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Adsorption behavior of cadmium ions from aqueous solution using pen shells

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ABSTRACT

Pen shells which have some functional groups like amide, amino and carboxyl groups were used as an adsorbent to remove cadmium ions from an aqueous solution. The functional groups in pen shells were investigated by FT-IR and the surface condition of pen shells and existence of cadmium ions onto the pen shells were confirmed by the SEM and EDX analyses. The highest adsorption capacity could be achieved as about 35.652 mg/g at the initial pH 4 of aqueous solution. Two adsorption isotherm models namely, Langmuir and Freundlich were used to fit the equilibrium data and the experimental data well follows the Langmuir isotherm model ($r^2 = 0.992$) and the maximum adsorption capacity (q_m) for cadmium ions was achieved as the 37.630 mg/g by the Langmuir model. Also, adsorption kinetics for cadmium on the pen shells followed pseudo second order rate equation with 0.999 of correlation coefficient and the calculated q_e value (35.594 mg/g) was in excellent agreement with the experimental q_e value (37.630 mg/g). Changing of temperature of the aqueous solution could not greatly affect during the adsorption process between cadmium ions and pen shells. Also, pen shells had a high selectivity to the cadmium ions In addition, the desorption efficiency of cadmium ions was about 98.0% at the 0.5 M of HCl and adsorption capacity of cadmium ions for reused pen shells can be still maintained at 31.65 mg/g level until the 2nd cycle. From the result, adsorption process using pen shells could be applied to the removal system of cadmium ions from aqueous solution and it was suggested that conventional treatment process using commercial ion-exchange resin can be sufficiently replaced with economical process using waste pen shells with comparative high adsorption capacity.

Introduction

Management of toxic metal ions in water system has been a major public concern. Especially, industrial sewages polluting water bodies with toxic metals such as lead, copper and cadmium put living world in danger and contaminate ecosystem of the earth including surface, sea and ground water resources. Among them, cadmium has been regarded as a latent metabolic toxicant by international agencies because it is so harmful to entire living organism and finally affects human health [1,2]. As cadmium does not biodegrade and accumulates within living organisms therefore, the excess cadmium caused the severe diseases like erythrocyte destruction, nausea, salivation, diarrhea, muscular cramps, renal degradation, chronic pulmonary problems, and skeletal deformities [3,4]. Furthermore, according to the International Agency for Research on Cancer, cadmium is known as a carcinogen [5]. Cadmium ions are generally generated from the industrial effluents coming from metal plating, battery manufacturing units, pesticides, paints, pigments, plastic, metallurgical and alloy industries [6,7]. It is recommended that the allowable concentration of cadmium for portable water is fixed by below the 0.003 mg/L [8]. Thus, it is necessary to remove cadmium ions from water or wastewater being discharged into the environment.

Many physical/chemical technologies to remove cadmium ions have been developed and applied to the water and wastewater system. The conventional treatment methods include ion exchange, reverse osmosis, coagulation–flocculation, solvent extraction and electrodialysis etc. [9–13]. However, these treatments have some disadvantages such as incomplete cadmium removal, high operating cost, prolonged executional period and generation of large amount of polluted toxic sludge that is essential to treat [14,15]. Among these techniques, adsorption method has been affected by many researchers in order to overcome shortcomings

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of these methods. This technology has an advantage of low operating cost, is effective in treating dilute solutions, produces no by-products in the environment and is largely insensitive to the type of toxic substance [16–19]. However, the application of this method for effluent treatment purposes may not be satisfied because of poor natural abundance and high cost of adsorbent itself. Recently, the adsorbents materials which have low cost and large quantities obtained from forestry, fishery and agriculture resources have attracted much attention to many workers. Some of the reported adsorbents include waste wool, peanut shells, eggshell, maize bran, soybean hulls, sugar beet pulp, cornstarch and cotton that they have been recognized as the potential alternative to traditional technologies for the removal of cadmium ions from the water and wastewater [20–23]. We have also conducted some studies on the removal of copper, lead, arsenic and silver ions from water and industrial wastewater by means of various wastes such as rice husk, sawdust, crab shell and exhausted coffee ground [24–27].

Along the sea shore of Korea, many fishery product manufacturers and a lot of restaurants discard pen shells as a waste and most of them are being dumped into landfill or incinerated. It is a kind of shellfish and well-known bivalve harvested in the West and Yellow Sea. Its adductor muscle and mantle are marketable as edible shellfish [28]. It is generally composed of 95% of calcium carbonate (C_aCO_3) and 5% of protein which has functional group like amide. From such economical viewpoint, we have prepared the pen shells as a novel adsorbent to remove cadmium ions from aqueous solution and furthermore, until now, the use as adsorbent of pen shells has not been tried.

In this study, pen shells were used as an adsorbent for the removal of cadmium ions from aqueous solution. Effect of various operation conditions on the cadmium removal and the surface condition onto pen shells were investigated by instrumental analysis. It is expected that the recycled pen shells would be an alternative solution satisfied with the low cost and large quantities as a novel adsorbent.

