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Adsorption studies of aqueous basic dye solutions using sepiolite

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ABSTRACT

Sepiolite, low cost, locally available and natural mineral was studied as an adsorbent for the removal of Basic Astrazon yellow 7GL from aqueous solutions and batch contact tests. The kinetics of the adsorption process was tested for the pseudo-first order, pseudo-second order reaction and intra-particle diffusion models. The rate constants of adsorption for all these kinetic models were calculated. Good correlation coefficients were obtained for the pseudo-second order kinetic model. Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were applied to the experimental equilibrium data by changing temperature. The isotherm constants were determined by using the linear regression of these models. The monolayer coverage capacities of sepiolite for basic dye were found to be in the range of 62.5–88.5 mg/g at different temperatures. Thermodynamic studies showed that the reaction for dye uptake by sepiolite is endothermic in nature. Based on the optimum parameters sepiolite was also used as adsorbent for raw wastewater treatment and found as efficient as dye color removal.

1. Introduction

Colored dye wastewater occurs as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. Colored effluents and dyes can cause toxic problems in several type of receiving media and can have acute or chronic effects on exposed organisms [1,2]. This kind of effluent is resistant to biological degradation. Therefore removal of dyes from aqueous effluents is a significant environmental issue. Precipitation, ion exchange, solvent extraction and filtration are the conventional methods for the removal of dyes from aqueous solutions [3]. All these methods have significant disadvantages i.e. incomplete ion removal, high-energy requirements and production of toxic sludge or other waste products that require further disposal. Adsorption processes have gained considerable attention in recent years to remove hazardous materials from wastewaters. Adsorption is a useful and simple technique, which allows gathering of both kinetic and equilibrium data without needing any sophisticated instrument. Moreover eco-friendly natural materials, which are less expensive and available in local natural resources, can be used in these processes. These natural minerals also have high affinity toward toxic species.

Sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$) is a natural clay mineral with formula of magnesium hydro-silicate. The unique porous structure allows penetration of organic and inorganic ions into the structure of sepiolite. The adsorption capacity of sepiolite is restricted to the external surface, which can be enhanced, by chemical processes [4] and heat treatment [5]. The enhanced surface area of sepiolite is given in the range of 263–426 m^2/g [6–8]. Naturally occurring low cost sepiolite as an adsorber offers great potential for removing dyes from aqueous dye effluents. Several works related to wastewater treatment using sepiolite have been studied. The adsorption of Acid Red 57 (AR57) onto surfactant-modified sepiolite was investigated in a batch system with respect to contact time, pH and temperature [8]. The removal of anionic dyes using calcinated sepiolite has been investigated [9]. It was found that calcination at higher temperature caused a decrease in the amount of adsorbed dye. Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated sepiolite surfaces has been explored [10]. Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals including sepiolite was also investigated [11]. The removal of dyes and surfactants from tannery wastewaters using sepiolite has also been investigated [12]. The capacity of sepiolite was found to be much greater than that of conventional adsorbents to remove anionic dyes normally used in the tannery.

Sepiolite, an efficient natural adsorbent, which is received from local resources and low cost materials, for the removal of hazardous dyes from aqueous solutions needs to be further examined for using process parameters. Therefore the aim of this paper is chosen to investigate kinetic, equilibrium and thermodynamic parameters of sepiolite to remove basic dye from aqueous solutions. On the other hand preliminary treatment of industrial dye wastewater obtained from a tank containing a mixture of exhaust dyeing solutions at a textile factory in Turkey (Gebze) was also examined based on the optimum parameters.

2. Material and methods

2.1. Chemicals and characterization of sepiolite

All chemicals used were analytical grade and used without further treatment. Deionised water was used in all experiments. Basic Astrazon

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yellow 7GL, provided by DyStar was used without purification. The structure of the dye is presented in Fig. 1.

Concentrations of dye in aqueous solutions were determined spectrophotometrically in the visible range of the spectrum. A UV–vis spectrophotometer (Hach Lange, DR 2800) with a 1-cm path length was used throughout the experiments. Initially, the maximum wavelength at which the maximum absorbance of dye in aqueous solutions was determined by scanning the light absorption curve and found as $\lambda_{max}=417$ nm. A calibration curve for basic yellow was obtained using the calibration range from zero to 50 mg/L at this wavelength. A 500 mg/L stock solution was prepared and consecutively diluted to give a series of dye solutions of known concentrations. Total organic carbon (TOC) measurements for raw textile wastewater experiments were performed by Hach-Lange IL 550 TOC analyzer.

