Original Research Article

REMOVAL OF HG (II) IONS FROM AQUEOUS SOLUTION BY ADSORPTION ON TO CROSSLINKED SODIUM ALGINATE BEADS

Dr. Tulika Dewangan
Department of Chemistry, Bharti College of Engineering & Technology
Durg (C.G.) – 491001 India

Abstract:
The removal of mercury ions from dilute aqueous solutions using cross linked sodium alginate beads as the adsorbent is reported in this article. The influence of various experimental parameters such as pH, initial metal ion concentration, contact time and solid to liquid ratio were studied. The adsorption data were applied to Langmuir and Freundlich isotherm equations and various static parameters were calculated. It was observed that the uptake of mercury ions was found to increase with time and that maximum adsorption was obtained within the first 60 minutes of the process. These results indicate that the cross linked sodium alginate beads have potential for removing mercury ions from industrial waste water.

Keywords: Adsorption isotherms, alginate, immobilization, sorption

Introduction

Quality of drinking water has become the main international subject. Presence of trace metals in drinking water has been related to certain type of cancers, cardiovascular diseases and other severe health problems in animals and human beings[1] .The heavy metal mercury is among the most Common pollutant found in industrial effluents. The major

sources of mercury pollution in the aquatic environment are industries such as chlor alkali, paint, pulp and paper, oil refining, electrical, rubber, processing, fertilizer, pharmaceutical and battery manufacturing[2].Mercury is generally considered to be one of the most toxic metals found in the environment. The major effects of mercury poisoning manifest as neurological and renal disturbances as it can easily pass the blood-brain barrier. Hence it is essential to remove mercury from waste waters before its transport and cycling into the environment. Several methods are employed to remove mercury form the industrial effluent. Some of them are chemical precipitation,

electrochemical methods, reverse osmosis, ion exchanges and adsorption.

Thus, the development of new, cost-effective, more environmentally friendly methods is needed. Biosorption of heavy metals by biomaterials has been suggested as a potential alternative to the existing physicochemical technologies for detoxification and recovery of toxic and valuable metals from wastewaters. Many biomaterials such as seaweed, micro-algae, fungi and various other plant materials have been studied for their mercury binding abilities [3-6]. Most reports related with the Hg (II) biosorption with dead fungal biomass have claimed that Hg(II) was removed from aqueous systems by "anionic adsorption". The cell walls of the microbial biomass are mainly composed of polysaccharides, proteins, and lipids, which contain functional groups such as carboxylate, hydroxyl, sulfate, phosphate and amino groups that bind to heavy metals [7].

The present work aims at investigating the removal of mercury ions from aqueous solutions by adsorption onto polymeric matrix composed of cross linked sodium alginate (SA) in the form of spherical beads. SA is abundantly available in nature. It can be found as a structural component of marine brown algae such as Macrocyst is pyrifera. SA is slowly soluble in cold water forming a viscous solution. This polysaccharide has many anionic or cationic groups in the structure; therefore, it exhibits a unique physical property by electrostatic interaction. Alginates are linear unbranched polymers containing b-(1,4)-linked D-mannuronic acid (M) and a (1,4)-linked L-guluronic acid (G) residues. Although these residues are epimers (D-mannuronic acid residues being enzymatically converted to L-guluronic after polymerization), and only differ at C_5, they possess very different conformations: D-mannuranic acid being C_1 with di equatorial links between them and L-guluronic acid being C_4 with biaxial inks between them. Bacterial alginates are additionally O-acetylated on the two and /or three positions of the D mannuronic acid residues. The bacteril O-acetylase may be used to O-acetylate the algal alginates, thereby increasing their water-binding. SA can be cross linked easily by using sodium ion [8-9].

Material and methods

Sodium alginate was obtained from Loba – Chemie, Mumbai, India and used as received. Other chemicals such as mercuric chloride, and calcium chloride ($CaCl_2$), cross linking agent for alginate (Loba -Chemie, Mumbai, India) were used of (A.R) grade. Double distilled water was used throughout the experiments.

