# INVESTIGATION OF SWELLING/ADSORPTION BEHAVIOR
OF CALCIUM ALGINATE BEADS

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The objective of this investigation was to study the biosorption of Cr (III) on calcium alginate and to determine the isotherms and kinetics of chromium biosorption. Using a batch system, the capacity for Cr (III) biosorption was investigated as a function of initial Cr (III) ions concentration, pH and contact time. The optimal pH for Cr (III) biosorption was 5.3. The data were correlated with Langmuir and Freundlich equations. Compared to this model, the Langmuir model best fit the experimental data ($R^2 > 0.989$). The results of this study demonstrated that the pseudo-second order model was more suitable than pseudo-first order model for Cr (III) biosorption onto calcium alginate. The thermodynamic parameters calculated were: change in free energy, in enthalpy, and in entropy of adsorption.
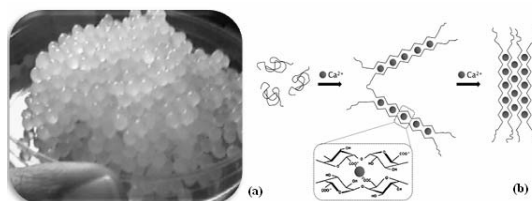
INTRODUCTION

Biosorbents, especially those derived from seaweed (macroscopic algae) and alginate derivatives, exhibit high affinity for many metal ions.[1] Because biosorbants are widely abundant (usually biocompatible, biodegradable, renewable and non-toxic) [2-4] and less expensive than industrial synthetic adsorbents, they hold great potential for the removal of toxic metals from industrial effluents.[5] In this study, calcium alginate (CA) beads were prepared by using sodium alginate (SA) as based biopolymer and chloride calcium (CaCl$_2$) as crosslinking agent.[5]

Sodium alginate is soluble in water forming viscous solution but its calcium form (calcium alginate hydrogel) is approximately water insoluble. Therefore, the present work aims at preparing a low-cost biopolymer adsorbent of commercial sodium alginate.

The work examines the utilization of the so-obtained calcium alginate (CA) for the removal of Cr (III) ions from their aqueous solutions under equilibrium conditions, taking into consideration the factors affecting the adsorption process and to what extent the adsorption data obey Langmuir and Freundlich adsorption isotherms.

Calcium alginate may be prepared in various forms, such as beads,[7] powders,[8] membranes [9] or fibers[1,10] and can be used as cell-immobilization support.[11] Bead particles have practical advantages in terms of applicability to a wide variety of process configuration and reusability.[2] Also, the alginate beads may be protonated[12] or doped with another metallic ion to obtain various bead properties.[13]

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MATERIAL AND METHODS

Chemicals

Commercial sodium alginate (Na-Alg) sample (Lot#4889401) purchased from Prolabo (France). Sodium chloride purchased from Prolabo. Distilled water was used to form all the aqueous solutions needed in these investigations. Cr(III) solution was prepared as stock solution from $CrCl_3.6H_2O$ salt and other concentrations were obtained by dilution. Concentrated hydrochloric acid and sodium hydroxide were used for pH adjustment. All chemicals used were of analytical purity grades.

Preparation of beads

Sodium alginate was dissolved in $0.1 mol.L^{-1}$ NaCl at a concentration of 2% (w/v) unless otherwise noted. The polymer solution was then added drop wise into gelation media of 250 mL $CaCl_2$ solution using a 5 mL hypodermic syringe under constant stirring at room temperature.[14] The beads, thus formed, were cured in the gelation medium for 24 hours and then taken out, followed by washing with distilled water and then allowed to dry at 45°C in limekiln for one night until no weight change was observed. The obtained beads have a diameter 2.5-3.0 mm.[15] The obtained beads were kept in desiccators for use (Fig. 1).

Swelling measurements using tea bag method

Ultimate absorbency (equilibrium swelling) of the beads samples was determined using the tea bag method described elsewhere.[16] Therefore; the equilibrium swelling values were reported as weight of fluid absorbed (0.9% NaCl) at equilibrium per 1g of dried sample (g/g). The

maximum absorbency or equilibrium swelling (ES) was measured and calculated using the following equation: [17]

$$ES \ (g/g) = \frac{W_s - W_d}{W_d} \tag{1}$$

where: W_s is the weight of the swollen beads and the W_d dry samples and, respectively.

