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Research paper

Removal of Methylene Blue from aqueous solutions by adsorption on Kaolin: Kinetic and equilibrium studies

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ABSTRACT

Removal of Methylene Blue (MB) from aqueous solutions is studied using a raw Algerian kaolin sample as a low-cost adsorbent. The effects of pH, contact time, dye concentration and temperature are all taken into consideration. The adsorption kinetics results are adjusted to best fit the pseudo-second order model. The experimental data are analyzed by Langmuir isotherms, revealing that the maximum adsorption capacity of MB on this kaolin sample equals 52.76 mg/g at T = 25 °C and pH = 6.0. The calculated thermodynamic data demonstrates that adsorption is spontaneous and enhanced at higher temperatures. Desorption studies with water indicate that the adsorbent could successfully retain MB, even after four cycles. From these results, it can be considered that the raw Algerian kaolin sample tested herein is effective in the removal of MB from aqueous solutions and moreover may be used as an alternative to high-cost commercial adsorbents.

1. Introduction

The textile industry is the major source of dyes and generates colored wastewater that is capable of causing severe water pollution. According to Allègre et al. (Allègre et al., 2006), dyeing 1 kg of cotton with reactive dyes requires an average of 70–150 L water, 0.6 kg NaCl and 40 g reactive dye. > 80,000 metric tons of reactive dyes are produced and consumed each year, but up to 20%–30% of these applied dyes (approx. 2 g/L) is not fixed to the fabric and thus contributes to the coloration and toxicity of the effluent. Such wastewater is commonly associated with a high pH (10 − 11) and temperature (50°–70 °C). Colored dye effluents are generally considered to be toxic to the animal and plant life of a particular region and habitat (Walsh et al., 1980). Moreover, almost all dyes are poorly biodegradable or resistant to environmental conditions and, therefore, create major problems in the treatment of wastewater stemming from the dyeing industry (Hao et al., 2000). As a final consideration, dyes cannot be completely removed by means of conventional biological treatment processes, such as activated sludge and anaerobic digestion: due to their low biodegradability, nearly 90% of reactive dyes remain unchanged after undergoing an activated sludge process. Several physicochemical technologies, including coagulation/flocculation, membrane separation, ion exchange, chemical oxidation, electrochemical techniques, adsorption and photocatalysis, have been studied for the purpose of removing dye from wastewater (Marrot and Roche, 2002; Allègre et al., 2006; Holkar et al., 2016).

Compared with the methods cited above, the adsorption of dyes from aqueous solution has proven to be an excellent approach to treating effluents as well as a cost-effective technique. After the seminal paper by Crini in 2006 (Crini, 2006), several reviews have compiled works dedicated to removing exhausted dyes from effluent water using low-cost adsorbents, e.g. natural minerals or biological species, agricultural byproducts, wastes from various industrial processes (Mondal, 2008; Gupta and Suhas, 2009; Rodríguez et al., 2012; Yagub et al., 2014; Ngulube et al., 2017). Adsorption kinetics describes the decrease in aqueous adsorbate concentration from solution versus reaction time variation. During the adsorption process, four distinct steps are considered: i) transport of the aqueous adsorbate to the film surrounding the adsorbent particle surface (this first step can be neglected if the system has been perfectly stirred); ii) external diffusion; iii) intra-particle diffusion; and iv) physical or chemical surface reactions (Gadd, 2009).

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Clay minerals act as good adsorbents owing to their high cation exchange capacity and high specific surface areas relative to their small particle size; moreover, these minerals offer the advantage of being abundant and available at lower cost. Their surface reactions therefore produce strong biochemical and ecological effects on soils and water, hence justifying use of these materials in decontamination and remediation treatments (Quintelas et al., 2011; Sánchez-Jiménez et al., 2012). Kaolin is the most abundant mineral in soils and sediments; it interacts with other soil elements in contributing to the mechanical stability of the soil column (Chen et al., 2000). Kaolin has been widely used in: ceramics manufacturing (Bouzerara et al., 2009; Schroeder and Erickson, 2014), dye adsorption (Harris et al., 2001), pesticides (Sanchez-Martin et al., 2006), metal ions (Gupta and Bhattacharyya, 2012), and oil well drilling due to its rheological properties (Au and Leong, 2013).

Methylene Blue (MB), a cationic dye, was selected herein because of its widespread application in textile dyeing and by virtue of being present in the human and veterinary pharmacopoeia for a long time (DiSanto and Wagner, 1972; Oz et al., 2010). Another well-known use of MB adsorption pertains to the determination of surface properties in either (hydrated) clays or activated carbon materials (Hang and Brindley, 1970; Raposo et al., 2009). The removal of Methylene Blue, one of the most extensively applied textile dyes, from aqueous media has recently been reviewed by Kannan and Sundaram (Kannan and Sundaram, 2001) for activated carbon, and by Rafatullah et al. (Rafatullah et al., 2010) for various kinds of low-cost adsorbents.

