

Fast removal of concentrated heavy metal ions using an alginate-poly(ethylene imine) biological adsorbent

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Abstract. Accumulation of heavy metals in aqueous environment has raised increasing concerns for public health. An alginate based biodegradable adsorbent was successfully developed for fast removal of heavy metals, and could adsorb 99.4% Cu(II) in 10 min when immersed in 10 mM Cu(II). Surface characteristics exhibited 25.65 wt% occupancy of Cu(II), further demonstrating the high adsorption capacity of the adsorbent. The adsorbent can be regenerated using either 10 wt% of Na₂CO₃ or 0.1 M HCl. Reusability under each condition did not show decrease. Adsorption of Fe(II) was also tested. The adsorbent showed 95% removal of Fe(II) in just 2 min. These results demonstrate successful design and preparation of a novel biodegradable adsorbent with a matrix of properties suitable for application in fast removal of heavily polluted waste water containing a high content of metal ions.

INTRODUCTION

Due to fast development of modern society, growing release of heavy metals has adversely impacted our aqueous environment. Accumulation of the heavy metals in food chain has raised increasing concerns for public health. Various methods, such as adsorption, ion-exchange, electrolysis and precipitation, have been applied to remove the heavy metals. Among these methods, adsorption has been suggested as a low cost solution. Biological material based adsorbent is bio-degradable and environmentally friendly, and therefore, advantageous over many other synthetic materials to reduce heavy metal pollution.

Alginate based biological adsorbent has been well studied for this application [1]. However, as it has been extensively reported, the alginate adsorbent is easy to disintegrate or dissolve during regeneration [2]. A method such as proper cross-linking is required if high stability of the adsorbent is demanded. Moreover, slow kinetics has further limited practical application of the adsorbent. Therefore, it is desirable to develop a kind of alginate adsorbent with fast adsorption kinetics and high stability so that the adsorbent can be reused after regeneration.

Poly(ethylene imine) (PEI) is a kind of polycationic polymer. It can form stable cross-linking with alginate, preventing the alginate structure from disintegration during regeneration process. Furthermore, the amino groups introduced by PEI can enhance adsorption via forming complexes with some metals. Therefore, an biological alginate based adsorbent was developed by crosslinking sodium alginate using PEI in this work. The adsorption kinetics was examined under a condition that contained a high concentration of Cu(II). Regenerating methods using either sodium carbonate or hydrogen chloride were compared and reusability of the adsorbent was further tested. The adsorption of Fe(II) ion was also examined.

MATERIALS AND METHODS

Materials

Sodium alginate, copper(II) chloride dihydrate, iron(II) sulfate heptahydrate, hydrogen chloride, sodium carbonate and sodium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. PEI (Mw ~ 70, 000) was

purchased from Sigma-Aldrich Co., Ltd.

Preparation of the adsorbents

Sodium alginate was dissolved in D.I. water and stirred at high speed with a magnetic stirrer to make 0.5 wt% homogeneous solution. The freshly prepared solution was subsequently freeze-dried to remove moisture. The resulting samples were first cross-linked with Copper(II) chloride dihydrate (0.323 g/g alginate) and then PEI (in mass ratios of about 1 PEI : 1 Copper(II) chloride dihydrate : 3 alginate). Samples were boiled for 30 minutes to speed up the cross-linking process.

Regeneration

For regeneration, either 0.1 M HCl (Li et al., 2013) or 10 wt% Na₂CO₃ solution was used. The adsorbent-ion complexes were immersed in 10 ml HCl or Na₂CO₃ solution and magnetically stirred. The regeneration process lasted 6 hour using HCl or 2 day using Na₂CO₃. After a certain period of time, aliquots of the solution were taken and centrifuged in micro-centrifuge for 1 min. The supernatant was removed for assay of metal concentration using Flame Atomic Absorption Spectroscopy (FAAS). After regeneration, the adsorbent was washed to remove unsorted metal. Finally, the adsorbent was obtained by centrifuge and depletion of the supernatant.

Adsorption of heavy metal

10 mL of Copper(II) chloride dihydrate solution (~ 10 mM) and adsorbent (0.03 g) were added to a 25 mL beaker and magnetically stirred for 10 min. 0.5 ml samples were taken out from the suspension every 2 min and centrifuged in micro-centrifuge for 1 min. The supernatant was removed for assay of metal concentration (C) using FAAS. The adsorption capacity (q, mg/g alginate) was calculated using the mass balance equation: $q = (C_0 - C) \cdot V \cdot M_w / m$, where C₀ is the initial concentration of the metal solution (mM), V is the volume of solution (L), M_w is the molecular weight of the metal ion and m is the amount of adsorbent (g).

Elemental analysis of the adsorbent

The elemental analysis of the adsorbent was performed after regeneration using Na₂CO₃ and re-adsorption of Cu(II) by a scanning electron microscope coupled with energy dispersive X-ray analysis (SEM-EDAX) as reported elsewhere [3] using a Nova NanoSEM 230 system (FEI, USA). The system can be used to acquire quantitative spot analysis and qualitative or quantitative X-ray elemental maps.

