

# Improvement of Water Quality Using Alginate/Montmorillonite Composite Beads

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**ABSTRACT:** The aim of this study is to explore naturally occurring sorbents that have high affinity for heavy metal treatment. In this respect, series of polymer-clay composite beads that consists of Na-alginate and montmorillonite clay were prepared using  $\text{CaCl}_2$  as crosslinker. The prepared composite bead was characterized by scanning electron microscope (SEM). Removal of lead from aqueous solution using this bead was then studied in batch adsorption experiments. The amount of lead removed was found to increase as the percent of Na-alginate increase in the composite beads. The experimental results also showed that the equilibrium contact time was obtained within  $\sim 100$  min with ( $t_{1/2}$ ) of 50% adsorption in less than 10 min. Lead adsorption was found to be strongly pH-dependent and display a maximum uptake capacity (244.6 mg/g) at pH 6 and minimum uptake (76.6 mg/g) at pH 1. Maximum lead adsorption was found to increase with increasing initial lead concentration in the feed solution and with decreasing temperature of experiment. Based on alginate-montmorillonite beads packed columns, a highly efficient method for Pb(II) removal from aqueous solution was developed. The effect of flow

rate on adsorption of 100 mg/L Pb(II) in the packed-bed column was investigated by changing the flow rate between 0.5 and 2.5 mL  $\text{min}^{-1}$ . The recovery of 100 mg/L Pb(II) in the packed-bed column was found to be 100% at flow rates 0.5 and 1 mL  $\text{min}^{-1}$  then lowered to be 93% and 84% at flow rates 1.5 and 2.5 mL  $\text{min}^{-1}$ , respectively. The effect of Pb(II) flow concentration ranging from 10 to 1000 mg/L on the adsorption of lead ions at constant flow rate 1.0 mL  $\text{min}^{-1}$  was also studied using column procedure. Technical feasibility for the uses of the prepared composite beads for the treatment of actual polluted wastewater samples collected from some industrial cities in Egypt was investigated. The evaluation of the system was performed by a complete analysis of heavy metals in the wastewater samples before and after the treatment process. The results showed a promising possibility for producing wastewater of better quality using such prepared beads. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2371–2378, 2011

**Key words:** polymer-clay composite; beads; lead; waste water; treatment

## INTRODUCTION

Till recent years, the surge of industrial activities has intensified more environmental problems as seen for example in the deterioration of several ecosystems due to the accumulation of dangerous pollutants such as heavy metals.<sup>1</sup> Heavy metals are still being used in various industries due to their technological importance. The effluents of industrial wastewaters often contain considerable amounts of such toxic and polluting heavy metals. It is well-known that heavy metals such as Hg, Pb, Cr, Ni, Cu, Cd, and Zn are usually associated with tendency to accumulate in living organisms and are highly toxic when adsorbed into body.<sup>2</sup> Lead contamination is known as one of the most pervasive and elusive environmental health threats, as considered by the fact that exposure Pb(II)

ions has been associated with death and disease in humans, birds and animals.<sup>3</sup> The majority of lead pollution has been through automobiles, battery manufacturers, cable coverings, radioactivity shields, plumbing fixtures, painting pigments, solder, ammunition, caulking, bearings, textile industry, printed circuit boards, electroplating, and petroleum industries.<sup>4,5</sup>

The adsorption processes are generally known to be one of the most effective techniques for removal of environmentally hazardous metals due to its low maintenance costs, high efficiency and ease of operation.<sup>6</sup> However, conventional adsorbent materials such as activated carbon and ion exchange resin are associated with several problems. Firstly, these materials are artificial and not degradable, which make their application from environmental perspective questionable. Secondly, their production is energy intensive. Therefore, there have been attempts to utilize low cost, naturally occurring adsorbents, to remove contaminants from wastewater.<sup>7,8</sup> These kinds of adsorbents, which are biological-based materials such as *Cephalosporium aphidicola*,<sup>5</sup> *Pinus sylvestris*,<sup>9</sup> *Saccharomyces*

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*cerevisiae*,<sup>10</sup> *Sargassum natans*,<sup>11</sup> *Botrytis cinerea*,<sup>12</sup> *Neurospora crassa*,<sup>13</sup> *Aspergillus niger*,<sup>14</sup> *R. arrhizus*,<sup>15</sup> *Bacillus* sp.,<sup>16</sup> alginate,<sup>17</sup> chitosan,<sup>18</sup> and carrageenan<sup>19</sup>; natural clay minerals such as kaolinite,<sup>20–23</sup> illite,<sup>24</sup> bentonite,<sup>25,26</sup> montmorillonite,<sup>20,23,27</sup> zeolite,<sup>28,29</sup> and sepiolite<sup>30,31</sup> have been used to remove heavy metal ions from aqueous solutions by adsorption.

