

PREPARATION AND APPLICATION OF A MAGNETIC COMPOSITE (Mn_3O_4/Fe_3O_4) FOR REMOVAL OF AS(III) FROM AQUEOUS SOLUTIONS

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ABSTRACT

The introduction of magnetic properties in adsorbent materials has the aim of improving solid-liquid separation processes. In this work, a magnetic composite was synthesized by precipitation of manganese oxide in presence of magnetite particles using O_2 as oxidant. The composite was shown to be chemically and physically stable in a wide range of pH values. The composite characterization indicated that the precipitated manganese phase is hausmannite (Mn_3O_4) and that magnetite does not go under any phase transformation during the synthesis. The composite was used to remove As(III) from aqueous solutions. The magnetic composite presents a maximum sorptive capacity of $15 \text{ mg}_{As} \text{ g}_{solid}^{-1}$ ($0.5 \text{ mg}_{As} \text{ m}^{-2}_{solid}$) in pH 7. The magnetic property of magnetite, which is attached to the active Mn_3O_4 , allows an easy removal of the sorbent particles from the solution.

Key-words: magnetic composite, manganese oxide, arsenic, adsorption.

INTRODUCTION

The increased quality water demand for human consumption and industrial support, allied to the stringent environmental laws have stimulated the development of new materials and methods for the treatment of contaminated aqueous solutions. Adsorption processes are often involved in applied technologies for water treatment. As desired features, the adsorbent should be low-cost, should have considerable contaminant adsorption and be easily recovered. The performance of powder adsorbents is sometimes limited when trace or sub-trace concentrations are concerned. In general, the best performance of the adsorbent is associated with smaller particles, since small particles possess large specific surface areas. However, the smaller the particles of the adsorbent, the more difficult their separation

from the aqueous solution is.

The challenge of separating high specific surface area powder adsorbents from solution could be addressed with the use of magnetic composites. Magnetic composites can be conveniently recovered by magnetic separation, avoiding the filtration steps, which currently still represent a barrier to the application of high performance advanced materials in environmental remediation processes and treatment of great volumes of aqueous solutions.

The literature has several works aiming the production of high performance adsorbents.¹ There are many works applying metal oxides to remove contaminants from waste-water. Iron, aluminum, titanium and manganese oxides are the most studied ones.²⁻⁷ Manganese oxides stand out for their useful properties since they have high surface areas and surface charges. Moreover, they are strong oxidants.

The use of powder magnetic manganese oxide composite as adsorbent may combine the excellent sorptive and oxidation properties of manganese oxide with the highly effective recovery of magnetic separation techniques. Nevertheless, very few works have been focusing on magnetic manganese oxide composites to be used in water treatment.⁸ Moreover, in these literature works, the magnetic composites are synthesized by precipitation of manganese dioxide in presence of magnetite by using expensive oxidants, such as potassium permanganate and hydrogen peroxide.

Considering the aforementioned context, the present work is aimed to synthesize low-cost magnetic manganese oxide composites that present chemical stability and physical integrity in stirred, solid-aqueous systems to be used as adsorbents in environmental systems.

EXPERIMENTAL

Synthesis of the magnetic manganese oxide composite

For the preparation of the composite by using O₂, deionized water pre-saturated with O₂ (24 h of air input) was put in contact with magnetite and a solution of MnCl₂·4H₂O. Magnetite was provided from Sigma-Aldrich (< 5 μm, 98%) being described as synthetic iron oxide Fe₃O₄. The reaction was carried out under alkaline conditions by addition of KOH and constant input of air. This was done to ensure complete oxidation of manganese ion. The resulting solid was separated from the liquid by using a magnet and washed using deionized water. The solutions were

analyzed by Atomic Absorption Spectrometry, AAS (Perkin Elmer Analyst A300), for iron and manganese content.

Evaluation of the composite chemical stability and physical integrity

The chemical stability of the composite is associated to its capacity of not dissolving in a wide range of pH values and the physical integrity of the composite is associated to the attachment of the different solids.

The chemical stability and physical integrity tests consisted of batch experiments in which 0.2 g of the magnetic composite was put in contact with 100 mL aqueous solutions in different pH values (from 2 to 12) and stirred during 24 h. The solid was separated from the solution by using a magnet. The solution was filtered and analyzed by AAS for Mn and Fe content

Characterization

Surface information of the magnetic composite were obtained by Raman spectroscopic analysis on a Horiba Jobin Yvon LABRAM-HR 800 spectrograph, equipped with a 633 nm helium-neon laser, 20 mW of power, coupled to an Olympus BHX microscope equipped with lenses of 10, 50 and 100X; by energy dispersive X-ray analysis (EDS) on a Thermo Noram (Quest) spectrometer; by X-ray diffraction analysis (XRD) on a Philips-PANalytical PW 1710 X-ray diffractometer equipped with a texture chamber and by Mössbauer spectroscopy on a conventional constant acceleration Mössbauer spectrometer (Halder) in transmission mode with a ^{57}Co (Rh) source. Measurements of the specific surface area were made by the BET (Brunauer-Emmett-Teller) – Multipoint method by nitrogen adsorption using a Quantachrome Autosorb-1.

Arsenic immobilization

In the batch arsenic sorption experiments, 0.3 g of the adsorbent material (magnetic composite) was added into the 250 mL Pyrex erlenmeyers flasks, filled with 100 mL of As(III) solution, and the vessels sealed with laboratory parafilm (Pechiney plastic packaging, USA). The As(III) stock solution was prepared by dissolving sodium NaAsO_2 in Milli-Q water. Initial As(III) concentrations varied from 0 until 250mg L^{-1} . Agitation at 200 rpm was provided by a thermostatic shaker, manufactured by New Brunswick Scientific Edison, USA. The temperature was

maintained at $(25 \pm 0.5)^\circ\text{C}$ and the solution at pH 7 for As(III). After 24h, the pH of the solutions was measured and the samples were separated from the liquid by using a magnet. The filtrate was assayed for total arsenic, iron and manganese directly by flame Atomic Absorption Spectroscopy, AAS (Perkin-Elmer Analyst A300). The solids were rinsed with Milli-Q water, dried in a desiccator at room temperature ($25 \pm 2^\circ\text{C}$) and stored for subsequent characterization.

RESULTS AND DISCUSSION

Evaluation of the composite chemical stability and physical integrity

The supernatants after magnetic separation of the solid samples stirred in pH 10 and pH 12 aqueous solutions were turbid (brown yellow) and had to be filtered twice in order to achieve clarification. EDS results have shown the presence of only manganese in the solid obtained after the filtration, indicating that the physical integrity of the magnetic composite was compromised in these pH values. In the pH values from 2 to 9, the supernatants after magnetic separation were not turbid and, therefore, the physical integrity was not compromised.

There was significant manganese dissolution only in pH 2 (49%). In pH values from 3 to 9 the solid was stable (less than 1% of manganese was dissolved).

It can be concluded that the composite has shown a good chemical stability and physical integrity in a wide range of pH values (i.e. from 3 to 9).

Characterization

The values of the specific surface area for commercial magnetite and for the prepared magnetic manganese oxide composite are 6 and $28 \text{ m}^2 \text{ g}^{-1}$, respectively. The results indicate that the manganese oxide formed has higher specific surface area than the commercial magnetite. The surface area of the composite could be increased increasing magnetite surface area. This may be done lately as part of the optimization of the synthesis.

Fig.1 shows the XRD diagrams of the composite. The diffraction pattern has shown the lines corresponding to the diffraction pattern of commercial magnetite and lines that correspond to the diffraction pattern of hausmannite (Mn_3O_4 – ICDD 80-0382).

The Raman spectrum of Mn_3O_4 (MnMn_2O_4 in spinel notation) is characterized

by a very sharp peak at 654 cm^{-1} . This peak corresponds to the Mn-O breathing vibration of divalent manganese ions in tetrahedral coordination. Two smaller peaks are located at $300\text{-}310$ and $350\text{-}360\text{ cm}^{-1}$. It also has a weak signal at 485 cm^{-1} .⁹ Raman spectrum of the solid filtered from the supernatant after magnetic separation of the composite sample stirred in pH 10 aqueous solution have also indicated the presence of hausmannite in the composite (Fig. 2). Despite the fact that MnO_2 is most used as an adsorbent and oxidant, Mn_3O_4 is easier to obtain and also presents acceptable sorptive and oxidative potentials.¹⁰⁻¹²

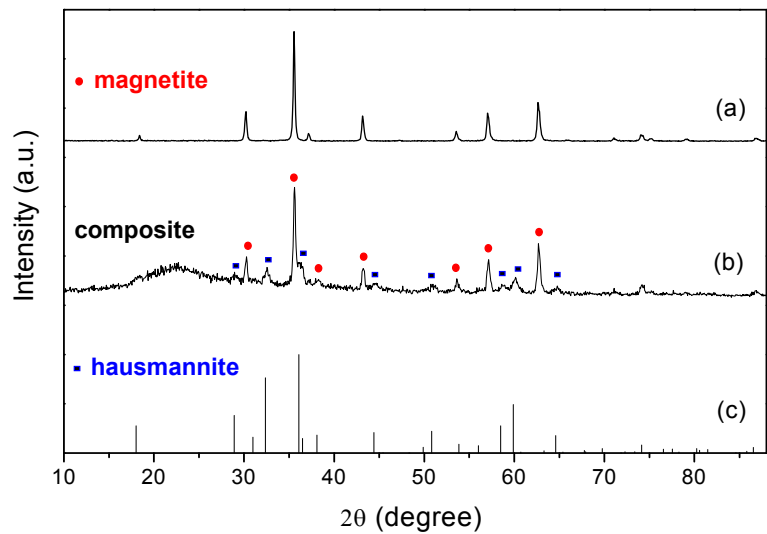


Fig. 1: X-ray powder diffraction patterns of (a) commercial magnetite, (b) the magnetic composite and (c) the main Bragg lines of hausmannite (Mn_3O_4 – ICDD 80-0382).

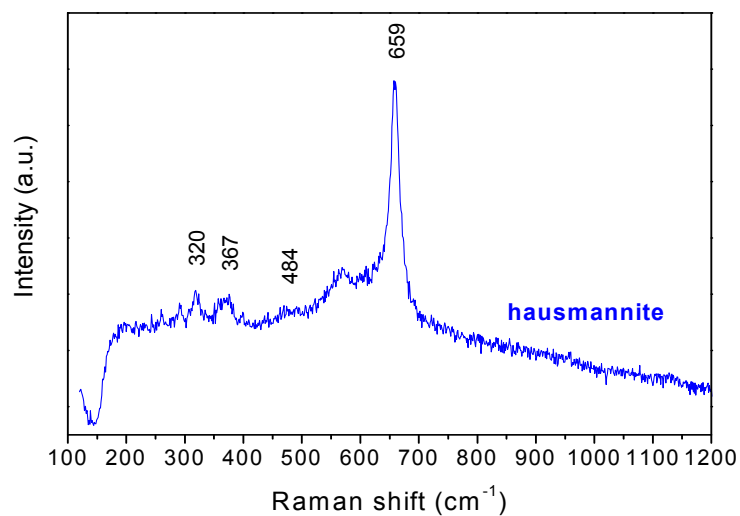


Fig. 2: Raman spectrum of the filtered solid in the pH 10 stability test for the magnetic composite.

Mössbauer results indicate that the ratio between the areas of tetrahedral and octahedral sites of the magnetite has not changed in the composite (Table 1, Fig. 3). Therefore, magnetite does not undergo any type of transformation during the synthesis, which insures the magnetic separation of the composite.

Table 1: Mössbauer hyperfine parameters of magnetite and the magnetic composite.

MAGNETITE			COMPOSITE		
	mag (T)	mag (O)		mag (T)	mag (O)
W (mm/s)	0.48	0.43	W (mm/s)	0.49	0.48
IS (mm/s)	0.54	0.19	IS (mm/s)	0.55	0.2
Q S(mm/s)	0.00	-0.02	Q S(mm/s)	0.01	-0.02
B _{HF} (T)	45.78	49.22	B _{HF} (T)	45.79	49.34
Area (%)	46.7	53.3	Area (%)	44.47	55.53
A _(O) /A _(T)	1.14		A _(O) /A _(T)	1.25	

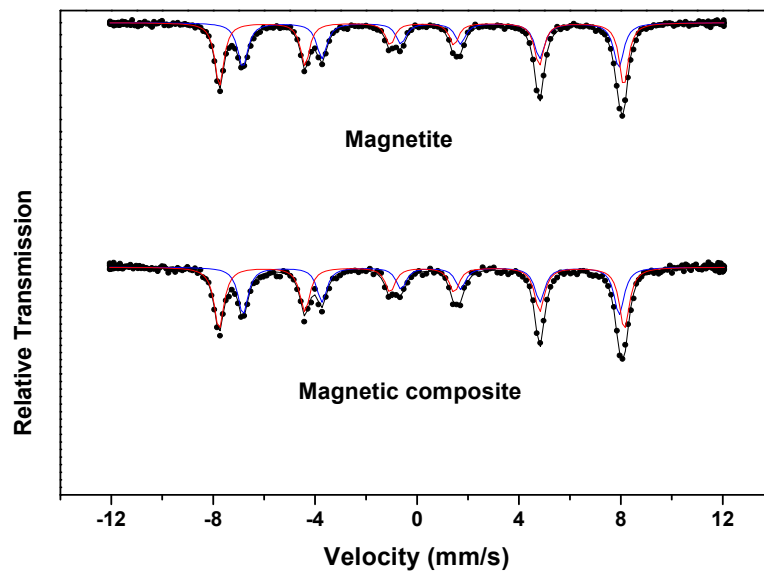


Fig. 3: Mössbauer spectra of commercial magnetite and the magnetic composite measured at 300 K.

Arsenic immobilization experiments

In the As(III) sorption test for the magnetic manganese oxide composite, the solid samples could be totally separated by the magnet. The pH values of the solutions increased from 7 to 8 during the test. The release of Mn(II) by the solid

increased with increasing As(III) initial concentrations until 100 mg L^{-1} and then became constant. The maximum release corresponded to 1% of the manganese in the solid. The solid in contact only with a pH 7 aqueous solution released 0.1% of the manganese. Thus, the presence of As(III) increases Mn(II) release. However, this release is not significant. The As(III) sorption isotherm shown in Fig. 4 indicates that both adsorption and precipitation are occurring. However, precipitation is occurring less than adsorption. Results observed by Dias et al.⁷, who studied the oxidation of As(III) by birnessite (a manganese dioxide), have confirmed that adsorption of arsenate ions onto hausmannite and oxidative precipitation of manganese arsenate in high concentrations of arsenic can occur. The maximum sorption capacity is 15 mg g^{-1} . This value is comparable to the value (14.7 mg g^{-1}) found for a raw material rich in Fe_2O_3 and MnO_2 with a higher specific surface area ($40.8 \text{ m}^2 \text{ g}^{-1}$)⁴, high compared to other synthetic Mn_3O_4 ¹⁰ and low compared to other values for synthetic manganese dioxides found in literature.⁵⁻⁷ However, this capacity could be improved by using magnetite particles with higher surface areas.

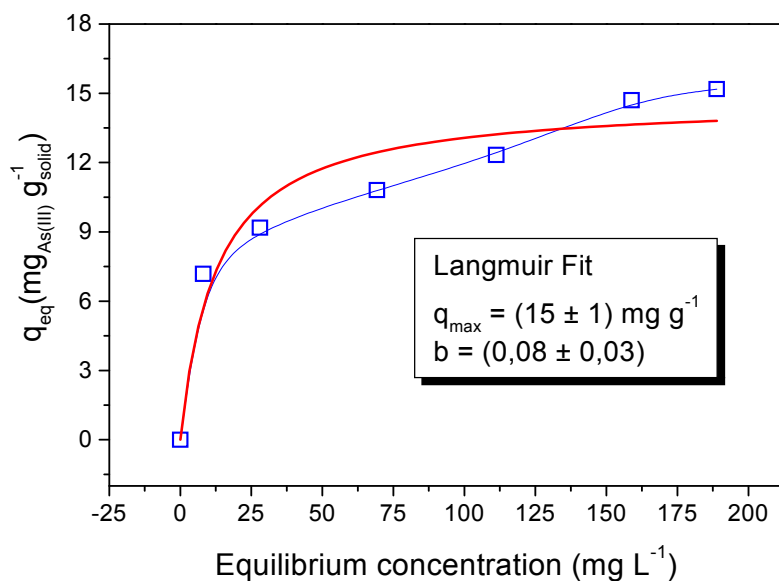


Fig. 4: Isotherm for As(III) sorption on the magnetic composite. Experimental conditions: pH 7, 300 rpm, 24 h, $(25 \pm 0.5)^\circ\text{C}$.

CONCLUSIONS

The results of the synthesis of manganese oxide (Mn_3O_4) coated magnetite have demonstrated that stable magnetic micro-sorbents can be generated which

allows the sorption of As(III) from aqueous solutions. The magnetic property of magnetite, which is attached to the active Mn_3O_4 , allows an easy removal of the sorbent particles from the solution.

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