Applied Clay Science 80–81 (2013) 46–51

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Removal of basic yellow cationic dye by an aqueous dispersion of Moroccan stevensite

Mohamed Ajbary [a], Alberto Santos [a], Victor Morales-Flórez [b,c,*], Luis Esquivias [b,c]

[a] Departamento de Ciencias de la Tierra, Universidad de Cádiz, Puerto Real, 11510 Cádiz Spain
[b] Instituto de Ciencia de Materiales de Sevilla, ICMS (CSIC-US), Av. Américo Vespucio 49, 41092 Seville, Spain
[c] Departamento de Física de la Materia Condensada, Universidad de Sevilla, Av. Reina Mercedes s/n, 41012 Seville, Spain

ARTICLE INFO

Article history:
Received 18 January 2012
Received in revised form 21 March 2013
Accepted 27 May 2013
Available online 22 June 2013

Keywords:
Adsorption kinetics
Basic yellow
Cationic dye
Stevensite
Wastewater

ABSTRACT

The aim of this study was to investigate the adsorption of basic yellow, a cationic dye, from aqueous solution by natural stevensite, with 104 m^2/g of specific surface area. The kinetics and the effects of several experimental parameters such as the pH of the solution, adsorbent dose and initial dye concentration were researched using a batch adsorption technique. The results showed that an alkaline pH favoured basic yellow adsorption and the adsorption reached equilibrium in about 20 min. It was concluded that the adsorption process was governed by the electrostatic interaction. The isothermal data were fitted by means of Langmuir and Freundlich equations, and a monolayer adsorption capacity of 454.54 mg/g was calculated. Finally, a good agreement was found between the pseudo-second order model and the experimental data. A high maximum adsorption capacity was obtained (526 mg/g) and a maximum surface density of ~9 dye molecules/nm^2 was estimated, involving a columnar arrangement of the adsorbed molecules.

1. Introduction

There are more than 100,000 commercially available dyes with over 7×10^5 t of dyes produced annually (Zollinger, 1987). It is estimated that 2% of them are discharged in effluent from manufacturing operations, while 10% are discharged from textile and associated industries (Easton, 1995). Even in small amounts, they are highly visible and have undesired effects to the environment. Furthermore, most dyestuffs are stable to light and oxidation (Mátivier-Pignon et al., 2003; Namasivayam et al., 2002; Orthman et al., 2003; Waranusantigul et al., 2003).

The removal of low levels of such compounds is difficult. Several treatment methods have been developed for decontamination purposes including coagulation, chemical oxidation, membrane separation, electrochemical processes, and adsorption techniques. The last one has been recognised as a cost-effective process to remove dyes from aqueous solution and it has been tested with many adsorbents; activated carbon has been the most commonly used adsorbent because of its high adsorption capacity. However, the operating cost of activated carbon adsorption is high (Leyva-Ramos, 1989; McKay, 1983; Pendleton and Wu, 2003; Singh et al., 2003; Tsai et al., 2001), though some strategies to reduce costs were also proposed (Kannan and Sundaram, 2001). Problems of regeneration and difficulty in separation from the wastewater after use are the two major concerns of using this material. Other commonly-used adsorbents are chitin (McKay et al., 1983), fly ash (Gupta et al., 1988), silica gels (Ahmed and Ram, 1992), peat (Allen, 1996; Ho and McKay, 1998), and more recently, heteropoly blue-intercalated layered double hydroxide (Bi et al., 2011). A wide compilation of the different considered strategies can be found in a review of Forgacs et al. (2004). However, the amount of adsorbed dye by these methods is not very high. To improve the efficiency of the adsorption processes, it is essential to develop more effective and cheaper adsorbents.

Clay minerals have a great potential to fix pollutants such as heavy metals, dye wastewater and organic compounds, and they are widely applied in many fields of science and technology, for example, for the removal of liquid impurities and the purification of gases with surfactant-modified montmorillonite as adsorbent agent (Juang et al., 2002), or the dyes and surfactants from tannery waste waters with natural and acid-activated bentonite and sepiolite (Espantaleón et al., 2003). Kaolin has also been considered for cationic dyes removal from aqueous solutions (Nandi et al., 2009). The porous structure of clay minerals can adsorb large amounts of colourant wastes and their use is justified by low cost, high specific surface area (SSA) and structural properties. Recent studies have been devoted to the mineralogical characterisation of stevensite from the Atlas Mountains of Morocco (called locally "Ghassoul" or "Rhassoul") and its possible applications in the water treatment field (Benhammou et al., 2005; Bouna et al., 2010; Elass et al., 2011; Elmchaouri and Mahboub, 2005). SSA of 150 m^2/g and 134 m^2/g, and adsorption capacities from 240 mg/g up to 600 mg/g were previously reported.

---

* Corresponding author at: Departamento de Física de la Materia Condensada, Universidad de Sevilla, Av. Reina Mercedes s/n, 41012 Seville, Spain. Tel.: +34 954550946.
E-mail address: vmorales@us.es (V. Morales-Flórez).

0169-1317/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.clay.2013.05.011

The objective of this work was to examine the effectiveness of this abundant stevensite material in the removal of basic dyes. Basic yellow (BY) (Wu et al., 2011) was selected as the modelled basic dye for this work. It is a dyestuff with $C_{15}H_{19}N_3O_4S$ as its molecular formula (M.W.: 337.4 g/mol), and its chemical name is 1-methyl-4-((methylphenylhydrazono) methyl) pyridinium methylsulphate.

