

Synthesis and Characterization of Alginate Based-Magnetic Nanocomposites

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ABSTRACT

Calcium alginate beads were synthesized through a cross-linking reaction between sodium alginate and calcium solutions. The effect of calcium concentration on the bead strength and chemical stability were investigated. Beads produced from a 0.5M Ca solution were robust and resistant to chemical dissolution. Co-precipitated magnetite nanocrystals were functionalized with meso-2,3-dimercaptosuccinic acid and dispersed inside the beads to form a magnetic polymer nanocomposite. The resulting nanocomposite can be used as sorbent for toxic aqueous species because of the ionic exchange capabilities exhibited by the alginate matrix and its synergistic interaction with functionalized magnetite nanoparticles. X-ray diffraction and Fourier Transform infrared spectroscopy confirmed the formation of the expected structures in pure beads and the corresponding nanocomposites. The magnetization of the nanocomposite was tuned by controlling the weight load of the magnetite phase within the alginate matrix.

Keywords: alginate, functionalized magnetite, DMSA, nanocomposite.

1 INTRODUCTION

Heavy-metals pollution of water bodies is a world-wide environmental concern. The toxicity of these metal species, even when they are present at low concentrations, makes their removal indispensable. Several alternatives involving the use of biodegradable materials have been developed to remove pollutants from water. Alginate-based compounds are among those environmental friendly compounds that exhibit sorption capabilities. Alginate is a polysaccharide extracted from brown seaweed that is composed by alternating blocks of guluronic (G) and mannuronic acids (M) groups. The solubility of alginate compounds in water depends on the type of cross-linked cations and pH. In particular, water-soluble sodium alginate can form gels in presence of divalent cations such as calcium or barium, which are preferentially bonded to the G-blocks in the alginate structure. This capability of hosting divalent cations in gel state allows the cross-linking of the alginate groups to form an egg-box like structure. The adsorption capability of the resulting structure is based on ionic exchange between protons of the free carboxylic functional

groups, mainly of the guluronic acid and metal ions in solution [1-4].

The sorption capability of some nanosize materials has also been addressed by several groups [1-3]. Magnetite, Fe₃O₄, nanoparticles (average crystallite size below 20nm) exhibit large specific surface area and suitable surface structure to interact with different types of metal ions in solution. The subsequent functionalization of these surfaces with meso-2,3-Dimercaptosuccinic Acid (DMSA) will enhance their adsorption capacity and selectivity for softer highly toxic metals like mercury lead, thallium and silver [5]. Besides, DMSA has been recognized as an excellent chelating agent for heavy metals. Despite of the well established sorption characteristic of magnetite, their actual application is limited by their nanometric size that makes their handling a very difficult task. The dispersion of these nanoparticles inside a porous matrix, like calcium alginate beads (CAB), should overcome this limitation. Accordingly, this work addressed the synthesis and characterization of CAB-magnetite nanocomposites to be used as a novel, inexpensive and environmental-friendly sorbent for a variety of heavy metal ions and oxyanions.

2 EXPERIMENTAL

2.1 Materials

Calcium alginate beads were produced by using low-viscosity sodium alginate and anhydrous calcium chloride. Magnetite nanoparticles were synthesized by using ferric chloride hexahydrate 97%, ferrous chloride tetrahydrate 99% and sodium hydroxide 98% (Alfa Aesar). Sodium oleate 98% (CTI), dimethylsulfoxide (DMSO) and meso-2,3-Dimercaptosuccinic Acid 98% (DMSA), were used to functionalize the magnetite surface. All reagents were used without further purification.

2.2 Synthesis of Calcium Alginate Beads

A 2% solution of low-viscosity sodium alginate was added drop-wise into a calcium chloride aqueous solution under gentle mechanical stirring. The beads were produced using different concentration of Ca ions (0.01M-0.5M) in order to investigate the effect of this parameter on the stability of resulting beads. Synthesized beads remained in contact with the calcium solution for 24 hours at room

temperature. At the end of this contact period, the beads were recovered, rinsed with deionized water and aerated to accelerate their drying. Dried beads were treated with nitric acid solution to convert the free carboxylic group of the alginate into its protonated form.

The chemical stability of the CAB was evaluated by contacting them with deionized water and aqueous solutions at pH 3, 5 and 8 and under room temperature conditions. Nitric acid and sodium hydroxide solutions were used to adjust the solutions pH. The beads were removed after 24 hours of contact and observed under the stereoscope to assess any change in volume or morphology with respect to the original state. Figure 1 shows the stereo images of the as-synthesized CAB using different concentrations of Ca ions.

