

Comparative equilibrium studies of sorption of Pb(II) ions by sodium and calcium alginate

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Received 29 August 2007; revised 5 December 2007; accepted 8 January 2008

Abstract

The absorption of Pb(II) ions from aqueous solution by different alginate compounds was studied in a batch sorption system. Water soluble sodium alginate and insoluble calcium alginate beads were investigated. The lead-binding capacity of both alginate compounds was highest within the pH range 6–8. The binding capacities and rates of Pb(II) ions by alginate compounds were evaluated. The Langmuir, Freundlich, and Bruneaur, Emmet and Teller (BET) sorption models were applied to describe the isotherms and isotherm constants. Sorption isothermal data could be well interpreted by the Langmuir model. The results obtained through the study suggest that alginate compounds are favorable sorbents. The largest amount of Pb(II) ions were bound by sodium alginate although the difference between two compounds was slight. Therefore, alginate substances may be considered as an alternative for sorption and removal of Pb(II) ions from wastewaters.

Key words: heavy metal; lead; equilibrium study; alginate; wastewater

Introduction

The effluents of industrial wastewaters often contain considerable amounts of toxic and polluting heavy metals. It is well known that heavy metals such as Hg, Pb, Cr, Ni, Cu, Cd, and Zn usually tend to accumulate in living organisms and are highly toxic when absorbed into body (Wan Ngah *et al.*, 2004). Releases of Pb(II) ions to the environment have been continuously increased as a result of industrial activity and technological development, posing a significant threat to the environment and public health because of toxicity, incremental accumulation in the food chain and persistence in the ecosystem (Markowitz, 2000). Owing to the wide use of heavy metals, including lead, the efficient removal of them from wastewaters is an important and widely studied research area where a number of technologies have been developed over the years (Deans and Dixon, 1992) including filtration, chemical precipitation, adsorption, electrodeposition, and membrane systems. All these approaches have their inherent advantages and limitation, but most of them either expensive or low effective, particularly, in dilute solutions (Schmuhl *et al.*, 2001). In recent years studies on polymers binding metal ions have increased significantly, where ion-exchange abilities are used in nuclear chemistry, electrochemistry, hydrometallurgy, and environmental protection (Kaminsk and Modrzejewska, 1997). Chelation

ion exchange takes advantage of the three-dimensional structure of the molecules to chelate and remove ions (Deans and Dixon, 1992). This approach is inherently attractive since only the toxic metals are removed while the harmless ions can be released into the environment. Some of the best chelation ion exchange materials are biopolymers. Biopolymers are industrially attractive because they possess a capability of lowering transition metal-ion concentration to parts per billion level, they are widely available and environmentally safe (Schmuhl *et al.*, 2001; Khotimchenko *et al.*, 2007). The group of biopolymers includes cellulose, pectin, carrageenans, lignin, some proteins, chitin, and alginates.

This study focuses on the alginate salts and their Pb(II) removing capacity in aqueous solutions. The retention of heavy metals on calcium alginate gels has become an increasing alternative technique to the treatment of aqueous effluents (Jodra and Mijangos, 2001). Alginic acid and its salts (alginates) occur mainly in marine brown seaweeds making main part of their polysaccharides and comprising up to 40% of the dry matter (Rossel and Srivastava, 1984). Red seaweeds belonging to the Corallinacea family also contain these substances (Okazaki *et al.*, 1982), and bacteria of the genera *Pseudomonas* and *Acetobacter* are known to contain acetylated alginates (Sabra *et al.*, 2001). By their chemical nature, alginates consist of a linear chain of (1–4)-linked residues of β -D-mannuronic acid and α -L-guluronic acid in different proportions and sequential

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arrangements. The most common arrangement is a block copolymer, in which long homopolymeric sequences of guluronic acid residues (G–G blocks) and similar sequences of mannuronic acid residues (M–M blocks) are intercalated between sequences of mixed composition (M–G blocks) (Sidsrod and Draget, 1996).

According to the “egg-box” model (Grant *et al.*, 1973), the metal binding mechanism of alginates is provided by formation of the covalent bonds between polysaccharide carboxyl groups and two valence metal ions. Since alginic acid rarely occurs in natural sources, the great interest is given to its salts. Usually sodium and calcium salts are used in experiments. In this case chelation is presented by ion exchange process between sodium/calcium ions and ions of heavy metals. As sodium and calcium possess quite different properties and form water soluble and insoluble alginates, respectively, it is of interest to compare these two types of alginate salts regarding their metal binding capacity.

