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Research paper

Adsorption of methylene blue from aqueous solution by kaolin and zeolite

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ABSTRACT

In the present study, kaolin and zeolite have been utilized as adsorbents for the removal of a cationic dye, methylene blue (MB), from aqueous solution within a batch process. Characterization of the two adsorbents was carried out by nitrogen adsorption–desorption experiments (specific surface area measurements by the BET method). The effects of various parameters such as initial MB concentration, contact time, adsorbent concentration, stirring speed, solution pH and salt concentration were examined and optimal experimental conditions were determined. The kinetic data were analyzed using pseudo-first-order and pseudo-second-order models. The mass transfer model in terms of interlayer diffusion was applied to the experimental data to examine the mechanisms of the rate controlling step. In order to determine the best-fit-isotherm, the experimental data were analyzed by the Freundlich, Temkin, and Dubinin–Radushkevich equation which are found to best represent the equilibrium data for kaolin and zeolite. The values of activation parameters such as free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were also determined. The results indicate that kaolin and zeolite could be interesting alternative materials with respect to more costly adsorbents used for dye removal.

1. Introduction

Many industries generate dye-bearing effluents during their production processes. Textile industries, in particular, are major consumers of water and release appreciable amounts of dyes in their effluents (Mohantry et al., 2006). The contamination of waste water with such dyes causes many important problems such as increasing the toxicity and chemical oxygen demand of the effluent, which has a detrimental effect on photochemical phenomena (Yasemin and Haluk, 2006). All of these dyes are synthetic and are composed by complex aromatic structures. Most of them can be carcinogenic and mutagenic, while they appear inert and non-biodegradable when discharged into waste streams (Ozer et al., 2007). Among them, MB is a cationic dye; whose risk related to its presence in waste water mainly arises from its harmful effect upon exposure to eyes, as well as possibility of nausea, vomiting and diarrhea (El-Sharkaway et al., 2007).

Research for control/removal of harmful dyes is being carried out by using different treatment technologies, e.g. chemical coagulation–flocculation (Pollock, 1973), different type of oxidation processes (Eilbeck and Mattock, 1985), biological process (Ledakowicz et al., 2001), membrane-based separation processes (Purkait et al., 2006), and adsorption (Purkait et al., 2007). Each of the above processes has their own benefits and limitations. Adsorption techniques have proven successful in removing colored organic species with activated carbon being the most widely used adsorbent due to its high capacity for the adsorption of organic materials (Chen et al., 2001; Markovska et al., 2001). However, due to its high cost and the difficulty of regeneration, cheaper, more effective adsorbents such as zeolite (Hana et al., 2009), clays like kaolin (Li et al., 2010) and bentonite (Almeida et al., 2009) are being considered as alternative low-cost adsorbents.

Adsorption of organic molecules to an adsorbent depends on various factors like temperature, pH of the solution, the structure and concentration of the adsorbing molecule, the ionic strength of the dispersion, and the structure of the adsorbent. However, adsorption over a surface with highly ionic character is mostly effective and very fast for a dye with opposite ionic character. Kaolin and zeolite are two examples of the very common low costs natural mineral adsorbent with ionic crystalline structure. Kaolin is one of the well-known low cost natural clays, available worldwide in rocks as crystalline structure. The use of kaolin as adsorbent may be very much economical. Many studies are carried out with different zeolites, due to its properties and characteristics (Melo et al., 2012; Peric et al., 2004; Wang and Zhu, 2006). The structure of zeolites consists of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedral. The aluminum ion (Al) is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (Na^+, K^+, or Ca^{2+}). These cations are exchangeable with certain cations in solutions (Barer, 1987).

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Within this context, the aims of the present work are to examine the applicability of two adsorbents, kaolin and zeolite, for the adsorption of MB dye from aqueous solution and to investigate the kinetics and mechanism of the adsorption process. The adsorption efficiency of MB was studied by optimizing experimental variables.

2. Materials and methods

2.1. Adsorbate and adsorbent

Methylene blue (3,7-bis (Dimethylamino)-phenazathionium chloride tetramethylthionine chloride) is a cationic dye with molecular mass of 373.9 g/mol, and the wavelength of 665 nm which corresponds to maximum adsorbance. The MB used in this work was the analytical grade one (Merck, Germany).

The adsorbents used in this study are, kaolin (Society of Tamazert — El Milia (Jijel-Algeria)) and zeolite (ECC International). The X-ray diffractograms (not presented) show that kaolin contains the largest amount of kaolinite (63%), muscovite (20%), quartz (11%) and a small amount of potassium feldspar (4%). The XRD pattern of the zeolite indicated the pure crystalline phase of zeolite 4A.

