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REMOVAL OF LEAD (II) IONS FROM AQUEOUS SOLUTION USING CALCIUM ALGINATE BEADS

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ABSTRACT

The removal of metal ions from wastewaters using biopolymers such as calcium alginate is currently gaining importance in the treatment of industrial wastewaters. The objective of this study was therefore to investigate the capacity of calcium alginate to adsorb Pb(II) ions from aqueous solution. The parameters investigated were the effects of initial solution pH, contact time and initial Pb(II) concentration. Results were fitted to both the Langmuir and Freundlich isotherms. The optimum pH of adsorption was 5.0 while the maximum adsorption was achieved within 60 minutes at initial Pb(II) concentration of 20 mg/L. The experimental results showed that the R^2 value for the Langmuir and Freundlich isotherms were 0.9868 and 0.8564 respectively. The maximum biosorption capacity Q^o was 26.52 mgg^{-1}. From the Freundlich plot the value of *n*, which indicates the sorption intensity, was calculated as 4.15. These results show that calcium alginate is a good adsorbent for the removal of Pb(II) ions from wastewaters.

Keywords: Adsorption, Alginate, Isotherm, Langmuir, Freundlich.

INTRODUCTION

Heavy metal ions can be discharged into the environment from a variety of industrial activities. The presence of these heavy metals in the environment can be detrimental to a variety of living species, including man. Industrial wastewaters are considered the most important source of heavy metal pollution (Sun *et al*, 2010). Lead contamination in the environment exists as an insoluble form, and the toxic metals pose serious human health problems. Lead fulfills no essential function in the human body. It can enter the human body through uptake of food, water and air. Conventional methods for Pb(II) removal are well established. Some of these methods include chemical precipitation, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon etc. (Mathieckal and Yu, 1999). However, they are not only costly but also involve the use of chemicals that generate wastes which may be either hazardous or toxic (Cabuk *et al*, 2005). Biosorption, which involves the use of microorganisms (i.e. fungi, bacteria, algae and yeasts) as adsorbents to remove metal ions from wastewaters offers a potential alternative to existing methods. Numerous studies have demonstrated that microorganisms have the ability to remove heavy metals from wastewater with better performance and lower cost compared with conventional technologies (Moon *et al*, 2006).

Biopolymers such as alginates can uptake metal ions from aqueous solutions. They possess all of the biosorbent advantages and compete with other traditional methods such as ion exchange and activated carbon (Vijaya *et al*. 2008). Alginates are linear polysaccharides found in many algal species especially in brown algae and are also produced by certain bacteria (Arica *et al*, 2001). This study was therefore carried out to investigate the biosorption capacity of calcium alginate beads for Pb(II) ions in aqueous solution and to provide optimization data for the establishment of pilot plants.

MATERIALS AND METHODS

Preparation of Calcium Alginate

100 mL of 4 % (w/v) sodium alginate was prepared in a volumetric flask and was shaken until it became properly dissolved. The sodium alginate slurry was dropped through a 10 mL syringe into 2% (w/v) $CaCl_2$ solution (Dong, 2004). Durable spherical beads of the alginates were formed immediately. The beads were washed with distilled water and stored at 4 °C in distilled water until further use.

Adsorption Experiments

1000 mg/L solution of Pb(II) was prepared by dissolving 1.5986g of $Pb(NO_3)_2$ in 1 dm^3 of solution. Lower working concentrations were prepared from the stock solution by appropriate dilution.