In this study the equilibrium of sorption of Pb(II) ions by sodium and calcium salts of alginic acid were investigated. The influence of experimental conditions such as pH, agitation period, agitation rate, and initial concentrations were studied. The Langmuir, Freundlich, and Brunauer, Emmet and Teller (BET) equations were used to fit the equilibrium isotherm. This will be useful for further application of system design in the treatment of practical waste effluents.

1 Materials and methods

1.1 Alginate preparation

Sodium alginate (type HV) without additives was obtained from Kelco (California, USA). Calcium alginate was prepared as follows. A 200-g of sodium alginate was suspended in 1,000 ml of 70% ethanol. With intensive shaking, 8 g of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 100 ml of 70% ethanol were added. Calcium alginate obtained was separated with a porous glass filter in a 40- μm mesh, rinsed with 500 ml of 70% ethanol, and dried at 60°C.

1.2 Alginate analysis

The uronic acid content of original sodium alginate and prepared calcium alginate was determined colorimetrically by the *m*-hydroxydiphenyl method and expressed in percentage (Blumenkrantz and Asboe-Haunsen, 1973). The calcium content in the calcium alginate sample was assayed using atomic-absorption spectrometry (Model AA-855, Nippon Jarrel Ash, Japan) and expressed in mg/g and mg equivalents/g of sample (Kostecka, 2000). The ratio of carboxyl groups forming a calcium salt was calculated as a calcium : uronic acid content ratio expressed in percentage and mg/g. Intrinsic viscosity of original sodium alginate was determined in 0.05 mol/L NaCl/0.005 mol/L Na-oxalate at 25.0°C and pH 6.0 using an Ubbelohde viscosimeter (Model HVU 482, Herzog, Germany). The intrinsic viscosity is related empirically to the molecular weight by the Mark-Howink relation (Kravtchenko and Pilnik, 1990).

1.3 Experimental procedures

Stock solutions (1.0 g/L) of Pb(II) ions was prepared by using analytical-reagent grade PbCl_2 (BDH). The stock solution was then diluted to give standard solutions of appropriate concentrations with controlled pH at 6.0 by addition of either 0.1 mol/L HCl or 0.1 mol/L NaOH. Batch sorption experiments were conducted in 250 ml beakers and equilibrated using a magnetic stirrer. Then 50 ml aliquots of these standard solutions were placed in 250 ml beakers and added with 50 ml of solution containing 0.2 g of dry sodium alginate or 50 ml of suspension with 0.2 g of dry calcium alginate. Removal of alginate compounds from Pb(II) solution was performed by centrifuging at 3,000 r/min for 10–20 min and following filtration through glass filter with a pore size 100–120 μm . Concentration of Pb(II) ions in supernatant was analyzed using an atomic absorption spectrophotometry method. The effect of Pb(II) sorption was studied in pH range 2–10. The pH of the initial solution was adjusted to the required pH value using either 0.1 mol/L HCl or 0.1 mol/L NaOH. Alginates were equilibrated at the particular pH for about 120 min at 400 r/min and at an initial Pb(II) concentration of 0.1 g/L using a bath controlled at 30°C. The effect of agitation period also studied to determine the optimum condition for sorption of Pb(II) ions. For batch kinetic studies 0.08 g calcium alginate or 8 ml of solution containing the same amount of dry sodium alginate were equilibrated at optimum condition as mentioned earlier. The sorption system was placed in 250 ml beakers and stirred by a magnetic stirrer. At preset time intervals, the aqueous samples (5 cm^3) were taken and the concentration of Pb(II) was analyzed.

Sorption equilibrium studies were conducted at optimum condition using a contact time of 120 min at pH 6 using a bath controlled at 30°C. Isotherm studies were conducted with a constant alginate preparation amount (0.1 g) and varying initial concentration of Pb(II) in the range of 0.1–1.0 g/L. Each experiment was at least duplicated under identical conditions.

