



Research Paper

Diffusion and agglomeration of iron oxide nanoparticles in magnetic calcium alginate beads initiated by copper sorption



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ABSTRACT

The contamination of aqueous solutions by heavy metals ions is an important environmental and social problem. During the last decade, cheap and environmentally friendly water treatment technologies based on the adsorption of ions by natural biosorbents were consequently proposed. Among them, magnetic biosorbents are of first interest due to their additional magnetic separation properties. The present study focuses on the bioadsorption of copper ions by magnetic alginate beads and on the associated modification of the beads. The ferromagnetic behaviour was achieved by including ferromagnetic Fe₃O₄ nanoparticles in calcium alginate beads. The role of iron oxide on the biosorption process was investigated by kinetic studies and demonstrates the minor role of iron oxide during the adsorption process. Kinetic data are very well fitted by a second-order model and isotherms correspond to the Langmuir model. Morphological and chemical characterizations of the beads after adsorption were performed by Scanning Electron Microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR) and X-Ray Photoelectron Spectroscopy (XPS). They demonstrate the presence of copper carboxylate complex in a unidentate form with or without Fe₃O₄ nanoparticles included in the beads. Moreover, they evidence the migration and the agglomeration of Fe₃O₄ nanoparticles toward the surface during copper adsorption. This phenomenon irretrievably changes the nature of the beads and has to be considered within the context of reusability of the sorbents.

1. Introduction

The contamination of aqueous solution by metal ions is of considerable concerns worldwide because of its impact on human health. Different methods already exist for the removal of toxic metal ions from aqueous solutions. They include chemical precipitation [1,2], coagulation and flocculation [3,4], membrane filtration [5,6] and ion exchange [7,8]. However, they are costly or inefficient at low metal concentration, and can also generate secondary wastes if organic solvents are used [9,10]. Within this context, adsorption of positive ionic species by biomaterials was proposed as a promising method due to its simplicity, efficiency and low cost [11–15]. Biomaterials have emerged as an attractive, sustainable, inexpensive and eco-friendly alternative for the treatment of contaminated water with organic and inorganic pollutants [16–18]. Among them, alginate has received a particular attention. It is a copolymer composed of α -L-glucuronic acid (G) and β -D-mannuronic acid (M) linked together in different sequences via 1–4

bonds. During the last decade, adsorption of several ions was studied by alginate in its insoluble form with calcium ion as cross linking agent [19–23]. It is now well accepted that the adsorption process is governed by the interaction between the carboxylate/hydroxyl groups of alginate and cations. The dominant chemical process during adsorption is the ion-exchange mechanism between calcium ions in alginate and metals (Cu, Ag ...) in the solution.

More recently, calcium-alginate magnetic adsorbents were developed due to their additional magnetic separation properties. Lim and Chen [24] demonstrated that alginate materials containing magnetite (Fe₃O₄) nanoparticles with a relatively high adsorption capacity of copper ions of 60.24 mg/g can indeed be easily separated from the solution by an external magnet. This method was also applied successfully to adsorption of lanthanum (III) [25]. However, while chemistry of metal adsorption by alginate is relatively well known [26], only a few studies have focused on the role of iron oxide nanoparticles on the adsorption process. Among them, the X-ray photoelectron spectroscopy

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(XPS) measurements performed on magnetic alginate after adsorption of Cu^{2+} and Pb^{2+} revealed an enhancement of metal oxide contribution in the O(1s) spectra suggesting the formation of metal oxides on the surface [27,28]. This result rarely appears in the studies devoted to adsorption of ions by non-magnetic alginate and could be explained by participation of iron nanoparticles in the adsorption process [27]. In contrast, Roger et al. [29] report no significant change of sorption associated with the integration of ferromagnetic nanoparticles in the polymer.

In the present study, to get further insights on the role of such iron oxide nanoparticles in the copper adsorption process, we present a kinetic study of adsorption by magnetic alginate beads together with a full set of chemical characterization of the material before and after adsorption. For that purpose, FTIR (Fourier Transform InfraRed spectroscopy), SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-ray analysis) and XPS measurements have been made on alginate immersed in copper solutions of different concentrations. The comparison between all the achieved results demonstrates that the copper adsorption by magnetite modified alginate beads is not as simple as discussed in most of the studies in the literature and it is indeed associated with agglomeration of nanoparticles on the surface of the beads.

2. Materials and methods

2.1. Chemicals

Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) supplied by Fluka was used as a crosslinking agent for alginate. Sodium alginate (SA) (W201502 from Sigma Aldrich), copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), iron (II, III) oxide (Fe_3O_4) with particle diameter below 50 nm, hydrochloric acid (37% aqueous solution) and sodium hydroxide (NaOH) were purchased from Sigma Aldrich. All chemicals were bought in analytical purity and used without further purification.

