

# Adsorption of silver ions from industrial wastewater using waste coffee grounds

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**Abstract**—Waste coffee grounds were used as an adsorbent to efficiently adsorb silver ions in actual industrial wastewater. It was found that the functional groups like  $\text{-COO}^-$  and  $\text{-OH}^-$  groups in coffee grounds play an important role in the adsorption of silver ions from the FT-IR spectra, and the SEM images and EDX spectra were used to investigate the surface onto waste coffee grounds and confirm the existence of silver ions onto the waste coffee grounds after adsorption of silver ions. The highest adsorption capacity and removal efficiency was achieved as about 46.2 mg/g and 92.4% at the initial pH 6 of wastewater. Two adsorption isotherm models, Langmuir and Freundlich, were used to analyze the equilibrium data. The Langmuir isotherm, which provided the best correlation for silver adsorption onto coffee grounds, showed that the maximum adsorption capacity and affinity constant was calculated as 49.543 mg/g and 1.134 L/mg, respectively. The adsorption was an exothermic reaction and the most equilibrium was achieved at less than 60 min. From these results, the waste coffee grounds have high possibility to be used as effective and economical adsorbent for silver adsorption.

Keywords: Coffee Grounds, Silver Ions, Adsorption, Industrial Wastewater, Removal

## INTRODUCTION

The excessive release of silver from industrial wastewater has caused a serious environmental problem, especially water. Monovalent silver ion is more toxic for fish than copper or mercury, and it is an extremely effective germicide [1]. The ecological systems with toxic silver have been finally exposing top-level predators to very high levels of pollution and therefore it will cause various diseases and disorders, such as the fatty degeneration of the liver and kidneys in the human body [2,3]. Nevertheless, silver has been widely applied in many industrial fields containing electroplating, communications, medical equipment and metal alloy industries, because it has the highest electrical and thermal conductivity, which results in a relative shortage of silver resources [4,5]. According to Purcell's report, while silver deposits in the world are sharply decreased, the extensive applications of silver ions have increased rapidly [6]. Therefore, silver in the effluents discharged from various industries has been necessarily recovered in terms of secure and recycling of resources.

Many methods have been developed to remove silver from industrial wastewater, including chemical precipitation, ion exchange, electrolysis, replacement, membrane and reverse osmosis [7,8]. In recent years, adsorption has attracted a great deal of attention because of low operating cost, generating of minimum amounts for sludge and high selectivity to specific metals. According to the literature survey, various kinds of adsorbents have been used to remove and recover silver from aqueous solutions or industrial waste-

water. To increase the adsorption capacity of silver ions, many chemically modified adsorbents, chelating and commercial ion exchange resins have been widely used [9-12]. Neudachina et al. studied the selective adsorption of silver ions over copper ions using sulfonethyl derivative based on chitosan [13]. However, these adsorbents have a problem concerning economic efficiency; therefore, recently, many works have focused on the use of low cost materials, including waste wool, peanut shells, crab shells, soybean hulls and cotton which are available in large quantities [14-16]. Inoue et al. applied acidothiurea leaching approach using biosorbent prepared from easily available agricultural waste to recover silver ions from printed circuit boards (PCBs) of mobile waste [17].

Coffee has become a popular beverage worldwide, including Korea, and significant quantities of coffee grounds are produced from the coffee manufacturing process. According to the United States Department of Agriculture (USDA), the annual global production capacity of coffee beans in the year 2012/2013 was estimated as exceeding 150 million of 60 kg bags, and in the future more production and waste of coffee ground are expected [18]. Most coffee grounds are burned as waste, which produces carbon dioxide, the greenhouse gas [19]. Therefore, extensive study on the efficient reuse/recycling of coffee grounds has been performed and until now, they have been used as soil remediation, removal of hazardous molecules from aqueous or gas phases, and wastewater desalination [20,21].

In this study, we used recycled waste coffee grounds to remove silver from industrial wastewater directly as a zero-cost adsorbent. The FT-IR and SEM-EDX of waste coffee grounds for before and after silver adsorption was examined to understand the possible adsorption mechanism. In addition, adsorption characteristics of waste coffee grounds for silver were investigated under the various

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experimental conditions of initial pH of wastewater, contact time, and temperature etc.

## MATERIALS AND METHODS

Five kinds of waste coffee grounds from different cafeterias located in the city of Gangneung in Korea were used. Overall, the composition of five different species of coffee grounds was similar, but the presence of composition may have been different due to the cistern water used in cafeterias for the preparation of coffee drinking [23]. They were thoroughly washed with deionized water and dried in an oven (JEIO TECH OF-22GW) at 80 °C for one day. Finally, they were sieved by molecular sieving with 80-100 mesh without any further treatment.

The industrial wastewater, including silvers used in this study, was obtained from the Toricom Company in the city of Chunan in Korea. All the chemical reagents were of analytical grade (Sigma Aldrich, U.S.A) and used without further purification.

FT-IR analysis was conducted with a Perkin Elmer 1725x spectrometer (U.S.A.) to confirm functional groups in coffee grounds for before and after adsorption of silver ions. Infrared spectra were recorded with a Bruker IFS 66 (1,000-4,000  $\text{cm}^{-1}$ ) spectrophotometer. Samples of 100 mg KBr disks containing 2% of beads of each sample were prepared less than 24 hours before recording. The morphology of the coffee grounds for before and after adsorption of silver ions was also studied to confirm surface condition and components onto the coffee grounds by a scanning electron microscope (SEM, Hitachi model S-4100, Japan) and energy dispersive X-ray spectroscopy (EDX, U.S.A.).

