Removal of copper (II) ions by adsorption onto crosslinked calcium alginate beads

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ABSTRACT

The removal of Copper (II) ions from aqueous solutions by adsorption onto crosslinked polymeric calcium alginate beads was studied at fixed pH (4.0) and room temperature (±25ºC). The progress of the adsorption process was monitored and various adsorption parameters were evaluated. The experiments were conducted to determine the pH profiles, time dependencies and capacities of copper uptake.

INTRODUCTION

The increased use of metals and chemicals in the process industries has resulted in the generation of large quantities of aqueous effluents that contain high levels of heavy metals, creating serious environmental disposal problems. Additionally, mining, mineral processing and extractive metallurgical operations generate huge volumes of toxic liquid waste[1].

Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as a contaminant in food, especially shellfish, lever, mushrooms, nuts and chocolates. Briefly, any processing or container using copper material may contaminate the product, such as food, water or drink. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well[2]. The accumulation of copper in the human liver is a characteristic of Wilson's disease, which produces neurological and psychiatric defects[3].

Thus, the removal of metal ions from dilute wastewaters has become an important and widely studied research area where a number of technologies have developed over the years[4]. These include methods such as precipitation, evaporation, electroplating, ion exchange and membrane processes[5,6]. These processes are expensive and also have other shortcomings such as incomplete removal of metals, limited tolerance to pH change, moderate or no metal selectivity, very high or low working levels of metals and production of toxic sludge or other waste products that also need disposal[7]. Therefore, the research for new and innovative technologies to remove toxic metals has focused on the metal removal capacities of various biological materials[8–10].

Biosorption, which is a property of certain type of inactive, dead microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions, is one of the most promising technologies involved in the removal of toxic metals from industrial waste stream and natural waters[11,12]. The most abundant polysaccharide in the

cell wall of brown sea weeds is alginic acid. Alginic acid is a polymer constituted by two uronic acids (b–1, 4D–mannuronic acid and a–1, 4–L guluronic acid) with molar ratio between the acids ranging from 0.25 to 2.5. Alginic acid is present in these seaweeds usually as calcium, magnesium, sodium and potassium salts, mainly in the cell wall. It is a structural polysaccharide with strong ion exchange properties. Alginate is a linear polyuronate, which can be crosslinked by using calcium ions. The sodium alginate gel is a cheap, nontoxic and abundantly available immobilization matrix.[13, 14].

Another important property of alginate is availability of binding sites for divalent cations due to the presence of amino, carboxyl, phosphate and sulfate functional groups on the molecule, which make it a potential adsorbent for removal of toxic metal ions from industrial effluents[15]. Thus, looking to the efficient adsorption affinity of alginate to variety of metal ions, the present study has been designed to evaluate metal ion removal performance of calcium alginate beads from synthetic effluents containing Cu(II) ions. The experiments were conducted to determine the pH profiles, time dependencies and capacities of copper uptake.

MATERIAL AND METHODS

Sodium alginate was obtained from Loba–Chemie, Mumbai (India) and used as received. Other chemicals such as copper sulphate and calcium chloride (crosslinking agent for alginate) (Loba Chemie, Mumbai, India) were used of high purity grade. Double distilled water was used throughout the experiments.

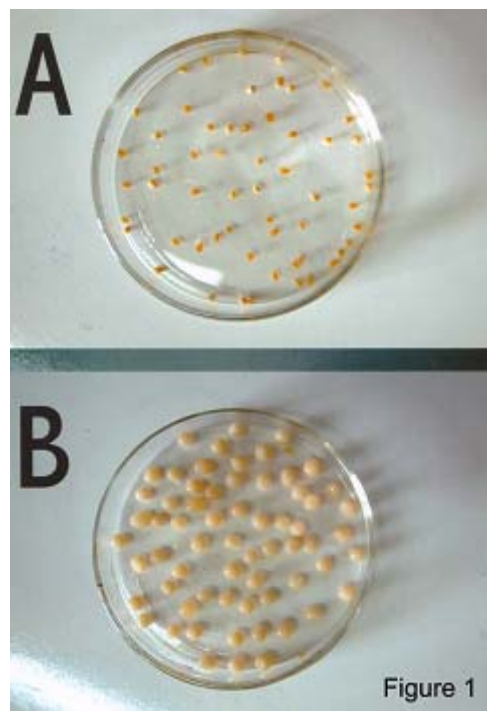### Preparation of polymeric Ca–alginate beads

