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Investigation of indium ions removal from aqueous solutions using spent coffee grounds

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This study used batch adsorption techniques to evaluate the potential suitability of spent coffee grounds as an environmentally friendly adsorbent for the removal of indium ions from aqueous solutions. In addition, we also investigated the effects of process parameters, such as, the solution pH, adsorbent dose, initial concentration of indium ions and the temperature on adsorption performance. The experimental data were fitted with several adsorption isotherm models to describe the adsorption process of indium ions onto the coffee grounds. The predictions of the Langmuir isotherm model satisfactorily matched the experimental observations. Besides, the kinetic data obtained at different initial concentrations were analyzed using pseudo-first-order and pseudo-second-order kinetic models. A pseudo-second-order model provided a good fit to the experimental results with correlation coefficients greater than 0.99. Thermodynamic parameters, including the Gibbs free energy, enthalpy and entropy, indicated that the indium adsorption of aqueous solutions onto coffee grounds was feasible, spontaneous and endothermic in the temperature range of 288 to 318 K.

Key words: Adsorption, indium ions, coffee grounds, isotherms, kinetics.

INTRODUCTION

Indium is a rare and valuable metal, which is evenly distributed in the earth's crust. It has no minerals of its own so, it has to be recovered as a byproduct from other metallurgical process, most commonly associated with ores of zinc, copper and tin. In recent years, over 60% of indium production over the world was consumed in the preparation of indium tin oxide (ITO) films. ITO films, which are composed of 90% of In_2O_3 and 10% of SnO_2 , are an optoelectronic material with the characteristics of transparency to visible light, electric conduction and thermal reflection. They are widely used in various optoelectronic devices for transparent conducting layers such as liquid crystal display (LCD), plasma displays and

solar cells (Alfantatazi and Moskalyk, 2003). Demand for indium has increased dramatically over the past 15 years, due largely to the growth of LCD, semiconductor materials, solar panels and other electronics market. Indium and its compounds have been found in the etching wastewater discharged from optoelectronic plants, and they are suspected to be carcinogenic to humans and damage the heart, kidney and liver (Carolyn et al., 2002). Therefore, the removal of indium ions from aqueous solutions has become a significant subject.

Most studies related to the extraction of metal ions from solid and liquid samples have employed chelation combined with solvent extraction (Chen et al., 2005). This method is also unfavorable because of the environmental contamination associated with the use of chemical solvents and the resulting health risks. Adsorption is considered quite promising in terms of its removal efficiency of metals from aqueous effluents. The most widely used

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industrial adsorbent is activated carbon. Activated carbons are very effective adsorbents, given their highly developed porosity, large surface area and high degree of surface reactivity (Dias et al., 2007; Hale and Adil, 2007). However, these methods have been found to be limited because they often involve high capital as well as operational costs and may be associated with the generation of secondary wastes, which present treatment problems (Aksu, 2002). In addition, strict new regulatory requirements on the use of organic solvents worldwide, motivated by health and environmental concerns, have prompted studies relating to the removal and separation of indium ions using methods such as electroanalytical techniques (Medvecky and Briancin, 2004), nanofiltration membranes (Wu et al., 2004), solid phase extraction (Tuzen and Soylak, 2006), supercritical CO₂ extraction (Chou and Yang, 2008), extraction resin (Gupta et al., 2007) and electrocoagulation techniques (Chou et al., 2009; Chou and Huang, 2009). More recently, great effort has been contributed to the development of new adsorbents that are byproducts of wastes from large-scale industrial operations and agricultural waste materials. Agricultural wastes are renewable, usually available in large amounts and potentially less expensive than other materials to manufacture diverse types of adsorbents. A number of agricultural waste materials used as low-cost adsorbents are available in different parts of the world. Such available adsorbents include corn cobs (Vaughan et al., 2001), saw dust (Sciban et al., 2006), coir dust (Shukla et al., 2006), coffee waste (Boonamnuyvitaya et al., 2004), banana leaf (Babarinde et al., 2012), rice and wheat bran (Montanher et al., 2005) and tea waste (Cay et al., 2004; Hossain et al., 2005), used in heavy metal removal from wastewaters. However, to date, there has been scarce research on the adsorption treatment for the removal of indium ions from aqueous solutions using agricultural waste materials out-side of our earlier study by tea waste (Chou et al., 2011).