2.2. Characterisation of the adsorbent

The surface physical proprieties of the adsorbents were characterized with Micrometrics model ASAP-2000, using N_2 as the adsorbate at 77 K. Prior to measurement, the samples were degassed at 393 K for 2 h. The specific surface area was calculated by the BET equation; the total pore volume (V_t) was estimated from nitrogen adsorption at a relative pressure of 0.98. The micropore volumes (V_{mic}) and micropore specific surface (S_{mic}) of samples were evaluated by the t-plot method. The external area (S_{ext}) was the deduction of S_{mic} from S_{BET} and the external volume (V_{ext}) was the deduction of V_{mic} from V_t. Based on the assumption of cylindrical pores, the average pore size (D_p) was estimated by the following equation:

$$D_p(\mathrm{nm}) = \frac{4 \times V_t}{S_{BET}} \times 1000. \quad (1)$$

The point of zero charge (PZC) of samples (kaolin and zeolite) used for the adsorption experiment was determined by the so-called pH drift method (Lopez-Raman et al., 1999). The pH of a deoxygenized dispersion (N_2 bubbling during 1 h) of the adsorbent (0.15 mg) in a NaCl aqueous solution (50 ml at 0.01 mol·L^{-1}) was adjusted to successive initial values between 2 and 12. The dispersions were stirred 48 h under N_2 and the final pH was measured and plotted versus the initial pH. The pH_{PZC} is determined at the value for which $pH_{final} = pH_{initial}$. pH of the solutions is maintained by using 0.1 N HCl and 0.1 N NaOH solutions.

2.3. Adsorption experiments

Adsorption experiments were carried out at ambient temperature in batch mode using a 2 L beaker. A stock solution of dye of concentration 500 mg/L was prepared by dissolving 0.5 g of solid dye in 1 L of deionized water (pH = 6.9). A standard method was followed to determine the dye concentration by using a UV–vis spectrophotometer. Initial dye concentrations of 4, 18, and 37 mg/L were used. For the study of how various parameters described next affect to the adsorption properties, an initial dye concentration of 7.5 mg/L was chosen. Effect of pH on dye removal was studied at different pH values between 2.0 and 12.0. To observe the effect of adsorbent content on dye adsorption, different amounts of adsorbents (varying from 0.1–3.0 g/L) were used. Effect of salt concentration was examined by using concentrations between 5.0 and 30.0 g/L of sodium chloride added to the dye solution. Agitation speeds of 200 to 800 rpm were used for analyzing the effect of turbulence on the dye adsorption. To calculate the activation parameters, experiments were carried out at three different temperatures (291 K, 313 K and 323 K). Unless otherwise specified, an adsorbent content of 1 g/L, stirring speed of 800 rpm and pH = 7 were maintained for these experiments. During the adsorption, the change of pH of the solution was almost negligible. All the samples were centrifuged at 7000 rpm for 5 min and analyzed by UV–vis spectrophotometry to determine residual dye concentration.

The amount of dye adsorbed per mass unit of adsorbent at time t, q_t (mg/g) and dye removal efficiency, R, were calculated as

$$q_t = \frac{(C_0 - C_t)}{M} V \quad (2)$$

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

where C_0 is the initial dye concentration (mg/L), C_t is the concentration of dye at time t, V is the volume of solution (in L) and M is the mass of adsorbent (in g). To determine the adsorption isotherms, 0.05 g of adsorbent was dispersed in 50 mL dye solution of different concentrations for 3 h (to confirm that equilibrium had been reached) with constant shaking at 291 K. After 3 h, the solution attained equilibrium and the amount of dye adsorbed (mg/g) on the surface of the adsorbent were determined.

3. Results and discussion

3.1. Characterization of adsorbents

The physical composition such as the specific surface area, micropore volume and pore size is most relevant to evaluate the capacity of adsorption by kaolin and zeolite. From Table 1, it could be seen that the BET surface area, micropore surface area and micropore volume of the zeolite were all lower than those of the kaolin. The zeolite is known as a microporous material, but the BET surface area (S_{BET} = 25 m^2/g) reported in Table 1 indicated that this zeolite is mainly macroporous and has a relatively small internal surface. Similar data was reported by Chutia et al. (2009) and Leyva-Ramos et al. (2008). It indicated that the specific surface area and pore size of adsorbents depend on the methods and conditions of production process.

3.2. Adsorption studies

3.2.1. Effect of contact time and initial dye concentration

The effect of initial dye concentration and contact time on the removal rate of MB on kaolin and zeolite is shown in Fig. 1. It may be observed from the figure that most of the dye adsorption takes place within the contact time of 5 min and becomes more gradual and almost reached equilibrium within 40 min. The rapid adsorption at the initial contact time is due to the availability of the negatively charged surface of adsorbent which led to fast electrostatic adsorption of the cationic MB from the solution at pH = 6.51. An increase of the initial dye concentration leads to an increase in the global adsorption capacity. This, as the initial dye concentration increases from 4 to 37 mg/L, the adsorption capacity of dye onto adsorbent changes from 3.3 to 30 mg/g of kaolin and 3.4 to 33.5 mg/g of zeolite.

Table 1
Textural properties obtained by N_2 adsorption/desorption studies.

Typical parameters	Kaolin	Zeolite
S_{BET} (m^2/g)	61.13	24.59
S_{ext} (m^2/g)	55.03	21.55
S_{mic} (m^2/g)	6.10	3.04
V_t (cm^3/g)	0.118	0.098
V_{mic} (cm^3/g)	0.003	0.0014
D_p (nm)	7.72	15.89