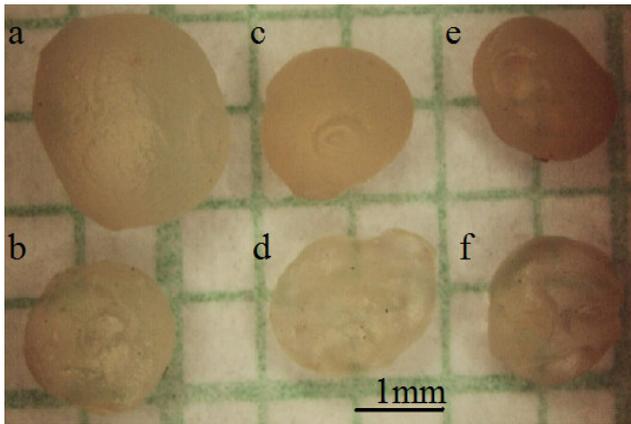
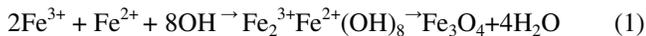


Figure 1: Stereo images of CAB synthesized from: 0.5M Ca, 0.2M Ca and 0.1M Ca solutions before, ('a', 'c' and 'e', respectively) and after, ('b', 'd' and 'f', respectively) acid treatment with 1.0M HNO₃.

2.3 Synthesis and Functionalization of Magnetite Nanoparticles

The aqueous solution containing iron (III) and iron (II) ions were added to a boiling sodium hydroxide solution. Two hours of contact were long enough to promote the dehydration and atomic rearrangement involved with the ferrite forming reaction (Equation 1).



In order to promote the adsorption of oleate species onto magnetite nuclei, the boiling aqueous suspension was contacted with 0.06M sodium oleate solution for an additional hour. Oleate-coated magnetite nanoparticles were washed with distilled water, dried at 60°C and suspended in 50mL of toluene. This suspension was mixed with a 4% v/w solution of DMSA in DMSO at a 1:1 volume ratio and sonicated for 24 hours. Recovered magnetic nanoparticles were washed with acetone, ethanol and water before drying at 60°C.

2.4 Synthesis of the Magnetic Nano-Composite

Suitable weights of functionalized magnetite nanoparticles were dispersed by sonication in sodium alginate prior to the addition of the Ca solution. Beads with 10%, 20%, 30% and 40% w/w weight loads of magnetite nanoparticles were produced by following a similar procedure as described in section 2.2.

2.5 Characterization Techniques

Structural characterization of pure magnetite, CAB and the corresponding composites were carried out in a Siemens D500 x-ray diffractometer (XRD) using the Cu-K α radiation. Fourier Transform Infrared (FTIR) measurements were undertaken in a MIRacle TM ATR FTS 1000 spectrometer in the transmittance mode. Magnetic properties were measured at room temperature (RT) and at a maximum applied field of 22kOe, using a Vibrating Sample Magnetometer (VSM) Lakeshore 7400 series.

3 RESULTS AND DISCUSSION

3.1 Stability of Calcium Alginate Beads

In general, CAB produced from 0.01M calcium chloride solution exhibited poor mechanical resistance and were easily fractured during handling. Moreover, the dried beads were soft and flake-like shaped. Consequently, these beads were not used for subsequent experimentation. Dried CAB produced by using 0.2M and 0.1M Ca solutions (Figures 1-c and 1-e, respectively) exhibited an average diameter of 1.5mm and were almost spherical. These initially spherical beads became irregular in shape after protonation (Figures 1-d and 1-f).

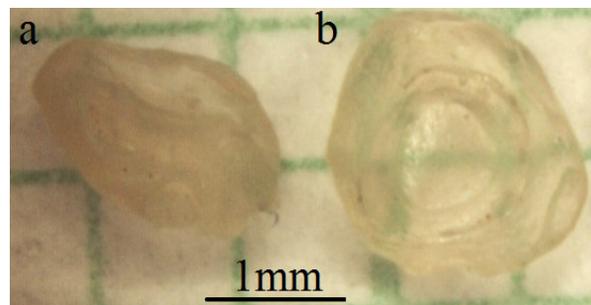


Figure 2: CAB prepared from 0.2M Ca solution after 24 hours contact in deionized water, (a) and at pH 3, (b).

The stability of CAB against chemical dissolution was strongly dependent of the solution pH. Beads prepared with 0.1M Ca were completely dissolved at pH 8 and 5 and although remained insoluble at pH 3, they became extremely brittle and easy to disaggregate during handling. CAB prepared from 0.2M Ca solutions were also quite unstable; they were completely dissolved (pH 8) or severely

deformed (pH 5). Although these CAB were not dissolved at pH 3 or in deionized water, a noticeable decrease in their size was noted (Figures 2-a and 2-b).

