



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

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ARTICLE INFO

Article history:

Received 26 July 2008

Received in revised form 5 January 2009

Accepted 3 February 2009

Available online 12 February 2009

Keywords:

Heavy metal

Electroplating wastewater

Bivalve mollusk shell

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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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.

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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 consciousness of cost effectiveness and public environmental protection, lower-cost, more efficient and safer adsorbents for the treatment of industrial wastewater contaminated with heavy metals are now in demand. To date, many such adsorbents 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 form 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (100 mg/L) and mixed metal (100 mg/L each $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$). 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 adsorbent, 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (500 mg/L) or $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (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-conducted 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 \pm 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.

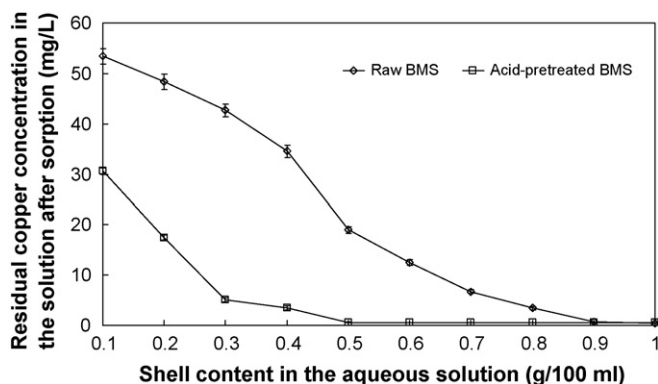


Fig. 1. Variation in copper removal with BMS dosage in the sorption system. Sorption was conducted for 90 min at 32 °C in 100 ml of solution containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (100 mg/L) and BMSs. The initial pH of the solution was adjusted to 5. BMS: bivalve mollusk shell. The error bars represent standard deviation of the mean from three batches of experiments.

3. Results and discussion

3.1. Copper removal efficiencies from the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ -containing solution

It has been reported that pretreatment of adsorbents by physico-chemical processes can improve the heavy metal removal efficiency [1,2]. Therefore, we evaluated the copper removal from 100 ml of solution that contained 100 mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ by raw and acid-pretreated BMSs (Fig. 1). The copper removal efficiency increased as the amount of BMSs used increased, regardless of whether the BMSs were raw or acid treated. Specifically, the copper removal efficiencies increased rapidly until a dose of 0.5 g/100 ml was reached. When the dose of BMSs reached more than 0.5 g/100 ml, the removal efficiencies performed by raw and acid-pretreated BMSs continued to increase at rapid and slower efficiencies, respectively. To reach a removal efficiency of ~99%, the doses need were 0.5 g/100 ml and 0.9–1 g/100 ml for raw and acid-pretreated BMSs, respectively, suggesting that acid pretreatment with H_2SO_4 can improve the copper sorption capacity of the BMSs.

In most cases, alkali and acid treatment of adsorbents enhances the metal sorption capacity, whereas acidic treatment has almost no influence on metal sorption [1,11–13], depending on the adsorbents and the process employed. For example, an increase in the sorption capability following acid pretreatment has been observed in the microbial biosorption of Cu, Cd and Zn by *Bacillus lentus*, *Aspergillus oryzae* and *Saccharomyces cerevisiae* [13] as well as when

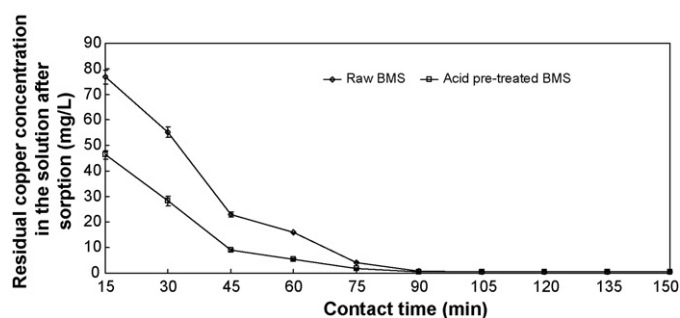


Fig. 3. Time courses of copper removal. Sorption was conducted at 32 °C in 100 ml of solution containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (100 mg/L) and BMSs (1 g). The initial pH of the solution was adjusted to 5. BMS: bivalve mollusk shell. The error bars represent standard deviation of the mean from three batches of experiments.

