Journal of Hazardous Materials B129 (2006) 244–252

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Adsorption of Acid Blue 193 from aqueous solutions onto DEDMA-sepiolite

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Received 25 May 2005; received in revised form 24 August 2005; accepted 27 August 2005
Available online 3 October 2005

Abstract

The adsorption of Acid Blue 193 (AB193) onto dodecylethyldimethylammonium (DEDMA)-sepiolite was investigated in aqueous solution in a batch system with respect to contact time, pH and temperature. The surface modification of DEDMA-sepiolite was examined by the FT-IR technique. The pseudo-first-order, pseudo-second-order kinetic models and the intraparticle diffusion model were used to describe the kinetic data and the rate constants were evaluated. The experimental data fitted very well with the pseudo-second-order kinetic model and also followed the simple external diffusion model up to initial 10 min and then by intraparticle diffusion model up to 75 min, whereas diffusion is not only the rate-controlling step. The adsorption capacities of natural sepiolite and DEDMA-sepiolite at pH 1.5 and 20 °C were (1.19 and 2.57) × 10^{-4} mol g^{-1}, respectively. The above results indicate that DEDMA-sepiolite has around two times higher adsorption capacity than natural sepiolite. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined. The Freundlich model agrees with experimental data well. The activation energy, change of Gibbs free energy, enthalpy and entropy of adsorption were also evaluated for the adsorption of AB193 onto DEDMA-sepiolite.

Keywords: Sepiolite; Adsorption; Acid dye; Surfactant; Kinetics; DEDMA-sepiolite

1. Introduction

The world-wide high level of production and use of dyes generates a large amount of colored wastewater, which gives cause for environmental concern [1]. Since a very small amount of dye in water is highly visible and may be toxic to aquatic creatures. Some toxic dyes for instance, benzidine or arlyamine based dyes are well known for their carcinogenity. Hence, the removal of color synthetic organic dyestuff from waste effluents becomes environmentally important. It is rather difficult to treat this kind of pollutants due to their synthetic origins and their mainly aromatic structure, which are biologically non-degradable. Among several chemical and physical methods such as coagulation, ultrafiltration, ozonation, oxidation, sedimentation, reverse osmosis, flotation, precipitation, adsorption process, adsorption is one of the effective techniques that have been successfully applied for color removal from wastewater due to its low maintenance costs, high efficiency and ease of operation [2–5].

Activated carbon is the most popular adsorbent for the adsorption process since it has a high surface area and thus it has a high adsorption capacity but due to difficulty and expensive of regeneration and the need of an alternative low-cost easily available adsorbent has encouraged the search for new adsorbent [6]. In this manner, natural clays for dye removal from wastewater such as sepiolite [7–10], kaolinite [11], montmorillonite [12], smectite [13] and bentonite [14,15] are being considered as alternative low-cost adsorbents. Such natural clays can be modified in a manner that significantly improves their capability to remove hydrophobic contaminants from solution. Hence, these adsorbents in this situation become organophilic since the organic functional groups of the quaternary ammonium cations are not strongly hydrated by water. These kinds of adsorbents are termed organoclays since the exchangeable inorganic cations (e.g. H^+, Na^+, Ca^{2+}) are replaced by organic cations such as quaternary ammonium compounds by ion-exchange reaction [16,17]. Hence, organoclays are powerful

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0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2005.08.037

adsorbents for a wide variety of environmental applications [18].

Most literature on dye removal is related to cationic dyes. To our knowledge, only little information exists on the use of organoclays, as an adsorbent especially sepiolite for dye removal and the data available about the removal of acid dyes onto sepiolite also needs to research [10] and the adsorption of Acid Blue 193 (AB193) onto dodecylethyldimethyl ammonium (DEDMA)-sepiolite has not been found in the literature.

Sepiolite is a fibrous hydrated magnesium silicate and a natural clay mineral with a unit cell formula $(Si_{12})(Mg_8)(O_{30})(OH)_4(OH)_2\cdot 8H_2O$ and a general structure formed by an alternation of blocks and tunnels that grow up in the fibre direction. Each block consists of two tetrahedral silica sheets enclosing a central magnesia sheet but the silica sheets are discontinued and inversion of the silica sheets that give rise to structural tunnels. These characteristics of sepiolite make it a powerful adsorbent for organic dye molecules. In addition, some isomorphic substitutions in the tetrahedral sheets of the lattice of sepiolite, such as Al^{3+} instead of Si^{4+} form negatively adsorption sites. Such sites are occupied by exchangeable cations that compensate for the electrical charge [8,19].