Coffee has become an established beverage all over the world, and large amounts of coffee grounds are discharged from food industries. The processing of coffee generates significant amounts of solid wastes, mainly coffee husks and spent coffee grounds from soluble coffee production. A portion of coffee grounds is recycled as materials for soil remediation or as adsorbents for odor. Nevertheless, most of the coffee grounds are burned as waste, which results in production of carbon dioxide, a green house gas (Hirata et al., 2002). Developing technology to reuse coffee grounds for useful purposes would promote this large amount of waste into new resource. Most available studies in the literature have used coffee waste as an adsorbent for the removal of various materials such as methylene blue (dye) (Hirata et al., 2002), heavy metals (Cd, Cu, Pb, Zn, Cr and Ni) (Azouaou et al., 2010; Boonamnuyvitaya et al., 2004; Ozdes et al., 2009; Sari et al., 2007, 2008), formaldehyde (Boonamnuyvitaya et al., 2005) and phenol (Namane et al., 2005). However, there are currently no studies on the

removal of indium ions using coffee waste as a potential adsorbent. Therefore, this study evaluated the adsorption potential of coffee grounds for the removal of indium ions from aqueous solutions. The optimum operating conditions, equilibrium data and kinetic data were processed to understand the adsorption mechanism of indium ions onto the coffee grounds.

EXPERIMENTAL

Adsorbent

The rejected coffee grounds collected from well-known chain stores in central Taiwan was used for the experiments. The collected coffee grounds wastes were washed several times with boiled water to remove any soluble dirtiness and colored components. The wet coffee grounds were then washed with de-ionized water and were dried at 85°C in-side a convection oven for 24 h. The dried coffee grounds were crushed and sieved to obtain a particle size in the range of 150 to 250 µm used in the adsorption experiments without any further modification. Finally, the resulting product was stored in air-tight container for further use. No other chemical or physical treatments were applied prior to adsorption experiments. The Fourier transform infrared (FTIR) analysis was used to identify the characteristic functional groups and the spectra of spent coffee grounds shown in Figure 1. The FTIR spectroscopic analysis indicated the broad band observed at 3366 cm⁻¹ was assigned to the stretching of O-H group due to inter- and intra-molecular hydrogen bonding of polymeric compounds, such as alcohols, phenols and carboxylic acid, as in pectin, cellulose and lignin. The O-H stretching vibrations occur within a broad range of frequencies indicating the presence of free hydroxyl groups and bonded O-H bands of carboxylic acids. The band at 2925 cm⁻¹ indicates symmetric or asymmetric C-H stretching vibration of aliphatic acids. The absorption peaks at 1745 cm⁻¹ was assigned to the resulting carboxyl linkage derived from xanthine derivatives such as caffeine. These shifts may be attributed to the changes in counter ions associated with carboxylate and hydroxyl, which are predominant contributors in metal ion uptake. These significant bands in the spectrum indicated the possible involvement of functional groups on the surface of the coffee grounds during the indium ions adsorption process.

Chemicals

The standard reference material used in the experiments was an indium standard solution [2% In(NO₃)₃ in HNO₃] from High-Purity Standards (SC, North Charleston, USA) with purity of at least 99%. Aqueous solutions containing indium ions were prepared by dissolving an appropriate quantity of indium nitrate in de-ionized water for adsorption experiments. The pH of the aqueous solution was adjusted by adding NaOH by Sigma-Aldrich (St. Louis, MO, USA).

Experimental equipment

The reactor cell was a 1.0L Pyrex glass equipped with a water jacket and magnetic stirrer, containing 0.5 L of indium ions solution. The temperature of the water jacket cell was controlled by continuously circulating water from a refrigerated circulating bath. The magnetic stirrer (Suntex, SH-301, Taiwan) was used in the reactor to maintain adequate mixing the indium ions solution during the adsorption process. The characteristics of the indium ions aqueous solution was determined using a pH meter (Sartorius,

