



Adsorption Studies of Lead Ions on Alginate-Calcium Carbonate Composite Beads

Neama A. Sobhy*, Nouran Y. Mohamed

Sanitary and Environmental Engineering Institute, Housing and Building National Research Center, Giza, Egypt
Email: neamaahmedriad@yahoo.com

Abstract Alginate-calcium carbonate beads was prepared by sol-gel method and characterized by Fourier transform infra-red spectroscopy (FT-IR) and scanning electron microscope (SEM) instruments. Adsorption potentials of lead ions have been studied on laboratory scale. The effects of contact time, adsorbents dosage, initial metal concentration and pH were studied at 298 K (25°C) in a single ion system. The highest percentage of lead removal was achieved in the pH 10 and at an initial concentration of 30 ppm lead concentration. Adsorption parameters were determined using both Langmuir and Freundlich isotherms, but the experimental data were better fitted to the Langmuir equation than to Freundlich equation.

The potential of Alginate-calcium carbonate composite beads for the removal of lead from aqueous solution was substantiated.

Keywords Alginate-calcium carbonate beads, lead removal, Langmuir and Freundlich isotherms

1. Introduction

Contamination of water with toxic compounds, such as heavy metals and dyes, even at low concentration, remains a serious environmental issue due to their dangerous effects on human health [1,2]. The use of heavy metals arises in various industries such as metallurgy, chemical industry, papermaking, electroplating, steel fabrication, anodizing baths, leather tanning, cement preservation, canning industries and textile [3,4]. These highly toxic metal ions including lead and chromium exert enormous effects on environment [5,6]. To overcome this serious problem, considerable attention has been paid to develop new approaches to remove toxic metal ions from polluted environmental matrices, e.g., physicochemical techniques namely precipitation, ion-exchange, electrochemistry, membrane ultrafiltration and chemical adsorption [7].

The search for alternative and innovative treatment techniques has focused attention on the use of biological materials such as algae, fungi, yeast and bacteria for the removal and recovery technologies and has gained importance during recent years because of better performance and low cost of these biological materials [8]. The metal sequestering ability of microorganisms such as yeast, fungi and bacteria that are generated in large quantities as waste byproduct from fermentation industries have been investigated and reported [9]. Biosorption technology based on the utilization of dead biomass offers certain major advantages such as lack of toxicity constraints, non-requirements of nutrients supply, and recovery of bound metal species by an appropriate desorption method [10]. Biopolymers are non-toxic, selective, efficient and inexpensive, and thus highly competitive with ion exchange resins and activated carbon [11].



The choice of biopolymer is a key factor in biosorption, which determines the mechanical strength and chemical resistance of the final biosorbent particle, which is to be utilized for successive sorption–desorption process [12]. Many biopolymers such as sodium alginate, glutaraldehyde, agarose, cellulose–acetate derived from microorganisms and plants are known to bind metal ions strongly and could be used for heavy metal adsorption [11]. But their biosorption potential for different metal ions and capacity of reusability in multiple adsorptions–desorption cycles has not been properly investigated.

The aim of this study was to investigate the Pb(II) biosorption profile of calcium alginate beads and to indicate factors that impact the sorption and elution characteristics of the beads. The characterization techniques involved are scanning electron microscopy analysis, Fourier Transform Infrared (FT-IR) analysis. The adsorption of lead ions onto alginate-calcium carbonate composite beads have been carried out in batch equilibrium conditions. The effects of different parameters including pH, contact time, stirring rate, and initial metal ion concentration have been investigated also.