Removal of Cr (III)

Batch studies

In batch experiment, 50 mL of Cr (III) ions solution was added to 0.1 g beads of CA (2) in 100 ml Erlenmeyer's flask. The experiment conditions were adjusted where; pH was 5 ± 0.2, temperature was $25 \pm 3°C$ and stirring rate was 250 rpm using environmental orbital shaker. Samples were taken at different contact times and the amount of the ions accumulated on the different beads was estimated. The quantitative determination of chromium was carried out using atomic absorption spectrophotometer (Zeenit 700) model Win AAS-version 3.17.0.

The percentage of adsorption (% E) and the adsorption amount of chromium (III) (q) were calculated according to equation (2) and (3).

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{2}$$

$$\% E = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{3}$$

where C_o and C_e are initial and equilibrium concentration of Cr (III) in the solutions, respectively ($mg.L^{-1}$), V is the volume of solution (L), and m is the mass of CA (2) (g).
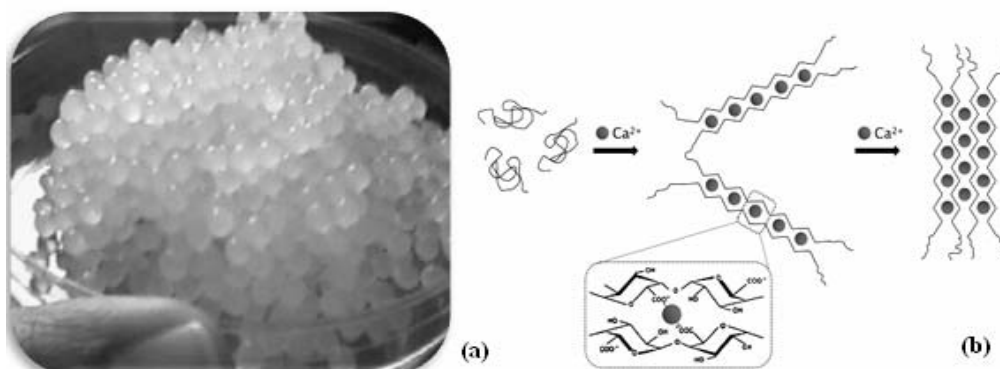

Fig. 1 – a) Photograph of Ca-alginate, b) Chemical structure of Ca- alginate and egg-box model.

The solution pH was measured by pH meter and was adjusted by adding dilute HCl or NaOH solution.

RESULTS AND DISCUSSION

Characterization of alginate

a) FTIR Spectroscopy

FTIR analysis was performed to examine the functional groups on the Ca-alginate beads. The IR spectra obtained for the samples in the 600-4000 cm^{-1} range, was shown in Fig. 2, the FT-IR spectrum of ca-alginate bead displays a number of absorption peaks. The broad peak around 3350cm^{-1} is an indicative of existence of bonded hydroxyl group. Characteristic absorption peaks around 2940 cm^{-1} due to C–H stretching. The absorption peak at 1740 cm^{-1} represent the stretching band of the free carbonyl double bond from the carboxyl functional group.[18] The peak around 1630 cm^{-1} is chelated stretching bond of C=O. It is reported that the carboxyl groups on biological polymer such as Ca-alginate bead have pK$_H$ values raging from 3.5 to 5.0,[19] and this carboxyl groups on CA bead play an important role in Cr(III) adsorption.

b) Swelling behavior r of CA beads

Although alginates are hydrophilic and water soluble anionic polysaccharides, but the Ca^{+2} ions induced cross linked beads of alginate are sufficiently stable in the aqueous media. It is the ion–exchange process between Na$^+$ and Ca^{+2} ions, which is supposed to be responsible for the swelling and subsequent degradation of the beads.[20]