The studies were carried out using a batch technique. The contact experiments were done in replicates in 100 mL conical flasks containing 50 mL of solution. The flask contents were mechanically agitated on a conical flask shaker at 150 rpm. The pH of the solutions were adjusted using 0.1 $moldm^{-3}$ NaOH and 0.1 $moldm^{-3}$ HNO_3. At the end of the reaction, the contents of the flask were separately filtered into polypropylene bottles using Whatman No 1 filter paper. The Pb(II) ion concentration in the solutions before and after contact with the adsorbent were determined using an Atomic Absorption Spectrometer (AA280AFS, Agilent Technologies, Santa Barbara, California, USA). The percentage metal removal (%) was calculated using the following equation:

$$\text{Removal \%} = \frac{(C_o - C_e)}{C_o} x\ 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The amount of each ion adsorbed was calculated from the difference between the added and equilibrium concentration by using the equation below (Babel and Opiso, 2007):

$$q_e = \frac{V(C_o - C_e)}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where q_e is the amount adsorbed in mg/g of the absorbent at equilibrium, C_o and C_e are the initial and the equilibrium concentrations in mg/L, respectively, *V* is the volume in litres of the solution used during the experiment and *M* is the mass of the adsorbent in grams.

The Effect of pH on the adsorption of metal ions from aqueous solution was studied by adding 100 mg each of the adsorbent into a 100 mL conical flasks containing 50 mL of 20 mg/L Pb(II) solutions. The pH of the samples were adjusted to different values: 3, 4, 5, 6, 7, 8, and 9 using 0.1 $moldm^{-3}$ HNO_3 and 0.1 $moldm^{-3}$

NaOH. The samples were agitated on a conical flask shaker for 120 minutes at 29 °C. The effect of contact time was investigated by varying the contact time from 10 – 150 minutes while keeping the other parameters constant (pH, 5.0; Adsorbent dosage, 100 mg; Temperature, 29 °C). The effect of initial metal ion concentration was determined by using Pb(II) solutions with concentrations ranging from 20 mg/L to 120 mg/L while keeping the other parameters constant.

Langmuir Adsorption Isotherm

This isotherm is often used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. It is expressed by the equation below.

$$\frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^o} \text{ .... } \quad (3)$$

Where K_L (L/g) is a constant related to the adsorption / desorption energy and Q^o (mg/g) is the maximum sorption upon complete saturation of the adsorption of the adsorbent (biosorbent) surface (Horsfall *et al*, 2004). A graph of C_e/q_e against C_e will have K_L (L/g) as the slope and Q^o (mg/g) as the intercept.

A dimensionless constant called the separation factor (R_L) was also calculated to test the favorability of adsorption which is an essential feature of the Langmuir isotherm (Hall *et al*., 1966). R_L is based on the equilibrium parameters and is defined as

$$R_L = \frac{1}{1 + K_L Co}$$

Where, K_L is the Langmuir isotherm constant and Co is the initial metal ion concentration (mg/L).

Hall *et al*. (1996) have shown through the use of mathematical calculations that the value of the parameter R_L indicates the type of isotherm involved as follows:

$R_L > 1$ Unfavorable; $R_L = 1$ Linear; $0 < R_L < 1$ Favorable; $R_L = 0$ Irreversible

Freundlich Adsorption Isotherm

The Freundlich isotherm was also used to correlate the adsorption equilibrium data in this work. The linearized form of the Freundlich equation is

$$logq_e = \quad logK_f + \frac{1}{n} logC_e \text{ .... } \quad (4)$$

Where q_e (mg/g) is the adsorption density, C_e is the concentration of metal ion in solution at equilibrium (mg/l), K_f and n are the Freundlich constants which determine the curvature and steepness of the isotherm (Akgerman and Zardkoohi, 1996). Also the value of *1/n* indicates the affinity of the adsorbate towards the biomass. A plot of *1og Ce* against *1og qe* gave the value of *1/n* and *1og* K_f from the slope and the intercept respectively.

