



Biosorption of uranium(VI) from aqueous solution using calcium alginate beads

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ABSTRACT

In this paper, sorption potentials of uranium ions were studied using alginate polymer beads in diluted aqueous solutions. The ability of alginate beads to adsorb uranium(VI) from aqueous solution has been studied at different optimized conditions of pH, U(VI) concentration, contact time, biomass dosage and temperature. In order to determine the adsorption characteristics, Langmuir, Freundlich, and Dubinin–Radushkevich adsorption isotherms were applied to the adsorption data. The thermodynamic parameters such as variations of enthalpy ΔH , entropy ΔS and variation of Gibbs free energy ΔG were calculated from the slope and intercept of $\ln K_d$ vs. $1/T$ plots. The results suggested that alginate beads could be suitable as a sorbent material for adsorption and removal of uranium ions from dilute aqueous solutions.

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1. Introduction

The increase in industrial activities has intensified environmental pollution and the deterioration of some ecosystems with the accumulation of pollutants such as heavy metals, synthetic compounds, waste nuclear liquids, etc. [1]. Mining and metallurgical waste waters are considered to be the major sources of heavy metal contamination. Therefore the need for economic and effective methods for the removal of metals from environmental samples has resulted in the development of new separation technologies [2]. It is considered to be a potential process for the removal of metals from solutions, not only for toxic metal removal, but also for radionuclides removal [3]. Biosorption is a term that describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution [4].

Synthetic polymers such as ion-exchange and chelating resins have been widely used as effective adsorbents to collect radionuclides, toxic metals, precious metals and base metals from aqueous solutions [5–7]. Recently, naturally occurring biopolymers have been known to exhibit excellent adsorption ability for multivalent metal ions [8,9]. Biosorption in algae has mainly been attributed to the cell wall properties where both electrostatic attraction and complexation play an important role. Alginate occurs in all brown algae. It may be present in both cell wall matrix and in the mucilage or intercellular material [4]. Alginate occurring

in brown seaweeds [10] is a biopolymer carrying carboxyl groups capable of forming complexes with metal cations. The ability of alginate to form gels by ion-exchange reaction with multivalent metal ions suggests its use as a metal adsorbent. Many recent studies have addressed the collection of heavy metals by alginic acid [11–13]. The alginic acid and alginates are thus likely to be potentially useful adsorbents for the removal of radionuclides from waste solutions. However, a limited amount of information is available concerning the uptake behavior of radionuclides on these polymer gels [14].

Alginate or alginate, the salt of alginic acid, is the common name given to a family of linear polysaccharides containing 1,4-linked β -D-mannuronic (M) and R-L-guluronic (G) acid residues arranged randomly along the chain. The salts of alginic acid or alginate with monovalent ions (alkali metals and ammonium) are soluble, whereas those with divalent or polyvalent metal ions (except Mg^{2+}) and the acid itself are insoluble [15]. The carboxylic groups are generally the most abundant acidic functional groups in the alginate polymer, and the sorption capacity of algae is directly related to the presence of these metal-binding sites. The most abundant other acidic functional group in brown algae is the sulfonic acid and hydroxyl groups [16]. In the presence of calcium or other divalent cations, alginate gels adopt a structure of cross-linked chains known as the “egg-box” model [17].

Alginate may be converted into a hydrogel via cross linking with divalent calcium ions as an “egg box” model where each divalent metal ion binds to two carboxyl groups as adjacent alginate molecules [18]. Some advantages of alginate beads are biodegradability, hydrophilicity, presence of carboxyl groups and natural origin. The presence of carboxyl groups in the alginate structure

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enhances the adsorption of many metal ions compared with other adsorbents [19].

Uranium is often released into the environment from mining and milling facilities [20]. Excessive amounts of uranium have found their ways into the environment through the activities associated with the nuclear industry. Uranium contamination poses a threat in some surface and groundwaters [21]. Hence the removal of uranium from wastewater is important not only for the nuclear industry, but also for environmental remediation [22]. There is a need in controlling the distribution of the heavy metals, especially uranium series radionuclides into the environment [23]. Microbial biomass can serve as efficient and safe biosorbent in treating the heavy metal pollution [24,25] and this property has been exploited to recover uranium from aquatic systems [26–28].