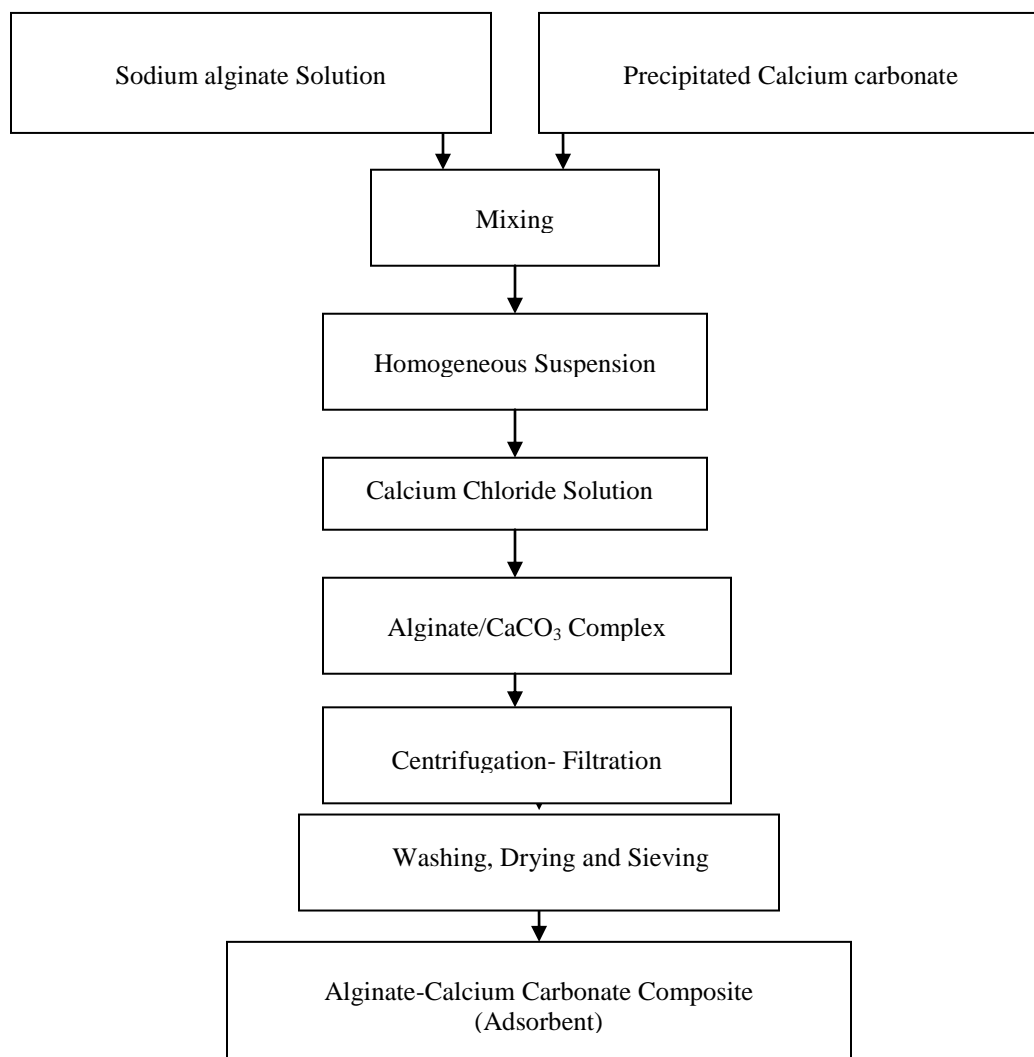


Figure 1: Flow sheet for adsorbent synthesis

2. Materials and Methods

2.1. Materials

Sodium alginate was obtained from Junsei Chemical Co (Japan). Analytical grade of $\text{Pb}(\text{NO}_3)_2$, was used for metal sorption experiments. All other chemicals used in this work were of analytical grade.

2.2. Adsorbent Preparation

Precipitated calcium carbonate was impregnated on sodium alginate gel to prepare adsorbent in the form of beads in aqueous calcium chloride solution. 5 g of commercial grade sodium alginate was dissolved in 200 ml of distilled water with vigorous stirring and heated at 40°C to get a gel like material. The fine calcium carbonate powder (20 g) was mixed thoroughly under constant mechanical stirring to get the homogeneous mixture. The suspension was injected drop wise into a 1 M solution of calcium chloride with the help of 25 mL syringe. Fine complex beads of alginate-calcium carbonate were obtained. The beads were separated from the solution through centrifuge process followed by filtration and drying for overnight at $(70\pm 2^\circ\text{C})$. The dried mass of beads was sieved and used as an adsorbent. The flow sheet of the process is demonstrated in Figure 1.

2.3. Batch Experimental System

Adsorption experiments were conducted by stirring the 50 mL of lead nitrate solution with concentration 20 mg/L with 0.6 g Alginate-Calcium Carbonate Composite in the capped conical flasks at $25\pm 2^\circ\text{C}$ for 120 min. and shacked at 150 rpm. The adsorption of lead nitrate were studied using Alginate-Calcium Carbonate Composite by batch technique. After equilibration, the suspension of the adsorbent was separated from the solution by filtration using filter paper Whatman No. 2 and the concentration of lead nitrate remaining in solution was measured using UV visible Spectrophotometer (ICE 3300, Thermo Scientific Ltd., UK). The percentage of removal efficiency was calculated using Equation 1. The amount of lead nitrate sorbed by weight of Alginate-Calcium Carbonate Composite was calculated using equation 2.

$$\text{Sorption (\%)} = (C_o - C_e) / C_o * 100 \quad (1)$$

Where C_o is the initial concentration of lead ions in solution, mg/l.

