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Removal of lead ions from aqueous solutions using sodium alginate-graft-poly(methyl methacrylate) beads

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ABSTRACT

The performance of a new adsorbent, sodium alginate-graft-poly(methyl methacrylate) in the form of calcium cross-linked beads has been evaluated for the removal of Pb^{2+} from aqueous solution. Characterization of the adsorbent was performed using Fourier transform infrared spectroscopy, scanning electron microscopy and laser diffraction technique. The Langmuir and Freundlich isotherm models were applied to describe the adsorption equilibrium process. The data obtained from the batch experiments using lead ion concentration from 200 to 1,000 mg/L could be well interpreted by the Langmuir model with maximum adsorption capacity of 526 mg/g. The data from the kinetic studies correlated with the second-order kinetic model. The regeneration experiments revealed that the beads could be successfully reused for multiple times. The adsorbent proved to be potentially excellent for application in the treatment of wastewater containing lead ions.

Keywords: Sodium alginate; Poly(methyl methacrylate); Lead ions; Beads; Regeneration

1. Introduction

Contamination of water by toxic heavy metals as a result of the discharge of untreated effluents is a global environmental problem, particularly more pronounced in developing countries. Heavy metals pollution in water has been threatening human health and aquatic organisms even at low concentrations [1]. Furthermore, heavy metals are not biodegradable and tend to accumulate in living organisms which lead to several disorders. In water streams, heavy metals may exist in the form of molecules or in solution as free ions, and chelated metal ligands [2]. Therefore, toxic metals must be removed from wastewater before discharging into the environment. Reported sources of heavy metals in the environment include fuel burning, industrial, agricultural, pharmaceutical, and domestic effluents. However, mining and manufacturing activities contribute greatly to the release of high concentrations of toxic heavy metals in the environment. The conventional methods for water treatment such as chemical precipitation [3], solvent extraction [4],

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ion-exchange [5,6], membrane technologies [7], and advance oxidation [8,9] are used for the removal of metal ions from aqueous solutions. However, these technologies have several disadvantages which include high energy requirements, proper monitoring and are not cost effective. Adsorption is considered to be the most effective technology because of ease of design and operation, high efficiency, and cost effectiveness [10–12]. Recently, removal of pollutants from waste streams by low-cost polysaccharides (biopolymers) has received considerable attention from many researchers [13], because the materials are cheap, non-toxic, biocompatible, and abundant in nature. Alginic acid or its salts called alginates are among the polysaccharides that occur in the cell walls of a large number of algal species. It is a copolymer consisting the residues of *β*-1,4-linked-D-mannuronic acid (M-block) and *α*-1,4-linked-L-guluronic acid (G-block) (Fig. 1) [14]. Sodium alginate possesses metal sequestering properties and can effectively sequester the dissolved metal ions in solutions quickly. It is an ideal material for the treatment of wastewater that contained heavy metal ions, due to its high content of carboxyl (COOH) and hydroxyl (OH) functional groups, which have high affinity as adsorptive sites as well as ion-exchange sites. Nevertheless, it has some limitations in terms of poor mechanical properties, prone to enzymatic degradation and can easily dissolve in aqueous media. To overcome these problems, chemical modification is necessary to improve its stability and mechanical strength. Sodium alginate is mostly converted to insoluble calcium alginate beads for the removal of heavy metal ions in aqueous medium; and this has been demonstrated in many studies to be an effective adsorbent [15–19]. Another method often used to modify sodium alginate is by grafting synthetic polymer on its backbone to develop a hybrid material with improved stability as well as enhanced adsorption capacity [20]. Singh et al. improved the physical properties as well as sorption capacity of *Cassia grandis* seed gum by the grafting of poly(methyl methacrylate) for the extraction of lead ions from aqueous solutions [21]. Removal of chromium(VI) using poly(methacrylate) functionalized guar gum was reported [22]. The material was found to be an effective sorbent in the removal of Cr(VI) from synthetic dye solution as well as from electroplating wastewater. Hydrogel was prepared by grafting itaconic acid with sodium alginate via free radical polymerization using gamma rays. The hydrogel showed high efficiency for removal of lead ions from aqueous solutions [23]. The grafting of itaconic acid as well as *in situ* crosslinking reaction which took place during polymerization was found to enhance the mechanical strength and sorption capacity of sodium alginate.