Fig. 3 depicts the swelling capacity for the alginate beads cross-linked in the 2% and 3% CaCl$_2$ solutions, in the pure distilled water (ED) and in water containing 0.9% NaCl (physiological water), their swelling behavior was studied at 30°C and pH 5.3. It is clear form the figure that the beads exhibit maximum fluid uptake of 96% and 4586% in the two solutions respectively. The results, indicate that the amount of Ca^{2+} ions released from the beads increases with the concentration of NaCl in the swelling media. This can be well attributed to the fact that with increase in number of Na$^+$ ions in the external solution, the ion exchange process is also enhanced, thus resulting in faster release of Ca^{+2} ions from the beads. In this way, number of Ca^{+2} diffusing out from the beads depends upon the concentration of NaCl in the external solution.

c) SEM images

Sample of Ca-alginate beads were examined by scanning electron microscopy (HITACHI S-4500, Acc Spot Magn 7.00 KV). Compared (a) and (b), CA(2) changes the surface morphology of sodium alginate and presents a dense structure, which is resulted from the crosslink reaction between sodium alginate and CaCl$_2$ solution. However, cracks appear at the dense structure of CA(2) after crosslinking, which means that some of the crossinking structure is broken.
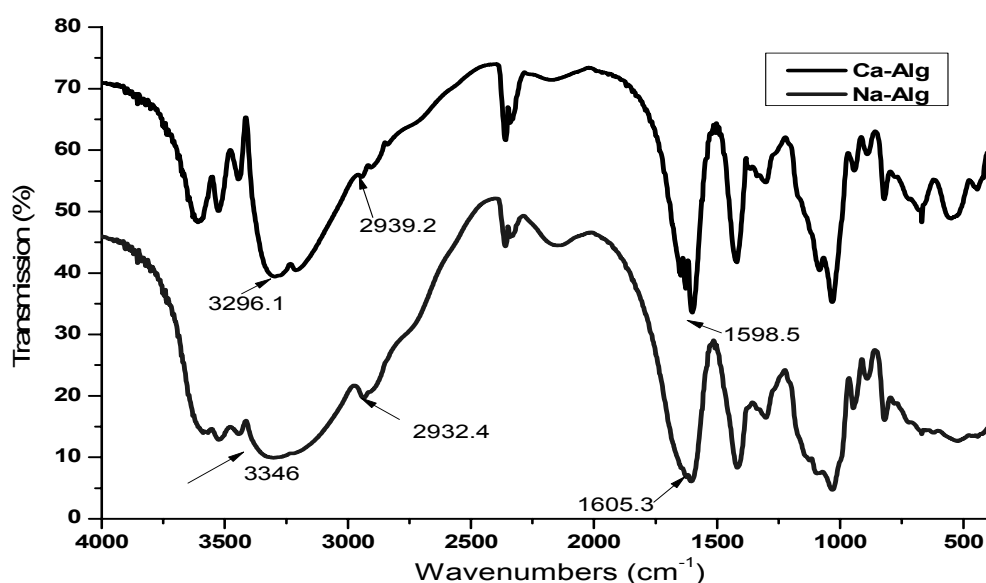