Alginate is a polysaccharide biopolymer composed of varying compositions of  $\beta$ -1,4 linked D-mannuronic acid (M) and L-guluronic acid (G). Because of its excellent features, medical and pharmaceutical industries have shown increased interest in this biopolymer. The extensive amount of research work that has been done on this system is due to the exceptional ability of sodium alginate to form durable, acid resistant beads upon exposure to aqueous solutions of bivalent ions like  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$ .<sup>32</sup> Alginate undergoes ionotropic gelation when these divalent cations interact ionically with blocks of guluronic acid residues, thus resulting in the formation of three-dimensional network, which is usually described by the “egg-box” model.<sup>32</sup> So far, adsorption property of alginate has been investigated for many heavy metal ions.<sup>17,33</sup>

Clay minerals possess a layered structure and are typically suspended in aqueous solutions as fine particles having average diameter of about 2  $\mu\text{m}$ .<sup>34</sup> Generally they have potential for ion exchange, being able to accommodate ionic and even nonionic foreign organic molecules.<sup>34</sup> Bentonite (B) as a representative clay mineral is clay mainly composed of montmorillonite, a 2 : 1 type of aluminosilicate. Its crystalline structure presents an alumina octahedral layer between two tetrahedral layers of silica, which by isomorphous substitutions, require cations, denominated exchange cations (Na, Ca, Mg, etc.), to compensate the negative layer charge. Cause of cation adsorption of clay minerals is that the presence of broken bonds around the edges of silica-alumina units would give rise to unsatisfied charges, which would be balanced by adsorbate cations.

The polymeric material can be modified with natural clay minerals in a manner that this significantly improves their capability to remove heavy metals from aqueous solutions.<sup>3,34–36</sup> These kinds of adsorbents are called polymer–clay composites, which are widely used in various areas of transportation, construction, and electronic products. They offer incredible combinations of stiffness and strength, which are difficult to attain separately from the main components.<sup>37</sup> They can be used as the excellent adsorbents for the adsorption technique due to the fact that they are low-cost and have high efficiency adsorbents for the adsorption of many pollutants.

The purpose of this study is to explore novel naturally occurring sorbents that have high affinity for heavy metal ions and fully exhibit their ability in a

wide range of metal concentration. For this reason, a series of alginate-montmorillonite composite beads is prepared and characterized. The removal of lead(II) ions from aqueous solution using the prepared beads by batch and column adsorption techniques has been investigated. The dynamic behavior of adsorption was examined on the effects of pH, contact time, temperature, and initial feed concentration.

## MATERIALS AND METHODS

### Materials

Sodium alginate and Pb(II) nitrate (99.6%) were supplied by Sigma-Aldrich. Clay was purchased from Aldrich. Calcium chloride was supplied by Acros Organics.

### Preparation of 2.5 wt % Na-alginate solution

A 25 g Na-alginate was added slowly to 975 g deionized water at 60°C under stirring condition. The solution was kept stirring for 4 h or longer until all Na-alginate is dissolved.

### Preparation of 2.5% clay suspensions

Suspension consists of 25 g of  $\text{Na}^+$  montmorillonite homogeneously dispersed in deionized water (975 g, 60°C) by continuous stirring over night followed by sonication for 3 h.

### Preparation of different Na-alginate/clay blend solution

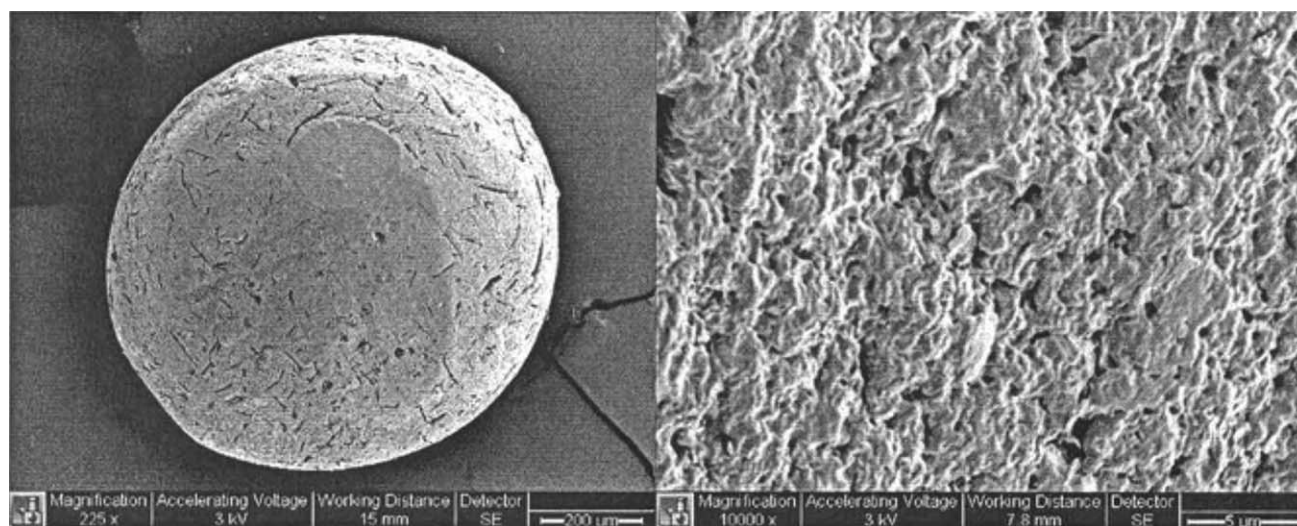
Solutions of the 2.5% Na-alginate were blended with 10, 30, 50, 70, and 90% wt % of the 2.5% clay suspension and mixed to homogenous solutions.

### Preparation of Na-alginate/clay crosslinked beads

The blend solutions were injected dropwise to 4% wt/v  $\text{CaCl}_2$  solution using 50 mL hypodermic syringe through a needle no. 21 under constant stirring at room temperature. Constant injection rate (2 mL/min) of the blend solutions was obtained using Syringe Infusion Pump22, Harvard Apparatus. The resultant alginate-clay beads were allowed to stand in the solution for 24 h at room temperature with gentle agitation on a magnetic stirrer. Finally, beads were taken out, washed several times with deionized water and then dried overnight at 30°C in a dust free chamber.

