

## REMOVAL OF CATIONIC DYE (BASIC RED 18) FROM AQUEOUS SOLUTION USING NATURAL TURKISH CLAY

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### ABSTRACT

In this study, the removal of a cationic dye, basic red 18, used in the textile industry with montmorillonite was investigated as a function of initial dye concentration, agitation speed, ionic strength, adsorbent dosage, pH and temperature. Adsorption process was attained to the equilibrium within 30 minutes. The adsorption capacity of basic red 18 increased with increasing ionic strength, initial dye concentration, pH, agitation speed, and temperature, but decreased with increasing adsorbent dosage. The experimental data were analyzed by Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich isotherms, and it was found that the isotherm data were reasonably correlated by Freundlich isotherm. Pseudo-first order, pseudo-second order, Elovich kinetic equations and intraparticle diffusion model were used to examine the experimental data of different initial conditions. It was found that the pseudo-second order kinetic equation described the data of dye adsorption onto montmorillonite very well. Furthermore, for the removal of basic red 18, a semi-empirical model was established. Thermodynamic analysis was carried out for basic red 18 onto montmorillonite. It was found that the adsorption processes were endothermic in nature. The values of  $E_a$ ,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  at 293 K for basic red 18 adsorption on clay were calculated as 27.635 kJ mol<sup>-1</sup>, 25.041 kJ mol<sup>-1</sup>, -0.090 kJ mol<sup>-1</sup> K<sup>-1</sup> and 51.412 kJ mol<sup>-1</sup>, respectively. The results indicated that montmorillonite could be employed as an alternative to commercial adsorbents in wastewater treatment for the removal of color and dyes.

**KEYWORDS:** Activation energy; Adsorption isotherm; Basic red 18; Freundlich isotherm; Montmorillonite; Pseudo-second-order kinetic.

### 1. INTRODUCTION

Environmental pollution control has been a concerned issue in many countries. The environmental issues surrounding the presence of color in effluent is continuing problem for dyestuff manufactures, dyers, finishers and water companies, because increasingly stringent color consent standard are being enforced by regulatory bodies to reduce the quality of color in effluent and water courses. One of the powerful treatment processes for the removal of dyes from water is adsorption. Adsorption techniques have been proven successful in removing colored organics (Kuleyin and Aydin, 2011; Kumar *et al.*, 2011; Rafatullah *et al.*, 2010). Adsorption is the separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. It is the process that takes place when a liquid or most commonly a gas known as the adsorbate accumulates on the surface of a solid adsorbent and forming a molecular film (Jain and Jayaram, 2010; Kumar *et al.*, 2010).

Many adsorbents have been tested on the possibility to lower dye concentrations from aqueous solutions, such as activated carbon (Rodríguez *et al.*, 2009), gallinaceous feathers (Sousa *et al.*,

2012), peat (Allen *et al.*, 2004), chitin (Akkaya *et al.*, 2007; Filipkowska *et al.*, 2002), clay (Fil, 2007; Nandi *et al.*, 2009), rice hulls (El-Maghraby and El Deeb, 2011), sludge ash (Weng and Pan, 2006), desert sand (Varlikli *et al.*, 2009), water hyacinth roots (Saltabaş *et al.*, 2012), and rice husk ash (Mane *et al.*, 2007; Verma and Mishra, 2010). Activated carbon is the most popular adsorbent and has been used with great success (Ahmad *et al.*, 2007; El-Halwany, 2010; Kilic *et al.*, 2011; Nuithitikul *et al.*, 2010; Yavuz and Aydin, 2006) and it's have high capacity for the adsorption of organic species. However, activated carbon suffers from high cost production and regeneration. Therefore, other adsorbents such as clays with higher surface areas are alternatives. Recent investigations have focused on the use of clays such as kaolinite (Dogan *et al.*, 2009), montmorillonite (Elaziouti and Laouedj, 2011; Fil *et al.*, 2012), sepiolite (Özdemir *et al.*, 2006), diatomite (Al-Ghouti *et al.*, 2009), illite (Pentrák *et al.*, 2012), bentonite (Jiang *et al.*, 2008) and perlite (Doğan and Alkan, 2003) to remove dyes.

Clay is a soil particle smaller than 0.002 mm or 2  $\mu\text{m}$ , with high specific area which mainly influenced the soil colloidal properties as well as stability of soil structure. Besides, it has high stability in both wet and dry conditions and in soil texture class. While colloid is a particle, which may be a molecular aggregate, with a diameter of 0.1 to 0.001 $\mu\text{m}$ , clay and soil organic matter are often called as soil colloids because they have particle sizes that are within, or approach colloidal dimensions. Clay minerals which are clay-sized hydrous aluminum silicates have a large interlayer space that can hold significant amounts of water and other substances. They encompassed of large surface area that allow swelling and shrinking. Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming clay. Montmorillonite, a member of the smectite family, is 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately 1 micrometer. The particle thickness is extremely small (~1 nm). It is the main constituent of the volcanic ash weathering product, bentonite. Montmorillonite's water content is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminum magnesium silicate hydroxide  $(\text{Na, Ca})_{0.33}(\text{Al, Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})\cdot n\text{H}_2\text{O}$ . Potassium, iron, and other cations are common substitutes; the exact ratio of cations varies with source (Fil, 2007; Rafatullah *et al.*, 2010; Tsai *et al.*, 2007).

