

# **SCIENCE & TECHNOLOGY**

Journal homepage: http://www.pertanika.upm.edu.my/

# Removal of Fe Ion from Polluted Water by Reusing Spent Coffee Grounds

#### Khairul Nizam Mohamed<sup>1,2\*</sup> and Lee Lai Yee<sup>1</sup>

<sup>1</sup>Department of Environmental Sciences, Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

<sup>2</sup>Environmental Forensics Research Unit (ENFORCE), Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

#### **ABSTRACT**

High concentration of iron (Fe) levels (above 1.0 mg/L) in water causes bad taste, staining and deposition in pipes and results in high turbidity in water supplies. Existing treatment technologies (which have been conventionally applied to remove Fe ions), are expensive and cause toxic sludge production. A set of experiments was carried out to evaluate the Fe uptake potential of spent coffee grounds by conducting batch tests in an aqueous solution through a biosorption process. Batch sorption studies were conducted based on pH, contact time, adsorbent dosage and adsorbent particle size. In addition, initial metal concentration was investigated. Flame atomic adsorption spectroscopy analysis revealed that the maximum adsorption recorded was 0.470 mg g<sup>-1</sup> by using 0.30 g of 210-355  $\mu$ m coffee with the maximum uptake percentage of Fe (92.9%) for 60 minutes at pH 4. Adsorption behavior of Fe ions on a surface of coffee grounds was well-interpreted by Langmuir model (R<sup>2</sup> = 0.999). A kinetic study indicated that the Fe ions uptake was well-fitted by the pseudo second-order reaction model with good correlation (R<sup>2</sup> = 0.993). The study offered an affirmative answer to the hypothesis of reusing eco-friendly and low-cost coffee grounds for removal of Fe ions from polluted waters.

Keywords: Adsorption, green technology, iron, spent coffee grounds, water pollution

ARTICLE INFO

Article history: Received: 03 December 2018 Accepted: 30 January 2019 Published: 24 July 2019

E-mail addresses:

k\_nizam@upm.edu.my (Khairul Nizam Mohamed) lee@ymail.com (Lee Lai Yee)

\* Corresponding author

INTRODUCTION

Scarcity of clean and clear water has become one of the world's major issues. In fact, the contamination of water directly affects the health of the environment. The presence of heavy metals in water bodies has become an afflictive issue that causes

this contamination. The rapid growth of economic activities in Malaysia, could increase the levels of these substances. According to Ramya et al. (2011), the effluent of leather and chemical industries, electroplating industries and dye industries could pollute water resources. Most of the metal ions are soluble in aqueous solutions and they are most likely to be non-biodegradable and persistent, therefore becoming more available and eventually affecting the quality of water. Recent reports on rising levels of total dissolved metals concentration in aquatic environments have highlighted the severity of water contamination (Idriss & Ahmad, 2012).

Iron (Fe) is known as one of the non-hazardous metallic elements that can be a nuisance in the water supply. Fe makes up at least five percent (5%) of the Earth's crust (Chandrakala et al., 2012). Fe can be found in the minerals hematite, magnetite, taconite and pyrite, and thus, it is widely used in the manufacturing of steel and in other alloys American Public Health Association (APHA, 2012). It is essential for health as it is significant in terms of being a functional part of hemoglobin in the human metabolism. As is also the case in plants, Fe plays a crucial role in the production of chlorophyll (Wang et al., 2010). From time to time, Fe causes trouble in water sources as water percolates through soil and rocks, dissolves minerals containing Fe into solution and carries along the uncontrolled effluent discharges from anthropogenic activities. In addition to its biological role and its importance for the development of the human body, Fe contributes to toxicity if it is found in amounts higher than normal in the human body after drinking water containing Fe concentrations above 200 mg/L. The presence of excess ferrous (Fe<sup>2+</sup>) causes production of free radicals These are highly reactive and are able to damage DNA, proteins, lipids, and other cellular components (Atasoy et al., 2011).

Chandrakala et al. (2012) reported that water contaminated with Fe would appear as a reddish brown slime and leave stains on laundry as well as table ware materials when the concentration of Fe in the water reached 0.30 mg/L. Stains or precipitates containing colloidal Fe may be severe enough to plug water pipes, pressure tanks, water softeners and water heaters (Seheimy & Sadek, 2009). In this case, a reduction in the available quantity of water supply can eventually be caused if the water is highly polluted with Fe. Ismail et al. (2013) suggested that the mean Fe ionic concentration found in the Penchala River was 1.35 mg/L during the period 1997 to 2009. When compared to Interim IIA/IIB and III standard for water supply in Malaysia, it was discovered that Fe concentration in the water supply had exceeded the acceptable limit of 1.00 mg/L. Apart from the natural input, sources of dissolved Fe are also emerging, in particular from the external inputs of anthropogenic activities. According to the Fifth Schedule of Environmental Quality (Industrial Effluent) Regulations 2009 under Malaysian Environmental Quality Act 1974, the acceptable limit for total Fe in the discharge of industrial effluent or mixed effluent is 1.00 mg/L for standard A compared to 5.00 mg/L for standard B.