### Characterization of the beads

The surface morphology of the polymeric beads was examined using scanning electron microscopy (SEM)



**Figure 1** SEM micrographs of alginate-clay (70/30) composite beads.

of a model FEI XL30 SEM-FEG (FEI company). The beads were initially dried in air at ambient temperature for 5 days before being analyzed. A fragment of the dried bead was sputter coated for 200 s. The surface of the sample was scanned at the desired magnification to study the morphology of the beads.

### Adsorption of Pb(II)<sup>+</sup>

#### Batch procedure

Adsorption of Pb<sup>2+</sup> from aqueous solutions was investigated in a batch experiments. The tests were done in 100 mL polyethylene bottles; previously cleaned with deionized water, dilute nitric acid and deionized water. In all the experiments, beads concentration was kept constant at 10 mg/25 mL within the bottles stirred magnetically at 600 rpm. Effects of the contact time, pH of the medium, initial Pb<sup>2+</sup> concentration, and temperature of the medium on the removal were studied. The suspensions were brought to the desired pH by adding 0.1 M NaOH and 0.1 M HNO<sub>3</sub>. The concentration of the metal ions in the aqueous phases after desired treatment periods were measured by using ICP, TELEDYNE instruments. The experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. Adsorption values (mg/g) were calculated as the difference in Pb<sup>2+</sup> ion concentration of the pre- and postadsorption solutions divided by the weight of dry beads according to:

$$\text{Adsorption capacity } Q = \frac{(C_0 - C_e)V}{W}$$

where  $C_0$  is the initial Pb<sup>2+</sup> concentration (ppm),  $C_e$  is the final or equilibrium Pb<sup>2+</sup> concentration (ppm),

$V$  is the volume of the Pb<sup>2+</sup> solution (mL) and  $W$  is the weight of beads (g).

#### Column procedure

The stopcock of the glass column (100 mm in length and 10 mm in diameter) was covered with a fritted glass disc. A total of 500 mg of Na-alginate/clay bead was slurred in water, and then poured into the column. A small amount of glass wool was placed on the disc to prevent loss of the beads during sample loading. In the first group of experiments, the effect of Pb<sup>2+</sup> concentration on adsorption was studied. Aqueous solutions in the range of 10–1000 ppm were circulated at constant flow rate 0.5 mL/min. In the second group of experiments, the effect of solution flow rate on the adsorption of Pb<sup>2+</sup> was investigated. For this purpose, 100 ppm Pb<sup>2+</sup> solutions were circulated at different flow rates, in the range of 0.5–2.5 mL/min. The concentration of the metal ions in the aqueous phases after desired column procedure were measured by using ICP.

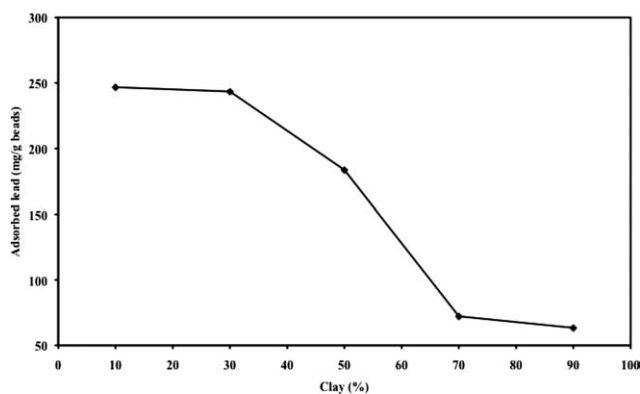
## RESULTS AND DISCUSSION

### Composite beads preparation

For the practical application, the utilization of bead particles has advantages in terms of applicability to a wide variety of process configurations even with dilute polluted streams and reusability for repeated runs following recovery.

An alginate solution is rapidly gelled upon contact with divalent cations and carboxyl groups of the alginate polymer chains.<sup>32,33</sup> By using this characteristic, various composite beads were prepared from different ratios of an alginate-montmorillonite clay mixture. The beads were then crosslinked by





**Figure 2** Effect of clay (%) on the adsorption of lead(II) onto alginate-clay composite beads; pH 5, time: 2 h, T: 25°C.

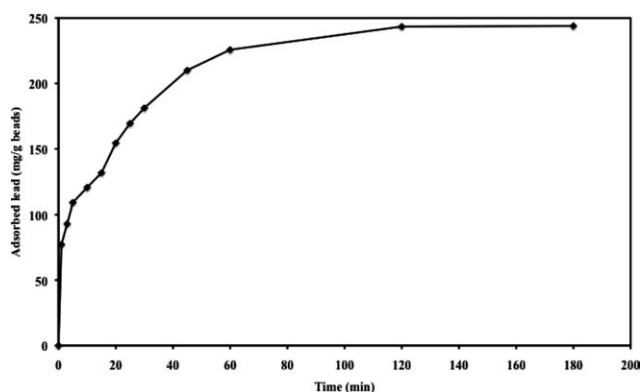
reaction with  $\text{CaCl}_2$ . Figure 1 shows the SEM image of the beads obtained.

### Adsorption properties

The feasibility of alginate-clay composite beads for the removal of heavy metal ions from aqueous solutions was demonstrated using Pb(II) as a model compound. Effect of adsorption time, pH, feed concentration, alginate-clay composition and temperature on the Pb(II) adsorption were investigated in batch procedure. Meanwhile, effect of solution flow rate and initial concentration were used to characterize the lead adsorption behavior in column procedure.

