KINETIC STUDYING of REACTIVE DYE ADSORPTION by DIFFERENT ORGANOCLAYS

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ABSTRACT

Adsorption is one of the most effective methods used to remove reactive dyes from wastewater and, different adsorbents such as activated carbons, biosorbents and clay minerals can be used for the adsorption.In this study, the adsorption of Reactive Red 141 dye on montmorillonite based commercial organoclay compounds and the organoclay modified with hexadecyltrimethylammonium bromide was investigated and a high color removal was observed. The adsorption kinetics were modelled using pseudo first and second order kinetic models. The pseudo-second kinetic model was found the best fitted.

KeyWords: Montmorillonite,modified organoclay, reactive dye, kinetic modeling.

1. INTRODUCTION

Nowadays, the effect of global warming is increasing and researches to protect the water resources are becoming more important. As a result of many finishing processes applied in textile industry, which is among the most water used industries, wastewater containing high concentrations of dye is released. Reactive dyes which are commonly used in textile industry, are difficult to remove from wastewater since they are water-soluble. Different color removal techniques are used for removal of reactive dyes; adsorption is one of the most effective methods used to remove reactive dyes. Adsorption is defined as a process of collecting soluble substances on a suitable interface in a solution. In the adsorption process the substance, which is adsorbed the dye, is called the adsorbent. Effectiveness and the cost are the most important parameters, when deciding to use a special application; it should be ensured that the adsorbent is economical, effective, accessible and abundant. These factors directly affect the cost of adsorption [1]. The most preferred adsorbents in industrial treatment are activated carbons. They are derived from natural materials such as wood, coconut shell, lignite or coal, but can be produced from any carbonized material [2]. Although it is an effective adsorbent, the production of activated carbon is difficult. In addition, the costs are high [3] due to this reasonalternative and more economic adsorbent species are commonly investigated.Some agricultural wastes, biodegradable materials and inorganic compounds are more economical adsorbents than potentially activated carbon, and many are known to be effective in adsorption [2]. Some of the agricultural wastes used as adsorbents are barley bark [15], eucalyptus wastes [4], wheat straw and corncob [5,6]. In recent years, the adsorbents of biological origin have also been attracted because they are more economical. For example; chitin-chitosan [7, 8], sawdust wastes [9, 10], carbonized wool [11] and activated sludge [12] are used as adsorbents [2]. In addition, low-cost inorganic materials are used as an effective adsorbent for dye removal. Examples include peat [13], ash [14], calcium metasilicate [15], activated aluminum [16], clay and bauxite [17]. Zeolite is also one of the important inorganic adsorbents [2]. Clay minerals in a certain crystalline structure are natural, fine-grained soils. Clay minerals can be found in different species such as montmorillonite, sepiolite and kaolin according to their composition and molecular structure. Natural clay minerals are cheap,

environmentally friendly and they have high adsorption capacity especially when they are modified. Clay compounds that are hydrophilic in nature are modified to gain organophilic properties and they are used in the removal of organic substances through the adsorption. The organo-montmorillonite complex is formed by the introduction of organic compounds having a polar or ionic structure between the unit layers of montmorillonite. In this study, commercial clays and an organoclay synthesized in the laboratory were used for adsorption of Reactive Red 141. A high color removal was observed and the adsorption kinetics of the organoclayswere investigated by using several kinetic models.The results showed that the adsorption kinetics of allorganoclays were described by the pseudo-second kinetic model.

2. MATERIAL AND METHOD

2.1 Material

Materials used in the adsorption and their properties are given in Table 1.

Table 1. Properties of materials used in adsorption.

Material	Type of Material	Chemical Structure
Reactive Red 141 dye (RR 141)	Reactive dye	$C_52H_34Cl_2N_{14}O_{26}S_8$
HDTMAB-Montmorillonite	Organoclay synthesized in laboratory	Montmorillonite modified with hexadecyltrimethylammonium bromide
Cloisite 5	Commercial organoclay	Bis (hyrogenated tallow alkyl) dimethyl, salt with montmorillonite
Cloisite 20	Commercial organoclay	Bis (hyrogenated tallow alkyl) dimethyl, salt with montmorillonite
Cloisite 20A	Commercial organoclay	Di (hyrogenated tallow alkyl) dimethyl, salt with montmorillonite

The dye, C.I. Reactive Red 141, was obtained from DyStar. The commercial organoclays, Cloisite 5, Cloisite20 and Cloisite 20A, were supplied from BYK Company.