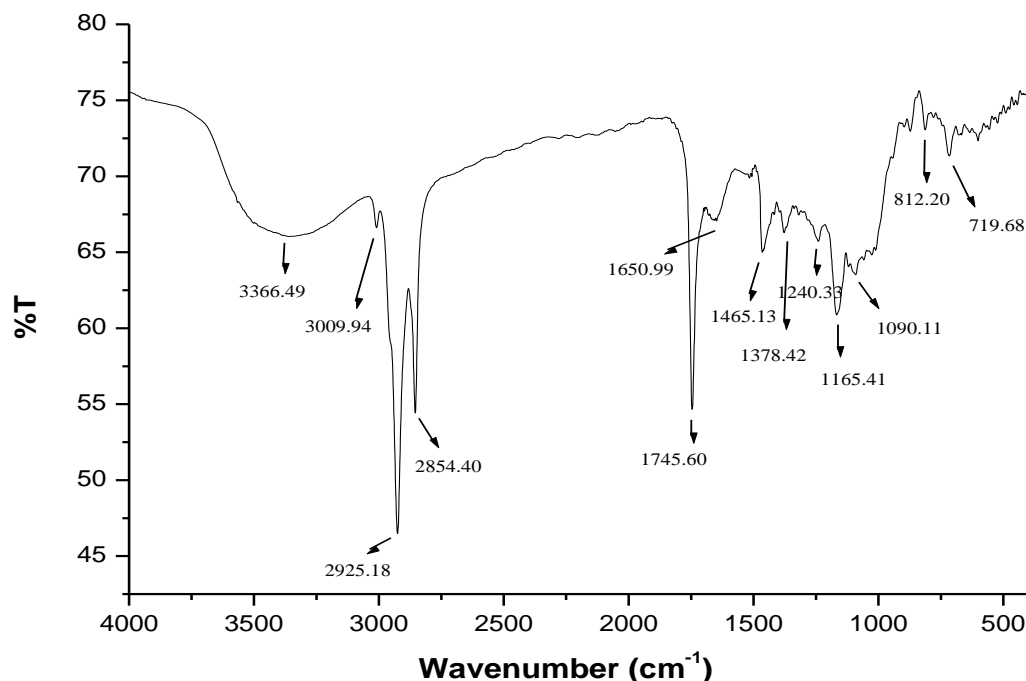


Figure 1. Fourier transform infrared spectroscopy of the spent coffee grounds.

Professional Meter PP-20, Germany) and by measuring conductivity (Eutech, CyberScan 510, Singapore). Physical characteristics of the prepared coffee grounds was carried out by nitrogen adsorption isotherms were obtained using BET surface area apparatus (Micromeritics, Gemini V, USA), surface area and porosity analyzer.

Experimental procedure

During each experimental run, 0.5 L of aqueous solution containing indium ions was placed into the reactor. The magnetic stirrer stirred the wastewater at a speed of 300 rpm. The adsorbent dose amount of 0.2, 0.25, 0.3 or 0.35 g L⁻¹ was added to the aqueous solution of indium ions used in the adsorption treatment process. The initial concentration used was in the range between 10 and 80 mg L⁻¹. A steady temperature of 288 to 318 K was maintained by circulating water from the refrigerated circulating bath through the water jacket. After adsorption treatment, the conductivity and pH of synthetic wastewater were measured with a multi-meter and pH meter respectively. The concentration of indium ions in each sample was measured three times with a flame atomic absorption spectrophotometer (Perkin-Elmer, AA-200, USA). An indium hollow cathode lamp operated at 20 mA was used as the light source. The wavelength was set at the 303.9 nm resonance line for indium. The amount of indium ions adsorbed by coffee grounds was calculated from the difference between the indium ions quantity added to the coffee grounds and the indium ions content of the supernatant using the following equation:

$$q_e = (C_0 - C_e) \frac{V}{M} \quad (1)$$

where q_e is the indium ions uptake (mg g⁻¹), C_0 and C_e are, respectively, the initial and final or equilibrium indium ions concentrations in the solution (mg L⁻¹), V is the volume of the

solution (L) and M is the mass of the coffee grounds.

RESULTS AND DISCUSSION

Effect of solution pH

Aqueous solution pH governs the speciation of metals and was identified as the most important parameter affecting metal adsorption onto adsorbent, this partly because hydrogen ions themselves are strongly competing with adsorbate. To characterize the effect of pH on indium ions adsorption, set of batch equilibrium experiments were investigated for values between 3.2 and 6.2. As seen in Figure 2, at pH of 3.2, the adsorption was very low and rapidly increases between pH 4.2 and 6.2. This phenomenon can be explained by the surface charge of the adsorbent and the H⁺ ions present in the solution. At lower pH values, the H⁺ compete with metal cation for the active sites of coffee grounds and therefore lower adsorption. The removals of indium ions increased rapidly at the pH range of 4.2 to 6.2 and almost reach 70%. However, a previous study reported that the indium ions get precipitated due to the formation of indium hydroxide at pH > 6 (Wood and Samsoni, 2006). A series of experiments were carried out to identify the dominant process indium ion removal between adsorption using the coffee grounds and hydroxide anions by pH adjustment using sodium hydroxide. As can be seen in Table 1, the indium ion removal efficiency were 2.5, 4.1, 13.7, and 22.5% when the pH value of the solution was adjusted using sodium hydroxide to different values of 3.2, 4.2,