RESULTS AND DISCUSSION

Effect of solution pH

The effect of the pH on the removal of Pb(II) ions from solution is presented in Fig. 1. As the figure shows, the highest removal percentage of Pb(II) was achieved at pH 5.0. The increase in Pb(II) removal with an increase in pH can be explained on the basis of a decrease in competition between protons and the metal cations for the surface sites and by the decrease in positive surface charge which results in a lower coulombic repulsion of the sorbing metal cation (Dianati – Tikali *et al*. 2004). Ozer and Ozer, (2003) and Ghorbani *et al*. (2008) have reported similar results

The effect of the contact time

The effect of the contact time on the removal of Pb(II) ions from solution is presented in Fig. 2. From the figure it can be seen that the removal percentage was highest at 60 minutes contact time and lowest at 150 minutes. As the adsorption process proceeded the adsorbate reached the saturation state and then the adsorbate tended to desorb back into the solution. Eventually the rates of adsorption and desorption became equal at equilibrium. When the system reached equilibrium, no net adsorption occurred further (Sari and Tuzen, 2008).

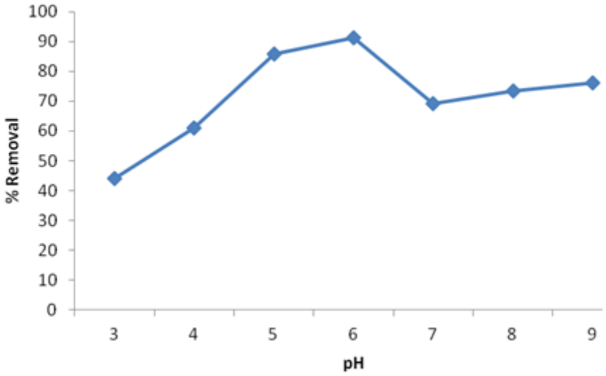

Fig. 1. Effect of solution pH on the removal lead (II) ions from aqueous solutions by calcium alginate

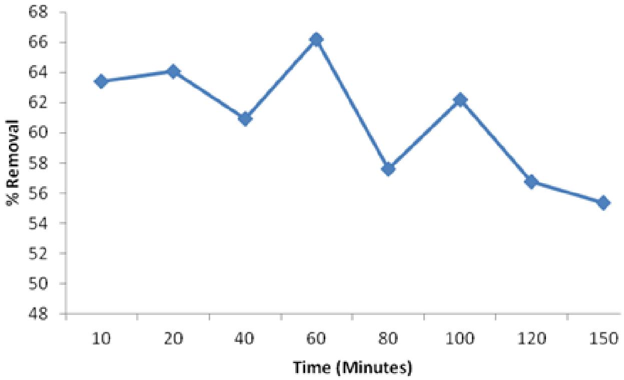

Fig. 2. Effect of contact time on the removal lead (II) ions from aqueous solutions by calcium alginate

The effect of initial metal ion concentration

The effect of initial metal ion concentration on the removal of Pb(II) ions from solution is shown in Fig. 3. From the figure it can be seen that the removal percentage of Pb(II) was highest at 20 mg/L concentration and decreased gradually afterwards with increase in the concentration of the ions. Occurrence of more unoccupied surface binding sites on the adsorbent at low concentration of metal ions could possibly be responsible for higher removal efficiency at low concentration. On the other hand, on increasing metal concentration, equilibrium between metal ions and the adsorbent's active sites were probably established very soon thus efficiency decreased due to the competitive effect of the metal ions for adsorptive sites (Zvinowanda *et al*. 2009).

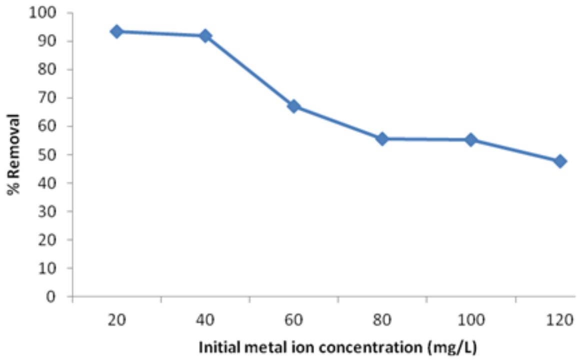

Fig. 3. Effect of initial metal ion concentration on the removal lead (II) ions from aqueous solutions by calcium alginate

