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Comparative study of Biosorption of Chromium and Lead Ions On to the Calcium Coss-linked alginate

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ABSTRACT: The objective of the present work included synthesis of nanoparticles of calcium cross-linked alginate by emulsion cross linking method and their characterization by techniques such as FTIR, TEM and XRD. In order to study the effect of factors like adsorbent dose, initial metal ion concentration, on the removal of chromium ions and lead ions from water using nanoparticles of alginate, a series of batch sorption experiments were conducted.

Keywords: Chromium, Lead, alginate, nanoparticles, adsorption, emulsion cross linking.

I. INTRODUCTION

Pure water is not easily available to all. Deprive sections of the Society Consume contaminated water and take ill periodically. Water pollution mainly occurs due to organic and inorganic wastages, sediments, radioactive materials, effluents, sewages and heavy metals .Among these pollutants, contribution of heavy metals is a major concern because of their toxicity , bioaccumulation , persistence and nonbiodegradable nature and large scale extraction of metal release more amount of hazardous wastes. Chromium is an essential nutrient for plants and animals metabolism. However, the increasing accumulation of chromium in the environment from industrial outputs has caused great concern. Chromium contaminated waste waters can originate from dyes and pigment manufacturing, wood preserving, electroplating and leather tanning industries. In India also, there are a large number of tanneries scattered all over the country and nearly 80% of these tanneries are engaged in the chrome tanning processes. Most of them discharge untreated wastewater into the environment. The current pattern of industrial activity alters the natural flow of materials and introduces novel chemicals into the environment.

Lead contamination of the environment is primarily due to anthropogenic activities making it the most ubiquitous toxic metal in the environment. Research on Pb has become a dominant topic for environmental and medical scientists for two obvious reasons .It has no known biological use. The selection of an effective and economic adsorbent in removal of toxic metals ion requires consideration of both conventional and non-conventional materials. The preceding discussion has motivated the authors to undertake the present study that aims at investigating the removal of Cr (VI) ions and lead ions from aqueous solution by adsorption onto the nanoparticles composed alginate.

II. MATERIAL AND METHODS

Biopolymer alginate was of high purity grade and purchased from local chemical suppliers. Calcium chloride was used as crosslinking agent. Silicon oil (Aldrich, USA) viscosity 10,000 (at 25^{o}C) was used as an oil phase for preparing the suspension. Chromium, lead and other Chemicals were of high purity grade and throughout the work; double distilled water was used for making solutions.

A. Preparation of Nanospheres

A known solution of Sodium Alginate were stirred on magnetic stirrer for about 20 min. 3 mL mixture of Calcium chloride and silicon oil was added drop wise into the suspension of Sodium alginate with the help of a syringe under constant stirring. Prepared nanoparticles were washed with acetone, then benzene and dried at 80 $^{\circ}$C for 48 h.

B. Adsorption Experiments

The adsorption was carried out by the batch contact methods. Firstly, the stock solution was prepared by dissolving 0.6 g of dichromate in 1 litre distilled water. Into 6mL of dilute stock solution (1:1), 100 mg of the swollen nanospheres were added as adsorbent.

The suspension was shaken in a rotary shaker (Tempstar, India) for 4 h which was found to be a sufficient time to attain equilibrium adsorption. After shaking is over, 3 mL supernatant was mixed with 1 mL reagent (NH_3 solution) and the amount of chromium was assayed spetrophotometrically. The adsorbed Cr (VI) and lead(II) was calculated by the following mass balance equation,

Adsorbed amount (mg/g = $(C_i – C_f)V/m$ …(1)

Where C_i and C_f being the initial and final concentration of Chromium and lead solution (mg/ml). V being the volume of adsorbed solution and m is the weight of swollen nanospheres (adsorbent).

C. Characterization

FTIR spectral Analysis. The presence of functional groups of the constituent biopolymer in the nanoparticles was confirmed by FTIR spectral analysis (Shimadzu, 1800).

Scanning Electron Micrograph (SEM). In order to study morphology of the prepared nanospheres, the SEM analysis of the microspheres surface was carried out (STEREO SCAN, 430, Leica SEM, USA).