agricultural and industrial waste such as blast-furnace slag and citric acid-modified soybean hulls has been used [14]. According to several previous studies, mollusk shells are not only composed entirely of inorganic matrices such as calcium [5] but also contain organic compounds such as aspartic acid-rich proteins [6,7]. Therefore, the increase in the copper removal efficiency of the BMS following acid pretreatment observed in this study may be related to the elimination of Ca^{2+} on the shell surface as well as to exposure of more functional groups that can bind metal ions to the shell surface.

3.2. Copper sorption potential of the BMSs

To estimate the copper sorption potential of the BMSs, a sorption experiment was conducted using 100 ml sorption systems that contained 1 g of BMSs and different initial concentrations of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (ranging from 100 mg/L to 1400 mg/L) (Fig. 2). For the raw BMS, good copper removal efficiencies were observed when the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentrations were less than 400 mg/L; however, the removal efficiencies declined sharply at higher concentrations. Specifically, when the initial concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was 400 mg/L, the copper removal efficiency reached 97.32%, which gave a copper sorption capacity of 38.93 mg/g. When the acid-pretreated BMS was evaluated, the copper removal efficiency remained at a high level, even when a high initial concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used. This was demonstrated by a 99.25% removal efficiency being observed when the initial concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was 1400 mg/L. This removal efficiency

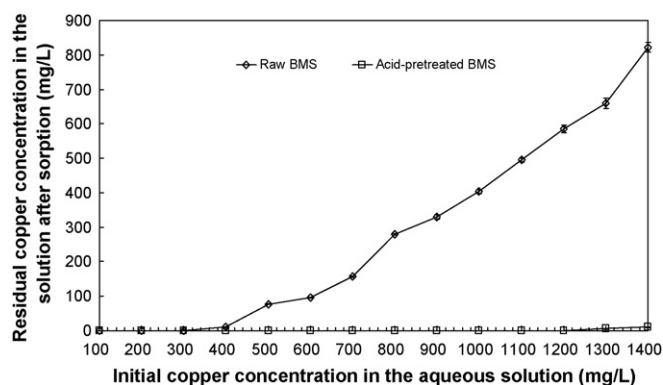


Fig. 2. Effect of initial concentrations of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ on copper removal. Sorption was conducted for 90 min at 32 °C in 100 ml of solution containing BMSs (1 g). The initial pH of the solution was adjusted to 5. BMS: bivalve mollusk shell. The error bars represent standard deviation of the mean from three batches of experiments.

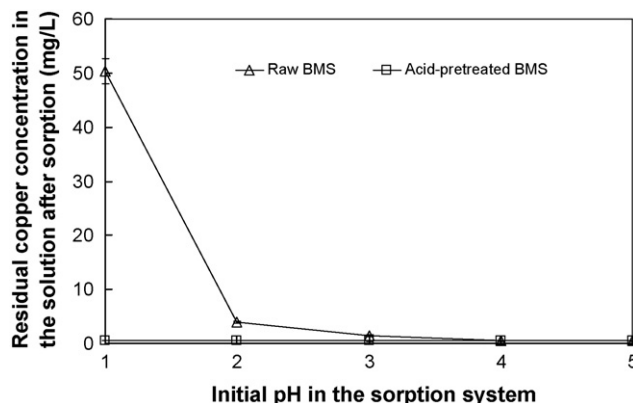


Fig. 4. Effect of initial pH of the solution on copper removal. Sorption was conducted at 32 °C in 100 ml of solution containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (100 mg/L) and BMSs (1 g). The initial pH of the solution was adjusted to different values. BMS: bivalve mollusk shell. The error bars represent standard deviation of the mean from three batches of experiments.

translated to a copper sorption capacity of 138.95 mg/g of the acid-pretreated BMSs. Prior to this study, the adsorbents with the highest reported copper sorption capacities were blast-furnace slag (133.35 mg copper/g) and citric acid-modified soybean hulls (154.9 mg copper/g) [14].

