

# MAGNETIC GRAPHENE OXIDE AS ADSORBENT FOR THE REMOVAL OF LEAD(II) FROM WATER SAMPLES

Hamid Rashidi Nodeh,<sup>a</sup> Wan Aini Wan Ibrahim,<sup>a\*</sup> Mohd Marsin Sanagi,<sup>a,b</sup>

<sup>a</sup>Separation Science and Technology Group, Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM, Johor Bahru, Johor, Malaysia

<sup>b</sup>Ibnu Sina Institute for Scientific and Industrial Studies, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

## Article history

Received

10 February 2015

Received in revised form

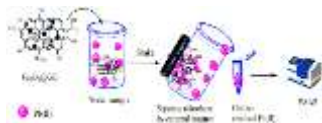
20 November 2015

Accepted

20 November 2015

\*Corresponding author  
wanaini@kimia.fs.utm.my,  
waini@utm.my

## Graphical abstract



## Abstract

Magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles were prepared on graphene oxide ( $\text{Fe}_3\text{O}_4/\text{GO}$ ) in situ in a one step process. The obtained  $\text{Fe}_3\text{O}_4/\text{GO}$  was used as an adsorbent for the removal of  $\text{Pb}(\text{II})$  from environmental water samples prior to flame atomic absorption spectroscopy measurement. The adsorption procedure was optimized as follows: 60 min adsorption time, 50 mL sample volume, solution pH 4.5, and 25 mg adsorbent dosage. Under the optimum conditions, the adsorption efficiency obtained was greater than 75% ( $C = 50 \text{ mg L}^{-1}$ ). The adsorption isotherm of  $\text{Fe}_3\text{O}_4/\text{GO}$  magnetic adsorbent was studied for  $\text{Pb}(\text{II})$  adsorption using two isotherm adsorption models namely Langmuir and Freundlich. The adsorption isotherm data fits well with Langmuir isotherm ( $R^2 = 0.9988$ ) rather than with Freundlich isotherm. The maximum adsorption capacity ( $q_m$ ) obtained was  $86.2 \text{ mg g}^{-1}$ . The results signified that the prepared  $\text{Fe}_3\text{O}_4/\text{GO}$  nanocomposite has a great adsorptive ability towards the  $\text{Pb}(\text{II})$  from environmental water samples.

Keywords: Magnetic nanoparticles; graphene oxide; lead(II); adsorption capacity; Langmuir isotherm model.

## Abstrak

Nanopartikel  $\text{Fe}_3\text{O}_4$  magnetik telah disediakan atas grafin oksida ( $\text{Fe}_3\text{O}_4/\text{GO}$ ) secara in-situ dalam proses satu langkah.  $\text{Fe}_3\text{O}_4/\text{GO}$  terhasil telah digunakan sebagai penjerap untuk penyingkiran  $\text{Pb}(\text{II})$  daripada sampel air alam sekitar, sebelum pengukuran dengan spektroskopi serapan atom nyata. Prosedur penjerapan telah dioptimumkan seperti berikut: 60 min masa penjerapan, 50 mL isipadu sampel, pH larutan 4.5, dan 25 mg dos penjerap. Di bawah keadaan optimum kecekapan penjerapan yang diperolehi adalah lebih besar daripada 75% ( $C = 50 \text{ mg L}^{-1}$ ). Kapasiti penjerapan penjerap magnetik  $\text{Fe}_3\text{O}_4/\text{GO}$  dikaji untuk penjerapan  $\text{Pb}(\text{II})$  menggunakan dua model penjerapan isoterma iaitu Langmuir dan Freundlich. Data penjerapan isoterma lebih sesuai dengan isoterma Langmuir ( $R^2 = 0.9988$ ) berbanding dengan isoterma Freundlich. Kapasiti penjerapan maksimum, ( $q_m$ ) ialah  $86.2 \text{ mg g}^{-1}$ . Keputusan mengesahkan bahawa nanokomposit  $\text{Fe}_3\text{O}_4/\text{GO}$  mempunyai keupayaan penjerapan yang tinggi terhadap  $\text{Pb}(\text{II})$  daripada sampel air alam sekitar.