C_e is the equilibrium concentration of lead ions in solution, mg/l.

$$Q_e \text{ (mg/l)} = (C_o - C_e) * V/m \quad (2)$$

Where Q_e is the equilibrium adsorption capacity, mg/g.

V is the volume of aqueous solution, L.

m is the dry weight of adsorbent, g.

2.4. Effect of operating parameters

2.4.1. Effect of pH

About 0.6 g of Alginate-Calcium Carbonate Composite was added to 20 mg/L of lead nitrate solution at different pH values (3-10) at temperature $25\pm 2^\circ\text{C}$ and the stirring of the solution was fixed at 150 rpm. The pH was adjusted using NaOH to provide an alkaline medium and HCl to provide acidic medium.

2.4.2. Effect of contact time

About 0.6 g of Alginate-Calcium Carbonate Composite dosage was added to 20 mg/L of lead nitrate solution at different contact times namely (30-180 minutes), temperature $25\pm 2^\circ\text{C}$, at pH 10 ± 0.2 and the stirring of the solution was fixed at 150 rpm.

2.4.3. Effect of adsorbent dose

About 0.6 g of Alginate-Calcium Carbonate Composite dosage was added to 20 mg/L of lead nitrate solution for 150 minute at different adsorbent dose (0.2-2 gm) at temperature $25\pm 2^\circ\text{C}$ and pH 10 ± 0.2 .

2.4.4. Effect of initial phosphate concentration

At room temperature, 0.6 g/L dosage of Alginate-Calcium Carbonate Composite, was added in solutions with different initial lead concentration (5.0, 10.0, 15, 20.0, 25.0, and 30.0 mg/L) at temperature $25\pm 2^\circ\text{C}$ and pH 10 ± 0.2 .



2.5. Adsorbent Characterization

The characterization of adsorbent material was made by Fourier transform infra-red spectroscopy (FT-IR) and scanning electron microscope (SEM) techniques.

FT-IR spectra of alginate-calcium carbonate composite shown of Figure (2) was recorded in the range of 4,000-400 cm^{-1} . The spectra exhibits several peaks with variable intensities merged to form a broad band in the functional group region between 3,200-3,600 cm^{-1} associated with stretching vibrations of free or bonded OH groups along with presence of inter and intra-molecular hydrogen bonding between these hydroxyl groups [13]. The distorted peaks of medium intensity corresponds to the asymmetric stretching vibrations of alkyl chains. Then relatively distorted small bands at 1,634, 1,465, 1,109 and 874 cm^{-1} are assigned to the stretching vibrations of the functional groups like C=O, -COOH and -OH [14]. It can be inferred from the FT-IR results that a strong bonding has occurred between functional groups of alginate and host material, that is, calcium carbonate.

The morphology of the adsorbent beads was observed by scanning electron microscope. SEM images from different areas of adsorbent material were taken at 15.0 kv with varying resolutions Figure (3). The SEM images indicate the formation of a composite material along with sites responsible for adsorption at the adsorbent interface.