Preparation of polymeric cross linked alginate beads

The sodium alginate beads employed as adsorbent were prepared by adding a solution of SA (1g in 25mL distilled water) into 50 mL of 0.05M calcium chloride solution. The SA solution was added drop wise using a syringe with constant stirring. The beads so produced were allowed to harden by leaving them in calcium chloride solution for 24h, then filtered, washed with double distilled water and stored at room temperature in double distilled water and used as such. A photograph of biopolymeric beads is shown in Figure 1.

Adsorption Experiments

In the present study, the adsorption of Hg (II) ions onto polymeric alginate beads was conducted by contact method [10-12].In brief, the swollen biopolymeric beads (0.2gm) were added to a 20mL known solution of Hg (II) ions of $50mgdm^{-3}$ concentration at pH 6 and room temperature (28 ^0C). The suspension was shaken in a wrist action shaking machine for 60 minutes, which was found to be a sufficient time to attain equilibrium adsorption. After shaking, the suspension was centrifuged in a centrifuge machine for 5 minutes and the amount of Hg (II) ions present in the supernatant was determined spectrophotometrically[13]using Systronics (Ahmedabad, India) spectrophotometer (visiscan–167). The amount of mercury adsorbed was determined by diphenyl

carbazone method[14] and the absorbance of the violet colored solution was measured at 560 nm .The amount of mercury adsorbed was calculated by the following mass balance equation

$$\text{Adsorbed amount (mg/g)} = \frac{(C_i - C_f)\ V}{m} \quad (1)$$

Where C_i and C_f are initial and final concentrations ($mgdm^{-3}$) of Hg(II)solution, respectively, v is the volume of metal ion solution, and m is the weight of swollen beads taken as adsorbent. For determining the progress of mercury adsorption by cross linked alginate beads from 20mL known solution of mercury ions of $50mgdm^{-3}$ concentration, the supernatant was analyzed for residual mercury after the contact period of 10, 20, 30, 40, 50, 60, 70 min. The effect of pH on mercury adsorption by alginate beads was determined at pH values of 2, 3, 4, 6, and 8. The effect of different doses of alginate beads ranging from 0.1 to 1.0g with 20mL of mercury solution of $50mgdm^{-3}$concentration was determined.

Desorption of Mercury from Sorbent

In order to desorb the metal ions, the beads loaded with Hg (II), were exposed to 2ml of 0.1M HCl for 15 minutes, centrifuged, and washed with double distilled water. The beads were then again exposed to HCl to strip any remaining mercury and then reused.

FTIR Spectra

The FTIR spectra of biopolymeric beads (before adsorption) (A) and after adsorption (B) was studied (refer to Figure 2).

Scanning Electron Micrograph (SEM)

In order to study morphology of the prepared polymeric beads, the SEM analysis of the polymeric beads surface was carried out (STEREO SCAN, 435, Leica SEM, USA)

Results and Discussion

FTIR

The characterization of polymeric beads was done by FTIR analysis. The FTIR spectra of bare (a) and mercury adsorbed bio polymeric beads (b shown in Figure 2), provide clear evidences of presence of alginate and Hg (II) as mercury chloride in the adsorbed beads. The spectra clearly marks the presence of hydroxyl group as confirmed by O–H stretching of hydroxyls at 3452cm ,C–O stretching of alcoholic OH at 1057cm and C(O) stretching of carboxylate ion at 1428 and 1351 cm, respectively. The spectra also mark the presence of methylene groups due to asymmetric stretch of $–CH_2$ groups.

Scanning Electron Micrograph (SEM)

The SEM image of metal ions adsorbed polymeric beads is depicted in Fig.3 which clearly indicates that the biopolymeric beads of microspheres are not much compatible and therefore, have resulted in a blend of heterogeneous nature. It is also visible from the image that blend surface has porous type morphology with voids ranging in width as large as 16 nm. This obviously accounts for good adsorbing property of biosorbents.