Kata kunci: Nanopartikel magnetik; grafin oksida; plumbum(II); kapasiti penjerapan; model isoterma Langmuir.

© 2016 Penerbit UTM Press. All rights reserved

## 1.0 INTRODUCTION

Due to presence of heavy metal ions in water samples determination and monitoring of metal ions require treatment process for removal [1]. Lead is one of the hazardous metal ions and critical pollution in air, water and soil. Lead can be discharge into the environmental via different ways, such as leaded gasoline, lead mining and processing, coal mining and processing, cosmetics, batteries and widespread application in the printing industry [2, 3]. Lead is a highly toxic metal, even at very low concentrations, so that the allowable level of Pb(II) in drinking water is 10 ng mL<sup>-1</sup> (set by European Union) [4]. Exposure through Pb(II) can lead to skin diseases, reproductive system disorders, cancer and so on [5]. Thus, determination, monitoring and removing Pb(II) from the environment to human and environmental protection is required.

Different types of technique have been reported to identify and remove Pb(II) from aqueous solution i.e., degradation, membrane filtration, oxidation, reduction, precipitation, ion exchange and adsorption [6, 7]. Among these technique, adsorption method is one of the outstanding techniques that have been used for toxic metal removal from aqueous media [8]. This is because adsorption method does not add secondary pollution to the environment as well as it is simple, fast, economic and environmental friendly [9]. Selection of an effective adsorbent in adsorption process is important. Graphene oxide (GO) with potential benefits have been used successfully as solid adsorbent for Pb(II) removal [10, 11, 12]. GO advantages which includes unique configuration of carbon atoms high surface area, single sheets and high adsorption affinity toward metal ions complexation since both sides of the sheets possess oxygen functional groups i.e., hydroxide, epoxy on the basal plane, and carboxyl [7, 13, 14]. Although GO provided high adsorption efficiency for Pb(II), but solid separation from aqueous media requires filtration, high speed centrifuge and this is costly, tedious and time consuming [15]. In order to overcome these problems, magnetic nanoparticles (MNPs) properly dispersed on adsorbent offer fast separation from water solution [13]. Magnetic materials provide low costs, fast, simple durability and high sorption efficiency toward trace and ultra-trace metal ions [16, 17].

The synthesised Fe<sub>3</sub>O<sub>4</sub>/GO adsorbent was examined for its feasibility in the adsorption of Pb(II) ions from water samples. Adsorption isotherm and kinetic models were applied as experimental adsorption capacity and contact time justification models, respectively.

## 2.0 EXPERIMENTAL

### 2.1 Chemicals and Reagents

Millipore water filtration system (Simplicity 185, 18.2 MΩ) from Merck (Darmstadt, Germany) was used for deionized water used for preparation of the standards and sample solutions. Iron(III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) and iron(II) chloride (FeCl<sub>2</sub>·4H<sub>2</sub>O) were prepared from Sigma Aldrich (St. Louis, MO, USA). Sodium hydroxide pellet (NaOH), hydrochloric acid (HCl 37.0%), Lead(II)nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>) was purchased from QReC (Selangor, Malaysia). Stock solution (1000 mg L<sup>-1</sup>) of Pb(II) was prepared in deionized water.

### 2.2 Instrument and Conditions

An Analyst 400 flame atomic absorption spectrometer (FAAS) was from Perkin-Elmer (Waltham, MA USA), equipped with a lead hollow cathode lamp to determine the absorption of Pb(II) ions in water solution. Deuterium lamp was used for background correction. The hollow cathode lamp was operated at 8.0 mA and the wavelength was set at 283.31 nm. The flame composition was operated with an acetylene flow rate of 1.8 L min<sup>-1</sup> and air flow rate of 10.0 L min<sup>-1</sup>.

