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# Adsorption characteristics of waste crab shells for silver ions in industrial wastewater

**Choong Jeon**†

Department of Biochemical Engineering, Gangneung-Wonju National University,
Jukhen-gil 7, Gangneung-si, Gangwon-do 210-702, Korea
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**Abstract**−Waste crab shells were used as an adsorbent to efficiently adsorb silver ions in actual industrial wastewater. The functional groups like -NHCO or $-NO_2$ groups in crab shells play an important role in the adsorption of silver ions. The highest removal efficiency was about 96% obtained from the 30 g/L of adsorbent concentration at initial pH 6.0 of waste solution. Langmuir sorption model was chosen to estimate the maximum uptake capacity and affinity constant of waste crab shells for silver ions, and its value was 5.21 mg/g-dry mass and 0.411 L/mg, respectively. Entire adsorption process was completed in 60 min, and removal efficiency of crab shells was higher than that of Amberlite IR 120 plus resin. The effect of temperature could be neglected in the range of 15.0-45.0 °C. Also, instrumental analysis such as SEM (scanning electron microscopy) photographs, EDX (energy dispersive X-ray) spectrum, and FT-IR spectrum were applied to investigate the surface condition and functional groups of crab shells.

Keywords: Crab Shells, Silver Ions, Adsorption, Wastewater, Recovery

## INTRODUCTION

Silver has been widely used in many fields such as electroplating, communications, chemical engineering, medical equipment, and electronic because of its excellent malleability, ductility, electrical and thermal conductivity [1,2]. However, reserve amounts of silver, which are generally connected with lead, copper and antimony deposits in the world, are dramatically decreased while the extensive applications of silver ions has increased rapidly [3]. In addition, a considerable amount of silver is lost in the effluents produced by various industries, which could be accumulating in living organisms through the food chain, and potentially doing harm due to the toxicity of silver ions [4]. According to the literature survey, exposure to silver ions induces an inhibition of active $Na^+$ and $Cl^-$ uptake and then ion regulation can fail due to inhibition of branchial $Na^+$-ATPase and $K^+$-ATPase in *crayfish* and *daphnids* [5,6]. Therefore, there is increased necessity for the effective removal and recovery of silver ions in wastewater discharged from the processes mentioned above, in terms of resources recycling [7-9].

A number of methods such as chemical precipitation, ion exchange, electrolysis, replacement, reverse osmosis, and adsorption to remove and recover silver ions from wastewater have been developed and applied to industrial wastewater. Among them, adsorption is one of the most promising techniques due to low operating cost, generating of minimum amounts for sludge and high selectivity to specific metals compared to others. Donia et al. have studied a chemically modified chitosan with magnetic properties, which can be used in silver recovery from aqueous solution [10]. Also, Kononova et al. have performed study on the recovery of silver ions from thiosulfate and thiocyanate leach solutions by means of anion exchange resins and activated carbon [11]. In spite of the many advantages of adsorption for the removal of silver ions from wastewater, the high cost of commercial ion exchange resin, activated carbon, and manufacturing for synthesis of adsorbent has been restrictive [12]. Hence, many studies have focused on the use of economical and facile adsorbents such as waste wool, peanut shells, vermiculite, soybean hulls, and cotton which are available in large quantities and may present higher potential as a novel adsorbent [13-15]. In 2013, a new approach to recovering silver ions from printed circuit boards (PCBs) of mobile waste by acidothiourea leaching followed by adsorption using biosorbent prepared from easily available agricultural waste was suggested by Inoue et al. [16].

Waste crab shells, which were easily obtained in the eastern coast of Korea, are mainly made up of 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 [17]. Until now, the main focus has been on the common heavy metal ion such as nickel, copper, and lead ions [18]. Our earlier work was also performed on the adsorption characteristics of arsenate ions using waste crab shells [19]. Unfortunately, there have been scarcely any works about removal and recovery of silver ions with waste crab shells.