Experimental

Pen shells were kindly obtained from restaurants located at the city of Gangneung in Korea. The shells were firstly washed several times in running water to remove dust and other impurities, then with deionized water and finally dried in an oven (JEIO TECH OF-22GW, Korea) at 80 °C for 1 day. To prepare the powdered pen shells, they were grinded using a blender with steel blades (Hanil Co., Korea) and sieved to 36-mesh screen and the other chemical treatment was not performed any more and finally kept in the desiccators for use. All the chemicals used in this study were analytical grade (Sigma–Aldrich) and deionized water obtained from the Milli-Q system (Millipore, Bedford, MA, USA) was used to prepare all the solutions.

To confirm existing and shifting of functional groups in the pen shells for before and after adsorption of cadmium ions, the Fourier Transform Infrared (FT-IR) analysis was applied and recorded by means of a Brucker IFS 66 (1000–4000 cm^{-1}) spectrophotometer. Samples of 100 mg KBr disks containing 2% of beads of each sample were prepared less than 24 h before recording. The SEM (Scanning electron microscopy, Hitachi model S-4100, Japan) photograph and EDX (Energy dispersive X-ray spectroscopy, U.S.A.) were also applied to confirm surface condition and component onto pen shells for before and after adsorption of cadmium ions.

In the batchwise processes, 10–100 mg of dried adsorbents was taken into the 250 mL conical flask together 10–100 mg/L of cadmium concentration. To prepare cadmium solution, cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$, MW: 308.48) was used. The flask was shaken vigorously in a shaking incubator (JEIO TECH, SI-600R, Korea) at the desired temperature, pH and time. The pH of cadmium solutions were measured using a pH meter (Orion 420A, U.S.A.) and controlled to 2.0–4.0 with 0.1 NH_4OH and HNO_3. When adsorption for cadmium ions from the aqueous solution approached to equilibrium state, the solution was centrifuged at 4000 rpm for 30 min to remove suspending pen shells by centrifuge (Gyrozen, Gyro 1236 MG), and then the cadmium concentration of supernatant was measured by using Atomic Absorption Spectroscopy (PerkinElmer A Analyst 100/A Analyst 700, U.S.A). Each sorption experiment was carried out three times and the average value was presented in the analysis. The adsorption capacity of cadmium ion for the adsorbent can be calculated based on the mass balance principle like following equation:

$$q_e = \frac{C_i V_i - C_e V_f}{m} \quad (1)$$

In the above equation, q_e represents the amount of cadmium ions adsorbed per unit mass of the pen shells (mg/g), the C_i (mg/L) and C_e (mg/L) are the initial and equilibrium cadmium ion concentrations, respectively. The V_i (L) and V_f (L) are the initial and final volumes of test solution, respectively and the m is the dry mass of the pen shells (g). To investigate the effect of initial pH of the solution including 100 mg/L of cadmium concentration on adsorption capacity of cadmium ions, 100 mg of pen shells was added to the solution at the pH 2.0, 2.5, 3.0, 3.5 and 4.0, respectively for 1 day to assure the equilibrium to be achieved. The experiment for the adsorption of cadmium ions was avoided above pH 5.0 due to the precipitation of cadmium ions as hydroxides [29,30]. This was certified by using MINEQL+ software that has a capability of calculating the equilibrium state of metals at various pH levels. The isothermal adsorption isotherm experiment was performed by agitating the mixture of pen shells and aqueous solution with different cadmium concentrations of 10, 30, 50, 70, 90 and 100 mg/L at the initial pH 4.0 of the solution for 1 day. The adsorption experiment for temperature change of the solution was performed for the 15, 25, 35 and 45 °C, respectively. Also, to investigate the effect of adsorption time, 100 mg of pen shells were added to 100 mL of aqueous solution with 100 mg/L of cadmium concentration for predetermined periods of 10, 30, 60, 120 and 180 min. Multi-metal adsorption capacity and selectivity experiment was carried out under the condition of 0.9 mM of each metal concentration (cadmium, lead, nickel, zinc, potassium, calcium and magnesium ions) in 100 mL of solution.

For the desorption experiment, previously adsorbed cadmium ions onto pen shells was transferred to a flask containing 100 mL of HCl solution. The mixture was shaken at 250 rpm using a rotary shaking incubator at room temperature for 24 h. The desorption efficiency of cadmium ions from the pen shells was calculated as the ratio between the amount of cadmium ions desorbed and amount of cadmium ions adsorbed.

In case of regeneration experiment, the adsorbent which metal was eluted to desorbing agent was thoroughly washed three times with deionized water to remove any traces of desorbing agent, and then mixed again in water containing cadmium ions for the next adsorption cycle. The above procedure was employed for three consecutive cycles.

Results and discussion

The FT-IR spectrum of pen shells for before and after adsorption of cadmium ions was shown in Fig. 1. The characteristic peak shown at the 2920 cm^{-1} was thought to indicate the stretching of the —OH groups bound to symmetric or asymmetric C—H stretching vibration of aliphatic acids [31,32]. The peak at the 2360 cm^{-1} and 1741 cm^{-1} means R—CN groups and carboxyl