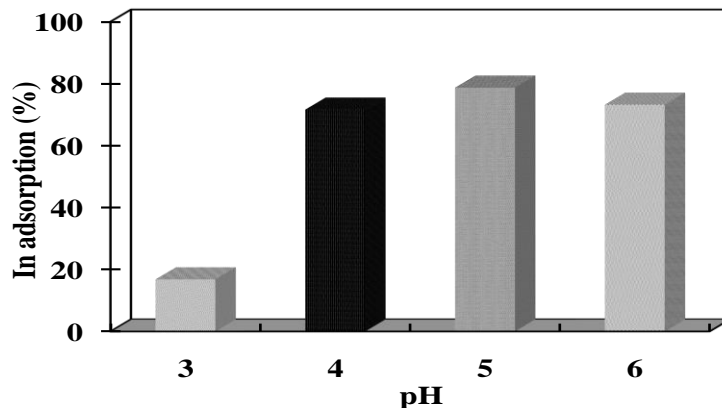


Figure 2. Effect of pH on the adsorption efficiency of indium ions ($C_0 = 20 \text{ mg L}^{-1}$, adsorbent dose = 0.25 g L^{-1} , $t = 300 \text{ min}$, $T = 298 \text{ K}$, agitation speed = 300 rpm).

Table 1. Comparison of indium ions adsorption efficiencies between coffee grounds and sodium hydroxide at various pH values of solution.

Parameters (%)	pH values of solution			
	3.2	4.2	5.2	6.2
Sodium hydroxide	2.5	4.1	13.7	22.5
Coffee grounds	14.4	67.6	65.1	50.7
Total	16.8	71.6	78.7	73.2

5.2, and 6.2 respectively. Under the same pH value of solution, the corresponding indium ions removal efficiency by adsorption using the spent coffee grounds was 14.4, 67.6, 65.1 and 50.7%, respectively. Consequently, as the pH value was greater than 6, the indium hydroxide was formed and this resulted in precipitation, therefore, the separation may not be due to adsorption, since the maximum pH value was selected to be lower than 6.1. In addition, the point of zero charge (PZC) of the biomass materials is pH dependent. A previous study reported that the PZC of spent coffee grounds was in the range of 3.4 to 3.6, and therefore, the pH values should be maintained at 4 to ensure a predominant negatively charged surface (Franca et al., 2009). Consequently, considering both the formation of indium precipitates and the PZC of coffee grounds, pH 4 provides the optimum performance for the adsorption of indium ions onto spent coffee grounds.

Effect of adsorbent dose

Adsorbent dose is an important parameter because it is used to determine the capacity of an adsorbent for a given initial concentration of the adsorbate at different operating conditions. To study the effect of adsorbent dose on the kinetics of indium ions adsorption is shown in Figure 3. The coffee grounds concentration was varied

from 0.2 to 0.35 g L^{-1} . The experimental results for all adsorbent doses showed a rapid initial adsorption rate followed by a slower rate.

Initially, the adsorption sites are open and the indium ions interact with accessible sites, thereby leading to an observed higher adsorption rate. Furthermore, the concentration gradient between the bulk solution and the solid-liquid interface was initially higher, resulting in a higher adsorption rate. However, after the initial period, slow adsorption may be due to slower diffusion of solute into the interior of the adsorbent. As expected, an increase in the coffee grounds quantity caused a decrease in the residual indium ions concentration at equilibrium, thereby increasing the adsorption removal efficiency from 53 to 95% as the coffee grounds dose was increased from 0.2 to 0.35 g L^{-1} . This trend can be explained by the fact that the number of adsorption sites or surface area increased with the quantity of adsorbent, resulting in a higher percent of metal removal at a high dose. However, as shown in Figure 4, the amount of indium ions adsorbed per unit weight of adsorbent (q) decreased from 26.5 to 4.7 mg g^{-1} when the adsorbent dose increased from 0.2 to 0.35 g L^{-1} . These experimental results were explained with at higher adsorbent doses the indium ions concentration in solution dropped to a lower value, and the system reached equilibrium at lower values of q , indicating the adsorption sites remained unsaturated.

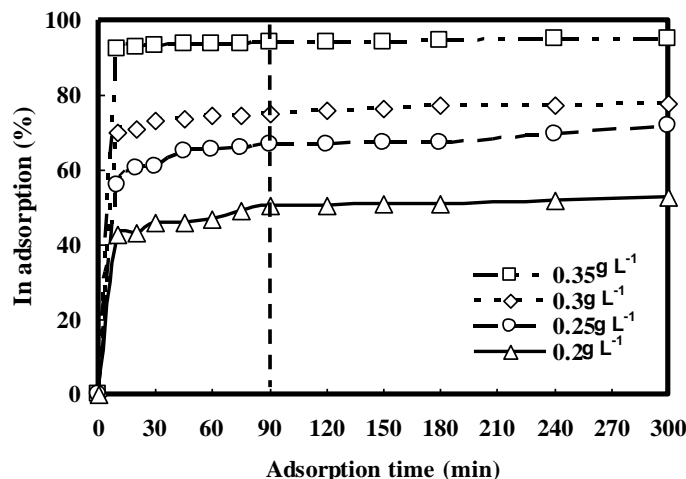


Figure 3. Effect of adsorbent dose on the adsorption efficiency of indium ions ($C_0 = 20 \text{ mg L}^{-1}$, $\text{pH} = 4.2 \pm 0.1$, $t = 300 \text{ min}$, $T = 298 \text{ K}$, agitation speed = 300 rpm).