Our intent was to examine the removal efficiency of noble silver ions from actual industrial wastewater by waste crab shells. And adsorption characteristics of waste crab shells for silver ions were investigated under various experimental conditions such as pH of wastewater, concentration of adsorbent, contact time, and temperature etc. All work was performed by Gangneung-Wonju National University, which is located in Gangneung-si.

## MATERIALS AND METHODS

Crab shells were obtained from a local company located in the city of Gangneung in Korea. They were crushed and passed by molec-

†To whom correspondence should be addressed.
E-mail: metaljeon@gwnu.ac.kr

**Table 1. Composition of wastewater**

| Components | Concentration (mg/L) |
|---|---|
| Ag(I) | 100 |
| Al(III) | 0.83 |
| Total Cr | 0.13 |
| K(I) | 0.09 |
| $CN^-$ | Not detected |
| $Cl^-$ | Not detected |

ular sieving with 80-100 mesh and then washed several times with deionized water and dried in an oven (JEIO TECH OF-22GW) at 80 °C for one day.

The actual industrial wastewater produced during the wet smelting process was obtained from the Toricom Company located in the city of Chunan in Korea. The composition of wastewater is given in Table 1, and the concentration of aluminum, chrome and potassium ions was very low compared to silver ions. Also, the concentration for anionic compounds was not detected. Therefore, the concentration for aluminum and chrome ions was not measured in this study. Meanwhile, the pH of wastewater was in very strong acidic condition at about 1.8. All of the chemicals used were of analytical grade (Sigma Aldrich, U.S.A) and deionized water was used to prepare all of solutions.

IR spectrum analysis was applied to confirm functional groups in crab shells. Infrared spectra were recorded with a Bruker 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. The SEM (Scanning electron microscopy, Hitachi model S-4100, Japan) photograph and EDX (Energy dispersive X-ray spectroscopy, U.S.A) were used to confirm surface condition and component onto the crab shells.

All sorption experiments were performed by batch-type with 100 mL conical flasks sealed with rubber stoppers and placed in a rotary shaking incubator (JEIO TECH, SI-600R, Korea) at the desired temperature and time. The initial pH of wastewater was adjusted using NaOH and $HNO_3$. Studying the adsorption of silver ions in basic media was avoided above pH 7.0 due to the precipitation of silver ions as hydroxides. When adsorption for silver ions in wastewater approached equilibrium state the solution was centrifuged at 4,000 rpm for 30 min to remove suspended crab shells by centrifuge (Gyrozen, Gyro 1236 MG, Korea), and then the 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 several times and the average value is presented. The removal efficiency and adsorption capacity of the crab shells for silver ions were calculated as the following equation, respectively:

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

where R.E is the removal efficiency of silver ions (%), Q is the adsorption capacity of silver ions (mg/g), $C_i$ is the initial concentration of silver ions in wastewater (mg/L), $V_i$ is the initial volume of wastewater (L), $C_f$ is the equilibrium concentration of silver ions (mg/L), $V_f$ is the final volume of wastewater (L), and m is the initial loading of crab shells (g).

The experiment for the pH effect was conducted with the 100 mL of industrial wastewater containing 100 mg/L of silver ion concentration, and the concentration of waste crab shells was 20 g/L. The temperature of wastewater was set as 25 °C and stirring speed of the solution was controlled as 300 rpm. The isothermal adsorption experiment was performed with the 100 mL of industrial wastewater containing silver ion concentration of 10, 30, 50, 70, 90 and 100 mg/L, and 1.0, 3.0, 5.0, 7.0, 9.0 and 10.0 g/L of waste crab shells went into the wastewater for each silver ion concentration, respectively. The initial pH and temperature of wastewater was set as 6.0 and 25 °C and stirring speed of the solution was controlled as 300 rpm. For the experiment on the effect of adsorbent concentration, 10.0, 15.0, 20.0, 25.0, and 30.0 g/L of crab shells concentration was applied to the wastewater with initial pH and temperature of 6.0 and 25 °C, respectively, and the stirring speed of the solution was controlled at 300 rpm. The temperature effect on removal efficiency of silver ions was observed for the 15, 25, 35, and 45 °C, respectively. For the experiment of adsorption time, 30.0 g/L of crab shells concentration was used for the 10, 30, 60, 120, and 180 min, respectively.