In order to remove the excess Fe ions, an efficient, cost-effective and environmentally-friendly technology is essential. A biosorption has been widely used for the removal of heavy metals (Chandrakala et al., 2012). There has been a practice of using low-cost materials as potential metal scavengers from solutions and wastewaters. Recently, numerous biosorbents have been studied, including: various agricultural waste (Egila et al., 2011); vegetable biomass (Tokimoto et al., 2005); dead macrophytes (Miretzky et al., 2005); oil palm biomasses (Khosravihaftkhany et al., 2013); as well as waste tea (Utomo & Hunter, 2010). According to Rose & Rajam (2012), the Fe<sup>2+</sup> ions sorptive potential of both wild jack and jambul barks has been investigated and can be used for the economic wastewater treatment.

In this study, spent coffee grounds have been selected as the biosorbent chosen to remove Fe ions from an aqueous solution. Almost 50% of coffee produced worldwide is processed for soluble coffee preparation (Ramalakshmi et al., 2009). A total of 45% of all the waste products in Malaysia were discarded into landfills composed of kitchen waste including coffee grounds (Economic Planning Unit, 2006). Previous researches have shown the possibilities of using coffee grounds for ion adsorption. The effectiveness of coffee grounds in removing heavy metals has been scientifically proven by Tokimoto et al. (2005), Ogata et al. (2011) as well as Imessaoudene et al. (2013). Research into lead (Pb) ion adsorption by coffee beans and coffee grounds had been proven by Tokimoto et al. (2005) through a study of Pb ion adsorption onto proteins contained in coffee grounds. Ogata et al. (2011) proved that carbonaceous material prepared from coffee grounds showed an acceptable adsorption capacity for fluoride (F-) ions. Strontium (Sr) uptake potential of spent coffee grounds was investigated by Imessaoudene et al. (2013) and revealed that the maximum adsorption was at pH 5 to 8 and temperature between 283 and 333 K respectively. The study also showed that the presence of carboxylic acid and amino group on a spent coffee ground surface played a vital role in Strontium (Sr) biosorption.

The effectiveness of spent coffee grounds as a biosorbent to remove Fe ions in a solution is the main objective of this study. The adsorption rates for five different parameters on the removal of Fe ions were also investigated. These parameters were: pH; contact time; size of adsorbent; adsorbent dosage and initial Fe ion concentration respectively. The biosorptive efficiencies in removing Fe ions of unmodified spent coffee grounds were compared with commercially available activated carbon and degreased coffee grounds. The results obtained from this study could be applied in such a way to be used as an alternative to the water treatment purposes.

#### MATERIALS AND METHODS

Since no significant difference was detected in adsorption capacity among several kinds of coffee grounds in the previous research of Tokimoto et al. (2005), spent coffee grounds

(SCG) were used in this study regardless of their manufacturers and origins. Each experiment was repeated in three runs in order to produce satisfactory results. Sensitivity and detection levels for the atomic absorption spectrometric (AAS) methods in measuring total Fe in water were 5 mg/L and 10  $\mu$ g/L, respectively (APHA, 2012).

## **Biosorbent Preparation**

The coffee grounds were soaked separately 24 hours in excess 0.3 mol dm<sup>-3</sup> HNO<sub>3</sub> (Egila et al., 2011). Adsorbent was then filtered and washed with Milli-Q water until neutrality was achieved. Degreased coffee grounds (DCG) were prepared by undergoing a 6 hours reflux using a Soxhlet extractor with diethyl ether solvent. The fat content of the coffee grounds was calculated by Equation (1) shown below.

$$F = (W - W_0) \times 100/M$$
 (1)

where F is the fat content (%), W is the weight of the flask (g),  $W_0$  is the weight of the flask plus a dried residue, and M is the weight of the sample coffee grounds (g) (Tokimoto et al., 2005).

# **Batch Sorption Analysis**

The batch sorption studies were analysed by placing 100 mL of the Fe ion solution of different pH into different contact times with a different weight of biosorbent and placed under shaking condition of 150 rpm at room temperature. At the end of the contact time, 30 mL of the sample was extracted from the conical flask and subjected to 4000 rpm centrifugation for 15 minutes in order to separate suspended particles and the supernatant. The concentration of metal ions in the solution both before and after biosorption was determined by AAS. Details of different parameters that had been applied in this sorption analysis are provided in Table 1.