All sorption experiments were batch-type with 100 mL conical flasks sealed with rubber stoppers and placed in a rotary shaking incubator (JEIO TECH, SI-600R, Korea) at desired temperature, pH and time. To find the optimum waste coffee grounds to use in the present study, an adsorption experiment for silver ions using five kinds of different species was performed. 0.1 g of each sample was agitated with 100 mL of wastewater with 50 mg/L of silver concentration at the initial pH 4.0. Each industrial wastewater with desired initial pH values (2.0, 3.0, 4.0, 5.0 and 6.0), which was adjusted by adding NaOH and  $\text{HNO}_3$  solutions, was prepared to examine the effect of pH on the adsorption capacity of silver ions. The investigation for the adsorption of silver ions was avoided above pH 7.0 due to the precipitation of silver ions as hydroxides [22]. The equilibrium adsorption isotherm was determined by agitating the mixture of coffee grounds and industrial wastewater with different initial concentrations (4, 10, 20, 30, 40 and 50 mg/L) for 24 h at the pH 6.0. To investigate the effect of contact time, 0.1 g of coffee grounds was added to 100 mL of wastewater with 50 mg/L of silver concentration for predetermined periods (10, 30, 60, 120, 180 min). In addition, the effect of temperature on adsorption capacity of silver ions was also observed (15, 25, 35, and 45 °C).

When adsorption for silver ions in industrial wastewater approached to equilibrium state, the mixture was centrifuged at 4,000 rpm for 30 min to remove suspending coffee grounds 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.).

The removal efficiency (R.E, %) and adsorption capacity ( $q_e$ , mg/g) were calculated using Eqs. (1) and (2), respectively:

$$\text{R.E} = \frac{C_i - C_e}{C_i} \times 100\% \quad (1)$$

$$q_e = \frac{C_i V_i - C_e V_f}{m} \quad (2)$$

where,  $C_i$  (mg/L) and  $C_e$  (mg/L) are the initial and equilibrium silver ions concentration, respectively.  $V_i$  (L) and  $V_f$  (L) are the initial and final volume of industrial wastewater.  $m$  (g) is the weight of adsorbent used in the experiment. All experiments were performed three times and the average was used in the analysis.

## RESULTS AND DISCUSSION

The composition for wastewater supplied from Toricom was analyzed and given in Table 1. The concentration of silver ions was very high at about 1,330 mg/L, while the concentration of aluminum and total chrome ions was very low at about 5.2 and 0.9 mg/L, respectively. Also, the concentration for anionic ions such as  $\text{CN}^-$  and  $\text{Cl}^-$  was not detected. In this study, the wastewater was properly diluted because of very high concentration of silver ions, and concentration for aluminum and chrome ions was not measured because their concentrations were very low, as compared to silver concentration. On the other hand, actual industrial wastewater-

Table 1. Composition of wastewater

Components	Concentration (mg/L)
Ag(I)	1,330
Al(III)	5.2
Total Cr	0.9
$\text{CN}^-$	Not detected
$\text{Cl}^-$	Not detected

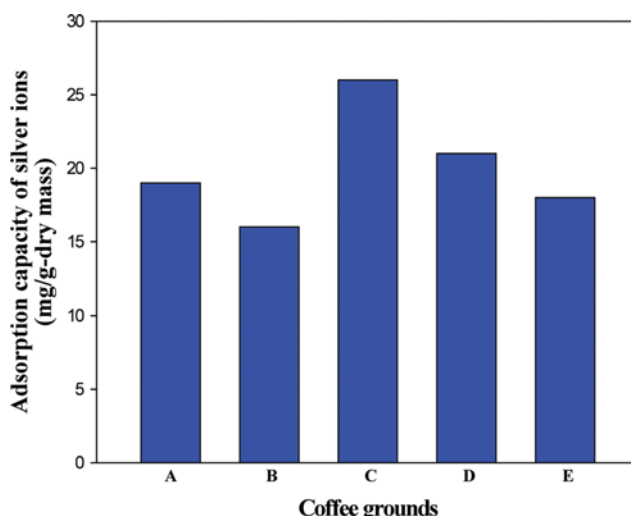


Fig. 1. Comparison of adsorption capacity for silver ions using various coffee grounds in industrial wastewater (Initial pH of wastewater: 4.0, initial concentration of silver ions: 50 mg/L, adsorbent concentration: 1.0 g/L, working volume: 0.1 L).

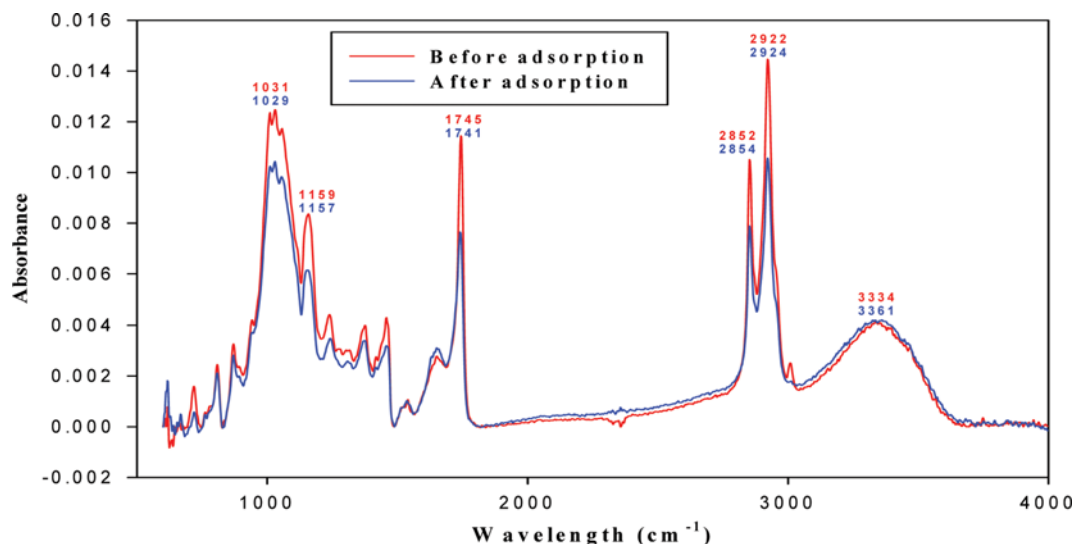


Fig. 2. FTIR spectra of coffee grounds before and after adsorption.

ter was very strong acidic condition as about pH 0.7.