This article will present the results obtained from experimental investigations performed on MB adsorption with a low-cost sorbent, i.e. natural raw (Algerian) kaolin, denoted here as KT3B. The effects of contact time, initial dye concentration, temperature, pH and adsorbent dosage on the static adsorption of the dye onto the KT3B kaolin sample will all be examined. The pseudo-first order and pseudo-second order models will be introduced to correlate the adsorption kinetics data of MB onto kaolin. Also, the equilibrium data will be analyzed using the Langmuir isotherm model and the adsorption thermodynamics will be evaluated. Moreover, the reuse of kaolin after MB desorption will be assessed in order to minimize the method's economic cost. This fundamental study will prove helpful for subsequent application in designing an adsorber for the treatment of dye-containing effluent discharged by the textile industry.

2. Materials and methods

2.1. Materials

The Tamazert kaolin deposit is located about 60 km north of the town of Jijel, in Eastern Algeria. A kaolin material originating from Tamazert, and industrially treated with sodium carbonate, was supplied by ENOF Ltd. (Algeria). The material was not ground because its grain size was already adequate for test purposes (i.e. ≤ 60 μm); it was only air dried, first at ambient temperature (25 °C) then at 110 °C in an oven. This raw kaolin sample will be denoted KT3B in the following discussion.

Methylene Blue (MB, or tetramethylthionine chloride, Fig. 1; CAS Number: 122965-43-9; Color Index number CI-52015), supplied by Panreac (Spain), was selected as an adsorbate and not purified prior to use. The MB molecular properties are: molar mass (319.85 g/mol), molar volume (241.9 cm^3/mol), width (14.3 Å), depth (6.1 Å), thickness (4 Å), and molecular diameter (0.8 nm), according to the evaluations conducted by Pelekani and Snoeyink (Pelekani and Snoeyink, 2000).

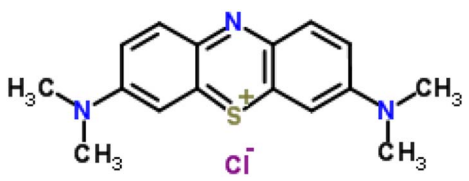

Fig. 1. The chemical structure of MB.

2.2. Characterization

The cation exchange capacity (CEC) of the KT3B sample was determined by relying on $BaCl_2$-triethanolamine (Primo-Yúfera and Carrasco Dorrién, 1981). The specific surface area (SSA) of the KT3B sample (previously outgassed at 200 °C for 8 h under 0.1 Torr vacuum) was determined by N_2 adsorption at 77 °K using a Micromeritics ASAP 2020 analyzer. The particle size distribution was measured with the MICRO-P laser granularity instrument (Malvern Instruments Ltd.).

An X-ray diffraction (XRD) analysis of the samples was carried out with a Powder X-ray Diffractometer (Bruker AXS) in the 2θ angle ranging from 2° to 65° incremented by a 0.025° step. A scanning electron microscopy (SEM) analysis of the samples was performed using a Philips SEM-505 scanning electron microscope, operated at 300 kV/SE and 50° inclination. We also made use of an Olympus BX50 polarizing microscope.

To estimate the pH of KT3B dispersion, the following procedure was adopted (Pansu and Gautheyrou, 2003): a 2:1 (v:w) water:KT3B dispersion was prepared and shaken for 24 h at 30 °C (Labwit ZWY-304); after 24 h, the dispersion was filtered through a Millipore 0.45 μm (Z227366 - Millex syringe filter units); and the pH of the filtrate was determined with a Jenway 3010 digital pHmeter. The FTIR spectra were obtained using a Spectrum GX spectrometer (Perkin-Elmer) at a 4 cm^{-1} resolution: undiluted KT3B samples in powder form were scanned and recorded between 4000 and 400 cm^{-1}.

Chemical components were obtained by dry chemical analysis. Real density (volumetric mass) was measured according to the pycnometric method. The loss on ignition (LOI) was determined by weighing the sample in a crucible both before and after overnight heating at 100 °C in a muffle furnace in order to remove water.

The point of zero charge (PZC) of the KT3B was determined (Noh and Schwarz, 1989) by applying a solid-to-liquid ratio of 1:1000. To carry this step out, 0.1 mg of KT3B was added to 100 mL of water at pH varying from 2 to 12 (adjusted with concentrated HNO_3 and NaOH) and then stirred for 24 h. Some of the physicochemical properties of the KT3B kaolin sample are presented in Table 1.

2.3. Analysis of Methylene Blue concentration

Methylene Blue ($C_{16}H_{18}ClN_3S{\cdot}2H_2O$, MB) was selected as the adsorbate species. The dye stock solutions were prepared by dissolving accurately weighted dye powder in Milli-Q water at a concentration of 1000 mg/L. The experimental solutions were derived by diluting the dye stock solutions in precise proportions to different initial concentrations. The pH of these solutions was adjusted to the desired value

Table 1
Composition of the raw kaolin sample KT3B.

Component	Content (mass%)
SiO_2	48.60
Al_2O_3	33.90
TiO_2	0.04
CaO	0.06
MgO	0.032
Fe_2O_3	0.90
Na_2O	0.08
K_2O	2.70
P_2O_5	0.14
MnO	0.35
LOI[a]	10.80

[a] Loss on ignition.