Table 1
Different parameters applied in sorption analysis of spent coffee grounds (SCG) on Fe ion

Parameters	Investigation
pH	pH 1 - pH 14
Contact time	30, 60, 180 and 360 minutes
Particle size of adsorbent	$210\text{-}355~\mu m,355\text{-}500~\mu m$ and $500\text{-}645~\mu m$
Adsorbent dosage	0.10, 0.20, 0.30, 0.40 and 0.50 g

Sorption data were calculated to get the amount of Fe adsorbed at equilibrium (mg/g) and the percent adsorption (%) based on both Equations (2) and (3) respectively.

$$q_e = (C_o - C_e) V / m \tag{2}$$

Uptake (%) = 
$$(C_o - C_e) / C_o \times 100\%$$
 (3)

where  $q_e$  is the amount of heavy metal ion adsorbed onto per unit weight of the adsorbent (mg/g),  $C_o$  and  $C_e$  are the initial and equilibrium metal ion concentration (mg/L), V is the volume of solution treated (L), M is the mass of the adsorbent (g) and C is the solution concentration at the end of adsorption (mg/L) (Imessaoudene et al., 2013).

An effect of initial concentration on various adsorbents was also carried out by varying each of the 100 mL of Fe ion concentration (0.3, 0.5, 0.7 and 1.0 mg/L) and shaken with 0.1 g of each adsorbent for one (1) hour at room temperature. The spent coffee grounds (SCG and DCG) and activated carbon (AC) were tested in this analysis.

The data were modelled using Freundlich and Langmuir models in order to describe adsorption equilibrium, surface properties and adsorbent affinity. By using these two models, clear descriptions on adsorption activities of mono-compound in metal ion by various materials were shown (Park et al., 2013). The logarithmic form of Freundlich model is given in Equation (4) following:

$$\log(q_e) = \log(K_F) + 1/n \log(C_e) \tag{4}$$

where  $K_F$  (L g-1) and n are the Freundlich parameters related to adsorption capacity and intensity, respectively. A plot of log  $q_e$  versus log  $C_e$  gives a straight line and  $K_F$  and n can be calculated from the slope and intercept.

Langmuir isotherm is commonly valid for monolayer adsorption onto a surface with homogeneous adsorption sites. The linear form of Langmuir isotherm is provided by Equation (5) following.

$$C_e/q_e = C_e/q_m + 1/K_L q_m (5)$$

where  $q_m$  is the maximum adsorption capacity (characteristic of the formation of monolayer's adsorbed molecules) (mg g-1) and  $K_L$  (L mg-1) is the equilibrium constant. This is a characteristic of adsorbent depending on the temperature and the experimental conditions. Using the constant  $K_L$ , a characteristic of Langmuir isotherm was determined where it was expressed in terms of separation factor and equilibrium parameter  $R_L$ , as shown in Equation (6) following. It can be employed to describe the affinity between the adsorbate and the adsorbent (Ahmadpour et al., 2010).

$$R_L = 1/1 + (K_L C_O) (6)$$

The parameter value  $R_L$  is shown where the adsorption is irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable  $R_L > 1$  (Gok et al., 2013). A plot of  $C_e/q_e$  versus  $C_e$  is a straight line with  $1/q_m K_L$  as intercept and  $1/q_m$  as slope. Hence,  $q_m$  and  $K_L$  can be calculated.

As for the investigation of the sorption rate law, kinetic data obtained in this study were analysed using pseudo first-order and pseudo second-order models respectively. According to Ramana et al. (2012), this model demonstrates the degree to which the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. Equation (7) below shows the equation of the pseudo first-order model;

$$1/q_t = k_1/q_e t + 1/q_e (7)$$

where  $q_t$  and  $q_e$  are the adsorption capacity at time t and equilibrium (mg g<sup>-1</sup>) respectively, t is the contact time (min) and  $k_1$  is the rate constant of pseudo first-order adsorption (mn<sup>-1</sup>). A plot of  $1/q_t$  (mg<sup>-1</sup> g) versus 1/t (min<sup>-1</sup>) gives a straight line and the values of calculated  $q_e$  and  $k_1$  constant can be calculated from the intercept and slope of the curve respectively.

