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Porous alginate aerogel beads for effective and rapid heavy metal sorption from aqueous solutions: Effect of porosity in Cu^{2+} and Cd^{2+} ion sorption

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HIGHLIGHTS

- Ca-alginate porous aerogel beads evaluated for the first time on metal sorption.
- Significantly enhanced sorption properties over non-porous xerogel beads.
- More efficient, 20% higher degree of active site saturation after sorption.
- Faster sorption, 99% removal achieved 600–800 min earlier.
- Multistage mechanism proposed for heavy metal sorption kinetics.

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ABSTRACT

Calcium alginate porous aerogel beads were prepared by sc-CO_2 drying, characterized and for the first time evaluated for their performance on metal ion sorption in comparison with their non-porous xerogel analogues. The aerogels were mainly mesoporous, also containing micropores and macropores with BET surface area of 419 $m^2\ g^{-1}$. The material exhibited enhanced sorption capacity with 20% higher degree of active site saturation after sorption compared to the xerogel beads and sorption values reaching 126.82 $mg\ g^{-1}$ for Cu^{2+} and 244.55 $mg\ g^{-1}$ for Cd^{2+}. The sorption kinetics exhibited a significant decrease in sorption time, with 99% removal achieved 600–800 min earlier than for xerogel beads. This behaviour indicates increased functional groups accessibility combined with increased flexibility due to the effect of porosity, facilitating chain rearrangement during ion exchange. A multistage mechanism for heavy metal sorption kinetics was suggested by the results of both Weber–Morris and film diffusion models.

1. Introduction

In the past few years alginate, a linear copolymer of a-L-guluronate (G) and a-D-mannuronate (M), which constitutes 10–40% of the dry weight of all species of brown algae, has been in the focus of research for its gelling and metal binding properties. Offering advantages such as biodegradability, hydrophilic properties, natural origin, and abundance combined with its ability to form stable hydrogels due to the presence of specially coordinated carboxylic binding sites, alginate has widely been used for the immobilization of algal biomass, microorganisms, or other specific sorbents (such as activated carbon) for various purposes, including heavy metal removal from wastewater [1].

Even though alginate has mainly been used as an immobilization agent, it plays a predominant role in metal sorption and has been reported to have excellent sorption capacity towards several heavy metal ions. In recent studies it has been shown that its sorption capacity greatly exceeds that of the actual sorbents immobilized in its matrix [2]. Due to this property, alginate has been previously studied not only concerning the mechanism of metal binding [3] and its metal sorption properties as a sorbent [4,5] but also as a composite membrane component [6,7].

However, dry alginate beads that have been used for heavy metal sorption is a rigid material with tight non-porous structure and due to the low diffusion coefficient of the material, the kinetics of sorption is somewhat slow [8]. Indeed, as noted by Lagoa and Rodrigues [8] the low porosity of dry alginate beads is its main drawback as a sorbent since it delays metal diffusion in the particle interior. Therefore, the use of the same material in a porous form would probably enhance its sorption kinetics properties. Such a porous form – the aerogel form – has already been prepared and studied by Valentin et al. [9] and since then it has been extensively characterized and recently has attracted considerable attention for

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its use in several fields such as catalysis, hydrocarbon sorption, and biomedical applications [1]. However the effect of porosity in its sorption properties has not been studied previously.

In this work, porous alginate aerogels prepared by supercritical CO_2 drying, were characterized and used for the sorption of Cu^{2+} and Cd^{2+}. Their sorption and kinetic properties were evaluated and compared with their xerogel analogues studied previously [2].

2. Materials and methods

2.1. Reagents and instrumentation

Sodium alginate was supplied by CEVA France extracted from *Laminaria digitata* collected from coastal areas around France with M/G ratio 1.5–1.7.

Stock and test metal solutions for sorption experiments were prepared using $CuSO_4{\cdot}5H_2O$ and $3CdSO_4{\cdot}8H_2O$ analytical grade and were used without further purification.

All experiments were performed in a Julabo SW22 shaking bath and metal concentrations were determined by Flame Atomic Absorption Spectrometry (FAAS) (GBC Avanta Σ).

The nitrogen adsorption isotherms at 77 K were performed in an automated volumetric system (AUTOSORB-1-Krypton version – Quantachrome Instruments). Prior to their measurement, the samples were outgassed at 60 °C for 48 h.

A Jeol JSM 7401F Field Emission Scanning Electron Microscope (SEM) was employed to characterize the surface morphology of the developed materials. The materials were subjected to gold coating prior to SEM imaging.