Particle Size Analysis. The size of the prepared nanospheres were determined by a particle size analyser (Fritsch Particle Sizer, Germany).

Surface Charge Analysis. As the nanospheres are composed of polyelectrolyte biomacromolecular, their surface bears a change which may be determined by EMF measurements. In order to determine the magnitude of surface charge, 1 g nanospheres are allowed to swell in 25 ml of distilled water and the chare developed over the surface was measured by pH/EMF meter (Systronics pH system 362, Ahmadabad, India). In a similar way, the Cr (VI) and lead (II) adsorbed nanospheres were also immersed into same volume of water and surface was determined.

III. RESULTS AND DISCUSSION

FTIR Spectra The Fourier transform infrared (FTIR) spectra of the sodium alginate and calcium alginate nanoparticles were recorded and compared (Fig. 1). Later bands are very significant and can be used for characterization of alginate structure from its derivatives and ingredients.

SEM Analysis. The morphology of the prepared alginate nanoparticles have been investigated by recording their scanning electrons micrograph as shown in Fig. 2.

Particle Size Analysis. The particles size analysis of the prepared nanospheres as determined by Dynamic Light Scattering measurements and the size distribution curve is shown in Fig. 3.

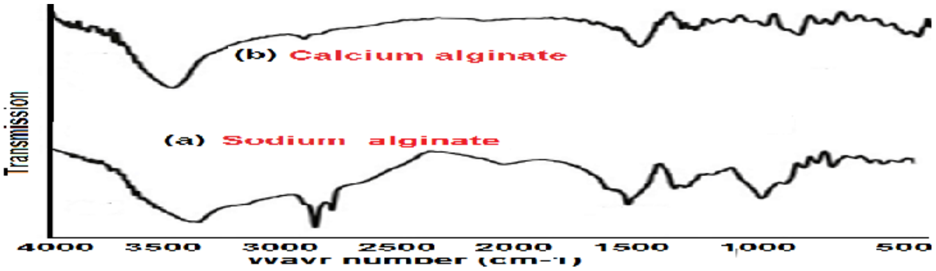

Fig. 1. FTIR spectra of (a) calcium cross linked alginate (nanoparticles) and (b) native sodium alginate.

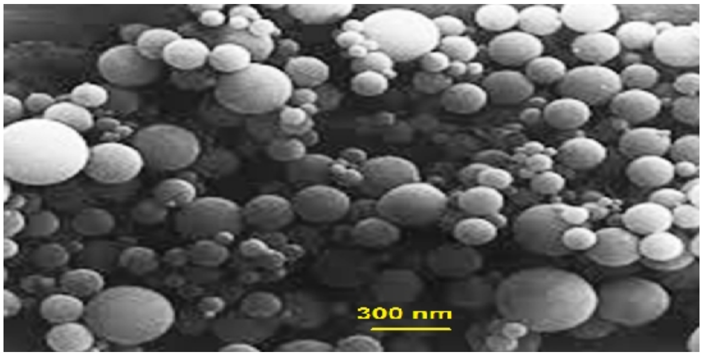

Fig. 2. Scanning electron micrograph (SEM) of calcium cross linked alginate nanoparticles.

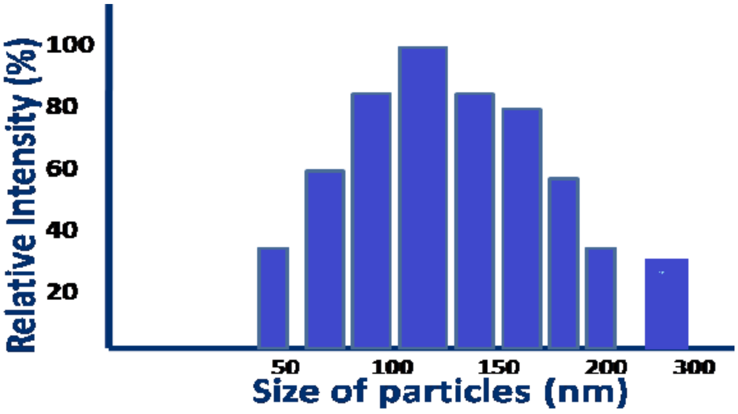

Fig. 3. Particle size distribution curve of calcium alginate nanoparticle.