2. Experimental

2.1. Sampling

The clay mineral was extracted from the Ghassoul mountains (Millot, 1954) and was considered as stevensite, or magnesian smectite (Benhammou et al., 2009; Caillère et al., 1982). The raw clay sample was crushed, ground, sieved through a 200 μm sieve, and dried at 110 °C in an oven for 2 h before use. Its chemical composition was determined by X-ray fluorescence (Philips PW 1666) spectroscopy. X-ray diffraction (XRD) experiments were performed using a Bruker diffractometer (D8 Advance) with a graphite monochromator and Cu Kα radiation. The intensities were measured in a 2θ range (3°–60°) with a step of 0.02° and a counting time of 5 s per step. Physisorption experiments were performed in a Micromeritics device model ASAP2010 at a constant temperature of 77.35 K. Samples were degasified at 150 °C under vacuum for 2 h prior to the experiment. The SSA and the pore size distribution were determined by the Brunauer–Emmett–Teller (BET) method and the Barret–Joyner–Hallenda (BJH) method, respectively.

2.2. Adsorption tests

Adsorption tests were carried out in a discontinuous reactor at room temperature, using a volume $V = 50$ ml of distilled water, containing the adsorbent material and the dye. The effect of the adsorbent dosage (m/V, where m is the adsorbent mass), the initial pH and the initial concentration of the dye on adsorption (C_0) were studied separately. The mixture was constantly stirred for a period of time fixed by kinetic tests and then filtered (0.45 μm cellulose nitrate filters, Sartorius).

The equilibrium concentration (C_e) was determined using a UV–visible spectrophotometer (JENWAY UV/VIS spectrophotometer model 6505) at the maximum absorbance wavelength ($\lambda_{max} = 412$ nm). The amount of metal adsorbed per unit mass of adsorbent, or adsorption capacity, was calculated as:

$$q_e = (C_0 - C_e) \times \frac{V}{m}. \tag{1}$$

The pH of the solution was adjusted by adding 0.1 M HNO_3 or 0.1 M NaOH solution as required. Blank tests (without dye) were done for each series of experiments as a reference. All experiments were performed twice.

3. Results and discussion

The chemical composition of the analysed stevensite-rich sample is summarized in Table 1. These results confirm the magnesium silicate nature of this mineral, with a maximum Mg/Si molar ratio of 0.83. Very low concentrations of Fe or Ca were also detected and Na was not detected in this analysis. The X-ray diffraction pattern showed that Mg-rich trioctahedral smectite, stevensite-15A, was the dominant phase, and minor proportions included reflections of quartz-α and dolomite (Fig. 1). Moreover, the presence of reflections corresponding to other minerals from the smectite group (montmorillonite, PDF files 00-011-0303 and 00-012-0219) was detected.

The analysis of the microstructure by nitrogen physisorption reveals the existence of channel-like pores (Kruk and Jaroniec, 2001).

Table 1
Chemical composition of clay.

Elements	Percentage present (mass %)
SiO_2	57.94
Al_2O_3	1.47
Fe_2O_3	0.43
MgO	32.46
CaO	0.34
Loss of ignition	7.36

The calculated SSA $S_{BET} = 104$ m^2/g, is roughly lower than those previously reported (Benhammou et al., 2005; Bouna et al., 2010; Elass et al., 2011), but almost an order of magnitude higher than other considered adsorbents as kaolin, for example (Nandi et al., 2009). The BJH analysis yielded a well defined typical pore size of 3.9 nm.

3.1. Effect of adsorbent dose (m/V)

In Fig. 2a, the amount of BY removed for a constant dye concentration $C_0 = 1$ g/l and different adsorbent doses is shown. It can be seen that this amount increased up to total adsorption. Obviously, the presence of more adsorption sites with higher adsorbent dosage allows the increase of the amount of removed dye. But raising adsorbent dose above 2 g/l, the increment of dye removal was very low until all the dye was removed (e.g. 99.96% of removal for adsorbent dose = 3 g/l).

3.2. Effect of initial pH

The pH is the most important factor affecting the adsorption process. To study the influence of pH on the adsorption capacity of stevensite, experiments were performed with the initial pH varying from 2 to 11, for $C_0 = 1$ g/l and adsorbent dose = 1.0 g/l. The results of the pH effect on the adsorption of BY onto stevensite are shown in Fig. 2b. It can be seen that the BY dye removal increased from 2 to 7 and then the removal remained almost the same at pH > 7. Two possible mechanisms of BY adsorption by the stevensite may be considered: electrostatic interactions between the surface groups of stevensite and the cationic dye, and a chemical reaction between the adsorbate and the adsorbent. At pH > 7, a significantly high electrostatic attraction existed between the negatively charged surface of the adsorbent and the cationic dye. As long as the pH of the system decreased, the number of positively charged sites increased, and the number of negatively charged sites decreased. Negatively charged sites on the adsorbent surface favoured the adsorption of cationic dye due to this interaction. On the other hand, the lower adsorption of BY at pH < 7 was due to the presence of excess H^+ competing

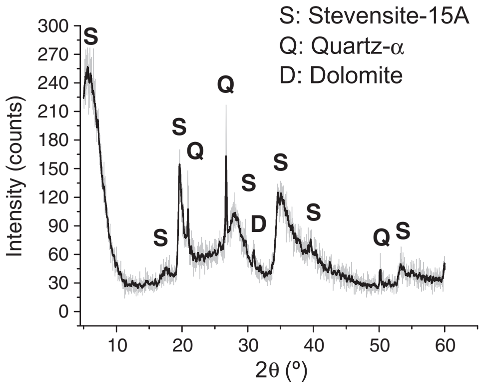

Fig. 1. X-ray diffraction pattern of natural stevensite. Black line was obtained by smoothing original data (grey line). S: stevensite-15A (PDF: 00-025-1498); Q: quartz-α (PDF: 01-089-8936); D: dolomite (PDF: 01-083-1530).