2.2. Aerogel alginate beads preparation

2% w/v sodium alginate solutions of were prepared by mixing the fine sodium alginate powder with distilled water while stirring. 0.1 L of the alginate solution was added dropwise into 0.5 L of 50 mmol L^{-1} $CaCl_2$ solution under gentle stirring at 25 °C. Ca-alginate hydrogel spheres were formed upon contact with the cross-linker solution and were left overnight to stabilize. The excess of cross-linker solution was removed by filtration and was washed several times with bi-distilled water. The resulting hydrogel beads were converted to alcogel via successive immersion in a series of ethanol–water solutions of increasing alcohol concentration (10%, 30%, 50%, 70%, 90%, and 100%) for 1 h for complete solvent exchange. The alcohol was exchanged by liquid CO_2 at 100 bar which was then brought to supercritical conditions at 45 °C and subsequently removed by a release valve in a controlled manner.

2.3. Potentiometric titration

Potentiometric titration was carried out using an auto-titrator (848 Titrino Plus, Metrohm). A selected mass of beads was initially suspended in 100 mL 1 N HCl overnight. After full protonation, the sample was washed with bidistilled water (400 mL) several times to remove the excess acid (until constant conductivity of the rinsing solution) and dried until constant weight. 100 mg of protonated beads were subsequently suspended in 50 mL of 0.1 M NaCl, in order to keep the ionic strength of the solution constant. Finally, the suspension was potentiometrically titrated adding 0.1 M NaOH stepwise. pH values were recorded after equilibration time of 30 min.

2.4. Metal binding batch experiments

The metal salts were dissolved in distilled water and stock solutions of different concentrations of single metal solutions were prepared. Samples of ≈0.1 g alginate beads were contacted with 100 mL of metal solution in 200-mL Erlenmeyer flasks under shaking at 190 rpm, at 25 °C. Known amounts of 0.5 M HNO_3 were added until the pH measured on a Metrohm 744 pH Meter was stabilized at 4.5. The samples were then left shaking for 24 h for complete equilibration and the metal content of the final solution was determined. The initial metal concentrations ranged from 5 to 1300 mg g^{-1}.

2.5. Sorption kinetics experiments

Stock metal solution of pH 4.5 was prepared by addition of a known quantity of 0.5 M HNO_3. Samples of ≈0.1 g alginate beads were contacted as described above for different contact times. The beads were then removed from the solution by filtering and metal concentrations were determined.

2.6. Aerogel beads pre-treatment

Aerogel beads exhibited high porosity and their pore volume after drying was filled with air. This resulted in floating samples that could not come in full contact with the solution, hence prior to both kinetic and sorption isotherm experiments aerogel beads were left in bi-distilled water for 48 h under vacuum for outgassing.

3. Results and discussion

3.1. Structural properties characterization

Nitrogen adsorption–desorption isotherms at 77 K were employed for the study of the prepared materials pore properties. The air dried xerogel beads showed no N_2 uptake at 77 K indicating the absence of a porous structure (data not shown). On the other hand, the corresponding isotherm of supercritical CO_2 (sc-CO_2) dried aerogel beads is presented in Fig. 1A. It is a type IV isotherm according to IUPAC classification, typical of mesoporous solids, with the presence of a hysteresis loop at high relative pressures confirming the presence of large mesopores. However, there is evidence of the existence of both microporosity and macroporosity. Specifically, at low pressures, a steep increase is observed due to micropore filling, while the significant upturn at pressures close to the vapour pressure can be attributed to large (presumably macro-) pores.

BET analysis was carried out for a relative vapour pressure of 0.01–0.3 and based on the calculated S_{BET} the aerogel fibril diameter, d, was estimated using the following equation [10]:

$$d = \frac{4000}{\rho_c \cdot S_{BET}} \qquad (1)$$

where S_{BET} ($m^2\ g^{-1}$) is the BET specific surface area, ρ_c (g cm^{-3}) is the density of the alginate, assuming a cylindrical shape of the fibrils. In the current study the Ca-alginate density used for calculation was 2.15 g cm^{-3} [10].

Moreover both Barrett–Joyner–Halendar (BJH) [11] analysis as well as the Density Functional Theory (DFT) analysis method were used to estimate the aerogels average pore size from the nitrogen desorption isotherm data, assuming cylindrically shaped pores [12].

The BET method is widely applied on adsorption data for specific surface area calculation, by estimating the number of molecules needed to form a monolayer adsorbed film. Several factors, such as surface-adsorbed phase interactions as well as the adsorbed molecules cross sectional area, have an effect on the results of the BET method. Especially for polymers, additional issues