Fig. 2 – FTIR spectra of Na-alginate and Ca-alginate beads.
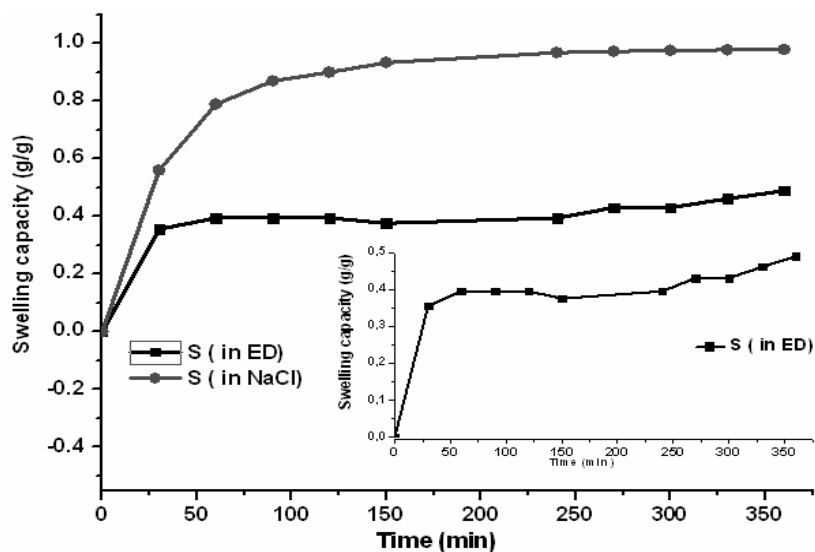
Fig.3 – Dynamic uptake of water as a function of time for the beads CA (2) in the medium of pH 5.3.
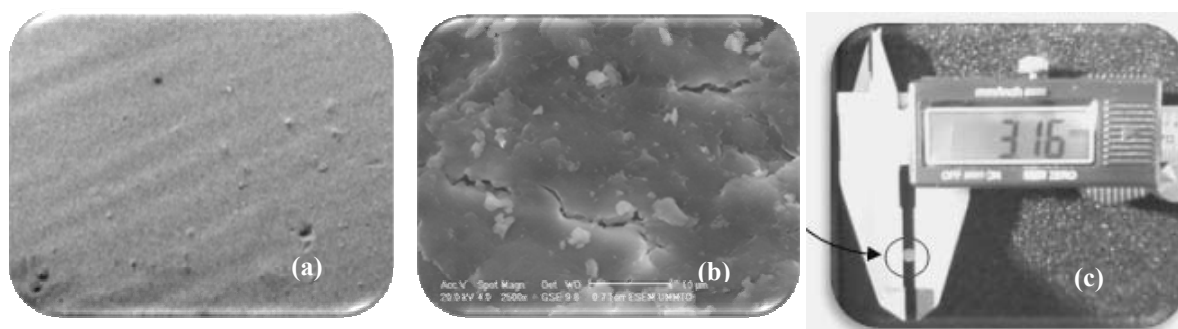

Fig. 4 – a) optical electron micrograph of SA (10x) , b) Scanning electron micrograph of CA(2) beads (2500x, 10μm),
c) particle size of beads by sliding equip of read digitel.

The fact is also revealed in the infrared spectra (Fig. 2) that Ca^{2+} released carboxyl groups after crosslinking. This may be caused by the exchange of ions in CA(2) and Ca^{2+} in the crosslinking solution.

The beads had a spherical shape and showed surface cracks probably caused by partial collapsing of the polymer network during drying. The mean particle size of the beads ranged from 2.50 to 3.16.± 0.02 mm (Fig. 4c).

Adsorption of Cr (III)

Effect of Contact time

Influence of contact time on Cr (III) adsorption with CA(2) can be seen in Fig. 5. The uptake of Cr(III) increases with contact time and the uptake equilibrium was attained within 80 minutes. At pH 5.3, the maximum Cr (III) uptake was estimated to be 96.2%, this resultat suggest that the solution pH is important in Cr (III) adsorption.

Effect of metal ion concentration

To understand the effect of time on the extent of adsorption, equilibrium concentrations of Cr (III) ions were determined at different time intervals with initial concentrations of 100, 200 and 300 mg.L^{-1}, keeping the pH, temperature and amount of biosorbent constant. The results are graphically presented in Fig. 6 for CA.

