



Research paper

Adsorption characteristics of montmorillonite clay modified with iron oxide with respect to methylene blue in aqueous media



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ABSTRACT

Montmorillonite clay modified with iron oxide (MtMIO) was prepared for use as an adsorbent of methylene blue dye. Structural characterization of MtMIO was performed by field-emission scanning electron microscopy, energy-dispersive spectroscopy, surface area measurements, zeta potential analysis and Fourier transform infrared spectroscopy. Batch experiments were carried out under different conditions of initial dye concentration, contact time and temperature to investigate the adsorption of methylene blue onto MtMIO. Adsorption isotherms were experimentally determined and the Freundlich and Langmuir models were used to fit the data, better results being obtained for the latter with a maximum adsorption capacity of 71.12 mg g⁻¹ at 333 K. Thermodynamic parameters, such as standard enthalpy, standard entropy and standard free energy changes were determined, indicating an endothermic and non-spontaneous process. Also, pseudo-first-order and pseudo-second-order kinetic models were applied, and the experimental data fitted the pseudo-second order model. The activation energy of +19.32 kJ mol⁻¹ was determined using the Arrhenius equation.

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1. Introduction

In the manufacturing of fabrics, leather, paper, cosmetics, polymers and food, among other items, large amounts of dyes are used to color the products, which are partly discharged in effluents with no previous treatment. The presence of dyes in effluents, even in low concentrations, is a major concern because they are highly visible, toxic to microorganisms and harmful to human health (Auta and Hameed, 2013; Kabra et al., 2013; Verma et al., 2012).

In recent decades, various methods have been developed for the removal of dyes from wastewaters, such as chemical oxidation, biodegradation, membrane separation, electrochemical processes, coagulation/flocculation and adsorption (Mondal et al., 2013; Vergili et al., 2012; Verma et al., 2012). Adsorption is considered an effective way to remove dyes from wastewater, since it is not destructive and easy to apply (Ahmad and Kumar, 2010; Anirudhan et al., 2010). The use of activated carbon as an adsorbent has a long history and it has been widely utilized for dye removal in wastewaters. However, due to its high cost, researchers have been studying alternative adsorbents (Ahmaruzzaman and Gayatri, 2010; Duman and Ayranci, 2010).

Magnetic adsorbents, which combine the adsorbent capacity of an adsorbent with the magnetic property of iron oxide, have been studied due to their great potential for application in several areas, such as the biological, medical, industrial and environmental fields (Durdureanu-

Angheluta et al., 2012; Zhao et al., 2012). Magnetic adsorbents have active sites with affinity for organic and/or inorganic compounds, being composed of an iron oxide core coated with organic or inorganic molecules. After the adsorption, magnetic adsorbents can be separated from the medium by a magnetic field (Mahdavian and Mirrahimi, 2010; Yamaura et al., 2004).

In this study, a magnetic adsorbent was obtained by modifying montmorillonite clay with iron oxide (MtMIO). The MtMIO produced was characterized and applied to methylene blue (MB) adsorption using the batch technique. The uptake time, initial concentration and temperature effects were investigated, as well as the equilibrium, kinetics and thermodynamics.

2. Materials and methods

2.1. Materials

Methylene blue (MB) dye, which has the chemical structure shown in Fig. 1, was used as the adsorbate. MB (basic blue 9, C.I. 52015) is a cationic dye with the molecular formula C₁₆H₁₈ClN₃S·3H₂O and a molar mass of 373.90 g mol⁻¹. Its electronic spectrum has a maximum absorbance peak in the visible region at a wavelength of 664 nm.

All solutions used were prepared with deionized water and all reagents were of analytical grade. Working solutions of MB were prepared from a stock solution of 2000 mg L⁻¹ to give the required initial concentrations (C₀ = 100 to 1000 mg L⁻¹) for each experimental run.

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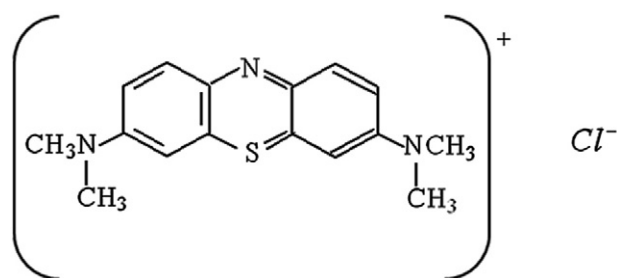


Fig. 1. The chemical structure of MB.

The montmorillonite clay (Mt) used in this study was supplied by the company Agetec Engenharia (Florianópolis, Santa Catarina – Brazil). Before the experiments the Mt was sieved to give a particle size range of 53–105 μm . The chemical composition was then determined by X-ray fluorescence spectroscopy and the major components of the Mt were SiO_2 (65.75%), Al_2O_3 (13.76%), Fe_2O_3 (6.80%), MgO (2.38%) and CaO (1.60%), with a loss on ignition of 7.64%.

