade one crawfish weighs approximately 1.5 oz (approximately 40 g) with around 15 to 20% as edible meat and the remaining exoskeleton of approximately 100 million lbs discarded, most frequently in rubbish dump. Clearly this is wasteful and given the green chemistry climate prevailing in the world, the utilization of this material could be both economically and environmentally important.

This work presents an investigation of ground crawfish exoskeleton for potential in removing chromium from aqueous solutions and is a continuation and extension of previous work initiated in this laboratory [6]. Chromium is considered an environmental pollutant because it is heavily used in different industrial settings. Therefore, it is commonly found in both soil and water, where both can become easily contaminated. However, unlike most metals chromium is different because its toxicity depends on its valence state [7].

Crustacean species display similar physical characteristics and there is also a similarity in the waste products (shells) of these species. In crawfish the chitin content is 23.5%. Chitin is found in the exoskeletons [8]. Additionally, the exoskeleton contains calcium carbonate and protein. Chitin is considered the main component in shells that allows metal removal from solutions because it contains functional groups such as amines, and hydroxyls. Chitin is a high-molecular weight

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polymer, which is insoluble in all mediums except for concentrated mineral acids. Chitin is considered environmentally friendly because it is considered nontoxic. The important adsorption mechanism for chitin is via dipole and electrostatic interactions. Chitin forms strong complexes with metals; therefore it is an important constituent for removing metals from the surface to deep waters in oceans [9]. The structure of chitin is shown in Fig. 1.

Vijayaraghavan et al. [9] conducted experiments using crab shell to determine if the particle size affects the uptake capacity and removal efficiency of metals. They determined that smaller particles provided much more surface area and as a result, those particles displayed higher metal uptake and removal efficiency. Low biosorption capability was experienced for the largest crab shell particle size [9].

The pH also plays a role in the biosorption process of metals. Generally, pH has a profound influence on adsorption of metals. However, there are cases where the pH does not significantly affect the adsorption capability of the sorbent [10]. Vijayaraghavan et al. performed adsorption experiments under several different pH conditions using crab shells. They reported that when the crab shell particle dose and agitation speed remained constant, the metal uptake was affected if the pH changed. They observed that as the pH increased the metal uptake increased as well. Many metal complexes in solution have a tendency to decrease their solubility when the pH increases. The sorption increases when the pH decreases. Therefore, it is important to find the optimum pH for metal complex solution [9].

It was observed for crab shell particles that the dose also affects the biosorption. This phenomenon was observed for cobalt and copper metals in a packed column of crab shells. It was determined that the removal efficiency improved when the biosorbent dosage increased. This phenomenon can be explained by the increased biosorbent surface area, which in turn results in increasing the number of binding sites. However, it is sometimes observed that the metal uptake decreases when the biosorbent dosage is increased, which is believed to be attributed to several factor due to complex interactions. The metal ions are not able to sufficiently bind with all of the exchangeable sites of the biosorbent, resulting in low metal uptake [11].

2. Methods and materials

2.1. Sample collection/preparation

Crawfish were collected from a farm in Southwest Louisiana and euthanized as described previously [5]. The tailmeat was removed and remaining skeletal rinsed in de-ionized water and stored at 4 °C prior to experimentation. The crawfish exoskeleton was ground in a mortar and pestle to a one hundred and fifty mesh size.

2.2. Instrumentation

Chromium determination was performed using Varian 715-ES (Varian, Inc., Walnut Creek, California) inductively coupled plasma-optical emission spectrometer (ICP-OES). A detailed description of the instrument, operating parameters for all metals determined in this work, calibration, and quality control/quality assurance program are detailed and described elsewhere [3–5]. A detection limit for chromium of around 1 μg/mL at a wavelength of 267.176 nm was obtained. Determinations of chromium in the samples were performed in triplicate with precision of around 0.5% or better.