Effect of pH

The procedures used are similar to those earlier reported[15]. Experiments were conducted at room temperature (28 ^{0}C)) study the effect of initial solution pH on the adsorption of metal ions by contacting 0.2g of the sodium alginate beads with 20mL of $50mgdm^{-3}$ mercury solution. The pH of each of the metal solutions was adjusted to the desired value with 0.1M hydrochloric acid. In the present study the adsorption experiments were conducted at pH values of 2, 3, 4, 5, and 6. The results are depicted in Figure 4, which clearly reveals that the optimum adsorption is noticed at pH 6 Different functional groups such as carboxyl ate group present on the adsorbent surface can play an important role for adsorption of mercury. At the lower pH value (pH<4), H ions may bind with negatively charged groups (COO^- ions) on the surface of beads, which may restrict the approach of metal cations as a consequence of the repulsive force. As the pH is increased, the legends such as carboxyl groups of alginate beads would be exposed increasing the negative charge density on the beads surface, thus increasing the attractions of Hg ions and

allowing the adsorption onto the surface of alginate beads.

Effect of Concentration and Adsorption Isotherms

Batch adsorption experiments were carried out using different mercury concentrations in the range of 1.25to50 mgdm^{-3}, and it was found that with the increase of mercury concentration, the amount of mercury adsorbed also increases. This observed increase is quite obvious as on increasing the concentration of solute, greater number of metal ions arrives at interface and thus get adsorbed. The highest metal uptake was found at 50mgdm^{-3} Initial mercury concentration, and above 50mgdm^{-3} concentration, the adsorption of mercury ions was found to decrease as a consequence of the progressive saturation of the binding sites (shown in Figure 5). The results obtained were analyzed using both[16 -17]. Freundlich and Langmuir isotherms. The Freundlich isotherm in linearized form is

$$\log a = \log k_f + 1/n \ \log C_e \qquad (2)$$

Where K_f and n are Freundlich Constants. The standard mathematical representation of Langmuir equation for adsorption of solute at solid-liquid interface is as follows

$$\frac{C_e}{a} = \frac{1}{a_s} K + \frac{C_e}{a_s} \qquad (3)$$

Where a is the adsorbed amount of mercury ions (mgg^{-1}) at equilibrium concentration Ce, as (mg dm^{-3}) is the adsorption capacity and K is the adsorption coefficient. The values of Freundlich and Langmuir constants (n, k_f, K, and as) are summarized in Table 1, which clearly suggests a favorable adsorption of mercury ions.

Effect of contact time

The progress of the adsorption process, monitored at different time intervals (0–70 min) using a constant mercury concentration of 50 mgdm^{-3}, is shown in Figure 6, which clearly reveals that the adsorption of mercury ions increases with the increase of time and then level so off after 1h. It has been observed that the rate of adsorption of mercury ions is almost constant up to 60 min and then slows down, which may be due to saturation of binding sites.

Effect of Solid-to-Liquid Ratio

In the present study, the solid-to-liquid ratio was studied by taking the different amounts of beads studied in the range of 0.2 to 1g, and it was observed that the amount of mercury adsorption decreases with the increasing amount of adsorbent beads (shown in Figure7). The decrease in the adsorbed amount of Hg (II) ions may be due to the reason that some of the beads surface may be inaccessible to the metal ions and thus lowering the adsorption. Similar types of results have been reported in literature [18].

Effect of Salt

In the present study, the effect of salts on the adsorption of Hg (II) ions was investigated by adding KCl to the mercury solution of 50 mgdm^{-3} concentration in the range of 0.005 to 0.1M. The results are shown in Figure 8, which shows that the amount of Hg (II) ions constantly decreases with the increasing concentration of KCl. The observed decrease in adsorption may be due to enhanced electro-static repulsion between mercury ions and added KCl as well as the fixed ionic centers of the alginate beads. The added ions (KCl) get preferably adsorbed on the surface of polymeric beads and thus exhaust the active sites and lower the adsorption [19].

Effect of Temperature

The effect of temperature on adsorption of Hg (II) ion by alginate beads was studied in the temperature range of 10 to 50^{0}C (shown in Figure 9). It was observed that adsorption of the Hg (II) ions increases from 10 to 30^{0}C while beyond 30 ^{0}C , the adsorption decreases. The increases in adsorbed amount of Hg (II) ions with increasing generated on the biopolymeric beads, due to the enhanced rate of protonation and deprotonation of functional groups and thus, bring about the increase in the adsorption of Hg (II) ions. At much higher temperatures (above 30^{0}C) ,the observed

decrease in the adsorption may be due to the weakening of the binding forces between metal cations and the active sites on present on the biopolymeric beads[20].