This study aims the feasibility of using alginate beads for the removal of uranium ions from aqueous solutions. The effects of different parameters such as initial pH, shaking time and initial uranium ions concentration and biopolymer dosage on the sorption were investigated. Equilibrium modeling was carried out using the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm equations.

2. Materials and methods

2.1. Reagents

The reagents used in the experiment were of analytical reagent (AR) grade. $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and sodium alginate powder was obtained from Merck and Fluka, respectively, and used without further purification. Distilled water (Millipore Ultra Pure Water System) was used in investigations. A solution of 1000 mg/L of uranium was prepared from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) by dissolving the salt in deionized distilled water. The stock solution was diluted to prepare working solutions. More diluted solutions were prepared daily as required.

To calibrate the pH-meter the buffer solutions (pH 4, 7 and 9) were used. The pH of each test solution was adjusted to the required value with diluted HNO_3 and Na_2CO_3 solutions at the start of the experiment. Reagent blank were run for every sample solution. Buffering was not used in the experiments due to unknown effects of buffer compounds on adsorption.

2.2. Instrumentation

Uranium(VI) concentrations were determined by UV–vis spectrophotometer (Shimadzu UV–vis 1601 Model Spectrophotometer). The adsorption experiments have been studied by batch technique using a thermostated shaker bath Model GFL-1083. Hanna Instrument 8521 Model pH meter was used to measure pH. A Hettich Zentrifugen Rotofix 32 Model digital centrifuge was used to centrifuge the samples. An oven (Electro-Mag M420 Model) was used to dry the samples.

2.3. Preparation of the alginate beads

Calcium alginate beads were prepared by dropwise addition of 2% of viscous sodium alginate solution (w/v) to 0.5 mol/L CaCl_2 solution, maintaining the temperature at 4 °C. After 1 h stirring, the resulting gel beads were stored in 0.5 mol/L CaCl_2 solution for 1 h at room temperature. Na-alginate reacts with CaCl_2 to form beads and cross-linked Ca-alginate was formed. During the process, the water soluble sodium alginate was converted into water insoluble calcium alginate beads. The resultant beads were stored after washing with de-ionized water to remove CaCl_2 from the bead surfaces. The beads were collected by filtration and the excess water was adsorbed on filter paper. The beads were then dried at room temperature for 48 h. The loss of weight after drying was 98% and was

accompanied by an average diameter reduction of alginate beads from 3.07 ± 0.16 to 0.71 ± 0.20 mm. Volume decreased $98 \pm 1.56\%$ after dried for 48 h at room temperature.

The advantages of using dry alginate beads instead of the gel type are ease of handling and storage, greater precision during weighing and greater stiffness.

2.4. Batch sorption experiments

All the sorption experiments were performed using 0.025 g of Ca-alginate beads suspended in 25 mL of $[\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ uranium solution in a polyethylene (PE) flask at selected pH. The flasks were shaken at different temperatures and mixing times. The solution was separated from the solids by filtration. Then the residual uranium(VI) ions in aqueous solution were determined spectrophotometrically using PAR (1-(2-pyridylazo-resorcinol)) method at 510 nm using spectrophotometer [29]. The amount of adsorbed uranium(VI) was calculated from the difference of the uranium concentration in aqueous solution before and after adsorption. The adsorption percentage (%) and distribution constant (K_d) (mL/g) were calculated using the following equations:

$$\% \text{Adsorption} = \frac{C_i - C_f}{C_i} 100 \quad (1)$$

where C_i and C_f are the concentrations of the metal ion in initial and final solutions respectively.

$$K_d = \frac{\text{amount of metal in adsorbent}}{\text{amount of metal in solution}} \frac{V}{m} \text{ mL/g} \quad (2)$$

where V is the volume of the aqueous phase (mL), m is the weight of the polymer gel beads (g).

All experiments were always performed in duplicates. The limit of experimental error of each duplicate was $\pm 5\%$.

3. Results and discussion

3.1. Properties of Ca-alginate

Alginate is a natural polymer and may be converted into hydrogels via cross-linking with divalent calcium ions. It has been preferred over other materials because of its advantages including biodegradability, hydrophilicity, presence of carboxylic groups and natural origin [30].