This study was calculated to investigate the adsorption capacity of locally available low-cost adsorbents montmorillonite from Balikesir of Turkey, for basic red 18 (BR 18) dye removal from aqueous solutions. Therefore, the dynamical behaviors of adsorption were measured on the effect of initial dye concentration, agitation speed, ionic strength, adsorbent dosage, pH and temperature. Experimental data were performed for isotherm models such as Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich. The adsorption rates were determined quantitatively and simulated by the Elovich, the pseudo-first-order and second-order models, and then adsorption mechanism was analyzed using intra-particle diffusion. Furthermore, thermodynamic activation parameters were also determined.

## 2. MATERIAL AND METHOD

Samples of montmorillonit were obtained from the Süd-Chemie (Balikesir, Turkey). Chemical composition and physical properties of montmorillonite were given in Table 1. Commercial quality cationic dye were obtained from Dyestar (Frankfurt, Germany) and used without any further purification. The structure of direct dye was given in Figure 1 (390.89  $\text{g mol}^{-1}$  molecular weight and molecular formula  $\text{C}_{19}\text{H}_{25}\text{ClN}_5\text{O}_2$ ). A stock solution of cationic dye was prepared in distilled water.

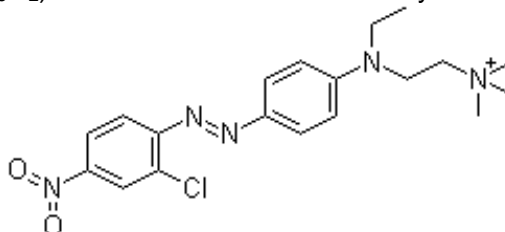


Figure 1. The structure of basic red 18

Table 1. Chemical composition of montmorillonite (a) and physicochemical properties of montmorillonite (b)

	Component	Weight (%)
(a)	SiO <sub>2</sub>	49.40
	Al <sub>2</sub> O <sub>3</sub>	19.70
	MgO	0.27
	CaO	1.50
	Fe <sub>2</sub> O <sub>3</sub>	0.30
	Na <sub>2</sub> O	1.50
	H <sub>2</sub> O	25.67
	Parameters	Value
(b)	Color	White
	Density (g cm <sup>-3</sup> )	2.3 – 3
	Transparency	Semi-transparent and opaque
	Brightness	Matt
	Surface Area (m <sup>2</sup> g <sup>-1</sup> )	95.36
	Reflective index	1 – 2

The influences of variables including initial dye concentration, agitation speed, ionic strength, adsorbent dosage, pH and temperature and on the adsorptive removal of Basic Red 18 (BR 18) were investigated in batch mode. In each experimental run, 100 ml of BR 18 solution of different concentrations between 25–750 mg L<sup>-1</sup> and varying amount montmorillonite were kept in a 250 ml erlenmeyer flask. A constant agitation speeds using an Edmund Bühler incubator from 100 rpm to 400 rpm and at different temperatures form 293 K to 333 K was maintained for all the adsorption experiment. Ionic strength of aqueous solutions was adjusted with NaCl at examining ion intensity experiments. The solution pH was adjusted by addition of dilute aqueous solutions of HCl (0.01M) or NaOH (0.01M) using a WTW multi 340i pH-meter. Samples were taken at different contact times to determine the time required to reach equilibrium. After centrifugation at 10000 rpm, the absorbance of the supernatant was measured at 484 nm (Ghazi *et al.*, 2003) using a Spekol-1100 UV-Vis spectrophotometer and then converted into concentration.

The adsorption equilibrium capacity of BR 18 was calculated using the following relationship:

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

where  $C_0$  (mg L<sup>-1</sup>) and  $C_t$  (mg L<sup>-1</sup>) is the dye concentration at initial and after equilibrium time respectively.  $V$  is the volume of the solution (L) and  $m$  is the mass (g) of montmorillonite.

The adsorption capacity of BR 18 was calculated for kinetic studies by the following equation:

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

where  $C_0$  (mg L<sup>-1</sup>) and  $C_t$  (mg L<sup>-1</sup>) is the dye concentration at initial and after time  $t$  respectively.  $V$  is the volume of the solution (L) and  $m$  is the mass (g) of montmorillonite.

### 3. RESULT AND DISCUSSION

#### 3.1. Adsorption isotherms

The equilibrium adsorption of dyestuffs can be mathematically expressed in terms of adsorption isotherms. The parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir, Freundlich, Elovich, Temkin and Dubinin–Radushkevich (D–R) isotherm equations were given in the Table 2 (Dubinin and Radushkevich, 1947; Elovich and Larionov, 1962; Freundlich, 1906; Langmuir, 1918; Temkin, 1941). Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

Table 2. Isotherm models equations (a) and kinetic models equations (b)

