

# Removal of Arsenic from Aqueous Solutions with Alginate Based-Magnetic Nanocomposites

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## ABSTRACT

Magnetite was synthesized by coprecipitation and functionalized with 2,3-Dimercaptosuccinic Acid (DMSA). The formation of the magnetite was confirmed using x-ray diffraction (XRD) whereas the nanoparticle functionalization was verified by infrared (IR) spectroscopy. Due their extremely small particle size, the recovery and handling of magnetite crystals from water becomes a very difficult and cumbersome task. Therefore, magnetite nanocrystals were immobilized in calcium alginate beads (CAB), to form a magnetic nanocomposite. In this work, the uptake capacity of CAB alone, DMSA-magnetite and CAB-(DMSA)magnetite for arsenite and arsenate species were evaluated. Maximum uptakes of 1.10mg/g sorbent and 1.04mg/g sorbent of arsenate and arsenite species, respectively, were achieved using functionalized DMSA-magnetite. The removal of arsenate and arsenite species using CAB alone was negligible.

**Keywords:** Arsenate, arsenite, calcium alginate beads, nanocomposite, DMSA-magnetite

## 1 INTRODUCTION

Contamination of water bodies is a world-wide concern. The main polluting agents are pesticides, hydrocarbons, heavy metals and oxyanions. Metal species can be contained in urban effluents (food plants, pharmaceutical facilities, cosmetics, cleaning products, etc.) or generated by industrial activities (mining and metallurgical plants, smelting of non-ferrous metals, burning of fossil fuels, timber treatment, paintings and electroplating, etc.). Metal removal from aqueous effluents can be accomplished by different strategies; besides physical (coagulation and sedimentation) or biological (metal removal by activated mud) treatment of wastewaters, other chemical routes including precipitation of metals as hydroxides, carbonates sulfides, can also be considered. The major inconveniences of these treatments are the formation of voluminous and unstable metal-bearing sludges [1-5].

Arsenic contamination of drinking water is a problem with potentially catastrophic effects on the long-term health of large populations. The natural occurrence of arsenic in water is directly related to arsenic complexes present in soils. Since arsenic in soils is highly mobile, once liberated,

may result in water contamination [6, 7]. Furthermore, arsenic species can produce diverse injurious effects in the humans such teratogenesis, mutagenesis and carcinogenesis. Their toxicity is related to their speciation: As (III) is more toxic than As (V).

The sorption capability of some nanosize materials has also been addressed by several groups [8, 9]. Magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles 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 [9]. Besides, DMSA has been recognized as an excellent chelating agent for heavy metals or oxyanions. Despite of the well established sorption capability of magnetite, its actual application has been 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. On this basis, the present work addressed the synthesis of CAB-magnetite nanocomposites and their evaluation as sorbent for arsenate and arsenite species from aqueous solutions.

## 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. Arsenic acid sodium heptahydrate salt and arsenic sodium oxide were used as the source of arsenic species. All reagents were used without further purification.

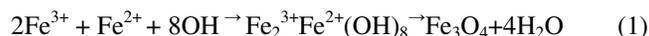
### 2.2 Synthesis of Calcium Alginate Beads

A 2% solution of low-viscosity sodium alginate was added drop-wise into a 0.2 M calcium chloride aqueous solution under gentle mechanical stirring. 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. Dry calcium alginate beads (CAB) were used to sorption of arsenate and arsenite.

## 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 distiller water, dried at 60°C and suspended in 50mL of toluene. This suspension was mixed with a 4% w/v 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. All magnetite used in the experiments was DMSA functionalized magnetite.

## 2.4 Synthesis of the Magnetic Nano-Composite

A 40% of magnetite nanoparticles were dispersed by sonication in sodium alginate prior to the addition of the Ca solution. Beads with 40% w/w weight loads of magnetite nanoparticles were produced by following a similar procedure as described in section 2.2.

## 2.5 Sorbent Characterization

Structural characterization of CAB-magnetite and CAB-magnetite nanocomposite were carried out in a Siemens D500 x-ray diffractometer (XRD) using the Cu-K $\alpha$  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.

## 2.6 As(III) and As(V) Adsorption Tests

One-hundred milliliters of 5mg/L arsenate or arsenite solutions were placed in polyethylene bottles and contacted with the sorbents on a reciprocal shaker. An additional sorption tests using 10 mg/L As was also carried out. The sorbents were added at concentrations of 1.5 g/L of CAB, 1.0g/L of DMSA-magnetite and 2.5g/L of CAB-(DMSA)magnetite. The initial pH was 6.0 in all experiments. Aliquots were taken at different contact times, preserved in 2% of nitric acid and analyzed in an Inductively Coupled Plasma- Mass Spectrophotometer (ICP-MS) from Agilent Technologies-7500ce to quantify the uptake capacity and the removal efficiency.

## 3 RESULTS AND DISCUSSION

### 3.1 Sorbents Characterization

CAB and CAB-(DMSA)magnetite are shown in figure 1. The average diameters of CAB fresh and dry are 3.5 mm and 1.2 mm, respectively. CAB-magnetite were 2mm in diameter.