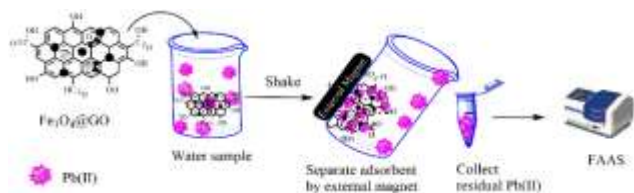
### 2.3 Synthesis of Fe<sub>3</sub>O<sub>4</sub>/GO

In the current study, magnetic graphene oxide was prepared using a simple one step method. Fe<sub>3</sub>O<sub>4</sub> MNPs were synthesised through co-precipitation method and simultaneously dispersed on GO sheets [18]. Briefly, GO (1 g), FeCl<sub>2</sub> (0.1 g) and FeCl<sub>3</sub> (0.2 g) were mixed in 50 mL de-ionized water and then sonicated for 30 min. Thereafter, the mixture was heated until 50°C with vigorous stirring and 5 mL of ammonia (25%) was added drop wise to it followed by an extra stirring for 5 h at room temperature. The product obtained (Fe<sub>3</sub>O<sub>4</sub>/GO) was then washed with distilled water (200 mL) and methanol (50 mL) and then oven dried at 80°C for 24 h.

### 2.4 Adsorption Experiments

#### 2.4.1 Adsorption Study

The adsorption of Pb(II) from water was performed by using batch equilibration method. Figure 1 shows a schematic procedure of the batch adsorption study. Initially the adsorbent dosage studied was from 5 mg to 100 mg and the solution pH was from 3 to 7 with 60 min adsorption time. Adsorption was studied using a fixed Fe<sub>3</sub>O<sub>4</sub>/GO dose (25 mg), solution pH 4.5, 50 mL water solution containing Pb(II) ions with different initial concentrations (10 - 150 mg L<sup>-1</sup>). After each adsorption treatment, an external magnet was applied for magnetic adsorbent separation from the solution. The residual concentration of Pb(II) in the water samples was measured using FAAS.



**Figure 1** Batch adsorption procedure of the proposed MSPE method

The adsorption capacity of the as-synthesised Fe<sub>3</sub>O<sub>4</sub>@GO adsorbent was calculated using equation (1) [19]:

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

where,  $q_e$  is the adsorption capacity (mg g<sup>-1</sup>),  $V$  is the volume sample (L),  $m$  is the adsorbent dosage (g),  $C_0$  is initial concentrations and  $C_e$  is residual concentrations after equilibrium of Pb (mg L<sup>-1</sup>).

### 2.4.2 Kinetic Study

Kinetic studies were carried out using different contact time between the adsorbent and Pb(II). Adsorption times used ranged between 5 and 120 min at a shaking speed of 250 rpm. Shaking was performed using an orbital shaker from Chung Shin RD (Taiwan, ROC). For experimental procedure, water samples used was 50 mL, 25 mg of adsorbent and 50 mg L<sup>-1</sup> concentration of the Pb(II). After the removal process, the residual concentrations of Pb(II) was determined by FAAS. Finally, Pb(II) adsorption capacity at the time { $q_t$  (mg g<sup>-1</sup>)} was calculated by using equation 2:

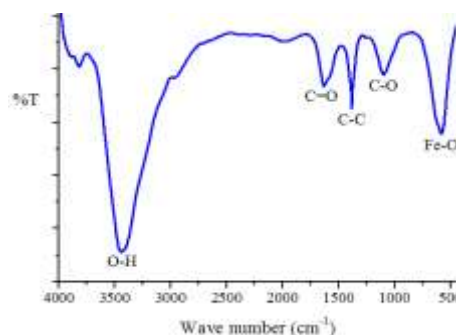
$$q_t = \frac{V}{m}(C_0 - C_t) \quad (2)$$

where  $q_t$  is the adsorption capacity at time,  $V$  is the volume sample (L),  $m$  is the adsorbent dosage (g),  $C_0$  is initial concentrations and  $C_t$  (mg L<sup>-1</sup>) is Pb(II) concentration at time  $t$ .

