



## Research articles

## Physical and arsenic adsorption properties of maghemite and magnetite sub-microparticles



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## ABSTRACT

The topotactic transformation from magnetite to maghemite sub-microparticles was demonstrated by a variety of techniques that include X-ray diffraction, Raman spectroscopy, electron microscopy, Mössbauer spectroscopy, magnetic measurements, and vis-NIR diffuse reflectance. The physical, chemical, and morphological properties of the particles were correlated with their adsorptive properties in water with respect to arsenic (V). The adsorptive properties of the iron oxide are increased by changing the crystal phases involved, specifically, the transformation of magnetite to maghemite. Maghemite sub-microparticles are capable of efficiently decreasing the arsenic content in water from 100 ppb to below the World Health Organization (WHO) guideline of 10 ppb.

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## 1. Introduction

Arsenic (As) is one of the most toxic elements present in the Earth's crust. In water, the presence of arsenic is a result of the strong influence of the rock-water interactions and the subsequent dissolution; by this mechanism, higher arsenic concentrations are introduced into groundwater [1]. However, anthropogenic activities such as mining, industry, and agriculture play an important role in the release of arsenic to the soil, water and air [2]. Arsenic pollution is a worldwide problem because people with continuous consumption of arsenic-polluted water develop arsenic-related diseases such as hypertension, cardiovascular diseases, diabetes, skin melanosis and keratosis and cancer in different organs [3]. Most notably, contaminated areas are in Argentina, Bangladesh, Chile, China, Hungary, India, Mexico, Romania, Taiwan, Vietnam and North America [1].

In order to decrease the impact of arsenic consumption by humans, different arsenic removal methods have been developed and used for water remediation [3,4]. Some methods are complex, costly, and inefficient for their use in developing countries. Therefore, it is necessary to develop an economically feasible and high efficient arsenic removal method. Due to their low cost and high affinity for different arsenic species, iron oxides have been extensively used for arsenic removal [5–8]. Because of their high surface area, nanoparticles (NPs) of different iron oxide phases such as hematite, goethite, ferrihydrite, magnetite, and maghemite, have been studied extensively for arsenic removal [3,5,7–10]. The specialized literature evaluates the role of different parameters on the arsenic removal properties of iron oxide NPs; some of them are the particle size [11], the source of the NPs [3], the phase transformation [10], etc. Research regarding the phase transformation of iron oxides is of great interest [10,12–14]. However, there is a lack of studies that relate a complete characterization of the involved iron oxide crystal phases with the arsenic adsorption properties. In this paper, magnetite and maghemite sub-microparticles (SMPs) are characterized, and their roles in the arsenic removal properties are evaluated. It was found that maghemite SMPs can decrease the arsenic content in water efficiently; i.e., from 100 ppb to below the World Health Organization (WHO) guideline of 10 ppb.

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## 2. Materials and methods

### 2.1. Synthesis of sub-microparticles

Magnetite SMPs were synthesized via the partial oxidation of Fe (II) species [15], and their oxidation at 370 °C yielded the maghemite SMPs. The synthesis of magnetite SMPs consisted of diluting 0.05 M of sodium citrate, 2 M of NaOH, and 0.5 M of KNO<sub>3</sub> in 190 mL of deionized water at room temperature (RT). This solution was heated at 100 °C for 10 min, and subsequently, 0.1 M of FeSO<sub>4</sub>·7H<sub>2</sub>O, previously dissolved in 10 mL of deionized water, was added. The reaction was stirred at 100 °C for one hour; after this time, the sample was washed three times with deionized water using magnetic decantation. Finally, the magnetite SMPs were dried at 45 °C for 24 h. For the preparation of maghemite SMPs, 1 g of the as-prepared magnetite SMPs were heated in a crucible at 370 °C during 30 min. Subsequently, the crucible was extracted from the furnace and cooled down to RT.

### 2.2. Characterization

The structural characterization was performed by X-ray diffraction (XRD) and Raman spectroscopy. XRD patterns were measured in a Bruker diffractometer in the Bragg-Brentano geometry using Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The powders were analyzed in the  $2\theta$  range from 10° to 80° using steps of 0.03°. The XRD patterns were indexed using the Crystallography Open Database (COD), and Rietveld refinement of the XRD patterns was done using the MAUD program v. 2.33. The Rietveld method combined with Fourier analysis for broadened peaks was employed, where the instrumental function was determined by measuring KCl free from defect broadening [16]. The Raman spectra were measured in a Witec CRC200 (laser  $\lambda = 514.5 \text{ nm}$ ). To minimize the structural changes promoted by the laser, a light intensity as low as 0.7 mW was used for the Raman characterization [17]. The structural and morphological characterization of the powders was studied by high-resolution transmission electron microscopy (HR-TEM) in an FEI-Titan 80–300 microscope. The Mössbauer characterization was performed with conventional Mössbauer equipment in the transmission mode with a Co<sup>57</sup> source in a rhodium matrix; 25 mg of the sample was placed in the sample holder with an internal diameter of 1.0 cm