Based on Ibrahim et al. (2012), the sorption mechanism which follows the second order reaction is the pseudo second-order model. The sorption rate is shown to be proportional to the square of the number of unoccupied sites. The equation of pseudo second order model is shown in Equation (8) below

$$t/q_t = 1/k_2 q_e^2 + t/q_e (8)$$

where  $q_t$  is the adsorption capacity at time t (mg g<sup>-1</sup>),  $q_e$  is the adsorption capacity at equilibrium (mg g<sup>-1</sup>), t is the contact time (min) and  $k_2$  is the rate constant of pseudo second-order adsorption (g mg<sup>-1</sup> min<sup>-1</sup>). A plot  $t/q_t$  (min mg<sup>-1</sup> g) against t (min) gives a straight line that will determine the values of  $k_2$  constant and  $q_e$  from the value of intercept and slope of the curve respectively

## RESULTS AND DISCUSSIONS

The present study has optimized the adsorption of spent coffee grounds (SCG) on Fe ions by analyzing this adsorption capacity at different solution conditions, namely: pH of solution; contact time; particle size and adsorbent dosage.

As shown in Figure 1a, the amount of Fe ions adsorbed by spent coffee grounds increased from pH 1 to 3. The measure was 0.286 at pH 1 and 0.458 mg g<sup>-1</sup> at pH 3, respectively. However, an equilibrium level of pH 3 to 7, (around 0.4 mg g<sup>-1</sup>) was achieved. As for the alkaline solution, its absorption was in decline from 0.3 mg g<sup>-1</sup> to pH 9 before remaining constant after pH 9 (Figure 1a). According to a previous study (Li et al., 2012), this might be due to the effect of initial concentration of hydrogen ions on the adsorption yield that depends on the adsorbent surface charge and on metals speciation. A significant difference (p < 0.05) between the initial solution pH was identified from statistical analysis.

The low uptake level of coffee grounds was recorded at acidic condition (pH 1, 59.0%). This could be due to the protonation of the exchange sites, negatively charged, by H<sup>+</sup> protons

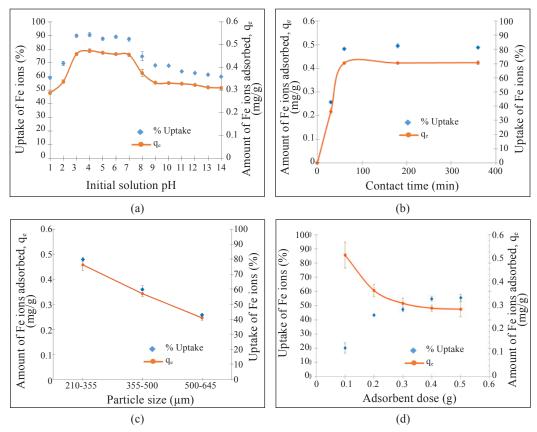


Figure 1. Effect of (a) different pH, (b) contact time, (c) particle size, and (d) dosage on the adsorption of Fe ions by SCG

that play a competitive part opposite the Fe<sup>2+</sup> ions. The presence of increasing mobility of hydrogen ions (H<sup>+</sup>) favored the preferential adsorption of H<sup>+</sup> compared to the metal ion (Ajmal et al., 2000). There was a plateau of Fe adsorption by spent coffee grounds at pH 3 to 7 (Figure 1a). This can be due to the sufficiency of the released sites of the H<sup>+</sup> protons guaranteed by the adsorbent excess matter (Imessaoudene et al., 2013). Therefore, adsorption of Fe by using spent coffee grounds is proven to be effective in polluted waters since most of the contaminated waters in wastewater treatment and polluted water sources have an acidic condition range of pH 4 to 6 as recorded by Al-Badaii et al. (2013). As shown in Figure 1a, the optimum pH for maximum percentage uptake of Fe ions (92.9%) at pH 4 was chosen for the next analysis.

There was a rapid drop in the percentage uptake of Fe ions between pH 7 and pH 9 (Figure 1a). However, this became slightly constant and bottomed out as the pH increased (pH>9) due to the weak interactive competition between coffee grounds and Fe ions which replace H<sup>+</sup> for formation of surface functional groups like -OH and -COOH (Egila et al., 2010). The reduction in uptake percentage was recorded as pH increases because

insoluble  $Fe(OH)_3$  formed easily in the retained remainder at alkaline conditions. Changes in metals speciation  $Fe^{2+}$  ions to  $Fe^{3+}$  ions were due to oxidation resulting in limitations in the uptake of Fe ions by adsorbent procedures as  $Fe^{3+}$  ions had weaker energy of hydration for adsorption (Keshtkar et al., 2012).

During the first 60 minutes, the capacity of biosorption increased dramatically and a major quantity of Fe (80.4%) was eliminated from the solution (Figure 1(b)). The instantaneous sorption showed the characteristic of physical adsorptions. The higher biosorption rate at the initial stage was attributed to the abundance of the active sites on biosorbent which were easily accessible by the ions (Seliman, 2012). After 60 minutes, the reaction became saturated and achieved an equilibrium state. This equilibrium was reached rapidly at the highest percentage uptake of Fe ions (82.5%). However, the extension (by this time up to 360 minutes) did not lead to an increase of the elimination percentage due to the exhaustion of binding sites on the substrate (Imessaoudene et al., 2013). The availability of these sites decreased as the contact time was prolonged, thereby causing difficulties in biosorption of the remaining empty external sites. Thus, a contact time of 60 min was fixed for further analysis to ensure the achievement of optimum reaction.