## RESULTS AND DISCUSSION

Various waste adsorbents such as crab shells, chestnut shell, tangerine, coffee grounds, and sawdust were used to compare the removal efficiency for silver ions. As shown in Fig. 1, the removal efficiency of crab shells for silver ions was the highest at about 6.6% at initial pH 1.6 of wastewater, although the value was very low. According to Atia's report, precious metals such as gold and silver can be well attached to the functional groups including nitrogen/sulfur [20].

To investigate functional groups of crab shells, FT-IR spectrum analysis was performed. As shown in Fig. 2, the IR peak shown at 3,408 $cm^{-1}$ is thought to represent the hydroxyl group and the characteristic peak appearing at 1,640 $cm^{-1}$ indicates amide groups (-NHCO

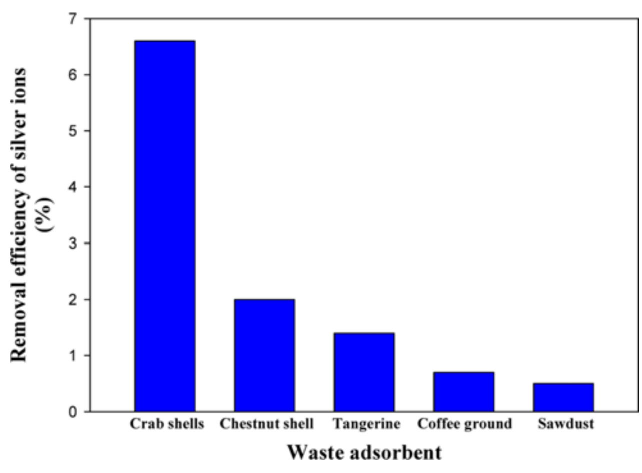



**Fig. 1. Comparison of removal efficiency for silver ions using various waste adsorbent in industrial wastewater (initial pH of wastewater: 1.6, initial concentration of silver ions in industrial wastewater: 100 mg/L, adsorbent concentration: 1.0 g/L).**

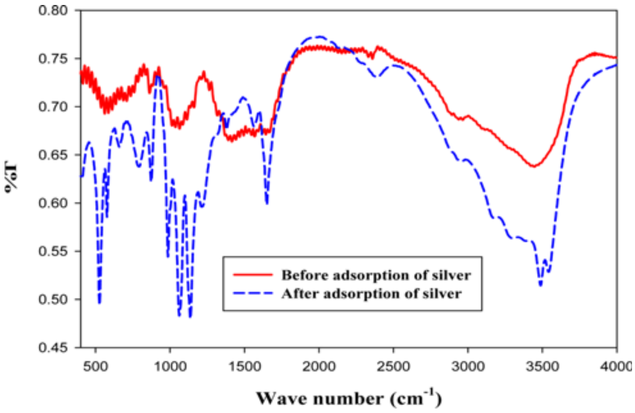



Fig. 2. FT-IR spectrum of waste crab shells.

stretching). Also, the peak of around 1,124 cm$^{-1}$ indicates $-NO_2$ group. The IR peak after adsorption of sliver ions was clearly different from that of no adsorption. Especially, the peak shown at 1,640 cm$^{-1}$ which indicates amide group was shifted to the higher value after adsorption of silver ions. Yeom et al. already reported that crab shells are mainly composed of calcium (22.3%) followed by phosphorus (3.1%), and magnesium (4.03%). Also, they revealed that crab shells have 53.8% of organic compounds, especially, 12.0% of protein and calcium which exist as the form of calcium carbonate [21]. From the analysis and literature survey, it was concluded that crab shells used in this study are composed of cellulose-like backbone, protein, calcium carbonate, and they have functional groups like -NHCO or $-NO_2$ groups which play an important role in the adsorption of silver ions.