The calcium alginate beads employed as adsorbent were prepared by dropwise addition of a solution of sodium alginate (1 g in 25 mL distilled water) into a 0.05 M calcium chloride solution. The addition was done with the help of a syringe with constant stirring. The beads so produced were allowed to harden by leaving them in $CaCl_2$ solution for 24 h and thereafter filtered and washed thrice with double distilled water. These biopolymeric beads were stored at room temperature in double distilled water and used as such. A photograph of both dry and swollen biopolymeric beads is shown in Fig.1.

Adsorption experiments

The adsorption was carried out by the contact method, as already described in literature[16–18]. In brief, the swollen biopolymeric beads (0.2 g) were added to a 20 mL known solution of $CuSO_4.5H_2O$ of 150×10^{-3} mole dm^{-3} concentration at constant pH 4.00 and temperature. The suspension was shaken for 3 h in a wrist action shaking machine which was found to be a sufficient time to attain equilibrium adsorption. After shaking the suspension was centrifuged, filtered and the amount of copper in the supernatant was determined spectrophotometrically[19]. The amount of Cu (II) adsorbed, was calculated by the following mass balance equation.

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

where C_i and C_f being the initial and final concentrations (g dm^{-3}) of copper sulphate solutions, respectively, V being the volume of metal ion solution and m is the weight of swollen beads taken as adsorbent.

Fig.1: Photograph depicting dry (A) and swollen (B) polymeric beads of Calcium alginate.

The progress of adsorption of Cu(II) ions on Ca–alginate beads was monitored by running several adsorption experiments under identical conditions and the amount of adsorbed copper was determined in each set one by one at different time intervals.

RESULTS AND DISCUSSION

FTIR spectra:

The polymeric crosslinked alginate beads were characterized by FTIR spectra. The FTIR spectra of unadsorbed and Cu(II) ion adsorbed polymeric beads are sown in Fig. 2 (A) and (B), respectively. The spectra provide clear evidences of presence of alginate in the beads as well as suggests how the Cu(II) ions bind to the carboxylate ions of alginate in the adsorbent beads.

The spectra clearly marks the presence of alginate as confirmed by the O–H stretching of hydroxyls at 3424 cm^{-1}, C–O stretching of alcoholic –OH at 1031 cm^{-1} and C–O stretching of –COOH group at 1413 cm^{-1}. The spectra also present a strong asymmetrical stretching band at 1642 cm^{-1} due to carboxylate anion of alginate.

In the spectra (b), a slight shift of carboxylate anion band from 1642 cm^{-1} to 1637 cm^{-1} is clearly seen, which may be due to the electrostatic binding of Cu (II) ions to anionic sites. Studies on concentration effect and adsorption isotherm

In order to understand the metal ion and polymeric beads interaction, adsorption experiments of different copper concentrations in the range 25 x 10^{-3} to 150 x 10^{-3} mole dm^{-3} were carried out and it was found that with the increase of copper concentration, the amount of copper adsorbed increases ,as on increasing the concentration of solute, greater number of metal ions arrive at the interface and thus get adsorbed[20].
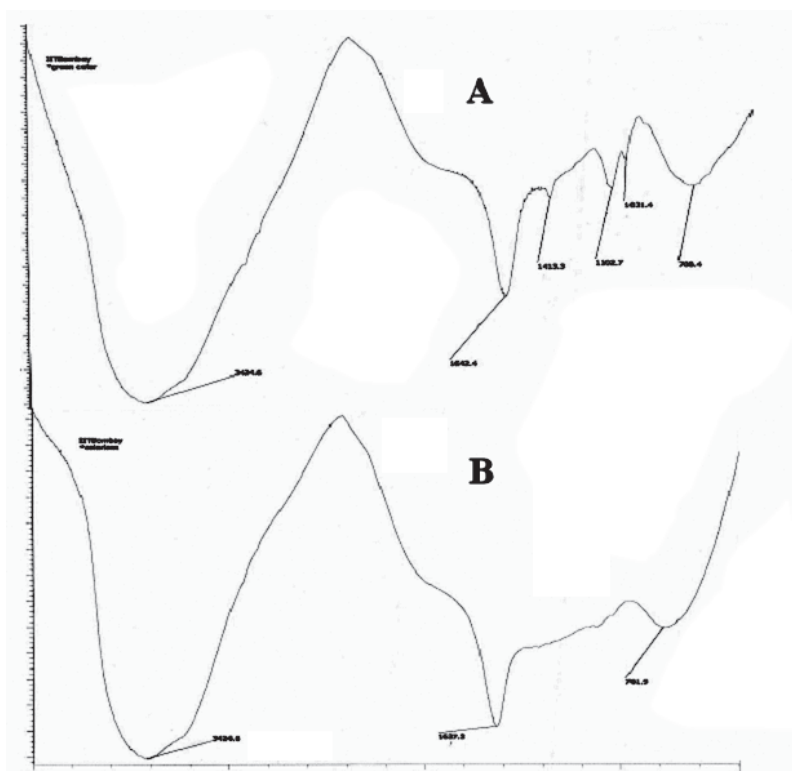