2.2. Modified adsorbent

Samples of MtMIO were prepared using iron oxide (IO) obtained by a method based on co-precipitation. For the iron oxide preparation, a solution of NH_4OH (1.0 mol L^{-1}) was slowly added to a solution comprising a mixture of FeCl_3 (2.0 mol L^{-1}) and FeSO_4 (1.0 mol L^{-1}) under mechanical stirring at 600 rpm, until the solution reached a pH of between 11 and 12. This procedure was adopted in order to obtain mainly magnetite instead of maghemite or hematite particles (Compéan-Jasso et al., 2008; Petcharoen and Sirivat, 2012). The magnetite particles (iron oxide – Fe_3O_4) were then removed from the solution and washed several times. In the next step, they were dispersed in 150 mL of deionized water, under agitation, with the addition of Mt, for 1 h. The resultant material (MtMIO) was vacuum-filtered, washed with deionized water until pH of around 7, dried in an oven at 50°C for 24 h, and then sieved to give a standard particle size in the range of 125–250 μm (120–60 mesh) (Petcharoen and Sirivat, 2012). The MtMIO was stored in a desiccator for characterization and batch adsorption experiments.

2.3. Characterization of adsorbent

Morphological studies were carried out using field-emission scanning electron microscopy (FE-SEM; JEOL microscope model JSM-6701F) coupled with energy-dispersive X-ray spectroscopy (EDS) for elemental analysis. The samples were sprinkled over a piece of conducting carbon tape and coated with a thin gold layer to give them conductive properties.

Fourier transformed infrared (FTIR) spectroscopy (ABB Bomem spectrometer, model 120) analysis was performed in the range of $4000\text{--}400 \text{ cm}^{-1}$. The samples were ground with KBr (analytical grade) and the mixture was pressed under vacuum conditions to produce disks for the FTIR analysis.

Zeta potential measurements were carried out using a Malvern Zetasizer Nano ZS analyzer (Malvern Instrument Ltd., Malvern Worcestershire, UK) equipped with a multipurpose autotitrator (model MPT-2, Malvern Instruments, Worcestershire, UK). Titration was performed from pH 10.0 to 2.0 with 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCl solutions under constant stirring.

The specific surface areas (SSA) of the samples were determined using an AUTOSORB-1 surface area analyzer, Quantachrome (Brunauer–Emmett–Teller – BET). Prior to the measurements, the samples were degassed at 573 K for 2 h, and then the nitrogen adsorption and desorption were measured at 77 K.

2.4. Batch adsorption experiments

Batch adsorption experiments were carried out in a set of glass flasks (80 mL) containing 50 mL of unbuffered MB solutions (pH 5.5–7.5) with different initial concentrations at three temperatures (308, 318 and 333 K) and with 0.1 g of adsorbent added to each solution. The pH measurements were monitored by using a laboratory pH meter model 827, Metrohm (USA). The MB solutions were kept under stirring using a mechanical stirrer built in our laboratory, with the speed calibrated by a manual tachometer at 450 rpm. The solutions were kept in thermal equilibrium by a thermostated system, with an outer circulating water bath (Nova Ética). Aliquots of 0.1 mL were withdrawn from the solutions over a period of 4 h, at predetermined time intervals during each run. These aliquots were then diluted, homogenized and centrifuged before the measurement of the supernatant absorbance. The absorbance was measured using a UV–vis spectrophotometer (Varian Cary 50 BIO spectrophotometer, USA) and a 1-cm path-length cell to monitor the absorbance at $\lambda_{\text{max}} = 664 \text{ nm}$, corresponding to the maximum absorbance. The MB concentrations at each time were estimated from a previously prepared calibration curve obtained by plotting the absorbance against the MB concentration of the solution. The batch adsorption was conducted for a contact period of 4 h, a time sufficient for the concentration of the solutions to reach a constant value.

The amount of MB adsorbed by MtMIO in each time interval, t , was calculated through the following mass balance equation:

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (1)$$

where C_0 is the initial liquid-phase MB concentration (mg L^{-1}); C_t is the liquid-phase MB concentration at time t (mg L^{-1}); V is the volume of the MB solution (ca. 0.05 L) and m is the mass of MtMIO used (ca. 0.1 g).

3. Results and discussions

3.1. Surface characterization

Fig. 2 shows micrographs of the Mt, IO and MtMIO. As can be seen in Fig. 2a, the Mt particles have irregular surfaces with undulations, indicating a crystalline-type order and stacking of sheets of the material. In the case of the IO (Fig. 2b), in the synthesis of the magnetite nanoparticles aggregates with relatively homogeneous distribution were formed. The magnetite nanoparticles have an average size of around 25 nm. Fig. 2c shows aggregates of the IO homogeneously distributed on the MtMIO surface, suggesting magnetite nanoparticles supported on the Mt surface. From Table 1, it can be observed that there is a substantial increase in the amount of iron on the surface of the clay after the chemical modification. The presence of iron on the MtMIO surface verifies that a thin layer of IO formed on the Mt surface due to electrostatic interactions. Also, according to Table 1 there was a lack of the elements Na, Mg and Al and a decrease in the Si content in the MtMIO, which also indicates that IO was adsorbed by the Mt surface covering the elements previously observed on the unmodified Mt surface. The IO particles are positively charged while the surface of Mt is negatively charged resulting in electrostatic interactions. These interactions may lead to a good dispersion of IO on the surface of Mt, as found by other authors (Yuan et al., 2009).

3.2. Surface properties

In this study, for IO, Mt and MtMIO the behavior of the surface charge was investigated in detail. Since the adsorption process is primarily driven by electrostatic forces, zeta potential ζ measurements provide key information to understanding the interaction between the adsorbent and the adsorbate. When the zeta potential is positive, the

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