	Isotherm	Mathematical equations	Eq.	References
(a)	Langmuir	$q_e = (q_m K_L C_e) / (1 + K_L C_e)$	(3)	(Langmuir, 1918)
	Freundlich	$q_e = K_F C_e^{1/n}$	(4)	(Freundlich, 1906)
	Elovich	$q_e / q_m = K_E C_e \exp(-q_e / q_m)$	(5)	(Elovich and Larionov, 1962)
	Temkin	$q_e = (RT/b) \ln(K_T C_e)$	(6)	(Temkin, 1941)
	Dubinin-Radushkevich	$q_e = q_m \exp\left[-B\left(RT \ln(1 + 1/C_e)\right)^2\right]$	(7)	(Dubinin and Radushkevich, 1947)
	Kinetic model	Mathematical equations	Eq.	References
(b)	pseudo-first order rate model	$\ln(q_e - q_t) = \ln q_e - k_1 t$	(8)	(Ho and McKay, 1998)
	pseudo-second-order rate model	$t/q_t = [1/k_2 q_e^2] + (1/q_e)t$	(9)	(Ho <i>et al.</i> , 1996)
	Elovich model	$q_t = \beta \ln(\alpha\beta) + \beta \ln t$	(10)	(McKay <i>et al.</i> , 1999)
	Intra Particle model	$q_t = k_{dif} t^{1/2} + C$	(11)	(Furusawa and Smith, 1974)

Correlation coefficients and constants of the isotherm models were given in the Table 3. As could be seen from table and Fig. 2, experimental results with the best fit Freundlich isotherm (Iyim and Güçlü, 2009). The capacity of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximum capacity of adsorption. As could be seen from experimental results maximum adsorption capacity of BR 18 dye onto montmorillonite clay was calculated as 530.645 mg g<sup>-1</sup> at pH: 4.0, 293 K temperature, 300 rpm agitation speed, 0.5 g L<sup>-1</sup> adsorbent dosage and 0 mol L<sup>-1</sup> NaCl ionic strength (Fig. 2). Comparison of the adsorption capacity of cationic dyes onto adsorbents such as clay species was shown Table 4 (Guiza *et al.*, 2004; Iyim and Güçlü, 2009; Jiang *et al.*, 2008; Karim *et al.*, 2009; Karim *et al.*, 2010; Tahir and Rauf, 2006; Wang and Zhang, 2011).

Table 3. Isotherm constants for basic red 18 adsorption onto montmorillonite

Langmuir isotherm		Freundlich isotherm	
K <sub>L</sub>	0.0614	K <sub>F</sub>	79.8475
q <sub>m</sub>	529.6330	n	3.3965
R <sup>2</sup>	0.970	R <sup>2</sup>	0.995
Temkin isotherm		Elovich isotherm	
K <sub>T</sub>	4.5766	q <sub>m</sub>	93.6938
b	42.3344	K <sub>E</sub>	1.0552
R <sup>2</sup>	0.879	R <sup>2</sup>	0.861
Dubinin-Radushkevich isotherm			
q <sub>m</sub>	262.3415		
B	7.806.10 <sup>-08</sup>		
R <sup>2</sup>	0.572		

### 3.2. Adsorption Kinetics

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer; kinetic models are used to test experimental data from the adsorption of BR 18 onto montmorillonite clay. The kinetics of dyes adsorption onto montmorillonite is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes. Thus, the kinetics of BR 18 adsorption onto montmorillonite were analyzed using pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic models were given in Table 2 (Furusawa and Smith, 1974; Ho and McKay, 1998; Ho *et al.*, 1996; McKay *et al.*, 1999). The conformity between experimental

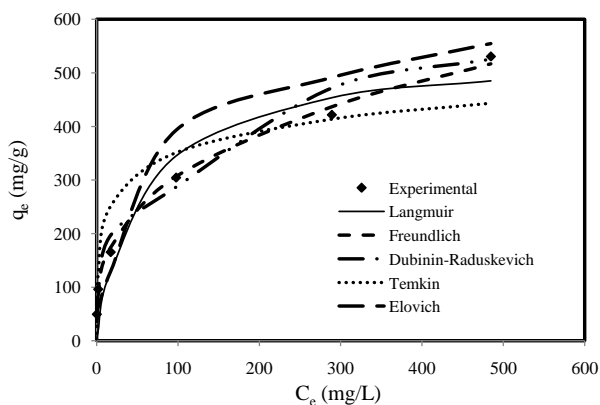


Figure 2. Comparison of isotherm models on dye adsorption on montmorillonite

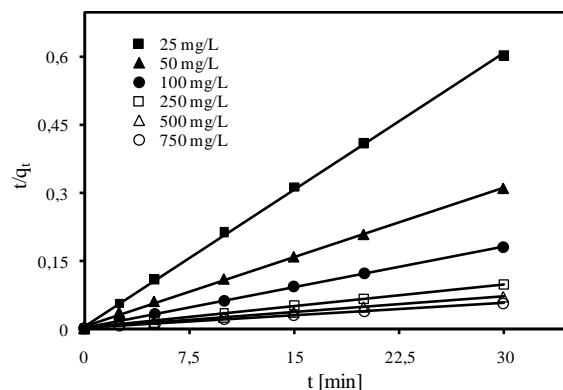


Figure 3. Pseudo-second-order kinetic models on dye adsorption on montmorillonite

Table 4. Comparison of the adsorption capacity of cationic dyes onto adsorbents such as clay