Fig. 2: FTIR spectra of biopolymeric beads (A) without adsorption, (B) with adsorption.

On increasing the concentration of copper sulphate solution above 150 x 10^{-3} mole dm^{-3}, the amount of copper adsorbed was found to decrease as a consequence of the progressive saturation of the binding sites.

In order to construct an adsorption isotherm, the adsorbed amount of copper was plotted against the equilibrium concentration of the adsorbate solution (Fig. 3). The following adsorption isotherms were considered :
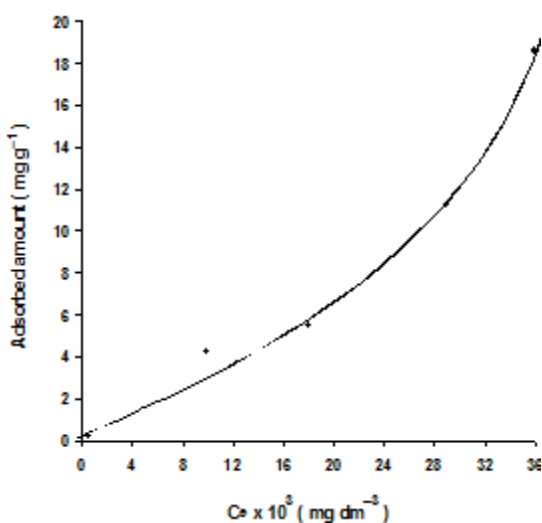
Fig. 3: Langmuir adsorption isotherm drawn between adsorbed amount of Cu (II) ions and equilibrium concentration of copper sulphate solution showing the adsorption of Cu (II) ions onto biopolymeric beads of Ca alginate = 0.2 g, pH = 4.0, Temp. = 30±0.2°C.

Langmuir Isotherm

A standard mathematical representation of Langmuir isotherm is as follows :

$$... \quad (2)$$

where a is the adsorbed amount of Cu (II) ions (mg g^{-1}) at equilibrium concentration C_e, a_s the adsorbed amount of metal ion at saturation (adsorption capacity) and K is the adsorption coefficient.

In the present work, the Langmuir isotherm is shown in Fig. 3, which clearly shows that the adsorption isotherm belongs to L–2 type which reveals that the adsorbed copper (II) increases with increasing concentration of copper sulphate and ultimately starts decreasing indicating saturation in the adsorbed amount. The values of K and a_s, determined from eq. (2) are summarized in Table 1, which clearly suggests a favourable adsorption of copper ions.

Table 1:

Langmuir and Freundlich constants	
1. Adsorption coefficient, K (mg^{-1} dm^3)	20.6
2. Adsorption capacity, a_s (mg g^{-1})	0.172
4. Predicted sorption, K_f (mg g^{-1})	20.89
5. Freundlich constant, n	5.0

Freundlich isotherm The Freundlich isotherm has the form

$$\text{Log } a = \log k_f + 1/n, \log C_e \qquad ... \quad (3)$$

$$\frac{C_e}{a} = \frac{1}{a_s} K + \frac{C_e}{a_s}$$

where k_f and n are Freundlich constants, characteristics of the system, indicating the adsorption capacity and adsorption intensity, respectively. k_f is the predicted quantity of adsorption per gram of the bio–polymeric beads at unit equilibrium concentration of copper sulphate solution and 1/n is the measure of the nature and strength of the adsorption process and the distribution sites. It has been shown using mathematical calculation that n values between 1 and 10 represent beneficial adsorption[21,22]. The values of n and k_f determined from eq. (3) are summarized in Table 1, which shows a favourable adsorption of copper ions.