3.3. Change in copper removal efficiency over contact time

It is important to optimize the contact time for heavy metal removal in industry. In this study, raw and acid-pretreated BMSs showed high copper removal efficiencies when the contact time was less than 90 min (Fig. 3). In addition, although longer contact enhanced the removal efficiency, this increase was not significant ($p > 0.05$). Specifically, the copper removal efficiencies after 90-min of contact were 99.33% and 99.94%, for raw and acid-pretreated BMSs, respectively, indicating a rapid copper sorption similar to the biosorption of fungal biomass [2].

3.4. The effect of initial pH on the copper removal efficiency

The pH is one of the most important environmental factors involved in the sorption of heavy metal ions. In this study, the copper removal efficiency of the raw BMSs was lowest when the initial pH was 1, only having 50%. However, this value then obviously increased and reached 96.1%, 98.6%, 96.1%, 99.5% and 99.5% at the initial pH of 2, 3, 4 and 5, respectively (Fig. 4). Conversely, the copper removal efficiencies of acid-pretreated BMSs were high (approximately 99.48–99.52%) throughout the entire range of tested pH values (Fig. 4). The optimal pH for the sorption of metal ions varies among systems. For example, the optimal pH value for the removal of copper by *S. cerevisiae* is 5–9 [15], whereas it is 1.5–9.0 for removal by industrial by-products such as iron/steel slag [14]. The effect of pH on the removal of heavy metals can usually be explained by strong influences on site dissociation at the surface of the adsorbents as well as by the solution chemistry of the heavy metals [2].

3.5. The effect of temperature on the heavy metal removal efficiency

Both raw and acid-pretreated BMSs showed stable and higher removal efficiencies in the range of 15–40 °C, reaching approximately 99.5% (Fig. 5). This result indicates that temperature has an effect on the biosorption of metal ions, but only to a limited extent within a certain range [2]. It is believed that sorption reactions are normally exothermic; therefore, the biosorption capacity increases as the temperature decreases [11]. However, this decrease

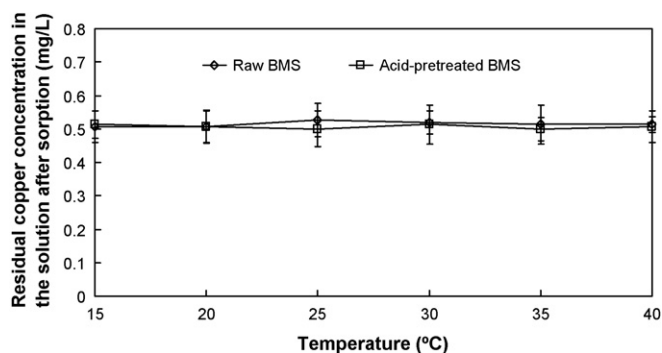


Fig. 5. Effect of temperature on copper removal. Sorption was conducted in 100 ml of solution containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (100 mg/L) and BMSs (1 g). The initial pH of the solution was adjusted to 5. BMS: bivalve mollusk shell. The error bars represent standard deviation of the mean from three batches of experiments.

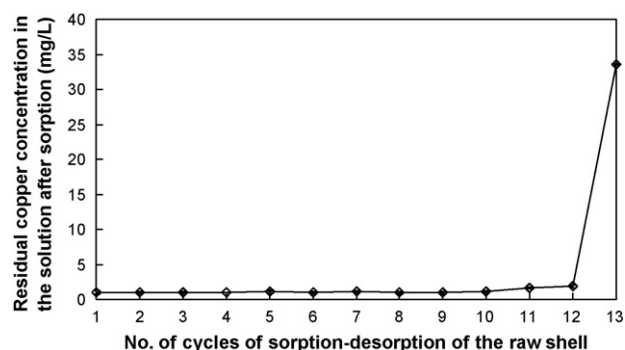


Fig. 6. Copper removal by raw BMSs in response to repeated sorption–desorption cycles. Sorption was conducted for 90 min at 32 °C in 100 ml of solution (initial pH 5) containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (100 mg/L) and BMSs (1 g). Desorption was conducted as described in Section 2. BMS: bivalve mollusk shell. The error bars represent standard deviation of the mean from three batches of experiments.