The concentration of adsorbed Cr (III) onto calcium alginate over time is depicted in Fig. 5. As shown in the Fig. 5, the amount of adsorbed Cr (III) ions increased with an increase in time, and equilibrium was attained at approximately 60 min. This suggested that, biosorption process is slow and reaches saturation within 60 min similar data was obtained by Loukidou (2004) and Abdel-Razek (2011).[21,22] At equilibrium, the cumulative removal percentage for Cr(III) concentration of 100, 200 and 300 mg.L^{-1} was 96.2, 94.3 and 91.8%, respectively. As shown in Fig. 5, the rate of biosorption onto pure calcium alginate (as mg.g^{-1}) increased from 48.9, 94.2, and 138.8 mg.g^{-1} as the concentration of Cr (III) ions increased from 100 to 300 mg.L^{-1}, respectively.
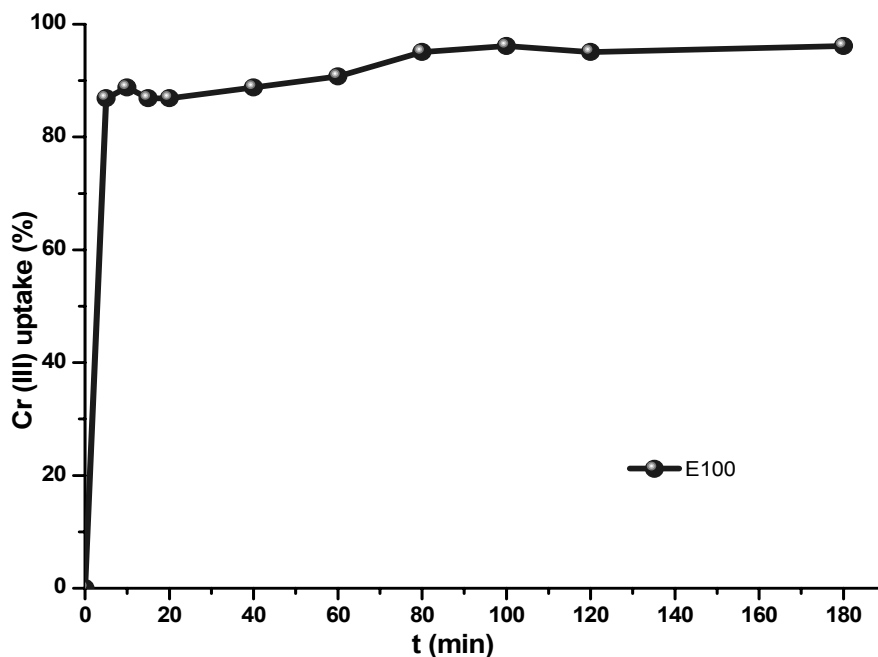
Fig. 5 – Effect of contact time on Cr (III) uptake by CA (2) (adsorbent dosage: 100 mg; pH 5.3;
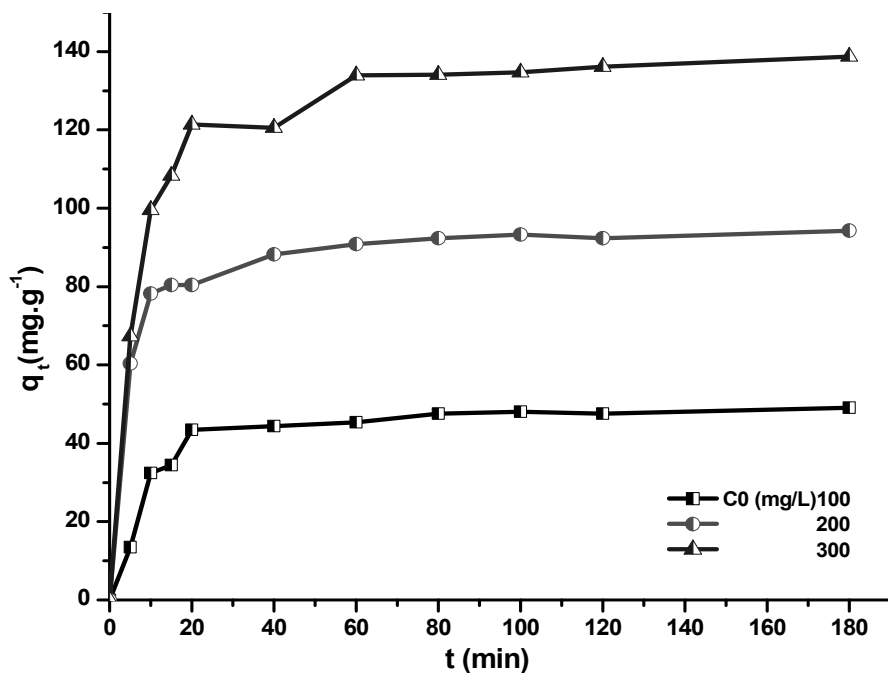initial Cr (III) concentration: 100 mg/L).

Fig. 6– Effect of contact time on Cr (III) adsorption capacity by the beads of CA (2)
(adsorbent dosage: 100 mg ; pH : 5.3; Initial Cr (III) concentration : 100 ,200 and 300 mg.L^{-1}).