**Time dependence studies for copper binding**

The progress of adsorption process monitored at different time intervals is shown in Fig. 4, which clearly reveals that the adsorption of Cu ions increases with the increase of time and then levels off after 3 h. It has been observed that the rate of adsorption is almost constant up to 2 h and then slows down.

pH profile studies for copper binding

The pH is an important parameter to affect biosorption of metal ions from aqueous solutions. The uptake of free ionic copper was found to increase with the increase of pH from 2.0 to 4.0, shown in Fig. 5 and above pH 5.0, the insoluble copper hydroxide started precipitating from the solution, thus making the adsorption studies impossible. In the present study, all the experiments were carried out with initial pH value 4.0, using 0.1 mol dm^{-3} HCl and 0.1 mol dm^{-3} NaOH.

At pH values lower than 3.0, Cu (II) removal was inhibited possibly as a result of the competition between hydrogen and copper ions on the adsorption sites.
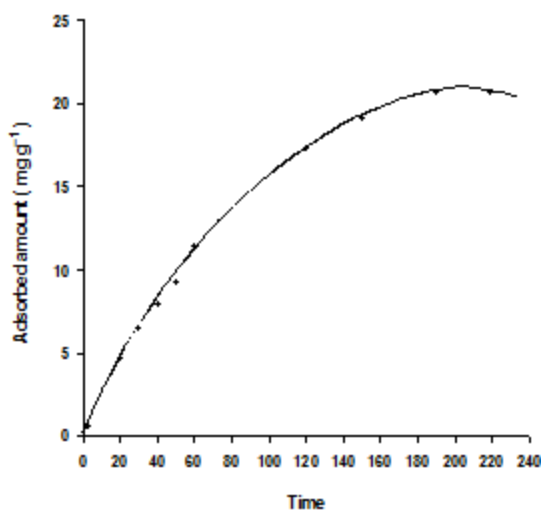
Fig. 4: Variation in the adsorbed amount of Cu(II) ions with time for fixed amount of Ca alginate beads = 0.2 g, pH = 4.0, Temp. = 30±0.2°C.
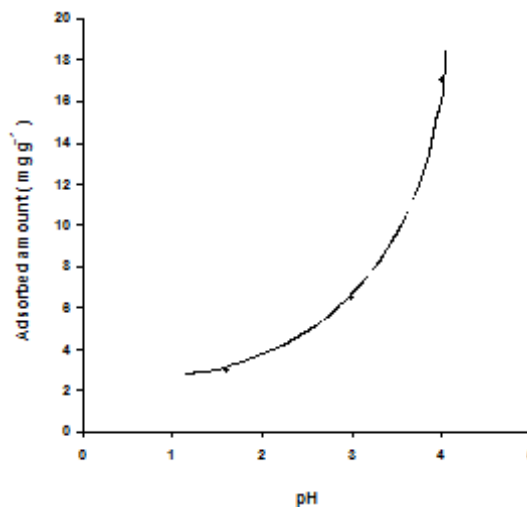
Fig. 5: **Effect of pH on the adsorption of Cu(II) ions onto biopolymeric beads of Ca alginate = 0.2 g, pH = 4.0, Temp. = 30±0.2°C.**

Crosslinked calcium alginate beads have proved to be a potential adsorbent for removal of Cu(II) metal ions from synthetic metal ion containing samples. The adsorption of copper ions is found to follow Langmuirian adsorption process as well as Freundlich isotherm equation. A high value of adsorption coefficient provides a strong quantitative evidence for the efficiency of the adsorbent beads under study. The process of removal of Cu(II) ions is significantly dependent on the experimental protocol. It is noticed that in the pH range 2–4, the adsorption is appreciably enhanced, whereas in the highly acidic medium (below pH 2) a negligible removal is obtained. The quantitative parameters of the adsorption process justify the selection of calcium alginate beads as effective adsorbent for bringing down metal ion induced toxicity of drinking water and industrial effluents.

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