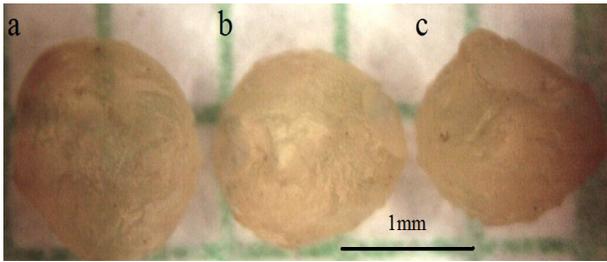


Figure 3: CAB synthesized from 0.5M Ca solution after contacting for 24 hours: in water, (a); in a pH 3 aqueous solution, (b); in a pH 5 aqueous solution, (c).

Those CAB synthesized from 0.5M Ca solution exhibited a well defined spherical shape with an average diameter of 0.2mm. The increase in size in these beads can be a consequence of the large amount of Ca species incorporated in the alginate structure. These beads were also dissolved at pH 8; however, they did not suffer any noticeable change in weight after contacting them with deionized water only or aqueous solutions at pH 3 or 5, (Figure 3). On this basis, a 0.5M Ca solution was selected to synthesize the beads to be used in the experimental work. The high solubility of the CAB in alkaline conditions can be rationalized as follows. In alkaline and neutral media the negatively charged carboxylate functional groups of the alginate would increase their affinity for metallic ions; therefore, Na^+ ions from NaOH would have been linked to the carboxylic groups of the alginate and decreased the stability of the egg box structure in this gel.

3.2 Synthesis of Magnetic Nanocomposites

Magnetite nanoparticles were homogeneously incorporated into the alginate matrix without any difficulty. Figure 4-a shows the image of one single particle of the CAB-magnetite nanocomposite. The bead was loaded with 10% w/w of magnetite nanoparticles. All beads were magnetic and exhibited a magnetic response proportional to the amount of incorporated nanoparticles.

3.3 XRD Characterization

Figure 5 shows the XRD patterns of magnetite powders, bare CAB and the corresponding nanocomposite synthesized with 10% w/w of magnetite nanoparticles. As Figure 5-a shows, all peaks corresponded to well-crystallized magnetite structure. The average crystallite size, estimated by the Scherrer's equation, was 12nm.

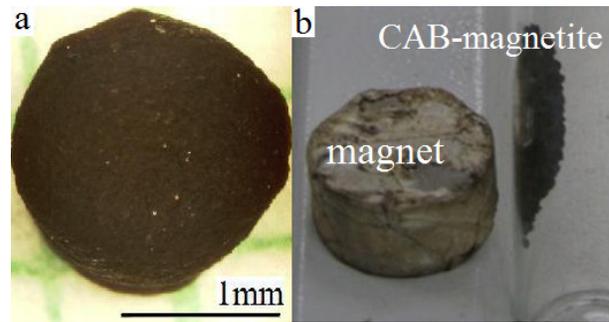


Figure 4: (a) CAB-magnetite nanocomposite bead bearing 10% w/w of magnetite. (b) CAB-magnetite nanocomposite in response to an external magnetic field.

The XRD pattern corresponding to bare CAB sample (Figure 5-b) showed a broad peak centered on 14° ; the presence of this peak would indicate some molecular ordering in the alginate structure. In turn, the formation of the magnetic composite is suggested by the co-existence of both calcium alginate and magnetite structures in the corresponding XRD pattern, shown in Figure 5-c. The presence of two well-defined peaks in this pattern, ($2\theta = 13^\circ$ and 16°), evidenced the molecular ordering in the alginate matrix was not affected by the presence of the disperse phase; i. e., the incorporation of magnetite nanoparticles did not interfere with the cross-linking reaction involved with the development of the calcium alginate structure.

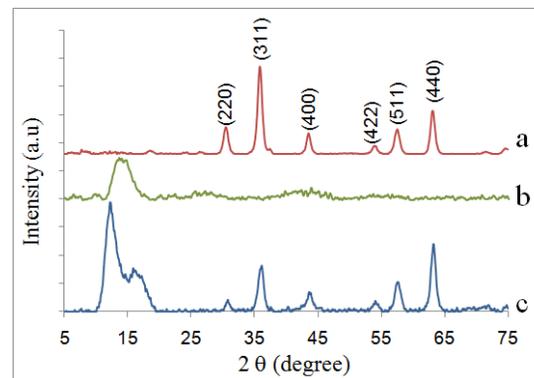


Figure 5: X-ray diffraction patterns for pure magnetite, (a); bare CAB, (b), and CAB- magnetite 10%w/w, nanocomposite, (c).