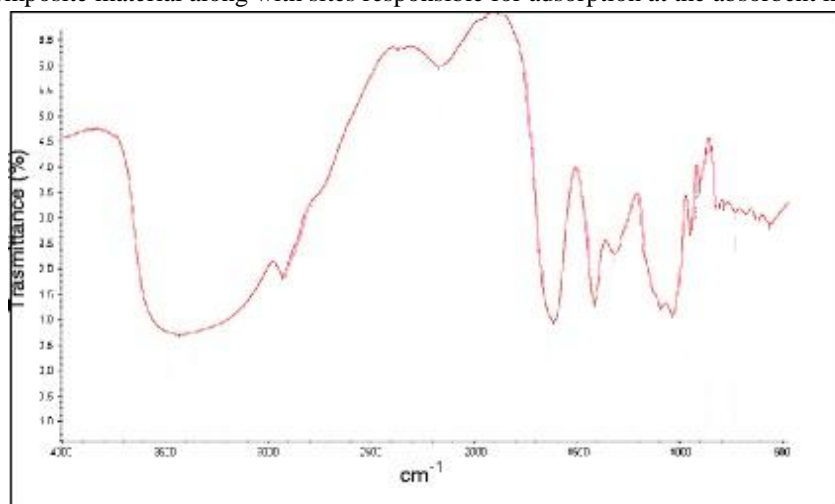


Figure 2: FTIR for Alginate-calcium carbonate composite beads surface

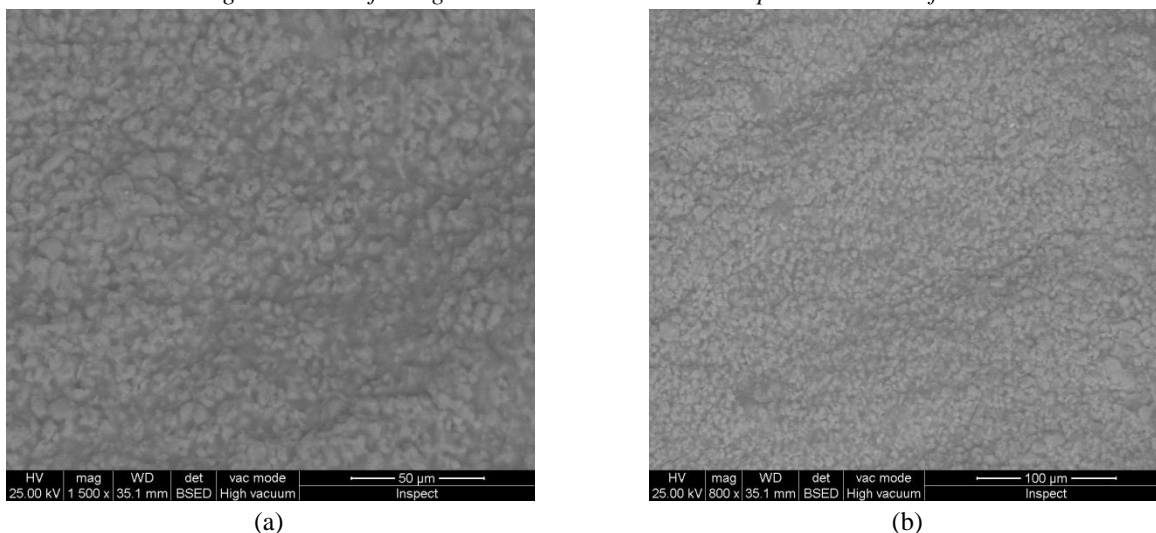


Figure 3: SEM image for Alginate-calcium carbonate composite beads surface

3. Results and Discussion

3.1. Effect of pH

The effect of variation in pH on the removal of lead ions has also been studied in the range from 2.0 to 12 using 0.1 % HCl and 0.1 % NaOH solutions that gave the maximum value of pH for our investigations. It is apparent from figure (4) that the lead removal shows maxima at pH 10 solution and then remains constant with further increase in pH from 10 to 12. Significant enhancement of adsorption was achieved at about pH 10 Figure (4).

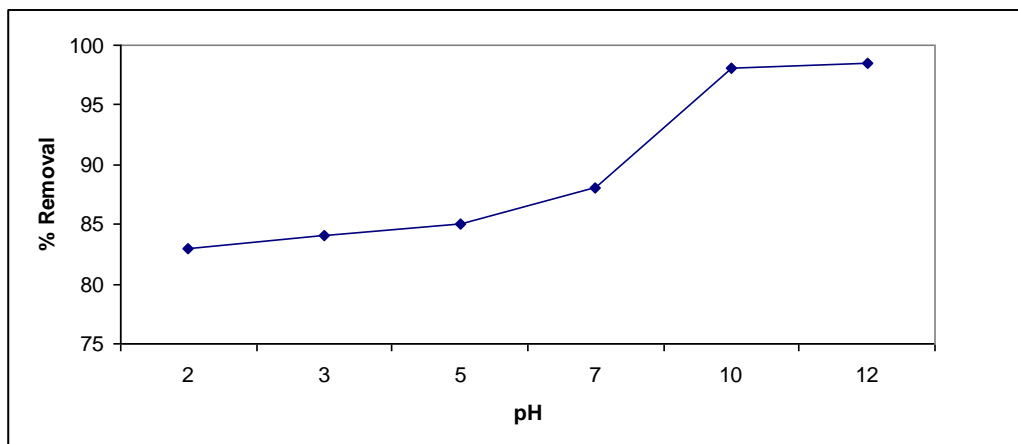


Figure 4: Effect of variation in pH on adsorption of lead ions on Alginate-Calcium Carbonate Composite