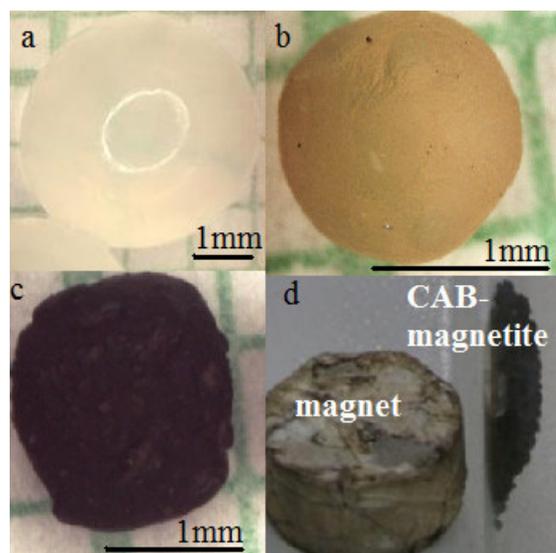


Figure 1: (a) 'Green'- CAB; (b) Dry CAB, (c) CAB-(DMSA)magnetite nanocomposite, and (d) CAB-magnetite nanocomposite in response to an external magnetic field.

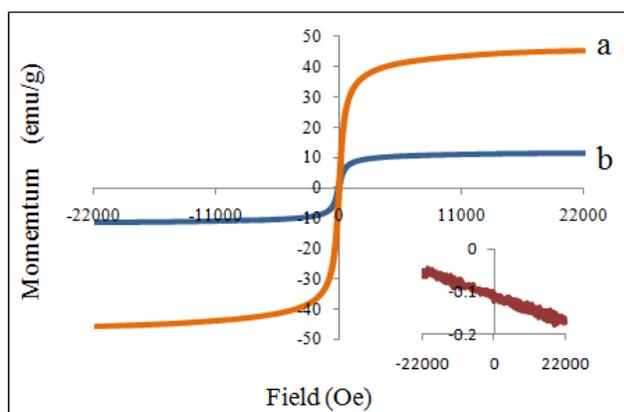


Figure 2: Room-temperature M-H loops for magnetite (a) and CAB-(DMSA)magnetite, 40% w/w (b). The inset corresponds to the M-H loop of bare CAB.

Magnetite structure was confirmed by XRD analysis. The average crystallite size, estimated by the Scherrer's equation, was 12nm. In turn, infrared analysis, not presented here, confirmed the functionalization of magnetite with DMSA. Two bands at  $1388\text{ cm}^{-1}$  and  $1575\text{ cm}^{-1}$  were observed in DMSA-magnetite, which were assigned to C=O bonding in the carboxylic groups of the DMSA structure. The absence of the bands between  $3000\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$ , 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. Magnetite nanocrystals exhibited a room-temperature saturation magnetization as high as 45emu/g (figure 2a); this value went down to 11emu/g for CAB-magnetite, 40% w/w, (figure 2b). The diamagnetic nature of pure CAB matrix is evidenced by the negative slope in the M-H data shown in the inset in the figure 2

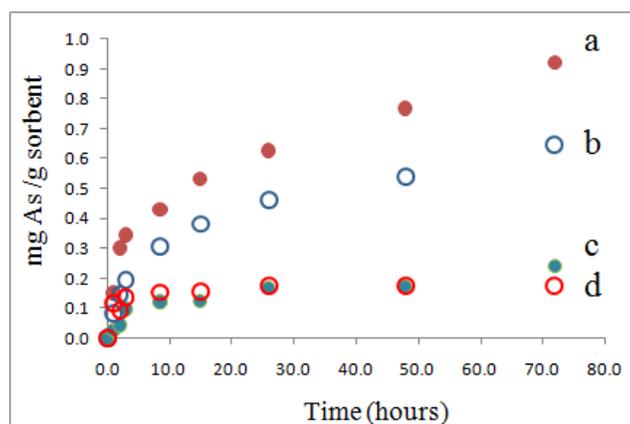


Figure 4: Adsorption kinetics using CAB-(DMSA)magnetite: Arsenate (a), Arsenite (b) and CAB: Arsenate (c), Arsenite (d). The uptakes are expressed on a dry bead basis. The initial As concentration was 5.0 ppm

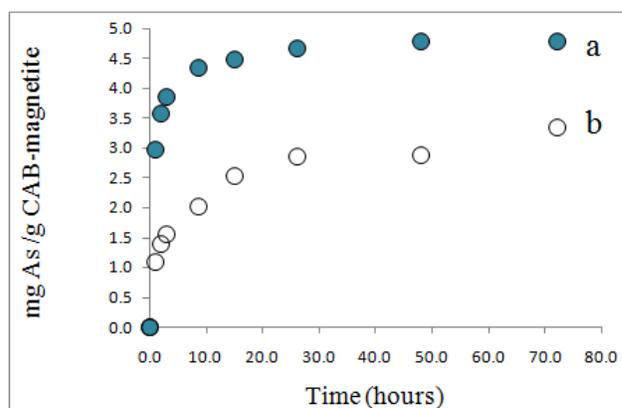


Figure 3: Adsorption kinetics of Arsenate (a), and Arsenite (b), species on DMSA-magnetite. The initial As concentration was 5.0 ppm.

