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The use of raw and acid-pretreated bivalve mollusk shells to remove metals from aqueous solutions

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ABSTRACT

Heavy metal removal from industrial wastewater is not only to protect living organisms in the environment but also to conserve resources such as metals and water by enabling their reuse. To overcome the disadvantage of high cost and secondary pollution by the conventional physico-chemical treatment techniques, environmentally benign and low-cost adsorbents are in demand. In this study, the use of raw and acid-pretreated bivalve mollusk shells (BMSs) to remove metals from aqueous solutions with single or mixed metal was evaluated at different BMSs doses, pH and temperatures in batch shaking experiments in laboratory conditions. When the BMSs were used to treat $CuSO_4{\cdot}5H_2O$ solution, the copper sorption capacities of the raw and acid-pretreated BMSs were approximately 38.93 mg/g and 138.95 mg/g, respectively. The copper removal efficiency (CRE) of the raw BMSs became greatly enhanced with increasing initial pH, reaching 99.51% at the initial pH 5. Conversely, the CRE of the acid-pretreated BMSs was maintained at 99.48–99.52% throughout the pH range of 1–5. Furthermore, the CRE values of the raw and acid-pretreated BMSs were not greatly changed when the temperature was varied from 15 °C to 40 °C. In addition, the CRE value of the raw BMSs was maintained for 12 cycles of sorption–desorption with a CRE of 98.4% being observed in the final cycle. Finally, when the BMSs were used to treat electroplating wastewater, the removal efficiencies (REs) of the raw BMSs were 99.97%, 98.99% and 87% for Fe, Zn and Cu, respectively, whereas the REs of the acid-pretreated BMSs were 99.98%, 99.43% and 92.13%, respectively. Ion exchange experiments revealed that one of mechanisms for metal sorption by the BMSs from aqueous solution is related to ion exchange, especially between the metal ions in the treated solution and Ca^{2+} from BMSs. Infrared absorbance spectra analysis indicated that the acid pretreatment led to occurrence of the groups (i.e. –OH, –NH, C=O and S=O) of negative charge in treated BMSs. Scanning electron microscopy revealed that acid pretreatment enabled the used BMSs to form the flake-shaped structure with smooth surfaces that can supply a better interface for binding metal ions.

1. Introduction

Heavy metal pollution is currently one of the most serious environmental problems worldwide. It is important to remove heavy metals from aqueous solutions such as electroplating waste water to protect living organisms in the environment, as well as to conserve resources such as metals and water by enabling their reuse. To date, several methods to remove heavy metals from aqueous solution have been developed including chemical precipitation and electrochemistry, ion exchange, membrane technologies, and the use of activated carbon as well as industrial, agricultural and fishery by-products [1,2]. However, chemical precipitation and electrochemistry, ion exchange, membrane technologies and activated carbon adsorption are extremely expensive and lead to secondary pollution and/or produce a large amount of sludge that is difficult to treat [2]. In addition, generally speaking, chemical precipitation and electrochemical treatments are ineffective, especially when the metal ion concentration in the aqueous solution is between 1 mg/L and 100 mg/L [2]. The use of microorganisms as biosorbents has many advantages over the aforementioned methods [2], but they do not allow separation of the metals from solution if the removal process is operated continuously or performed in dynamic continuous-flow sorption systems. Even though the problems of separation associated with microbial removal systems can be solved by immobilization, such immobilization operations increase the cost of remediation and

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can result in many problems associated with desorption [3]. Due to the increasing consciousnesses of cost effectiveness and public environmental protection, lower-cost, more efficient and safer absorbents for the treatment of industrial wastewater contaminated with heavy metals are now in demand. To date, many such absorbents have been studied, including chitosan, zeolites, clay, and waste products from industrial operations such as fly ash, coal and oxides [1], and agricultural wastes such as palm shells [4].

Bivalve mollusk shells (BMSs), as discarded by-products during sea food processing, are very common round the coasts of China and can be therefore gotten free from the local markets and industries. It is well-known that BMSs contain a large amount of organic compounds and macromolecules, such as chitin that can forms the framework for other macromolecular components [5–9], strongly implying that BMSs have a potential of adsorption for metal ions. In Guangxi of China, there are many copper-mining and -processing industries, which discharge a considerable amount of copper-containing wastewater. During development of environmentally benign and low-cost adsorbents for removal of heavy metal from the aqueous solution, we found that BMSs could efficiently remove copper from the $CuSO_4{\cdot}5HO_2$ solution by adsorption. The aim of this study is to characterize the ability of BMSs to remove metals from aqueous solution and then evaluate potential of treatment of actual electroplating wastewater.

2. Materials and methods

2.1. Materials

BMSs used in this study were collected from local markets in Nanning. The samples were then brushed and washed to remove any adhered materials, after which they were pulverized and then sieved through 100 meshes.