The objective of the present work is to study the removal of lead ions from aqueous solutions by sodium alginate-graft-poly(methyl methacrylate) beads. The beads were formed using a simple encapsulation method that enables the ionic interactions between guluronate blocks (G-blocks) of the graft copolymer and calcium ions. The characterization of the beads

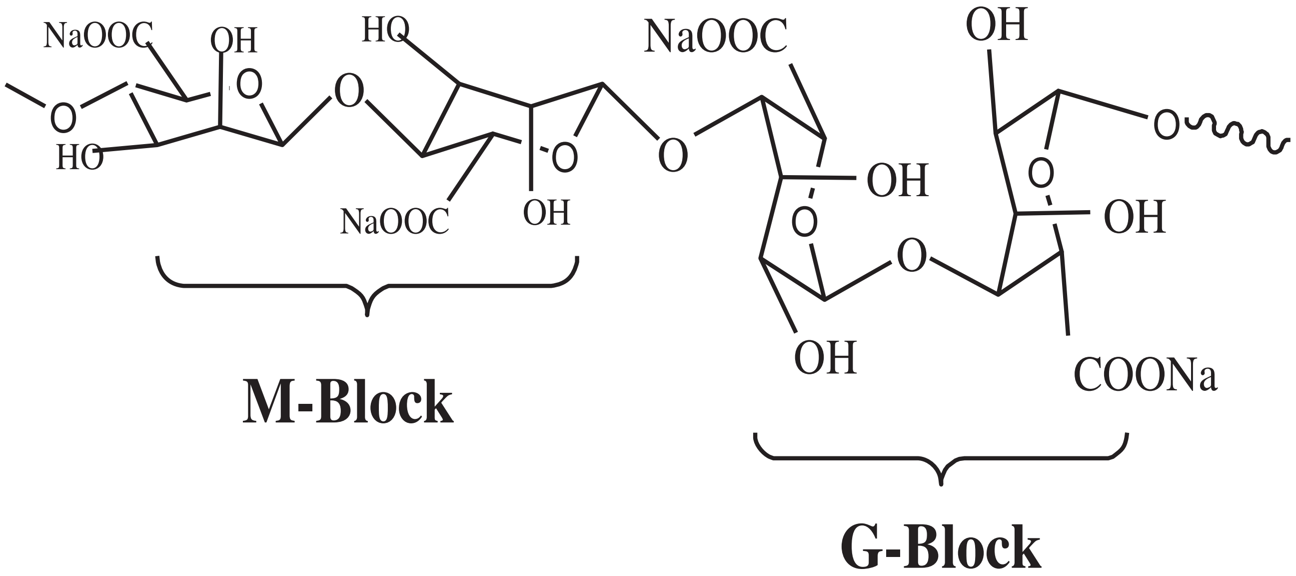

Fig. 1. Molecular structure of sodium alginate.

was conducted, and the effect of initial pH, adsorption kinetics, and adsorption isotherms were studied.

2. Materials and methods

2.1. Materials

Sodium alginate with medium molecular weight, methyl methacrylate (MMA), and benzoyl peroxide (BPO) were purchased from Sigma–Aldrich (USA), MMA monomer was distilled under reduced pressure prior to use. BPO was further purified by dissolving in chloroform and precipitated in excess methanol. Lead ions standard (1,000 mg/L) was purchased from Merck (Selangor, Malaysia). Methanol and acetone were from QRëc (Selangor, Malaysia). All other chemical reagents were of analytical grade from various suppliers and used as received.