A. Results on adsorption studies

Effect of metal ion concentration and Kinetics. The effect of initial concentration of Cr solution on its adsorption onto prepared alginate nanospheres has been studied by increasing the metal ion concentration in the range 0.5 to 8.0 mg/L and monitoring the amounts of adsorbed Cr ions over the span of time period up to 60 min. The results are presented in Table 1 and Fig. 4 which clearly reveal that as the time increases, the amount of adsorbed Cr ions also increases and ultimately levels off.

Table 1: Data showing the variation in the amounts of adsorbed Cr ions with increasing concentration of metal ion solutions.

Time (min)	**Adsorbed Cr (mg/g) at Various Initial Concentrations of Cr solution (mg/L) ×100**						
	0.5	**1.0**	**1.5**	**2.0**	**5.0**	**7.5**	**8.0**
10	0.8	1.6	2.5	3.9	5.6	6.5	7.8
20	1.3	2.8	4.5	6.2	10.2	11.8	13.2
30	2.0	4.5	6.6	8.4	13.6	14.9	16.2
40	2.6	5.8	7.8	9.8	16.8	17.8	19.4
50	3.4	6.4	8.8	11.2	18.8	20.2	21.4
60	4.0	7.0	10	12.0	23.0	25.0	25.0
90	4.0	7.0	10	12.0	23.0	25.0	25.0
120	4.0	7.0	103.9	12.0	23.0	25.0	25.0

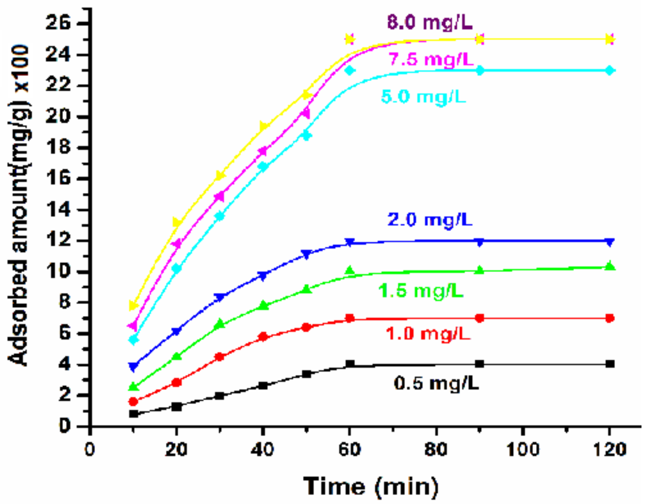

Fig. 4. Graphs showing the variation in the amount adsorbed Cr with time at different initial metal ion concentrations.

'The effect of initial concentration of lead ions (mg/L) on the adsorbed amount has been investigated by varying the initial concentration of Pb ions in the range 25 to 800 mg/L and determining the amount of adsorbed lead ions (mg/g). The results are summarized in Table 2 and Fig. 5 which clearly reveals that the amount of adsorbed metal ions increases with increasing metal ion concentration. The results are quite expected and may be explained by the fact that with increasing concentration of metal ions, the number of lead ions approaching the solution-alginate nanoparticles interface increases which results in greater adsorption.

Table 2: Effect of concentration of metal ions and kinetics.

Co mg/L	Time in min Amount of adsorbed Pb (x/m) mg/g							
	15	**30**	**45**	**60**	**90**	**120**	**150**	**180**
25	2.6	4.3	6.2	7.1	8.8	9.6	10.2	10.2
50	4.8	7.6	9.1	10.8	13.2	14.6	15.4	15.4
100	7.1	11.8	15.1	16.6	19.8	21.2	22.3	22.3
200	9.5	15.4	21.2	23.6	27.6	28.7	29.2	29.2
400	10.2	17.1	22.4	27.2	34.2	38.3	39.4	39.4
800	12.6	19.8	26.9	32.4	40.8	44.2	45.6	45.6