Conclusions

Biopolymeric beads composed of cross linked sodium alginate prove to be an effective adsorbent for removal of mercury ions from aqueous solution. The adsorption of mercury ions follows Langmuir equation as well as the Freundlich equation. The high value of adsorption coefficient provides a strong quantitative evidence for the efficiency of the adsorption beads under study. The adsorption attains an equilibrium stat us after 60minutes and decreases with increasing solid to liquid ratio. The adsorption of Hg (II) is quite sensitive to pH of the suspension and shows an optimum uptake value at pH 6.0. The quantitative parameters of the adsorption process justify the selection of sodium alginate beads as effective adsorbent for bringing down metal ion-induced toxicity of drinking water and industrial effluents. The polymeric adsorbent beads of sodium alginate could be repeatedly used in the adsorption studies by adsorption–desorption cycle without detectable losses in their initial adsorption capacities.

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Table 1

Static and Kinetic parameters for adsorption of Hg (II) ions onto biopolymeric beads

S. No.	Parameter	Value
1	Adsorption coefficient, K (g^{-1} dm^{-3})	5.4
2	Adsorption capacity, a_s (mg g^{-1})	2.12
3	Predicted sorption , k_f (mg g^{-1})	0.549
4	Freundlich constant, n	6.41
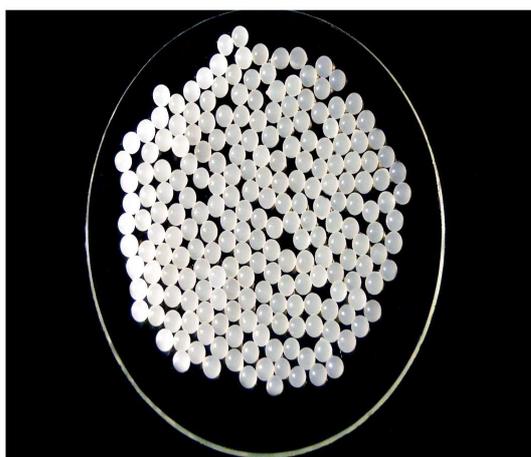
Figure 1 A photograph showing (a) dry and (b) swollen beads

Fig.2. (A) FTIR spectra of biopolymeric beads before adsorption
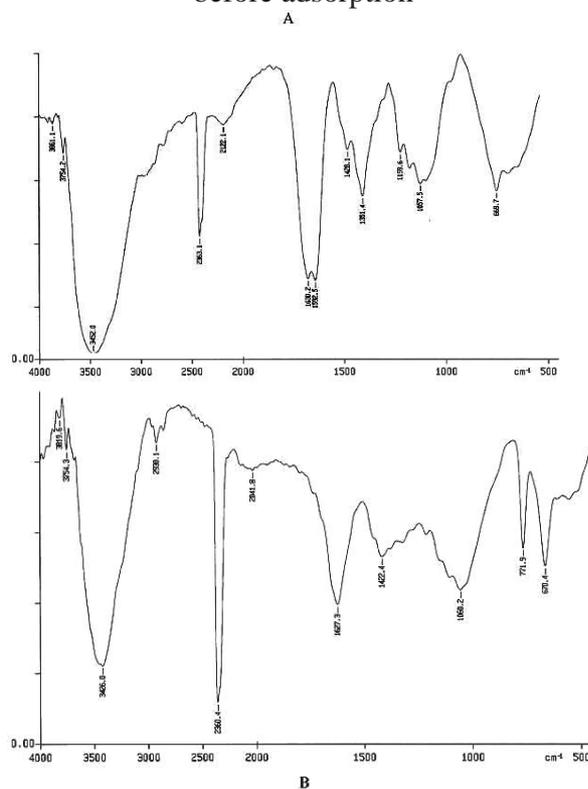
Fig.2.(B) FTIR spectra of biopolymeric beads, after adsorption.

