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Adsorption behavior of silver ions from industrial wastewater onto immobilized crab shell beads

Choong Jeon *

Department of Biochemical Engineering, Gangneung-Wonju National University, Jukhen-gil 7, Gangneung-si, Gangwon-do 210-702, South Korea

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ABSTRACT

To efficiently remove silver ions from industrial wastewater, powdered crab shells were immobilized as a bead form by entrapment method using polyvinyl alcohol and boric acid. The beads with 2.0 mm of diameter and 11.124 m^2/g of surface area were stable until 45 °C and pH 10.0 in wastewater without untangling. In addition, the beads have excellent mechanical strength and swelling characteristics. The highest removal efficiency was 83% for silver ions and can be obtained from 4.0 g of crab shell contents into the beads. The Langmuir isotherm model showed significant fit to the equilibrium adsorption data and maximum adsorption capacity of 2.951 mg/g of silver ions was achieved at the pH 6.0 of wastewater. The breakthrough point was appeared around 70 (1.0 mL/min) and 120 bed volumes (0.5 mL/min), respectively, and 6 bed volumes of 1.0 M HNO_3 solution was required to get desorption efficiency of 95% in continuous process. Also, the bed volume for silver ions of firstly reused crab shell beads was 110 and the value shows possibility for reuse.

Introduction

Toxic metals discharged from industrial wastewater have been become a serious problem over the world because they are not biodegradable and therefore remain in ecological systems and in the food chain indefinitely, exposing top-level predators to very high levels of pollution [1]. Especially, the monovalent silver ion is more toxic for fish than copper or mercury, and it is an extremely effective germicide [2]. In addition, the concentration of silver in the human body increased to toxic levels will cause various diseases and disorders, such as the fatty degeneration of the liver and kidneys [3]. Among the toxic metals, silver has been widely used in various industrial fields including electroplating, photography, coinage and metal alloy industries because of its excellent electrical, thermal conductivity, malleability, ductility and photosensitivity [4,5]. However, reserve amount of silver which is generally connected with lead, copper and antimony deposits in the world are dramatically decreased while the extensive applications of silver ions increased rapidly and considerable amount of silver are lost in the effluents produced by various industries [6,7].

Many conventional methods, such as chemical precipitation, ion exchange resin, oxidation and separation membrane have been used to remove and recovery silver ions from industrial wastewater, however, they are partially not economical and efficient at low silver concentrations [8–10]. Therefore, novel and most promising techniques such as adsorption have been widely studied. Adsorption has some advantages, such as high efficiency, simple operation and easy recovery/reuse of adsorbent over other methods. In recent years, economical and easily obtained adsorbents, such as waste wool, peanut shells, vermiculite, soybean hulls and cotton have been applied to the industrial wastewater [11–13]. We also reported that the waste crab shells which were easily obtained in the eastern coast of Korea have an excellent ability to adsorb silver ions in industrial wastewater [14].

Although some adsorbents could economically remove silver ions in industrial wastewater, the use of powdered adsorbents could not accept for the continuous operation using packed-bed column operation due to the cracking of powdered adsorbents and pressure drop occurred during operation [15]. Therefore, it is necessary for the powdered adsorbents to immobilize as a bead form to have good mechanical strength and preserve adsorptive properties similar to those of commercial activated carbon or ion exchange resins. Many immobilization methods for adsorbent have been developed and, among them, entrapment method has some advantages, such as easy and low cost operation over others.

* Tel.: +82 33 640 2405; fax: +82 33 641 2410.
E-mail address: metaljeon@gwnu.ac.kr

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Generally, agar, polyacrylamide, sodium alginate, polyvinyl alcohol and k-carrageenan have been used as chemicals for entrapment [16,17]. Especially, the polyvinyl alcohol (PVA) is a raw material of vinylon and can be produced industrially rather cheaply. PVA also offers various advantages over the conventional immobilization methods, such as low cost, high durability and chemical stability and non-toxicity to viable cells. Up to now, several methods of immobilization using PVA have been reported and among them, PVA-boric acid method has been widely used to immobilize several adsorbent [18,19].

In this work, crab shells was immobilized by PVA-boric acid method and immobilized crab shells was used to remove and/or recover silver ions discharged from industrial wastewater under batch and continuous operation using packed-bed column. The basic data obtained from this study could be helpful for the understanding of the adsorption process and will provide the possibility for application of various industrial wastewaters with silver ions.

Materials and methods

Crab shells used in this study were kindly obtained from the local company located in the city of Gangneung in Korea and pretreatment methods and chemical composition for crab shells were well presented in our previous study [14]. The industrial wastewater was obtained from the Toricom Company located in the city of Chun-An in Korea and composition of the wastewater was given in Table 1. As shown in Table 1, the concentration of aluminum, total chrome and potassium ions was very low, compared to silver ions. Therefore, measurement of concentration for aluminum and chrome ions was not done in this study. Also, any anionic compounds were not detected. All of the chemicals used in this study were of analytical grade (Sigma Aldrich, U.S.A.) and deionized water was used to prepare all of solutions.