2.1.1. Graft copolymerization reaction

Sodium alginate was dissolved in 100 mL of distilled water by stirring in a three-necked round bottom flask (250 mL) under a nitrogen atmosphere. Thereafter, the required quantity of BPO (dissolved in acetone) was added dropwise into the reaction flask, followed by addition of MMA monomer. The polymerization was allowed to proceed for the specified time after which the reaction mixture was poured into methanol (300 mL). The precipitate was filtered and dried in a vacuum oven at 60°C. The products thus obtained were finally extracted with acetone in a Soxhlet apparatus for 24 h to dissolve the homopolymer completely and the graft copolymer alginate-graft-poly(methyl methacrylate) (Alg-g-PMMA) was finally dried under vacuum to a constant weight. The percentage of grafting was determined by the following equation:

$$\text{Percentage grafting} = \frac{\text{weight of graft copolymer} - \text{weight of alginate}}{\text{weight of alginate}} \times 100 \quad (1)$$

By varying various reaction parameters, such as time, temperature, and monomer concentration, graft copolymer samples with different grafting percentages were synthesized using BPO initiator. The maximum percentage grafting that could be obtained was 212% using the concentration of BPO, MMA, and sodium alginate of 4.13×10^{-3} mol/L, 7.99×10^{-1} mol/L, and 1% w/v, respectively. The optimum reaction temperature and time were 80°C and 2 h, respectively. The sample synthesized under optimum conditions was selected for the preparation of the beads for lead adsorption studies.

2.2. Preparation of the beads

The beads were prepared using a simple method by dispersing 2 g of the crushed graft copolymer (Alg-g-PMMA) into stirred 100 mL of distilled water by mechanical stirring at a rate of 1,500 rpm. The resultant colloidal solution obtained was dropped into a stirred 250 mL of $CaCl_2$ solution (0.1 mol/L) using a syringe; and solid gel beads were immediately formed. The beads were allowed to stay in the $CaCl_2$ solution for overnight to stabilize. Subsequently, the beads were washed with excess distilled water to remove $CaCl_2$ from the surfaces. Thereafter, the beads were dried at 60°C in a vacuum oven.

2.3. Characterization

2.3.1. FTIR analysis

The infrared spectra were obtained in the range of 450–4,000 cm^{-1} using Perkin Elmer 400 Fourier transform infrared spectroscopy (FTIR) spectrometer. The dried samples were pulverized and mixed with KBr and pressed by hydraulic compression that formed transparent pellets.

2.3.2. SEM and beads size analysis

Scanning electron microscope (SEM) micrographs were taken with a JEOL-JSM 6390LV (JEOL Ltd, Japan) to examine the morphology and surface structure of the beads. The beads were sputtered with a thin coat of silver under vacuum. The particle size distribution of the dried beads was determined using a Horiba Instruments (Partica LA-950) laser scattering particle size distribution analyzer, which determines particle size by measuring the rate of fluctuations in laser light intensity scattered by particles as they diffuse through a fluid.

2.4. Batch adsorption experiments

The required concentration of Pb^{2+} solutions was prepared from the standard stock solution of Pb^{2+} (1,000 mg/L) with distilled water. Adsorption studies were carried out using a 250 mL Erlenmeyer flask. The flasks were agitated on orbital shaker set at 200 rpm. A known amount of adsorbent was added in the sample solution whose concentration and pH were determined. After the flasks were shaken for specified time and then filtered, the remaining lead ions were then analyzed using atomic absorption spectrophotometer (AAnalyte 400). Kinetic studies were conducted at 200 mg/L metal ion concentration and 0.1 g adsorbent amounts. Separate flasks were prepared for each time interval and one flask was taken at specified time. The percent adsorption and the amount of metal ion adsorbed by the adsorbent at equilibrium were calculated using Eqs. (2) and (3), respectively.

$$\text{Percentage removal } (\%) = \frac{C_o - C_f}{C_o} \times 100 \tag{2}$$

$$q_e(\text{mg/g}) = \frac{C_o - C_e}{W(\text{g})} \times V(L) \tag{3}$$

where C_o is the initial lead ions concentration (mg/L), and C_f is the lead ions concentration in the solution (mg/L) at the end of adsorption, C_e is the equilibrium concentration of metal ion in solution (mg/L), V is the volume of metal ion solution used (L), and W is the weight of the adsorbent used (g).