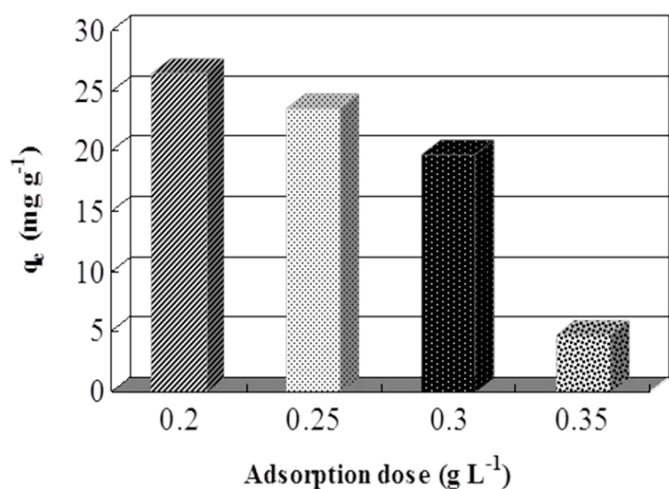


Figure 4. Effect of adsorbent dose on the adsorption capacities of indium ions ($C_0 = 20 \text{ mg L}^{-1}$, $\text{pH} = 4.2 \pm 0.1$, $t = 300 \text{ min}$, $T = 298 \text{ K}$, agitation speed = 300 rpm).

Effect of initial concentration

The initial concentration provides an important driving force to overcome mass transfer of the pollutant between the aqueous and solid phases. The relationship of contact time and adsorption efficiency of indium ions onto coffee grounds at different initial indium ions concentrations is shown in Figure 5. The experiment results revealed that all initial concentrations show rapid initial adsorption rate followed by a slow rate. The adsorption efficiency was very fast (from 0 to 30 min), increasing from 27 to 91%, with an indium ions concentration range of 10 to 80 mg L^{-1} . The fast adsorption at the initial stage was probably due to open adsorption sites allowing easy interaction with the metal ions. As time increased the adsorption

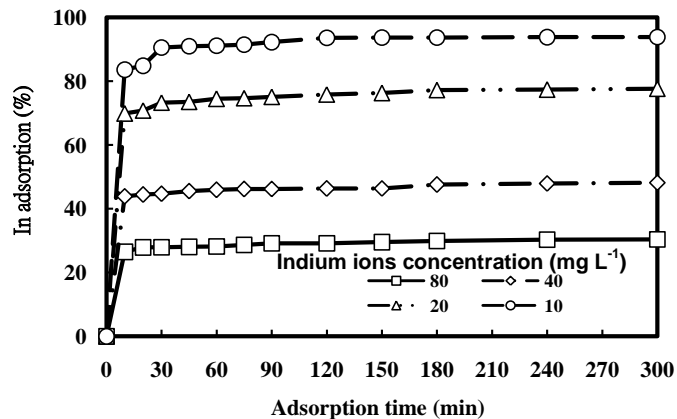


Figure 5. Effect of initial concentration on the adsorption efficiency of indium ions (adsorbent dose = 0.3 g L^{-1} , $\text{pH} = 4.2 \pm 0.1$, $t = 300 \text{ min}$, $T = 298 \text{ K}$, agitation speed = 300 rpm).

removal efficiency proceeded at a slower rate, and eventually the adsorption removal approached equilibrium within 90 min in all cases. The removal efficiencies corresponding to equilibrium adsorption increased from 29 to 92% when the initial concentration decreased from 80 to 10 mg L^{-1} . These observations imply that the ratio of surface active sites to the total metal ions in the solution at low initial concentration is high, and therefore, all metal ions may interact with the adsorbent and be removed from the solution. However, as shown in Figure 6, the equilibrium adsorption capacity increased from 15.6 to 40.5 mg g^{-1} with an increase in the initial concentration from 10 to 80 mg L^{-1} . These experiment results were explained base on the fact that, as the initial concentration increased the mass transfer driving force became larger, resulting in higher indium ions adsorption.

