



Preparation and evaluation of hydrotalcite-iron oxide magnetic organocomposite intercalated with surfactants for cationic methylene blue dye removal

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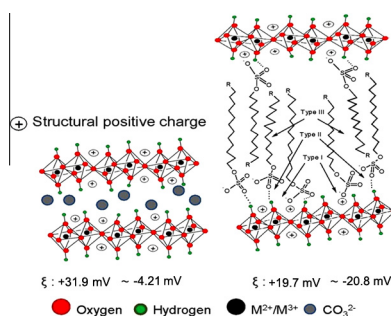
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HIGHLIGHTS

- Proposed mechanism of interaction between hydrotalcite and surfactants.
- Organocompounds, HT-iron oxide interspersed with surfactants, are novel in literature.
- Application of HT-iron oxide interspersed with surfactants on adsorption of cationic dye.
- Study of the zeta potential versus pH indicates that the hydrophobic interaction acts on the adsorption process.

GRAPHICAL ABSTRACT



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ABSTRACT

Cationic dye adsorption by hydrotalcite-iron oxide magnetic modified with dodecylsulfate (DS) and dodecylbenzenesulfonate (DSB) anionic surfactants was examined using methylene blue (MB) dye as compound model in aqueous solutions and compared to the adsorption capacity of non-modified hydrotalcite (HT). The magnetic adsorbents were named by HT-CO₃/Fe, HT-DS/Fe and HT-DSB/Fe. These were characterized by infrared spectroscopy (IR), X-ray diffractometry (XDR), zeta potential and atomic adsorption spectrometry. The effects of the adsorbent dosage, contact time, pH and initial concentrations of the dye were evaluated. In accordance with the obtained results, the pseudo-second order kinetic model can fittingly describe the adsorption processes. The MB removal percentages by adsorbents HT-CO₃/Fe, HT-DS/Fe and HT-DSB/Fe were 9%, 91%, and 82%, respectively, for the initial dye concentration of 150 mg/L of MB. Free energy variations, during MB adsorption were -25.88 and -27.40 kJ/mol for HT-DS/Fe and -26.36 and -27.80 kJ/mol for HT-DSB/Fe suggesting the spontaneity of the adsorption process. The positive value of ΔH° suggests that interaction of the AM dye adsorbed by the organocompounds HT-DS/Fe and HT-DSB/Fe is an endothermic process. The Dubinin-Radushkevich model indicated that the adsorption process is probably physisorption for both organocompounds.

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1. Introduction

The efficient removal of organic dye stuffs in industrial polluted water has been always a hot and challenging issue in the field of environmental remediation and pollution control. Among various physical and chemical approaches, the adsorption technique is more widely used for being of low cost, simple and efficient for dye removal [1]. Several types of porous materials such as anionic clays, have received attention as potential adsorbents. The term “anionic clays” is used to designate Layered Double Hydroxides (LDHs) [2].

Layered Double Hydroxides (LDHs) are mixed metal hydroxides that have general formula expressed as $[M_1^{2+}_{1-x}M_2^{3+}_x(OH)_2]^{x+}A_{x/n}^{n-} \cdot mH_2O$, where M^{2+} and M^{3+} represent, respectively, di and trivalent metal cations, A^{n-} a charge anion n , x the molar ratio between di and trivalent cations, $M^{2+}/(M^{2+} + M^{3+})$, and m , the number of water molecules. The crystalline structure of these compounds consists of positively charged layers $[M_1^{2+}_{1-x}M_2^{3+}_x(OH)_2]^{x+}$, similar to the brucite layered structure ($Mg(OH)_2$), and an interlayered negative region composed of anions and water molecules, $A_{x/n}^{n-} \cdot mH_2O$ [2,3].

The most important class of LDHs is the hydrotalcites (HT), presenting the general formula $[Mg_{1-x}^{2+}Al_x^{3+}(OH)_2]^{x+}[A_{x/n}^{n-} \cdot mH_2O]^{x-}$ where x may have value between 0.17 and 0.33. Anions (A^{n-}) and interlayered water molecules can be exchanged for other anions, which makes hydrotalcites good anionic exchangers [2,4].

A wide variety of inorganic or organic anions can be intercalated in the HT interlayer space. The adsorbent property of the HT surface can be modified through the exchange of inorganic interlayered anions for organic anions such as anionic tensioactives (originating the organocomposite) [5,6]. When anionic surfactants like dodecylsulfate (DS) and dodecylbenzenesulfonate (DSB) are intercalated to HT, the space between layers increases and alteration of interlayer superficial properties from hydrophilic to hydrophobic occur. The hydrophobic nature and accessibility of the interlayer region of organocomposites make these materials promising candidates for adsorption of non-ionic organic pollutants [7–10]. However, the removal of cationic organic species, by LDH, from aqueous solutions is little reported in the literature [5].

Magnetic technology is a promising solution due to easy removal of adsorbent/adsorbed from aqueous solution through application of a magnetic field, which naturally reduces costs and time spent in the extraction of the absorbing material [11].