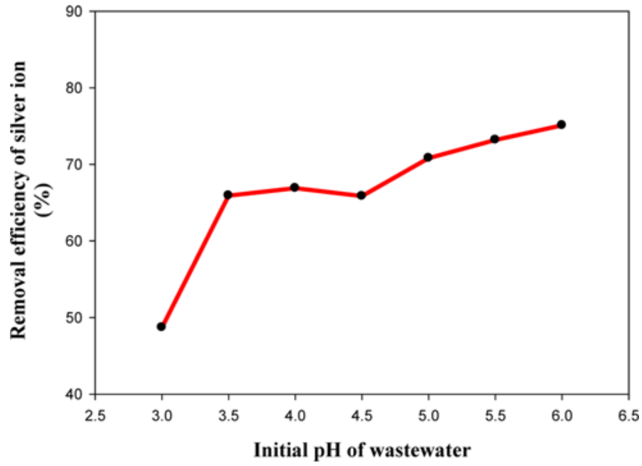
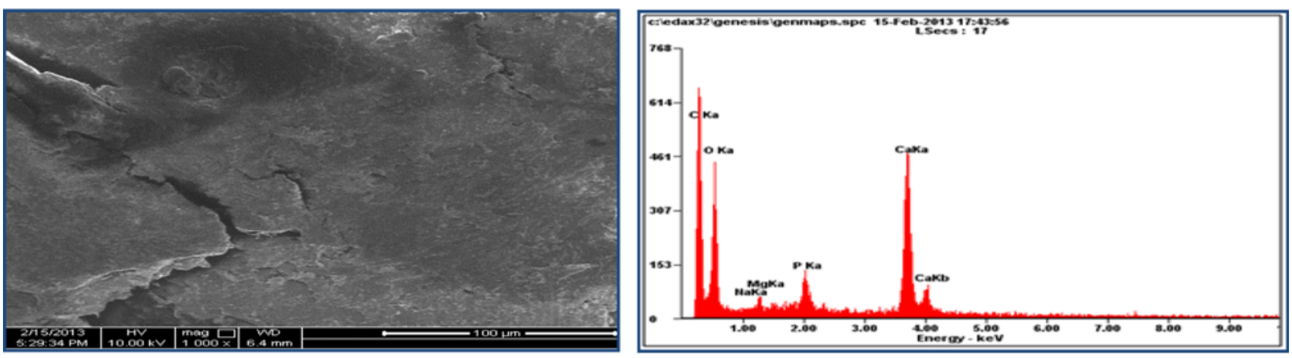
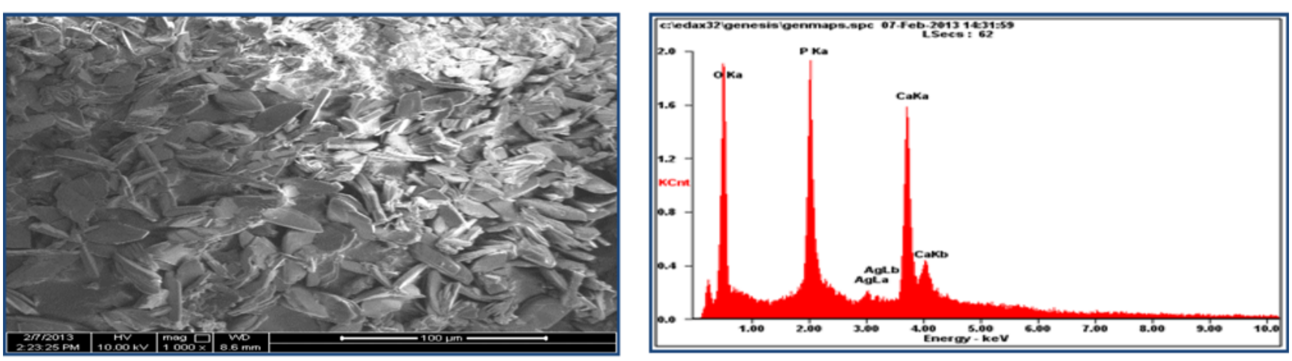