3. Results and discussion

3.1. Characterization

3.1.1. Infrared spectroscopy

FTIR spectrum of sodium alginate (Fig. 2(a)) showed a broad absorption band at 3,426 cm^{-1} due to O–H stretching vibration which indicates the presence of hydroxyl groups. The absorption band observed at 1,600 and 1,407 cm^{-1} are characteristics of carbonyl group resonance stretchings of carboxylic salt (asymmetric and symmetric, respectively) [24,25]. The band located at 1,028 cm^{-1} was assigned to the stretching vibration of C–O. The IR spectrum of the graft copolymer (Fig. 2(b)) had additional absorption bands at 2,994 and 1,730 cm^{-1} due to the stretching of C–H of methyl groups and ester carbonyl stretching, respectively. This result substantially confirmed the grafting of MMA onto sodium alginate.

3.1.2. Morphology of the beads

The beads prepared in this work were analyzed for their sizes using the light scattering method. A SEM micrograph of the bead is shown in Fig. 3 and it is obvious that the beads have spherical shape with rough surface and porosity. The average mean distributions of the bead size were 1.2 ± 2 mm as measured using a laser diffraction scattering method as can be seen in Fig. 4 and SEM analysis indicates similar diameter.

3.1.3. Adsorption of Pb^{2+} ions onto Alg-g-PMMA beads

The ability of biosorbents toward adsorption of heavy metal ions is not based on one mechanism. It involves a complex process such as complexation, ion-exchange, coordination, chelation, adsorption by physical forces, and entrapment in the spaces of the polysaccharide network [26]. Besides, physicochemical properties and chemistry of the contact solution may

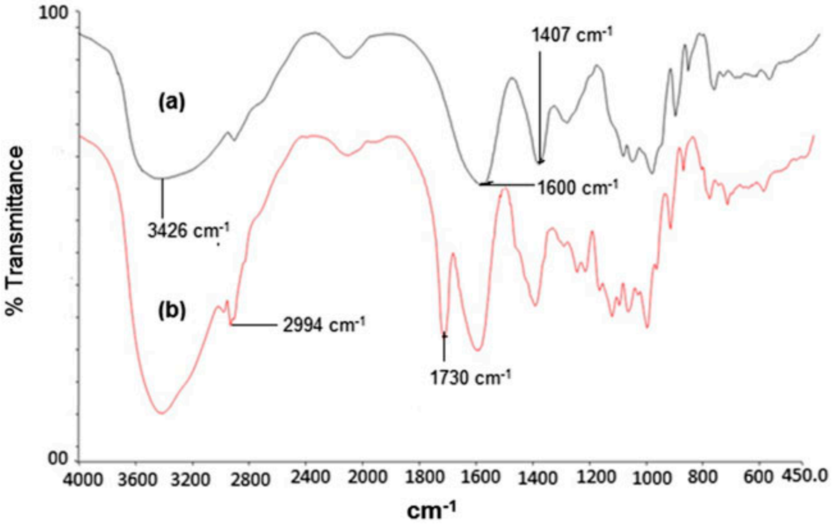

Fig. 2. IR Spectra of (a) sodium alginate and (b) the graft copolymer (Alg-g-PMMA).

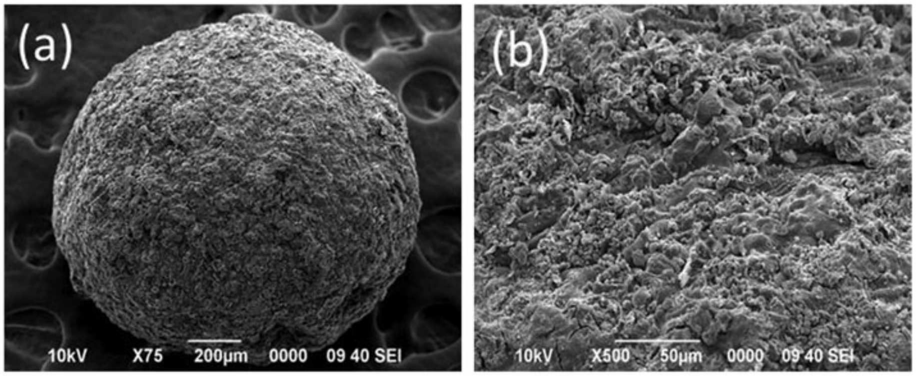

Fig. 3. SEM image of (a) Alg-g-PMMA bead and (b) surface structure of Alg-g-PMMA bead.