The crude clay which consists of montmorillonite was obtained fromTokatReşadiye region of Turkey.

Hexadecyltrimethylammonium bromide (HDTMAB) $[CH_3(CH_2)_{15}N(CH_3)_3Br]$ which is used as organic cation (quaternary ammonium) was purchased from Merck with 99% purity.

2.2 Method

2.2.1 Modification ofClay

First the impurities such as iron oxide and silica were removed from crude clay by a sedimentation method. Then the samples were dried in an oven at 60°C and pulverized to pass through a 530 µm sieve. The cation exchange capacity (CEC) of bentonite is 0.91 meq/g [18]. Clay-water dispersion and a solution containing HDTMB in amount equal to 100% of CEC of the clay were prepared according to the method given in the literature[19] and then they were mixed. The dispersion was subjected to microwave irradiation for 5 min at 360 W in a microwave oven. After that the modified clay was washed with distilled water and filtered to

remove the surfactants which do not react with clay. This step was carried out until the amount of HDTMAB observed in the filtrate was no longer considerable. The amount of surfactant in the filtrate was determined by the methyl orange method [20]. After the washing step, the sample was dried by a LabconcoFreeZone 2.5 model freeze-dryer at a temperature of -45°C and a pressure of 0.06 mbar for 8 h [21].

2.2.2 Adsorption Studies

Adsorption studies were carried out by shaking the dispersions containing 100 mg/l of Reactive Red 141and 1 g/l ofadsorbent, over a time interval of 0–24 h. At the end of the adsorption time, the supernatants of the solutions were separated by centrifugation. The residual dye concentration in the supernatant liquid was analyzed using a UV-Vis spectrophotometer (Perkin-Elmer Lambda 25) at 519 nm.

The adsorption capacity (mg/g), q_e, of the adsorbent was calculated by [21]:

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

whereC_0, initial dye concentration in liquid phase (mg/l); C_e, the equilibrium concentration (mg/l);V, total volume of dye solution used (L); m, mass of adsorbent used (g).

2.2.3 Adsorption Kinetics

In this study, two ofthe most frequently used kinetic models, pseudo-first-order and the pseudo-second-order kinetic models, were used.

The pseudo-first-order kinetic model is given by Equation 2:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

By taking q_t =0 at t = 0 and q_t=$q_t$at time t, the integrated form of Eq. 2 becomes

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_1 t \tag{3}$$

where$q_t$isthe amount of adsorbed dye at time t, and k_1 is the rate constant of first-order sorption.The parameters of the equation can be obtained from the linear plot of $ln(q_e-q_t)$ vs. t.

Another model for the analysis of sorption kinetics is the pseudo-second-order kinetic model. This model is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

wherek_2 is the pseudo-second-order rate constant of sorption. By taking q_t =0 at t = 0 and q_t=$q_t$at time t, the integrated form of Eq. 4 becomes

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

The plot of t/q versus t gives a straight line with a slope of $1/k_2 q_e^2$ and an intercept of $1/q_e$. [21].

3. RESULTS AND DISCUSSION

The changes in adsorbed amounts with time are given in Figure 1 for the different organoclay types. The time to reach the plateau is approximately 3-4 h. The values of the correlation coefficient imply that the adsorption of the reactive dye on the organoclay is described by a pseudo-second-order equation (Table 2).

