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

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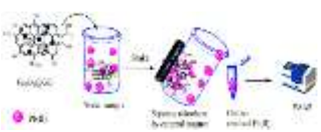
Graphical abstract



Abstract

Magnetic Fe_3O_4 nanoparticles were prepared on graphene oxide (Fe_3O_4/GO) in situ in a one step process. The obtained Fe_3O_4/GO was used as an adsorbent for the removal for Pb(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 mg L^{-1}). The adsorption isotherm of Fe_3O_4@GO magnetic adsorbent was studied for Pb(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 mg g^{-1}. The results signified that the prepared Fe_3O_4/GO nanocomposite has a great adsorptive ability towards the Pb(II) from environmental water samples.

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

Abstrak

Nanopartikel Fe_3O_4 magnetik telah disediakan atas grafin oksida (Fe_3O_4/GO) secara in-situ dalam proses satu langkah. Fe_3O_4/GO terhasil telah digunakan sebagai penjerap untuk penyingkiran Pb(II) daripada sampel air alam sekitar, sebelum pengukuran dengan spektroskopi serapan atom nyala. 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 diperoleh adalah lebih besar daripada 75% (C = 50 mg L^{-1}). Kapasiti penjerapan penjerap magnetik Fe_3O_4/GO dikaji untuk penjerapan Pb(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 mg g^{-1}. Keputusan mengesahkan bahawa nanokomposit Fe_3O_4/GO mempunyai keupayaan penjerapan yang tinggi terhadap Pb(II) daripada sampel air alam sekitar.

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

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^{-1} (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 aqeous 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_3O_4/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 ($FeCl_3.6H_2O$) and iron(II) chloride ($FeCl_2.4H_2O$) were prepared from Sigma Aldrich (St. Louis, MO, USA). Sodium hydroxide pellet (NaOH), hydrochloric acid (HCl 37.0%), Lead(II)nitrate ($Pb(NO_3)_2$) was purchased from QReC (Selangor, Malaysia). Stock solution (1000 mg L^{-1}) 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^{-1} and air flow rate of 10.0 L min^{-1}.

2.3 Synthesis of Fe_3O_4/GO

In the current study, magnetic graphene oxide was prepared using a simple one step method. Fe_3O_4 MNPs were synthesised through co-precipitation method and simultaneously dispersed on GO sheets [18]. Briefly, GO (1 g), $FeCl_2$ (0.1 g) and $FeCl_3$ (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_3O_4/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_3O_4/GO dose (25 mg), solution pH 4.5, 50 mL water solution containing Pb(II) ions with different initial concentrations (10 - 150 mg L^{-1}). 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.

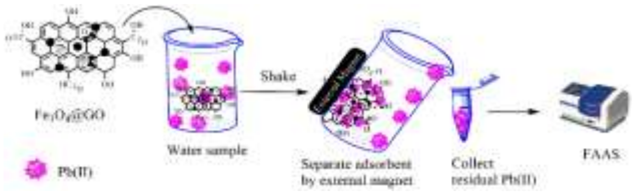


Figure 1 Batch adsorption procedure of the proposed MSPE method

The adsorption capacity of the as-synthesised Fe_3O_4@GO adsorbent was calculated using equation (1) [19];

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

where, *qe* is the adsorption capacity (mg g^{-1}), V is the volume sample (L), m is the adsorbent dosage (g), C0 is initial concentrations and Ce is residual concentrations after equilibrium of Pb (mg L^{-1}).

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^{-1} 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^{-1})} was calculated by using equation 2:

$$q_t = \frac{V}{m}(C_o - C_t) \qquad (2)$$

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^{-1}) 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^{-1}, 1720 cm^{-1}, 1490 cm^{-1}, 1200 cm^{-1} and 580 cm^{-1} which are related to O-H, C=O, C-C, C-O and Fe-O, respectively. These evidences provided the presence of Fe_3O_4 nanoparticles on the GO surface.

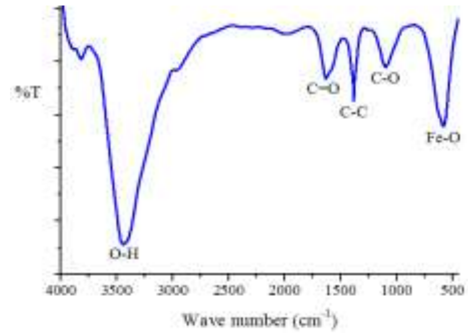


Figure 2 FTIR spectroscopy of the as-synthesised Fe_3O_4/GO adsorbent

3.2 Adsorption Study

Adsorption study was carry out using different concentrations of Pb(II) (10 - 150 mg L^{-1}) 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_3O_4/GO was studied by using adsorption models namely Langmuir and Freundlich.

