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Removal of Basic Red 18 onto modified sepiolite: Equilibrium, adsorption kinetics and thermodynamic studies

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ABSTRACT

The adsorption of Basic Red 18 (BR 18) from aqueous solution onto KF modified sepiolite was carried out as a function of pH, initial dye concentration, contact time and temperature. The equilibrium data were evaluated according to Langmuir and Freundlich models. The experimental results showed that the best correlation was obtained on Freundlich model. The adsorption kinetics was examined with pseudo-first order, pseudo-second order and intraparticle diffusion models. The result was best fitted for pseudo-second order kinetic model. Thermodynamic investigations were also performed to determine $\Delta H°$, $\Delta G°$ and $\Delta S°$. The results indicated that the adsorption of BR 18 was exothermic and spontaneous.

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1. Introduction

Dyes are widely used as colorant in textile, paper, photography and leather industries [1,2]. Textile industries are the largest generators of wastewater because these industries use up a large amount of water. Water contaminated with dyestuff is known to be toxic to the environment and dangerous for aquatic life [3,4]. Hence, disposal of dyestuff contaminating water with appropriate methods is very important. These methods include adsorption, coagulation, precipitation, oxidation, bacterial biodegradation and biosorption [5-10]. Among these, adsorption has been reported to be an effective process to eliminate water containing dyestuff [11]. Numerous adsorbents have been investigated for removal of dye from aqueous solution. Some of these are activated carbon [12,13], gypsum [14-16], zeolite [17], colemanite [18], bentonite [19], peat [20,21] and flyash [22,23].

Sepiolite is a natural clay mineral with formula of $Mg_8Si_{12}O_{30}(OH)_4(OH_2)4·8H_2O$[24,25]. Sorption of sepiolite is higher than the other clay. Due to the sorptive and structural properties, sepiolite is used in decolorizing, deodorizing, drug, ceramic production and catalytic reaction, *etc.* [1]. A number of investigations on sepiolite have been reported and continue to be carried out intensively [1,24-28]. In this study, the removal of BR 18 onto KF/sepiolite was investigated. The pH, initial dye concentration, contact time and temperature effects were explored. The adsorption studies were analyzed by Langmuir and Freunlich models. Equilibrium data were assessed by pseudo-first order, pseudo-second order and intraparticle diffusion models. Thermodynamic parameters such as $\Delta H°$, $\Delta G°$ and $\Delta S°$ were also estimated.

2. Experimental

2.1. Adsorbent materials and dye solution

Sepiolite used in this study was obtained from Eskisehir, Turkey. The chemical composition of sepiolite was determined by XRF (Rigaku ZSX Primus II) and given in Table 1. Sepiolite was modified with KF. The KF/Sepiolite materials were prepared as mentioned in reference [29]. The dye named Basic Red 18 (BR 18) was obtained from DyStar. The chemical structure of BR 18 is given in Figure 1. Dye stock solution was prepared by dissolving 250 mg of BR 18 in 1 L deionized water. The dye solutions used in the study were obtained by diluting stock solution. pH of the solutions was adjusted by 0.01 M HCl and 0.01 M NaOH.

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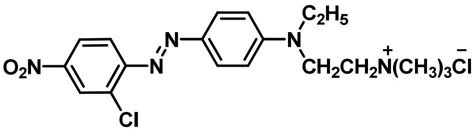
Table 1. Chemical composition of sepiolite.

Component	Chemical analysis (%)
MgO	28.76
Al_2O_3	0.08
SiO_2	58.58
SO_3	0.22
CaO	1.14
Fe_2O_3	0.04
NiO	0.23
Weight loss	10.97



2-[{4-[(*E*)-(2-Chloro-4-nitrophenyl)diazenyl]phenyl}(ethyl)amino]
-*N*,*N*,*N*-trimethylethanaminium

Figure 1. Chemical structure of BR 18.