Adsorption kinetics

To evaluate the isotherm models, 1 g.L^{-1} of the biosorbent were stirred in a solution of Cr (III) at a pH of 5.3 and an initial Cr (III) concentration ranging from 100 to 300 mg. L^{-1} for 180 min. Kinetics of adsorption using different models was studied by many workers. The adsorption data were analyzed by the following two important isotherms: the Langmuir and Freundlich isotherms.

a) Langmuir isotherm

The relationship between adsorption capacity of the beads and chromium concentration can be expressed using the Langmuir adsorption equation.[23]

$$q = q_{max} \frac{bC_e}{1+bC_e} \qquad \text{(non-linear form)} \qquad (4)$$

$$C_e/q_e = 1/b \cdot q_{max} + C_e/q_{max} \qquad \text{(linear form)} \qquad (5)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent ($mg.g^{-1}$), C_e the equilibrium concentration of solute in the bulk solution ($mg.L^{-1}$), q_{max} the monolayer adsorption capacity ($mg.g^{-1}$), and b is the constant related to the free energy of adsorption/desorption (b α $e^{-\Delta G/RT}$). High values of b are reflected by the steep initial slope of a sorption isotherm and indicate a high affinity for

the adsorbate. In terms of implementations, sorbents with highest possible q_{max} and high b are the most desirable.

b) Freundlich isotherm

The Freundlich equation may be written as: [24]

$$q_e = K_F \times C_e^{(1/n)} \qquad \text{(non-linear form)} \qquad (6)$$

$$\text{Log } q_e = Log K_F + (1/n) Log C_e \qquad \text{(linear form)} \qquad (7)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent ($mg.g^{-1}$), C_e the equilibrium concentration of solute in the bulk solution ($mg.L^{-1}$), K_F the constant indicative of the relative adsorption capacity of the adsorbent ($mg.g^{-1}$), and

$1/n$ is the constant indicative of the intensity of the adsorption.

The values of the isotherm constants and maximum biosorption capacities (q_{max}) are provided in Table 1.

Table 1

Isotherm parameters for Cr (III) ions biosorption onto calcium alginate.

CA(2) pH = 5.3 25°C	Langmuir Model				Freundlich Model				ΔG_{ads} (K.J.mol^{-1})
	q_m (mg.g^{-1})	b (L.mg^{-1})	R^2	SD	1/n	K_F (mg .g^{-1})	R^2	SD	
	270.3	0.049	0.989	0.003	0.637	18.29	0.978	0.032	- 6.401

As shown in Table 1, the values of the correlation coefficients indicated that the Langmuir model best fit Cr (III) biosorption onto calcium alginate. The adsorption process was found to obey Langmuir adsorption isotherm, thus on plotting C_e versus $1/q_e$ (Fig. 7) a straight line with correlation coefficient (R^2) of 0.989 was obtained. The values of Langmuir constants for CA(2), q_{max} and b were calculated and found to equal 270 $mg.g^{-1}$ and 4.9×10^{-2} $L.mg^{-1}$, respectively. The Langmuir isotherm model provides a more realistic description of adsorption by organic material because it accounts for different types of binding sites and their interactions, surface heterogeneity and the energy of the biosorbent surface.

The thermodynamic parameters of the sorption process (i.e., Gibbs energy (ΔG_0, kJ.mol^{-1}), have been determined using the Van't Hoff equation (8):

$$\Delta G = - RT \ln K_c \qquad (8)$$

K_c is the Langmuir equilibrium constant (b coefficient, Table 1), R is the universal gas

constant (8.314 J. mol^{-1}K^{-1}), and T is the absolute temperature (K).