The metal accumulation (q) was determined as follow:

$$q_e = (C_0 - C_e)V/W \quad (1)$$

where, C_0 (mg/L) is the initial Pb(II) concentration, C_e (mg/L) is the final or equilibrium Pb(II) concentration, V (ml) is the volume of the Pb(II) solution and W (g) is the weight of the dry samples of calcium or sodium alginate.

The amount of the metal bound by the alginate compounds was expressed in mg per g of the dry sorbent.

2 Results and discussion

2.1 Alginate substrate

The uronic acid concentration of the sodium and calcium alginate used in experiment was 77.3%. The intrinsic viscosity of original sodium alginate used for preparation of calcium alginate was 1,270 ml/g. Calculated molecular weight of the original sodium alginate and calcium alginate used in experiments was 403×10^3 Da. The calcium content

of the calcium alginate sample was 7.25%. This indicates 82.5% of carboxyl groups in preparation are presented in calcified form, which means calcium content in the sample is 38 mg/g of the polysaccharide. Calcium alginate beads were not soluble in water.

2.2 Effect of pH

The pH of solution strongly affects the sorption capacity of any binding material including the alginate derivatives regarding Pb(II) ions. Therefore, the measurement of the sorption capacity at various pH values means estimation of selectivity of alginate compounds to protons in comparison to Pb(II) ions. Fig.1 shows the effects of pH on the lead binding with sodium alginate and calcium alginate. The maximum lead uptake by sodium alginate was found within the pH range of 4–8 whereas it is for calcium alginate was found within pH 6–8. At pH values higher than 8 there was a dramatic decrease of the uptake capacity of all compounds, as a result of unstable polysaccharides (Lofgren *et al.*, 2002) and an insoluble Pb(II) hydroxide formation which barely be bound via ion exchange mechanism. Below pH 8, sorption gradually increases with the rise of pH. This could be explained by the phenomenon that the lower the pH, the more protons are available to carboxyl groups, reducing the number of binding sites in the alginate molecule.

2.3 Effect of agitation period

Figure 2 shows the effects of agitation period on the metal uptake of alginate. The time required to reach equilibrium can be found with different Pb(II) uptake values obtained after various batch sorption periods. The

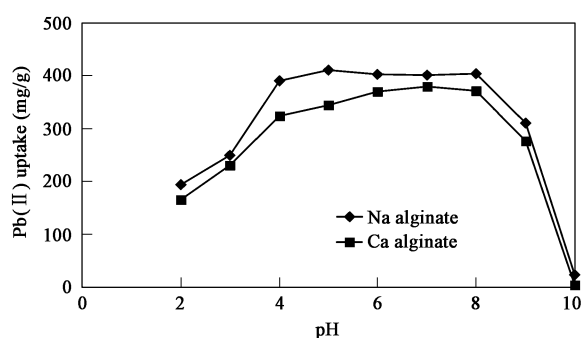


Fig. 1 Effect of pH on the Pb(II) uptake of calcium and sodium alginates.

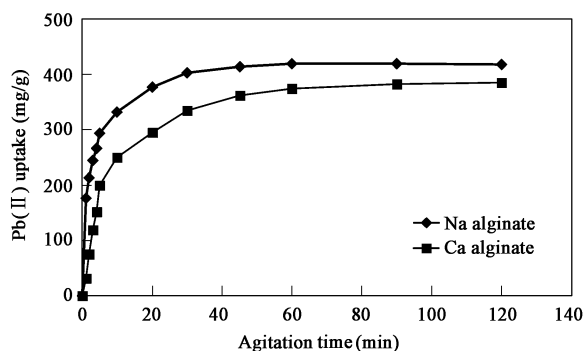


Fig. 2 Effect of agitation period on the Pb(II) uptake of calcium and sodium alginates.

amount of Pb(II) bound by sodium and calcium alginates increases within the beginning of agitation period and attains equilibrium at about 60 min. The main differences in the sorption rates between these compounds were observed within the first minutes of the agitation period. Therefore, during the first minute of the period soluble sodium alginate bound 42% of their highest uptake under given conditions whereas insoluble calcium alginate bound only 8%. In 10 min the differences of the Pb(II) uptake between soluble and insoluble alginate substances became insignificant. The longer period required for calcium alginate to bind Pb(II) ions is probably dependent on the rate of metal diffusion into alginate beads.