3.4 FT-IR Measurements

FTIR measurements were carried out in order to: (i) verify the actual functionalization of magnetite nanoparticles with DMSA, and (ii) confirm the development of expected structures in the CAB. The spectra for pure and DMSA-coated magnetite are shown in Figure 6-a and 6-b, respectively. The bands at 1388 cm^{-1} and 1575 cm^{-1} observed in DMSA-magnetite were assigned to C=O bonding in the carboxylic groups of the DMSA

structure. For the same spectra, the absence of the bands between 3000cm^{-1} and 2850cm^{-1} , which correspond to the stretching modes of C-H in the oleate species, would evidence the actual exchange between oleate and DMSA ligands on the nanocrystals surface.

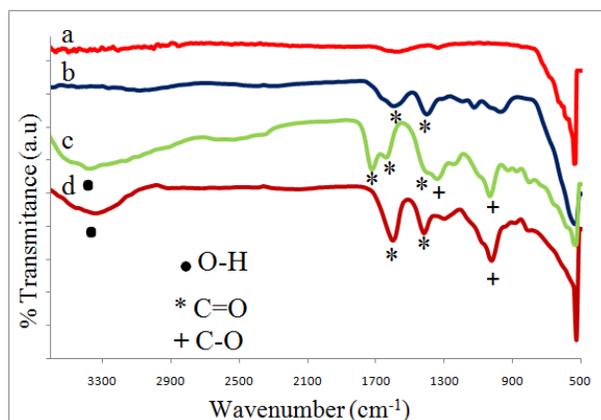


Figure 6: FTIR spectra of: 'clean' magnetite, (a); DMSA-magnetite, (b); bare CAB (c) and CAB-magnetite 10%w/w, nanocomposite, (d).

Figures 6-c and 6-d show the FTIR spectra of bare CAB and CAB-magnetite composite, respectively. The bands in the 1400cm^{-1} - 1750cm^{-1} range can be assigned to the C=O bond in carboxylic acid. The bands corresponding to the C-O (1000cm^{-1} - 1050cm^{-1}) and O-H (3500cm^{-1} - 3300cm^{-1}) bonding, corresponding to carboxylic and hydroxyl groups in the alginate structure, were also be observed.

3.5 Magnetization Measurements

Pure magnetite nanocrystals exhibited a room-temperature saturation magnetization as high as 60emu/g . This value went down to 45emu/g after functionalizing the magnetite with DMSA. This drop in magnetization could have been caused by the deposition of a non-magnetic DMSA shell surrounding the surface of the nanoparticles. The M-H loops corresponding to CAB-magnetite composites synthesized at various weight loads of the disperse phase are presented in Figure 7. The diamagnetic nature of the pure CAB matrix is evidenced by the negative slope in the M-H data shown in the inset. As observed, the maximum magnetization of the composites was dependent on the weight load of magnetite nanoparticles in the polymeric matrix; the corresponding magnetization saturation varied from 3.5emu/g to 11.5emu/g when this weight load was increased from 10% up to 40%, respectively. Evidently, the magnetization of the CAB-magnetite nanocomposite can be easily tuned by homogeneous dispersion of magnetite nanoparticles inside the alginate matrix and the suitable selection of the weight fraction of magnetic nanoparticles.

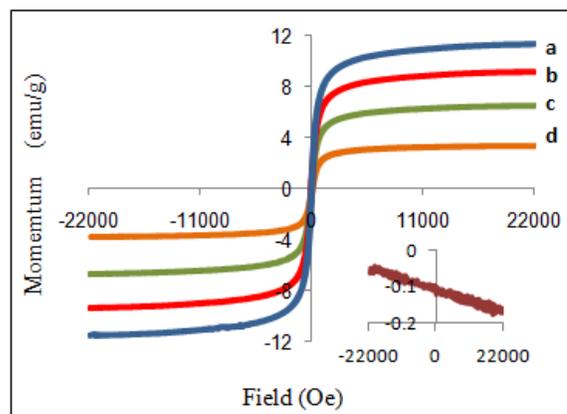


Figure 7: Room-temperature M-H loops for nanocomposites synthesized at different weight loads of magnetite: 40% w/w, (a); 30% w/w, (b); 20% w/w, (c) and 10% w/w (d). The inset corresponds to the M-H loop of bare CAB.

4 CONCLUDING REMARKS

Robust and mechanically resistant CAB were synthesized using a cross-linking 0.5M calcium solution. The actual functionalization of 12-nm magnetite nanocrystals with DMSA through a ligand exchange reaction in toluene was also verified. Produced nanocomposites exhibited a maximum magnetization that was dependent on the weight load of the magnetite nanoparticles in the matrix of calcium alginate beads. Ongoing works are focused on the evaluation of these magnetic nanocomposites as sorbent for water cleaning.

5 ACKNOWLEDGMENTS

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