The Gibbs energy is negative and it means that the reaction is spontaneous but becomes consistently favorable with the decrease of Langmuir equilibrium constant. The spontaneous and exothermic behaviour was also observed by several authors studying the adsorption of trivalent and hexavalent chromium in different biosorbents.[25, 26]

The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L[27, 28] on different systems as given by Eq. (9).

$$R_L = \frac{1}{1+bC_0} \qquad (9)$$

where: b is the Langmuir constant, C_0 the initial concentration, and R_L indicates the shape of the isotherm to be: irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavourable ($R_L > 1$). Fig. 8 shows that Cr sorption of all types of adsorbent in this study is favourable.
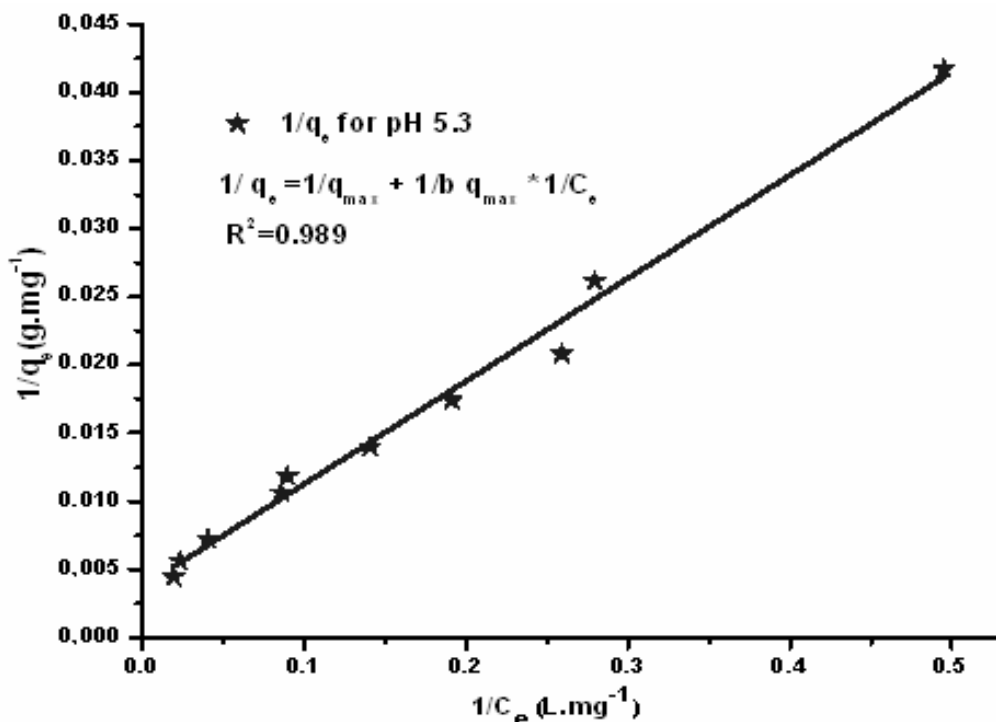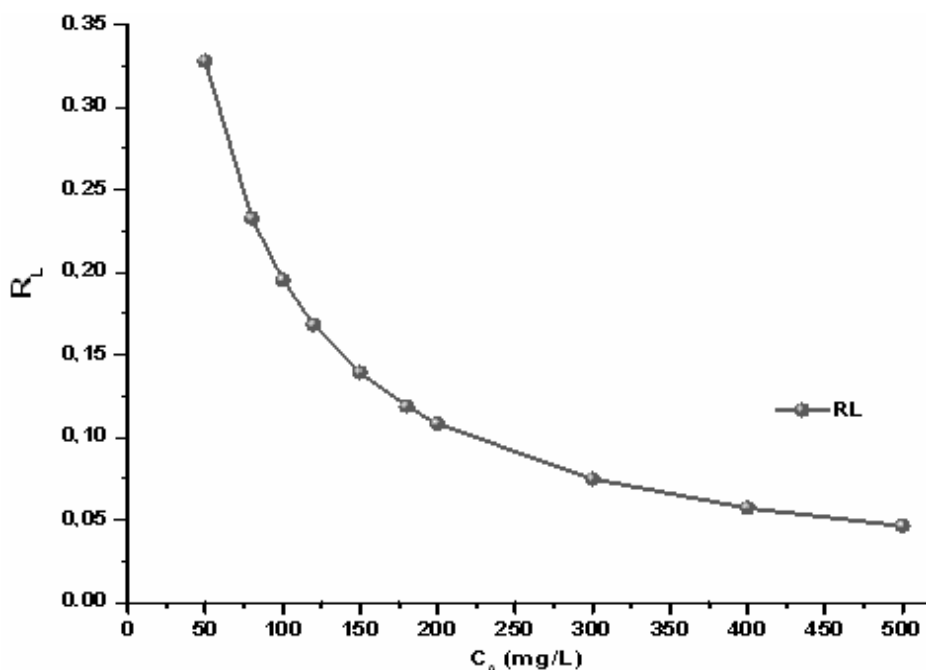
Fig. 7 – Langmuir adsorption isotherm of Cr (III) onto CA.