2.2. Preparation of magnetic alginate beads (MABs)

The sodium alginate (SA) solution was prepared by adding 0.75 g of SA into 50 mL of distilled water under vigorous stirring for 30 min at 80 °C. In order to elaborate magnetic alginate beads (MABs) that incorporate 20% (w/w) of magnetite, 0.1875 g of Fe_3O_4 nanoparticles was added to the SA solution. The obtained mixture was then placed in ultrasonic bath for 90 min at room temperature to obtain a homogeneous mixture. Subsequently, the solution was slowly dropped into 100 mL of 2% CaCl_2 bath. This leads to precipitation of magnetic alginate droplets due to ionic crosslinking property of Ca^{2+} ions. The obtained beads are spherical with an average diameter of 2 mm. Note that the objective of this study is to understand the copper adsorption process by the MABs. It is clear that the bead size could be modified according to the chosen applications. The produced MABs were then allowed to rest and harden for 24 h at room temperature without agitation. They were then filtered and rinsed with deionized water several times to remove the excess of calcium. They were finally dried in an oven at 55 °C for 2 days. As shown in Fig. 1 of the Supplementary information, the obtained MABs can be easily manipulated by an external magnet and are thus suitable for magnetic separation. The same procedure is followed to elaborate pure alginate beads (ABs) without adding magnetite nanoparticles to the sodium alginate solution. Similar synthetic methods have already been described [30–33].

2.3. Adsorption measurements

The kinetic of adsorption was carried out at room temperature with a fixed copper (II) concentration of approximately 75 mg/L. The aqueous solution of Cu (II) was prepared by dissolving 73.8 mg (± 0.1) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water in a 250.00 mL (± 0.23) volumetric

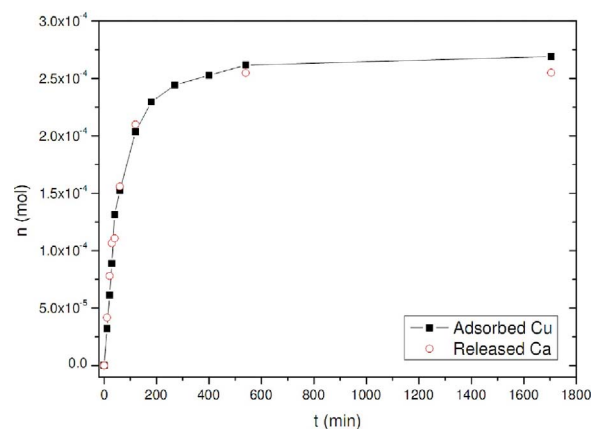


Fig. 1. Amounts of adsorbed Cu^{2+} by MABs and released Ca^{2+} in the solution versus time (L concentration).

flask. An amount of 0.300 g (± 0.001) of magnetic alginate beads were then added to the copper solution and stirred using a rotary shaker at 250 rpm, a room temperature of 298.4 K (± 2.0), a pressure of 1 atm and a pH of 5.10 (± 0.01). A sample of 2.00 mL (± 0.01) was taken by a variable pipette during this process. During the first two hours, samples were taken at regular time intervals of 10 min. Subsequently, the sampling process occurred every 3 h until reaching the time limit of 24 h. Each sample was diluted by adding 13.000 mL (± 0.001) of distilled water. The diluted solution was then placed in a 15 mL vial for the AAS analysis. The dilution factor was used to determine the concentration from the AAS measurements. The AAS analysis of the sample taken at time 0 (before adding the adsorbent dose to the solution) allowed us to determine the initial concentration of copper in the solution. The pH of the solutions was measured at the beginning and at the end of each experiment and adjusted to 5.10 (± 0.01) by using sodium hydroxide or hydrochloric acid. The zero point charge (ZPC) value was obtained by plotting pH_{final} vs $\text{pH}_{\text{initial}}$ and it was found to be 6.5. Consequently, the adsorbent surface is slightly positively charged. During these AAS measurements, the concentration of copper and calcium ions in the solution were obtained as per the below formula:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_t is the copper solution concentration at the time t , and C_0 the initial concentration.

The isotherm experiments were performed by varying the initial copper concentration in the range of 15–500 mg/L. At each concentration level, a 250.0 mL (± 0.2) of copper solution was placed into a 500 mL Erlenmeyer flask. Subsequently, 0.300 g (± 0.001) of magnetic alginate beads was added to the flask and stirred using a rotary shaker at a speed of 250 rpm, a pressure of 1 atm, a pH of 5.10 (± 0.1) and a room temperature of 298.4 K (± 2.0). The sampling continued until reaching the time limit of 24 h. The desired sample volume was taken by a variable pipette and was diluted by distilled water in a 50.0 mL (± 0.6) volumetric flask. Then, the diluted solutions were placed in a 15 mL vial for the AAS analysis. The dilution factor was used to determine the copper concentration in the samples from the AAS reading. In this case, the adsorption capacity (q_e) is defined as the amount of copper cations adsorbed per unit mass of adsorbent at equilibrium (mg/g). It is given by the relation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where C_0 and C_e are the initial and the equilibrium concentrations of copper solution, respectively. V is the volume of the copper solution and W is the total weight of the adsorbent including Fe_3O_4 nanoparticles.

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