and measured at RT. The Normos software package [18] was used for fitting the Mössbauer spectra. The magnetic properties were measured at RT in an alternating gradient magnetometer (AGM Micromag 2900) manufactured by Princeton Measurements; 180 first-order reversal curves (FORC's) were obtained, and the FORC diagrams were processed and analyzed with the FORCinel software package [19].

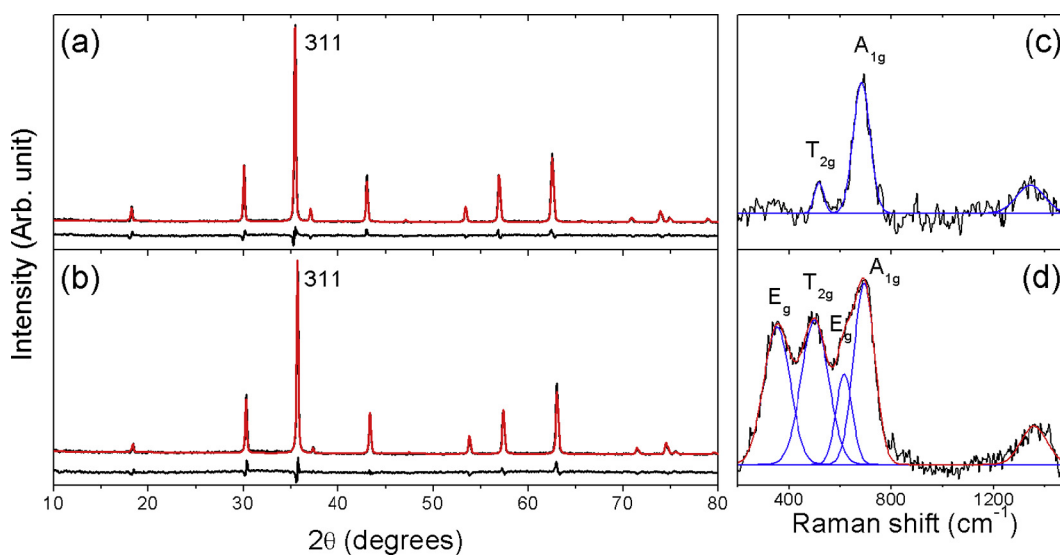
### 2.3. Arsenic adsorption tests

The adsorption kinetics study was carried out in plastic flasks with 50 mg of SMPs and 50 mL of a 100 ppb aqueous solution of As(V) at a pH of 6. Changes in the arsenic concentration were monitored at different times. After the adsorption time, the SMPs were separated by magnetic decantation, and the clear solutions were used for the determination of the remaining arsenic concentration. The concentration of arsenic was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with a Thermo Jarrell Ash instrument. The arsenic adsorption isotherms were realized at RT, pH = 6, and using 50 mg of maghemite SMPs mixed with 50 mL solutions of As(V) in concentrations of 0.1–10 mg/L. It was determined that the As(V)/SMPs systems reached equilibrium in less than 48 h. After 48 h of continuous shaking at 28 rpm, the mixtures were centrifuged, filtered through 0.2  $\mu\text{m}$  cellulose filters and, finally, the remaining arsenic concentration in the solution was determined by ICP-AES.

## 3. Results and discussion

### 3.1. Structural characterization

The structural characterization of the samples was done by a set of complementary techniques such as XRD, Raman spectroscopy, HR-TEM, and Mössbauer spectroscopy. The XRD patterns of the samples are shown in Fig. 1a and b. In the case of the SMPs prepared via the partial oxidation of Fe(II) species, it can be observed that all the detected diffractions can be indexed to the inverse spinel crystal structure of magnetite with space group  $Fd-3m$ , COD number 9002316 [20]. On the other hand, for the oxidized sample, all the detected diffractions can be indexed to inverse spinel structure of the vacancy disordered maghemite (space group  $Fd-3m$ ),



**Fig. 1.** XRD and Raman spectra of the samples. SMPs prepared via the partial oxidation of Fe(II) species: (a) XRD pattern, and (c) Raman spectra. SMPs oxidized at 370 °C: (b) XRD pattern, and (d) Raman spectra. The measured and calculated powder patterns, and their difference are included in (a) and (b). For the Raman spectra, the deconvoluted components are included as blue lines. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)

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