Effect of temperature

The major effect of temperature on the adsorption process is influenced by the diffusion rate of adsorbate molecules and the internal pores of the adsorbent particle. Increasing temperature caused an increase in the diffusion rate of the adsorbate molecules across the external layer and within the internal pores of the adsorbent particle due to a decrease in the viscosity of the solution. Besides, changing the temperature can alter the equilibrium capacity of the adsorbent for the adsorbate (Alkan et al., 2008). To investigate the effect of the temperature (288, 298, 308 and 318K) on the indium ions adsorption, the experiments were conducted at constant concentrations of indium ions (20 mg L^{-1}) and different times. Figure 7 illustrates the relationship between contact time and adsorption removal efficiency of indium ions onto coffee grounds at different temperatures. As time increases, the adsorption removal efficiency proceeded at a slower rate,

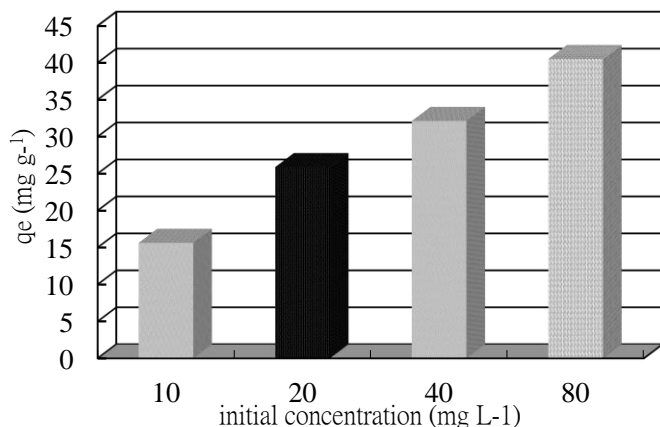


Figure 6. Effect of initial concentration on the adsorption capacities of indium ions (adsorbent dose = 0.3 g L⁻¹, pH = 4.2 ± 0.1, t = 300 min, T = 298 K, agitation speed = 300 rpm).

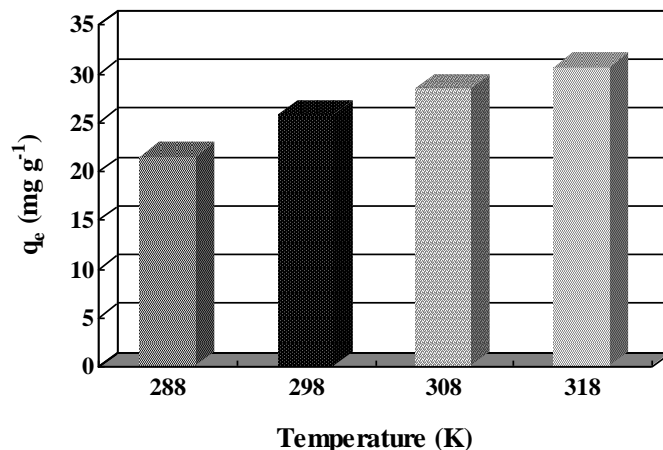


Figure 8. Effect of temperature on the adsorption capacities of indium ions (C₀ = 20 mg L⁻¹, adsorbent dose = 0.3 g L⁻¹, pH = 4.2 ± 0.1, t = 300 min, agitation speed = 300 rpm).

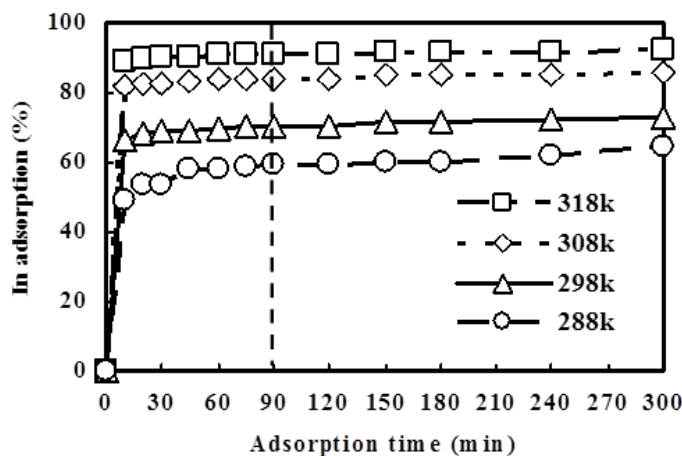


Figure 7. Effect of temperature on the adsorption efficiency of indium ions (C₀ = 20 mg L⁻¹, adsorbent dose = 0.3 g L⁻¹, pH = 4.2 ± 0.1, t = 300 min, agitation speed = 300 rpm).

and the adsorption removal approached equilibrium within 90 min in all cases. As seen in Figure 6, the removal efficiencies corresponding to equilibrium adsorption increased from 65 to 92% when the temperature was increased from 288 to 318 K. Similar results were observed for equilibrium adsorption capacity, which increased from 21.5 to 30.7 mg g⁻¹ when the temperature was increased from 288 to 318 K, as shown in Figure 8. This phenomenon indicates that indium ions removal by adsorption processes on coffee grounds is endothermic in nature and favors a high temperature. This may be due to the mobility of indium ions, which increases generally with increasing temperature. An increasing number of molecules may also gain enough energy to interact with active sites at the solid-liquid surface. Furthermore, increasing temperature may cause a swelling effect of the coffee

internal structure advancing metal ions to penetrate further (Chou et al., 2011).

