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Research Paper

Removal of methyl violet from aqueous solution using a stevensite-rich clay from Morocco

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ABSTRACT

An inexpensive and easily available Moroccan natural clay, called locally Ghassoul, was employed for adsorption of methyl violet, a cationic dye, in aqueous solution. The experiments were carried out in a batch system to optimize various experimental parameters such as pH, initial dye concentration, contact time, temperature and ionic strength. The experimental data can be well represented by Langmuir and Freundlich models. The Langmuir monolayer adsorption capacity was estimated as 625 mg/g at 298. Kinetic analyses showed that the adsorption rates were more accurately represented by a pseudo second-order model. Intraparticle diffusion process was identified as the main mechanism controlling the rate of the dye sorption. In addition, various thermodynamic activation parameters, such as Gibbs free energy, enthalpy, entropy and the activation energy were calculated. The adsorption process was found to be a spontaneous and endothermic process. The obtained results confirmed the applicability of this clay as an efficient and economical adsorbent for cationic dyes from contaminated water.

1. Introduction

Industries such as textile, leather, paper, plastics, etc., use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater (Ravi et al., 2005). It is estimated that more than 100,000 commercially available dyes with over 7×10^5 tones of dyestuff produced annually (Pearce et al., 2003; Rafatullaha et al., 2010). Their presence in water, even at very low concentrations, is highly visible and undesirable and may significantly affect photosynthetic activity in aquatic life (Gücek et al., 2005). The synthetic origin and complex aromatic structures of dyes make them stable and difficult to be biodegraded (Forgacs et al., 2004).

Treatment processes for contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation/adsorption (Churcley, 1998; Coro and Laha, 2001; Ferrero, 2007; Kang et al., 2000; Stephenson and Sheldon, 1996). Of the numerous techniques mentioned, the adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater, offering significant advantages like the low cost, availability, profitability, ease of operation and efficiency, in comparison with conventional methods especially from economical and environmental points of view (Banat et al., 2003; Gupta and Suhas, 2009).

Many adsorbents have been tested to reduce dye concentrations from aqueous solutions. Currently, the most common procedure involves the use of activated carbons (Azizian et al., 2009; Rodríguez et al., 2009; Wu et al., 2005) as adsorbents because of their higher adsorption capacities. Despite the prolific use of activated carbon for wastewater treatment, carbon adsorption remains an expensive process, and this fact has recently prompted growing research interest into the production of low-cost alternatives. Various workers have exploited substances such as fly ash (Janos et al., 2003; Suna et al., 2010), activated carbon prepared from agricultural waste material (Baccar et al., 2010; El-Sheikh and Newman, 2004; Hameed, 2008; Yunus, 2006), perlite (Dogan et al., 2004; Dogan and Alkan, 2003), sepiolite (Alkan et al., 2005; Ugurlu, 2009), kaolinite (Karaoğlu et al., 2010), bentonite (Tahir and Rauf, 2006), chitosan (Kamari et al., 2009), as potential adsorbents for dye containing waters.

In this work, we attempt to investigate the potential of an abundant Moroccan clay, called locally Ghassoul, as an adsorbent of a cationic dye from aqueous solutions. This mineral clay (also known as Rassoul or Ghasoul) comes from the only deposit in the world, located at the East side of the Middle Atlas Mountains, in the Moulouya valley, approximately 200 km away from Fes (Benhammou et al., 2009). For several centuries, Ghassoul clay has been used in natural cosmetic products (soap, shampoo, skin conditioner). Currently, it is marketed for its detergent and grease-removing properties.

The geochemical characterization and the origin of the Ghassoul clay formation were studied by Chahi et al. (1997, 1999). The mineralogical composition of Ghassoul clay shows that the raw Ghassoul clay consists

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mainly of a Mg-rich trioctahedral smectite, stevensite, together with quartz and dolomite (Benhammou et al., 2009). A strong correlation was established between the adsorption of ionic dyes onto stevensite from Jbel Rhassoul clay and the nature of surface charge (Bouna et al., 2010). At pH 2–12, stevensite particles are formed of negatively charged layers responsible via Coulombic attractions of the strong retention of cationic dyes (Bouna et al., 2010).

This Moroccan clay has been the subject of several recent studies in order to develop new industrial applications. Bejjaoui et al. (2010) were interested in the development of cordierite ceramics by mixing andalusite and Ghassoul clay. Benhammou et al. (2005a,b, 2007) studied the adsorption of heavy metals in aqueous solution on raw and on organic- and inorganic-modified Ghassoul. El Ass et al. (2010) studied the adsorption of Basic dye in aqueous solution on raw Ghassoul. Elmchaouri and Mahboub (2005) studied the synthesis and characterization of Al-pillared stevensite.

In the present study, we aimed to evaluate the potentiality of this Moroccan clay for the removal of a cationic dye (methyl violet) from aqueous solutions. Therefore, batch experiments were performed. The effects of contact time, initial dye concentration, ionic strength, solution pH, and temperature were investigated. Equilibrium and kinetic analysis were conducted to determine the factors controlling the rate of adsorption and to find out the possibility of using this material as low-cost adsorbent for dye removal.