The procedure to get immobilized crab shell beads is as follows; firstly, some amount of crab shells, 2.5 g of PVA (MW: 1500) and 50 mL of distilled water were mixed under stirring to get a uniform mixture at 50 °C for 2 h. Secondly, the mixture was added dropwise to the 100 mL of mixed solution including 5.4 g of boric acid and 10 mL of glutaraldehyde (25% solution) with stirring by means of syringe pump (78-8110 INT, Kd Scientific) to get uniform beads and then the beads were separated from the mixed solution after aging process for 24 h. Finally, the bead washed with deionized water several times and dried at room temperature for 24 h.

The physical properties for the beads were investigated by the method already described in our previous work [20]. The swelling characteristics such as distention index and swelling ratio were measured from the weights and the volumes of dried and swollen crab shell beads respect to time and the values were calculated by following equations (1) and (2):

$$\text{Distention index} = \frac{V_s}{W_d} \tag{1}$$

$$\text{Swelling ratio} = \frac{(W_s - W_d)}{W_d} \tag{2}$$

Table 1
Composition of industrial wastewater.

Components	Concentration (mg/L)
Ag(I)	100
Al(III)	0.83
Total Cr	0.13
K(I)	0.09

where V_s is the volume of the swollen beads, W_s and W_d are the weight of the swollen and dry beads, respectively. Each sample was examined four times.

The SEM (Scanning electron microscopy, Hitachi model S-4100, Japan) photograph and EDX (Energy dispersive X-ray spectroscopy, Oxford INCA, U.S.A.) were also used to confirm surface condition and component onto the bead for before and after adsorption of silver ions.

All batch sorption experiments were performed with 100 mL conical flasks sealed with rubber stoppers and placed in a rotary shaking incubator (JEIO TECH, SI-600R, Korea) at desired temperature and time. The experiment for the effect of crab shells content in the beads on the removal efficiency of silver ions was done by 0.1 g of various beads with different amount of crab shells in the beads. The isothermal adsorption experiments were also carried out at the desired initial silver concentration and pH of wastewater. The desired pH was controlled by dilute NaOH and HCl solution and adsorption time was set to 24 h which is enough time to get an equilibrium state. After 24 h, the solution was centrifuged at 4000 rpm for 30 min to remove suspending crab shell beads by centrifuge (Gyrozen, Gyro 1236 MG, Korea), and then concentration of silver ions in supernatant was analyzed by Atomic Absorption Spectroscopy (Perkin-Elmer A Analyst 100/A Analyst 700, U.S.A.). Each sorption experiment was done three times and the average value is presented. The removal efficiency (R) and adsorption capacity (Q) of the crab shell beads for silver ions were calculated as following equations (3) and (4), respectively:

$$R\ (\%) = \frac{(C_i - C_f)}{C_i} \tag{3}$$

$$Q\ (\text{mg/g}) = \frac{(C_i \times V_i - C_f \times V_f)}{m} \tag{4}$$

where C_i and C_f are the silver ion concentration in the wastewater before and after adsorption (mg/L), V_i and V_f are the wastewater volumes before and after adsorption (L), and m is the dry weight of the immobilized crab shell bead (g).

Continuous adsorption experiments using borosilicate glass column with 1.0 cm of diameter and 10 cm of height was performed at room temperature. 1.5 g of immobilized crab shell beads was packed in a column and industrial wastewater was constantly conducted across the column by Acuflow Series II high-pressure liquid chromatograph (U.S.A.). Flow direction was up-flow, as is the case in most column operations and flow rate was controlled as 0.5 (retention time: 2.4 min) and 1.0 mL/min (retention time: 1.2 min) [21]. Influent concentration of silver ions was set as 10 mg/L and influent pH of wastewater was maintained as 6.0. For the regeneration experiments, 1.0 M of HNO_3 solution was used. Effluent samples were automatically collected by Spectra/Chrom CF-1 fraction collectors and concentration of silver ions was measured by Atomic Absorption Spectroscopy.

Results and discussion

Generally, adsorption capacity for metals of immobilized adsorbent much lower than that of powdered adsorbent as functional groups concerned binding to metals in adsorbent is consumed when immobilization reaction happens [22]. Therefore, it is very important to have any amount of adsorbent into immobilized bead. Table 2 shows that it is possible to make uniform immobilized bead until 4.0 g of crab shells into the bead and the content was chosen as the optimal manufacture condition for immobilization of crab shells. Fig. 1 shows the immobilized crab shell beads produced at the 4.0 g of crab shells content and the