2.4 Effect of agitation rate

The influence of agitation rate on the binding of lead by alginate compounds was studied using following stirring speeds: 100, 200, 300, 400, and 500 r/min. It was found that agitation rate has no influence on the values of lead uptake by sodium alginate and calcium alginate.

2.5 Equilibrium studies

Removal of lead by sodium alginate and calcium alginate as a function of initial metal concentration was studied at pH 7. Since the data for the curve are obtained at the same temperature, the curve is an isotherm. Therefore, there is a defined distribution of the metal ions in the sorption system, which can be expressed by one or more isotherms (Findon *et al.*, 1993). Fig.3 shows the sorption curve indicating the amount of lead ions bound to the alginate molecules increasing with the increase of the initial metal concentration. The isotherms are characterized by the initial region, which is represented as being concave to the concentration axis.

The isotherm reaches a plateau, which can typically be described by the Langmuir isotherm (2). The results were analyzed with Langmuir, Freundlich, and BET adsorption isotherms. The Langmuir equation is often used to describe equilibrium sorption isotherm, which is valid for monolayer sorption with a finite number of identical sites and is given by:

$$C_e/q_e = (C_e/q_{\max}) + (1/q_{\max})b \quad (2)$$

where, q_{\max} (mg/g) is the maximum sorption at monolayer, C_e (mg/L) is a final equilibrium concentration of Pb(II), q_e

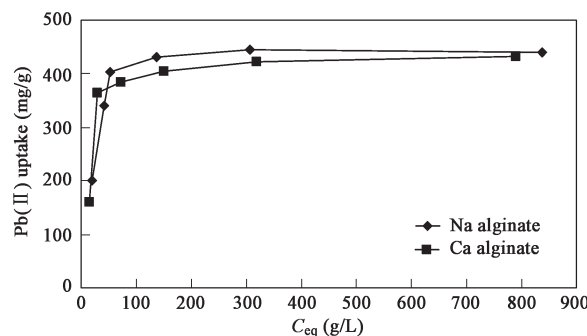


Fig. 3 Equilibrium sorption of Pb(II) from aqueous solution using calcium and sodium alginates.

(mg/g) is the amount of Pb(II) bound per unit weight of the alginate compound at final equilibrium concentration, b (ml/mg) is the Langmuir constant related to the affinity of binding sites (ml/mg) and is considered as a measure of the energy of sorption.

The following linearized plot of the Langmuir equation was used in this study:

$$C_e/q_e = (C_e/q_{\max}) + (1/q_{\max})b \quad (3)$$

which gives q_{\max} and b .

The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where, K_F (mg/g) and n are Freundlich constants indicating sorption capacity and intensity, respectively. K_F and n can be determined from linear plot of $\log q_e$ against $\log C_e$.

The BET equation is given by:

$$\frac{C_e}{(C_0 - C_e)q_e} = \left(\frac{1}{Bq_{\max}} \right) + \left(\frac{B-1}{Bq_{\max}} \right) \left(\frac{C_0}{C_e} \right) \quad (5)$$

where, q_{\max} (mg/g) is the maximum adsorption at monolayer, C_e (mg/L) is the equilibrium concentration of Pb(II), C_0 (mg/L) is the saturation concentration of the solute, q_e (mg/g) is the amount of Pb(II) adsorbed per unit weight of the alginate compounds at equilibrium concentration and B is the BET constant expressive of the energy of interaction with surface.

Calculated results of the Langmuir, Freundlich, and BET isotherms are given in the Table 1. The results show that sorption of Pb(II) by alginate compounds were better correlated ($R^2 > 0.98$) with the Langmuir equation as compared to Freundlich and BET equation within studied concentration range. It can be explained by the presence of finite number of homogenous binding sites on the alginate molecules, which is the basic condition of the Langmuir

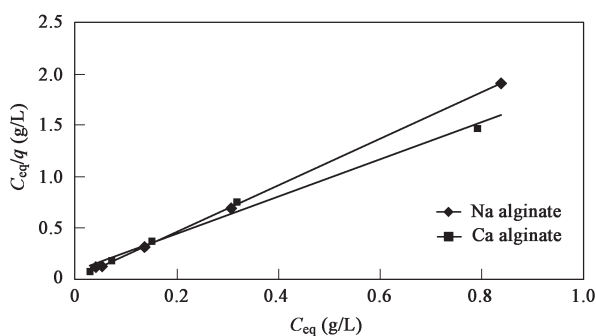


Fig. 4 Langmuir plot for the sorption of Pb(II) by calcium and sodium alginates.