in biosorption capacity at higher temperatures likely occurs due to damage to the active binding sites in the biomass [16]. Such differences between the results likely resulted from differences in the nature of adsorbents and/or species of metals.

3.6. Cycle of sorption–desorption in the BMS

In practice, regeneration and reuse of the adsorbents not only decreases the operational cost, but also provides additional benefits through the recovery of heavy metals. In this study, copper desorption efficiencies of up to 99% were attained using both raw and pre-treated BMSs (data not show). In addition, the copper removal efficiencies of the raw BMSs were maintained for 12 cycles of sorption–desorption (Fig. 6) with a copper removal efficiency of 98.4% being observed in the final cycle.

3.7. Metal removal from the mixed metal solution by BMSs

Industrial effluent usually contains various ionic components. Therefore, we examined the ability of the BMSs to remove metals from solutions containing a mixture of metals (Fig. 7). For raw BMSs, the order of removal efficiencies were as follows: Fe (99.99%) > Cu (98.62%) > Zn (26.81%) > Cd (14.5%). The acid-pretreated BMSs exhibited removal efficiencies of 99.99%, 99.45%, 69.53% and 30.21% for Fe, Cu, Zn and Cd, respectively. This differ-

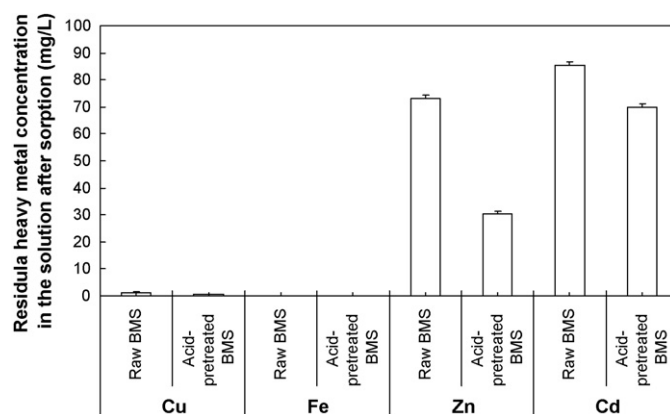


Fig. 7. Metal removal from mixed metal solution by BMSs. Sorption was conducted for 90 min at 32 °C in 100 ml of mixed heavy metal solution (initial pH 5) containing BMSs (1 g). BMS: bivalve mollusk shell. The error bars represent standard deviation of the mean from three batches of experiments.

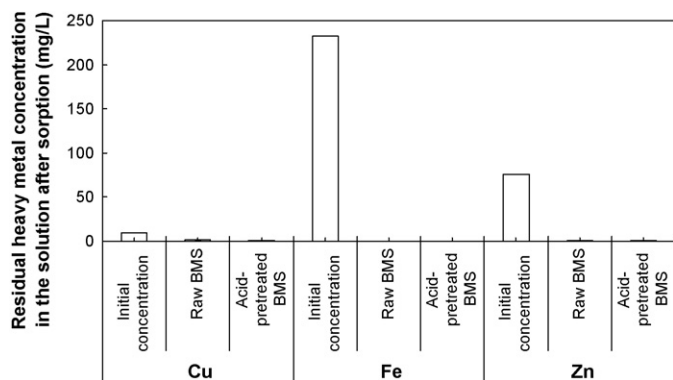


Fig. 8. Metal removal from electroplating wastewater by BMSs. Sorption was conducted for 90 min at 32 °C in 100 ml of wastewater (initial pH 5) containing by BMSs (1 g). BMS: bivalve mollusk shell. The error bars represent standard deviation of the mean from three batches of experiments.

ence of different metals in the removal efficiencies likely resulted from selective and/or competitive sorption, which is a phenomenon that is often observed in similar experiments [1,2]. It is believed that competitive biosorption occurs as a result of competition between similar species with the same charge for binding sites [17].