Fig. 4   Effect of pH on the adsorption of Hg (II) ions onto polymeric beads of Sodium alginate = 0.2 g, temp. = 28 ^{o}C.
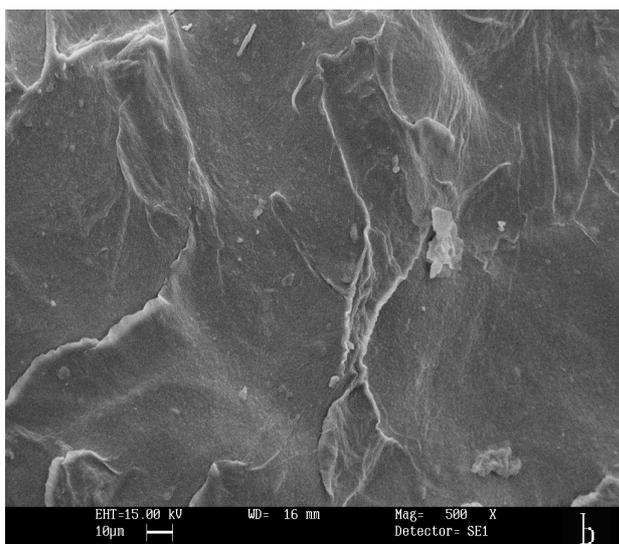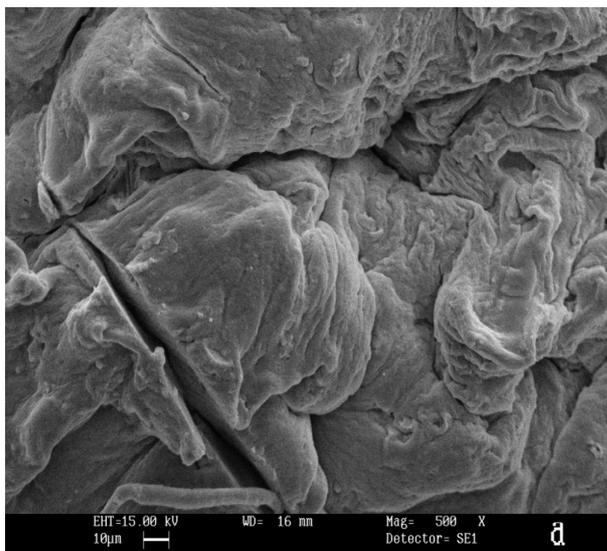
Fig.3. SEM image of the microspheres surface 3. (a) native (unadsorbed) , 3. (b) adsorbed Hg(II)
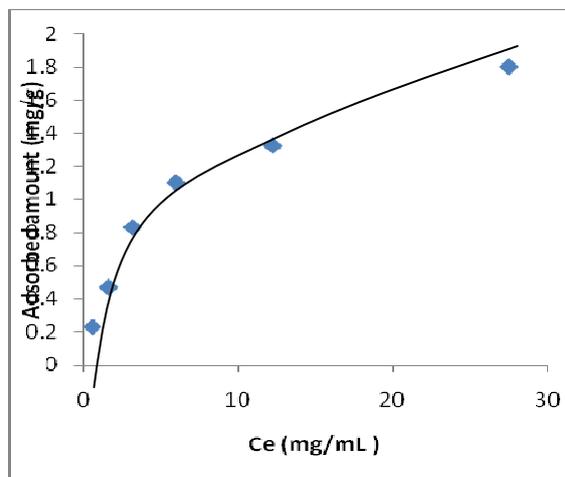
Fig. 5   Langmuir adsorption isotherm drawn between adsorbed amount of Hg (II)ions and equilibrium concentration of mercury solution showing the adsorption of Hg (II) ions onto polymeric beads
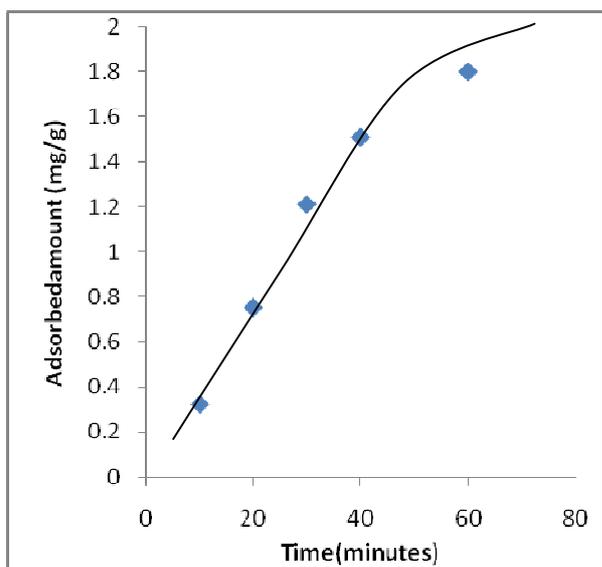
Fig.6 Variation in the adsorbed amount of Hg (II) ions with time for fixed amount of alginate beads = 0.2 g, pH = 6.0, temp. = 28 $^{\circ}$ C.
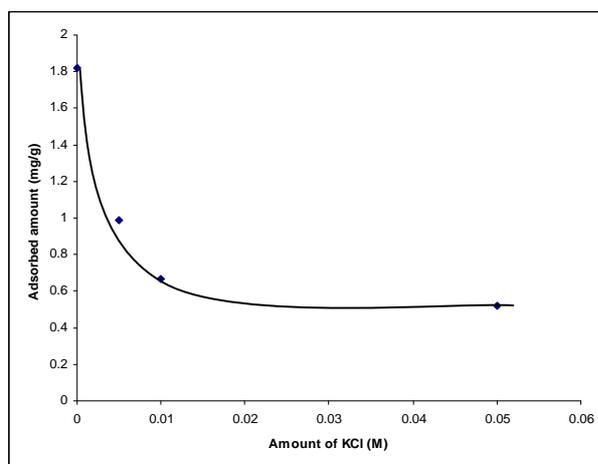