Adsorbent	Adsorbant	Maximum adsorption capacity ( $\text{mg g}^{-1}$ )	Ref.
Bentonite	Malachite Green	7.716	(Tahir and Rauf, 2006)
Na-Bentonite And Ca-Bentonite	Basic Violet 14	147.9 and 100	(Jiang <i>et al.</i> , 2008)
Crude And Purified Clay	Methylene Blue	50 and 68,5	(Karim <i>et al.</i> , 2010)
Natural Clay	Nile Blue And Brilliant Cresyl Blue	25 and 42	(Iyim and Güçlü, 2009)
Cu(II)-Loaded Montmorillonite	Crystal Violet	114.3	(Wang and Zhang, 2011)
Moroccan Clay	Basic Red 46	54	(Karim <i>et al.</i> , 2009)
Natural Clay	Neutral Red, Methyl Violet, Methyl Green And Methylene Blue,	567, 526, 427 and 300	(Guiza <i>et al.</i> , 2004)
Montmorillonite	Basic Red 18	530.645	In this study

data and the model-predicted values was expressed by the correlation coefficients ( $R^2$ , values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of dye adsorption onto clay. The linear plots of  $t/q_t$  versus  $t$  showed good agreement between experimental and calculated  $q_e$  values at all experimental conditions than other models (Table 5). The correlation coefficients for the second-order kinetic model were greater than 0.995 which led to believe that the pseudo-second-order kinetic model provided good correlation for the adsorption of BR 18 onto montmorillonite (Dogan *et al.*, 2007; Doğan *et al.*, 2006; Fil and Özmetin, 2012). The obtained results were shown for initial BR 18 concentrations in Figure 3.

Besides for adsorption on the outer surface of adsorbent, there is also a possibility of transport of adsorbate dye from the solution to the pores of the adsorbent due to vigorous agitation during the adsorption process. It is probably reasonable to assume that the rate is not limited by mass transfer of BR 18 from the aqueous solution liquid to the clay particle external surface. One might then base that the rate limiting step may be film or intra-particle diffusion. The most commonly used technique for identifying the mechanism involved in the adsorption process is by using intra-particle diffusion model (Wu *et al.*, 2009) was given by Table 2. The  $R^2$  values were given in Table 5 were close to unity indicating the application of this model. This may confirm that the rate-limiting step is the intraparticle diffusion process. The linearity of the plots demonstrated that intraparticle diffusion played a significant role in the uptake of the adsorbate by adsorbent.

### 3.3. Effect of initial adsorbate concentration on adsorption process

The influence of the initial concentration of basic red 18 (25-750 mg L<sup>-1</sup>) on the adsorption rate using montmorillonite was studied. The experiments were carried out at 0.5 g L<sup>-1</sup> adsorbent dose, at 300 rpm agitation speed, at 0 mol L<sup>-1</sup> NaCl concentration, at 293 K temperature and at pH: 4.0 for 30 min (Fig. 4). The percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of adsorbent increased with increase in dye concentration in the test solution for different concentrations (25-750 mg L<sup>-1</sup>) at the same time (min). The increase in adsorption with the increase in BR 18 concentration is due to the driving force that initial concentration provides to overcome the mass transfer resistance between the aqueous and solid phases. The adsorption rate was high at early adsorption period due to availability of large number of vacant site which increased the concentration gradient between the adsorbate in the solution and adsorbate on the adsorbent surface (Zohra *et al.*, 2008). Similar results were observed in the literature (Karadag *et al.*, 2007; Unuabonah *et al.*, 2008).

### 3.4. Effect of agitation speed on adsorption process

Adsorption studies were carried out with an orbital incubator at pH: 4.0, which is initial pH of the dyed solution. Basic red 18 dye solution was 100 mg L<sup>-1</sup>. The agitation speed varied from 100 to 400 rpm. The adsorption efficiency increased because of increasing kinetic energy between the dye molecules and the montmorillonite particles (Fig. 5). Thus, the adsorption efficiency increased with increasing agitation speed and the dye removal efficiency was maximal at 400 rpm. The effect of agitation rate onto the montmorillonite was shown in Fig. 5. The BR 18 dye adsorbate on per gram of the montmorillonite increased because of increasing kinetic energy between the dye molecules and the montmorillonite particles. The dye adsorption capacities for different agitation rates (100, 200, 300 and 400 rpm) were obtained as 140.933, 153.634, 165.586 and 172.564 mg g<sup>-1</sup>, respectively (Nandi *et al.*, 2009).

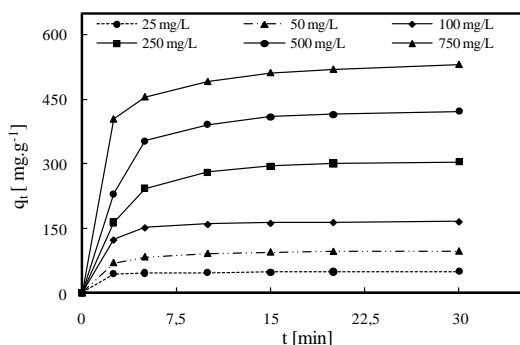


Figure 4. Effect of initial dye concentration on dye adsorption on montmorillonite (Conditions: agitation speed 300 rpm, adsorbent dosage 0.5 g L<sup>-1</sup>, temperature 293 K, ionic strength 0 mol L<sup>-1</sup> NaCl, solution pH: 4.0)