2.2. Procedure

Batch adsorption experiments were performed onto KF/sepiolite (0.1 g) in a 100 mL beaker containing 50 mg/L dye solution to specify the pH, initial dye concentration, contact time and temperature. At the end of adsorption, dye solutions were centrifuged 4000 rpm for 10 min and remaining liquid dye solution was analyzed by UV-Vis spectrophotometer (Shimadzu 1601) at 489 nm. The amount of adsorbed dye onto KF/sepiolite (*q* in mg/g) and the removal efficiency (%) were determined by Equation (1) and (2).

$$q = \frac{(Co-Ce)V}{M} \tag{1}$$

$$Removal\ \% = \frac{(Co-Ce)}{Co}\times 100 \tag{2}$$

C_o and C_e represent the initial and dye concentrations at equilibrium (mg/L), respectively. *V* is the volume dye solution (L) and *M* is the mass of adsorbent (g) [14,24].

3. Results and discussion

3.1. Influence of pH

The pH of the dye solution has a significant effect on the adsorption process. The surface charge of the adsorbent and the ionization degree of adsorbate are affected by pH. The influence of pH on BR 18 adsorption was investigated at pH = 4, 6, 8 and 10 values (Figure 2). As seen in Figure 2, the adsorption capacity of BR 18 increased with pH and maximum adsorption was found to be at pH = 8 (23.6 mg/g), then the adsorption capacity began to decrease with increasing pH, and optimum pH was found to be 8. Deniz *et al.* and Bulut *et al.* reported similar behavior previously [14,15]. Higher pH value may enhance KF/sepiolite surface charge and facilitates the dye adsorption. Being excess H^+ at lower pH results the displacement of the cationic dye group which causes low adsorption [14].

3.2. Influence of initial dye concentration

The influence of initial concentration of BR 18 onto KF/sepiolite was carried out concentration range of 25-150 mg/L. The obtained data are given in Figure 3. As shown in Figure 3, the removal efficiency of BR 18 decreased with increasing concentration. It downed from 99.7 to 54.3 %. In contrast, adsorption capacity (*q*) increased with increasing of BR 18 concentration. The *q* value increased from 12.50 to 40.25 mg/g in 25-150 mg/L dye concentration range. The decreasing in removal efficiency at high dye concentration is in consequence of saturation of the adsorbent pore [6,14].

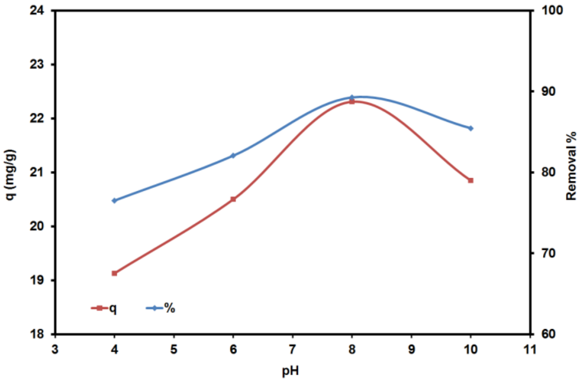


Figure 2. Effect of pH on BR 18 adsorption by KF/sepiolite (50 mg/L dye concentration, temperature 20 °C, contact time 60 min).

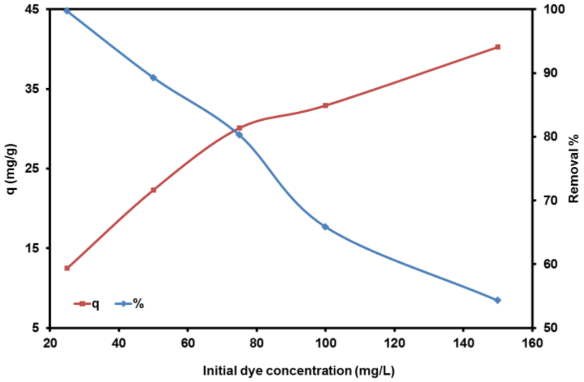


Figure 3. Effect of initial dye concentration on BR 18 adsorption by KF/sepiolite (pH = 8, temperature = 20 °C, 60 min).

3.3. Influence of contact time

The influence of contact time on removal of BR 18 and adsorption capacity were investigated. The effect of the contact time was given in Figure 4. It can be seen from Figure 4 that the adsorption and removal efficiency increasing with increased time. It was observed that the removal of dye and the adsorption of dye were fast for the first 10 min and afterward it keeps going slow land lastly reaches equilibrium. The initial fast adsorption is perhaps consequence of plenty of available surface pore.