**Fig. 4.** Effect of pH on removal efficiency for silver ion using waste crab shell (concentration of waste crab shell: 20 g/L, initial concentration of silver ion: 100 mg/L, stirring speed: 300 rpm).

Fig. 3 shows the SEM (scanning electron microscopy) and EDX (energy dispersive X-ray) for crab shells which have (a) before adsorption of silver ions (b) after adsorption of silver ions. As shown in SEM, the electron dense part which is thought to be silver adsorption appeared at the (b), as compared with (a). To verify whether the electron dense part on the surface of the crab shells is made up of silver ions, EDX analysis was applied. While the EDX (a) for virgin crab shells did not show the characteristic peak of silver ions, (b) for the crab shells after adsorption clearly appeared the peak of




(a) Before adsorption of silver ions




(b) After adsorption of silver ions

Fig. 3. SEM and EDX of crab shells.

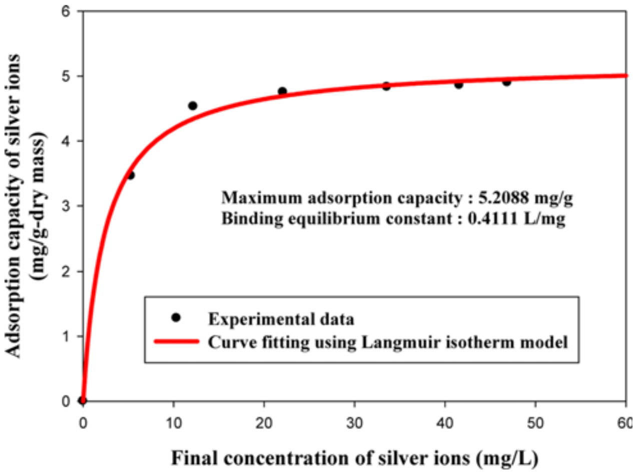



**Fig. 5. Isothermal adsorption curve of crab shells for silver ions (working volume: 100 mL, initial pH of wastewater: 6.0, stirring speed: 300 rpm).**

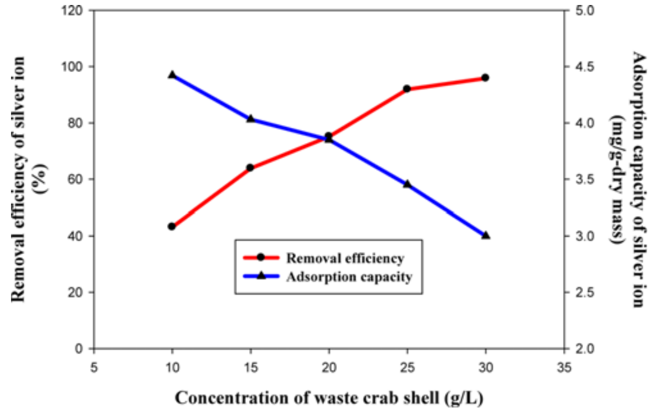



**Fig. 6. Effect of concentration of waste crab shells on the removal efficiency and adsorption capacity for silver ions (initial concentration of silver ion: 100 mg/L, initial pH of wastewater including silver ion: 6.0, stirring speed: 300 rpm).**

silver ions. Therefore, the existence of silver ions onto the surface of the crab shells by the result was proved.