3.2. Effect of contact time

The effect of stirring time on the removal of lead ions was studied by varying the time of stirring from 30 to 180 minutes for the optimum equilibrating time, pH adjusted at 10 and stirring rate 150 rpm. Results in Figure (5) show that the equilibrium in adsorption of lead ions is attained at about 150 minutes of stirring time. Therefore, the optimum stirring time of 150 minutes has been chosen for all investigations throughout the study.

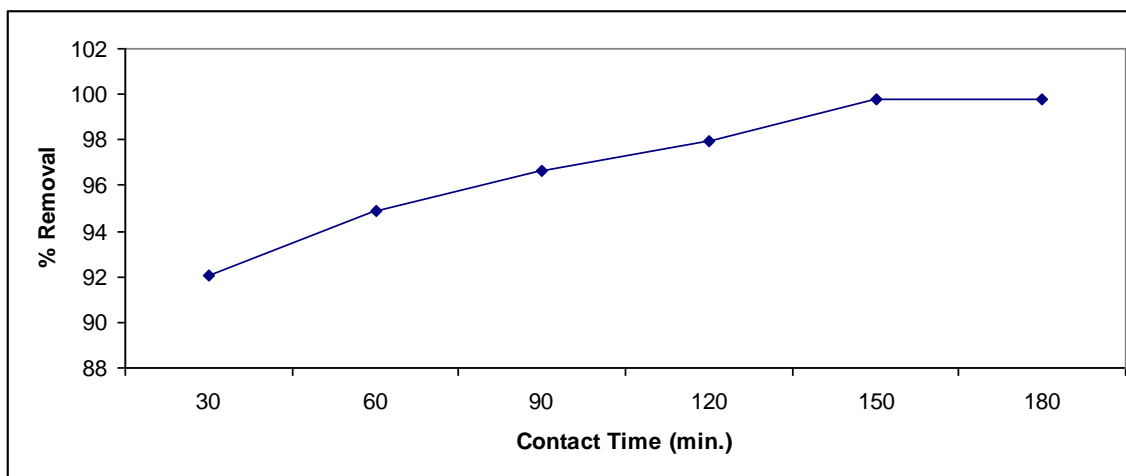


Figure 5: Effect of contact time on adsorption of lead ions on Alginate-Calcium Carbonate Composite

3.3. Effect of adsorbent dose

The effect of adsorbent dose on the removal of lead ions was studied by varying adsorbent dose from 0.2 to 2 gm at $25 \pm 2^\circ\text{C}$. The pH of solution adjusted at 10 and time 150 minutes. It is observed that the maximum adsorption obtained at 2 gm as shown in Figure (6).



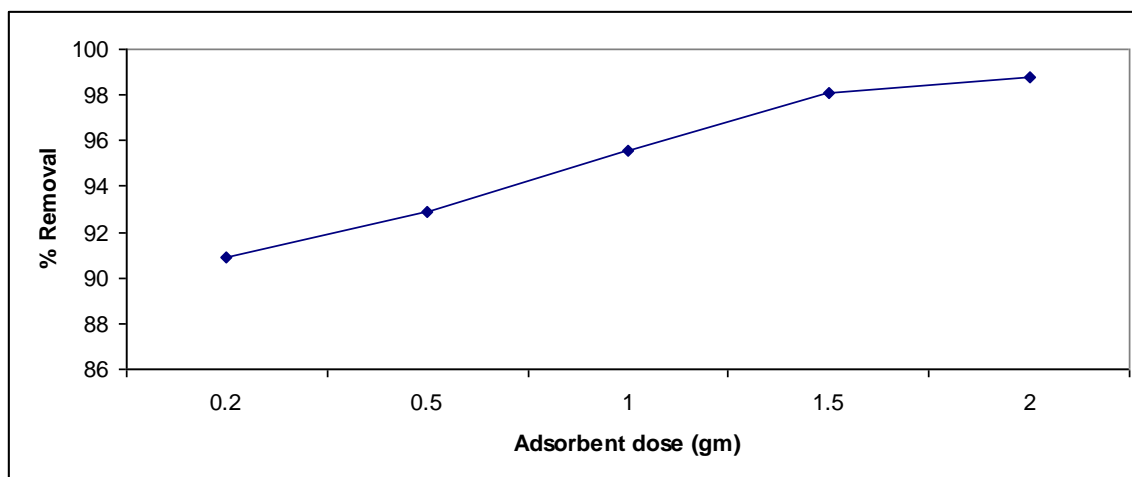


Figure 6: Effect of adsorbent dose on adsorption of lead ions on Alginate-Calcium Carbonate Composite