#### Effect of various alginate-clay ratios

The results of the experiments with varying clay ratio in the composite beads on the Pb(II) adsorption are illustrated in Figure 2. With a decrease in the clay percentage from 90 to 10%, the amount of lead(II) ions removal increased from 63.4 to 246.8 mg/g and approximately reaching a plateau at 30% clay content.



**Figure 3** Time dependent for the adsorption of lead(II) onto alginate-clay (70/30) composite beads; pH 5, T: 25°C.

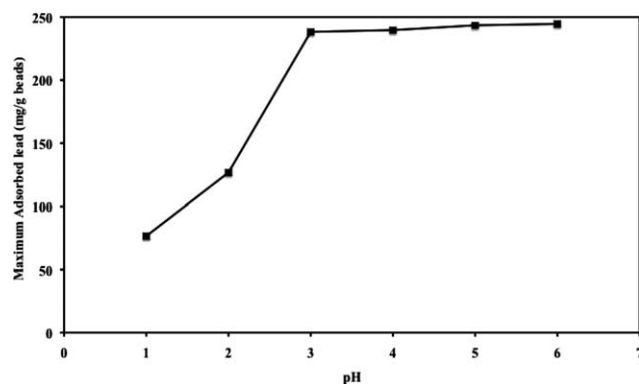
For alginate, metal ions could be adsorbed by ion exchange to carboxyl groups on alginate chains.<sup>33</sup> Also, Assaad et al.<sup>38</sup> revealed that clay retains aqueous metals by ion exchange, and that Mt-Na and Mt-K are more effective than Mt-Mg and Mt-Ca with maximum metal removal of 26.5 mg/g by Mt-K.<sup>38</sup> Therefore, the increase in maximum Pb(II) uptake with increasing alginate contacts indicates that metal ions are adsorbed on the hybrid gel beads by ion exchange with hydrogen ions on the binding sites formed by carboxyl groups on alginate. The Na- elements on montmorillonite coexisting in the gel beads are thought to mainly support the matrix structure by interacting with the carboxyl groups on alginate.<sup>33</sup>

#### Equilibrium adsorption time

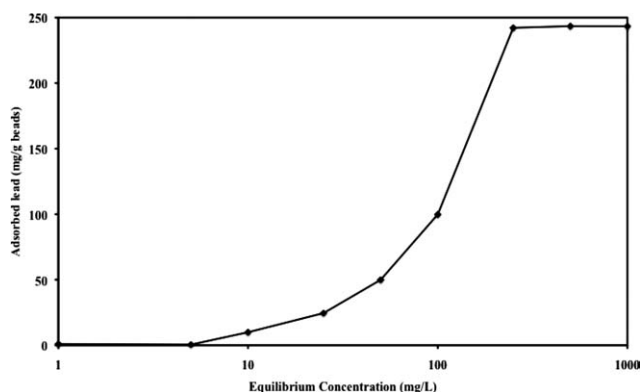
Time dependence of Pb(II) adsorption from aqueous solution onto alginate-clay (70 : 30 wt/wt) composite beads was determined. High adsorption rate is observed at the beginning of adsorption process, and then saturation value (i.e., adsorption equilibrium) is gradually reached within  $\sim 100$  min (Fig. 3). However, the time ( $t_{1/2}$ ) of 50% sorption was less than 10 min indicating a quite fast adsorption of Pb(II) onto the composite beads.

#### Effect of pH

The mechanism of pH dependence of lead(II) ions uptake may be explained by the nature of the composite surface metal binding sites. Figure 4 shows the effect of pH on the removal of lead(II) ions onto alginate-clay (70 : 30 wt/wt) composite beads adsorbent from aqueous solution. It is observed that almost no change in the adsorption capacity with increasing pH of the metal solution during the adsorption process up to pH 3–6 and the maximum lead(II) ions removal was observed at pH 6. The



**Figure 4** Effect of pH for the adsorption of lead(II) ions onto alginate-clay (70/30) composite beads; time: 2 h, T: 25°C.



**Figure 5** Effect of equilibrium Pb(II) concentration on adsorption (%) of Pb(II) ions on alginate-clay (70/30) composite beads; pH 5, time: 2 h, T: 25°C.

adsorption of metal as a function of initial pH clearly indicated that solution pH played an important role in the adsorption of lead(II) ions by the composite bead.<sup>19</sup> Under highly acidic conditions (pH = 1–2), the adsorption of lead(II) ions is not so important, since the metal binding sites on the adsorbent were closely associated with  $\text{H}_3\text{O}^+$  and restricted the approach of metal cations as a result of the repulsive forces. However, the adsorption increased with increasing solution pH, since more metal binding sites could be exposed with negative charges, with subsequent attraction of metal ions with positive charge and adsorption occurring onto the composite surface. Experiments were carried out up to pH value of 6 due to the fact that metal precipitation occurred at higher pH values.

#### Equilibrium adsorption of Pb(II)

For the alginate-clay composite beads, the equilibrium adsorption of Pb(II) is illustrated in Figure 5. The amount of Pb(II) ions adsorbed per unit mass of the composite beads (i.e., adsorption capacity) increased with increasing the initial concentration of Pb(II) ions, and a saturation adsorption value is achieved (243.5 mg/g beads), which represents maximum adsorption capacity of the alginate-clay composite beads.