The characteristics of the adsorption behavior are generally inferred in terms of both adsorption kinetics and equilibrium isotherms. The adsorption isotherms are also an important tool to understand the adsorption mechanism for the theoretical evaluation and interpretation of thermodynamic parameters [20,21].

In this study, the removal of Acid Blue 193 (AB193) from aqueous solutions using the low-cost material sepiolite as the adsorbent by batch adsorption techniques has been investigated. The common Langmuir and Freundlich equations were used to fit the equilibrium isotherm. The dynamic behavior of the adsorption was examined on the effect of initial dye concentration, temperature and pH. The adsorption rates were determined quantitatively and stimulated by the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models and were also tested for validity. The thermodynamic parameters also deduced from the adsorption measurements in the present study are very useful in elucidating the nature of adsorption.

2. Materials and methods

2.1. Materials

A commercial textile dye AB193 (Isolan Dark Blue 2-SGL; CI 15707) was obtained from Dystar, Turkey and used without further purification. The chemical structure of AB193 is illustrated in Fig. 1. Sepiolite was provided from Eskisehir, Turkey. It was crushed, ground, sieved through a 63 μm sieve, and dried at 110 °C in an oven for 2 h prior to use. The cation exchange capacity (CEC) and surface area determined by the methylene blue method [22] were 299.4 mmol kg^{-1} and 234.3 m^2 g^{-1}, respectively.

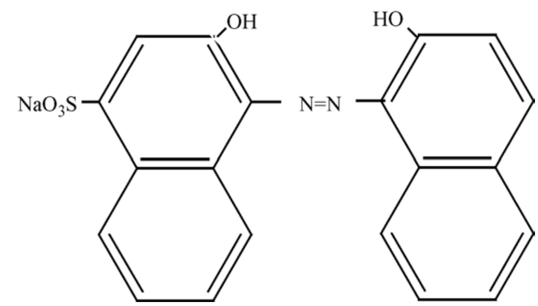

Fig. 1. Chemical structure of AB193.

2.2. Material characterization

The chemical analysis of sepiolite was determined by using an energy dispersive X-ray spectrometer (EDX-LINK ISIS 300) attached to a scanning electron microscope (SEM-Cam Scan S4). The crystalline phases present in the sepiolite were determined by using X-ray diffractometer (XRD-Rigaku Rint 2000) with Cu Kα radiation.

FT-IR spectra for sepiolite and DEDMA-sepiolite were recorded (KBr) on a Jasco FT-IR-300E Model Fourier transform infrared spectrometer to confirm the surface modification.

2.3. Preparation of DEDMA-sepiolite

The Na^+-exchanged form of clay was prepared by stirring samples for 24 h with 1 M NaCl. This was followed by several washings with deionized water and filtered to remove the excess NaCl and other exchangeable cations from the clay. The clay was then resuspended and filtered until a negative chloride test was obtained with 0.1 M $AgNO_3$.

A 20 g of the Na-saturated clay was dispensed in 0.5 dm^3 of distilled water. Dodecylethyldimethylammonium (DEDMA) bromide was used as a surfactant. DEDMA-sepiolite was prepared by adding quantities of the respective bromide salts equal to twice the cation exchange capacity of the sepiolite and stirring for 24 h. The clay was then washed with deionized water until free of salts and a negative bromide test had been obtained with 0.1 M $AgNO_3$ and it was grounded, sieved through a 63 μm sieve, and dried at 110 °C in an oven for 2 h and was used for the adsorption studies [23].

2.4. Adsorption experiments

The pH experiments were carried out by 50 ml of a 3.5×10^{-4} M dye solution with 0.05 g of natural sepiolite and DEDMA-sepiolite and the pH was carefully adjusted between 1 and 9 with adding a small amount of dilute HCl or NaOH solution using a pH meter (Fisher Accumet AB15). The dye solutions were stirred using a mechanical magnetic stirrer in a 100 ml erlenmeyer sealed flash with parafilm to avoid evaporation. The optimum pH was then determined as 1.5 and used throughout all adsorption experiments, which were conducted at various time intervals and temperatures (20, 30, 40 and 50 °C) to determine when adsorption equilibrium was reached and the maximum