The higher specificity of polyguluronic acid residues for divalent metals is explained by its “zigzag” structure where the Ca^{2+} ions can accommodate more easily. The alginates are thought to adopt an ordered solution network, through inter-chain dimerization of the polyguluronic sequences in the presence of calcium or other divalent cations of similar size (Fig. 1). The rod-like shape of the poly-l-guluronic sections results in an alignment of two chain sections yielding an array of coordination sites, with cavities suitable for calcium and other divalent cations because they are lined with the carboxylate and other oxygen atoms of G residues [31]. The regions of dimerization are terminated by chain sequences of polymannuronic acid residues. As a result, several different chains may become interconnected and this process promotes gel network formation. The higher the degree of linkage, the greater the resulting viscosity occurs [32].

A schematic representation of the alginate’s structure is given in Fig. 1, which shows the “egg-box junction” of this configuration. It should be noted that this particular structure of the alginates leaves free carboxylic functional groups in the H-form, which may interact with metal ions [33].

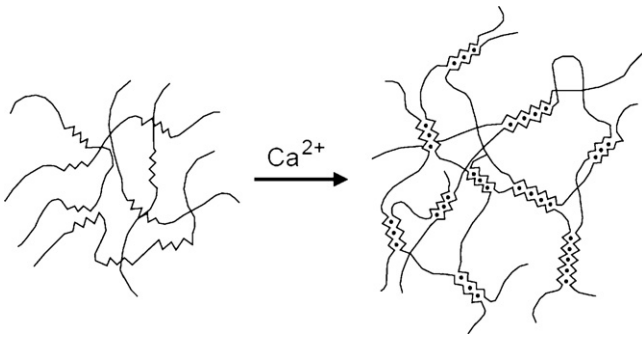


Fig. 1. Schematic representation of the calcium-induced gelation of alginate in accordance with the “egg-box” structure [34].

3.1.1. Surface morphology

The scanning electron microscopy (SEM) image of the surface of the calcium alginate beads are shown in Fig. 2 (a) at 100 \times magnification and (c) at 2200 \times magnification. After uranium sorption, SEM image of Ca-alginate beads are shown in Fig. 2 (b) at 100 \times magnification and in Fig. 2 (d) at 2200 \times magnification. As seen from figures the calcium alginate beads generally have a spherical shape. The average size of gel particles estimated from SEM image was in the region of 0.6–1.05 mm. Pores with different size were observed as shown from Fig. 2. These pores are very suitable places for the sorption of uranium ions. The calcium alginate beads are stable in terms of their morphology after uranium sorption.

3.2. Effect of initial pH

Earlier studies on heavy metal biosorption have showed that pH is an important parameter affecting the biosorption process. It also influences the precipitation of metal ions and ionization of surface functional groups. The effect of initial pH on uranium ion

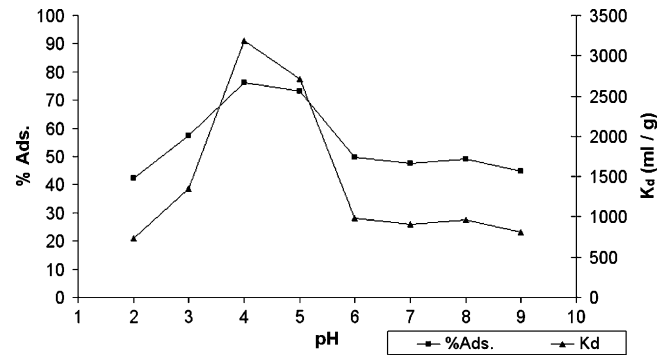


Fig. 3. The effect of pH on adsorption of U(VI) onto calcium-alginate (U : 25 mg/L, m : 25 mg, V : 25 mL, t : 120 min, T : 25 $^{\circ}$ C).

biosorption of Ca-alginate was studied at 25 mg/L initial uranium concentration at 25 $^{\circ}$ C. The effect of the pH on U(VI) adsorption by calcium-alginate was studied in the pH region between 2.0 and 9.0. For that purpose, the pH values of uranium solutions were adjusted to a range of 2.0–9.0 prior to the experiments. As seen in Fig. 3, the adsorption of uranium increases from 42% to 76% with an increase in pH of the solution from 2.0 to 4.0 and then decreases to 50% at pH 6.0.

