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Research paper

Adsorption study of reactive dyes onto porous clay heterostructures

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ABSTRACT

The present research evaluates the adsorption of reactive dyes, Remazol Violet 5R (RV5R) and Acid Blue 25 (AB25), using Porous Clay Heterostructures (PCHs) prepared from natural bentonite. Natural bentonite, PCH with silica pillars (Si-PCH) and PCH with silica-zirconia (SiZr-PCH) were characterized by elemental analysis, XRD, N_2 adsorption-desorption at −196 °C, FT-IR, TG and XPS. The adsorption experiments were carried out in a stirred tank in order to evaluate the effect of pH, contact time and initial concentration. The adsorption isotherms were well fitted by Langmuir (L), Langmuir-Freundlich (LF) and Redlich Peterson (RP) models. The equilibrium data were described using the Langmuir-Freundlich model for both dyes and both materials, obtaining a maximum adsorption capacity of 209.9 mg g^{-1} and 265.9 mg g^{-1} for AB25 using Si-PCH and SiZr-PCH, respectively. In the case of RV5R, the maximum adsorption capacity was 127.07 mg g^{-1} and 185.7 mg g^{-1} for Si-PCH and SiZr-PCH, respectively. The adsorption process takes place by electrostatic interactions between the silanol groups of the PCHs with functional groups of the dyes, such as amine or hydroxyl. From the obtained results, it can be concluded that PCHs showed to be a promising material for the adsorption of dye.

1. Introduction

In the last decades, the widespread contamination of groundwater and soils as a consequence of synthetic organic chemicals, e.g. dyes coming from the textile and related industries, has been considered an important issue worldwide (İyim and Güçlü, 2009). Dyes can be classified as a function of the charge in anionic, cationic and non-ionic compounds. Among them, anionic dyes are widely used as colorant in the textile industry in wool, silk, acrylic, leather or nylon. These dyes are formed by aromatic compounds with nitrogen or sulfur centers leading to an obvious coloration. Nonetheless, these compounds are harmful and potential human carcinogen, even at low concentrations. The use of colorants in the textural industry generates effluents highly colored which provoke numerous operational problems in municipal wastewater treatment due to high biological oxygen demand (BOD) and high chemical oxygen demand (COD), high conductivity and alkaline nature of these effluents (Ozturk et al., 2009). In addition, the presence of metal together with the dyes in the wastewater can provoke a microbial inhibition.

The treatment of the wastewaters depends on the physicochemical properties of the dye as well as the treatment technology selected (Abbassi et al., 2013). Several methodologies have been proposed to diminish the content of colorant of wastewater such as membrane separation, flocculation-coagulation, ozonation, oxidation, sedimentation, reverse osmosis, flotation, precipitation, and aerobic or anaerobic treatment (Leodopoulos et al., 2014; Yagub et al., 2014). However the most of them are infeasible due to their high cost or low efficiency.

The adsorption is a usual method to the treatment of wastewater for dye removal due to the availability of adsorbents, its simplicity in operation and high efficiency (Almeida et al., 2009).

Actually, the dyes adsorption is focused in the use of natural solid materials, which can be able to remove pollutants from contaminated water with low-cost. In this sense, it has been proposed clay minerals, siliceous materials or zeolites as natural absorbents by physical and/or chemical interactions with the dyes. Among them, clay minerals, and specially bentonites, have shown to be interesting adsorbents with low cost materials, large availability, thermal and chemical stability in a wide range of pH and interesting properties in the adsorption field (Abbassi et al., 2013). Bentonite is formed mainly by montmorillonite, which displays a lamellar structure where Si^{4+} species are partially replaced by Al^{3+} species in the tetrahedral positions and Al^{3+} species are partially substituted by Mg^{2+} or Fe^{2+} species in octahedral positions. This fact gives rise to the development of negative charges in the layers, which are balanced by the presence of Na^+, K^+ or Mg^{2+} cations strongly hydrated located in the interlayered space (Brindley, 1980). Montmorillonite has been treated or modified with several methods to improve its physicochemical properties. Thus, it has been proposed the acid treatment to improve the specific surface area of this smectite (Al-Khatib et al., 2012; Pentrák et al., 2012; Toor et al., 2015) or the