## 3.0 RESULTS AND DISCUSSION

### 3.1 Characterization

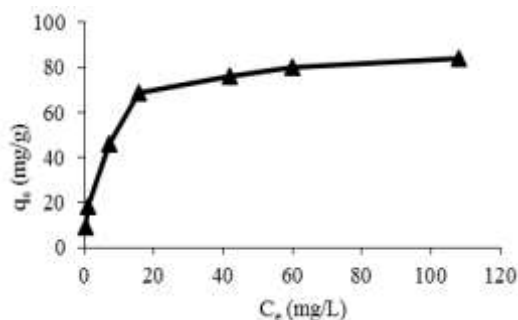
The prepared adsorbent was characterized by using FTIR spectroscopy. Figure 2 shows the peaks at 3450 cm<sup>-1</sup>, 1720 cm<sup>-1</sup>, 1490 cm<sup>-1</sup>, 1200 cm<sup>-1</sup> and 580 cm<sup>-1</sup> which are related to O-H, C=O, C-C, C-O and Fe-O, respectively. These evidences provided the presence of Fe<sub>3</sub>O<sub>4</sub> nanoparticles on the GO surface.



**Figure 2** FTIR spectroscopy of the as-synthesised Fe<sub>3</sub>O<sub>4</sub>/GO adsorbent

### 3.2 Adsorption Study

Adsorption study was carry out using different concentrations of Pb(II) (10 - 150 mg L<sup>-1</sup>) at pH 4.5 (Figure 3). When the concentration of Pb(II) was increased,  $q_e$  also increased until it reached equilibrium at higher concentrations since at high concentration adsorption sites were saturated. The adsorption mechanism of Pb(II) on the Fe<sub>3</sub>O<sub>4</sub>/GO was studied by using adsorption models namely Langmuir and Freundlich.



**Figure 3** Equilibrium adsorption capacities for Pb(II) sorption using the as-synthesised Fe<sub>3</sub>O<sub>4</sub>/GO as adsorbent

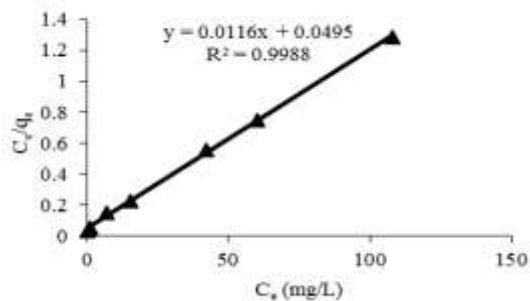
#### 3.2.1 Langmuir Isotherm

Langmuir model provide unique surface and monolayer adsorption that control by chemisorption. Langmuir model was considered by using equation (3),  $q_m$  is the maximum adsorption capacity (mg g<sup>-1</sup>).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m} \quad (3)$$

where  $q_e$  is the experimental adsorption capacity that was obtained from equation (1),  $k_L$  is Langmuir constant (L mg<sup>-1</sup>) and  $C_e$  is the residual concentration in the solution after removal process. The theoretical adsorption capacity or  $q_m$  was obtained by plotting  $C_e/q_e$  versus  $C_e$  (Figure 4).  $q_m$  and  $k$  can be obtained from the slope of line and intercept, respectively. The

calculated parameters (i.e.,  $q_m$ ,  $k_L$ ,  $K_F$  and  $R^2$ ) from these two models are given in Table 1.



**Figure 4** Langmuir linearity for adsorption model of Pb(II) sorption by using  $Fe_3O_4/GO$  as adsorbent.

### 3.2.2 Freundlich Isotherm

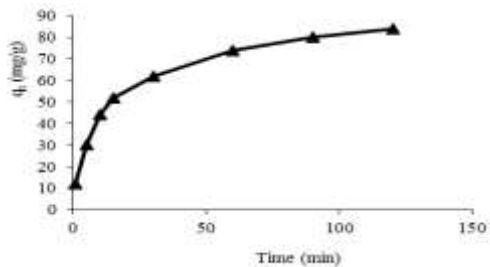
Freundlich model shows heterogeneous surface adsorbent and multilayer adsorption is controlled by physisorption (i.e. van der Waal's interaction). Freundlich model is obtained from equation (4),

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (4)$$

Where  $K_F$  is the adsorption capacity ( $(\text{mg/g})(\text{L/mg})^{1/n}$ ),  $n$  is the constant that shows heterogeneity. The coefficient of determination ( $R^2$ ) was obtained by plotting  $\text{Log } q_e$  versus  $\text{Log } C_e$ . The values of  $K_F$  and  $n$  can be obtained from the intercept and slope, respectively. The calculated values from these models are given in Table 1. Finally, Table 1 result shows that the Langmuir model is more favorable for adsorption studies since high correlation of  $R^2$  was obtained.

