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Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters

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ABSTRACT

This research involved the efficient adsorption of an anionic dye (Reactive Red 120) by natural untreated clay, a low-cost material abundant in highly weathered soils. The adsorption kinetics was investigated using the parameters such as contact time, stirring speed, initial dye concentration, initial pH, ionic strength, and solution temperature. According to these experiments the maximum removal is observed after 80 to 100 min. The results showed that acid pH is favorable for the adsorption of dye and physisorption on broken edges of clay particles seemed to play a major role in the adsorption process. It was found that the rate of adsorption decreases with increasing temperature and the process is exothermic. The adsorption kinetics followed the pseudo-second-order equation for the dye investigated in this work. Furthermore the thermodynamic activation parameters such as the enthalpy and entropy were determined. Compared to adsorption experiments on other clays, the results show that the Fouchana natural clay is an efficient adsorbent for Reactive Red 120 dye.

1. Introduction

There are more than 100 000 types of dyes commercially available, with over 7×10^5 tons of dyestuff produced annually, which can be classified according to their structure as anionic and cationic [1]. In aqueous solution, anionic dyes carry a net negative charge due to the presence of sulphonate ($SO^{-}{}_3$) groups, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulfur containing groups [2]. Due to their strong interaction with many surfaces of synthetic and natural fabrics, reactive dyes are used for dyeing wool, cotton, nylon, silk, and modified acrylics [3]. Discharging dyes into the hydrosphere can cause environmental damage as the dyes give water an undesirable color [4] and reduce sunlight penetration, with some dyes also being toxic/carcinogenic [5]. A considerable amount of research on wastewater treatment has focused on the elimination of reactive dyes, essentially for three reasons: firstly, reactive dyes represent 20–30% of the total dye market [6]; secondly, large fractions of reactive dyes (10–50%) are wasted during the dyeing process (up to 0.6–0.8 g dye/dm^3 can be detected in dyestuff effluent) [7]; thirdly, conventional wastewater treatment methods, which rely on adsorption and aerobic biodegradation, were found to be inefficient for complete elimination of many reactive dyes [1]. Furthermore, it is difficult to remove reactive dyes using chemical coagulation due to the dyes' high solubility in water [8]. Adsorption with activated carbon appears to be the best prospect for elimination of this dye. Despite its effectiveness, this adsorbent is expensive and difficult to regenerate after use. There is a need to produce relatively cheap adsorbents that can be applied to water pollution control. Therefore, many researches in recent years have focused on the use of various low-cost adsorbents to replace activated carbon [9]. A wide variety of low cost materials, such as clay minerals [10], bagasse fly ash [11], wood [10], maize cob [12] and peat [13] are being evaluated as viable substitutes for activated carbon to remove dyes from colored effluents.

Clays have a high adsorption capacity due to their lamellar structure which provides high specific surface areas [14] and possibility to adsorb ions and polar organic molecules on particle external site and in interlayer positions [15,16]. Adsorption and desorption of organic molecules in the clays are primarily controlled by surface properties of the clay and the chemical properties of the molecules [17]. Natural clay exhibits a negative charge of structure which allows it to adsorb positively charged dyes but induces a low adsorption capacity for anionic dyes. Thus literature mostly reports on cationic dye adsorption by clay and very few studies have been devoted to anionic dye adsorption onto natural clay ([18], [19], [20], [21]) or treated clay (see e.g., [22], [23]).

In a previous work [24], we investigated the adsorption of wastewater dyes from a Tunisian dyeing industry onto a natural

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untreated clay from the Fouchana region (Tunisia), and we showed Fouchana clay's great potential to treat these dye-rich industrial effluents. The aim of the present work was to focus on the adsorption of a specific anionic dye, Reactive Red 120 (RR 120) which is commonly used in the Tunisian textile industry, and to investigate the effect of parameters including contact time, stirring speed, initial dye concentration, initial solution pH, ionic strength, and solution temperatures on the dye adsorption capacity of Fouchana clay. Therefore adsorption kinetics and isotherm studies were undertaken to determine the adsorbate removal rate and the maximum adsorption capacity of the untreated clay. The thermodynamic activation parameters, such as enthalpy, entropy and the free energy, were also investigated and surface properties were determined to provide insights to the adsorption reactions and mechanisms.

2. Experimental

2.1. Materials

The reactive dye C.I. Reactive Red 120 used as adsorbates is a bifunctional dye (bis(monochloro-s-triazine)) incorporating azo-based chromogens which structure is shown in Fig. 1. The wavelength of maximum absorbance (max) for RR 120 is 535 nm. Reactive Red 120 has a molecular weight and solubility of 1470 g mol^{-1}. The clay used in this study as dye adsorbent was collected from the Fouchana region (North-East of Tunisia). The specific surface area (Ss) of Fouchana clay and its exchange capacity (CEC) were measured by the BET method and by the Metson method (AFNOR NF X 31–130 [25].) respectively (Table 1). Major elements compositions of the bulk and <2 μm sample fractions were obtained by ICP-AES analyses (Jobin Yvon JY 124) [26] (Table 1). Fouchana clay is a mixture of expanding clay (smectite and interlayered illite/smectite) and non expanding clay (kaolinite and illite), poor in non clay minerals (mainly quartz, calcite and gypsum).