3.8. The removal of metals from electroplating wastewater by BMSs

To examine the potential for the use of BMSs for the removal of heavy metals from actual industrial wastewater, we evaluated the ability of BMSs to remove metal from electroplating wastewater obtained from a local industry. We found that both raw and acid-pretreated BMSs effectively removed Fe, Zn and Cu from the electroplating wastewater (Fig. 8). Specifically, when raw BMSs were evaluated, the removal efficiencies were 99.97%, 98.99% and 87% for Fe, Zn and Cu, respectively, whereas the removal efficiencies were 99.98%, 99.43% and 92.13%, respectively, when the acid-pretreated BMSs were evaluated. Compared to the status (light brown) before treatment, the treated wastewater presented colorless owing to removal of a large amount of Fe.

It should be pointed out that the efficiencies of Cu removal by raw and acid-pretreated BMSs were higher in the solution containing only $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Fig. 1) than in the electroplating wastewater (Fig. 8), this is because removal of the individual metal ions in the solution with multiple metal salts is usually affected by other metal ions due to interference effects, such as competing for adsorption sites [18,19].

3.9. Ion exchange in metal sorption by BMSs

To understand the mechanisms underlying metal sorption by BMSs, ion exchange experiments were conducted in the solutions containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$. Accompanying evident decrease in Cu or Cd concentration in the solutions treated by sorption using acid-pretreated BMS the net increments of Na and Ca concentrations in the treated solution were also obvious, but the increment of the former was much higher than that of the latter (Fig. 9A and B). In the solutions treated by sorption using raw BMS, the removal efficiencies of Cu and Cd were relatively lower while the net increments of Na and Ca concentrations were so little that they could be neglected (Fig. 9A and B). These results suggest that one of mechanisms for metal sorption by the BMSs from aqueous solution is related to ion exchange, especially between metal ions in the treated solution and Ca^{2+} from the BMSs.

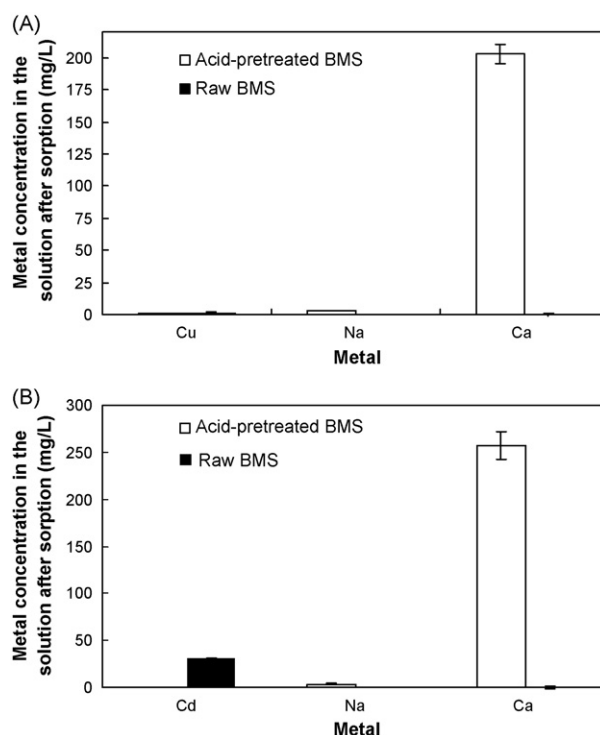


Fig. 9. Concentrations of specific metals in the metal salt-containing solution after treatment by sorption with BMSs. (A) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ -containing solution; (B) $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ -containing solution. The Cu and Cd concentrations presented in the Figure indicate the residual concentrations in the solution after sorption. The Na and Ca concentrations shown in the Figure indicate the net increments of both metals in the solution after sorption, which were calculated by subtracting metal concentrations in the control solution from concentrations of corresponding metals in the solution after sorption. The error bars represent standard deviation of the mean from three batches of experiments. The detailed experimental procedures were described in Section 2.