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incorporation of bulky cations in the interlayered spacing to favor the electrostatic interaction between the bulky cations and the dyes (Tong et al., 2010; Kıranşan et al., 2014; Anirudhan and Ramachandran, 2015; Grundgeiger et al., 2015). However, the acid treatment leads to the partial digestion of the clay together with the loss of the silanol groups, which causes a decrease of available active sites that should interact with the dye. With regard to the intercalation with bulky cations located in the interlayer spacing, the presence of these bulky cations provokes a drastic decline of the available specific surface area.

In order to improve the adsorption capacity of the montmorillonite, several methods, such as the synthesis of pillared interlayered clays (PILCs) with the use of polyoxocations (Vaccari, 1999), have been proposed. In 1995, Galarneau et al. described the synthesis of a porous material, denoted as PCH, from cationic exchange of the cations located in the interlayer spacing by a bulky cation, which produces the expansion of the interlayer spacing, and subsequent formation of silica pillars intercalated between two adjacent layers (Galarneau et al., 1995). Recently (Cecilia et al., 2013) have proposed a new method of synthesis with the incorporation of zirconium in the pillars. This method allows the control of the pore size leading to materials with high surface area (>600 m^2 g^{-1}) with high micro- and mesoporosity. The chemical behavior of the PCH can be modified by the insertion of heteroatoms such as Al, Zr or Ti in the pillars, which produces an increasing of the acidity and provides to the material a higher thermal and mechanical stability (Cecilia et al., 2013). In addition, these materials display higher hydrophilicity than the natural clays, which improves the performance in the adsorption and catalysis, thereby generating their extensive use in the removal of different compounds (Roca Jalil et al., 2013).

The present research describes the synthesis and characterization of porous clay heterostructures, which contains silica or silica-zirconium pillars, from a natural bentonite. These materials have been evaluated as adsorbents in the removing azo dyes in aqueous solutions in batch adsorption experiments.

2. Material and methods

2.1. Dyes

Dye Remazol Violet 5R (trisodium; (3Z)-5-acetamido-3-[[2-hydroxy-5-(2-sulfonatooxyethylsulfonyl) phenyl] hydrazinylidene]-4-oxonaphthalene-2,7-disulfonate - $C_{20}H_{16}N_3Na_3O_{15}S_4$) with molar mass of 735.6 g mol^{-1}, UV–visible $\lambda_{max} = 562$ nm. Dye Acid Blue 25 (2-Anthracenesulfonic acid, 1-amino-9,10-dihydro-9,10-dioxo-4-(phenylamino), monosodium salt - $C_{20}H_{13}O_5N_2SNa$) with molar mass of 416.4 g mol^{-1}, UV–visible $\lambda_{max} = 605$ nm. The dyes used were obtained from Sigma-Aldrich with a high degree of purity. The structures of dyes are shows in Fig. 1. Remazol Violet 5R is formed by an aromatic framework with aryl, amide and sulfonic groups, while Acid Blue 25 is also formed by an aromatic structure with amine and sulfonic groups.

2.2. Porous clay heterostructures synthesis

The synthesis of the porous clay heterostructures (PCHs) were carried out following the procedure described by (Cecilia et al., 2013) in a previous research.

The starting bentonite was supplied by Minas de Gador S.A. from “Sierra de Gador” (Spain). The raw bentonite was purity to obtain the montmorillonite fraction by a sedimentation process. Later, the montmorillonite fraction was treated with a NaCl solution (1 M) for 24 h to generate the homoionic Na-montmorillonite.