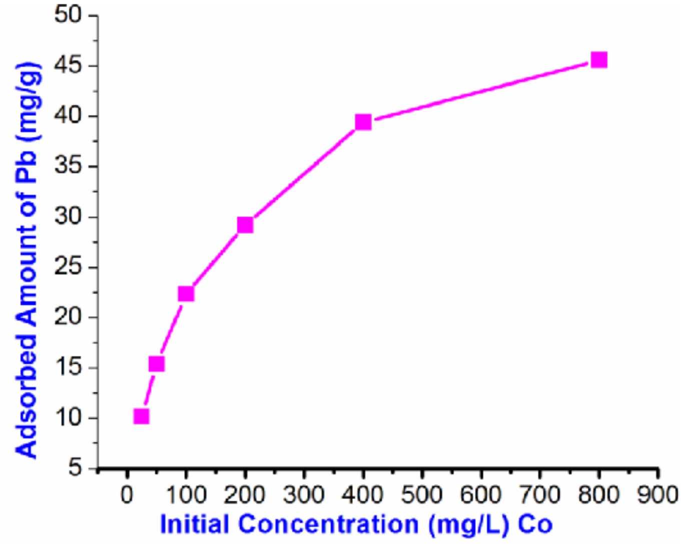

Fig. 5. Adsorption isotherm showing the effect of initial concentration of metal ions on the adsorbed amount of Pb.

B. Adsorption Isotherms

Langmuir model (chromium). The effect of equilibrium concentration of metal ions on the amount of the adsorbed Cr ions may quantitatively be dealt with several adsorption isotherm models among which the Langmuir equation has been the most frequently and successfully applied. According the Langmuir equation,

$$q_e = q_m K_L C_e / 1 + K_L C_e \ldots\ldots \quad \ldots(2)$$

Table 3: Data showing typical adsorption isotherm in accordance to equation 2.

Co	(x/m)	Ce	Ce/(x/m)
0.5	0.04	0.001	0.025
1.0	0.07	0.003	0.0428
1.5	0.10	0.005	0.05000
2.0	0.12	0.008	0.0667
5.0	0.23	0.027	0.117
7.50	0.25	0.050	0.200
8.0	0.25	0.055	0.220

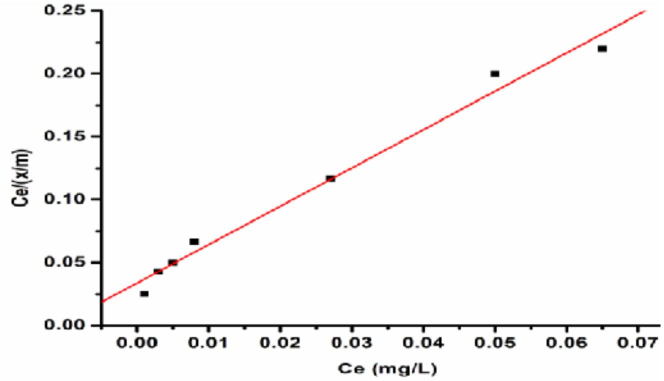

Fig. 6. A typical adsorption isotherm drawn in accordance to Eq. 2.

Thus, a plot drawn between the equilibrium concentration and the adsorbed amount depicts a typical type of adsorption isotherm which is a commonly reported isotherm in the literature. More popularly, the equation may also be represented by the following linear form,

$$Ce/qe= 1/q_m K_L + C_e/q_m \qquad ...(3)$$

The linearized plot is shown in Fig. 6 which clearly indicates that the adsorption data very well follow Langmuir model. The values of adsorption coefficient K_l and adsorption efficiency qm have been calculated from the eq. 3 and the values have been found to be 0.34 and 145, respectively.

Langmuir Model (Lead). The effect of equilibrium concentration of metal ions on the amount of the adsorbed Pb ions may quantitatively dealt with several adsorption isotherm models among which the Langmuir equation has been the most frequently and successfully applied. According the Langmuir equation, (eq. 3)

Thus, a plot drawn between the equilibrium concentration and the adsorbed amount depicts a typical type of adsorption isotherm which is a commonly reported isotherm in the literature.

Table 4: Data showing the variation in adsorbed amounts of Pb with initial concentration of the metal ion solution for plotting Langmuir adsorption isotherms.