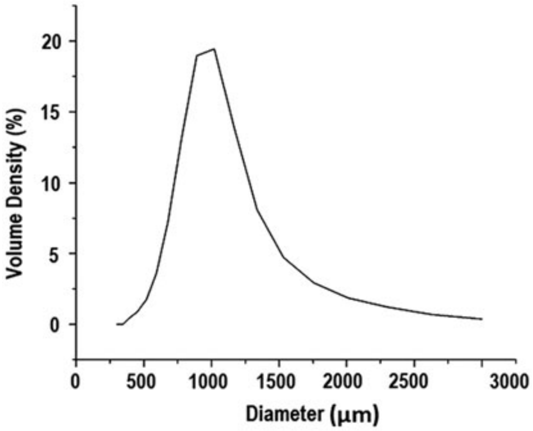

Fig. 4. Size distributions of Alg-g-PMMA beads.

also affect the adsorption process. The carboxyl groups are abundant acidic functional groups on alginate. The adsorption capacity is directly related to the presence of these groups on the alginate backbone. Metal adsorption capacity of alginate was enhanced by the presence of poly(methyl methacrylate) grafted, which provides additional adsorptive sites. Because of the many possible interactions in the adsorption processes, the mechanisms of the lead ions adsorption are quite complex that may range from complexation, ion-exchange, or hydrophobic interactions (Fig. 5). In addition, the physicochemical nature of the metal ion also contributes significantly. Because it has been proven that metal binding strength of Pb^{2+} showed great affinity to all available carboxyl groups both in polyguluronate and polymannuronate blocks [27].

3.1.4. Effect of initial pH on Pb^{2+} adsorption

The pH value of the solution is one of the most important parameters affecting the adsorption of heavy metals in aqueous solutions. It affects not only the active sites of the adsorbent, but also the solubility of the metal ions in solution. It is known that the carboxyl groups of mannuronic and guluronic blocks of alginate tend to be ionized at pH values of >4 (pK_a range, 3.4–4.5). The initial pH of the solution was varied from 2 to 6 as shown in Fig. 6. It was observed that adsorption of the metal ions reached a climax at pH 4. The decreased adsorption of Pb^{2+} at lower pH may be due to the competition between protons and metal ions in the solution. Therefore, pH 4 was taken as the optimum for lead ions adsorption and used in all subsequent adsorption experiments.

3.1.5. Adsorption isotherms studies

The adsorption isotherm represents the relationship between the amount adsorbed by a unit of adsorbent and the amount of adsorbate remaining in the solution at equilibrium. The Langmuir and Freundlich isotherm models were selected for adsorption isotherm studies. The Langmuir model is valid for monolayer adsorption and expressed in the linear form as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b \times q_{max}} \tag{4}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g) per unit weight of the adsorbent; b is the Langmuir constant relating the free energy of adsorption (L/mg); q_{max} is the maximum monolayer uptake capacity of the adsorbent. The essential characteristics of the Langmuir adsorption can be expressed in terms of a dimensionless constant referred to as separation factor or equilibrium parameter for predicting whether an adsorption system is favorable or unfavorable. R_L is calculated using the equation below:

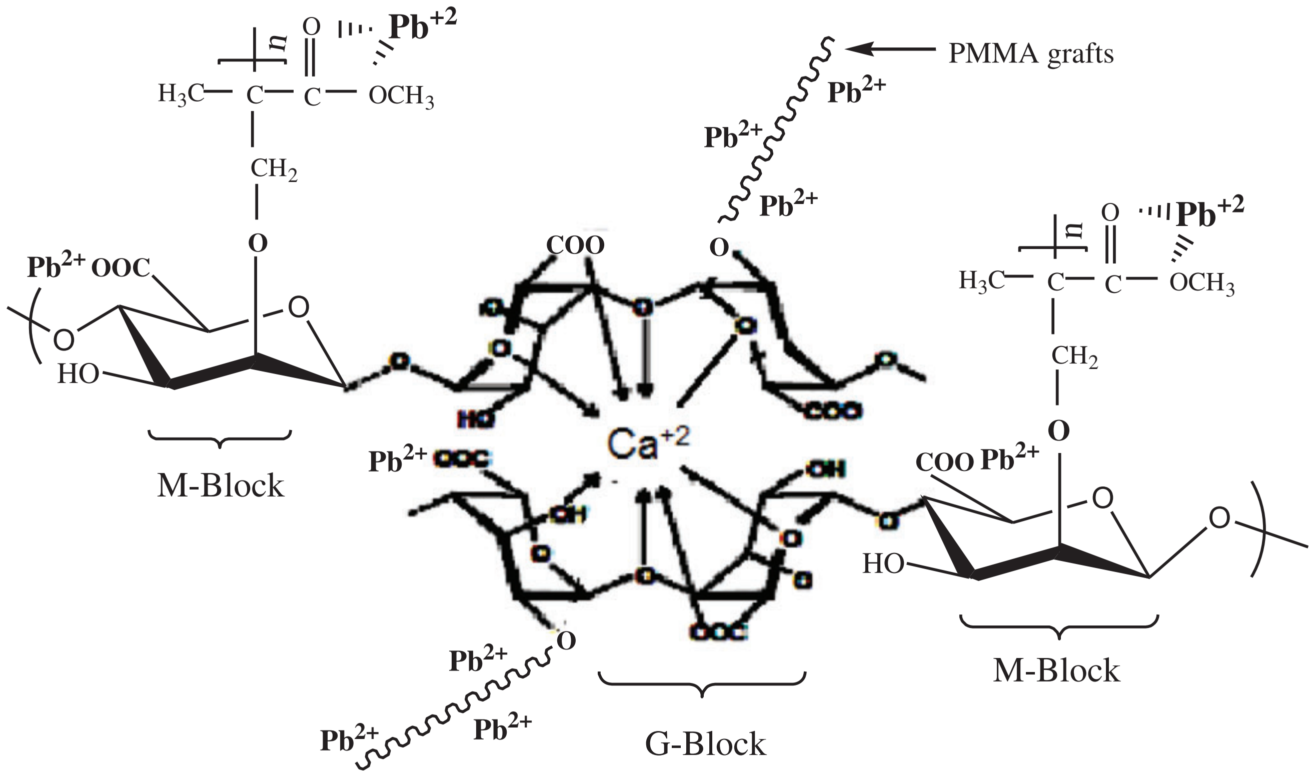

Fig. 5. Model for interaction between the Pb^{2+} and the graft copolymer beads (Alg-g-PMMA).

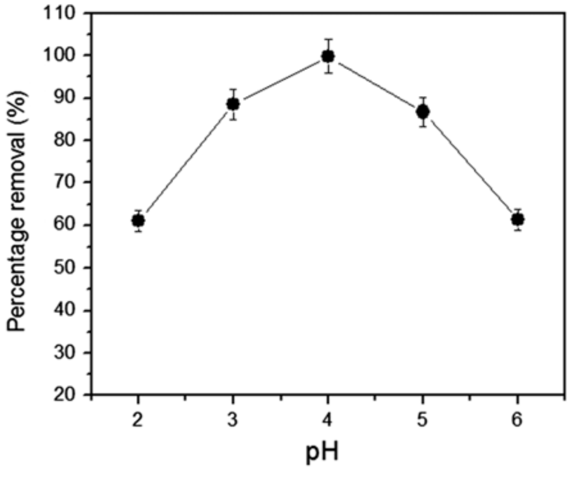

Fig. 6. Effect of pH on Pb^{2+} percentage removal by Alg-g-PMMA beads. Conditions: Pb^{2+} concentration = 100 mg/L; adsorbent dose = 0.1 g; batch volume = 50 mL; contact time = 60 min.

$$R_L = \frac{1}{1 + bC_o} \tag{5}$$

where C_o is the initial Pb^{2+} concentration (mg/L). If R_L value lies between $0 < R_L < 1$, the adsorption is favorable [28].