From the viewpoint of application, it is important to develop an appropriate mathematical model for describing the equilibrium behavior of a beads-metal system to guide the further treatment process for actual contaminated water. Each adsorption isotherm is characterized by certain constants express the surface properties and affinity of the sorbent and can also be used to find the sorption capacity of beads. Several isotherm equations have been used for the equilibrium modeling of sorption systems. Among these, two are commonly used and have been applied for this study, Langmuir and Freundlich isotherms.

Both represent the equilibrium amount of metal removed as a function of the equilibrium concentration of metal ions in the solution, corresponding to the equilibrium distribution of ions between aqueous and solid phases as the initial concentration increases while keeping the adsorbent weight constant. The linearized Langmuir equation assumes the form:

$$C_e/q_e = 1/(Q_e K_L) + (1/Q_e)C_e$$

where ( $C_e$ ) is the metal concentration in aqueous solution at equilibrium (mg/L).

( $q_e$ ) is the experimental amount of adsorbed metal at equilibrium (mg/g).

( $Q_e$ ) is the calculated amount of adsorbed metal at equilibrium (mg/g).

( $K_L$ ) is the Langmuir constant (L/mg).

By plotting ( $C_e/q_e$ ) versus ( $C_e$ ), ( $Q_e$ ), and ( $K_L$ ) can be determined from the slope and intercept of the obtained straight line, respectively.

While, the linearized logarithmic Freundlich equation assumes the form:

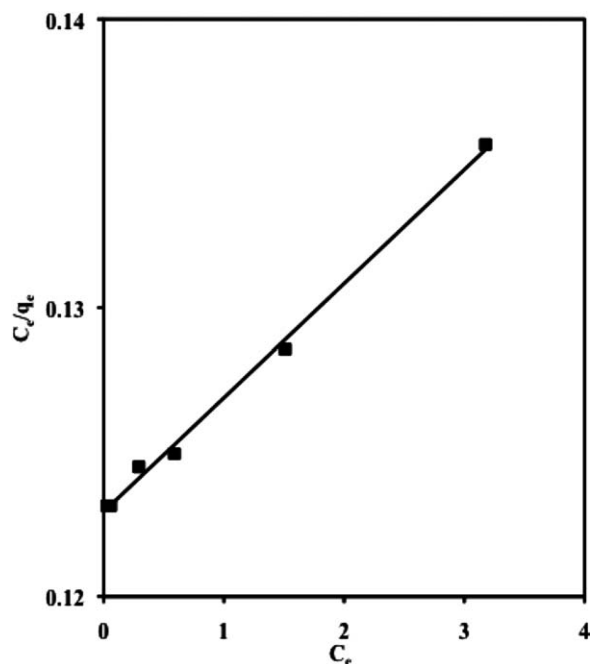
$$\text{Log } q_e = \text{Log } K_F + (1/n)\text{Log } C_e$$

where ( $K_F$ ) is the Freundlich constant indicating adsorption capacity.

( $n$ ) is the Freundlich constant indicating adsorption intensity.

By plotting ( $\text{Log } q_e$ ) versus ( $\text{Log } C_e$ ), ( $n$ ) and ( $K_F$ ) can be determined from the slope and intercept of the obtained straight line, respectively.

The linearized Langmuir and Freundlich adsorption isotherms corresponded to  $\text{Pb}^{2+}$  removal by the prepared beads are represented in Figures 6 and 7. Whereas Table I represents the correspondent constants along with the correlation coefficients ( $R^2$ ) associated at each linearized model. As can be observed, the high ( $R^2$ ) values that nearly approach unity reveal that both Langmuir and Freundlich models are very suitable for describing the adsorption equilibrium of the tested metal. The calculated ( $Q_e$ ) from Langmuir plots define the maximum capacity of the alginate-clay for Pb(II) removal in the level of the low concentrations that are used to plot the relation. As can be observed from Table I, the calculated ( $Q_e$ ) value match with the experimental one ( $q_e$ ) that are determined in the level of high concentrations. These results reflect the applicability of beads in the treatment of water samples that contain low and high concentrations of metal ions. The magnitude of ( $K_F$ ) and ( $n$ ) values, Freundlich constants, reflects the easy removal of the metal under investigation from water by the beads.<sup>33</sup> The higher ( $K_F$ ) value indicates high adsorption capacity and is found to be proportional to the actual high sorption capacity ( $q_e$ ). Also, ( $n$ ) value that is greater than

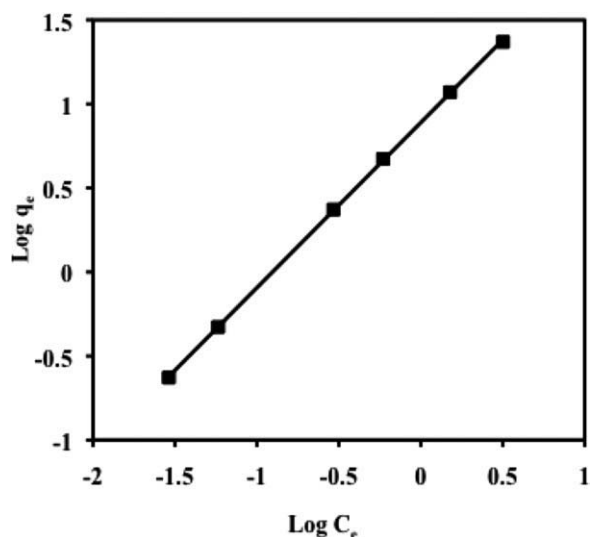


**Figure 6** Linearized Langmuir adsorption isotherms for lead(II) using alginate-clay (70/30).

unity indicate the favourability of the beads to remove lead from water.