Thermodynamic studies

The effect of temperature on the sorption capacity of the indium ions from the aqueous solution was evaluated at the temperatures range of 288 to 318 K. Thermodynamic parameters, such as the Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0), were calculated and were used to determine whether or not the adsorption process was spontaneous. The ΔG^0 was calculated by the following equation:

$$\Delta G^0 = -RT \ln K_d \quad (2)$$

Where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature (K), K_d is the distribution coefficient (q_e/C_e) (L g⁻¹), q_e and C_e are the equilibrium concentrations of indium ions for the adsorbent (mg g⁻¹) and the solution (mg L⁻¹) respectively. The relationship between ΔG^0 , ΔH^0 and ΔS^0 can be expressed by the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (3)$$

Combining Equations 2 and 3 leads to:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (4)$$

At each temperature, the corresponding C_e values at

Table 2. Thermodynamic parameters of the indium ions adsorption on the coffee grounds at different temperatures.

Temperature (K)	Thermodynamic equilibrium constant (K_d)	ΔG^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	ΔH^0 (kJ mol ⁻¹)
288	2.649	-2.267		
298	4.355	-3.644		
308	8.899	-5.597	173.22	47.72
318	16.87	-7.471		

different fixed values of q_e were calculated. The thermodynamic parameters of ΔH^0 and ΔS^0 were calculated from respectively. The Gibbs free energies at different temperatures were calculated from Equation 2.

The values of ΔG^0 , ΔH^0 and ΔS^0 for the indium ions adsorption onto the coffee grounds at different temperatures are given in Table 2. Table 2 shows negative values of ΔG^0 and positive values of ΔH^0 which indicate that the indium ions adsorption process is a spontaneous and endothermic process. The positive value of ΔS^0 suggests an increased randomness at the solid-solution interface occurs in the internal structure of adsorption of indium ions from solution onto coffee grounds. The positive values of ΔH^0 indicate the presence of an energy barrier in the adsorption process.

Adsorption isotherms

Analysis of the equilibrium data is important to develop an adsorption isothermal equation, which would accurately represent the results and be used for design purposes (Aksu, 2002). In order to confirm the mechanism of the adsorption process the adsorption isotherms are one of the most important data. These equilibrium models often provide some insight into both the adsorption mechanism and the surface properties and affinity of the adsorbent. In this study, two of the most commonly used adsorption isotherms (Langmuir and Freundlich) were applied to establish the relationship between the amounts of indium ions adsorbed onto the coffee grounds. The Langmuir model was originally developed to represent chemisorption at a set of well-defined localized adsorption sites with the same adsorption energy, independent of the surface coverage, and with no interaction between adsorbed molecules. This model assumes that a monolayer deposition is formed on a surface with a finite number of identical sites and that there is no interaction between metals adsorbed on adjacent binding sites. The mathematical expression for the Langmuir isotherm is (Langmuir, 1916):

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

where a_L (mg g⁻¹) is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity, C_e (mg L⁻¹) is the equilibrium liquid-phase concentration, K_L (L mg⁻¹) is a direct measure of the intensity of adsorption, and q_e (mg g⁻¹) is the amount adsorbed at equilibrium. From a plot of $1/q_e$ versus $1/C_e$, K_L and a_L can be determined from the slope and intercept of the resulting straight line.

The Freundlich adsorption isotherm is typically based on adsorption on the heterogeneous surfaces with sites that have different energy of adsorption. The isotherm model has theoretical implications that are not restricted to monolayer formation and provide a basis for understanding non-linear adsorption. The mathematical expression for the Freundlich mode is (Freundlich, 1906):

$$q_e = K_f C_e^{1/n} \quad (6)$$

where K_f [(mg g⁻¹)(L mg⁻¹)^{1/n}] and n (dimensionless) are Freundlich constants which account for all factors affecting the adsorption capacity and intensity respectively. K_f can also be defined as the adsorption coefficient and represents the quantity of indium ions adsorbed onto adsorbent per unit equilibrium concentration. $1/n$ is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption (Jiang et al., 2002). The Freundlich constants K_f and $1/n$ are determined from the intercept and slope respectively, of the linear plot of $\ln q_e$ versus $\ln C_e$.