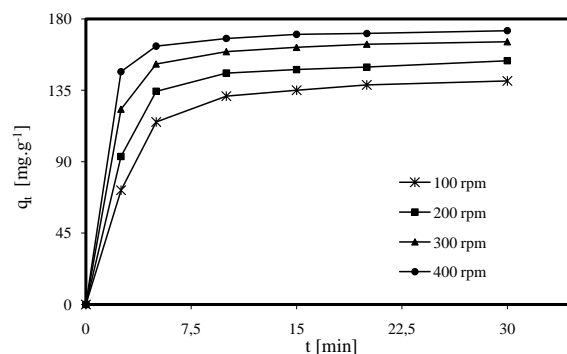


Figure 5. Effect of agitation speed on dye adsorption on montmorillonite (Conditions: initial dye concentration 100 mg L<sup>-1</sup>, adsorbent dosage 0.5 g L<sup>-1</sup>, temperature 293 K, ionic strength: 0 mol L<sup>-1</sup> NaCl, solution pH: 4.0)

### 3.5. Effect of ionic strength on adsorption process

As shown in Fig. 6, adsorption of BR 18 on montmorillonite increased upon addition of small quantities of salt. The effect of ionic strength on dye adsorption onto montmorillonite surface was studied on 0 M, 1x10<sup>-1</sup> M, 1x10<sup>-2</sup> M, and 1x10<sup>-3</sup> M NaCl solutions at pH: 4.0, 300 rpm agitation speed, 293 K temperature, 0.5 g L<sup>-1</sup> adsorbent dosage and 100 mg L<sup>-1</sup> initial adsorbate concentration. Theoretically, when the electrostatic forces between the adsorbent surface and adsorbate ions were attractive, as in this system, an increase in ionic strength will decrease the adsorption capacity. Conversely, when the electrostatic attraction is repulsive, an increase in ionic strength will increase adsorption (Fil and Özmetin, 2012; Wang and Zhang, 2011). The experimental data from this study did not follow this convention, as the adsorption of negatively charged dye molecules on positively charged montmorillonite increased with NaCl addition. The increase in dye removal after NaCl addition can be attributed to an increase in resolution of BR 18 in solution.

Table 5. Kinetic constants for basic red 18 adsorption onto montmorillonite

Parameters						Kinetic models					
Ionic strength (mol L <sup>-1</sup> NaCl)	Adsorbent dosage (g/100 ml)	Temperature (K)	Initial dye concentration(mg L <sup>-1</sup> )	pH	Agitation speed (rpm)	Pseudo – second – order			Pseudo – first – order	The Elovich Equation	Intra-particle
						$h=k_2 \times q_e^2$ mg g <sup>-1</sup> min <sup>-1</sup>	$k_2 \times 10^3$ g mg <sup>-1</sup> min <sup>-1</sup>	R <sup>2</sup>	R <sup>2</sup>	R <sup>2</sup>	R <sup>2</sup>
0	0.050	<b>293</b>	100	4.0	300	346.021	0.012279	0.999	0.914	0.830	0.857
0	0.050	<b>303</b>	100	4.0	300	471.921	0.015231	1.000	0.886	0.802	0.821
0	0.050	<b>313</b>	100	4.0	300	612.745	0.018027	1.000	0.793	0.813	0.805
0	0.050	<b>323</b>	100	4.0	300	929.368	0.026116	1.000	0.793	0.776	0.810
0	0.050	<b>333</b>	100	4.0	300	1997.204	0.052535	1.000	0.770	0.627	0.646
0	0.050	293	<b>25</b>	4.0	300	146.007	0.058929	1.000	0.744	0.993	0.878
0	0.050	293	<b>50</b>	4.0	300	152.625	0.015836	0.999	0.973	0.922	0.704
0	0.050	293	<b>100</b>	4.0	300	346.021	0.012279	0.999	0.914	0.830	0.857
0	0.050	293	<b>250</b>	4.0	300	256.345	0.002553	0.996	0.986	0.894	0.896
0	0.050	293	<b>500</b>	4.0	300	396.825	0.002085	0.996	0.954	0.847	0.872
0	0.050	293	<b>750</b>	4.0	300	825.764	0.002857	0.999	0.913	0.972	0.885
0	<b>0.025</b>	293	100	4.0	300	342.231	0.008396	0.999	0.934	0.896	0.889
0	<b>0.050</b>	293	100	4.0	300	346.021	0.012279	0.999	0.914	0.830	0.857
0	<b>0.075</b>	293	100	4.0	300	337.952	0.021113	1.000	0.882	0.824	0.642
0	<b>0.100</b>	293	100	4.0	300	277.085	0.027836	1.000	0.864	0.820	0.444
0	0.050	293	100	4.0	<b>100</b>	117.261	0.005464	0.995	0.958	0.853	0.904
0	0.050	293	100	4.0	<b>200</b>	187.371	0.007603	0.998	0.871	0.812	0.879
0	0.050	293	100	4.0	<b>300</b>	346.021	0.012279	0.999	0.914	0.830	0.857
0	0.050	293	100	4.0	<b>400</b>	616.143	0.047260	1.000	0.837	0.864	0.780
0	0.050	293	100	<b>4.0</b>	300	346.021	0.012279	0.999	0.914	0.830	0.693
0	0.050	293	100	<b>6.0</b>	300	444.642	0.014174	1.000	0.919	0.877	0.835
0	0.050	293	100	<b>8.0</b>	300	438.596	0.012418	1.000	0.764	0.918	0.802
0	0.050	293	100	<b>10.0</b>	300	400.320	0.010465	0.999	0.906	0.897	0.749
<b>0</b>	0.050	293	100	4.0	300	346.021	0.012279	0.999	0.914	0.830	0.857
<b>0.001</b>	0.050	293	100	4.0	300	389.712	0.013119	0.999	0.895	0.833	0.901
<b>0.010</b>	0.050	293	100	4.0	300	473.709	0.015154	1.000	0.917	0.846	0.916
<b>0.100</b>	0.050	293	100	4.0	300	481.464	0.012543	1.000	0.868	0.837	0.916