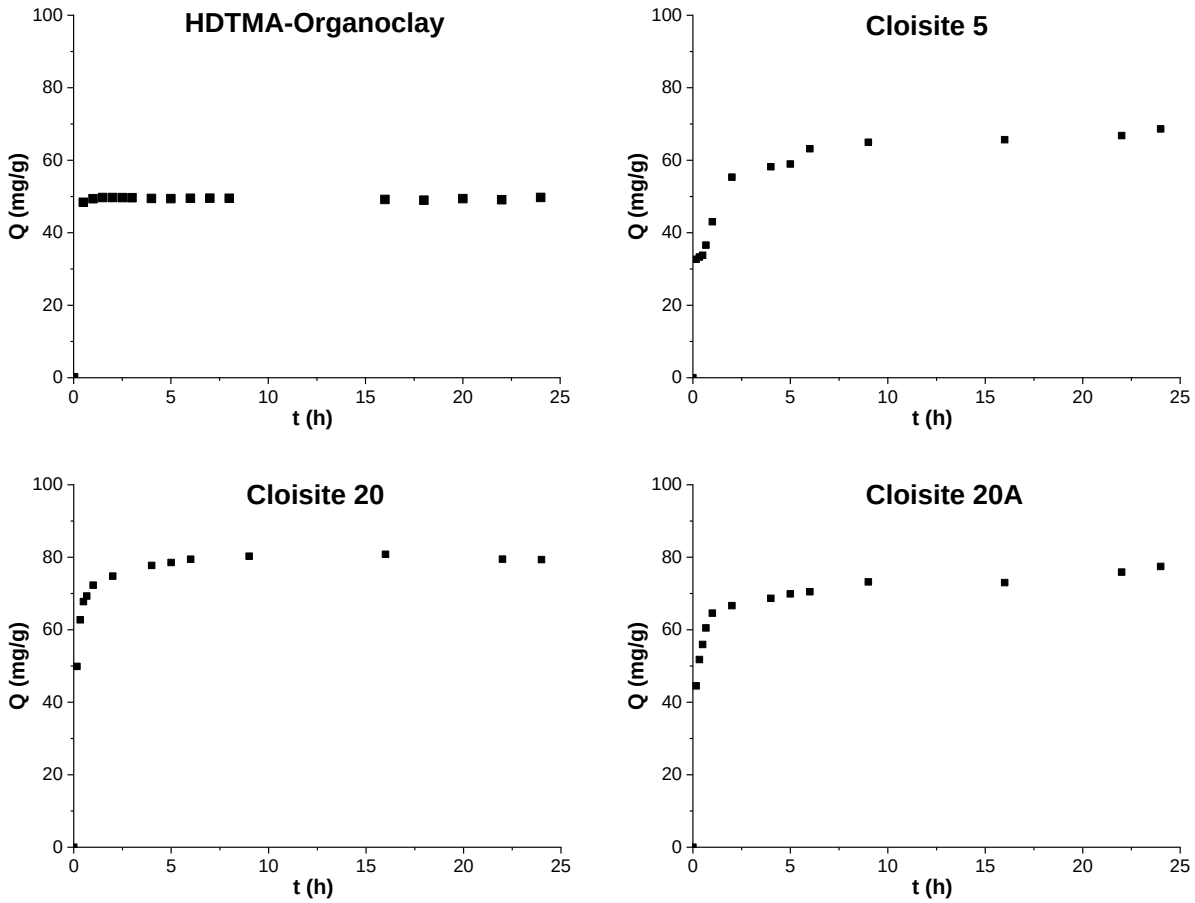

Figure 1. Amounts of the dye adsorbed versus contact time for HDTMAB-organoclay, Cloisite 5, Cloisite20 andCloisite 20A

Table 2. Parameters of the pseudo first and second order equations

Adsorbent type	Pseudo first order kinetic model			Pseudo second order kinetic model		
	q_e(mg.g^{-1})	k_1 (s^{-1})	R^2	q_e(mg.g^{-1})	k_2 (dm^3 mol^{-1} s^{-1})	R^2
HDTMAB-organoclay	54,35	6,34	0,039	49,26	0,0491	0,999
Cloisite 5	68,64	0,32	0,840	68,64	0,028	0,999
Cloisite 20	79,37	1,46	0,947	79,37	0,060	0,999
Cloisite 20A	77,46	0,26	0,842	77,46	0,060	0,999

4. CONCLUSION

In this study, kinetic behavior of different oganoclay types for adsorption of Reactive Red 141 were investigated.The results of kinetic modelling studies showed that adsorption kinetics of all organoclay types fitted to the pseudo second order kinetic model.It was observed that the commercial organoclayshave higher adsorption capacity than the organoclay modified with HDTMAB.

ACKNOWLEDGEMENT

The authors would like to gratefully acknowledge the financial support for this research received through Project no. 109M752 of The Scientific and Technical Research Council of Turkey (TUBITAK); through Project no. DPT-2007 K 120780 of the T.R. Prime Ministry State Planning Organization; and through Project no. 10MUH034 of Ege University's scientific research projects.

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