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Removal of As(V) from aqueous solutions by waste crab shells

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Abstract−Waste crab shell, which has some functional groups like -NHCO or NO_2 groups, was used as an adsorbent to remove arsenate ions (As (V)). The functional groups in crab shells were confirmed by FT-IR analysis. Waste crab shell had a high uptake capacity of 35.92 mg/g-dry mass for arsenate ion at pH 4, and the regression curve using the Langmuir isotherm equation fit well with the experimental data. The effects of pH, loading of crab shells, and time on uptake capacity of arsenate ions were also investigated. The adsorption capacity of arsenate ions was increased as the pH value was increased because the amount of negative arsenic species increased as the pH value was increased. Waste crab shells could remove arsenate ions of about 45% with 0.5 g of loading amount, and adsorption of arsenate ions was almost completed in 30 min when initial concentration of arsenate ions was 100 and 9.3 mg/L, respectively. Considering recycling of crab shell, it could be an economical and promising adsorbent.

Key words: Crab Shell, Removal, Arsenate Ions, Recycling, Adsorption

INTRODUCTION

Management of hazardous waste is a major public concern and arsenic is one of the priority pollutants in waste discharges. It is widely known to be highly detrimental to human beings and animals, causing several neurological, dermatological, gastrointestinal, and cardiorenal diseases [1-4]. To remove the As(V), many physical/chemical treatment methods have been applied to arsenic-contaminated wastewaters. Among them, flocculation treatment has been widely used [5]. Other treatments such as solvent extraction, chemical precipitation, ferrihydrite precipitation, iron coprecipitation and reverse osmosis have also been used to remove arsenic species from aqueous solutions [6-8]. However, these treatments suffer from incomplete removal, high cost and energy of the process itself. In 1990, novel techniques for removing metals based on biosorption using microorganism such as algae or bacteria were reported [9,10]. This technology has the advantage of low operating cost, is effective in treating dilute solutions and generates minimum amounts of effluent. But their use for effluent treatment purposes may not be satisfactory because of their poor natural abundance. Recently, for metal removal, many studies have been performed focusing on using waste such as waste wool, peanut shells, soybean hulls, and cotton which are available in large quantities and may present higher potential as inexpensive sorbents [11,12]. Our earlier work also characterized lead ion adsorption by means of chemically modified sawdust, which is forestry waste [13]. On the other hand, the use of crab shells, which is seafood waste, has been focused on removal of metals. Crab shells are composed of mainly calcium carbonate, chitin along with some proteins and well known to possess rigid structure, excellent mechanical strength and ability to withstand extreme conditions employed during regeneration [14]. Chitin and its deacetylated form (Chitosan) have been used as effective biosorbents for metal removal. According to a literature survey, crab shells were effectively used to remove various metals such as nickel, copper, and cobalt ions [15,16]. Unfortunately, however, there is little study on As(V) removal using crab shells.

The aim of the research is to investigate the possibility as a novel adsorbent for waste crab shells to remove As(V) in wastewater. The effect of various environmental conditions on the removal of As(V) was also investigated.

MATERIALS AND METHODS

Crab shells were obtained from a local company located in the city of Gangneung in Korea. The shells were washed several times and dried in an oven (JEIO TECH OF-22GW) at 80 °C for 1 day. All the reagents were analytical grade (Sigma Aldrich) and deionized water was used to prepare all the solutions.

All sorption experiments were performed by batch-type in 100 mL of arsenate (V) solution in a shaking incubator (JEIO TECH, SI-600R, Korea) at room temperature for 1 day. To prepare arsenate (V) solutions, sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) was used and purchased from Sigma-Aldrich. The initial concentration of As(V) was set as the 100 mg/L. The pH of arsenate solution was adjusted periodically to 4.0 by using NH_4OH and HNO_3. When the pH of arsenic solution was maintained as 4.0, the solution was centrifuged at 4,000 rpm for 30 min to remove suspending crab shells by centrifuge (Gyrozen, Gyro 1236 MG), and then arsenate concentration of supernatant was analyzed by means of atomic absorption spectroscopy (Perkin-Elmer A Analyst 100/A Analyst 700, U.S.A). Each sorption experiment was performed three times and the average value is presented. The uptake capacity of arsenic ions was calculated as the following equation:

$$Q=(C_i \times V_i - C_f \times V_f)/m$$

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Where Q is the uptake capacity of arsenic ions (mg/g), C_i is the initial concentration of arsenic ions (mg/L), V_i is the initial solution volume (L), C_f is the final concentration of arsenic ions (mg/L), V_f is the final solution volume (L), and m is the initial loading of crab shells (g). The experiment for ionic strength of waste crab shells was carried out by NaCl solution varied with 0.02-0.1 M.