To find the optimum adsorbent, five kinds of waste coffee grounds were used to adsorb silver ions and the result is shown in Fig. 1. Silver adsorption capacity for each waste coffee ground did not show great difference at about 16-26 mg/g; however, waste coffee grounds obtained from the C cafeteria, which showed the highest adsorption capacity at about 26 mg/g, was selected in terms of economic feasibility and it was applied to all adsorption experiments in the study. The BET surface area of coffee grounds obtained from the C cafeteria was 4.574 m<sup>2</sup>/g (data not shown).

To investigate which functional groups of waste coffee grounds were responsible for silver adsorption, FT-IR spectra analysis for solid samples before and after the adsorption process was carried out. As shown in Fig. 2, the broad bands observed at the 3,330 and 3,430 cm<sup>-1</sup> were thought to represent the stretching of O-H group due to inter- and intra-molecular hydrogen bonding of polymeric compounds, such as alcohols, phenols and carboxylic acids as in pectin, cellulose and lignin [23]. The O-H stretching vibrations happened within a broad range of frequencies, indicating the presence of free hydroxyl groups and bonded O-H bands of carboxylic acids [24,25]. The characteristic peak appearing at the 2,920 cm<sup>-1</sup> indicates symmetric or asymmetric C-H stretching vibration of aliphatic acids [24,26]. The absorption peaks at 1,744 and 1,745 cm<sup>-1</sup> were assigned to the resulting carboxyl linkage derived from xanthine derivatives including caffeine [27]. The characteristic peak around 1,383 cm<sup>-1</sup> appeared due to the COO<sup>-</sup> symmetric stretching vibration and the bands in the range of 1,200-900 cm<sup>-1</sup> were assigned to m(S=O), indicating the existence of sulfur [28]. The characteristic peaks of 3,334, 2,922, 2,852, 1,745, 1,159 and 1,031 cm<sup>-1</sup> for before adsorption had shifted to 3,361, 2,924, 2,854, 1,741, 1,157 and 1,029 cm<sup>-1</sup>, respectively, due to silver adsorption. These shifts may be attributed to the changes in counter ions associated with carboxylate and hydroxylate anions, suggesting that acidic groups including carboxyl and hydroxyl play an important role in metal adsorption [29]. Therefore, it was concluded that waste coffee grounds used in this study have functional groups like COO<sup>-</sup>

and OH<sup>-</sup> groups which play an important role in the silver adsorption. In addition, sulfur also contributed to the binding to silver ions, to some extent.

To investigate the surface structure of waste coffee grounds for before and after silver adsorption, morphological analysis was carried out by SEM and EDX. As shown in Fig. 3(a), coffee grounds have a porous and homogeneous structure with a deep pore and are mainly composed of carbon (61.60%) and oxygen (38.40%). However, in the case of (b), after silver adsorption, electron dense parts, which are thought to be silver adsorption, appeared on the SEM images, and EDX spectra analysis showed that the characteristic peaks for silver ions which have 19.82% clearly emerged.

In adsorption study, aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the adsorbent [30]. Therefore, it has been identified as the most important variable affecting metal adsorption onto adsorbent; this is partly because hydrogen ions themselves are strongly competing with metal ions [31]. The effect of initial pH value of wastewater on the adsorption capacity and removal efficiency of waste coffee grounds for silver ions was conducted and the result is shown in Fig. 4. The study on pH effect beyond 7.0 was excluded because insoluble silver-hydroxide-precipitate was observed in the wastewater. The precipitation effect was almost the same as Wang's report [22]. It can be seen that the adsorption capacity and removal efficiency of waste coffee grounds for silver ions increased with the increasing pH value. Especially, the highest adsorption capacity and removal efficiency was achieved as about 46.2 mg/g and 92.4% at the pH 6. In the case of low pH (pH<3.0), adsorption capacity and removal efficiency were very low because of the competition adsorption for the COO<sup>-</sup> and OH<sup>-</sup> sites between protons (H<sup>+</sup>) and silver ions (Ag<sup>+</sup>). According to Yurtsever and Azouaou's reports, phenolic and carboxylic groups into the waste coffee grounds play an important role in adsorption of metals including silver [5,23]. Therefore, if adsorption of waste coffee grounds for silver ions could be done by two different functional groups, the mechanism is as follows:

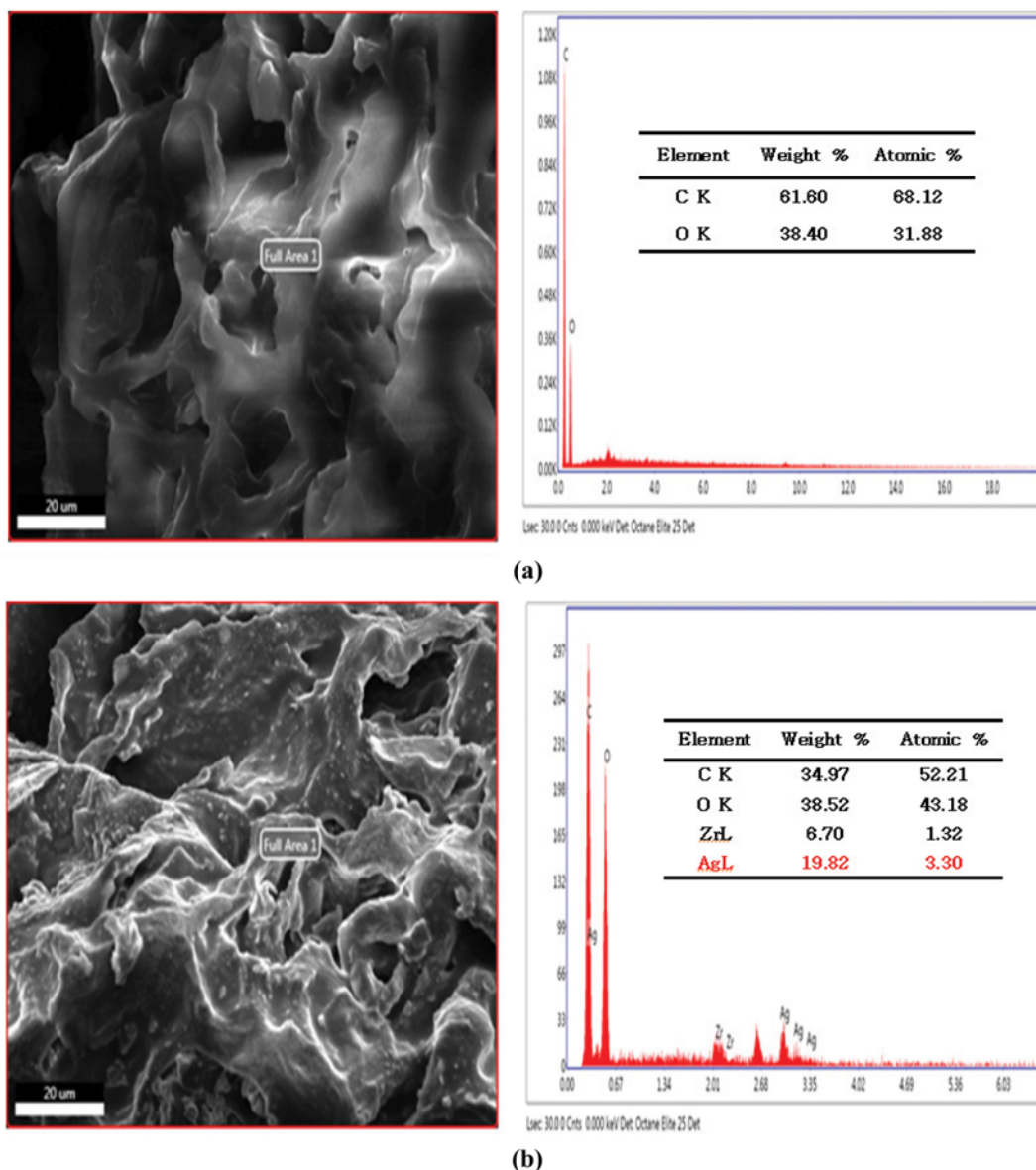


Fig. 3. SEM and EDX of waste coffee grounds.

(a) Before adsorption of silver ions, (b) after adsorption of silver ions



From the result, the optimum initial pH of wastewater was selected as 6.0 and the pH was applied to the future adsorption experiments.

The adsorption isotherm is important from both a theoretical and a practical point of view. To optimize the design of an adsorption system to remove the metal ions, it is important to establish the most appropriate correlations of the equilibrium data of each system [32]. In this study, two classical adsorption models, Langmuir and Freundlich isotherms, were applied to describe silver adsorption equilibrium. Generally, the Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. The Langmuir model is based on the assumption of adsorption homogeneity, such as equally available adsorption sites,

monolayer surface coverage and no interaction between adsorbed species, while the Freundlich model is the empirical relationship whereby it is assumed that the adsorption energy of a protein binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied [33]. The Langmuir and Freundlich model can be expressed as Eqs. (5) and (6), respectively:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_e K_L C_e} \quad (5)$$

$$\text{Log} q_e = \text{Log} K_f + \frac{1}{n} \text{Log} C_e \quad (6)$$

where  $q_e$ ,  $q_m$  and  $K_L$  are adsorption capacity (mg/g) corresponding to metal ion concentration ( $C_e$ ), maximum adsorption capacity of metal ions (mg/g) and Langmuir adsorption constant (L/mg),

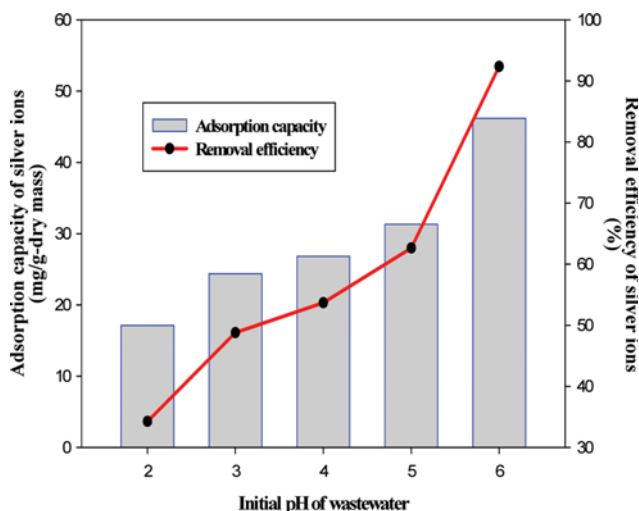


Fig. 4. Effect of pH on adsorption capacity and removal efficiency of silver ions using coffee grounds (Initial concentration of silver ions: 50 mg/L, concentration of coffee grounds: 1.0 g/L, working volume: 0.1 L).