### 3.6. Effect of adsorbent dosage on adsorption process

The effect of adsorbent amount on the uptake of the dye was measured for dye concentration  $100 \text{ mg L}^{-1}$ , and different quantity of clay ( $0.25, 0.50, 0.75$  and  $1.00 \text{ g L}^{-1}$ ) at pH 4, 300 rpm agitation speed and 293 K temperature (Figure 7). In general, it was found that by increasing the amount of the adsorbent the adsorption rate increased. This increase was most significant when the amount of adsorbent increased from ( $0.25$ - $1.00 \text{ g L}^{-1}$ ). Maximum dye removal was achieved within 30 minutes after which a decrease in BR 18 concentration was negligible. Increase in dye removal percentage with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. But, when was increased adsorbent dosage from  $0.25 \text{ g L}^{-1}$  to  $1.00 \text{ g L}^{-1}$ , adsorption capacity decreased from  $198.701 \text{ mg g}^{-1}$  to  $98.868 \text{ mg g}^{-1}$ . This may be attributed to the availability of more sorption sites due to higher amount of the sorbent. At higher montmorillonite to solute ratios, there is a very fast sorption onto the sorbent surface that produces a lower solute concentration in the solution compared to the sorbent to solute concentration ratio is lower (Vimonses *et al.*, 2009). At the beginning of the process the rate of dye removal by the clay was fast during the first 10 min and then decreased gradually.

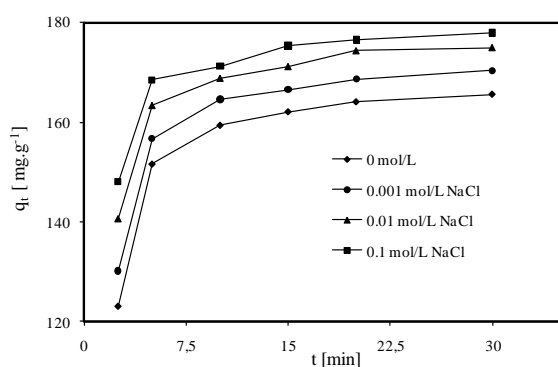


Figure 6. Effect of ionic strength on dye adsorption on montmorillonite (Conditions: initial dye concentration  $100 \text{ mg L}^{-1}$ , adsorbent dosage  $0.5 \text{ g L}^{-1}$ , temperature 293 K, agitation speed 300 rpm, solution pH: 4.0)

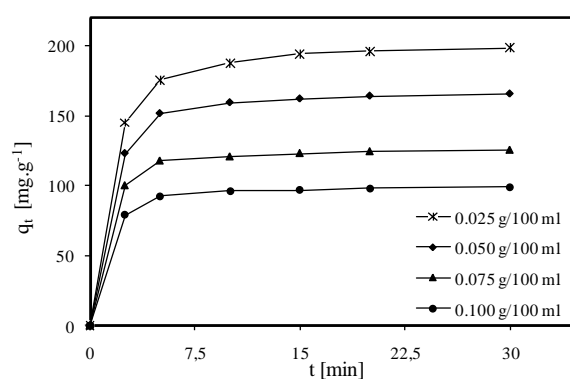


Figure 7. Effect of adsorbent dosage on dye adsorption on montmorillonite (Conditions: initial dye concentration  $100 \text{ mg L}^{-1}$ , agitation speed 300 rpm, temperature 293 K, ionic strength  $0 \text{ mol L}^{-1}$  NaCl, solution pH: 4.0)

### 3.7. Effect of initial solution pH on adsorption process

The pH value of the solution is an important parameter for the adsorption processes, and the initial pH value of the solution has significant influence compared to than the final pH. To study the effect of pH on BR 18 adsorption, the experiments were carried out at  $100 \text{ mg L}^{-1}$  initial dye concentration with  $0.5 \text{ g L}^{-1}$  adsorbent dosage at 293 K and 300 rpm agitation speed. In general, initial pH value may enhance or depress the uptake. This is attributed to the charge of the adsorbent surface with the change in pH value. Figure 8 showed the relationship between the pH value and the adsorption capacity of BR 18. It could be seen from the figure that as the solution pH increased, the adsorption capacity increased. Increasing solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites and enlarges the attraction between dye and adsorbent surface, (Karim *et al.*, 2009). Generally, the net positive charge decreases with increasing pH value lead in the decrease in the repulsion between the adsorbent surface and the dye thus, improving the adsorption capacity.

### 3.8. Effect of solution temperature on adsorption process

The effect of temperature on the removal of BR 18 dye was investigated effect of solution temperature (293, 303, 313, 323 and 333) K at pH: 4.0, 300 rpm agitation speed,  $0.5 \text{ mg L}^{-1}$  adsorbent dosage,  $0 \text{ mol L}^{-1}$  NaCl salt concentration and  $100 \text{ mg L}^{-1}$  initial adsorbate concentration. The results were graphed in Fig. 9. From this figure, it has been observed when increased solution temperature from 293 K to 333 K, adsorption capacity of BR 18 onto montmorillonite increased from  $165.586 \text{ mg g}^{-1}$  to  $194.311 \text{ mg g}^{-1}$ . The kinetic energy between the dye molecules and the montmorillonite particles increased with increasing the temperature of the solution. The collision



frequency between adsorbent and the dye molecules increased then the dye molecules electrostatically adsorbed onto the surface of the adsorbent particles (Weng and Pan, 2007).