3.10. Infrared absorbance spectra and ultrastructure of BMSs

To gain further insight into the mechanisms of high efficiencies of heavy metals, we compared the infrared absorbance spectra between raw and acid-pretreated BMSs. The result indicated that the raw BMS itself possesses many reactive groups (Fig. 10A), but acid-pretreated BMSs presented more groups (Fig. 10B). Significant differences between materials were unique groups present in acid-pretreated BMSs, which were $-\text{OH}$ and $-\text{NH}$ at the wavelength range of $3750\text{--}3000\text{ cm}^{-1}$, C-H , $-\text{CH}_3$, $-\text{CH}_2$ and $-\text{COOH}$ at $3000\text{--}2700\text{ cm}^{-1}$, C=O at $1900\text{--}1650\text{ cm}^{-1}$, C=C and C=N at $1675\text{--}1500\text{ cm}^{-1}$, and S=O at $\sim 1200\text{ cm}^{-1}$. In these groups, Interested were those of negative charge, including $-\text{OH}$, $-\text{NH}$, C=O and S=O . The presence of the group S=O (Fig. 10B) in acid-pretreated BMSs indicated an effect of acid pretreatment. These groups of negative charge can directly bind metal ions. All these results also consolidate a viewpoint that chemical treatments can release and modify binding sites in the biomass [20].

To definite the basic characteristics of raw and acid-pretreated BMSs, we observed the structures of BMSs before and after acid pretreatment using SEM. SEM results indicated that BMSs used were approximate particles with rough surface before acid pretreatment (Fig. 10C) but presented the flake-shaped structure with smooth surfaces after acid pretreatment (Fig. 10D), suggesting occurrence of chemical reaction during acid treatment. Obviously, the flake-shaped structure with smooth surfaces can supply a better interface for binding metal ions.