Parallel experiments without the biomatrix were carried out under the similar experimental conditions and it was observed that there was no precipitation of metal ion. This confirms that the decrease in the concentration of metal ion was due to biosorption and not because of the formation of insoluble hydrolysed species of the metal ions. Efficient sorption of uranium was noted to be between pH 4 and 5 of the aqueous solutions

Algal biomasses contain high content of carboxyl groups from mannuronic and guluronic acids on the cell wall polysaccharides, which suggests that the biosorption process could be influenced by changes in the solution pH [35]. The Ca-alginate beads have a

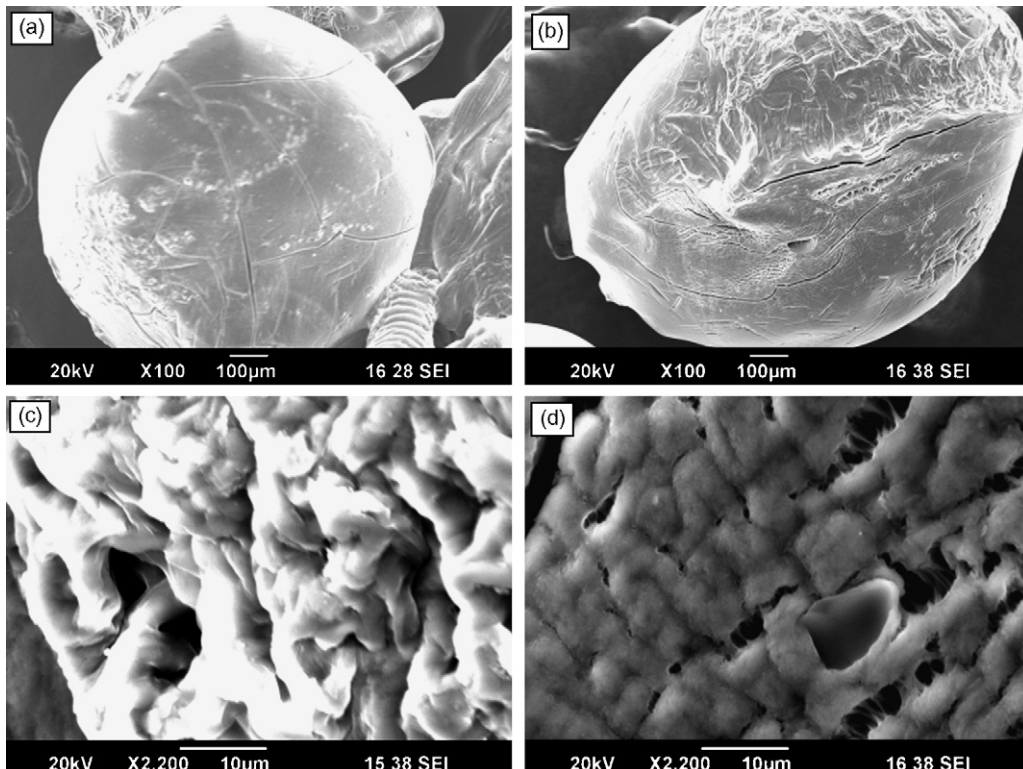


Fig. 2. SEM image of covalently Ca-alginate beads before (a, c) and after (b, d) uranium sorption.

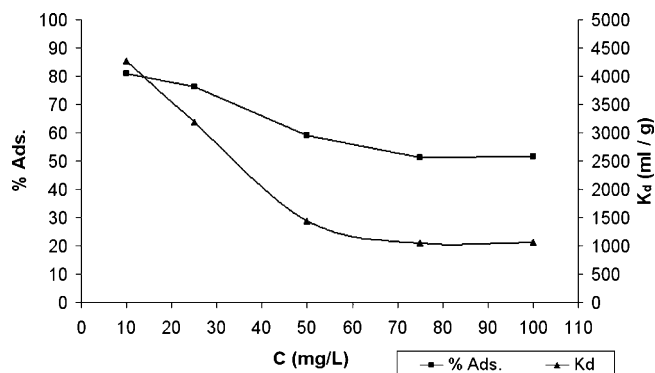


Fig. 4. Variations of adsorption (%) and K_d vs. initial uranium concentration (m : 25 mg, V : 25 mL, t : 120 min, pH : 4.0, T : 25 °C).

maximum sorption (76%) at pH 4.0. The high adsorption levels of the Ca-alginate beads between pH 4 and 5 indicate. At low pH , the uranyl exists primarily as a mononuclear, aqueous ionic species. In general, uranyl becomes highly hydrolyzed and forms oligomeric solution species with increasing pH [36].