#### Effect temperature

It is well known that temperature has a great influence on any chemical process so that it may enhance or retard such process depending on the nature of the reactants and/or the products.<sup>39</sup> The effect of temperature on the adsorption of Pb(II) ions was studied at 25, 40, 55, and 70°C. From Figure 8, it has been observed that the adsorption of Pb(II) from



**Figure 7** Linearized Freundlich adsorption isotherms for lead(II) using alginate-clay (70/30).

**TABLE I**  
Langmuir and Freundlich Equilibrium Parameters for Pb(II)<sup>+</sup> Removal by the Prepared Alginate-Clay Bead

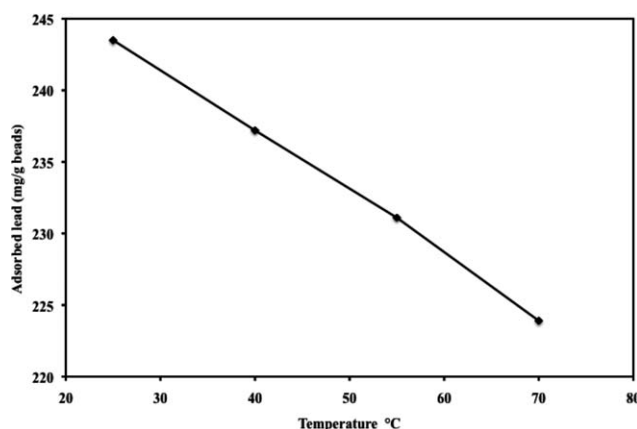
Freundlich parameters			Langmuir parameters			$q_{e(\text{exp})}$ (mg/g)
$K_F$	$n$	$R^2$	$K_L$ (L/mg)	$Q_c$ (mg/g)	$R^2$	
7.75	1.02	0.99	0.034	238.1	0.99	243.5

aqueous solution is affected by the reaction temperature. The figure shows an unexpected result as the adsorption of lead ions slightly decreased with increasing temperature. This might be due to the fact that the electrostatic interaction between Pb(II) ions and alginate is lower at higher temperatures.<sup>40</sup>

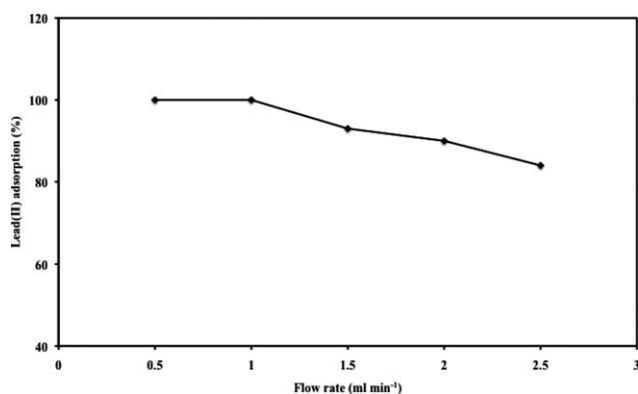
#### Column procedure

Based on alginate-montmorillonite beads packed columns, a highly efficient method for Pb(II) removal from aqueous solution was developed. The stopcock of the glass column (100 mm in length and 10 mm in diameter) covered with a fritted glass disc and filled with 500 mg alginate-clay (30 : 70 wt/wt) composite bead was used. The effect of flow rate and Pb(II) flow concentration on adsorption of Pb(II) in the packed-bed column was investigated.

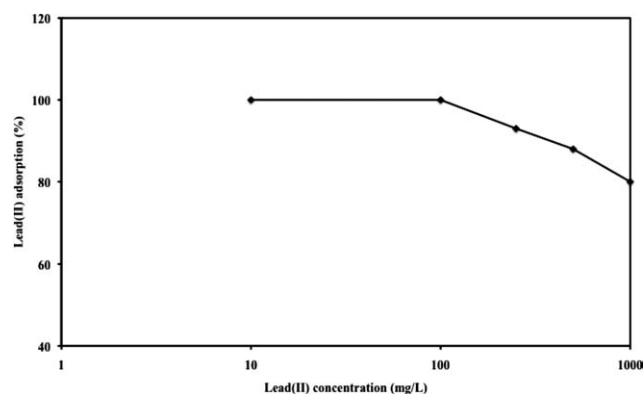
*Effect of flow rate.* The flow rate of the Pb(II) solution through the packed-bed column is a very important parameter for controls the time of adsorption and analysis. Using the column procedure, the effect of flow rate on sorption of Pb(II) in the packed-bed column was investigated by changing the flow rate between 0.5 and 2.5 mL min<sup>-1</sup>. The results show that the flow rate has high influence on the sorption of Pb(II). At initial concentration of 100 mg/L, Pb(II) can be 100% adsorbed by alginate-clay (30 : 70 wt/wt) composite beads at a flow rate below 1.0 mL min<sup>-1</sup>. Above 1.0 mL min<sup>-1</sup>, the recovery was



**Figure 8** Effect of temperature on the adsorption of lead(II) onto alginate-clay (70/30) composite beads; pH 5, time: 2 h.



