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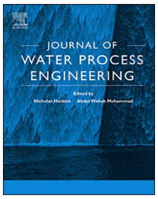

pH-sensitive magnetic alginate/γ-Fe_2O_3 nanoparticles for adsorption/desorption of a cationic dye from water

Delphine Talbot, Sébastien Abramson, Nebewia Griffete, Agnès Bée*

Sorbonne Université, CNRS, Laboratoire PHENIX, F-75005 Paris, France

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ABSTRACT

In this study, magnetic alginate nanoparticles (AlgMNP) were synthesized using a simple and green two-step method, which can be easily developed on an industrial scale. First, coprecipitation of both ferric and ferrous ions in alkaline medium followed by oxidation of magnetite into maghemite leads to a stable colloidal dispersion called ferrofluid. A sodium alginate solution was then added to the ferrofluid in order to obtain the magnetic nanocomposite. This approach combines the advantages of a biopolymer with magnetic properties of the maghemite nanoparticles. The morphology, structure, size and composition of the magnetic nanoparticles were characterized by means of atomic absorption spectrometry, transmission electron microscopy, X-ray diffraction, Fourier-transform-infrared spectroscopy and thermogravimetric analysis. Adsorption is one of the most efficient treatments for the removal of pollutants from wastewater. But the development of efficient and environmental friendly adsorbent still remains challenging. Using AlgMNP as a magnetic adsorbent could be a suitable response to this challenge. Its adsorption efficiency was investigated by using methylene blue as pollutant. The effects of pH, contact time, and initial concentration of the dye on adsorption were investigated. The high adsorption capacity with respect to the dye in a wide pH range (273 mg/g) was explained by the way magnetic nanoparticles bind to the alginate chains. We assumed an organization with alginate strands decorated by the magnetic nanoparticles leaving the adsorption sites of the particles more accessible rather than a configuration with a complete coating of magnetic nanoparticles by alginate. The reusability was successfully demonstrated through 10 adsorption/desorption cycles.

1. Introduction

Among the different technologies used for the removal of pollutants from industrial effluents, adsorption is considered to be an efficient and economic process easy to implement. However, the preparation of adsorbents that can efficiently remove pollutants, while exhibiting green properties and facilities for industrial development still remains challenging [1]. Moreover, separating adsorbents from water after pollutants extraction remains a laborious and time-consuming step. Using magnetic adsorbents makes it possible to overcome these difficulties. Indeed, these materials can be easily extracted from the treated water by applying a simple magnetic process reducing the risk of secondary pollution of the environment by waste accumulation [2].

Magnetic nanoparticles and more particularly iron oxide nanoparticles have been widely studied and used since a long time in many fields such as hyperthermia, magnetic drug delivery, magnetic resonance imaging, data storage, environmental remediation and so on [3–10]. These applications often need a surface engineering of the magnetic nanoparticles and the research of appropriate compounds to introduce additional functionalities to the nanoparticles attracts more and more attention. Nevertheless, it is still a challenge to synthesize functionalized magnetic nanoparticles in a controlled manner, especially when green and large-scale conditions are required [11].

Composites based on natural polymers are in focus as green adsorbents and among them, alginate seems to be a good candidate due to its strong adsorption properties. Alginate, mainly extracted from brown algae, is a water-soluble linear polysaccharide, which combines features of abundant resources, low-cost, biocompatibility and biodegradability. This natural polyelectrolyte is composed of β-D-mannuronate (M) and α-L-guluronate (G) units arranged in blocks rich in G units (G-block) or M units (M-block) separated by blocks of alternating G and M units (MG-block) [12]. Alginates are extensively used in biotechnologies, medicine or food industry [13,14]. It is mainly their gelling properties that are at the origin of their industrial applications. Due to this ability

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* Corresponding author at: Sorbonne Université, laboratoire PHENIX, Campus Pierre et Marie Curie, case 51, 4 place Jussieu, F-75005 Paris, France.
E-mail addresses: delphine.talbot@sorbonne-universite.fr (D. Talbot), sebastien.abramson@sorbonne-universite.fr (S. Abramson), nebewia.griffete@sorbonne-universite.fr (N. Griffete), agnes.bee@sorbonne-universite.fr (A. Bée).

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to form stable hydrogels, alginates can encapsulate different materials [15], which can strengthen their adsorption properties or confer them other properties, such as, for example, magnetic properties when magnetic nanoparticles are trapped in the polymer matrix [16–19]. Therefore, alginate is currently a hot topic for environmental research and many polymer nanocomposites are developed for applications in this field [20–24].

Recently, different methods have been reported for the synthesis of magnetic alginate-nanoparticles [25–29]. Two types of strategies are usually adopted: the magnetic nanoparticles are either synthesized in-situ in the alginate matrix, or synthesized separately (co-precipitation, hydrothermal treatment, etc.) and subsequently added to the alginate solution (so-called two-step method). However, in most of these materials, magnetic nanoparticles consist in magnetite (Fe_3O_4), which is readily oxidizable and especially unstable in acidic environment [30], which complicates the regeneration of this kind of materials. In addition, they are mainly used for biomedical applications [28].

This study reports the synthesis of alginate/maghemite nanoparticles (AlgMNP) for the adsorption of water pollutants. The use of maghemite (γ-Fe_2O_3) instead of magnetite as magnetic core is of particular interest because of the much larger stability of this phase. In addition to the green character and the adsorption sites of alginate, magnetic properties of the nanoparticles allow their fast extraction from complex environmental samples with a simple magnetic process. The two-step method described here consists first in the preparation of size-controlled maghemite nanoparticles (MNP) dispersed in diluted nitric acid to form a stable ferrofluid. Alginate solution is then added to the ferrofluid to obtain the magnetic adsorbent. Alginate is bound to the surface of the MNP through its carboxylate functions; the remaining carboxylate groups can then be used to adsorb pollutants in water. This method, easy to implement, is an attractive approach for effective clean-up procedure because it does not use toxic products and can be developed at an industrial scale. Moreover, there is no need of centrifugation or filtration steps due to the magnetic properties of the materials used. The potential use of AlgMNP for water treatment was investigated through adsorption experiments, methylene blue being chosen as a model of pollutant. Dyes are compounds widely used in the industry and their presence in effluents is of serious concern because of their toxic effects for both environment and human health [31]. The influence of pH, contact time, dye concentration on adsorption efficiency was studied. The reusability of the magnetic composite was demonstrated through adsorption/desorption cycles. We made a special effort to understand the interactions between the dye and the adsorbent. A good knowledge of our system and the control of the synthesis parameters enabled us to predict the number of active sites involved in the adsorption of the pollutant, which was then compared with the experimental results.

2. Experimental

2.1. Chemicals

Sodium alginate was purchased from Sigma Aldrich. The weight average molar weight (M_w) and the number average molar weight (M_n), obtained by gel permeation chromatography, are respectively 2.74×10^5 g/mol and 1.49×10^5 g/mol, leading to a polydispersity index (I_P) equal to 1.8. The amount of carboxylate functions of alginate (pKa = 3.4–4.2 [32,33]) was obtained from the dosage of their sodium counterions ($[Na]_{alg}$) by atomic absorption spectrometry with a Perkin–Elmer Analyst 100 apparatus. It is equal to 4.2 ± 0.1 mmol/g_{alg}.

Methylene blue (MB) was purchased from Sigma-Aldrich (M = 373.9 g/mol). Stock solutions of MB were obtained by dissolving the powder in distilled water. Their concentrations were measured by spectrophotometry at $\lambda = 664$ nm using a UV–vis UVIKON XL Secoman apparatus; the extinction coefficient ε_{664} is 83,243 $molL^{-1}\,cm^{-1}$.