The metal ion binding in biosorption could be attributed to several mechanisms such as ion exchange, complexation, electrostatic attraction and microprecipitation. For algae biomass, ion exchange has been considered as a main mechanism responsible for metal sequestering [37]. The ion exchange mechanism of uranyl ions binding to the biomass is complicated since that the uranium cation UO_2^{2+} is hydrolyzed in aqueous solutions within the range of the sorption system pH . Portioning of the hydrolysed uranium species depends on the solution pH and the total uranium concentration in the solution. In the range of acidic to near neutral pH values, four major hydrolysed complex ions, UO_2^{2+} , $(UO_2)_2(OH)_2^{2+}$, UO_2OH^+ , $(UO_2)_3(OH)_5^+$ exist in the solution [38].

According to Collins and Stotzky, the hydrolyzed species can obviously be sorbed better than the free hydrated ions. Particularly the monovalent hydrolyzed ions, compared with the divalent hydrolyzed ions, have even higher affinity to the biomass in ion exchange with protons because they could replace single protons on separate binding sites in the biomass [39]. The percentage of UO_2^{2+} in Ca-alginate increases with increasing pH of the system up to pH 4.0. The lower pH suppresses the enhancement of uranium biosorption occurring normally because of the hydrolyzed ions.

The uranium uptake reached a maximum at pH 4.0 before decreasing. Therefore, pH 4.0 was selected for further experiments.

3.3. The effect of initial uranium concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of uranium between the aqueous and solid phases. The biosorption of U(VI) was carried out at different initial concentrations ranging from 10 to 100 mg/L at pH 4.0 for Ca-alginate beads and the sorption yield are shown in Fig. 4. The sorption has a maximum at 81% at the lowest uranium concentration (10 mg/L), i.e., the sorption is more efficient in dilute solutions. The absolute amount of uranium uptake is greater at the higher uranium concentrations.

3.4. Effect of contact time

The effect of contact time on the sorption of U(VI) ions on calcium alginate beads was investigated over time intervals from 15 up to 240 min. Fig. 5 shows the sorption yield as a function of contact time. As seen from Fig. 5, it reached a maximum at about 90 min, and almost remained constant up to 240 min. In general, about 80% of the total metal ion sorption was achieved within 90 min. Therefore,

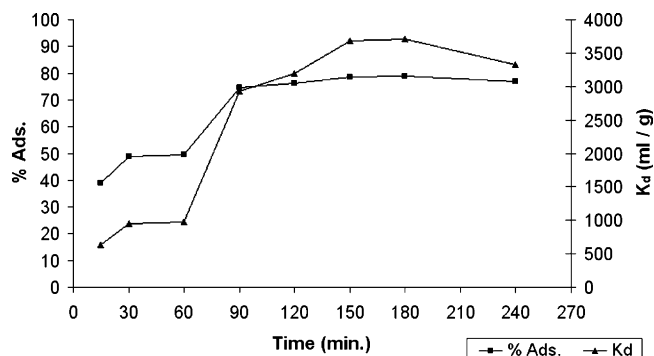


Fig. 5. Variation in adsorption (%) and K_d of U(VI) on the Ca-alginate beads as a function of contact time (U : 25 mg/L, m : 25 mg, V : 25 mL, pH : 4.0, T : 25 °C).

in subsequent equilibrium experiments, 120 min was deemed more than sufficient to establish equilibrium and used in all subsequent measurements.

3.5. Effect of biomass dosage

The effect of calcium alginate dosage on the biosorption of U(VI) ions was studied using different biomass dosage in the range of 0.5–15 g/L (Fig. 6). Fig. 6 shows the variation of the biosorption yield vs. alginate concentration. Results showed that the biosorption efficiency is highly dependent on the calcium dosage of the solution. Biosorption of the uranium ions was attained a maximum at 10 g/L biomass dosage, then became constant. This trend could be explained as a consequence of a partial aggregation of biomass at higher biomass concentrations, which results in a decrease in effective surface area for the biosorption. Therefore, the optimum biomass dosage was selected as 10 g/L for further experiments.