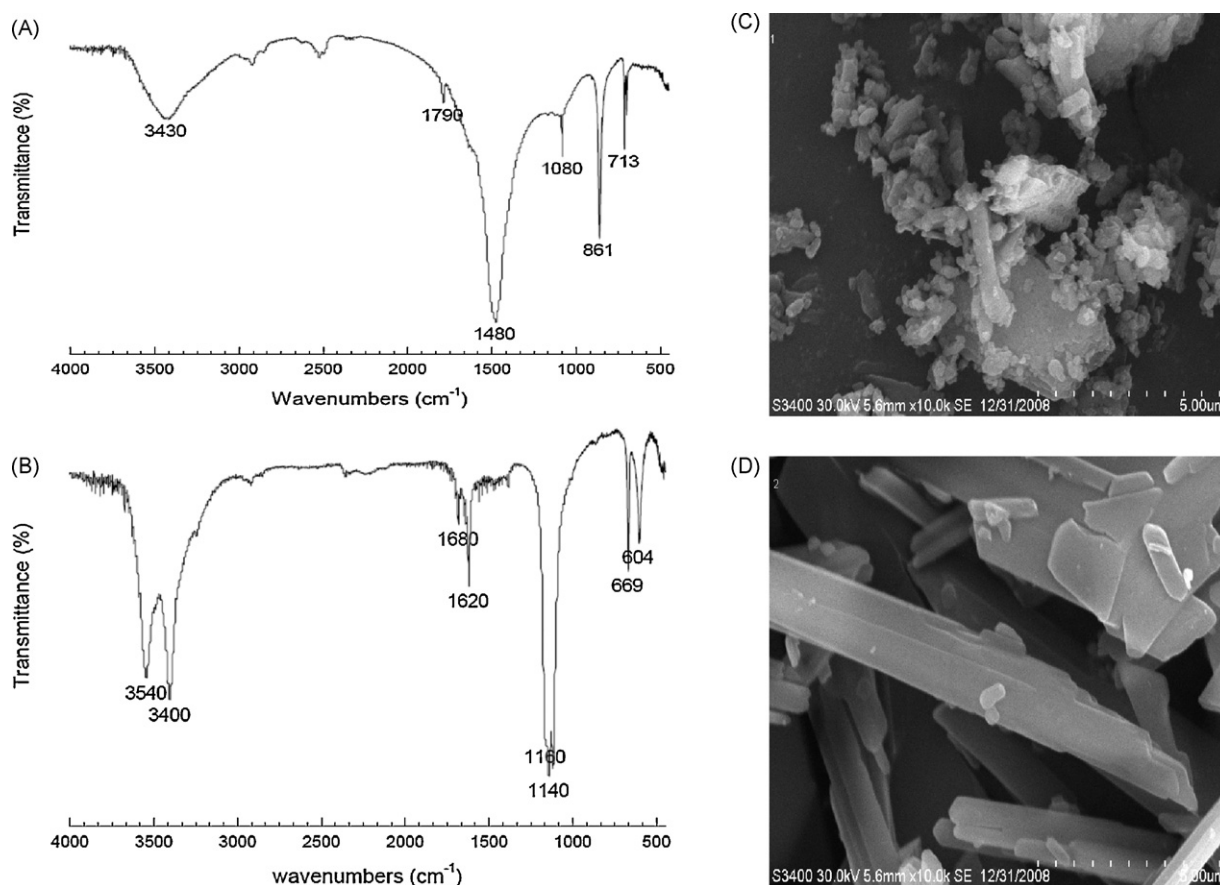


Fig. 10. Infrared absorbance spectra and ultrastructure of BMSs. Infrared absorbance spectra: (A) raw BMSs; (B) acid-pretreated BMSs. Ultrastructure: (C) raw BMSs; (D) acid-pretreated BMSs. Infrared absorbance spectra were analyzed by the Fourier transform infrared spectroscopy. The ultrastructure was observed by SEM. The detailed experimental procedures were described in Section 2.

4. Conclusions

Both raw and acid-pretreated BMSs effectively removed heavy metals from the tested solutions, but the acid-pretreated BMSs were far more efficient. In addition, when $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solutions with initial pH values of 1–5 were treated, the copper removal was found to be pH-dependent for the raw BMSs but not for the acid-pretreated BMSs. Moreover, the copper removal efficiency was found to be temperature-independent for both raw and acid-pretreated BMSs when samples were treated at temperatures ranging from 15 °C to 40 °C. The copper sorption capacities of the raw and acid-pretreated BMSs were approximately 38.93 mg/g and 138.95 mg/g, respectively. Furthermore, the BMSs were found to have high removal and desorption efficiencies for 12 cycles of sorption–desorption. In the sorption, the net increments of Na and Ca were marked. The acid pretreatment enabled the BMSs to present some unique groups of –OH, –NH, C=O and S=O. SEM results indicated that acid pretreatment enabled the used BMSs to form the flake-shaped structure with smooth surfaces.

These findings together with the result of removal of heavy metals from the electroplating wastewater indicate that BMSs are a very promising adsorbent that can be used for the removal of heavy metals from electroplating wastewater, and suggest 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 the BMSs. In addition, improvement of metal removal efficiencies by acid pretreatment is not only due to occurrence of the groups (i.e. –OH, –NH, C=O and S=O) of negative charge but also probably because of the flake-shaped structure with smooth surfaces in acid-pretreated BMSs.

Acknowledgements

We thank the members of our laboratory for suggestions and advice during the preparation of this manuscript. This research was supported by grants from the Development Program for Guangxi Science and Technology (0895003-8 and 0443001-20), the Director's Fund of the Guangxi Key Laboratory of Subtropical Bioresource Conservation and Utilization (07-04) and the Science Foundation of the Key Laboratory of the Ministry of Education for Microbial and Plant Genetic Engineering (J0701).

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