The pH of a solution has an important role in metal ion adsorption. This is partly because hydrogen ions themselves are strongly competing with metal ions [22]. The effect of pH value on removal efficiency of silver ions is shown in Fig. 4. It can be seen that the removal efficiency of crab shells for silver ions increased with the increasing pH value. At low pH values (pH<3.5), the low removal efficiency may be explained as the competition adsorption for the -NHCO and $-NO_2$ sites between protons ($H^+$) and silver ions ($Ag^+$).

A static equilibrium test was performed to study the isothermal adsorption of crab shells for silver ions at initial pH 6 of the waste solution. In Fig. 5, the adsorption capacity increased with growing the final concentration of silver ions until it reached saturation. Generally, the adsorption isotherms reveal the specific relation between the concentration of sorbent and its sorption degree onto adsorbent surface at constant temperature [23]. We chose the Langmuir sorption model to estimate the maximum uptake capacity, and the affinity constant of waste crab shells for silver ions and regression curve fit well with the experimental data as the 0.988 of correlation coefficients ($r^2$). The maximum uptake capacity ($q_{max}$) and affinity constant was 5.21 mg/g-dry mass and 0.411 L/mg, respectively. Silver adsorption has been studied with various adsorbents. In Table 2, the maximum adsorption capacity of crab shells has been compared to other adsorbents. Although a direct comparison is difficult due to the varying experimental conditions employed in those studies, it can be concluded that the adsorption of silver ions onto waste crab shells is as effective as other adsorbents. Especially, in terms of recycling of marine waste, waste crab shells have advantage of economic feasibility, as compared with other sorbents when selecting an adsorbent for removal of silver ions.

**Table 2. Comparison of maximum adsorption capacity for silver ions with various adsorbents**

| Adsorbent | Maximum adsorption capacity (mg/g-dry mass) | Reference |
|---|---|---|
| Coke | 4.9 | [24] |
| Peat | 10.8 | [24] |
| Low-rank Turkish coals | 1.87 | [25] |
| Expanded perlite | 8.46 | [4] |
| Crab shells | 5.21 | This study |

The effect of adsorbent dosage on the removal efficiency of silver ions at initial pH 6.0 of waste solution is shown in Fig. 6. This figure shows that adsorbent dosage has an important role in the adsorption process. The removal efficiency of silver ions sharply increased with the increasing of crab shells concentration, and the maximum value was the 96% obtained from the 30g/L of adsorbent concentration. The increase in the removal efficiency may be attributed to the fact that an increase in adsorbent dosage means increasing the ratio of adsorbent weight/solution volume, and therefore, the adsorption is higher because of the increasing of mass for solid phase [4]. Meanwhile, adsorption capacity of silver ions decreased with the increasing of adsorbent concentration, which causes an increase of unsaturated sorption site for metal ions [26].

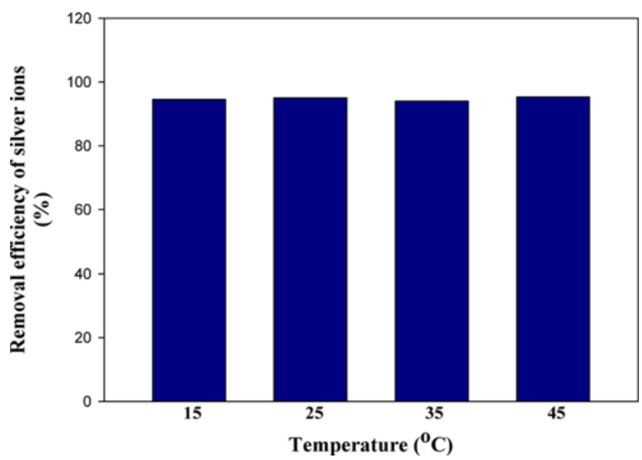



**Fig. 7. Effect of temperature on removal efficiency of silver ions using waste crab shell (initial concentration of silver ion: 100 mg/L, concentration of waste crab shell: 30 g/L, initial pH of wastewater: 6.0, stirring speed: 300 rpm).**