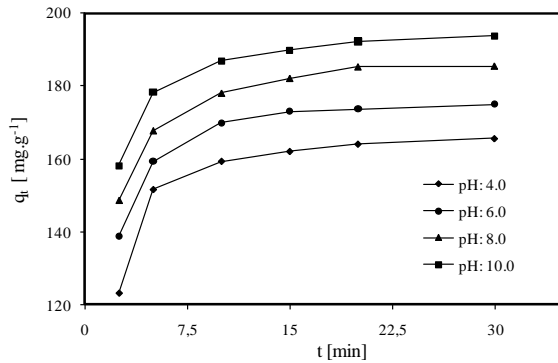


Figure 8. Effect of solution pH on dye adsorption on montmorillonite

(Conditions: initial dye concentration  $100 \text{ mg L}^{-1}$ , adsorbent dosage  $0.5 \text{ g L}^{-1}$ , temperature  $293 \text{ K}$ , agitation speed  $300 \text{ rpm}$ , ionic strength  $0 \text{ mol L}^{-1} \text{ NaCl}$ )

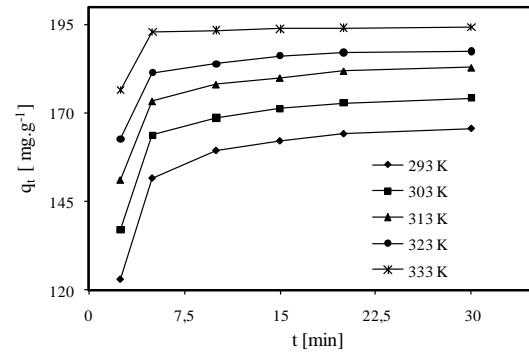


Figure 9. Effect of temperature on dye adsorption on montmorillonite

(Conditions: initial dye concentration  $100 \text{ mg L}^{-1}$ , adsorbent dosage  $0.5 \text{ g L}^{-1}$ , agitation speed  $300 \text{ rpm}$ , ionic strength  $0 \text{ mol L}^{-1} \text{ NaCl}$ , solution pH:  $4.0$ )

### 3.9. Activation parameters and thermodynamic parameters

#### 3.9.1. Activation Energy

Adsorption rate constant temperature dependence can be given as follows (Al-Ghouthi *et al.*, 2005):

$$\ln k_2 = \ln k_0 - \frac{E_a}{R_g} \frac{1}{T} \quad (12)$$

where  $k_2$  is the pseudo-second-order constant ( $\text{g mol}^{-1} \text{ min}^{-1}$ ),  $k_0$  is the rate constant of adsorption ( $\text{g mol}^{-1} \text{ min}^{-1}$ ),  $E_a$  is activation energy of adsorption ( $\text{kJ mol}^{-1}$ ),  $R_g$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the solution temperature (K). Plotting of  $\ln k_2$  against the reciprocal temperature gives a reasonably straight line, the gradient of which is  $-E_a/R_g$ . From Eq. (12), the activation energy,  $E_a$ , is  $27.635 \text{ kJ mol}^{-1}$  (Fig. 10). The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. Low activation energies ( $5\text{--}50 \text{ kJ mol}^{-1}$ ) are characteristics for physical adsorption, while higher activation energies ( $60\text{--}800 \text{ kJ mol}^{-1}$ ) suggest chemical adsorption (Nollet *et al.*, 2003).

#### 3.9.2. Thermodynamic parameters

Free energy ( $\Delta G^\ddagger$ ), enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) of activation can be calculated by Eyring equation (Laidler and Meiser, 1999):

$$\ln \left( \frac{k_2}{T} \right) = \left[ \left( \frac{k_b}{h} \right) + \frac{\Delta S^\ddagger}{R_g} \right] - \frac{\Delta H^\ddagger}{R_g} \frac{1}{T} \quad (13)$$

where  $k_b$  and  $h$  are Boltzmann's and Planck's constants, respectively. According to Eq. (13), a plot of  $\ln(k_2/T)$  versus  $1/T$  should be a straight line with a slope  $\Delta H^\ddagger/R_g$  and intercept  $[\ln(k_b/h) + \Delta S^\ddagger/R_g]$ .  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were calculated from slope and intercept of line, respectively (Fig. 11). Gibbs energy of activation may be written in terms of entropy and enthalpy of activation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T \cdot \Delta S^\ddagger \quad (14)$$

$\Delta G^\ddagger$  was calculated at  $293 \text{ K}$  from Eq. (14). It is found that the values of the free energy ( $\Delta G^\ddagger$ ), enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) of activation is  $51.412 \text{ kJ mol}^{-1}$ ,  $25.041 \text{ kJ mol}^{-1}$  and  $-0.090 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. The free energy of activation,  $\Delta G^\ddagger$  have also been computed at  $293 \text{ K}$  (Table 6).