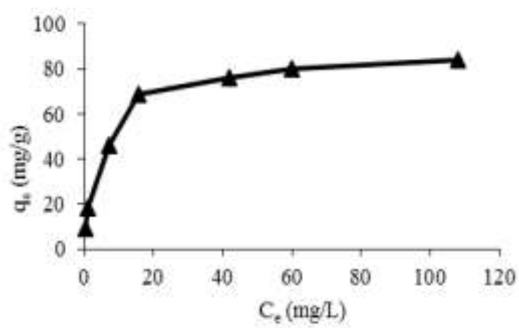


Figure 3 Equilibrium adsorption capacities for Pb(II) sorption using the as-synthesised Fe_3O_4/GO as adsorbent

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^{-1}).

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

where q_e is the experimental adsorption capacity that was obtained from equation (1), k_L is Langmuir constant (L mg^{-1}) 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.

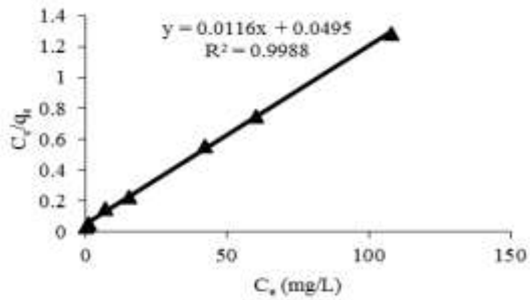


Figure 4 Langmuir linearity for adsorption model of Pb(II) sorption by using Fe_3O_4/GO as adsorbent.

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),

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

Where K_F is the adsorption capacity ((mg/g)(L/mg)$^{1/n}$), n is the constant that shows heterogeneity. The coefficient of determination (R^2) was obtained by plotting Log q_e versus 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.

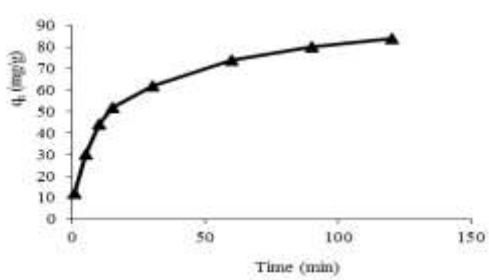


Figure 5 Effect of contact time in adsorption capacity for Pb(II) sorption by using Fe_3O_4/GO as adsorbent.

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]:

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

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

Where q_e is the equilibrium adsorption capacity (mg g^{-1}) (theory), q_t is adsorption capacity (mg g^{-1}). k_t (1/min) and k_2 (g/mg/min) are the pseudo constants for first-order and second-order, respectively. In pseudo-first-order model the values of q_e and k_t 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.

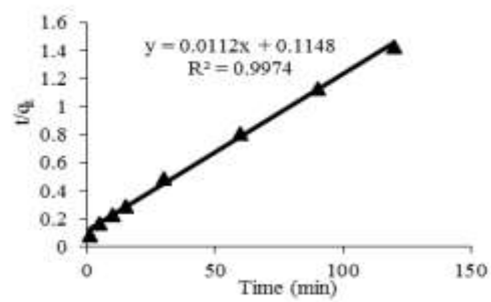


Figure 6 Pseudo-second-order rate linearity for adsorption of Pb(II) sorption by using Fe_3O_4/GO as adsorbent

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 :

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

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.

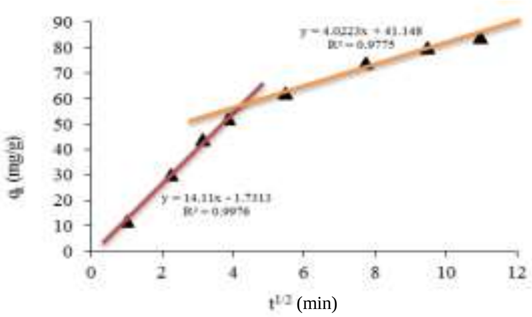


Figure 7 Intra-particle diffusion model for adsorption of Pb(II) sorption by using Fe_3O_4/GO as adsorbent.

4.0 CONCLUSIONS

The adsorption nature of magnetized graphene oxide (Fe_3O_4/GO) as an adsorbent was studied for Pb(II) adsorption from aqueous solution. The adsorption capacity obtained was 82 mg g^{-1} 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

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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_3O_4/GO as adsorbent.

Analyte	Langmuir Isotherm			Freundlich Isotherm		
	q_m (mg g^{-1})	**K (L mg^{-1})**	**R^2**	**K_F (mg/g)(L/mg)$^{1/n}$**	***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^{-1})	**k_1 (min^{-1})**	**R^2**	**q_e (mg g^{-1})**	**k_2 (g. mg^{-1} min^{-1})**	**R^2**
	46.1	0.027	0.9869	89.28	0.097	0.9974

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