### 3.3 Kinetic Study

The experiment for kinetics study was carried out using different contact time effects on the adsorption of Pb(II) on the adsorbent. Figure 5 shows that the adsorption capacity increase fast until 15 minute thereafter it's going up slowly until it reached equilibrium. The kinetic models were carried out by pseudo-first-order, pseudo-second-order and intra-particle diffusion models.



**Figure 5** Effect of contact time in adsorption capacity for Pb(II) sorption by using  $Fe_3O_4/GO$  as adsorbent.

### 3.3.1 Pseudo First Order & Second Order Models

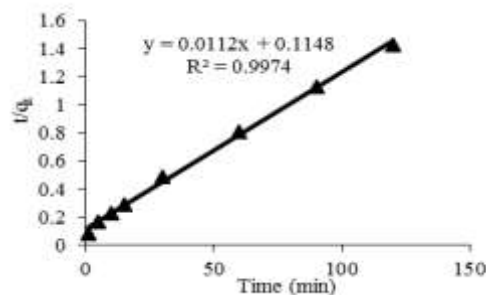
The pseudo-first order rate and pseudo-second order rate are generally expressed by equation 5 & 6 [20]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_t} \quad (6)$$

Where  $q_e$  is the equilibrium adsorption capacity ( $\text{mg g}^{-1}$ ) (theory),  $q_t$  is adsorption capacity ( $\text{mg g}^{-1}$ ).  $k_1$  ( $1/\text{min}$ ) and  $k_2$  ( $\text{g}/\text{mg}/\text{min}$ ) are the pseudo constants for first-order and second-order, respectively. In pseudo-first-order model the values of  $q_e$  and  $k_1$  can be calculate from intercept and slope of the linearity that plotting  $\ln(q_e - q_t)$  versus  $t$ . In pseudo-second-order model, the values of  $q_e$  and  $k_2$  can be obtained from slope and intercept of linearity that plotting  $t/q_t$  versus  $t$  (Figure 6).

Table 1 show that the pseudo-second-order rate can be applied for experimental data and adsorption mechanism studies because high correlation is obtained for  $R^2$  and value of  $q_e$  (theory adsorption) is close to experimental  $q_e$ .



**Figure 6** Pseudo-second-order rate linearity for adsorption of Pb(II) sorption by using  $Fe_3O_4/GO$  as adsorbent

### 3.3.2 Intra-Particle Diffusion

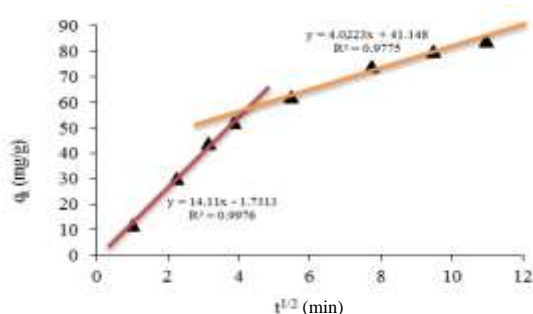
Intra-particle diffusion provide adsorption rate, mass transfer, adsorption part and equilibrium part [21] generally expressed by equation 7 :

$$q_t = k_{id} t^{1/2} + C_i \quad (7)$$

Where  $k_{id}$  is constant for intra-particle diffusion rate and  $C_i$  is adsorption boundary layer thickness. Values were calculated from by plotting of  $q_t$  versus  $t^{1/2}$ .

Figure 7 shows that two steps were involved in intra-particle diffusion model, i.e. mass transfer (first stage) and equilibrium part (second stage), respectively. This trend shows adsorption of Pb(II) on  $Fe_3O_4/GO$  was conducted in two steps High linearity ( $R^2 > 0.97$ ) of both parts indicated that the experimental results can be fitted well with the intra-particle diffusion model.

First part with a sharp slope showed that the adsorption rate is fast and adsorption is favorable on the surface. The second part with slow slope shows that the adsorption rate is slow and intra-particle diffusion is not involved in adsorption.