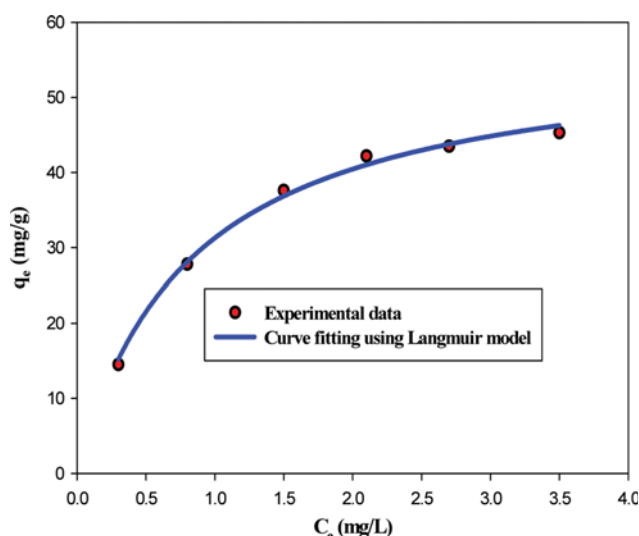


Fig. 5. Isothermal adsorption curve of waste coffee grounds for silver ions using Langmuir isotherm model (Initial pH of wastewater: 6.0, working volume: 100 mL).

respectively. Also, the  $K_f$  is a constant related to the adsorption capacity and  $1/n$  is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of material. Figs. 5 and 6 show the isothermal adsorption curves of waste coffee grounds for silver ions using two isotherm models, respectively, at initial pH 6.0 and 25 °C of wastewater. From the regression result using Langmuir model, the  $q_m$  and  $K_L$  parameters for silver ions were achieved as 49.543 mg/g and 1.134 L/mg, respectively, and regression curve fit well with the experimental data together with the 0.995 of correlation coefficients ( $r^2$ ), as shown in Table 2. The comparison of maximum adsorption capacity of the waste coffee grounds with that of various adsorbents for silver ions is given in Table 3, and it is found that the waste coffee grounds have a high

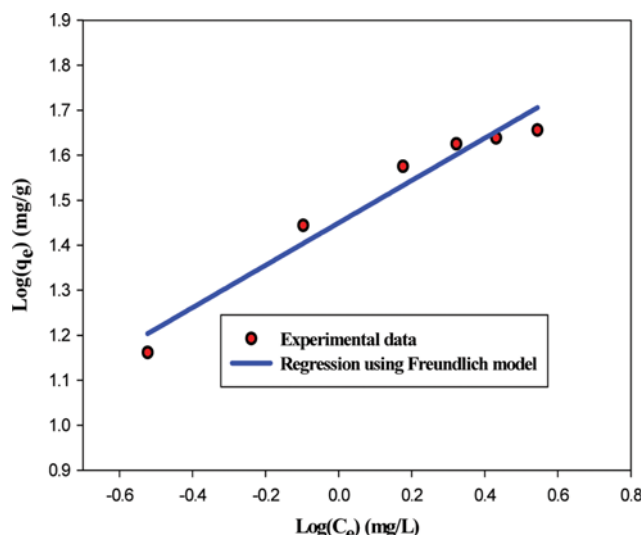


Fig. 6. Isothermal adsorption of waste coffee grounds for silver ions using Freundlich isotherm model (Initial pH of wastewater: 6.0, working volume: 100 mL).

Table 2. Isotherm adsorption model parameters of waste coffee grounds for silver ions

Langmuir isotherm model			Freundlich isotherm model		
$q_m$ (mg/g)	$K_L$ (L/mg)	$r^2$	$1/n$	$K_f$ (L/g)	$r^2$
49.543	1.134	0.995	0.471	14.754	0.953

Table 3. Comparison of maximum adsorption capacity for silver ions of waste coffee grounds with various adsorbents for silver ions

Adsorbent	Maximum adsorption capacity (mg/g)	Reference
Valonia Tannin Resin (VTR)	97.08	[5]
Calcium alginate beads	52.00	[34]
Natural clinoptilolites	31.44	[35]
Peat	10.80	[36]
Coffee grounds	49.54	This study

adsorption capacity as comparable with that of the other adsorbents. Therefore, considering the low cost of this natural adsorbent (waste), it can be used as an alternative material to recover silver ions in wastewater. Also, the values of  $1/n$  and  $K_f$  for silver ions were obtained from the Freundlich model as 0.471 and 14.754 L/g, respectively. The correlation coefficient ( $r^2$ ) was 0.953 and lower than that of Langmuir model. Therefore, we concluded that the isotherm adsorption for silver ions of waste coffee grounds well follows the Langmuir isotherm model. Fig. 7(a) shows the effect of temperature on adsorption capacity for silver ions of waste coffee grounds. The adsorbed amount of silver ions slightly decreases when increasing temperature in the range of 15.0–45.0 °C. It means that low temperature is in favor of silver ions removal by adsorption onto coffee grounds. This effects indicates that an explanation of the adsorption mechanism concerned with the removal of sil-