Thermodynamical parameters were evaluated for BR 18 ions and showed that the adsorption of the dye is endothermic in nature. The positive value of  $\Delta H^\ddagger$  showed that adsorption was favorable at higher temperature and the presence of possible chemisorptions phenomenon. The positive values of the Gibbs free energy change ( $\Delta G^\ddagger$ ) confirm that the adsorption process was not spontaneous

whereas the negative values of the entropy ( $\Delta S^*$ ) confirm that the decreased randomness at the solid-solute during adsorption process.

Table 6. Thermodynamic parameters of basic red 18 adsorption onto montmorillonite

	T (K)				
	293	303	313	323	333
$\Delta G^*$ (kJ mol <sup>-1</sup> )	51.412	52.312	53.212	54.112	55.012
$\Delta H^*$ (kJ mol <sup>-1</sup> )	25.041				
$\Delta S^*$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	-0.0900				

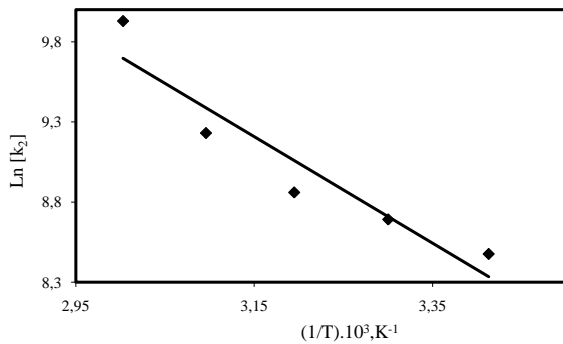


Figure 10. Arrhenius plots for adsorption of dye on montmorillonite

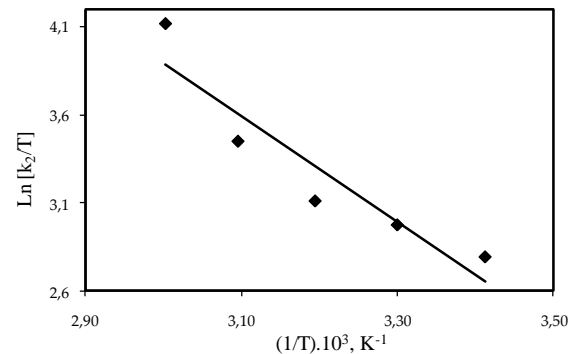


Figure 11. Plots of  $\ln(k_2/T)$  versus  $1/T$  for adsorption of dye on montmorillonite

### 3.10. Semi-empirical model for adsorption of BR 18 onto montmorillonite

Adsorption capacity data obtained by a mass balance equation obeyed the pseudo-second-order equation, and selected parameters were effective onto the adsorption capacity and rate. Hence, based on Eq. (9), an semi-empirical kinetic model including effects of initial dye concentration, solution pH, agitation speed, adsorbent dosage, ionic strength, temperature, and contact time was developed using 162 items of experimentally obtained results by means of Statistica 6.0 programme and given as follows:

$$\frac{t}{q_t} = 1.782 \times [H^+]^{0.0112} \times (AS)^{-0.1708} \times (AD)^{0.6858} \times [I]^{1.43E-7} \times [C_0]^{-0.8668} \times \exp\left(\frac{4.267}{T}\right) \times t^{0.9495} \quad (15)$$

where  $[H^+]$  is hydrogen ions concentration (mol L<sup>-1</sup>),  $(AS)$  is agitation speed (rpm),  $(AD)$  is the adsorbent dosage (g L<sup>-1</sup>),  $[I]$  is NaCl concentration (mol L<sup>-1</sup>),  $C_0$  is the initial dye concentration (mg L<sup>-1</sup>),  $T$  is the reaction temperature (K), and  $t$  is the contact time (min). The correlation between experimentally obtained ( $t/q_t$ ) and predicted ( $t/q_t$ ) was given in Fig. 12.

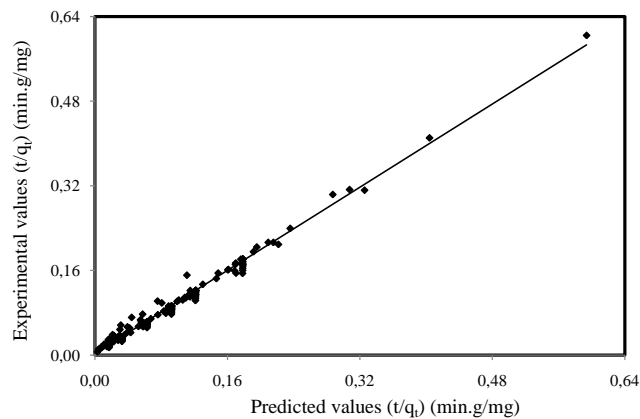


Figure 12. Correlation between experimental and statistically predicted  $t/q_t$  values

#### 4. CONCLUSIONS

The results of this investigation showed that Turkish clay montmorillonite has a suitable adsorption capacity for the removal of BR 18 from aqueous solutions. The experimental results were fitted well with Freundlich isotherm model. The data indicate that the adsorption kinetics follow the pseudo-second-order rate with intraparticle diffusion as one of the rate determining steps. Adsorption capacity increased that with increasing pH, temperature, agitation speed, initial dye concentration and ionic strength but, decreased that with increasing adsorbent dosage in spite of the increase percent removal. The activation parameters of the adsorption process helped in predication of how the adsorption of dye molecules might vary with temperature changes. The present study concludes that the montmorillonite could be employed as low-cost adsorbents as alternatives to commercial activated carbon for the removal of color and dyes from wastewater.

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