3.4. Effect of initial metal concentration

Adsorption studies were carried out on a fixed weight of Alginate-Calcium Carbonate Composite 0.6 g with varying lead concentrations from 5 to 30 mg/L. It is observed from our studies that the lead removal efficiency increases with increasing lead concentrations and rises to maxima up to around 25 to 30 mg/L as shown in Figure (7). Further, it is observed that lead removal efficiency does not show any significant change after lead concentration of 30 mg/L. [15] have shown that such behavior is anticipated due to the buffering properties of lead compounds.

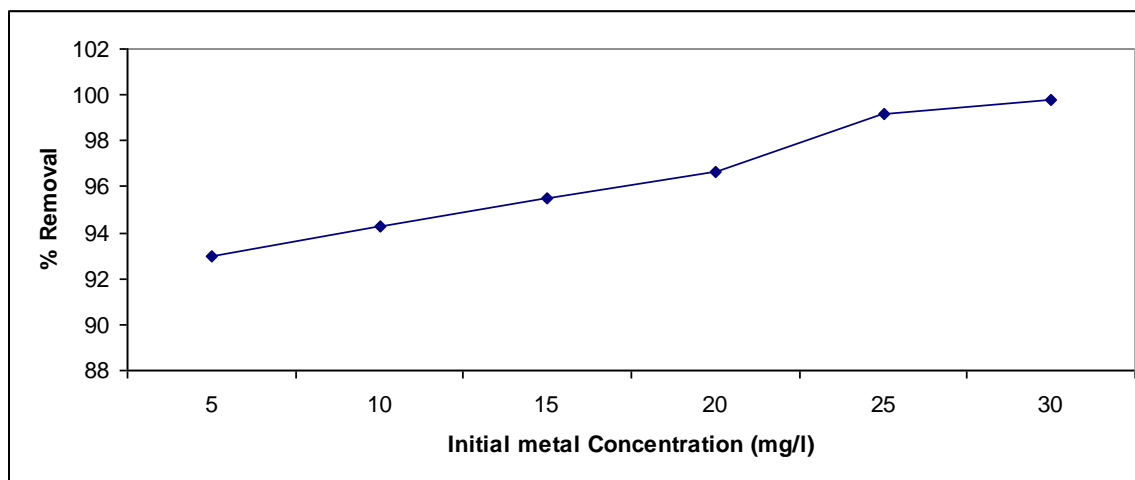


Figure 7: Effect of initial metal concentration on adsorption of lead ions on Alginate-Calcium Carbonate Composite

3.5. Adsorption models

3.5.1. Adsorption isotherm

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents so are critical for design purposes; therefore, the correlation for equilibrium data using an equation is essential for practical adsorption operation [16].

Two isotherm equations were adopted in this study as follows:



3.5.1.1. Langmuir isotherm equation

The Langmuir equation is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbent molecules on the adsorbent surface, that the energy of adsorption is constant [17]

The Langmuir equation is defined as:

$$Q_e = (b \cdot Q_m \cdot C_e) / (1 + b \cdot C_e) \quad (3)$$

And in linearized form is:

$$C_e / Q_e = (C_e / Q_m) + (1 / (b Q_m)) \quad (4)$$

Where “ Q_m ” and “ b ” are Langmuir constants related to the adsorption capacity and sorption energy, respectively. “ C_e ” is the equilibrium concentration in mg/l, and “ Q_e ” is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). The plots C_e / Q_e against C_e are shown in Figure (8). The adsorption of lead ions on Alginate-Calcium Carbonate Composite give a straight line. It is clear that the linear fit is fairly good and enables the applicability of Langmuir model.