**Figure 7** Intra-particle diffusion model for adsorption of Pb(II) sorption by using Fe<sub>3</sub>O<sub>4</sub>/GO as adsorbent.

## 4.0 CONCLUSIONS

The adsorption nature of magnetized graphene oxide (Fe<sub>3</sub>O<sub>4</sub>/GO) as an adsorbent was studied for Pb(II) adsorption from aqueous solution. The adsorption

**Table 1** Langmuir, Freundlich, pseudo-first order rate and pseudo-second order models constants and coefficient of determination for adsorption of Pb(II) by using Fe<sub>3</sub>O<sub>4</sub>/GO as adsorbent.

Analyte	Langmuir Isotherm			Freundlich Isotherm		
	$q_m$ (mg g <sup>-1</sup> )	$K$ (L mg <sup>-1</sup> )	$R^2$	$K_F$ (mg/g)(L/mg) <sup>1/n</sup>	$n$	$R^2$
Pb(II)	86.21	0.234	0.9988	18.17	2.63	0.9462
	Pseudo-first-order			Pseudo-second-order		
	$q_e$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_e$ (mg g <sup>-1</sup> )	$k_2$ (g. mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
	46.1	0.027	0.9869	89.28	0.097	0.9974

## References

- [1] Sahmetlioglu, E., Yilmaz, E., Aktas, E., Soylak, M. 2014. Polypyrrole/Multi-Walled Carbon Nanotube Composite For The Solid Phase Extraction Of Lead (II) In Water Samples. *Talanta*. 119: 447-451
- [2] Naseem, R., Tahir, S. S. 2001. Removal Of Pb(II) From Aqueous/Acidic Solutions By Using Bentonite As An Adsorbent. *Water Research*. 35 (16): 3982-3986.
- [3] Mashhadizadeh, M. H., Amoli-Diva, M., Shapouri, M. R., Afrazi, H. 2014. Solid Phase Extraction Of Trace Amounts Of Silver, Cadmium, Copper, Mercury, And Lead In Various Food Samples Based On Ethylene Glycol Bis-Mercaptoacetate Modified 3-(Trimethoxysilyl)-1-Propanethiol Coated Fe<sub>3</sub>O<sub>4</sub> Nanoparticles. *Food Chemistry*. 151: 300-305
- [4] Community, E. 1998. Council Directive 98/83/EC of 3 November 1998 On The Quality Of Water Intended For Human Consumption. *Official Journal of the European Communities* L330: 32-54.
- [5] Hu, R.; Wang, X., Dai, S., Shao, D., Hayat, T., Alsaedi, A. 2015. Application Of Graphitic Carbon Nitride For The Removal Of Pb(II) And Aniline From Aqueous Solutions. *Chemical Engineering Journal*. 260: 469-477.
- [6] Deng, X., Lü, L., Li, H., Luo, F. 2010. The Adsorption Properties Of Pb(II) And Cd (II) On Functionalized Graphene Prepared By Electrolysis Method. *Journal of Hazardous Materials*. 183: 923-930.
- [7] Chawla, J., Kumar, R., Kaur, I. 2015. Carbon Nanotubes And Graphenes As Adsorbents For Adsorption Of Lead Ions From Water: A Review. *Journal of Water Supply Research and Technology*. 64: 641-659.
- [8] Daneshvar, T. G., Shemirani, F. 2013. Magnetic Multi-Wall Carbon Nanotube Nanocomposite As An Adsorbent For Preconcentration And Determination Of Lead(II) And Manganese(II) In Various Matrices. *Talanta*. 115: 744-750.
- [9] Ali, I., 2012. New Generation Adsorbents For Water Treatment. *Chemical Reviews*. 112: 5073-5091.
- [10] Pang, S., Liu, S., Su, X. 2015. An Ultrasensitive Sensing Strategy For The Detection Of Lead(II) Ions Based On The

capacity obtained was 82 mg g<sup>-1</sup> for Pb(II) at pH 4.5 for 60 min. Adsorption isotherm analysis has been studied by Langmuir and Freundlich models. The results obtained provided the Langmuir model is more favorable for adsorption mechanism through chemisorption process.