**Figure 9** Effect of flow rate on the adsorption of Pb(II) on the alginate-clay (70/30) composite beads; Pb(II) concentration: 100 mg/L, pH 5, T: 25°C.



**Figure 10** Effect of Pb(II) initial concentration on adsorption (%) of Pb(II) ions on alginate-clay (70/30) composite beads; flow rate: 0.5 mL min<sup>-1</sup>, pH 5, time: 2 h, T: 25°C.

lowered to be 93% at 1.5 mL min<sup>-1</sup> and even 84% at 2.5 mL min<sup>-1</sup>, as shown in Figure 9. At higher flow rates, the contact time of lead ions with the column materials is shorter. So the flow rate of 1.0 mL min<sup>-1</sup> was chosen for column procedures.

*Effect of Pb(II) flow concentration.* The effect of Pb(II) flow concentration on the adsorption of Pb(II) ions was studied using column procedure. At constant flow rate of 1.0 mL min<sup>-1</sup>, the concentration of Pb(II) ions in the flow solution was 10, 100, 250, 500, and 1000 mg/L (Fig. 10). Lead recoveries for above concentrations were 100, 100, 93, 88, and 80%, respectively. Thus, 100 mg/L was the maximum

Pb(II) concentration in which quantitative adsorption of lead is possible. At higher concentrations the recovery decreased.

#### Wastewater treatment

Rapid industrial development during recent time has caused increased environmental pollution. The removal of toxic heavy metal contaminants from industrial wastewaters is one of the most important environmental issues to be solved today. For this reason, the synthesized alginate-clay (30 : 70 wt/wt) composite bead was then applied for the treatment

**TABLE II**  
Chemical Analysis Data for Wastewater Samples Before and After Treatment Process

Sample	<sup>a</sup> Heavy metal ion (ppm)								
	Al	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
Shoubra El-Khama									
1	Before	8.9	<0.01	<0.01	52.1	10.9	<0.0004	0.45	0.04
	After	0.1	<0.01	<0.01	8.68	1.41	<0.0004	<0.0008	<0.0001
	(%)	99			83	87		~ 100	~ 100
2	Before	3.2	3.1	0.08	0.84	0.07	20.5	0.03	0.2
	After	<0.04	0.8	<0.01	<0.01	0.02	1.24	<0.0008	0.02
	(%)	~ 100	74	~ 100	~ 100	71.5	94	~ 100	90
10th of Ramadan									
3	Before	8.7	<0.01	0.08	2.7	0.34	0.02	0.03	0.05
	After	0.21	<0.01	<0.01	<0.01	<0.003	<0.0004	<0.0008	<0.0001
	(%)	97.5		~ 100	~ 100	~ 100	~ 100	~ 100	~ 100
4	Before	2.4	0.09	<0.01	4.1	0.17	0.13	0.02	0.42
	After	0.05	<0.01	<0.01	0.15	<0.003	<0.0004	<0.0008	0.01
	(%)	98	~ 100		96	~ 100	~ 100	~ 100	98
El-Obour									
5	Before	1.5	0.06	0.08	0.96	0.09	<0.0004	<0.0008	0.12
	After	<0.04	<0.01	<0.01	<0.01	<0.003	<0.0004	<0.0008	<0.0001
	(%)	~ 100	~ 100	~ 100	~ 100	~ 100		~ 100	~ 100
6	Before	0.14	<0.01	0.2	0.1	0.02	<0.0004	0.15	0.04
	After	<0.04	<0.01	<0.01	<0.01	<0.003	<0.0004	<0.0008	<0.0001
	(%)	~ 100		~ 100	~ 100	~ 100		~ 100	~ 100

<sup>a</sup> The relative standard deviation (%RSD) was 0.02–0.14% for triplicate analysis.

of actual industrial wastewaters. Six samples were collected from three industrial cities (Shoubra El-Khama, 10th of Ramadan and El-Obour) near capital Cairo, Egypt. Analysis of heavy metals for such samples by ICP reveals high concentration of aluminum, chromium, copper, iron, manganese, nickel, lead and zinc as shown in Table II. So, 100 mL of these wastewater samples were loaded into 500 mg alginate-clay in packed column system. A 1.0 mL min<sup>-1</sup> was used as the flow rate. Treatment process was continued until the entire 100 mL sample introduced into the column. Generally, the treatment must provide water of better quality. After treatment process, alginate-clay beads were able to remove from 97.5 to ~ 100% of Al, 74 to ~ 100% of Cr, ~ 100% of Cu, 83 to ~ 100% of Fe, 87 to ~ 100% of Mn, 94 to ~ 100% of Ni, ~ 100% of Pb, and 90 to ~ 100% of Zn, resulting in a satisfactory removal of heavy metals in the wastewater samples under investigation. The data also shows the high efficiency of the beads for metal removal even in very low concentrations.

### CONCLUSIONS

Series of polymer-clay composite beads that consists of Na-alginate and montmorillonite clay were prepared and characterized. Removal of lead from aqueous solution using this bead was then studied in batch adsorption experiments. The amount of lead removed was found to increase as the percent of Na-alginate increase in the composite beads. The experimental results also show that the equilibrium contact time was obtained within ~ 100 min. Lead adsorption was found to be strongly pH-dependent and display maximum uptake at high pH, high initial lead concentration in the feed solution and low temperature. Based on alginate-montmorillonite beads packed columns, a highly efficient method for Pb(II) removal from aqueous solution was developed. Technical feasibility for the uses of the prepared composite beads for the treatment of actual polluted wastewater samples collected from some industrial cities in Egypt was investigated. The results showed a promising possibility for producing wastewater of better using such prepared beads.