As the adsorbent particle size increased, adsorption capabilities decreased (Figure 1(c)). This led to the decrease of 37.1% in Fe uptake between the finest particles (210-355  $\mu$ m) and the largest particles (500–645  $\mu$ m) (Figure 1(c)). This result highlighted the resemblance in the behavior of spent coffee grounds compared to those of other biosorbents, such as fluoride (Ogata et al., 2011) and strontium (Imessaoudene et al., 2013). In this case, it can be suggested that the Fe ion adsorption was strongly affected by the presence of surface functional groups. The spent coffee grounds achieved maximum percentage uptake of Fe ion (79.9%) with the smallest mean diameter of 210-355  $\mu$ m and the largest specific surface area. Surface area is one of the functional properties that may influence the amount of Fe ions adsorbed onto coffee grounds.

Adsorbent dosage is one of the factors that influence the adsorbent's adsorption capacity for a given initial concentration of metal ion solution (Imessaoudene, et. al., 2013). Figure 1d shows the percentage removal of Fe ion and adsorption capacity of spent coffee grounds over a variety of dosages for a fixed initial concentration of 0.5 mg/L Fe solution. The decrease in adsorption capacity was the result of an increase in dosage. When more adsorbent was added, the Fe ion concentration remained unchanged. According to Kamal et al. (2010), the ratio of numbers of adsorption sites to the number of Fe ions would rise as the adsorbent dosage increased and result in more adsorption sites that were not adsorbed. Other than that, the decrease in adsorption capacity was due to the particle aggregation of excessive adsorbents that decrease the total surface area of coffee grounds. Therefore, the Fe ions must penetrate deeper in the intra-particulate active sites by meeting a much larger resistance (Gogoi et al., 2013).

Percentage of removal is equally as important as adsorption capacity. The percentage of removal (20.2-55.2%) increased as dosage was increased (0.1-0.5 g) (Figure 1d). The greater the surface area, the greater the number of adsorption sites. In this present study, a dosage of 0.3 g was chosen because it showed the closest value between the adsorption capacities  $(0.259 \text{ mg g}^{-1})$  with a considerable percentage of Fe removal of 47.4%.

Figure 2 shows the effect of initial Fe ion concentration on the removal efficiency of three different adsorbents, specifically: spent coffee grounds (SCG); degreased coffee grounds (DCG); and activated carbon (AC). DCG (after removal of fat) achieved the highest adsorption capacity (0.748 mg g<sup>-1</sup>) at the high concentration of Fe ions (1.0 mg/L). The SCG adsorbed approximately half the amount of Fe ions (0.415 mg g<sup>-1</sup>) hence less than DCG. With the removal of fat content in coffee grounds (11.2%), DCG could adsorb more Fe ions compared to the SCG. A previous study carried out by Tokimoto et al. (2005) had also proven that fat in coffee grounds could not adsorb lead (Pb) ions. Therefore, the experimental results in this study and previous studies suggested that fat contained in SCG is not responsible for adsorption of heavy metals. This study demonstrates a better way to use SCG for Fe ion removal by eliminating fat content in coffee grounds prior to adsorption activities.

Although Activated Carbon (AC) has been applied in water treatment to a great extent, this present study has revealed that lesser Fe ions were adsorbed compared to DCG (Figure 2). This indicates that the adsorption capabilities of SCG and AC had similar efficiency for removal of Fe ions at concentrations of 0.5-0.7 mg/L (Figure 2). Easily available SCG can be used as an alternative to the expensive AC in the water treatment process.

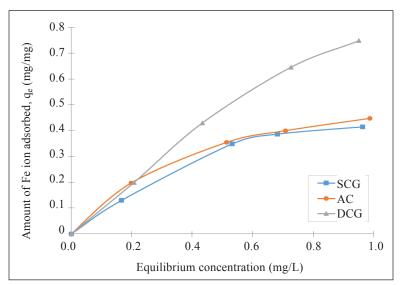


Figure 2. Effect of various Fe ion concentrations by using different adsorbents on the adsorption of Fe ions (Condition: 0.1 g of each adsorbent in 100 mL of Fe solution at pH 4 for 60 min)

### **Adsorption Isotherms**

Sorption data explain adsorbent performances while adsorption isotherms describe the equilibrium distribution of solute between solution and adsorbent. This can provide an estimation of adsorbent efficiencies and the market value. The Freundlich and Langmuir were tested and the results are presented in Figure 3 below.