Sepiolite samples used in this work were obtained from Eskişehir, Turkey. The main characteristics of sepiolite were described previously [13]. All samples were grounded and washed with distilled water in order to remove the surface dust. Selected 40–80 mesh sized natural sepiolite was used throughout the experiments. As the adsorption being a surface phenomenon, the smaller particle sizes offered comparatively larger surface areas and hence higher dye removal at equilibrium, therefore the 40–80 mesh size fraction of sepiolite was selected because of its high removal capacity as well as easy handling.

2.2. Batch experiments

Adsorption studies were performed by batch experiments (Fig. 2). All batch-technique experiments were carried out in 100 mL glass flasks by mixing 0.1 g of sepiolite with 50 mL of dye solution in the conical flasks. The initial concentration of 50 mg/L was used for kinetic experiments. In order to evaluate kinetic data, separate flasks were prepared for each time interval and only one flask was taken for desired time. The solution and adsorbent were separated through the standard filter designed for a wide range of laboratory applications (MF-Millipore membrane filter, mixed cellulose ester, 0.45 μm). Final dye concentrations were then measured in the equilibrium solution.

Four sets of isotherm plot were obtained using three different temperature values (25–60 °C) to evaluate thermodynamic data. Each isotherm consisted of six dye concentrations varied from 25 mg/L to 500 mg/L.

The concentration of the adsorbed species on the adsorbent in the batch contact test (Fig. 2) was calculated using the following mass-balance equation;

$$m(q_e-q_0) = V(C_0-C_e) \tag{1}$$

q_0 and q_e are the initial and equilibrium amount of dye adsorbed per unit weight on the adsorbent (mg/g) where initially q_0 is equal to zero.
C_0 and C_e is the initial and equilibrium dye concentration in solution (mg/L),

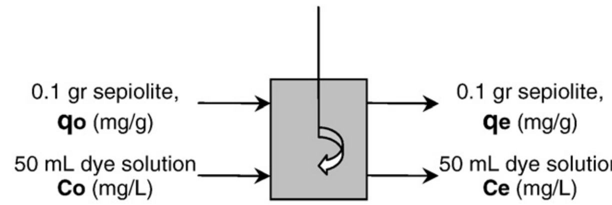

Fig. 2. A single-stage batch adsorption experimental set-up.

m is the mass of adsorbent used (g)
V is the volume of solution (L)

All these parameters, except, q_e which were calculated from mass-balance equation (Eq. (2)), were measured experimentally.

$$q_e = \frac{V}{m}(C_0-C_e) \tag{2}$$

2.2.1. Zeta potential measurements

In order to indicate the molecular interaction between dye and sepiolite, zeta potentials of related samples were measured at 22 ± 1 °C using a Zeta Meter 3.0. The unit converts the electrophoretic mobility of particles into zeta potential terms, itself automatically.

0.1 g of sepiolite was mixed with 50 mL of 50 mg/L dye solution in the conical flasks and agitated for 60,120 and 180 min at 225 rpm. Also a washed 0.1 g sepiolite was mixed with 50 mL deionized water in 100 mL glass flask and agitated for 24 h at 225 rpm. The suspensions were kept still for 5 min to settle and the measurements then were conducted. Each data point is an average of approximately 10 measurements. The results are given Table 1. As clearly seen from the table, adsorption is mainly due to counter ion effect between dye and sepiolite.

2.3. Adsorption kinetic models

The chemical kinetics describes reaction pathways until reaching the equilibrium whereas chemical equilibrium gives no information about pathways and reaction rates. Adsorption kinetics shows the dependence on the physical and/or chemical characteristics of the adsorbent material which also influence the adsorption mechanism [14]. In order to investigate the mechanism of adsorption, several different models have been used at different experimental conditions for adsorption processes.

2.3.1. Pseudo-first order model

This was the first equation for the sorption of liquid/solid system based on solid capacity [15,16]. In most cases, the pseudo-first order equation does not fit well for the whole range of contact time. This model may be represented;

$$\frac{dq_t}{dt} = k(q_e-q_t) \tag{3}$$

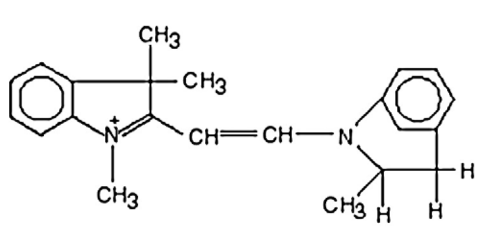

Fig. 1. Structure of dye ($C_{22}H_{25}ClN_2$, formula weight 229 g/mol).

Table 1
Zeta potential measurements.

Sample	Zeta potentials
Sepiolite + deionized water (24 h)	−36.2 mV
Sepiolite + 50 mg/L dye (60 min.)	−23.3 mV
Sepiolite + 50 mg/L dye (120 min.)	−19.9 mV
Sepiolite + 50 mg/L dye (180 min.)	−11.9 mV