Table 1 Langmuir, Freundlich, and Brunauer, Emmet and Teller (BET) isotherm constants and correlation coefficients of Pb(II) binding capacity of sodium and calcium alginate

Sample	Langmuir			Freundlich			BET		
	b (ml/mg)	q_{\max} (mg/g)	R^2	K_F (mg/g)	n	R^2	q_e (mg/g)	B	R^2
Na alginate	204.08	442.8	0.9997	0.717	16.13	0.777	52.3	13.749	0.7576
Ca alginate	22.62	551.1	0.9885	0.748	9.28	0.8568	111.2	5.106	0.9501

Table 2 R_L values based on the Langmuir equation

Pb(II) initial concentration (mg/ml)	R_L value	
	Na alginate	Ca alginate
0.2	0.0239	0.1810
0.4	0.0121	0.0995
0.6	0.0081	0.0686
0.8	0.0061	0.0524
1.0	0.0049	0.0423

sorption model. Fig.4 shows the langmuir plot for the sorption of Pb(II) by calcium and sodium alginates. According to calculated Langmuir parameters highest binding capacity is characteristic of calcium alginate although sodium alginate possesses a little lower sorption activity. The sorption coefficient b that is related to the apparent energy of sorption for sodium alginate was quite greater than that of calcium alginate.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is used to predict if an adsorption system is “favourable” or “unfavourable”. The separation factor, R_L is defined by:

$$R_L = 1/(1+bC_0) \quad (6)$$

where, C_0 (mg/ml) is the initial Pb(II) concentration and b (ml/mg) is the Langmuir adsorption equilibrium constant. If the results are in the range between 0 and 1, the adsorption can be considered as favorable. The R_L values of both alginate compounds studied were in the range of $0 < R_L < 1$ (Table 2), which indicates that the sorption of Pb(II) by these substances are favorable. The mechanism of sorption is to be elucidated by binding of the metal ions with carboxyl groups located on the alginate molecules and acting as the binding sites. The results show that intensity of binding processes and sorption capacity does not depend on solubility of the compound but closely relates to the number of the carboxyl groups in its structure (Grant *et al.*, 1973). This implies formation of the junction zones between carboxyl groups of alginate and Pb(II) according to the “egg-box” model.

The main difference between the samples of the alginate compounds is the metal ion bound to the initial sample of polysaccharide. Sodium is a one-valence metal and its bonds with polysaccharides are easily broken. Chemical bonds between alginate and calcium are much stronger and Ca(II) is competing with Pb(II) ions. Therefore, comparison of the Pb(II)-binding activity of these two salts of alginate is interesting. It was found earlier that affinity of alginate to Pb(II) is much higher than to Ca(II) (Hartmeier *et al.*, 1992; Jodra and Mijangos, 2001). Therefore, the ion-exchange process occurs due to the release of Ca(II)

ions pectate molecule with the simultaneous binding of the Pb(II) ions. Results of the measurement of the Pb(II) sorption capacity showed that both polysaccharides binds similar amount of Pb(II) ions under given conditions. However, evaluation of the results with use of Langmuir model showed that coefficient of affinity of sodium alginate is 9 times higher than that of calcium alginate. This may be explained by the presence of intensive ion-exchange process in the case of calcium alginate reducing its affinity.

3 Conclusions

Alginates are the favorable materials for removal of Pb(II) from disposal materials and wastewaters. Binding of the Pb(II) ions is a fast process being most efficient within the pH range of 6 and 8. Both sodium alginate and calcium alginate can bind a large amount of Pb(II) ions, but affinity of calcium alginate to Pb(II) is much lower. Despite its high sorption capacity calcium alginate may be less effective than sodium alginate. It can be concluded that compounds based on sodium alginate are effective substances for the collection of metal ions in higher concentrations. The next steps of the studies should be performed to estimate lead binding capacity of these compounds in extremely low metal concentrations.

Acknowledgements

This work was supported by the Federal Agency of Science and Innovation of the Ministry of Education and Science of Russian Federation (State contract No. 02.512.11.2090).

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