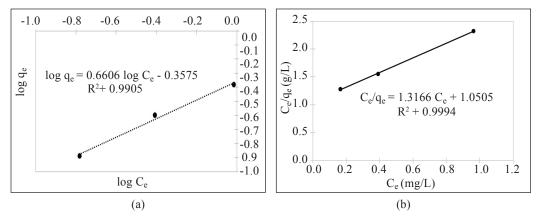


Figure 3. (a) Linear Freundlich adsorption isotherm and (b) linear Langmuir adsorption isotherm for Fe ions adsorption by SCG

The goodness of fit of the experimental data worked out for the two types of isotherms are summarized in Table 2. Both the Freundlich and Langmuir plots were linear with correlation coefficients of 0.991 and 0.999 (Figure 3) respectively. As a result, the data were in line with the models. Our results suggested that adsorption seems to take place according to the Freundlich model with a satisfactory value of  $R^2$  (0.991). However, the n value does not fall in between 0 and 1 (1.796). This could indicate that the Fe adsorption by the spent coffee grounds was not favorable to the studied conditions of the Freundlich model. The deviation from linearity of the biosorption of spent coffee grounds for Fe ion in a solution using the Freundlich model indicates the poor bond energies existing between Fe ion and coffee grounds.

It may be suggested that a better Fe adsorption ( $R^2$ =0.999) was Langmuir model as compared to the Freundlich model. Consequently, the possible assumptions related to this biosorption phenomenon, as stated by Gok et al. (2013). The calculated  $R_L$  values (0.453-0.828) for Fe ions indicate that the biosorption of SCG is favorable. A comparison of  $q_m$  values obtained in this study indicated that the Fe adsorption by spent coffee grounds is less favorable compared to other biosorbents. This is mainly because most biosorbents which had undergone intensive chemical pretreatment prior to adsorption eventually achieved better adsorption capabilities compared to spent coffee grounds.

Table 2
The values of parameters for Freundlich and Langmuir isotherms

Freundlich			Langmuir			
$K_{\mathrm{F}}$	N	$\mathbb{R}^2$	$K_L (L \text{ mol}^{-1})$	$R_{L}$	$\mathbb{R}^2$	q <sub>m</sub> (mg g <sup>-1</sup> )
0.530	1.796	0.958	2.803	0.263 - 0.543	0.9501	0.615

## **Adsorption Kinetics**

There are a number of models that can be applied to demonstrate the mechanism of sorbent sorption by a solute. In order to conduct a better investigation of the mechanism, characteristic constants of Fe sorption by spent coffee grounds (SCG) were ascertained by applying both pseudo first-order equation and a pseudo second-order equation (Figure 4).

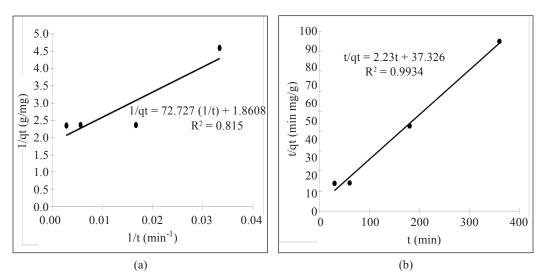


Figure 4. A pseudo first-order (a) and pseudo second-order (b) kinetic fit for adsorption of Fe ions onto SCG

The values of  $K_1$ ,  $q_e$ ,  $R^2$  (correlation coefficient for pseudo first-order sorption kinetics) and  $q_e$ ,  $K_2$ , H, and  $R^2$  (correlation coefficient for pseudo second-order sorption kinetics) have been tabulated in Table 3. Adsorption rates were found to conform to pseudo second-order kinetics with good correlation. The use of the pseudo first-order equation proved to be less compatible through our experimental data with regard to values  $R^2 = 0.815$  (Table 3). Pseudo first-order showed a significant difference between experimental  $q_e$  and calculated  $q_e$  of this model. On the other hand, pseudo second-order seemed more compatible to the results ( $R^2 = 0.993$ ) where correlation coefficient of the curve  $t/q_t$  according to t is close to the unit 1. There was no significant difference between experimental  $q_e$  and calculated  $q_e$  of pseudo second-order model (p-value = 0.2381 > 0.01).

Table 3
The values of parameters for pseudo first-order and pseudo second-order kinetic models

qe	Pseudo first-order con			Pseudo second-order constants			
experimental	qe calculated	K1	R2	qe calculated	K2 (g mg <sup>-1</sup>	H (mg g <sup>-1</sup>	R2
$(mg g^{-1})$	$(mg g^{-1})$	(min <sup>-1</sup> )		$(mg g^{-1})$	min <sup>-1</sup> )	min <sup>-1</sup> )	
	( 00 /	,		( 00 /	,	,	

Consequently, the pseudo second-order was selected in this study and it showed that adsorption might be restricted by valence forces (Ramana et al., 2012). According to Kırbıyık et al. (2012), the biosorption process occurs on localized sites with no interaction between maximum biosorption and biosorbates. Thus, the reaction involved in this study corresponds to a saturated monolayer of biosorbates onto the biosorbent surface.