IR spectrum analysis was applied to confirm functional groups in crab shells. Infrared spectra were recorded with a Brucker IFS 66 (1,000-4,000 cm^{-1}) spectrophotometer. Samples of 100 mg KBr disks containing 2% of beads of each sample were prepared less than 24 hours before recording.

RESULTS AND DISCUSSION

1. FT-IR Spectrum Analysis of Waste Crab Shells

To investigate functional groups of crab shells, FT-IR spectrum analysis was done. As shown in Fig. 1, the IR peak shown at 3,408 cm^{-1} is thought to represent the hydroxyl group, and the characteristic peak at 1,640 cm^{-1} indicates amide groups (-NHCO stretching). Also, the peak of around 1,384 cm^{-1} means NO_2 groups. Yeom already reported that crab shells are mainly composed of calcium (22.34%) followed by phosphorus (3.08%), and magnesium (4.03%). Also they revealed that crab shells have 53.8% of organic compounds, especially, 12.0% of protein. In general, calcium exists as the form of calcium carbonate ($CaCO_3$) [17]. According to the FT-IR spectrum analysis and literature survey, it can be said that crab shells are composed of cellulose-like backbone, protein, calcium carbonate and they have some functional groups like -NHCO or NO_2 groups which play an important role in the removal of As(V). Srivastava et al. performed biosorption studies on removal and recovery of arsenic from aqueous system by means of a biomass which has functional groups of amino acids (NH_3) [18].

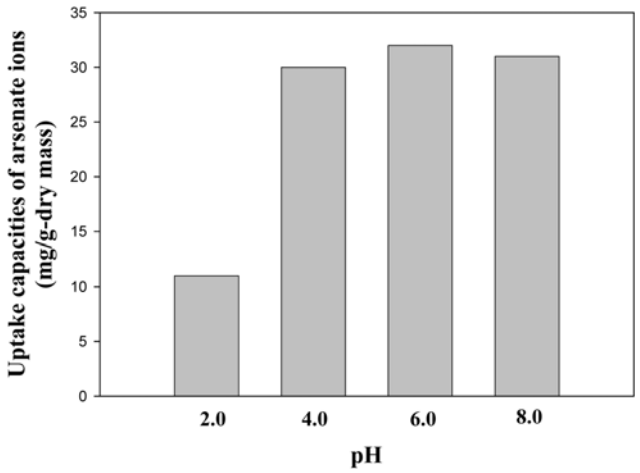

Fig. 2. Effect of pH on uptake capacities of arsenate ions using waste crab shell (Initial concentration of arsenate ions: 100 mg/L, Working volume: 100 mL).

2. Batch Sorption of Arsenate Ions Using Waste Crab Shells

The effect of pH on uptake capacity of arsenate ions is shown in Fig. 2. It can be seen that the adsorption capacity of arsenate ions was increased as the pH values were increased. In general, at lower pH values, $H_2AsO_4^-$ is the predominant species and the amount of negatively arsenic species increased as the pH value was increased [18]. Therefore, the anions would be easily expected to interact more strongly with the crab shells carrying positive charges.

Fig. 3 shows the isothermal adsorption curve to As(V) ions using waste crab shells at pH 4. The amount of crab shells was differently added according to initial concentration of As(V). The Langmuir sorption model was chosen to estimate the maximum uptake