2. Materials and methods

2.1. Adsorbents and dye solution

Ghassoul clay was treated before using in the experiments as follows: a distilled water suspension of the clay was dispersed for approximately 4 h and then cleaned several times with de-ionized water. The fine fraction was collected by repeated dispersion, sedimentation and siphoning techniques (El Ass et al., 2010). The solid sample was dried at 105 °C for 24 h, ground then sieved by 140 μm sieve.

Methyl violet was dried at 70–80 °C for 5 h to remove moisture and then was dissolved in distilled water. Methyl violet solution was allowed to stand for 1–2 days until the absorbance of the solutions remained unchanged (Dogan and Alkan, 2003). The structure of this dye is shown in Fig. 1 (Hameed, 2008).

2.2. Adsorption measurements

Adsorption studies were performed by the batch technique to obtain rate and equilibrium data. All adsorption experiments were performed at temperature 25 °C and dye solution pH 7.5, except those in which the effects of temperature and pH were investigated. An adsorbent dose of 1 g/L was kept constant for all of the adsorption experiments.

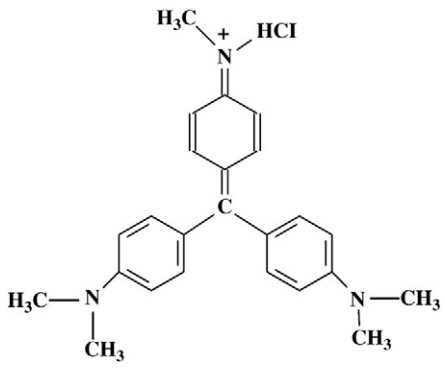

Fig. 1. The structure of methyl violet.

Adsorption experiments were carried out by shaking 50 mg Ghassoul sample with 50 ml aqueous solutions of methyl violet of desired concentrations at various pH and ionic strength. The preliminary experiment revealed that about 100 min was required for the adsorption process to reach equilibrium. Therefore, a contact period of 120 min was finally selected for all of the equilibrium tests. The solution and solid phase were separated by centrifugation at 4000 rpm for 15 min. A 10-ml aliquot of the supernatant was removed and analyzed for methyl violet by a Shimadzu 160 UV–visible spectrophotometer at the wave length of 585 nm. The adsorption capacity of dyes was then calculated using the relation:

$$q_e = \frac{C_o - C_e}{m} \cdot V$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium time, respectively. V (L) is the volume of the solution, and m (g) is the mass of adsorbent used.

For kinetic studies, 0.5 g of Ghassoul clay was added into 0.5 L of methyl violet solution with different initial concentrations (200–1000 mg/L). The dye adsorption amounts were determined by analyzing the solution at appropriate time intervals. The effect of temperature on the adsorption kinetic was carried out by performing the adsorption experiments at various temperatures (25, 45, and 55 °C).

Blanks containing no methyl violet were used for each series of experiments. Each experimental point was an average of three independent adsorption tests.

3. Results and discussions

3.1. Characterization of Ghassoul clay

The sample clay used in this study comes from a tertiary formation of Jbel Ghassoul located at the East of the middle Atlas, in Morocco. Mineralogical identification was performed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer (Cu Kα radiation, λ = 1.5418 Å). The XRD pattern of raw Ghassoul clay (Fig. 2a) showed that the dominant phase is the stevensite with the presence of quartz and dolomite. The XRD pattern of the fine fraction (Fig. 2b) show (i) an increase in the abundance of stevensite, indicating that the clay fraction of the Ghassoul clay consists mainly by phyllosilicates (ii) significant decrease in the abundance of quartz and disappearance of dolomite. The chemical composition of the raw Ghassoul clay and its fine mineral fraction are presented in Table 1. These results show that the fine fractions are principally made up of SiO_2 (58.16 wt.%) and MgO (27.44 wt.%). Al_2O_3 is notably concentrated in the fine clay mineral fraction (4.48 wt.%). The large amount of CaO (12.13 wt.%) measured in the raw clay may be ascribed partly to the dolomite recognized in XRD patterns, but particularly to gypsum. Indeed, gypsum has been reported to be present in the Rhassoul clay deposit by several authors (Benhammou, 2005). The surface area of fine mineral fraction, measured by the N_2-BET method, is 137 m^2/g. This high value, compared with other clays, reveals the existence of a high porosity responsible for the strong capacity of this material to fix some cations (Benhammou et al., 2005a). the pH of zero point charge, $pH_{ZPC} = 2.0$ the same result was found by Benhammou (2005a,b) and Bouna et al. (2010). The cation exchange capacity is 79 meq/100 g, relatively large, compared to the value for natural stevensite (41 meq/l00 g), reported by Takahashi et al. (1997).

3.2. Adsorption studies

3.2.1. Effect of solution pH

pH is one of the most important factors which control the adsorption capacity of dye on clay surfaces. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent