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Magnetic chitosan/clay beads: A magsorbent for the removal of cationic dye from water

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ABSTRACT

A magnetic composite material composed of magnetic nanoparticles and clay encapsulated in cross-linked chitosan beads was prepared, characterized and used as a magsorbent for the removal of a cationic dye, methylene blue (MB), from aqueous solutions. The magnetic properties of these beads represent an advantage to recover them at the end of the depollution process. The optimal weight ratio R=clay: chitosan for the removal of MB in a large range of pH was determined. For beads without clay, the maximal adsorption capacity of MB occurs in the pH range [9–12], while for beads with clay, the pH range extends by increasing the amount of clay to reach [3–12] for $R>0.5$. Adsorption isotherms show that the adsorption capacity of magnetic beads is equal to 82 mg/g. Moreover, the kinetics of dye adsorption is relatively fast since 50% of the dye is removed in the first 13 min for an initial MB concentration equal to 100 mg/L. The estimation of the number of adsorption sites at a given pH shows that the main driving force for adsorption of MB in a large range of pH is the electrostatic interaction between the positively charged dye and the permanent negative charges of clay.

1. Introduction

During the last few decades, the treatment of effluents has become a challenge in the environmental field due to the presence of numerous pollutants in the environment coming from human activity. Indeed, the processes currently used for the removal of pollutants have to be improved to increase their efficiency in terms of abatement of pollution, of decrease of sludge production and, sometimes for recovering materials of economical interest. Among the methods used for the water treatment, adsorption process is currently considered as an efficient and economic method for the removal of pollutants. Its easy handling and its minimal sludge production are important assets to use such a process in the water treatment although its success is strongly dependent of the chosen adsorbent. Adsorption studies with green, efficient and low-cost adsorbents have already shown remarkable results but efforts are still needed to find a way for separating pollutants and adsorbents from the water being treated. In this framework, magnetic composites attract increasing research attention due to both their adsorption efficiency and their magnetic properties. Indeed, magnetic systems can be easily separated and collected by applying an external magnetic field allowing removal of pollutants from water but also recovery of the adsorbent, thereby preventing an increase in the turbidity of the water being treated. Researchers have developed many systems combining a magnetic material with other compounds. We focus therefore our attention on magnetic composites based on biopolymer and clay. Due to their environmental-friendly properties, the combination of clay and biopolymer appears as an attractive way to develop materials with properties that are inherent to the different components. Among natural polymers, chitosan is a good candidate to develop organic–inorganic hybrid materials. Chitosan is the deacetylated product of chitin, a natural polymer found in the cell wall of fungi or in the exoskeletons of crustaceans and insects. Chitosan is a copolymer composed of D-glucosamine and N-acetyl-D-glucosamine units. Its adsorption properties are mainly governed by the acid-base properties of the amine group. In particular, the formation of protonated groups $R–NH_3^+$ contributes to the solubility of chitosan in acid medium. To prevent this dissolution, a crosslinking agent is used, that contributes to maintain chitosan into a bead form, even in acid medium. Indeed, cross-linking produces inter chains linkages using covalent bonding between the polymer chains, which induces the formation of a three dimensional network. The mobility of the chains of the

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polymer is then reduced and it becomes insoluble in water [1]. Clays are also low-cost adsorbents that are often used as cations exchanger due to their net negative charge [2]. If adsorption of pollutants by magnetic chitosan [3–5] or chitosan–clay composites [6,7] has been widely studied in the literature, there is much less work with magnetic chitosan–clay composites [8–10]. Moreover, the nature of adsorption sites and the adsorption mechanisms have not gained enough attention.

In the present study, the use of chitosan (CS) beads containing magnetic nanoparticles and clay appears as an improving way to develop materials efficient for adsorption of both anionic and cationic pollutants. The magnetic nanoparticles aid to separate the adsorbent from wastewater after use. The magnetic material which was used for this study is a ferrofluid consisting of magnetic nanoparticles of maghemite bearing surface charges, whose the nature and the number vary with the pH of the medium. In a previous work, magnetic chitosan beads without clay were used for the removal of methyl orange (MO), an anionic dye [11]. MO adsorption occurs in a pH range [3–7], whereas no MB adsorption occurs in this pH range. The encapsulation of clay within the beads aims to extend the pH range for adsorption of MB. Finally, according to the pH value and the quantity of clay in the beads, the magsorbent can remove MB or MO separately or together. These two dyes have been used as models to understand the behavior of cationic and anionic pollutants due to the easiness to determine their concentration in water by UV–vis spectrophotometry. But they also represent a significant source of water pollution since they are present in the effluents of many industries such as textile, food processing, cosmetics… Magnetic composites were characterized by TGA, atomic absorption spectrometry and X-ray diffraction. Moreover, for a better understanding of the adsorption mechanisms, an estimation of the amounts of adsorption sites has been done. Batch experiments were then carried out to investigate the effects of pH value, contact time, amount of encapsulated clay and initial dye concentration on the adsorption of the dyes by the magnetic beads.

2. Materials and methods

2.1. Materials

We used a clay made available by the company "Eau & Industrie". It is mainly composed of montmorillonite and will be subsequently called MMT. Its cationic exchange capacity (CEC), determined by adsorption of methylene blue, is equal to 0.47 ± 0.03 mmol/g_{MMT} (47 mequiv/100 g). CEC represents the amount of negative adsorption sites of MMT (N^{-}_{MMT}), which remains constant in the whole pH range.

Chitosan (CS) was characterized by its degree of deacetylation (DDA) (ratio of amino units to total units). It was supplied by Sigma with a DDA of 73.1%. The amino content of chitosan, equal to 4.4 ± 0.2 mmol/$g_{CS,}$ was determined as previously by potentiometric titration [11]; the deduced value of DDA is equal to $71 \pm 4\%$ in accordance with the value given by the supplier. A mean value of 6.2 is presented in the literature for the pKa of amino groups of chitosan [12]. To estimate the amount of positive adsorption sites of chitosan at a given pH (N^{+}_{CS}), we considered chitosan as a weak acid. By assuming that the amino content of chitosan represents the maximum positive adsorption sites ($N^{+}_{CS,max}$), N^{+}_{CS} was estimated from the following equation: $N^{+}_{CS} = N^{+}_{CS,max}/10^{pH\text{-}pKa}$.

Magnetic material was a ferrofluid composed of maghemite (γ-Fe_2O_3) nanoparticles synthesized according to the Massart's method [13,14] and dispersed in diluted nitric acid (pH ≈ 2). This magnetic material is a polydisperse system of rocklike nanoparticles, which can be described as spheres. The magnetization curve of the ferrofluid was obtained at room temperature using a homemade vibrating sample magnetometer. The mean diameter of the magnetic nanoparticles (d_0) and their polydispersity index (σ), deduced from a two-parameter fit of the magnetization curve, are equal to 7.5 nm and 0.4 respectively [15]. The iron concentration of the ferrofluid, obtained by atomic absorption spectrometry, is equal to 1.49 ± 0.03 mol/L (119.2 $g_{maghemite}$/L). The stability of the ferrofluid comes from surface charges due to the ionization of hydroxyl groups at the surface of the nanoparticles. Surface density of charges of the nanoparticles could be controlled through pH variations. At the point of zero charge (PZC) located at about pH 7.3, the net surface charge of the particles is zero. At this point, the electrostatic repulsions between uncharged particles do not exist any more and ferrofluid flocculates. Under acidic conditions (pH < PZC) protonation of surface hydroxyl groups leads to a positive surface while their deprotonation leads to a negative surface under alkaline conditions (pH > PZC). Potentiometric measurements allow calculating the amount of charges due to the nanoparticles for a given pH, which represents the adsorption sites of the nanoparticles [16]. After synthesis, the pH value of the ferrofluid was close to 2, the hydroxyl groups are protonated and the particles are then cationic ones with nitrate counterions.

Methylene blue (MB) was purchased from Sigma-Aldrich. Stock solutions of MB were obtained by dissolving the powder in distilled water. Their concentrations were measured by using a UV-visible Hitachi U2000 spectrophotometer at $\lambda = 664$ nm. The extinction coefficient ε_{664} is equal to 83243 mol L^{-1} cm^{-1}. Dye solutions of different initial concentrations were then prepared by diluting the stock solution.

2.2. Magnetic beads synthesis and characterization methods

The synthesis protocol of the magnetic chitosan beads with encapsulated clay was adapted from the one used previously to obtain magnetic chitosan beads without clay [11]. Briefly 15 mL of ferrofluid were added under stirring to a solution containing 3 g (m_{CS}) of chitosan dissolved in acetic acid; the weight ratio m_{CS}/m_{magh} was equal to 1.2 ± 0.1, m_{magh}, being the weight of maghemite determined from the iron concentration of the ferrofluid. m_{MMT} g of clay were then added in the mixture to obtain a weight ratio $R = m_{MMT}/m_{CS}$ varying from 0 to 1.3. The mixture was then dropped into NaOH. After that an alkaline epichlorohydrin solution was used as a cross-linking agent to form the chitosan gel. No release of both magnetic nanoparticles and clay was observed in the NaOH bath and during the cross-linking step. The beads were gathered with a magnet and washed with ethanol and deionized water until the $AgNO_3$ test proved the absence of residual chloride ions in the solution. The ready-for-use beads were stored in deionized water and carefully characterized before studying their adsorption properties. Their mean diameter and size distribution were obtained from digitized photographs in combination with image analysis software (ImageJ). The iron content of the beads was analyzed by atomic absorption spectrometry using a Perkin-Elmer AAnalyst100 apparatus. X-ray diffraction studies of air-dried beads (70 °C) ground to powder were performed on a Rigaku Ultima IV diffractometer using Cu Kα radiation. Thermogravimetric analysis were carried out with a SDT Q600 TA Instruments, the heating rate was 10 °C/min. The moisture content (%hum = $(m_W - m_d)/m_W$) of the beads was determined from the weights of wet (m_w) and dried (m_d) beads.

2.3. Adsorption experiments

Batch adsorption experiments were carried out at room temperature (≈ 20 °C). Wet magnetic beads ($m_{beads} \approx 0.5$ g) were added to 5 mL of MB at an initial concentration C_0. The pH of the