



Magnetic mesoporous silica for water remediation: Synthesis, characterization and application as adsorbent of molecules and ions of environmental concern



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ABSTRACT

Magnetic mesoporous silicas (NSMSiO₂) were synthesized by coating nano-sized magnetite (NSM) particles with mesoporous silica shells. The effects of the NSM loading on the morphology, charge development and adsorption properties of the synthesized composites were investigated. Both the shape and the size of aggregates strongly changed as NSM/SiO₂ molar ratio increased, i.e., from plates to spherical-like particles, in agreement with reduction on the silica shell thickness. The shell acted as a protective agent that minimized alteration of the magnetite structure and avoided magnetite dissolution in acidic media. The composites have a significant adsorption capacity towards a humic acid and the cationic dye malachite green, showing that they can adsorb both, anionic and cationic species. HA seems to enter the pores and bind the NSM cores, whereas malachite green binds mainly the silica shell. The effect of Ca²⁺ concentration on the adsorption capacity of the synthesized composite was also evaluated and discussed. The magnetic property of the materials facilitates the recuperation of the adsorbent from aqueous environments.

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1. Introduction

The interactions between environmentally active molecules, such as humic substances, dyes, pesticides, etc. and synthetic adsorbents constitute an area of research of extreme importance in the field of straightforward technological applications as well as in basic science [1]. For example, it is known that the existence of humic acids (HA) in drinking water may lead to color, taste and odor problems, and to biological instability of drinking water in distribution systems. In fact, HA is generally recognized as the major precursor of strongly carcinogenic disinfection by products formed in chlorinated or chloraminated drinking water or water treatment [2]. Another example is the release of dyes and pigments from manufacturing and textile industries. These species are, in general, relatively stable to light, oxidizing agents and heat, and their presence in wastewaters offers considerable resistance to their biodegradation, upsetting aquatic life [3]. Moreover, the dye

may enter into the food chain and could possibly cause carcinogenic, mutagenic and teratogenic effects on humans [4].

Because all mentioned species cannot be effectively removed by the conventional treatments used in drinking water supply, it is of great interest to develop effective adsorbents as antidotes or filters for their removal from poisoned circulation systems or contaminated environments. In this respect, mesoporous silica can be a good adsorbent due to its high surface area (>200 m² g⁻¹), ordered frameworks, narrow pore size distribution (2 – > 10 nm, higher than zeolites), high thermal stability and easy regeneration and reusability [5,6]. Due to these properties, mesoporous silicas are very good base materials for catalysis [7], bioseparation [8], drug delivery [9], medical contrasting [10], food technology [11], biomedicine [12] and separation of environmental pollutants [13]. In fact, it is well documented that the pore morphology of silica and its reactivity towards different molecules strongly depends on the synthesis conditions, e.g., pH, temperature, type and concentration of surfactant used as template, etc. [14].

In order to extend their potential applications, functionalized mesoporous silicas with magnetic iron-based nanoparticles have attracted special attention during the last decade because of their interesting magnetic properties. In addition, it is known that

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covering the iron core with a silica shell or layer protects it from erosion and oxidation and, thus, increasing its chemical stability [9]. Among all the studied magnetic nanoparticles, nano-sized magnetite (NSM) is one of the most investigated systems due to the broad range of potential applications in various fields, including high-density magnetic recording, ferrofluids, magnetic resonance imaging, and as biomedical materials [15] and adsorbents [16].

As adsorbents, magnetic mesoporous silica composites were used on the removal of several species, such as DNA, boron, heavy metals, phenols, etc. [8,13,17]. However, the silica shells had to be modified in almost all cases with organic molecules, some of them of a controverted toxicity, in order to increase the adsorption efficiency. In addition, the possible role of the NSM core as adsorbent in the composite has not been yet evaluated.

The aim of this article is to present a study of the synthesis and sorption properties of magnetic mesoporous silicas, prepared by modifying NSM with mesoporous silica. The effects of NSM content of the synthetic composites on the morphology, charge development, sorption of HA and the cationic dye malachite green (MG) are evaluated. Moreover, the adsorption data obtained at a variety of pH, ionic strength and Ca^{2+} concentration are used to gain insights into the mechanisms that govern the adsorption process and into the factors that promote or prevent it. The obtained results will also serve as a basis for further synthesis of new materials for pollution control.

2. Materials and methods

2.1. Chemicals

Cetyltrimethylammonium *p*-toluene sulfonate or tosylate (CTAT, MW = 455.7 g mol^{-1}), Pluronic F68 (PEO₇₆PPO₂₉PEO₇₆, MW = 8400 g mol^{-1} , with PEO and PPO being the poly(oxyethylene) and the poly(oxypropylene) chain units, respectively) and tetraethyl orthosilicate (TEOS, 99%) were purchased from Aldrich. Ferrous chloride tetrahydrate was obtained from Merck. Ferric chloride hexahydrate, hydrochloric acid, nitric acid, sodium hydroxide, calcium chloride and sodium chloride were purchased from Anedra. The HA used for adsorption experiments was extracted from an alfalfa-cultivated soil (INTA Manfredi experimental station, Córdoba, Argentina) and purified according to the procedures recommended by the IHSS. Its elemental composition is C (54.43%), H (4.00%), N (1.62%), and O (39.95%). The ash content of the sample is 1.18% and the total acidity is 9.90 mmol g^{-1} of which 4.71 mmol g^{-1} is ascribed to carboxylic groups and 5.19 mmol g^{-1} to phenolic groups. More information about the general characteristics of this HA sample can be found elsewhere [18]. Malachite green (acetate salt form, MW = 463.5 g mol^{-1}) was obtained from Sintorgan. Molecular structures of HA and MG are shown in the [Supplementary Material \(SM, see SM Fig. S1\)](#).

All chemicals were of analytical grade and used as received. Milli-Q water was used for the preparation of solutions.

2.2. Synthesis of materials

2.2.1. Mesoporous silica (SiO_2)

SiO_2 was prepared using a procedure similar to that described in an earlier work [14] with an exception in the method of template removal, i.e., solvent extraction was used here instead of calcination in air furnace as in Ref. [14]. Briefly, 11.6 mL of TEOS were mixed with 2 mL of water and stirred in an autoclave flask for 10 min at 500 rpm. At the same time, 38 mL of Pluronic F68-CTAT mixed solution were prepared with a 1:3 M ratio by adding the desired amount of surfactants to water. This mixed template was stirred in a conical flask at 35 °C to form a transparent solution and then it

was left at room temperature. To obtain the mesoporous material, 20 mL of a 1.38 M NaOH solution were added dropwise to the TEOS solution under stirring and 2 min later the surfactant solution was incorporated. The final pH of the mixture was 11.8. The resulting gel, whose composition was 1 TEOS:0.53 NaOH:0.011 CTAT:0.0037 F68, was stirred for 5 min and then left for 48 h in an autoclave at 100 °C. In order to remove the template, the gel was filtered and washed three times with 80 mL of an acidified ethanol solution at 60 °C (400 μL of concentrated HCl solution in 240 mL of a 96% ABV ethanol solution) and then several times with distilled water at room temperature up to neutrality. Finally, the solid was dried at 40 °C overnight.

2.2.2. Nano-sized magnetite (NSM)

NSM was chemically synthesized using a modification of the method described by Illés and Tombácz [19]. Briefly, 100 mL of 0.5 M FeCl_3 and 0.275 M FeCl_2 solutions were respectively prepared by adding the desired amount of hydrate iron salts to water and bubbled during 30 min with N_2 in order to remove dissolved O_2 . Both solutions were mixed and filtered by using 0.2 μm pore-diameter cellulose acetate filters (Osmonic). To obtain the NSM particles, 107 mL of a 2.05 M NaOH solution were added to the iron salts solution in two portions, the first half drop by drop and the second half suddenly under rigorous stirring and N_2 bubbling. The formed black-brown suspension was stirred for a few minutes, and then transferred into 1 L of water. After that, the suspension was washed with water several times to eliminate alkaline impurities from the synthesis and finally acidified with a HCl solution down to pH 3.5 to complete peptization. The stock suspension, whose concentration was determined to be 7.52 g L^{-1} , was stored in the dark at room temperature.

2.2.3. Magnetic mesoporous silica (NSMSiO₂)

Three composites with different NSM loading (called NSMSiO₂-1, NSMSiO₂-2, and NSMSiO₂-3) were prepared by adding the desired amount of the dry NSM to the F68/CTAT solution and then sonicating to complete suspension of the material. The resulting suspension was added to the TEOS + NaOH solution, and the system was treated as described for SiO_2 . The NSM content of NSMSiO₂-1, NSMSiO₂-2, and NSMSiO₂-3 was 6, 14, and 35wt., respectively, as measured by UV-VIS spectroscopy using the thiocyanate colorimetric method [20] after extracting the Fe ions from the solid with concentrated HNO_3 [21].

2.3. Characterization of synthesized materials

The synthesized materials were characterized by scanning and transmission electron microscopy (SEM and TEM); XRD; FT-IR spectroscopy; electrophoretic mobility; magnetic measurements; and the N_2 -BET method for surface area, pore volume and pore diameter determination. SEM was performed using an EVO 40-XVP microscope. The samples were prepared on graphite stubs and coated with a ca. 300 Å gold layer in a PELCO 91000 sputter coater. TEM was performed using a JEOL 100 CX II transmission electron microscope, operated at 100 kV with magnification up to 450,000 \times . Observations were made in a bright field. The powders were placed on 2000 mesh copper supports. XRD patterns were obtained using a Philips PW 1710 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and graphite monochromator operated at 45 kV, 30 mA and 25 °C; the angle step and counting time were 0.02°(2 θ) and 1 s, respectively. FT-IR experiments were recorded in a Nicolet FT-IR Nexus 470 Spectrophotometer. To avoid co-adsorbed water the samples were dried under vacuum until constant weight and then they were diluted with KBr powder before the FT-IR spectra were recorded. The hydrodynamic size and zeta potential of the

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