The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as:

$$\ln q_e = \ln K_F + n \ln C_e \tag{6}$$

where K_F indicates adsorption capacity (mg/g) and n is an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorption.

The equilibrium data fitted well to the Langmuir isotherm due to the high coefficient of determination ($R^2 = 0.9991$) (Fig. 7) as compared to Freundlich model ($R^2 = 0.8215$). The results indicate surface homogeneity of the adsorbent and monolayer adsorption. From Langmuir model, the maximum monolayer adsorption capacity (q_{max}) was found as 526 mg/g indicating that the adsorbent had high capacity to remove Pb^{2+} ions. R_L and b were calculated to be 0.005 and 0.613 mg/L, respectively, thus adsorption is favorable. The Freundlich constant K_F and n were calculated to be

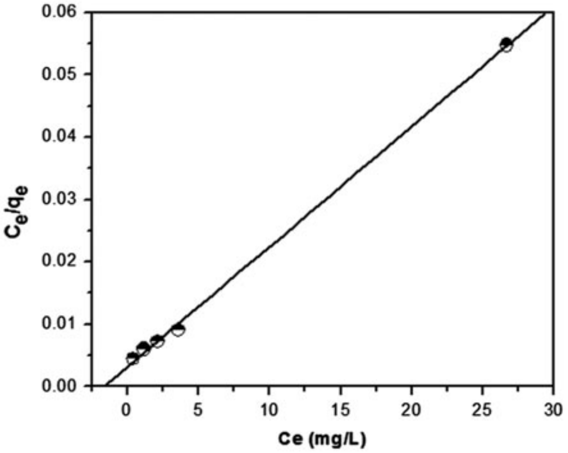

Fig. 7. Langmuir adsorption isotherm of Pb^{2+} by Alg-g-PMMA beads.

179 mg/g and 2.40, respectively (Figure not shown). Coefficients of determination and equilibrium constants are summarized in Table 1.

3.1.6. Kinetic studies

Kinetics of metal adsorptions govern the rate at which the adsorption is taking place as well as the efficiency of the adsorbent. In order to investigate the rate constant of the adsorption process the two most widely applied kinetic models were selected and studied; pseudo-first-order model (Eq. (7)) and pseudo-second-order model proposed by Ho and McKay [29] which are based on the assumption that the adsorption follows second-order chemisorption (Eq. (8)).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

where q_e and q_t are the amount adsorbed (mg/g) at equilibrium and at time t, respectively, k_1 (min^{-1}) is the pseudo-first-order rate constant and k_2 (g/mg/min) is the pseudo-second-order rate constant. The k_1 was calculated by plotting log $(q_e - q_t)$ vs. t and

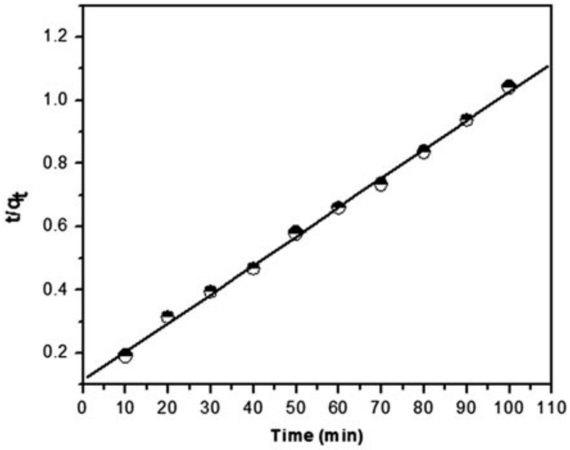

Fig. 8. Pseudo-second-order kinetics. Conditions: pH 4; Pb^{2+} concentration = 200 mg/L; batch volume = 50 mL; adsorbent dose = 0.1 g.