In a typical PCH synthesis, 2.5 g of Na-montmorillonite was treated with 9 g of hexadecyltrimethylammonium bromide (HDTMBr) (Aldrich) in 100 mL of *n*-propanol (99.9%, VWR). After 3 days under stirring, the solution was filtered and was washed with distilled water to remove the non-intercalated HDTMBr. The solid was redissolved in 250 mL of water for 24 h. After this time, a solution of 0.9 g of hexadecylamine (90%, Aldrich), used as co-surfactant, was dissolved in 25 mL of *n*-propanol solution, added to the mother solution and stirred for 24 h. The Si-pillars located between adjacent layers of montmorillonite were formed by the incorporation of a solution of 11.1 mL tetraethylorthosilicate (TEOS) (98, Aldrich), as silicon source. The formation of Si—Zr pillars with a molar ratio Si/Zr = 5 were generated by the addition of a solution of 9.4 mL of TEOS and 2.25 mL of zirconium propoxide (70%, Aldrich) dissolved in both cases in *n*-propanol (50 vol.%). The obtained gel was stirred during 72 h and then was filtered and washed with water-ethanol and dried at 60 °C in air for 12 h. Finally, the surfactant was removed by the calcination at 550 °C with a rate of 1 °C min^{-1} during 6 h. Elemental analysis CNH were carried out to ensure the complete combustion of the surfactant.

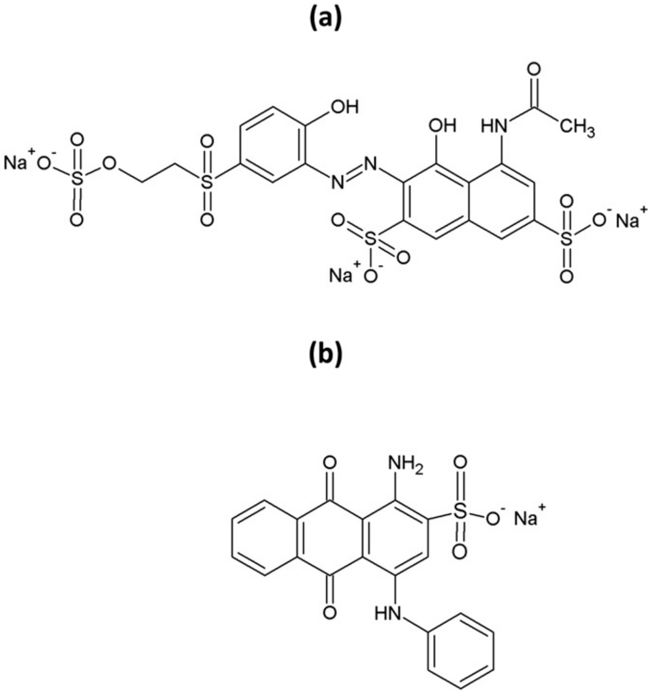

Fig. 1. Chemical structure of the Remazol Violet 5R-RV5R (a) and Acid Blue 25-AB25 (b).

2.3. Characterizations of porous clay heterostructures

The purified montmorillonite was examined by scanning electron microscope (SEM) using a JEOL SM-6490 LV combined with X-ray energy dispersive spectroscopy (EDX). The samples were gold sputtered in order to avoid charging of the surface. Elemental composition of the bentonite was achieved by the average of EDX chemical analyses of 40 grains.

X-ray powder patterns for the samples were collected on a X'Pert Pro MPD automated diffractometer (PANalytical B.V.) equipped with a Ge (111) primary monochromator (strictly monochromatic CuKα_1 radiation) and an X'Celerator detector with a step size of 0.017°. The powder patterns were recorded between 10° and 70° in 2θ with a total measuring time of 30 min. Low angle measurements were obtained with the same configuration maintaining the divergence and anti-divergence aperture at 1/16° and with Soller of 0.02 rad. Measurements were carried out between 0.5–10° in 2θ with a step size of 0.017°.

The textural parameters (S_{BET}, V_P and d_P) were evaluated from the nitrogen adsorption-desorption isotherms at −196 °C as determined by an automatic ASAP 2020 system from Micromeritics. Prior to the measurements, samples were outgassed at 200 °C and 10^{-4} mbar overnight. Surface areas were determined by using the Brunauer–Emmett–Teller (BET) equation and a nitrogen molecule cross section of 16.2 Å^2.