Fig. 8 – Evaluation of R_L as a function of initial Cr(III) ion concentration.

The values of R_L at this adsorbent dose and temperature were found to be less than 1 and greater than 0 indicating the favorable adsorption of Cr(III) on both of the adsorbents used for Cr(III) removal.

Moreover, the adsorption process was also found to obey Freundlich adsorption isotherm,[24] thus on plotting $logC_e$ against $logq_e$ (Fig. 9) a straight line with a correlation coefficient (R^2) of 0.978 was obtained.

The values of Freundlich constants for CA(2), K_F and n were calculated and found to equal 18.29 and 1.5698, respectively. As shown from the results, the value of n is 1.5698 (*i.e.* $0 < n < 10$) showing that the adsorption of trivalent chronium onto Ca-alginate beads is favorable.
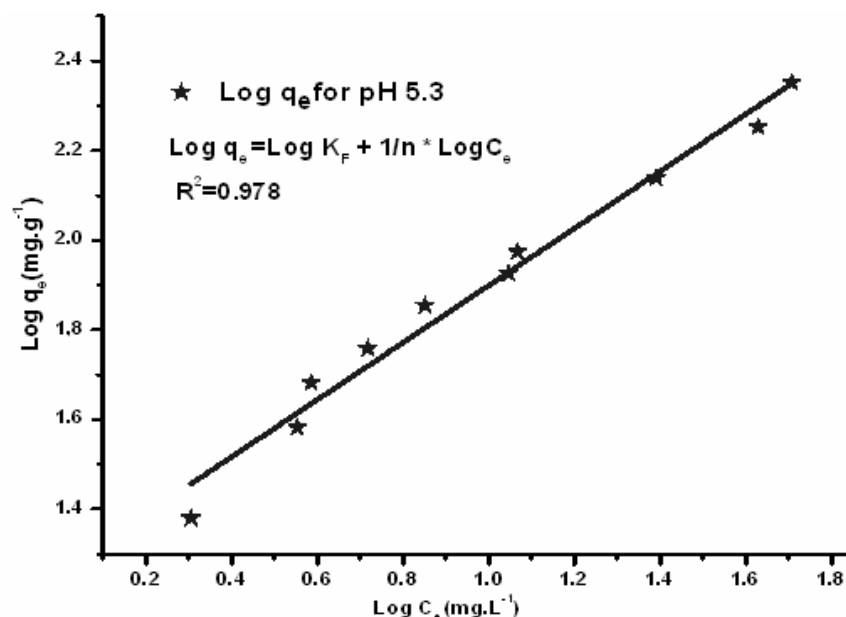
Fig. 9 – Freundlich adsorption isotherm of Cr (III) onto CA (2).

CONCLUSION

In the above work, calcium alginate (2%) was synthesized and it exhibited excellent swellibilty in biological fluids. It is found that swelling of CA(2) beads is governed by the ion-exchange process. In this way, these beads gave excellent chronium removal efficiency. The Langmuir model is an appropriate adsorption isotherm, with the maximum adsorption capacity of 270.2 mg.g^{-1} at pH 5.3.

In conclusion, it has been shown that the use calcium alginate for chromium ion removal appears to be technically feasible, ecofriendly and with high efficacy. The adsorbent can be regenerated by using acid (0.1M of HNO_3 or HCl), and therefore can be reused. This adsorbent can be a good candidate for adsorption of not only chromium ions but also other heavy metal ions in wastewater stream. Finally, it can be concluded that out of the bead sample, namely calcium alginate, later exhibits more stability and bears potential for being used as bioadsorbent support for the removal of toxic metals from industrial effluents.

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