Available online at www.sciencedirect.com

SCIENCE DIRECT®

Colloids and Surfaces A: Physicochem. Eng. Aspects 277 (2006) 90–97

COLLOIDS AND SURFACES A

www.elsevier.com/locate/colsurfa

Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite

Adnan Özcan*, E. Mine Öncü, A. Safa Özcan

Department of Chemistry, Faculty of Science, Anadolu University, 26470 Eskişehir, Turkey

Received 26 July 2005; received in revised form 29 October 2005; accepted 5 November 2005
Available online 15 December 2005

Abstract

In the present study, natural sepiolite was used as an adsorbent for the investigation of the adsorption kinetics, isotherms and thermodynamic parameters of an acid dye (Acid Blue 193, AB193) from aqueous solution at various pHs, temperatures and concentrations. Two simplified kinetic models, first-order and pseudo-second-order, were used to predict the adsorption rate constants. It was found that the kinetics of the adsorption of AB193 onto natural sepiolite at different operating conditions was the best described by the pseudo-second-order model. The rate parameters of the intraparticle diffusion model for adsorption were also evaluated and compared to identify the adsorption mechanisms. Adsorption isotherms and equilibrium adsorption capacities were determined by the fittings of the experimental data to three well-known isotherm models including Langmuir, Freundlich and Dubinin-Radushkevich (D-R). The results showed that the D-R model appears to fit the adsorption better than other adsorption models for the adsorption of AB193 onto natural sepiolite. The equilibrium constants were used to calculate thermodynamic parameters, such as the change of free energy, enthalpy and entropy.

Keywords: Sepiolite; Adsorption; Acid dye; Kinetics; Isotherm

1. Introduction

Synthetic dyes are being gradually used in the textile, paper, cosmetics, pharmaceutical and food industries. The removal of color from textile effluents, which are toxic, to pollute water and to cause severe damage human beings, is a major problem because of the difficulty in treating such wastewaters by conventional waste treatment methods, such as coagulation, chemical oxidation, membrane filtration, solvent extraction, chemical precipitation, osmosis, etc. These methods have not been very successful since dyes are stable to light, oxidizing agents, high capital cost and operational costs or secondary sludge disposal problem and aerobic digestion. Adsorption has been proved to be an excellent way to treat textile waste effluents, offering significant advantages like the cheapest, easy availability, most profitable, easy of operation and most efficient, over may conventional methods especially from an economical and environmental point of view [1–4].

Activated carbon is widely used as an adsorbent due to its high surface area, high adsorption capacity, but it is relatively high price, which limits their usage [5]. For this reason, many researchers have investigated low-cost, locally available, biodegradable substitutes made from natural sources to remove dyes from wastewater [3,6–10]. Clays, such as sepiolite [11,12], zeolite [13], montmorillonite [14], smectite [15] and bentonite [5,16,17] are being considered as alternative low-cost adsorbents.

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. However, the silica sheets are discontinued and inversion of these silica sheets gives rise to tunnels in the structure. These characteristics of sepiolite make it a powerful

* Corresponding author. Tel.: +90 222 3350580x5815; fax: +90 222 3204910.
E-mail addresses: aozcan@anadolu.edu.tr (A. Özcan), emoncu@anadolu.edu.tr (E.M. Öncü), asozcan@anadolu.edu.tr (A.S. Özcan).

0927-7757/$ – see front matter
doi:10.1016/j.colsurfa.2005.11.017

adsorbent for organic dye molecules. In addition, some isomorphic substitutions in the tetrahedral sheets of the lattice of the 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 [18,19].

Several studies were achieved using natural sepiolite as an adsorbent including catalyst support, wastewater treatment, solid wastes, reducing the toxic effect of some heavy metals and pesticides [20]. Most literature on dye removal is related to cationic dyes. To our knowledge, compared with cationic dyes, only little information exists on the use of natural sepiolite, as an adsorbent for the removal of anionic dyes and also needs to research. The water-soluble anionic dyes are commonly used to dye fabrics like wool, nylon and silk. Due to the weak interactions between the negatively charged surface in clays and anionic dyes, a few studies on the adsorption of acid dyes have been carried out using sepiolite as an adsorbent [11,12,21], but none of them has investigated the kinetics, isotherms and thermodynamics of adsorption of Acid Blue 193 (AB193) onto natural sepiolite.