The pH was measured using a Eutech Instruments (Cole-Parmer Instruments Company, Vernon Hills, Illinois) pH meter with appropriate calibration.

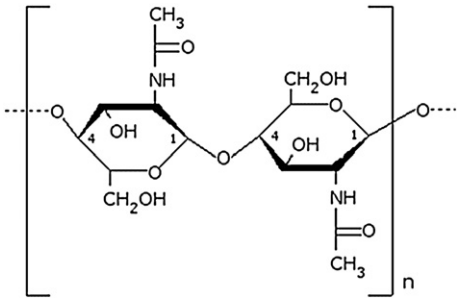

Fig. 1. Structure of chitin.

2.3. Procedure

Ground crawfish was added to aqueous solutions of chromium, with different volumes and concentrations. Initially, the optimum contact time was established before proceeding to the subsequent experiments. Environmental conditions such as pH, salinity and selected co-ion (lead) were also examined to determine the effect on the crawfish adsorption. Since crustacean species exhibit similar components, commercially available ground shrimp chitin (Sigma Aldrich, St. Louis, Missouri) was used for comparison purposes.

Chromium or chromium/lead contaminated water samples were prepared to yield specific concentrations, and in some experiments they were buffered to yield specific pH's or to desired salinity concentrations.

Typically a solution was prepared by dissolving accurately approximately 0.3849 g of chromium nitrate $Cr(NO_3)_2 \cdot 9\ H_2O$ in a known volume with deionized water to yield a chromium concentration of 100 μg/mL. Experimental trials were performed with dilutions of this solution to prepare different chromium concentrations and volumes. The volumes that were used were 250 mL, 500 mL and 1000 mL.

To investigate whether chromium absorption by the crawfish shell would be affected by pH, chromium contaminated aqueous solutions were prepared with buffer solutions with pHs of 5.5, 7.0 and 9.0. A 0.10 M acetate buffer was prepared by mixing 7.67 g of sodium acetate (Fluka anhydrous) and 0.91 mL of acetic acid in a 1-liter flask and diluting with deionized water. A 0.10 M of Tris buffer was prepared by mixing 12.1114 g of tris(hydroxymethyl)methylamine (Sigma Chemical Company, St. Louis, Missouri, 99.0–99.5%) and 4.61 mL of hydrochloric acid (Fisher Scientific) in a 1-liter flask and diluted with deionized water. A 0.10 M boric acid/NaOH buffer was prepared by mixing 6.55 g of boric acid (Sargent-Welch Powder, Technical) and 2.0 g of sodium hydroxide pellets, (97+%, A.C.S. reagent) in a 1-liter flask and diluted with deionized water. The calculated pH values for the buffer solutions were verified using an Oakton Waterproof pH tester, which were calibrated using Thermo Scientific Orion pH buffers 4.01, 7.00, and 10.01.

A stock solution of 100 μg/mL of chromium was prepared by using 0.3848 g of chromium nitrate with the acetate buffer to a volume of 500 mL. The previous steps were repeated for the remaining buffers.

After the buffered stock solutions were prepared they were used to make 2 μg/mL and 8 μg/mL solutions of chromium from the stock solution to a 1-liter volume with the appropriate buffer solution.

To investigate whether salinity affects the absorption by the crawfish shell uptake sodium chloride (99+%, A.C.S. reagent) and chromium nitrate solutions were prepared. A 15 mg/mL solution of NaCl was prepared by measuring 30 g of NaCl into a 1-liter volumetric flask and diluted with deionized water. A 30 mg/mL solution of NaCl was prepared by measuring 60 g of NaCl into a 2-liter volumetric flask and diluted with deionized water.

A stock solution of 100 μg/mL of chromium was prepared using 0.3848 g of chromium nitrate. The chromium nitrate was then placed into a 500 mL volumetric flask and diluted with the 15 mg/mL NaCl solution to the 500 mL mark. The previous steps were repeated for the 30 mg/mL solution.