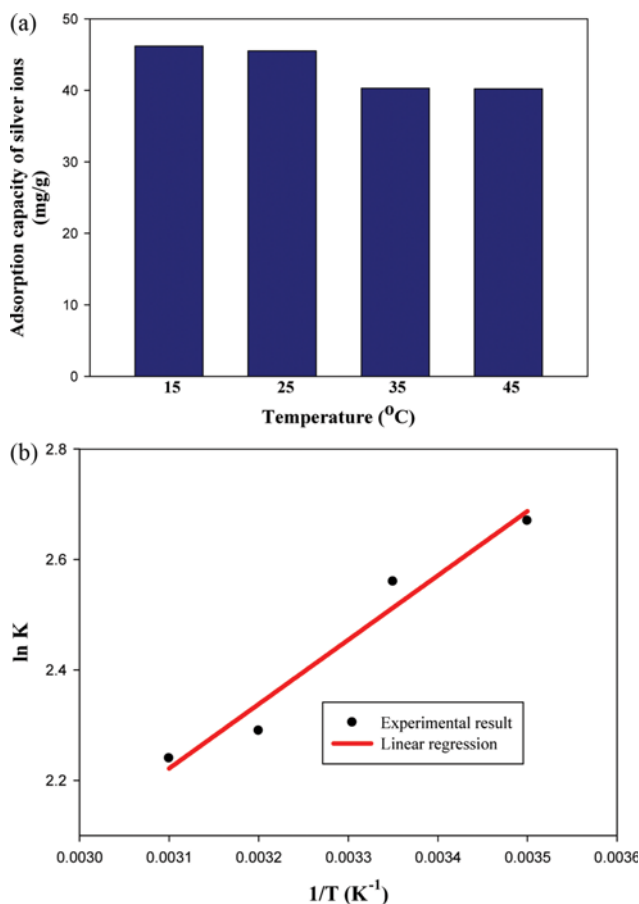


Fig. 7. (a) Effect of temperature on adsorption capacity of silver ions using coffee grounds (Initial concentration of silver ions: 50 mg/L, concentration of coffee grounds: 1.0 g/L, initial pH of wastewater: 6.0, stirring speed: 300 rpm). (b) Linear regression of  $\ln K$  versus  $1/T$  obtained for the adsorption of silver onto coffee grounds.

ver ions onto coffee grounds involves a physical process to some extent, in which adsorption arises from electrostatic interaction, which is usually associated with low adsorption heat [37]. The results also imply that the adsorption process has an exothermic reaction and quite the same result was reported by Sari et al. and Azouaou et al. [16,23]. From the result, the optimum temperature was chosen as 25.0 °C (room temperature), in which it is not necessary to have temperature control. Otherwise, thermodynamic parameters can be determined using the equilibrium constant  $K$ , which depends on temperature. The change in Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) associated with the adsorption process was calculated using the following equations:

$$\Delta G = -RT \ln K \quad (7)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

where  $R$  is the universal gas constant (8.314 J/mol·K) and  $T$  is absolute temperature (K). Eq. (8) is used to predict the process enthalpy and entropy by regression analysis of  $\ln K$  versus  $1/T$  plotting and

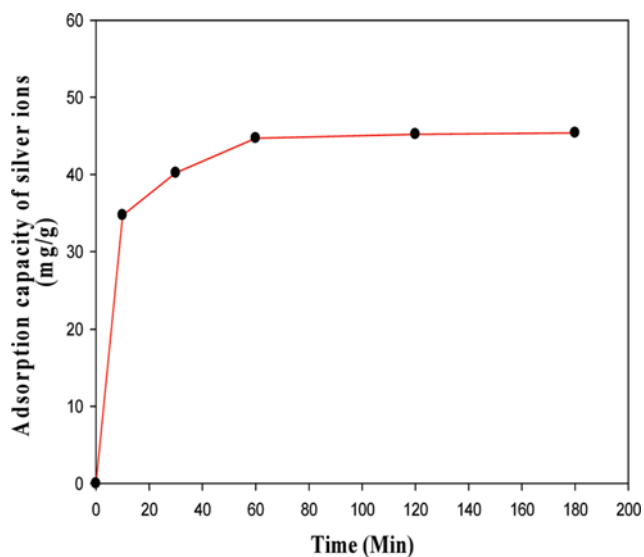


Fig. 8. Adsorption capacity for silver ions of coffee grounds with time (Initial concentration of silver ions: 50 mg/L, coffee ground concentration: 1.0 g/L, initial pH of wastewater: 6.0).

the graph is shown in Fig. 7(b). The values of enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were found to be, respectively,  $-9.683$  KJ/mol and  $-11.546$  J/mol·K. The negative value of  $\Delta H$  for silver adsorption confirmed that the adsorption process was exothermic. And the negative value of  $\Delta S$  implied that silver ions in wastewater was in a much more chaotic distribution compared to the relatively ordered state of solid phase [23]. Similar results have been found in previous works [38,39]. Gibbs free energy change ( $\Delta G$ ) was between  $-6.396$ ,  $-6.345$ ,  $-5.925$  and  $-5.866$  KJ/mol for temperatures of 288, 298, 308 and 318 K, respectively.

The effect of contact time on adsorption capacity for silver ions of coffee grounds was studied, and the results are shown in Fig. 8. The slope of the lines combining the data points in the figure reflected the adsorption rates. The silver adsorption increased sharply with the increasing of adsorption time, and then followed by a relatively slow phase. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid and then, as lower adsorption would follow, as the available adsorption sites gradually decreases, which is consistent with studies reported before [40]. From the result, it was found that most of adsorption for silver ions of coffee grounds was completed within 60 min, which shows superiority, as compared with Hanzlik's report that an equilibrium adsorption time for the silver removal using several adsorbents was 5 hr [41].