2.2. Kinetic experiment

Adsorption kinetic experiments were carried out using mechanic stirrer by agitating 1 L solution (agitation speed, 19 C and natural pH = 6.3) of a constant dye concentration with 0.2 g of clay (<2 μm) at a constant stirring speed of 450 rpm. Samples of 5 mL were collected each 20 min and were then centrifuged for 20 min at 3000 rpm. The left out concentration in the supernatant solution was analyzed using a spectrograph (Jobin Yvon, TRIAX 320) by monitoring the absorbance changes at a wavelength of maximum absorbance (535 nm).

We investigated the effect of pH (3 to 9), salt concentration (0.1–1 mol L^{-1}), temperature (19 °C, 30 °C, 40 °C, 50 °C), dye concentration (5, 15, 25 mg L^{-1}), and stirring speed (225, 450, 750 rpm) on dye removal.

The amount of dye adsorbed per unit weight of Fouchana clay at time t, q_t (mg g^{-1}) was calculated as

$$q_t = (C_0 - C_t)\mathrm{V} / \mathrm{m} \quad (1)$$

where C_0 and C_t are the initial and liquid-phase concentrations of dye solution (mg L^{-1}) respectively at any time t; qt is the dye concentration on adsorbent at any time t (mg g^{-1}), V the volume of dye solution (L), and m (g) the mass of clay sample.

Table 1
Physical and chemical characteristics of Fouchana clay.

Parameter	Unit	Bulk sample	<2 μm
Specific surface	m^2 g^{-1}	–	80
CEC	Cmol kg^{-1}	22.3	34.3
Smectite and interstratified	%	22	60
Kaolinite	%	11	30
Illite	%	3	10
Non clay minerals	%	64	–
SiO_2	(w)	57.3	52.1
CaO	% (w)	4.54	1.01
Na_2O	% (w)	0.44	0.02
Al_2O_3	% (w)	15.4	22.7
MgO	% (w)	1.58	2.17
Fe_2O_3	% (w)	6.90	9.15
K_2O	% (w)	2.22	2.46
TiO_2	% (w)	0.81	0.916

3. Results and discussion

The adsorption of dye from aqueous phase onto a solid surface can be well described as a reversible reaction under an equilibrium condition established between the two phases [27]. The rate at which the species are removed from the solution onto an adsorbent surface is an important factor for designing treatment plants. Thus, in order to characterize the adsorption process of dye on clay, we have discussed the effect of parameters such as contact time, stirring speed, initial dye concentration, initial solution pH, ionic strength, and solution temperatures on the removal rate of dye onto clay from aqueous solution.

3.1. Effect of contact time and initial dye concentration

The removal of dye was rapid in the initial stages of contact time and gradually decreased with time until equilibrium (Fig. 2). The rapid adsorption observed during the first 10 min is probably due to the abundant availability of active sites on the clay surface, and with the gradual occupancy of these sites, the sorption becomes less efficient. It appears from Fig. 2 that the contact time needed to reach equilibrium conditions was 80 to 100 min. This is in accordance with the results obtained in dye adsorption experiments onto different types of adsorbents as for example kaolinite [28], powdered activated sludge [29] or aerobic granules [30]. From Fig. 2 it was clear that the removal of dye was dependent on the concentration of the dye. The adsorption capacity increased with increasing initial dye concentration and the process was faster at higher concentrations. The shapes of the curves are similar and approximately independent on the initial dye concentration (Fig. 2). This indicates a monolayer formation of the

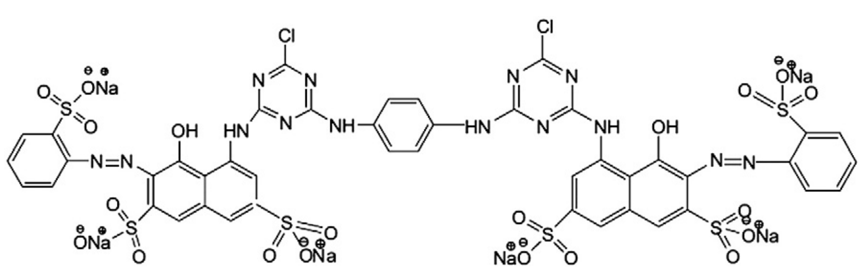

Fig. 1. Chemical structure of diazo C.I. Reactive Red (RR 120).