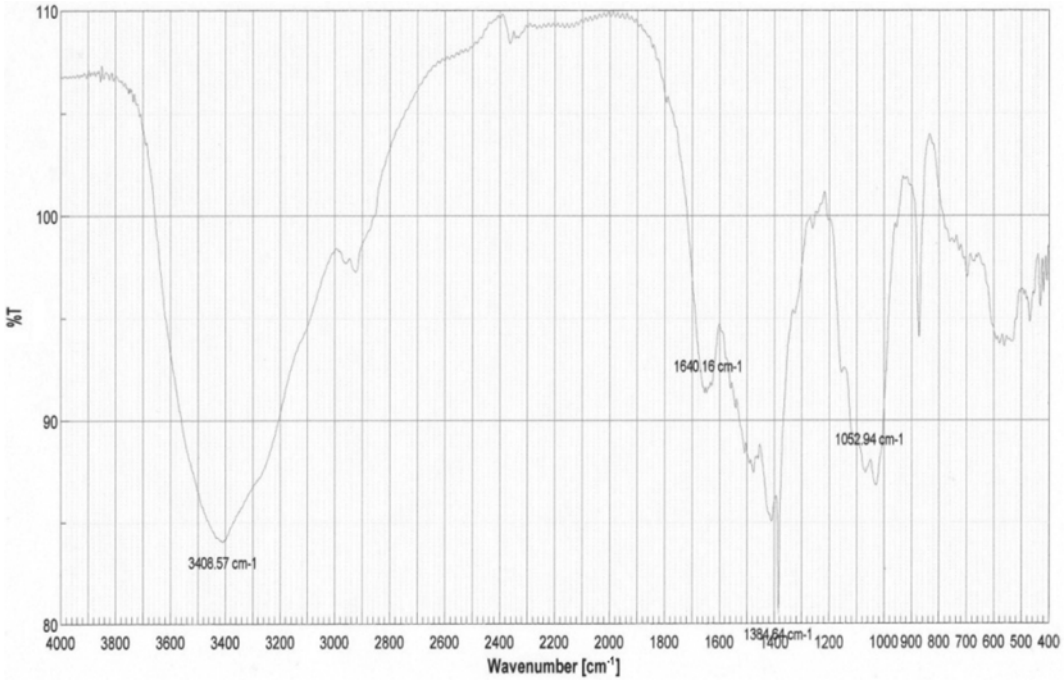

Fig. 1. FT-IR spectrum of waste crab-shells.

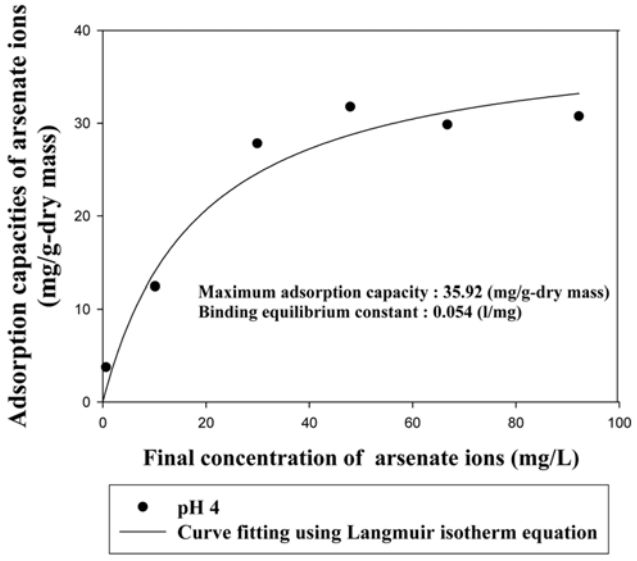

Fig. 3. Isothermal adsorption curve of arsenate ions using waste crab shell (Working volume: 100 mL).

capacity and conditional binding equilibrium constant of As(V) ions by means of waste crab shells. The maximum uptake capacity (q_{max}) was 35.92 mg/g-dry mass and conditional binding equilibrium constant was 0.054 L/mg. Regression curve using the Langmuir isotherm equation fit well with the experimental data. As(V) adsorption has been studied by various investigators, using a variety of different adsorbents. In Table 1, the respective adsorption efficiencies of

Table 1. Comparison of adsorption capacity of As(V) from aqueous solutions using various adsorbents

Adsorbent	pH	Maximum adsorption capacity (q_{max})	Reference
Waste crab shells	4.0	35.92	This study
Fly ash	4.0	27.78	[19]
Bauxite	3.5	12.6	[20]
Activated alumina	3.6	12.34	[21]

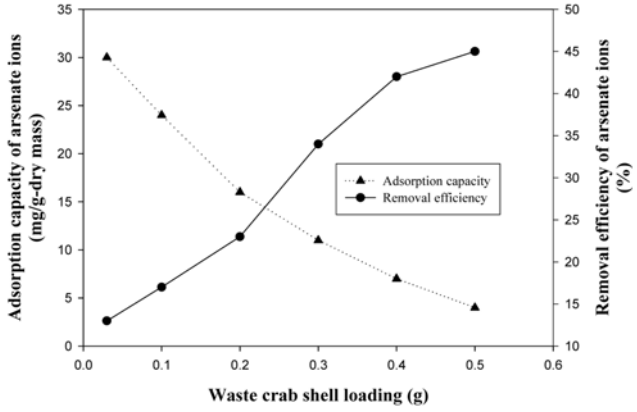

Fig. 4. Adsorption capacity and removal efficiency of arsenate ions using waste crab shell (Initial concentration of arsenate ions: 100 mg/L, Final pH of arsenate ion solution: 4.0).