### References

- Park, D.; Yun, Y.; Jo, J. H.; Park, J. M. *Ind Eng Chem Res* 2006, 45, 5059.
- Wan Ngah, W. S.; Kamari, A.; Koay, Y. J. *Inter J Bio Macro* 2004, 34, 155.
- Solener, M.; Tunali, S.; Ozcan, A. S.; Ozcan, A.; Gedikbey, T. *Desalination* 2008, 223, 308.
- Ake, C. L.; Mayura, K.; Huebner, H.; Bratton, G. R.; Phillips, T. D. *J Toxicol Environ Health Part A* 2001, 63, 459.
- Tunali, S.; Akar, T.; Özcan, A. S.; Kiran, I.; Özcan, A. *Sep Purif Technol* 2006, 47, 105.
- Dubey, S. S.; Gupta, R. K. *Sep Purif Technol* 2005, 41, 21.
- Aksu, Z.; Acikel, U.; Kutsal, T. *J Chem Tech Biotechnol* 1997, 70, 368.
- Doğan, M.; Alkan, M.; Onganer, Y. *Water Air Soil Poll* 2000, 120, 229.
- Ucun, H.; Bayhan, Y. K.; Kaya, Y.; Cakici, A.; Algur, O. F. *Desalination* 2003, 154, 233.
- Huang, C. P.; Huang, C. P.; Morehart, A. L. *Water Res* 1990, 24, 433.
- Holan, Z. R.; Volesky, B. *Biotechnol Bioeng* 1994, 43, 1001.
- Akar, T.; Tunali, S.; Kiran, I. *Biochem Eng J* 2005, 25, 227.
- Kiran, I.; Akar, T.; Tunali, S. *Process Biochem* 2005, 40, 3550.
- Jianlong, W.; Xinmin, Z.; Decai, D.; Ding, Z. *J Biotechnol* 2001, 87, 273.
- Fourest, E.; Roux, J. C. *Appl Microbiol Biotechnol* 1992, 37, 399.
- Tunali, S.; Çabuk, A.; Akar, T. *Chem Eng J* 2006, 115, 203.
- Gotoh, T.; Matsushima, K.; Kikuchi, K. *Chemosphere* 2004, 55, 57.
- Jin, L.; Bai, R. *Langmuir* 2002, 18, 9765.
- Shawky, H. A.; El-Hag Ali, A.; El Sheikh, R. A. *J Appl Polym Sci* 2006, 99, 2904.
- Srivastava, S. K.; Tyagi, R.; Pant, N.; Pal, N. *Environ Technol (Lett)* 1989, 10, 275.
- Orumwense, F. F. O. *J Chem Technol Biotechnol* 1996, 65, 363.
- Chantawong, V.; Harvey, N. W.; Bashkin, V. N. *Asian J Energy Environ* 2001, 2, 33.
- Gupta, S. S.; Bhattacharyya, K. G. *Appl Clay Sci* 2005, 30, 199.
- Echeverría, J. C.; Zarranz, I.; Estella, J.; Garrido, J. J. *Appl Clay Sci* 2005, 30, 103.
- Naseem, R.; Tahir, S. S. *Water Res* 2001, 35, 3982.
- Donat, R.; Akdogan, A.; Erdem, E.; Cetisli, H. *J Colloid Interf Sci* 2005, 286, 43.
- Barbier, F.; Duc, G.; Petit-Ramel, M. *Colloids Surf A: Physicochem Eng Aspects* 2000, 166, 153.
- Zamzow, M. J.; Eichbaum, B. R.; Sandgren, K. R.; Shanks, D. E. *Sep Sci Technol* 1990, 25, 1555.
- Ouki, S. K.; Cheeseman, C.; Perry, R. *Environ Sci Technol* 1993, 27, 1108.
- Brigatti, M. F.; Lugli, C.; Poppi, L. *Appl Clay Sci* 2000, 16, 45.
- Bektasf, N.; Agaem, B. A.; Kara, S. *J Hazard Mater* 2004, 112, 115.
- Bajpai, S. K.; Tankhiwale, R. *React Funct Polym* 2006, 66, 645.
- Gotoh, T.; Matsushima, K.; Kikuchi, K. *Chemosphere* 2004, 55, 135.
- Ulusoy, U.; Simsek, S.; Ceyhan, O. *Adsorption* 2003, 9, 165.
- Liu, A.; Xie, T.; Yang, G. *Macromol Chem Phys* 2006, 207, 701.
- Dogan, M.; Turhan, Y.; Alkan, M.; Namli, H.; Turan, P.; Demirbas, O. *Desalination* 2008, 230, 248.
- Xie, W.; Hwu, J. M.; Jiang, G. J.; Buthelezi, T. M.; Pan, W.-P. *Polym Eng Sci* 2003, 43, 214.
- Assaad, E.; Azzouz, A.; Nistor, D.; Ursu, A. V.; Sajin, T.; Miron, D. N.; Monette, F.; Niquette, P.; Hausler, R. *Appl Clay Sci* 2007, 37, 258.
- El-Hag Ali, A.; Shawky, H. A.; El-Sayed, M. H.; Ibrahim, H. *Separat Purif Technol* 2008, 63, 69.
- Chang, Y.; Chen, D. *J Colloid Interface Sci* 2005, 283, 446.