To further understand the adsorption mechanism of the metal adsorption process and judge the performance of adsorbents used for metal ions adsorbed, pseudo first-order and pseudo second-order models were used to describe the kinetics of silver adsorption onto the coffee grounds [22]. The pseudo first-order kinetic model can be expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (9)$$

where,  $q_e$  (mg/g) and  $q_t$  (mg/g) are the amounts of silver ions ad-

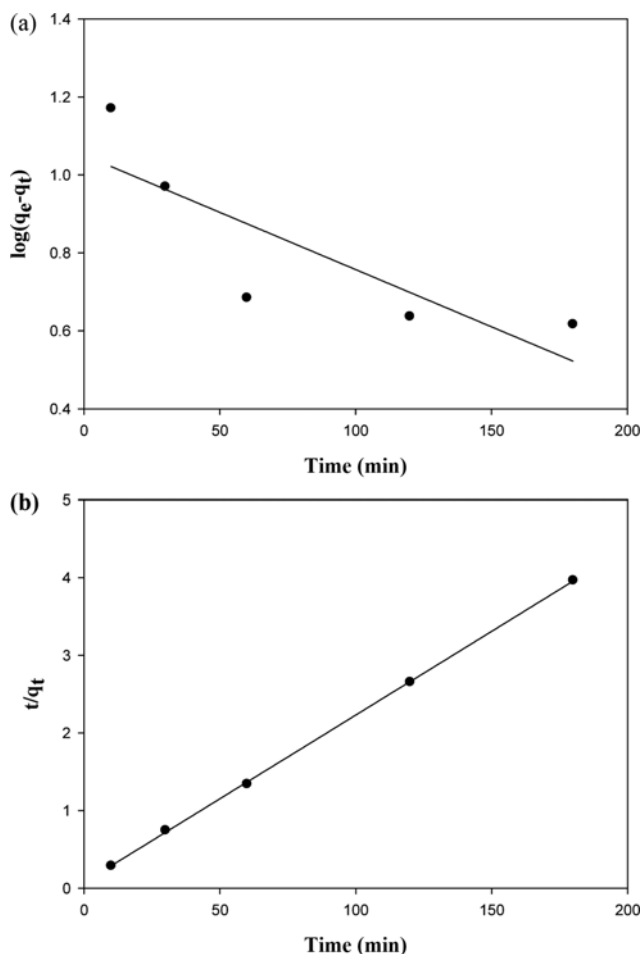


Fig. 9. (a) Pseudo first-order kinetic plots of the adsorption data. (b) Pseudo second-order kinetic plots of the adsorption data.

sorbed at equilibrium and time  $t$ , respectively;  $k_1$  is the pseudo first-order rate constant. The  $q_e$  and rate constant  $k_1$  can be calculated by plotting the  $\log(q_e - q_t)$  versus  $t$ , as shown in Fig. 9(a). The  $r^2$  value is 0.7018, so the plot shows non-linear behavior. The calculated  $q_e$  value is 11.25 mg/g and not in agreement with the experimental data (49.54 mg/g). From the result, the adsorption of silver ions does not follow pseudo first-order kinetics.

The pseudo second-order models can be represented as the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where,  $k_2$  is the pseudo second-order rate constant of adsorption. The slope and intercept of the linear plot  $t/q_t$  versus  $t$  yield the val-

ues of  $q_e$  and  $k_2$ , as shown in Fig. 9(b). From the linear regression, correlation coefficients ( $r^2$ ) and several parameters were obtained and the values are summarized in Table 4. As seen, the obtained  $r^2$  value is 0.9998 and the calculated  $q_e$  value (46.29 mg/g) is in excellent agreement with the experimental  $q_e$  value (49.54 mg/g). Therefore, we concluded that the adsorption of silver ions onto the coffee grounds kinetics was in accordance with the pseudo second-order model. Similar results have been found in previous works [38,42].

## CONCLUSIONS

Untreated waste coffee grounds were used to adsorb silver ions in industrial wastewater. From the FT-IR spectra analysis, it was found that the waste coffee grounds have functional groups like  $\text{COO}^-$  and  $\text{OH}^-$  groups, which play an important role in silver adsorption. The existence of silver ions onto adsorbent was confirmed by SEM images and EDX spectra. Coffee grounds have a porous and homogeneous structure with a deep pore and are mainly composed of carbon (61.60%) and oxygen (38.40%). After silver adsorption, electron dense parts, which are thought to be silver adsorption, appeared on the SEM images and EDX spectra analysis showed that the characteristic peaks for silver ions which have 19.82% clearly emerged. The adsorption capacity for silver ions of coffee grounds increased when increasing pH value of wastewater from 2.0 to 6.0 and the highest adsorption capacity and removal efficiency were achieved as about 46.2 mg/g and 92.4% at the pH 6. To evaluate adsorption behavior for silver ions of waste coffee grounds, the Langmuir and Freundlich sorption model were used and the maximum adsorption capacity and affinity constant for silver ions of waste coffee grounds were calculated as the 49.543 mg/g and 1.134 L/mg, respectively. Also, the isotherm adsorption for silver ions of waste coffee grounds well follows the Langmuir isotherm model, as compared with Freundlich model. The adsorbed amount of silver ions slightly decreased when increasing temperature in the range of 15.0–45.0 °C, and the value of enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) was found to be, respectively,  $-9.683$  KJ/mol and  $-11.546$  J/mol·K. Thus, the adsorption process has an exothermic reaction. Most of the adsorption for silver ions of coffee grounds was completed within 60 min and the kinetics was in accordance with the pseudo second-order model. From these results, we concluded that the adsorption process using waste coffee grounds can be sufficiently applied to the adsorption/recovery system for silver ions in actual industrial wastewater treatment system; and furthermore, the technique could replace conventional treatment processes such as solvent extraction and ion exchange resin.

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## REFERENCES

1. A. R. Jacobson, M. B. McBride, P. Baveye and T. S. Steenhuis, *Sci. Total Environ.*, **345**, 191 (2005).
2. G. Aragay, J. Pons and A. Merkoci, *Chem. Rev.*, **111**(5), 3433 (2011).