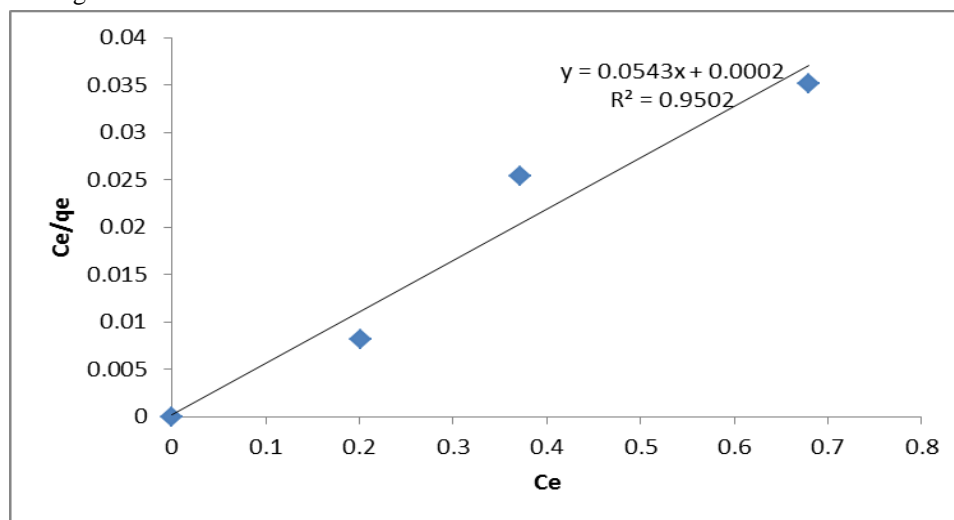


Figure 8: Langmuir isotherm plot for adsorption of lead ions on Alginate-Calcium Carbonate Composite

Table 1: Langmuir constants calculated from Langmuir isotherm

R^2	q_m	b
0.952	18.41	271.5

3.5.1.2. Freundlich isotherm equation

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.

$$Q_e = k \cdot C_e^{1/n} \quad (5)$$

and in linearized form is :

$$\log Q_e = \log k + (1/n) \log C_e \quad (6)$$

Where “ C_e ” is the equilibrium concentration in mg/l, “ Q_e ” amount of adsorbate adsorbed per unit weight of adsorbent (mg/g), “ k ” is a parameter related to the temperature and “ n ” is a characteristic constant for the adsorption system under study. The plots of $\log Q_e$ against $\log C_e$ are shown in Figure (9), the adsorption of lead ions onto Alginate-Calcium Carbonate Composite give a straight line; values of “ n ” between 2 and 10 show good adsorption [18].



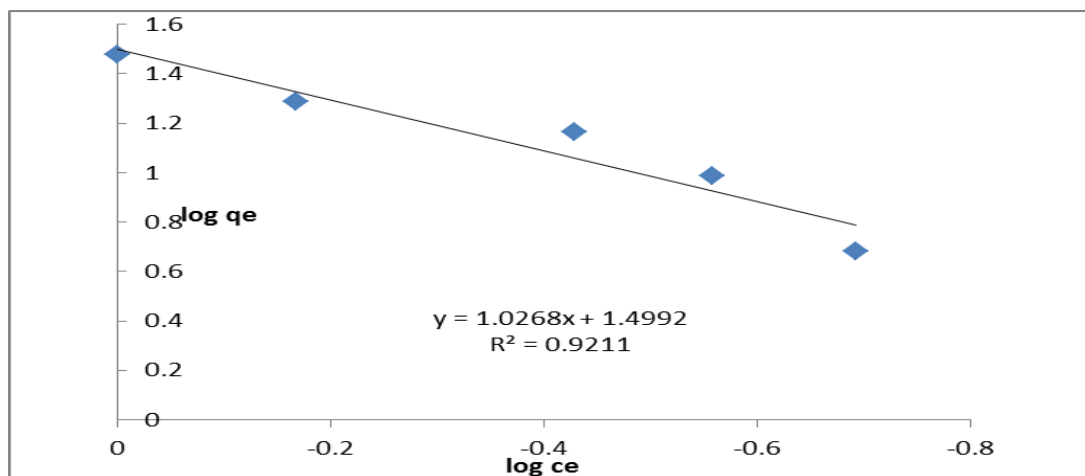


Figure 9: Freundlich isotherm plot for adsorption of lead ions on Alginate-Calcium Carbonate Composite

As can be observed, experimental data were better fitted to Langmuir equation, and therefore it is more suitable for the analysis of kinetics.