3.6. Effects of cations

Industrial application of a biosorption process must deal with the fact that heavy metal-bearing waste streams often contain other ions that may interfere the uptake of the radioactive metal ions of interest. Multiple metal ion solution was prepared containing U(VI), Th(IV), Al(III), Ni(II), Cd(II), Cu(II), Fe(III), Zn(II), Mn(II), and Pb(II). The experiments were conducted to evaluate the effect of some cations on the biosorption of uranium by calcium alginate beads. The concentration of U(VI) was 25 mg/L, while the concentration of the other metal ions were 10 mg/L in the solution. Experiments were carried out with 1 g/L biomass dosage having a pH 4.00. Shaking time and temperature of the solution were 120 min and 25 °C, respectively. The concentration of metal ions in the solution was measured by PerkinElmer Optima 2000 DV

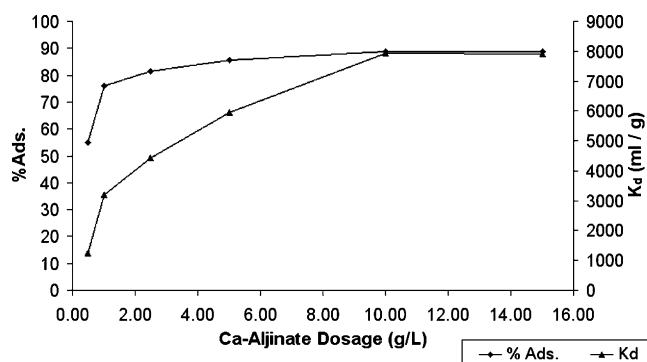


Fig. 6. Effect of biomass dosage on the biosorption of U(VI) ions on the Ca-alginate beads (U : 25 mg/L, t : 120 min, pH : 4.0, T : 25 °C).

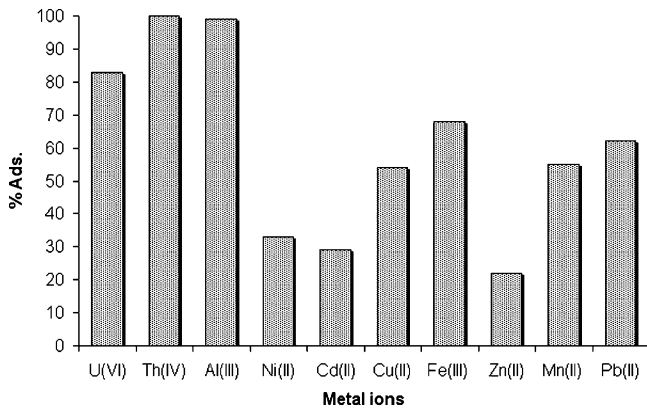


Fig. 7. Effect of cations on uranium uptake by calcium alginate (initial uranium concentration = 25 mg/L, initial metal ion concentration = 10 mg/L, m : 25 mg, V : 25 mL, pH: 4.0, t : 120 min, T : 25 °C).

ICP-OES. All the experiments were carried out in duplicate and the mean value was noted. Fig. 7 displays uranium adsorption by the Ca-alginate beads in the presence of the other metal ions. It is evident that the uranium uptake by calcium alginate was not affected by these metals mentioned. The bars (Fig. 7) represent metal uptakes as a percentage. Uptakes of uranium, thorium and aluminum ions were recorded as 83%, 100% and 99%, respectively. As a result, it can be concluded that the other cations could not interfere the biosorption of uranium ions by calcium alginate beads.

3.7. Sorption isotherms

The sorption data have been subjected to different sorption isotherms namely Freundlich, Langmuir and Dubinin–Radushkhevich. The data fit the Freundlich and Langmuir isotherms (Table 1), but do not fit the Dubinin–Radushkhevich (R^2 : 0.7426) isotherm.

3.7.1. Langmuir isotherm

The Langmuir theory was first used to describe the adsorption of gas molecules onto metal surfaces [40]. However, this model has also found successful application in many other sorption processes. The basic assumption of the Langmuir model is that the amount of metal ions adsorbed can be expressed by

$$q_e = \frac{X}{m} = \frac{Q_0 b C_e}{1 + b C_e}, \quad (3)$$

where X is the initial concentration of solute minus the final concentration of solute in solution at equilibrium (mg/L) and m is the concentration of adsorbent (g/L).