The applicability of the isotherm equations was compared using the correlation coefficient (R^2). The Langmuir and Freundlich constants for the adsorption of indium ions onto coffee grounds are presented in Table 3. It can be seen from the experimental data ($R^2=0.99$) values that the Langmuir isotherm model has a better fit than Freundlich isotherm model for indium ion adsorption. In this study, this result indicated that the adsorption of indium ions by coffee grounds was apparently with monolayer coverage of adsorbed molecules.

Adsorption kinetic modeling

The adsorption kinetic is one of the most important information that can be helpful to understand the mechanisms of indium ions adsorption and describes the

Table 3. Langmuir and Freundlich isotherm constants for adsorption of indium ions onto the coffee grounds.

Langmuir isotherm			Freundlich isotherm		
K_L (L mg ⁻¹)	a_L (mg g ⁻¹)	R^2	K_F ((mg g ⁻¹) (L mg ⁻¹) ^{1/n})	n	R^2
0.023	181.8	0.98	4.647	1.18	091

adsorption efficiency of the adsorbent. A number of adsorption kinetic models have been developed to describe the kinetics of metal removal. In order to investigate the reaction mechanism of adsorption processes such as mass transfer by using two different adsorption kinetic models which are pseudo-first-order model and pseudo-second order model. The conformity between experimental data and the model-predicted values was expressed according to the linear regression correlation coefficient value R^2 .

The first-order rate equation of the Lagergren model is one of the most widely used expressions for describing the adsorption of a solute from a solution (Lagergren, 1898). The pseudo-first-order equation can be expressed by Equation 7:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the amounts (indium ions) adsorbed on the adsorbent at equilibrium and at any time t , respectively, and k_1 (min⁻¹) is the rate constant of the pseudo-first-order model.

The pseudo-first-order model considers the rate of occupation of the adsorption sites which is assumed to be proportional to the number of unoccupied sites. The values of k_1 and q_e can be obtained from the slope and intercept respectively from the linear plot of $\ln(q_e - q_t)$ and t . The adsorption rate constants determined from the pseudo-first-order model for different initial indium ions concentrations are listed in Table 3. From the results obtained, we observed that the correlation coefficients for the first-order kinetic model were relatively lower than those obtained for the second-order kinetic model for all different initial indium ions concentrations. Furthermore, the calculated q_e values are all low compared with experimental q_e values. These results indicate that the pseudo-first-order kinetic model might be insufficient to describe the mechanism of indium ions adsorption onto the coffee grounds.

The pseudo-second-order kinetic model is based on the adsorption equilibrium capacity and can be given by Equation 8 (Ho and McKay, 1998):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where k_2 (g mg⁻¹ min⁻¹) is the rate constant of the pseudo-

second-order equation, q_e (mg g⁻¹) is the maximum adsorption capacity and q_t (mg g⁻¹) is the amount of adsorption at time t (min).

The values of the correlation coefficients (R^2) for the pseudo-second-order kinetic model obtained in all cases were above 0.99, and the calculated q_e values were in agreement with the experimental q_e values. The adsorption rate constants determined from the pseudo-second-order model for the different adsorption dose are listed in Table 4. Higher correlation coefficients were obtained for the pseudo-second-order kinetic model than for the first-order model. These results indicate that the second-order kinetic model can suitably be applied to predict the adsorption process of indium ions onto coffee grounds.

Conclusions

The experimental results of this study indicate that coffee grounds are environmentally friendly adsorbent for the removal of indium ions adsorption from aqueous solution. The following conclusions were drawn based on the presented information:

- (1) The optimum adsorption removal efficiencies of indium ions were significantly influenced by the solution pH, adsorbent dose, the initial concentration and the temperature, using coffee grounds as an adsorbent.
- (2) The positive value of ΔH^0 indicates that the adsorption process is endothermic in nature and the positive value ΔS^0 showed the increase in the degree of freedom or increase in the disorder of adsorption process.
- (3) The indium ions adsorption process was modeled using adsorption isotherm models. The adsorption equilibrium data showed best fit with the Langmuir adsorption isotherm model.
- (4) The adsorption rate was rapid over an initial period and then decreased gradually and reached equilibrium within 90 min in all the cases, indicating that the indium ions adsorption of the aqueous solution onto coffee grounds was best described using the pseudo-second-order kinetic model at the different adsorbent dose.

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Table 4. Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated, and experimental q_e values at different adsorbent dose.

Adsorbent dose (g L ⁻¹)	$q_{e,exp}$ (mg g ⁻¹)	First-order model			Second-order model		
		k_1 (min ⁻¹)	q_e (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
0.2	11.41	0.027	9.46	0.80	0.015	11.51	0.99
0.25	10.13	0.021	7.78	0.70	0.022	10.71	0.99
0.3	6.14	0.027	3.88	0.61	0.051	6.31	0.99
0.35	3.49	0.034	1.99	0.71	1.052	3.54	0.99

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