Langmuir Isotherm

The Langmuir isotherm for the biosorption of Pb(II) by calcium alginate is shown in Fig. 4. The value of the coefficient of determination, R^2, for the Langmuir plot was found to be 0.9868. The Pb(II) ions therefore, exhibited a good fit of their equilibrium data for the Langmuir model which indicates a monolayer adsorption. Maximum biosorption capacity Q^o as calculated from the Langmuir plot was 26.52 mgg^{-1}. The values of the separation factors, R_L, presented in Table 1 (i.e. $0 < R_L < 1$) indicate that the adsorption process was a favourable one (Hall *et al*., 1966).

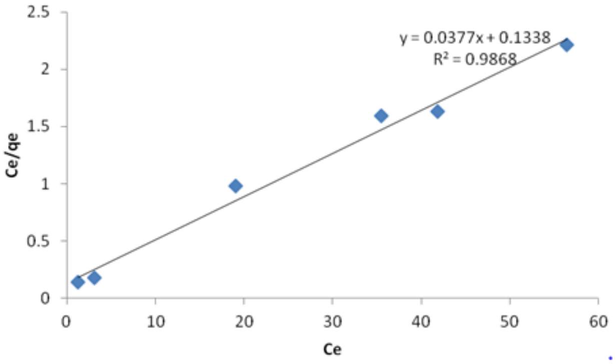

Fig. 4. Langmuir Isotherm for the removal lead (II) ions from aqueous solutions by calcium alginate

Table 1: Separation Factors (R_L), for the removal of Pb(II) ions from solution by calcium alginate beads

Initial Pb(II) ion concentration (mg/L)	Separation factor (R_L)
20	0.15
40	0.09
60	0.06
80	0.04
100	0.03
120	0.02

Freundlich isotherm

The Freundlich isotherm plot for the adsorption reaction is presented in Fig. 5. The value of the determination coefficient, R^2, was found to be 0.8564 which shows that the biosorption of Pb(II) ions onto the biosorbent had a good fit for both isotherms since the values are close to unity. The value of *n* was calculated from the slope of the Freundlich plot between Log qe and Log Ce. The value was 4.15 Lmg^{-1}. This value of *n* lies between 1 and 10 and according to Treybal (1980) this indicates a beneficial adsorption

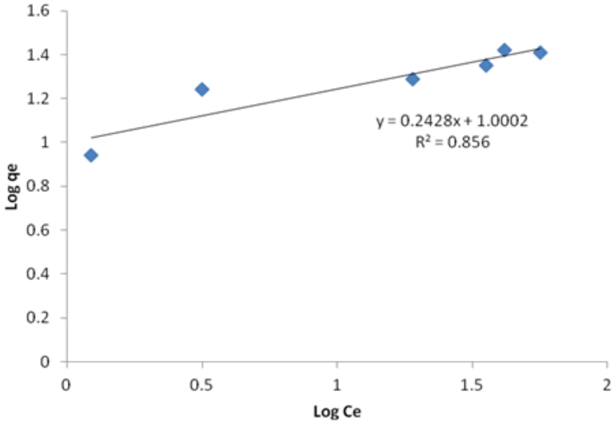

Fig. 5. Freundlich Isotherm for the removal of lead (II) ions from aqueous solutions by calcium alginate

Conclusion

The results of this study showed that the maximum biosorption was achieved at pH of 5.0. Also maximum adsorption was achieved at 60 minutes of contact time of the adsorbate with the adsorbent. Adsorption was higher at lower working solution concentrations than at higher concentrations. The adsorption isotherms plotted for the data showed that the experimental data fitted the Langmuir ($R^2 = 0.9868$) isotherm better than the Freundlich isotherm indicating a monolayer adsorption. These results indicate that Pb(II) ions removal by calcium alginate is a low cost wastewater treatment option and can be effectively used in small scale treatment plants.

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