2.2. Preparation of magnetic nanoparticles

A two-step procedure was used to obtain AlgMNP. In the first step, maghemite (γ-Fe_2O_3) nanoparticles (MNP) were synthesized according to the Massart's method [34,35] by alkaline co-precipitation performed by rapid addition of concentrated ammonium hydroxide (20%, 1 L) in an aqueous stoichiometric mixture of $FeCl_2$ and $FeCl_3$ obtained by mixing 180 g of Fe(II) salt (0.9 mol) and 715 mL of Fe(III) solution (1.5 mol) in acidic medium (HCl). The resulting dark black magnetite (Fe_3O_4) was then stirred in nitric acid (360 mL, 2 moL/L), oxidized into maghemite by a boiling solution of $Fe(NO_3)_3$ (323 g, 1.3 mol) and, after washing, dispersed into water leading to a stable magnetic fluid called ferrofluid. The pH value of the resulting suspension is about 2. At this time, nanoparticles are positively charged with nitrate counterions. In the second step, alginate solution (18 g/L) was added to the diluted ferrofluid to obtain the alginate-bound maghemite nanoparticles. Preliminary studies were carried out to optimize the ratio $R = \frac{m_{Alg}}{m_{MNP}}$ (m_{Alg} being the introduced weight of alginate and m_{MNP}, the weight of maghemite nanoparticles calculated from the iron concentration of the ferrofluid). Then, the reaction mixture was stirred for 30 min with an orbital shaker at 50 °C. The alginate-bound maghemite nanoparticles were recovered from the reaction mixture by centrifugation (20 min, 7500 rpm) or by using a permanent magnet with a surface magnetization of 800 G (typical value of the magnetic field at 1.5 cm from a cylindrical Nd/Fe/B magnet with a diameter of 2.5 cm and a height of 1 cm). Then, nanoparticles were washed three times using distilled water and dried 48 h in an oven at 70 °C.

2.3. Characterization

The size and morphology of the magnetic nanoparticles were observed by transmission electron microscopy using a Jeol model JEM 100 CX at 100 kV. The magnetic size distribution of the nanoparticles, which can be approximated by a lognormal law, was obtained by fitting magnetization curves parameters and led to the mean diameter d_{Aim} (ln $d_{Aim} = <\ln d>$) and distribution width σ_{Aim} of the nanoparticles [36]. The experimental device for the magnetic measurements was based on the one described by S. Foner [37]. X-ray diffraction (XRD) on dried samples using a Rigaku Ultima IV apparatus with a copper anode (Cu K_α radiation, $\lambda = 1.54178$ Å) was performed to identify the crystallographic structure and size of the nanoparticles. The equivalent iron concentration of the ferrofluid ([Fe]) was determined by atomic absorption spectrometry using an air-acetylene flame (Perkin Elmer AAnalyst 100 apparatus). Before measurements, magnetic nanoparticles were heated to ebullition in concentrated hydrochloric acid ($\approx$12 mol L^{-1}) until total dissolution of the nanoparticles into iron (III) ions was achieved. The amount of alginate bound on nanoparticles was estimated from the thermogravimetric analysis (TGA) performed on dried nanoparticles in air atmosphere with a heating rate of 10 °C/min (TA Instruments SDT Q600). FT-IR spectra of pure alginate, MNP, and AlgMNP were recorded in KBr discs in the range of 4000–400 cm^{-1} on a Bruker Tensor 27 to check the binding of alginate to maghemite nanoparticles.

2.4. Adsorption/desorption experiments

Batch adsorption experiments were carried out at room temperature ($\approx$20 °C). 100 mg (m) of dried AlgMNP (R = 0.14) were added to 10 mL (V) of MB at initial concentration C_0, pH of the samples being adjusted using either HNO_3 or NaOH solutions. After stirring using an orbital shaker (IKA KS 260) (2 h to reach equilibrium), nanoparticles were removed magnetically from MB solution. The concentration of MB remaining in solution at equilibrium (C_{eq}) or at a given time t (C_t) was measured by UV–vis spectrophotometry at 664 nm. We checked for each measure that there was no change in the BM spectrum. In