The test solution samples used included ones containing $CuSO_4{\cdot}5H_2O$ (100 mg/L) and mixed metal (100 mg/L each $CuSO_4{\cdot}5H_2O$, $Fe_2(SO_4)_3$, $ZnSO_4{\cdot}7H_2O$ and $CdCl_2{\cdot}2.5H_2O$). All of the inorganic chemicals used in this study were of analytical grade. In addition, all solutions used in this study were prepared using distilled deionized water and then adjusted to the required initial pH values by adding HCl or NaOH.

Electroplating wastewater was provided by a local electroplating factory. The wastewater, which was analyzed by atomic absorption as described below, had a pH of 3 and contained Cu^{2+} (9.4 ± 0.1 mg/L), Fe^{3+} (232.7 ± 1.2 mg/L) and Zn^{2+} (75.5 ± 0.8 mg/L). This wastewater presents light brown owing to having a higher concentration of Fe.

2.2. Pretreatment of the BMSs

Prior to use as an absorbent, the powered BMSs were washed for 10 min at 100 rpm with distilled deionized water, after which they were collected by centrifugation at 2000 rpm for 5 min. Next, the BMS precipitate was dried at room temperature. An aliquot of the dried BMS precipitate was also acid-treated for 60 min at 100 rpm by soaking the solution in 1 M H_2SO_4, after which the resulting BMS was collected by centrifugation. Another aliquot of the dried BMS precipitate, as a control, was parallel-treated with distilled deionized water.

2.3. Sorption experimental procedures

Sorption experiments were conducted in batches in 250-ml Erlenmeyer flasks that contained 100 ml of solution containing the metal salt(s) or 100 ml of the actual electroplating wastewater. The powered BMSs were then added to each flask, which was subsequently sealed with a cap and shaken for the required time at 200 rpm at the indicated temperatures. The flasks were centrifuged at 4800 rpm for 5 min immediately after treatment, after which the supernatant was collected. The residual concentration of the specific metals in the supernatant was then determined by atomic absorption analysis.

The removal efficiency of specific heavy metal was calculated as: $Q = C_0 - C_1/C_0$, where Q is the removal efficiency of the specific metal (%), C_0 is the initial concentration of the specific metal in solution (mg/L), and C_1 is the residual concentration of the specific metal in solution after sorption (mg/L).

2.4. Sorption–desorption experimental procedures

Following sorption as described above, 100 ml of the solution containing $CuSO_4{\cdot}5H_2O$ (100 mg/L) and raw BMSs (1 g) was centrifuged. The resulting supernatant was then analyzed for the presence of residual copper by atomic absorption. Next, the precipitated BMS particles were dried and subjected to the desorption experiment, which was conducted at room temperature as follows: the BMSs (1 g) loaded with Cu from the sorption reaction were added to 50 ml of 0.5 mM ethylenediamine tetraacetate solution and then washed for 30 min at 32 °C by shaking at 100 rpm. Next, the sample was centrifuged, after which the copper concentration of the supernatant was determined. This procedure was then repeated 13 times using the same raw BMSs.

2.5. Ion exchange analysis in metal sorption by BMSs

Sorption was done in 500-ml Erlenmeyer flasks that contained 200 ml of solution containing 200-mesh-sieved BMSs (5 g), and $CuSO_4{\cdot}5H_2O$ (500 mg/L) or $CdCl_2{\cdot}2.5H_2O$ (500 mg/L). The conditions used were for 2 h at 37 °C by shaking at 100 rpm. After sorption, the resulting sorption solution was centrifuged at 3000 rpm for 5 min immediately, and the supernatant was then collected. The concentration of the specific metals in the supernatant was then determined by atomic absorption analysis. The control for sorption was parallel-coducted in the solution only containing BMSs.

2.6. Atomic absorption assay

The atomic absorption assay used to analyze the metals in the solution was conducted on a Hitachi Z-8000 atomic absorption spectrophotometer (Hitachi, Tokyo, Japan) equipped with a graphite tube atomizer following standard procedures [10]. All assays were conducted in triplicate and reported in the mean values ± the standard deviation.

2.7. Analysis of infrared absorbance spectra of BMSs

Raw and acid-pretreated BMSs prepared as the indicated methods were dried at 70 °C, and analyzed for infrared absorbance spectra to characterize the functional groups in BMSs. Infrared absorbance spectra were determined by the Fourier transform infrared spectrometer (Nicolet, USA) as the method of potassium bromide pellet. All parameters for analysis were default settings.

2.8. Scanning electron microscopy (SEM)

Raw and acid-pretreated BMSs were prepared as the indicated methods and observed on a HITACHI EDAX S-3400N scanning electron microscope according to the standard procedures.