The study of adsorption equilibrium, isotherms and kinetics is essential in supplying the basic information required for the design and operation of adsorption equipments for wastewater treatment. Various models have been put forward to describe or predict the adsorption kinetics. The resistance models, such as the first-order, pseudo-second-order and intraparticle diffusion models and the adsorption isotherms including Langmuir, Freundlich and Dubinin-Radushkevich (D-R) provide a detailed description of the adsorption.

The objective of this work is to study the adsorption of Acid Blue 193 (AB193) from aqueous solutions onto natural sepiolite. The effects of temperature, pH, contact time and concentration were examined and the kinetic and the thermodynamic data were also evaluated.

2. Materials and methods

2.1. Materials

A commercial textile dye AB193 (Isolan Dark Blue 2-SGL; C.I. 15707) was obtained from Dystar, Turkey and used without further purification. The chemical structure of AB193 is illustrated in Fig. 1. The adsorbent used in this work was provided from Dolsan, Eskişehir-Turkey. It was crushed, ground, sieved through a 63-μm size sieve and samples collected from under the sieve and dried in an oven at 110 °C for 2 h before use. Natural sepiolite was characterized with respect to its cation-exchange capacity (CEC) and surface area by the methylene blue method [22,23] and they were found as 299 mmol kg^{-1} and 234.3 $m^2\ g^{-1}$, respectively.

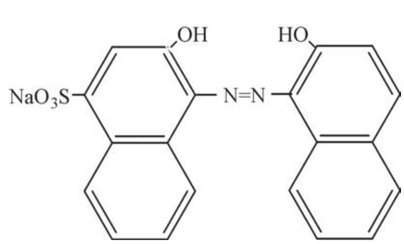

Fig. 1. The chemical structure of AB193.

2.2. Material characterization

The chemical analysis of natural sepiolite was conducted 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 sepiolite were determined via X-ray diffractometry (XRD-Rigaku Rint 2000) using Cu Kα radiation.

2.3. Adsorption experiments

All pH experiments were conducted by mixing 50 ml of a 3.5×10^{-4} mol dm^{-3} aqueous dye solution with 0.05 g of natural sepiolite at 25 °C and at various pH values in the ranges 1–11. The solution pH was carefully adjusted by adding a small amount of HCl or NaOH solution and measured using a pH meter (Fisher Accumet AB15), while the dye solutions contained in 100 ml erlenmeyer flasks closed with parafilm to avoid evaporation were stirred using a mechanical magnetic stirrer. Once the optimum pH had been attained, kinetic studies were conducted at this pH value for increasing periods of time, until no more dye was removed from the aqueous phase and equilibrium had been achieved. After such time (60 min), the samples were filtered to remove any organic or inorganic precipitates formed under acidic or basic conditions and the equilibrium concentrations ascertained by spectrophotometer (Shimadzu UV-2101PC) at the respective λ_{max} value, which is 609 nm for AB193. The amount of the dye adsorbed onto natural sepiolite was determined by the difference between the initial and remaining concentrations of dye solution.

In order to study the adsorption isotherms for 120 min to allow attainment of equilibrium at a constant temperature of 20 °C and kinetics for time intervals at various temperatures a 0.05 g of natural sepiolite were kept in contact with 50 ml of dye solution of various concentrations.

3. Results and discussion

3.1. Chemical composition of sepiolite

The chemical composition of natural sepiolite obtained by using EDX analysis given in Table 1 indicates the presence of silica and magnesium oxide as major constituents along with traces of aluminium, potassium, sodium, iron and titanium oxides in the form of impurities. XRD results combined with EDX analysis show that most of the magnesium is in the form of sepiolite and calcium and some of magnesium are in the form of dolomite. XRD also showed the presence of free quartz in natural sepiolite. It is thus expected that the adsorbate species will be removed mainly by SiO_2 and MgO.