A linear form of this equation is

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}, \quad (4)$$

where C_e is the equilibrium concentration of metal in solution, q_e is the amount of metal ions sorbed onto adsorbent, and Q_0 and b are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum sorption capacity (Q_0) represents monolayer coverage of sorbent with sorbate, and b represents enthalpy of sorption and should vary with temperature [41]. The

Table 1
Isotherm parameters of metal ion adsorption on Ca-alginate beads.

Langmuir parameters			Freundlich parameters		
Q_0 (mg/g)	b (l/g)	R^2	K (mg/g)	n	R^2
400	48.83	0.9918	1311	491	0.9431

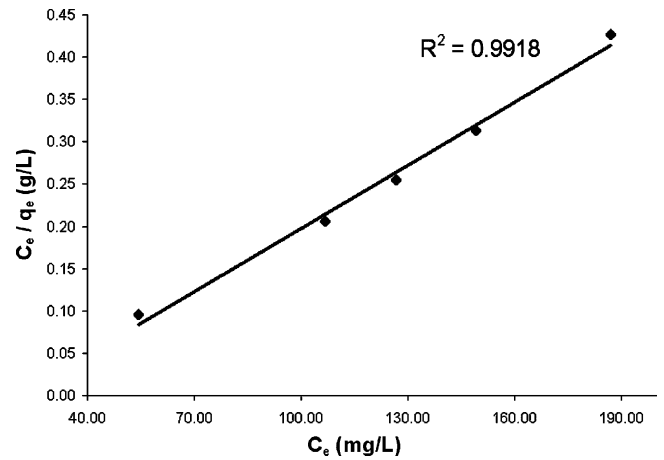


Fig. 8. Langmuir sorption isotherm of UO_2^{2+} ions on Ca-alginate beads (m : 25 mg; T : 298 K; pH: 4.00; t : 120 min; V : 25 ml).

equilibrium data for metal cations over the concentration range from 10 to 100 mg/L at 298 K has been correlated with the Langmuir isotherm (Fig. 8). A linear plot is obtained when C_e/q_e is plotted against C_e over the entire concentration range of metal ions investigated. The Langmuir model parameters and the statistical fits of the sorption data to this equation are given in Table 1. The Langmuir model effectively described the sorption data with all R^2 values >0.99 (Table 1). The adsorption isotherms of UO_2^{2+} exhibit Langmuir behavior, which indicates a monolayer adsorption. The maximum monomolecular capacity is found to be 400 mg/g for UO_2^{2+} at 298 K.

3.7.2. Freundlich isotherm

The Freundlich adsorption isotherm was tested in the following linearized form:

$$\log C_{ads} = \log K + \frac{1}{n} \log C_e \quad (5)$$

by plotting $\log C_{ads}$ vs. $\log C_e$. C_{ads} is the amount of solute adsorbed, C_e is the amount of solute in solution and K and n are constants. The sorption data is obeyed the Freundlich isotherm (Table 1). From the slope and intercept of straight portion of the plot the values of Freundlich parameters are calculated and results are represented in Fig. 9.

The $1/n$ value is usually dependent on the nature and strength of the adsorption as well as the distribution of active sites. The Freundlich sorption isotherm gives an expression encompassing the

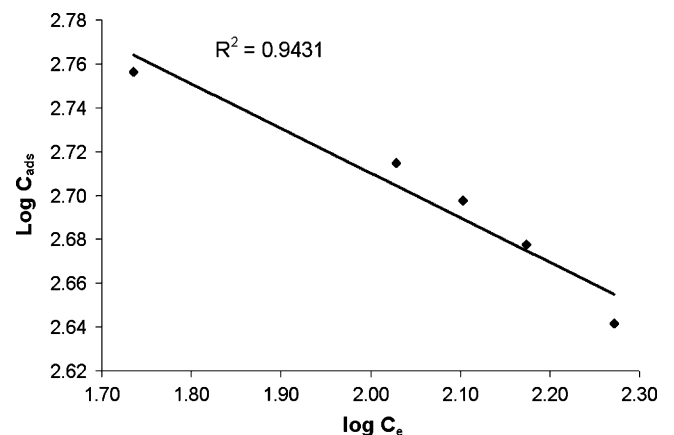


Fig. 9. Freundlich sorption isotherm of UO_2^{2+} ions on Ca-alginate beads (m : 25 mg; T : 298 K; pH: 4.00; t : 120 min; V : 25 ml).

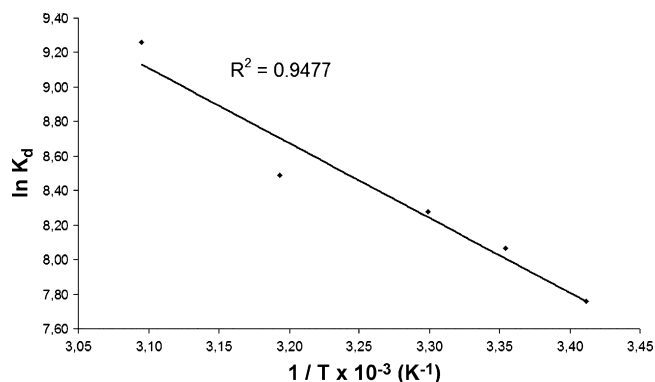


Fig. 10. Influence of temperature on the thermodynamic behaviour of adsorption of uranium on Ca-alginate beads.

surface heterogeneity and the exponential distribution of active sites and their energies. This isotherm does not predict any saturation of the sorbent by the sorbate thus infinite surface coverage is predicted mathematically, indicating a multilayer sorption of the surface [42,43].

3.8. Thermodynamic studies

The thermodynamic parameters of the adsorption process are obtained from experiments at various temperatures. It is essential to clarify the change of thermodynamic parameters.

The influence of temperature variation on the sorption of UO_2^{2+} ions on Ca-alginate beads from aqueous solution was examined using 120 min and 25 mg Ca-alginate beads in 25 mL of sorptive solution from 293 to 323 K. Thermodynamic parameters were calculated for this system using the following equation [44–46]:

$$\ln K_d = \left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{RT} \right) \quad (6)$$

where K_d is distribution coefficient, ΔH , ΔS and T are the enthalpy, entropy, and temperature in Kelvin, respectively and R is the gas constant. The plot of $\ln K_d$ against $1/T$ for UO_2^{2+} is shown in Fig. 10. The values of enthalpy (ΔH) and entropy (ΔS) were obtained from the slope and intercept of $\ln K_d$ vs. $1/T$ plots, which were calculated by a curve-fitting program. Gibbs free energy (ΔG) was calculated by using the following equation

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

The values of the thermodynamic parameters for the sorption of UO_2^{2+} on Ca-alginate beads are given in Table 2.

The positive value of enthalpy change, ΔH , shows the adsorption of uranium(VI) ions is an endothermic nature. The numerical value of ΔG decreases with an increase in temperature as shown in Table 2, indicating that the reaction is spontaneous and more favorable at higher temperatures. In addition, the positive entropy favours complexation and stability of sorption. The resultant effect of complex bonding and steric hindrance of the sorbed species eventually increases the enthalpy and entropy of the system [47].

Table 2
Thermodynamic parameters for the adsorption of uranium on Ca-alginate beads.

ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)				
		293 K	298 K	303 K	313 K	323 K
36.00	0.19	-18.92	-19.85	-20.79	-22.66	-24.53

4. Conclusions

The removal of uranium ions from aquatic solutions was carried out using classical adsorption techniques. Ca-alginate beads were applied to remove uranium ions from the solution. The results of this study showed that Ca-alginate beads can be successfully used for uranium recovery from aqueous solutions. The percent adsorption (%) and distribution constant (K_d) for uranium ions were 91 ± 1 and 10043 ± 834 mL/g respectively under the optimized experimental conditions.

Biosorption equilibrium was fit Langmuir equation better than Freundlich equation, and it did not fit Dubinin–Radushkevich model. From the thermodynamic study, the positive value of enthalpy change (36.00 kJ/mol) means that the interaction between uranium ions and Ca-alginate beads is endothermic in nature. Values of entropy and Gibbs free energy change suggested that the adsorption of uranium on Ca-alginate is a spontaneous process and it corresponded to an increase in the randomness of adsorbed species. Ca-alginate beads are natural and cheap, and can be utilized successfully in removal of uranium ions from dilute aqueous solutions.

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