#### **CONCLUSIONS**

Results from this study have proven the ability of spent coffee grounds in removing total Fe ions. About 92.9% of Fe ions in the concentration of 0.5 mg/L were successfully adsorbed by 0.10 g of spent coffee grounds at optimum conditions of pH 4 in 60 minutes. The ability of spent coffee grounds in removing total Fe ions showed it to be suitable as an alternative material for replacing commercially available adsorbents for the removal of Fe ions in polluted water. This innovative green technology is necessary due to increasing environmental awareness for sustainable management processes.

#### **ACKNOWLEDGEMENTS**

This study was funded by the Universiti Putra Malaysia (IPM 9435200). We are grateful for the assistance from all the laboratory staff of the Faculty of Environmental Studies, UPM during the sampling and analysis procedures.

#### REFERENCES

- Ahmadpour, A., Zabihi, M., Tahmasbi, M., & Bastami, T. R. (2010). Effect of adsorbents and chemical treatments on the removal of strontium from aqueous solutions. *Journal of Hazardous Materials*, 182(1-3), 552-556.
- Ajmal, M., Rao, R.A., Ahmad, K., & Ahmad, R. (2000). Adsorption studies on citrus reticulate (fruit peel of orange). Removal and recovery of Ni (II) from electroplating wastewater. *Journal of Hazardous Materials*, 79(1-2), 117-131.
- Al-Badaii, F., Othman, M. S., & Gasim, M. B. (2013). Water quality assessment of the Semenyih River, Selangor, Malaysia. *Journal of Chemistry*, 2013, 1-10.
- American Public Health Association. (2012). *Standard methods for the analysis of water and wastewater* (20th ed.). Alexandria, Virginia: APHA.

- Atasoy, N., Mercan, U., Alacabey, I., & Kul, A. R. (2011). Levels of heavy metals and certain macro elements in potable and tap water at Van City Center. *Journal of Biology and Chemical*, 39(4), 391-396.
- Chandrakala, G., Abhishek, B., Kumar, Ch V., S. K., Meera, I., Naidu S. V., & Rao, M. N. (2012). *Ageratum conyzoides* leaf powder for decontamination of iron (III) removal, adsorbent characterization and equilibrium modelling. *Journal of Environmental Research and Development*, 7(1A), 1-10.
- Economic Planning Unit. (2006). Ninth Malaysia Plan 2006–2010. Putrajaya: Author.
- Egila, J. N., Dauda, B. E. N., & Jimoh, T. (2010). Biosorptive removal of cobalt (II) ions from aqueous solution by *Amaranthus hydridus* L. stalk wastes. *African Journal of Biotechnology*, *9*(48), 8192-8198.
- Egila, J. N., Dauda, B. E. N., Iyaka, Y. A., & Jimoh, T. (2011). Agricultural waste as a low cost adsorbent for heavy metal removal from wastewater. *International Journal of the Physical Sciences*, 6(8), 2152-2157.
- Gogoi, R., Barbhuiya, H. A., & Borah, S. (2013). Rediscovery of impatiens laevigata var. grandifolia (Balsaminaceae) from NE India. *Taiwania*, 58 (4), 311-315.
- Gok, C., Gerstmann, U., & Aytas, S. (2013). Biosorption of radiostrontium by alginate beads: Application of isotherm models and thermodynamic studies. *Journal of Radioanalytical and Nuclear Chemistry*, 295(1), 777-788.
- Ibrahim, H. S., Ammar, N. S., Soylak, M., & Ibrahim, M. (2012). Removal of Cd (II) and Pb (II) from aqueous solution using dried water hyacinth as a biosorbent. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 96, 413-420.
- Idriss, A.A., & Ahmad, A.K. (2012). Concentration of selected heavy metals in water of the Juru River, Penang, Malaysia. *African Journal of Biotechnology*, 11(33), 8234-8240.
- Imessaoudene, D., Hanini, S., & Bouzidi, A. (2013). Biosorption of strontium from aqueous solutions onto spent coffee grounds. *Journal of Radioanal Nuclear Chemistry*, 298(2), 893-902.
- Ismail, Z., Salim, K., Othman, S. Z., Ramli, A. H., Shirazi, S. M., Karim, R., & Khoo, S. Y. (2013). Determining and comparing the levels of heavy metal concentrations in two selected urban river water. *Elsevier Journal* of Measurement, 46(10), 4135-4144.
- Kamal, M. H. M. A., Azira, W. M. K. W. K., Kasmawati, M., Haslizaidi, Z., & Saime, W. N. W. (2010). Sequestration of toxic Pb (II) ions by chemically treated rubber (*Hevea brasiliensis*) leaf powder. *Journal of Environmental Sciences*, 22(2), 248-256.
- Keshtkar, A. R., Kafshgari, F., & Mousavian, M. A. (2012). Binary biosorption of uranium (VI) and nickel (II) from aqueous solution by Ca-pretreated *Cystoseira indica* in a fixed-bed column. *Journal of Radioanal Nuclear Chemistry*, 292(2), 501-512.
- Khosravihaftkhany, S., Morad, N., Teng, T. T., Abdullah, A. Z., & Norli, I (2013). Biosorption of Pb (II) and Fe (III) from aqueous solutions using oil palm biomasses as adsorbents. *Water Air Soil Pollution*, 224(3), 1455.
- Kırbıyık, Ç., Kılıç, M., Çepelioğullar, Ö., & Pütün, A. E. (2012). Use of sesame stalk biomass for the removal of Ni (II) and Zn (II) from aqueous solutions. *Water Science & Technology*, 66(2), 231-238.