Fig.8 Effect of addition of salts on the adsorption of Hg (II) ions onto polymeric beads of Sodium alginate = 0.2 g, pH = 6.0, temp. = 28 $^{\circ}$C .
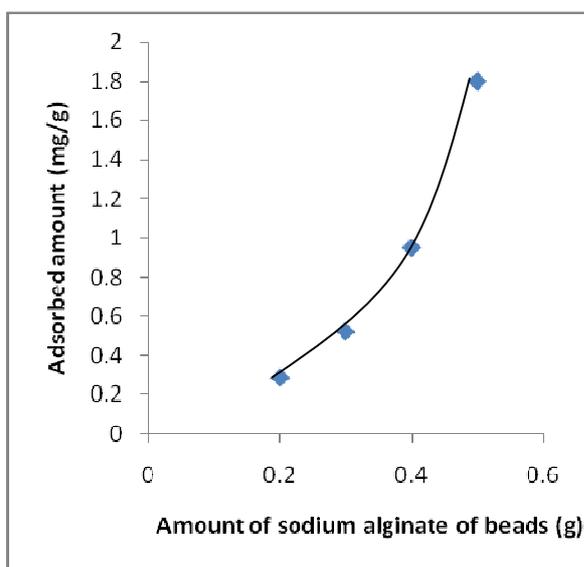

Fig.7 Effect of solid to liquid ratio on the adsorption of Hg (II) ions onto polymeric beads of Sodium alginate = 0.2 g, pH = 6.0, temp. 28 $^{\circ}$C .
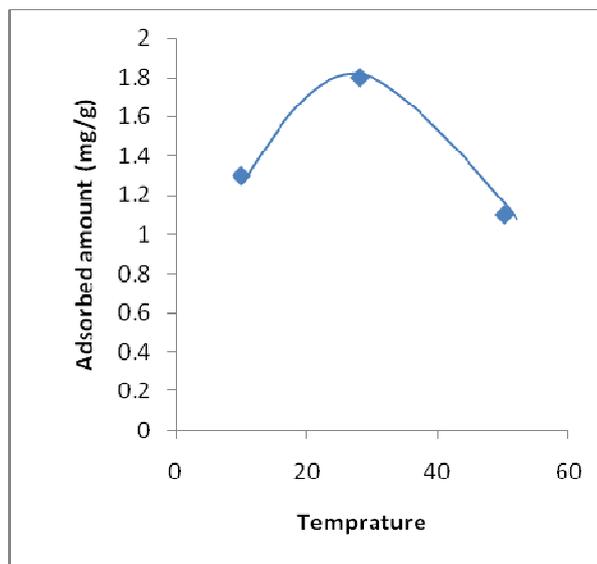

Fig.9 Influence of temperature on the adsorption of Hg (II) ions onto polymeric beads of Sodium alginate = 0.2 g, pH = 6.0