The combination of iron oxide and HT composite was developed to improve HT separation in aqueous solution [2,11–13]. HT intercalated by dodecylsulfate (DS) and dodecylbenzenesulfonate (DSB) anionic surfactants and added with magnetic properties was nominated as HT-DS/Fe and HT-DSB/Fe, respectively, and magnetic hydrotalcite as HT-CO₃/Fe. Several magnetic adsorbent materials have been reported in literature when studying the adsorption of the dye AM [14–16]. However, to the best of our knowledge, the adsorbents synthesized in this work, the modified HTs-iron oxide, have not been reported in literature for the adsorption of waters contaminated by cationic organic species.

Therefore, as the removal of cationic organic species by LDH is scarcely reported in the literature and associated with the magnetic properties of organocomposites, the purposes of this study were (1) to synthesize the two organocomposites, with dodecylsulfate (DS) and dodecylbenzenesulfonate (DSB) surfactants intercalated in the HT, added with magnetic properties, (2) to propose a possible interaction mechanism between surfactants and HT and (3) to evaluate the adsorption performance of the prepared materials, HT-DS/Fe and HT-DSB/Fe, as for the capacity of removing

cationic methylene blue (MB) dye from water, comparing with the adsorption capacity of HT-CO₃/Fe.

2. Materials and methods

2.1. Materials

Both metal nitrates, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, sodium hydroxide, sodium carbonate, sodium dodecylsulfate (DS) and sodium dodecylbenzenesulfonate (DSB), iron(III) chloride hexahydrate and ferrous sulfate heptahydrate were used and obtained from Sigma Aldrich. The dye methylene blue was purchased from Vetec (Rio de Janeiro, Brazil). Deionized water was used in all stages of this work. All solutions were prepared with analytical grade reagents and high purity deionized water produced with a Milli-Q[®] system (Millipore, Bedford, MA, USA).

2.2. Synthesis and modification of HT by surfactants

The organocomposites, $[Mg_3Al(OH)_8][CH_3(CH_2)_{10}CH_2(C_6H_4)SO_3] \cdot nH_2O$ and $[Mg_3Al(OH)_8][CH_3(CH_2)_{10}CH_2SO_4] \cdot nH_2O$ were obtained by the co-precipitation method in N₂ atmosphere. An aqueous solution (100 mL) containing 0.06 mol of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.02 mol of $Al(NO_3)_3 \cdot 9H_2O$ (Mg/Al = 3 ratio) was added drop by drop to an alkaline solution (500 mL) containing 0.16 mol of NaOH, 0.05 mol of sodium dodecylsulfate or 0.15 mol of dodecylbenzenesulfonate. The obtained suspensions were hydrothermally treated at 80 °C for 24 h, and the precipitates were washed with distilled water and dried at 60 °C. Samples were denominated HT-DS and HT-DSB.

For comparison purposes, hydrotalcite, $[Mg_3Al(OH)_8]_2CO_3 \cdot nH_2O$ (HT-CO₃) was prepared by the variable pH co-precipitation method, as described in the literature [9,10].

2.2.1. Synthesis of the composite and organocomposites/iron oxide

The products, HT-CO₃, HT-DS and HT-DSB were combined with iron oxide properties to produce the magnetic adsorbents HT-CO₃/Fe, HT-DS/Fe and HT-DSB/Fe, respectively. In the synthesis of the HT-CO₃/Fe magnetic composite, a quantity of hydrotalcite obtained at a mass ratio of HT-CO₃:iron oxide of 1:0.3 was adjusted. Thus, 400 mL of a HT-CO₃ suspension, with $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ was prepared at proportions of 0.50; 0.10 and 0.25 mol, respectively. The suspension was heated to 70 °C and the iron oxide precipitation was obtained by addition of 30 mL of 0.15 mol of NaOH. The obtained material (HT-CO₃/Fe) was washed with deionized water and dried in oven at 70 °C for 18 h. After preparation, HT-CO₃/Fe presented magnetic properties when tested with a 0.3 T magnet, where all material was attracted to the magnet. [2]. Analogously, the organocomposites HT-DS/Fe and HT-DSB/Fe were prepared, being unprecedented in the literature.

2.2.2. Characterization of prepared materials

The infrared spectrometry analysis was carried out directly on the sample using a VARIAN 660 infrared spectrophotometer, outfitted with a total attenuated reflectance PIKE GladiATR accessory in the region 400–4000 cm⁻¹. The X-ray diffraction analyses were carried out in an X-ray Diffraction model System (X' Pert PRO, PANalytical) using Ni filter, Co- α ($\lambda = 1.78890 \text{ \AA}$) radiation and 3–70° (2 θ) angular variation. For the determination of magnesium, aluminum and iron content in the composite and magnetic organocomposites, 12 mL of aqua regia were added, (1 V) HNO₃:(3 V) HCl to samples of 0.100 g of each material, HT-CO₃/Fe, HT-DS/Fe and HT-DSB/Fe. Subsequently, samples were submitted to digestion

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