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Research paper

Effect of chemical modification of palygorskite and sepiolite by 3-aminopropyltriethoxisilane on adsorption of cationic and anionic dyes

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A B S T R A C T

A study has been performed on the removal of representative cationic and anionic dyes, methylene blue and metanil yellow, from aqueous solutions using fibrous clay minerals grafted with amine groups using (3-aminopropyl)triethoxysilane as functionalizing agent. Parameters affecting dye uptake, including contact time and dye concentration, the desorption process, pH and the recovery of both the dyes and the adsorbents, were evaluated. The adsorption capacities were 49.48 and 47.03 mg/g for grafted palygorskite and 60.00 and 59.78 mg/g for grafted sepiolite, for methylene blue and metanil yellow dyes, respectively. Adsorption of the anionic dye was enhanced by the grafting process. Grafted clay mineral adsorbents proved to be efficient to remove the contaminants from a real wastewater from textile industry within 30 min. Both adsorbents showed good reusability and the maximum adsorption capacity was maintained stable after a 2-cycle test. Thus, hybrid adsorbents based on fibrous clay minerals can efficiently be applied in adsorption/desorption cycles for removal of dyes.

1. Introduction

Water pollution, mainly due to industrial processes, is one of the most serious environmental problems in modern society (Anandkumar and Mandal, 2011). Many industries, such as paper and pulp, cosmetics, paints and pigments, plastics, leather tanning and textile, generate huge amounts of *colored effluents* which contain considerable amounts of toxic substances (Ozer et al., 2007; Demirbas et al., 2008).

Palygorskite (*Pal*) and sepiolite (*Sep*) are fibrous clay minerals whose basic structure can be described as 2:1 ribbons laterally linked to each other by single basal oxygens (Galán and Singer, 2011). The structure of Pal is similar to that of Sep except that a shorter *b* dimension incorporates only two linked pyroxene-like chains in the ribbon width, instead of three for Sep. This unique structural arrangement results in a large specific surface area (higher than 200 m^2/g) and good adsorption capacity for several organic compounds (Önal and Sarikaya, 2009; Galán and Singer, 2011).

Grafting of organo-alkoxides containing various groups, such as amine, mercapto or chlorine, among others, on different matrices has been recently reported by several authors, e.g., on silica (Linneen et al., 2014; Tiozzo et al., 2014), alumina (Afkhami et al., 2011; Saha and Sarkar, 2012), or zeolites (Bezerra et al., 2014), as well as layered (Tonlé et al., 2007; Önal and Sarikaya, 2009; Letaief et al., 2011; Wayde et al., 2011) or fibrous clay minerals (Letaief et al., 2011). The functionalizing molecules promote specific properties of the inorganic matrices providing or enhancing interesting properties to the grafted materials, making them potentially applicable in environmental remediation of various pollutants such as dyes, pesticides, heavy metals and drugs.

As indicated above, dyes are released into effluents from textile, leather, shoes polish, wood stain, paper, food and cosmetic industries, among others (Ozer et al., 2007; Demirbas et al., 2008; Anandkumar and Mandal, 2011). Metanil yellow, MY (monosodium salt of 3-(4-anilinophenylazo)benzenesulfonic acid, Fig. S1) is manufactured for textile industries and other purposes, and although it is non-permitted for coloration of food, it is extensively used in India and other countries (Nagaraja and Desirajut, 1993; El–Rehim et al., 2012). The environmental damage due to synthetic azo dyes is of increasing concern due to their serious health effects on animals and human beings. MY has carcinogenic effects due to the changes that can promote in the DNA synthesis (Nagaraja and Desirajut, 1993; Jain et al., 2003). Methylene blue, MB (3,7-bis(dimethylamino)-phenothiazin-5-ium chloride, Fig. S1), has practical application in the textile industry and has been used in a

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large number of studies as model of cationic dyes (Jain et al., 2003; Ozer et al., 2007; Demirbas et al., 2008; Anandkumar and Mandal, 2011).

Several methods for treatment of dye-containing wastewater have been developed recently, including adsorption on various matrices (Jain et al., 2003; Ozer et al., 2007; Demirbas et al., 2008; Anandkumar and Mandal, 2011), advanced oxidation processes (AOP) such as Fenton and photo-Fenton (Sahoo and Gupta, 2012; Barbosa et al., 2015) or electrochemical treatments (Gupta et al., 2007), among others. Removal and recovery of dyes from solutions by a simple and versatile adsorption method is certainly an emerging field of research, because adsorption is a clean operation and can completely remove the dyes even from dilute solutions (Ozer et al., 2007; Demirbas et al., 2008; Anandkumar and Mandal, 2011; Galán and Singer, 2011). The most commonly used adsorbent is activated carbon, due to its very high specific surface area and large amount of adsorption sites on the surface. However, commercially available activated carbons are very expensive. Alternatively, modification of natural clay minerals by organic groups can improve their adsorption capacity and make them suitable for the adsorption of various compounds. In fact, several issues related to the preparation and application of hybrid materials based on fibrous clay minerals have been addressed, as the use of long- or short-chain organic compounds containing different functional groups, thus tailoring the hydrophobicity, the affinity of the functional groups for different organic and inorganic pollutants, the mechanism of partitioning at the solid/solution interface, etc. (Frost and Mendelovici, 2006; Frost et al., 2010; Galán and Singer, 2011; Xue et al., 2011; Ruiz–Hitzky et al., 2013; Matusik and Wścisło, 2014).