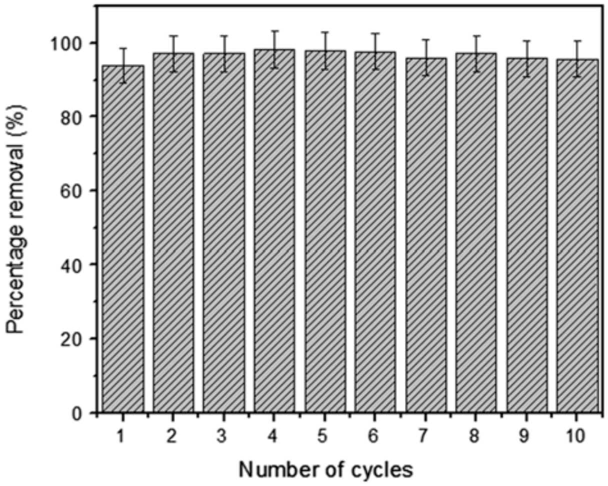

Fig. 9. Adsorption cycles of the adsorbent. Conditions: Pb^{2+} concentration = 100 mg/L; adsorbent dose = 0.1 g, batch volume = 50 mL; desorption solution = 0.1 M HNO_3 (10 mL), contact time = 60 min.

Table 1
Equilibrium constants and coefficients of determination for adsorption of lead ions onto Alg-g-PMMA beads

Langmuir model				Freundlich model		
q_{max} (mg/g)	R_L	b (L/mg)	R^2	K_F (mg/g)	n	R^2
526	0.005	0.613	0.999	179	2.40	0.821

Table 2
Kinetic constants and coefficients of determination for adsorption of Pb^{2+} onto Alg-g-PMMA beads

Pseudo-first-order model			Pseudo-second-order model		
q_{max} (mg/g)	k_1 (min^{-1})	R^2	q_{max} (mg/g)	k_2 (g/mg/min)	R^2
139.8	0.081	0.911	109.8	0.00096	0.999

Table 3
Pb^{2+} uptake for different adsorbents and the pH of optimum adsorption

Adsorbent materials	Lead uptake (mg/g)	pH	Refs.
Calcium alginate beads	416	4	[19]
CG-*graft*-PMMA	126	2	[21]
Alginate-*graft*-itaconic acid	255	5	[23]
Calcium alginate beads	374	4.5	[27]
Activated calcium alginate beads	228	4	[30]
Magnetic alginic acid beads	300	4	[31]
Activated GDKGM	191	5	[32]
Alg-*graft*-PMMA beads	526	4	Present study

k_2 was calculated by plotting t/q_t vs. t, and the observed data give a straight line indicating pseudo-second-order kinetics for the adsorption (Fig. 8). Coefficients of determination and rate constant have been summarized in Table 2.

3.1.7. Reusability of the adsorbent

The regeneration of adsorbent may be a crucial step in the wastewater treatment in order to recover the metal ions and the wastewater treatment process becomes cost-effective. Adsorption-desorption cycles were repeated for ten consecutive times using metal ion concentration of 100 mg/L, HNO_3 (0.1 M, 10 mL) as desorption solvent and 0.1 g of the adsorbent. The adsorbent was thoroughly washed with distilled water before the next cycle. It was observed that in the first cycle, the percentage removal was 92%, but in the subsequent cycles, percentage removal was found to be greater than 96%. This could be attributed to increase the surface porosity of the adsorbent as a result of interaction with the desorption solvent (HNO_3), which forms hydrogen bonds that replace the metal ions from egg-box structure. The results showed that the material proved to be excellent in the removal of the metal ions after nine cycles with no significant loss of adsorption capacity (Fig. 9). Furthermore, adsorption capacity of lead ions using Alg-g-PMMA beads has been compared with earlier reports in the literature (Table 3).

4. Conclusion

Alg-g-PMMA beads developed are proved to be effective and stable in the removal of lead ions from aqueous solutions. The beads have a great potential as an adsorbent for the treatment of lead ions' effluent. The adsorption process was depended on the initial pH and metal concentration. The optimum pH for the adsorption of the metal ions is 4.0. Adsorption data were described well by Langmuir isotherm model than did Freundlich and the adsorption followed a second-order kinetic model. The adsorbent could be regenerated for several times using dilute nitric acid (HNO_3, 0.1 M). This study concluded that the material could be utilized as cost-effective adsorbent for Pb^{2+} remedy from industrial effluent.

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