Co (mg/L)	(x/m)(mg/G)	Ce (mg/L)	Ce/(x/m)
25	10.2	15.2	1.49
50	15.4	34.6	2.25
100	22.3	77.7	3.48
200	29.2	170.8	5.84
400	39.4	359.6	9.12
800	45.6	754.4	16.54

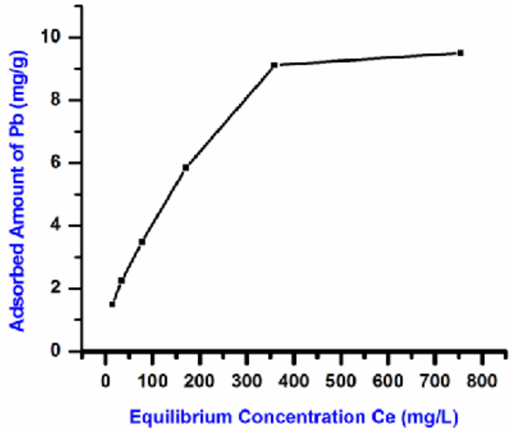

Fig. 7. A typical adsorption isotherm drawn in accordance to Eq. 3.

More popularly, the equation may also be represented by the following linear form Table 4. The linearized plot is shown in Fig. 8 which clearly indicates that the adsorption data very well follow the Langmuir model. The values of adsorption coefficient K_L and adsorption efficiency q_m have been calculated from the Eq. 3 and the values have been found to be 0.025 and 40 mg/L, respectively.

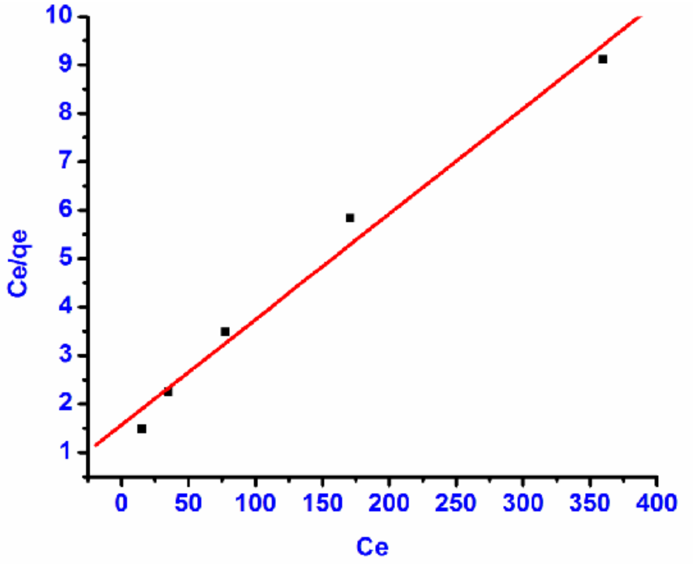

Fig. 8. A plot drawn between Ce and Ce/qe in accordance to the linearized Langmuir equation.

CONCLUSIONS

Chemical crosslinking of a water/oil suspension of a sodium Alginate produces regular shaped nanospheres of size up to 150 nm. The prepared nanospheres show potential for the removal of Cr ions from aqueous solutions.

The adsorption of Cr ions onto the water–swollen nanospheres increases with increasing initial metal ion concentration in the range 0.5 to 8.0 mg/L and monitoring the amounts of adsorbed Cr ions over time period up to 60 min. It is noticed that in the higher concentration range (8 mg/L) with the increase in time, the adsorbed amount nearly levels off. The adsorption process is found to follow Langmuir adsorption isotherms equation characterized by the appearance of a well marked plateau portion.

The adsorption of Pb^{2+} ions onto the water–swollen nanospheres increases with increasing initial metal ion concentration in the range 1.0 to 8.0 mg/mL. It is noticed that in the higher concentration range (8 mg/mL), the adsorbed amount nearly levels off.

The adsorption process is found to follow Langmuir adsorption isotherms equation characterized by the appearance of a well marked plateau portion. The arrival of plateau is further confirmed by surface coverage–concentration plot which also exhibits more than 99 percent surface coverage in the metal ion concentration range 6 to 8 mg/mL.

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