Kinetic study indicated that the pseudo-second-order rate model is more favorable for adsorption mechanism studies. This model also provided chemisorption adsorption for Pb(II) in 60 min. The experimental and theoretical results showed that the synthesised adsorbent is an ideal candidate for Pb(II) removal from water with high adsorption capacity and satisfactory removal efficiency (>75%). The proposed method is fast, simple, environmental friendly and low cost method.

## Acknowledgement

The authors gratefully acknowledged the Ministry of Higher Education Malaysia for financial support through the Research University Grants No. 04H22 and 10J43. H. R. Nodeh is grateful to UTM for the UTM IDF scholarship.

- Intermolecular G-Quadruplex And Graphene Oxide. *Sensors and Actuators B: Chemical*. 208: 415-420.
- [11] Zawisza, B., Sitko, R., Malicka, E., Talik, E. 2013. Graphene Oxide As A Solid Sorbent For The Preconcentration Of Cobalt, Nickel, Copper, Zinc And Lead Prior To Determination By Energy Dispersive X-Ray Fluorescence Spectrometry. *Analytical Methods*. 5: 6425-6430.
- [12] Dong, Y. L., Liu, Q. F., Zhou, X., Gao, S. T., Li, J. C., Ma, J. J. 2013. Application Of Graphene As A Sorbent For Preconcentration And Determination Of Trace Amounts Of Lead In Water Samples Prior To Flame Atomic Absorption Spectrometry. *Asian Journal of Chemistry*. 25 (11): 6267-6269
- [13] Li, L., Fan, L., Duan, H., Wang, X., Luo, C.. 2014. Magnetically Separable Functionalized Graphene Oxide Decorated With Magnetic Cyclodextrin As An Excellent Adsorbent For Dye Removal. *RSC Advances*. 4: 37114-37121.
- [14] Jung, H. S., Lee, M.Y., Kong, W. H., Do, I. H., Hahn, S. K. 2014. Nano Graphene Oxide-Hyaluronic Acid Conjugate For Target Specific Cancer Drug Delivery. *RSC Advances*. 4: 14197-14200.
- [15] Wan Ibrahim, W. A., Nodeh, R. H., Aboul-Enein, H. Y. Sanagi, M. M. 2015. Magnetic Solid-Phase Extraction Based On Modified Ferum Oxides For Enrichment, Preconcentration, And Isolation Of Pesticides And Selected Pollutants. *Critical Reviews in Analytical Chemistry*. 45: 270–287..
- [16] Abd Ali, L. I., Wan Ibrahim, W. A., Sulaiman, A., Sanagi, M. M., 2014. Adsorption Studies Of Nickel(II) Metal Ions Uptake Using Fe<sub>3</sub>O<sub>4</sub> Magnetic Nanoadsorbent. *Jurnal Teknologi*. 71(5): 99-101.
- [17] Sohrabi, M. R., Matbouie, Z., Asgharinezhad, A. A., Dehghani, A., 2013. Solid Phase Extraction Of Cd(II) And Pb(II) Using A Magnetic Metal-Organic Framework, And Their Determination By FAAS. *Microchimica Acta*. 180: 589-597.
- [18] Lu, W., Wu, Y., Chen, J., Yang, Y., 2014. Facile Preparation Of Graphene-Fe<sub>3</sub>O<sub>4</sub> Nanocomposites For Extraction Of Dye From Aqueous Solution. *CrystEngComm*. 16: 609-615.
- [19] Yanhui Li, Q. D., Tonghao Liu, Jiankun Sun, Yonghao Wang, Shaoling W., Zonghua, W. Y. X., Linhua, X., 2013. Methylene Blue Adsorption On Graphene Oxide/Calcium Alginate Composites. *Carbohydrate Polymer*. 95: 501– 507.
- [20] Li, L., Li, X., Duan, H., Wang, X., Luo, C., 2014. Removal Of Congo Red By Magnetic Mesoporous Titanium Dioxide-Graphene Oxide Core-Shell Microspheres For Water Purification. *Dalton*. 43: 8431-8438.
- [21] Ngadi, N., Ee, C. C., Yusoff, N. A., 2013. Removal Of Methylene Blue Dye By Using Eggshell Powder. *Jurnal Teknologi*. 65(1): 63-71.