Table 2: Freundlich constants calculated from Freundlich isotherm

R^2	k	n
0.92	0.011	0.66

4. Conclusions

The developed Alginate-calcium carbonate beads adsorbent material was prepared by sol-gel method can effectively be used for the removal of lead ions from wastewater. It is inferred from this research work that alginates modified with calcium carbonate could be an effective alternative material to recover lead ions from contaminated water. Experimental data were better fitted to Langmuir equation, and therefore it is more suitable for the analysis of kinetics.

References

- [1]. Dutta, K. (2017). Aromatic conjugated polymers for removal of heavy metal ions from wastewater: a short review. *Environ Sci Wat. Res.*, 3:793–805.
- [2]. Abdel-Halim, E.S., Al-Deyab, S.S. (2011). Removal of heavy metals from their aqueous solutions through adsorption onto natural polymers. *Carbohydr Polym.*, 84:454–8.
- [3]. Eladlani, N., Dahmane, E., Ouahrouch, A., Rhazi, M., Taourirte, M. (2018). Recovery of chromium (III) from tannery wastewater by nanoparticles and whiskers of chitosan. *J Polym Environ.*, 26:152–7.
- [4]. Kan, C.C., Ibe, A.H., Rivera, K.K.P., Arazo R.O., De Luna M.D.G. (2017). Hexavalent chromium removal from aqueous solution by adsorbents synthesized from groundwater treatment residuals. *Sustain Environ Res.*, 27:163–71.
- [5]. Liu, W., Zhang, J.S., Jin, Y.J., Zhao, X., Cai, Z.Q. (2015). Adsorption of Pb(II), Cd(II) and Zn(II) by extracellular polymeric substances extracted from aerobic granular sludge: efficiency of protein. *J Environ Chem Eng.*, 3:1223–32.
- [6]. Shahabuddi, S., Tashakori, C., Kamboh, M.A., Korrani, Z.S., Saidur, R., Nodeh, H.R., et al. (2018). Kinetic and equilibrium adsorption of lead from water using magnetic metformin-substituted SBA-15. *Environ Sci Wat. Res.*, 4:549–58.
- [7]. Wang, S.Y., Vincent, T., Roux, J.C., Faur, C., Guibal, E. (2017). Pd(II) and Pt(IV) sorption using alginate and algal-based beads. *Chem Eng J.*, 313:567–79.
- [8]. Kratochvil, D. and Volesky, B. (1998). Advances in the biosorption of heavy metals. *Trends Biotechnol.*, 16:291–302.

- [9]. Volesky, B. and Holan, Z.R. (1995). Biosorption of heavy metals: selection of biomass type. *Rev. Biotechnol. Prog.*, 11:235–250.
- [10]. Gadd, G.M. (1990). Fungi and Yeasts for metal accumulation. In: Ehrlich, C.L. et al. (eds.), *Microbial Mineral Recovery.*, McGraw Hill, New York., 249– 276.
- [11]. Wilde, E.W., and Benemann, J.R. (1993). Bioremoval of heavy metals by the use of microalgae. *Biotechnol. Adv.*, 11:781– 782.
- [12]. Bai, S.R., and Abraham, T.E. (2001). Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigricans*. *Bioresource Technol.*, 79: 73 – 81.
- [13]. Bernard, E., Jimoh, A., Adigure, J.O. (2013). Heavy metals removal from industrial wastewater by activated carbon prepared from coconut shell. *Res. J. Chem. Sci.*, 3:3-9.
- [14]. Kirova, G.M., Velkova, Z., Gochev, V. (2012). Copper (II) removal by heat inactivated streptomycetes fradiae biomass: surface chemistry characterization of the biosorbent. *J. Biosci. Biotech.*, 20:77-82.
- [15]. Zhao, Y., Wang, J., Luan, Z., Peng, X., Liang, Z., and Shi, L. (2009). Removal of phosphate from aqueous solution by red mud using a factorial design. *Journal of Hazardous Materials*, 165(1–3): 1193–1199.
- [16]. Hashem, M.A. (2007). Adsorption of lead ions from aqueous solution by okra wastes. *Int J Phys Sci.*, 2(7):178–84.
- [17]. Badillo Almaraz, V., Trocellier, P., Davila Rangel, I. (2003). Adsorption of aqueous Zn(II) species on synthetic zeolites. *Nucl Instrum Methods Phys Res.*, 210:424–8.
- [18]. Panday, K.K., Prasad, G., Singh, V.N. (1985). Copper (II) removal from aqueous solutions by fly ash. *Water Res.*, 19(7):869-73.