- Li, Q., Liu, Y., Cao, X., Pang, C., Zhang, Z., Wang, Y., Liu, Y., & Hua, M. (2012). Biosorption characteristics of uranium (VI) from aqueous solution by pomelo peel. *Journal of Radioanal Nuclear Chemistry*, 298(3), 67-73.
- Miretzky, P., Saralegui, A., & Cirelli, A. F. (2005). Simultaneous heavy metal removal mechanism by dead macrophytes. *Chemosphere*, 62(2), 247-254.
- Mussatto, S.I., Carneiro, L.M., Silva, J. P. A., Roberto, I. C., & Teixeira, J. A. (2011). A study on chemical constituents and sugars extraction from spent coffee grounds. *Carbohydrate Polymers*, 83(2), 368-74.
- Ogata, F., Tominaga, H., Yabutani, H., & Kawasaki, N. (2011). Removal of fluoride ions from water by adsorption onto carbonaceous materials produced from coffee grounds. *Journal of Oleo Sciences*, 60(12), 619-625.
- Park, Y., Shin, W. S., & Choi S. J. (2013) Removal of cobalt and strontium from groundwater by sorption onto fishbone. *Journal of Radioanalytical and Nuclear Chemistry*, 295(1), 789-799.
- Ramalakshmi, K., Rao, L. J. M., Takano-Ishikawa, Y., & Goto, M. (2009). Bioactivities of low-grade green coffee and spent coffee in different in vitro model systems. *Food Chemistry*, 115(1), 79-85.
- Ramana, D. K. V., Reddy, D. H. K., Yu, J. S., & Seshaiah, K. (2012). Pigeon pea hulls waste as potential adsorbent for removal of Pb (II) and Ni (II) from water. *Chemical Engineering Journal*, 197, 24-33.
- Ramya, R., Sankar, P., Anbalagan, S., & Sudha, P. N. (2011). Adsorption of Cu (II) and Ni (II) ions from metal solution using crosslinked chitosan-g-acrylonitrile copolymer. *International Journal of Environmental Sciences*, *1*(6), 1323-1338.
- Rose, E. P., & Rajam, S. (2012). Equilibrium study of the adsorption of iron (II) ions from aqueous solution on carbons from wild jack and jambul. *Journal of Advance Applied Science Research*, 3(2), 1889-1894.
- Seheimy, A. E. H. A., & Sadek, M. E. S. (2009). Iron impact management on October 31<sup>st</sup> to November 4th 2009. *Journal of Chemica Acta*, 1(1), 40-43
- Seliman, A. (2012). Affinity and removal of radionuclides mixture from low-level liquid waste by synthetic ferrierites. *Journal of Radioanalytical and Nuclear Chemistry*, 292(2), 729-738.
- Tokimoto, T., Kawasaki, N., Nakamura, T., Akutagawa, J., & Tanada, S. (2005). Removal of lead ions in drinking water by coffee grounds as vegetable biomass. *Journal of Colloid and Interface Science*, 281(1), 56-61.
- Utomo, H. D., & Hunter K.A. (2010) Adsorption of divalent copper, zinc, cadmium and lead ions from aqueous solution by waste tea and coffee adsorbents. *Environmental Technology*, 27(1), 25-32.
- Wang, C., Kong, H., Wang, X., Wu, H., Lin, Y., & He, S. (2010). Effects of iron on growth and intracellular chemical contents of *Microcystis aeruginosa*. *Biomedical and Environmental Sciences*, 23(1), 48-52.