### 3.2 Adsorption Experiments

The uptake capacity of DMSA-Magnetite were 4.78mgAs/g sorbent and 3.34mgAs/g sorbent for As(V) and As(III) species, respectively, when the initial As concentration was 5 mg/L. The corresponding removal efficiencies were 95.7% and 32.3%. The sorption mechanism for the removal of the As ions by DMSA-magnetite could involve metal ions chelation with carboxylic acid functional groups or sulfur atoms present in the DMSA structure. Other conditions are presented in the figure 3 and table 1. As figure 4 shows, the adsorption was delayed when CAB-(DMSA)magnetite were used instead. The removal efficiencies for arsenate and arsenite species went down to 45.9% and 32.3%. Evidently, the diffusion of aqueous solutions towards magnetite particles would have been hindered by the matrix limited porosity.

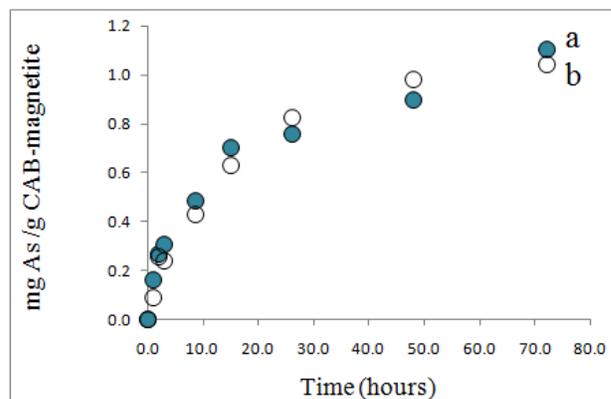


Figure 5: Sorption kinetics of Arsenate (a), and Arsenite (b), species on CAB-(DMSA)magnetite. The uptakes are expressed on a dry bead basis. The initial As concentration was 10.0 ppm

Table 1: Adsorption of arsenate and arsenite by CAB, DMSA-magnetite, and CAB-(DMSA)magnetite

Sorbent	Arsenate					Arsenite				
	**Concentration mg/L		*pH	% Sorption	Uptake Capacity mg As / g Sorbent	**Concentration mg/L		*pH	% Sorption	Uptake Capacity mg As / g Sorbent
	Initial	Final	Final			Initial	Final	Final		
CAB	5	4.6	5.9	7.2	0.24	5	4.7	5.9	5.3	0.17
DMSA-Magnetite	5	0.2	3.8	95.7	4.78	5	1.7	3.8	66.8	3.34
CAB-(DMSA)Magnetite	5	2.7	4.0	45.9	0.92	5	3.4	4.0	32.3	0.65
	10	7.2	4.2	27.6	1.10	10	7.4	4.1	26.1	1.04

\* initial pH = 6; \*\* All analysis performed by ICP-MS. Contact time= 72 hours.

CAB alone was also evaluated to assess its individual contribution to the adsorption process based on its well known sorption capability [3-4]. The CAB alone could only remove 7.2% of arsenate and 5.3% of arsenite (figure 4).

Additional adsorption experiments were performed solutions containing 10 mg/L of As species. CAB-(DMSA) was used as the sorbent (figure 5). The uptake capacities for were 1.10mg/g sorbent for arsenate and 1.04mg/g sorbent for arsenite. As the data in figure 5 shows, the adsorption process is very fast at the beginning of the contact period; however, in a second stage the process slows down without reaching equilibrium. The fast sorption rate during the first hours can be attributed to the immediate contact between As species and magnetite nanoparticles located near the surface of the beads. At these sites get saturated, the As ions must diffuse through the beads pores, becoming the rate-controlling step.

#### 4 CONCLUDING REMARKS

Our results suggest that DMSA-magnetite immobilized in CAB can remove arsenate and arsenite from aqueous solutions. The maximum uptake capacities of arsenate and arsenite species by CAB-(DMSA)magnetite were 1.10mg/g sorbent and 1.04mg/g sorbent, respectively. The amount of arsenate and arsenite removed by the CAB alone was insignificant. The suspected mechanism for the removals of the arsenate and arsenite species by the magnetite would involve metal chelation by the two carboxylic acid functional groups or the two sulfur atoms present in the DMSA structure. The use of CAB-(DMSA)magnetite nanocomposites has the potential to be used for the removal of arsenate and arsenite species from contaminated aqueous solutions. Ongoing works are focused on the enhancement of the specific surface area of beads as well as the increase on their porosity as attempt to accelerate the adsorption of As species..

#### 5 ACKNOWLEDGMENTS

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