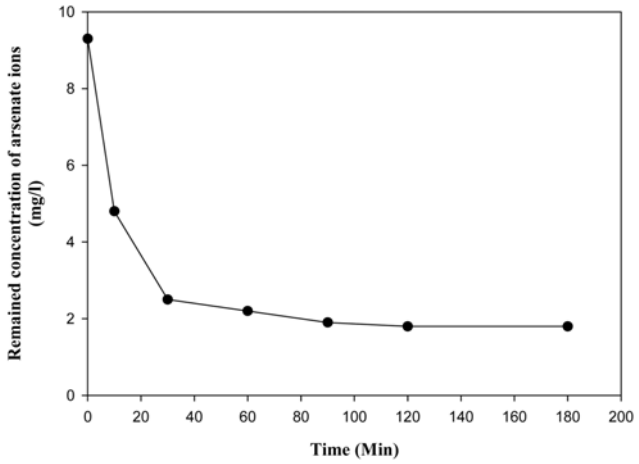

Fig. 5. Concentration change of arsenate ions with time (Initial concentration of arsenate ions: 9.3 mg/L, Working volume: 100 mL).

common ion exchange adsorbents are presented for comparison with the studied waste crab shells. Many of these adsorbents, such as activated carbon, natural zeolites or ion-exchange resins, have been applied in several practical metal recovery applications. Although a direct comparison between the studied waste crab shells with those obtained in literature is difficult, due to the varying experimental conditions employed in those studies, the waste crab shells used in this study shows high adsorption capacity, as compared with other adsorbens.

Fig. 4 shows effect of waste crab shell loading on the adsorption capacity and removal efficiency, which is defined as ratio of final/initial concentration of arsenate ions at pH 4. As loading increased, the removal efficiency of arsenate ions increased, while the adsorption capacity of arsenate ions decreased. In general, unsaturated sorption site for metal ions increased as adsorbent loading increased [22].

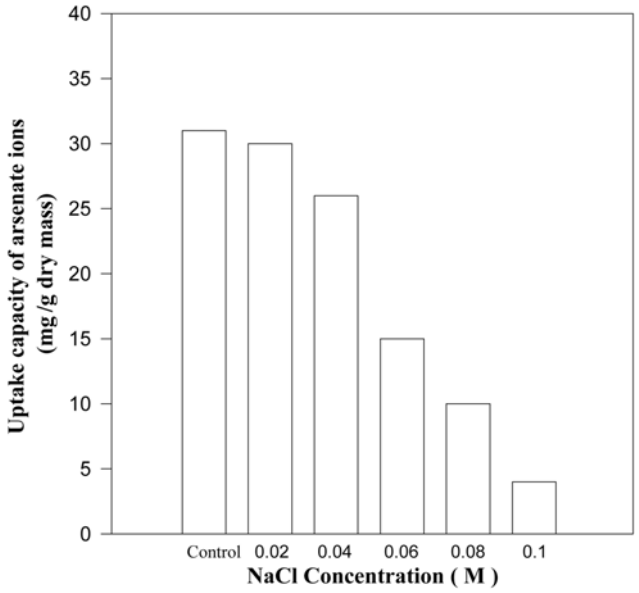

Fig. 6. Effect of ionic strength on the arsenate uptake capacities of waste crab shells (Initial concentration of arsenate ions: 100 mg/L, Final pH of arsenate ion solution: 4.0).

In terms of removal efficiency, waste crab shells could remove arsenate ions of about 45% with 0.5 g. Considering crab shell is waste, it must be an economical and promising adsorbent.

Kinetics experiments show that the adsorption of arsenate ions increases with time. As shown in Fig. 5, the adsorption of arsenate ions was rapid 30 min of contact time after which the rate slowed down as equilibrium approached at 120 min of contact time. No further increase in sorption was observed with further increase of contact time up to 180 min.

The effect of ionic strength on the arsenic adsorption by waste crab shells was also investigated by adding NaCl to the experimental solution. As shown in Fig. 6, as the concentration of NaCl increased, the uptake capacity of arsenate ions was decreased. Changing ionic strength influences adsorption in at least two ways: first, by affecting the interfacial potential and therefore the activity of electrolyte ions and adsorption; and second, by affecting the competition of the electrolyte ions and adsorbing anions for available sorption sites [23]. It can be explained that the added Cl^- could also compete with the $H_2ASO_4^-$ anion for the positively charged binding sites. Similar results were observed for biosorption of arsenate ions [24].

CONCLUSIONS

For the purpose of recycling waste crab shells, they were used as an adsorbent to remove arsenate ions (As(V)). Waste crab shells are composed of cellulose-like backbone, protein, calcium carbonate and they have some functional groups like -NHCO or NO_2 groups which play an important role in the removal of As(V). The uptake capacity of arsenate ions was increased as the pH values were increased. The maximum uptake capacity (q_{max}) for arsenate ions was 35.92 mg/g-dry mass, which shows high uptake capacity, as compared with other adsorbents. Waste crab shells could remove arsenate ions of about 45% with 0.5 g of loading amount and adsorption of arsenate ions was almost completed in 30 min when initial concentration of arsenate ions was 100 and 9.3 mg/L, respectively. Of course, the 45% of removal efficiency for As(V) is not satisfactory; however, the possibility of waste crab shells as a novel adsorbent could be sufficient in the arsenic removal process.

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