The adsorption of cationic and anionic species on one single matrix has attracted a great interest in recent years, and hybrid compounds are good candidates for this purpose, as they show high versatility and usability, as well as increased performance by combining the properties of the matrix with the functionality of the organic compound. Taking into account the importance of environmental studies based in natural clay minerals, the adsorption of cationic and anionic dyes (methylene blue, MB, and metanil yellow, MY) on two fibrous clay minerals, sepiolite and palygorskite, organofunctionalized with the alkoxide 3-aminopropyltrietoxysilane (APTES), has been studied in the present work. Our main purpose was to verify and to understand the effect of chemical modification of these two fibrous natural clay minerals (palygorskite and sepiolite) with aminosilanes on their adsorption properties.

2. Experimental

2.1. Materials

The adsorbates MB (C.I.: 52015, chemical formula: $C_{16}H_{18}ClN_3S.xH_2O$, MW: 333.6 g/mol, maximum absorbance λ = 665 nm) and MY (C.I.: 13065, chemical formula: $C_{18}H_{14}N_3NaO_3S$, MW: 375.38 g/mol, maximum absorbance λ = 440 nm) were supplied by Sigma-Aldrich.

2.2. Purification of fibrous clay minerals

The fibrous clay minerals used in this work were palygorskite from Attapulgus, Georgia, USA (Clay Minerals Society), also known as attapulgite, and sepiolite from Vallecas, Madrid, Spain, commercially available as PANGEL, and kindly supplied by TOLSA, S.A. Both were purified according to the dispersion-decantation method (Bizaia et al., 2009), obtaining very pure clay minerals (Fig. 1). In the formulation of the samples, purified palygorskite and sepiolite are abbreviated as *Pal* and *Sep*, respectively.

2.3. Synthesis of the amino-hybrid clay minerals

The hybrid organic-inorganic materials were obtained by keeping a mass of 10.0 g of the precursor (Pal or Sep) in the presence of 50.0 cm^3 of (3-aminopropyl)triethoxysilane (APTES) for 48 h at 180 °C and under nitrogen atmosphere (without using any solvent, as APTES is a liquid). So, the clay mineral:APTES mass/volume ratio used was 1:5. The resulting materials were washed twice with toluene, then 5 times with ethanol and finally 5 times with water and oven-dried at 80 °C for 24 h; they were named as Pal-APTES and Sep-APTES, respectively.

2.4. Adsorption experiments

2.4.1. Kinetic studies

The adsorption kinetics was determined by analyzing the adsorptive uptake of the dyes from aqueous solutions at several time intervals. Volumes of 5.0 cm^3 of solutions of each dye with an initial concentration of 25 mg/dm^3 were poured in glass tubes and mixed with 0.05 g of each adsorbent, at room temperature, and with continuous magnetic stirring. At predetermined time intervals, between 0.1 and 60 min, the solid phase was separated by centrifugation at 3500 rpm. The dye concentration in the supernatant liquid was analyzed by UV–visible spectroscopy, using a Hewlett-Packard Model 8453 diode array spectrometer, determining the absorption at 665 nm for MB and 440 nm for MY, these being their respective maximum absorbance wavelengths. The amount of MB and MY adsorbed by the functionalized hybrid fibrous clay minerals was calculated by Eq. (1):

$$q_t = V \cdot (C_0 - C_t)/m \quad (1)$$

where q_t (mg/g) is the amount of dye adsorbed at time t (min), C_0 (mg/dm^3) is the initial concentration of the dye in the solution, C_t

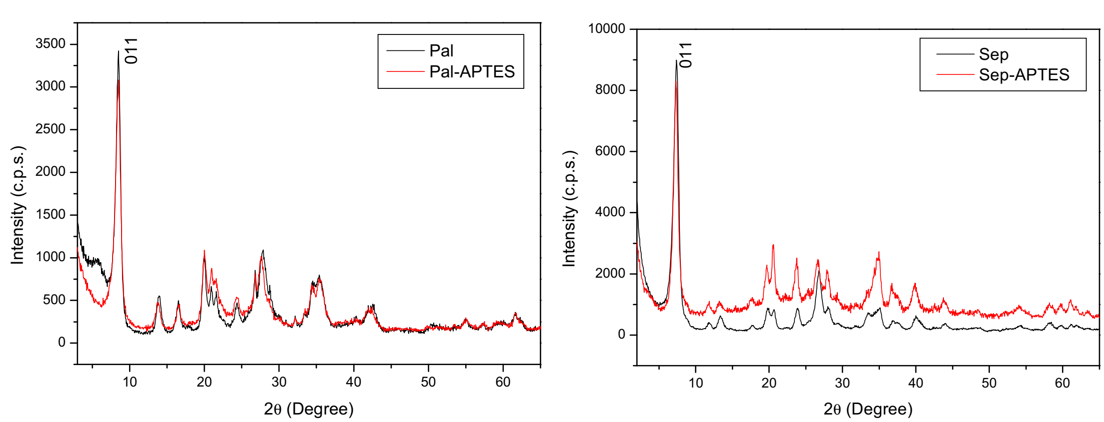

Fig. 1. X-ray powder diffraction patterns of parent clay minerals and of the APTES-functionalized solids.