Table 4. Adsorption kinetic parameters for silver adsorption onto coffee grounds

Kinetic model	$q_e$ (mg/g) calculated	Rate constant	$r^2$
Pseudo first-order	11.25	0.0067 ( $\text{min}^{-1}$ )	0.7018
Pseudo second-order	46.29	0.0063 (g/mg·min)	0.9998

3. P. L. Drake and K. J. Hazelwood, *Annal. Occupa. Hygi.*, **49**, 575 (2005).
4. Z. Celik, M. Gulfen and A. O. Aydin, *J. Hazard. Mater.*, **174**(1-3), 556 (2010).
5. M. Yurtsever and I. A. Sengil, *Trans. Nonferrous Met. Soc. China.*, **22**, 2846 (2012).
6. T. W. Purcell and J. J. Peters, *Environ. Toxicol. Chem.*, **17**, 539 (1998).
7. K. S. Shin, E. M. Choi and T. S. Hwang, *Desal.*, **263**, 151 (2010).
8. C. Y. Wang, B. Y. Fang, M. H. Yao and Y. D. Zhao, *Sens. Actua. B. Chem.*, **228**, 643 (2016).
9. M. A. Abd El-Ghaffar, Z. H. Abdel-Wahab and K. Z. Elwakeel, *Hydrometal.*, **96**, 27 (2009).
10. G. X. Li, X. L. Ma, J. Sun and M. R. Huang, *Langmuir*, **25**, 1675 (2009).
11. A. M. Donia, A. A. Atia and K. Z. Elwakeel, *Hydrometal.*, **87**, 197 (2007).
12. O. N. Kononova, A. G. Kholmogorov, N. V. Danilenko, N. G. Goryaeva, K. A. Hatnykh and S. V. Kachin, *Hydrometal.*, **88**, 189 (2007).
13. Y. S. Petrova, A. V. Pestov, M. K. Usoltseva and L. K. Neudachina, *J. Hazard. Mater.*, **299**, 696 (2015).
14. C. Jeon, *Korean J. Chem. Eng.*, **31**, 446 (2014).
15. T. Vaughan, C. W. Seo and W. E. Marshall, *Bioresour. Technol.*, **78**, 133 (2001).
16. A. Sari and M. Tuzen, *Micropor. Mesopor. Mater.*, **170**, 155 (2013).
17. K. Inoue, M. Gurung, B. B. Adhikari, H. Kawakita, K. Ohto and S. Alam, *Hydrometal.*, **133**, 84 (2013).
18. T. Halstead, U.S. Department of Agriculture, <http://www.fas.usda.gov/psdonline/circulars/coffee.pdf> (2012).
19. T. Tokimoto, N. Kawasaki, T. Nakamura, J. Akutakawa and S. Tanada, *J. Colloid. Interface Sci.*, **281**, 56 (2005).
20. M. G. Plaza, A. S. Gonzalez, C. Pevida, J. J. Pis and F. Rubiera, *Appl. Energy*, **99**, 272 (2012).
21. K. Benrachedi, K. Bensouali and H. Houchati, *Desalin.*, **239**, 122 (2009).
22. S. Wang, H. Li, X. Chen, M. Yang and Y. Qi, *J. Environ. Sci.*, **24**, 2166 (2012).
23. N. Azouaoui, Z. Sadaoui, A. Djaafri and H. Mokaddem, *J. Hazard. Mater.*, **184**, 126 (2010).
24. M. Iqbala, A. Saeeda and S. I. Zafar, *J. Hazard. Mater.*, **164**, 161 (2009).
25. R. Gnanasambandam and A. Protor, *Food Chem.*, **68**, 327 (2000).
26. T. Li, H. Yang, Y. Zhao and R. Xu, *Chin. Chem. Lett.*, **18**, 325 (2007).
27. K. Kaikake, K. Hoaki, H. Sunada, R. P. Dhakal and Y. Baba, *Biore-sour. Technol.*, **98**, 2787 (2007).
28. M. Baek, C. O. Ijagbemi, O. Se-Jin and D. Kim, *J. Hazard. Mater.*, **176**, 820 (2010).
29. R. Ashkenazy, L. Gottlieb and S. Yannai, *Biotechnol. Bioeng.*, **55**, 1 (1997).
30. E. Malkoc, Y. Nuhoglu and M. Dunder, *J. Hazard. Mater.*, **138**, 142 (2008).
31. Y. M. Ren, X. Z. Wei and M. L. Zhang, *J. Hazard. Mater.*, **158**, 14 (2008).
32. K. Gholamreza, *Appl. Clay Sci.*, **90**, 159 (2014).
33. K. Shen and M. A. Gondal, *J. Saudi Chem. Soc.*, **87**, 654 (2013).
34. E. Torres, Y. N. Mata, M. L. Blazquez, J. A. Munoz, F. Gonzalez and A. Ballester, *Langmuir*, **21**, 7951 (2005).
35. S. Coruh, G. Senel and O. N. Ergun, *J. Hazard. Mater.*, **180**, 486 (2010).
36. P. Hanzlik, J. Jehlicka, Z. Weishauptova and O. Sebek, *Plant Soil Environ.*, **50**, 257 (2004).
37. I. Kula, M. Ugurlu, H. Karaoglu and A. Celik, *Bioresour. Technol.*, **99**, 492 (2008).
38. L. C. Manuella, F. de A. N. Ambrosio, N. S. Eric and V. G. A. Melissa, *J. Clean. Prod.*, **112**, 1112 (2016).
39. X. Huang, N. Gao and Q. Zhang, *J. Environ. Sci.*, **19**, 1287 (2007).
40. N. Y. Mezenner and A. Bensmaili, *Chem. Eng. J.*, **147**, 87 (2009).
41. J. Hanzlik, J. Jehlicka, O. Sebek, Z. Weishauptova and V. Machovic, *Water Res.*, **38**, 2178 (2004).
42. E. Nakkeeran, N. Saranya, M. S. Giri Nandagopal, A. Santhiagu and N. Selvaraju, *Int. J. Phytoremediation*, **18**(8), 812 (2016).