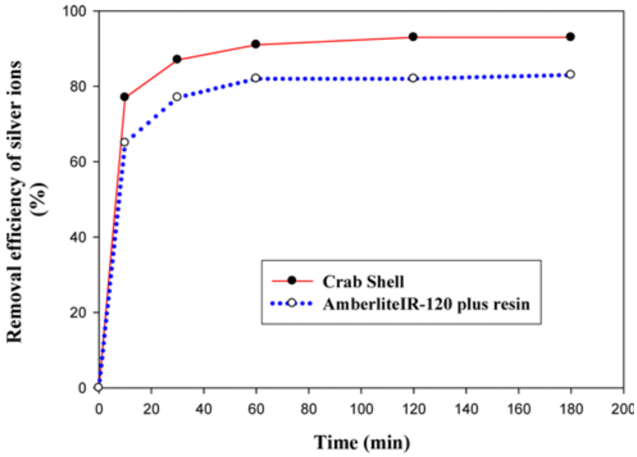



**Fig. 8. Removal efficiency of silver ions for crab shell and amberlite IR-120 plus resin (initial concentration of silver ions: 100 mg/L, adsorbent concentration: 30 g/L, initial pH: 6.0, stirring speed: 300 rpm).**

Fig. 7 shows the effect of temperature on removal efficiency of crab shells for silver ions. The removal efficiency hardly changed in the range of 15.0-45.0 °C, which means that the effect of temperature could be neglected during the research process. It is also well known that the temperature of actual wastewater is generally in the range of 25.0-40.0 °C. Therefore, silver adsorption using crab shells has the advantage of applicability for actual wastewater treatment regardless of the temperature of the waste solution. And it reflected that the adsorption of crab shells for silver ions is not dominated by physical adsorption, which is largely affected by temperature [2]. Quite the same result was reported by Zhou et al [27].

The effect of time on removal efficiency for silver ions by the crab shells and Amberlite IR 120 plus resin, which is well known as a commercial cation exchange resin, is shown in Fig. 8. The slope of the lines combining the data points in the figure reflects the adsorption rates. The silver adsorption increased dramatically with the increasing of adsorption time, and then was followed by a relatively slow phase. All adsorption was completed in 60 min for both adsorbents. Hanzlik et al. reported that the equilibrium adsorption time for the silver removal using several adsorbents was 5 hr [28]. In addition, removal efficiency of crab shells was higher than that of Amberlite IR 120 plus resin. It shows that the adsorption process using crab shells can be applied to the recovery system for silver ions in an actual wastewater treatment system, and furthermore, the technique could sufficiently replace a conventional treatment process such as solvent extraction and ion exchange resin.

## CONCLUSIONS

Waste crab shells were employed to effectively adsorb silver ions in actual industrial wastewater. The removal efficiency of crab shells for silver ions increased with the increasing of pH value. Langmuir sorption model was chosen to estimate the maximum uptake capacity and affinity constant of waste crab shells for silver ions; its value was 5.21 mg/g-dry mass and 0.411 L/mg, respectively. The removal efficiency of silver ions sharply increased with the increasing of crab shells concentration, with the maximum value, 96%, obtained from the 30 g/L of adsorbent concentration at initial pH 6.0 of waste solution. Also, the removal efficiency hardly changed in the range of 15.0-45.0 °C and the entire adsorption process was completed in 60 min. In addition, removal efficiency of crab shells was higher than that of Amberlite IR 120 plus resin. From these results, we concluded that the adsorption process using crab shells can be applied to the recovery system for silver ions in actual wastewater treatment system; furthermore, the technique could sufficiently replace conventional treatment processes such as solvent extraction and ion exchange resin.

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