RESULTS AND DISCUSSION

Adsorption of copper(II) ion

At a high loading of Cu(II) (~ 10mM), the alginate-PEI adsorbent exhibited fast adsorption kinetics, reducing the metal concentration down to 0.16 mM after just 2 min (Fig. 1a). The percentage of metal removal was more than 98% (Fig 1b). The adsorbent can further remove copper to an extent as high as 99.4% after 10 min, and reached a capacity of 202 mg/g alginate. In comparison, the adsorption rate by freeze-dried sodium alginate adsorbent was much slower, showing only 15.7%, 24.6% and 64.3% removal of Cu(II) after 2, 10 and 60 mins, respectively (Fig. 1b). It has been suggested that equilibrium adsorption of Cu(II) can be achieved within 60 min using an adsorbent via molecular imprint technique [4]. During our preparation, the target ion was also incorporated into the adsorbent, under which condition the adsorbent could form coordinated geometry for fast adsorption based on the charges and sizes of the target ion. Moreover, our adsorbent exhibited even faster adsorption than a nano-sized carbon immobilized alginate bead that can remove 80%-95% metal in 2 hour as reported elsewhere [5]. Therefore, the adsorbent here should be very useful to remove Cu from the concentrated waste water.

Regeneration

In order to examine the reusability of the adsorbent, two regenerating methods were explored. Fig. 2 shows that when the PEI-alginate adsorbent was regenerated using sodium carbonate, the adsorption capacity could reach 201

mg/g alginate, which is comparable to that from first run (202 mg/g alginate). If the adsorbent was regenerated using 0.1 M hydrogen chloride, it showed adsorption capacity of 4.6 mg/g alginate, which was 23% of that using sodium carbonate. The adsorption capacity did not reduce after a 2nd regeneration cycle, suggesting the adsorbent was reusable under either regenerating conditions (Fig. 2). As shown in Table 1, surface characteristics of the adsorbent demonstrated a high content of Cu(II) (25.65 Wt%) after regeneration using Na_2CO_3 and re-adsorption of Cu(II), confirming high capacity of the adsorbent for Cu(II) adsorption. Only 1.18 Wt% Cl^- was present on the surface, suggesting Cu(II) was in a complex with the adsorbent, probably via interaction with COO^- group of alginate.

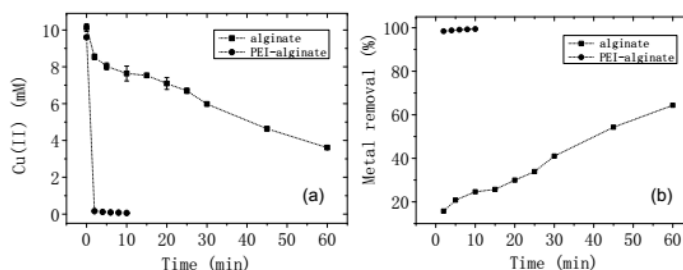


FIGURE 1. Removal of Cu(II). (a) Concentration of Cu(II) in solution; (b) removal percentage.

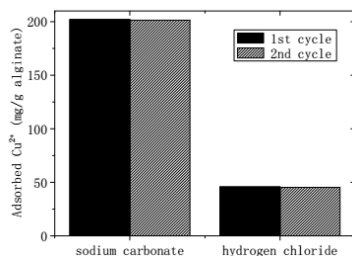


FIGURE 2. Reusability of the adsorbent after regeneration.

Hydrogen chloride regenerating process was rapid (Fig. 3) though the adsorption capacity was alleviated than Na_2CO_3 regenerated adsorbent. Compared to slow release of Cu(II) using the sodium carbonate, the released Cu(II) quickly approached 6.7 mM within 5 min using hydrogen chloride, showing the potential of this process for enrichment of copper metal in a system as reported elsewhere [6]. The elution mechanism might involve the ion-exchange of Cu(II) with Na^+ or H^+ [7]. From our experiments, the tightness of the complexes between the adsorbent and cations was in the order of H^+ -alginate > Cu(II)-alginate > Na^+ -alginate. As a result, the adsorbent could be regenerated with HCl fast but the regenerated adsorbent had less capacity for Cu(II) adsorption.

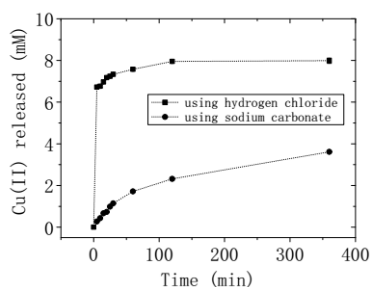


FIGURE 3. Desorption kinetics during regeneration.

Adsorption of ferrous ion

The capacity of this adsorbent for adsorption of other metal ion such as Fe(II) was also tested (Fig. 4). Similar to adsorption of Cu(II), the adsorption of Fe(II) was also rapid, reaching 95% removal in just 2 min, broadening application of the adsorbent. Fe ions are discharged in a large amount by steel factory, copper etching solution, and

paint industries, etc. They may be not only harmful to aquatic organisms [4] but also to human health. The fast adsorption kinetics made our adsorbent particularly useful for removal of Fe ions from concentrated waste water quickly.

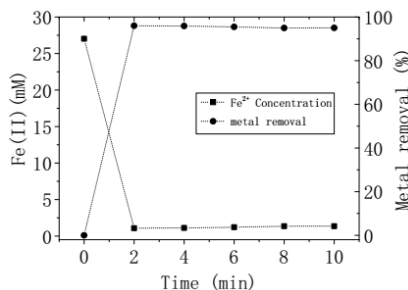


FIGURE 4. Adsorption of Fe(II).

CONCLUSION

A biological adsorbent was successfully developed by crosslinking alginate using PEI. Fast adsorption kinetics was obtained with 99.4% removal of Cu(II) within 10 min when the adsorbent was immersed in 10 mM Cu(II) solution. The adsorption capacity of Cu(II) reached 201 mg/g alginate. Surface characteristics of the adsorbent demonstrated a high content of Cu(II) (25.65 Wt%), confirming the high capacity for adsorption. Furthermore, the adsorbent also showed high capacity and fast removal of Fe(II), indicating potential of this biodegradable option for application in fast removal of different heavy metals.

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