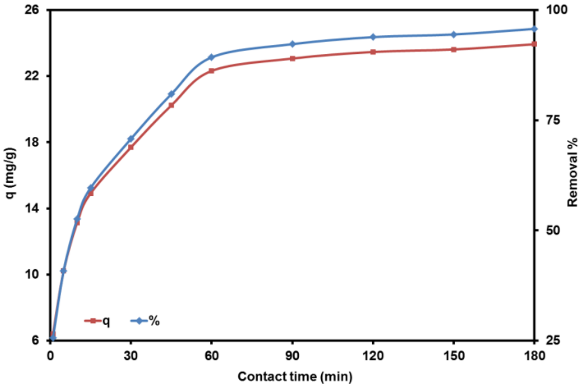


Figure 4. Effect of contact time on BR 18 adsorption by KF/sepiolite (pH = 8, C_o = 50 mg/L, Temperature = 20 °C).

3.4. Influence of temperature

Temperature is one of the most important parameter in adsorption and gives valuable information about some thermodynamic parameter such as Gibbs free energy, enthalpy and entropy. The influence of temperature on adsorption was researched at 20, 40 and 60 °C. As shown in Figure 5, the adsorption capacity decreased with increasing temperature. This means that, the adsorption of BR 18 on KF/sepiolite was an exothermic. Similar results were also noted in previous studies [18,26,30].

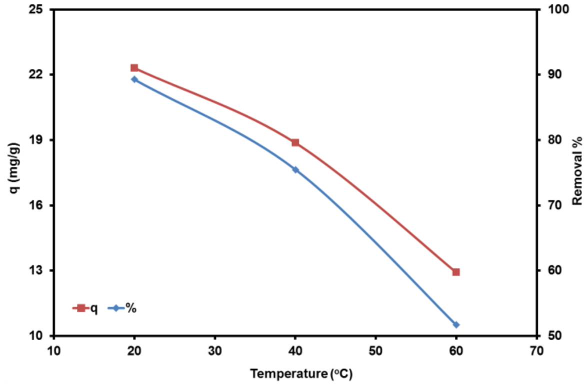


Figure 5. Effect of temperature on BR 18 adsorption by KF/sepiolite (pH = 8, C_o = 50 mg/L and contact time of 60 min).

3.5. Adsorption isotherm

Adsorption isotherms give information about adsorption mechanism. In present study, the adsorption experiments data were searched for Langmuir and Freunlich isotherms.

The mathematical equation of Langmuir isotherm can be expressed as [14];

$$\frac{C_e}{q_e} = \frac{1}{bq_n} + \frac{C_e}{q_m} \tag{3}$$

where q_m, b, C_e and q_e represent monolayer adsorption capacity (mg/g), Langmuir constant (L/mg), equilibrium dye concentration (mg/L) and amount dye adsorbed (mg/g), respectively. Plotting C_e/q_e *vs* C_e gives a straight line and from slope q_m and the intercept b can be found. Langmuir isotherm includes a dimensionless factor called R_L-defines the favorability of the adsorption process. R_L is given as [27];

$$R_L = \frac{1}{1+bC_0} \tag{4}$$

The adsorption process is unfavorable if R_L>1, linear if R_L=1, favorable if 0< R_L<1, and irreversible if R_L=0.

In present study, the monolayer adsorption capacity (q_m) was found to be 41.6 mg/g, Langmuir isotherm constant (b) is 0.3 L/mg, R_L is 0.06 meaning that the adsorption process was favorable with r^2 of 0.988.

Freundlich model is one of the oldest known adsorption isotherm defines that the adsorption occurs on heterogeneous surfaces [31]. Linear form of Freundlich adsorption equation is [1]:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{5}$$

where K_F = Freundlich isotherm constant (mg/g), n = adsorption intensity; C_e = the equilibrium concentration of adsorbate (mg/L) and q_e = the amount dye adsorbed at equilibrium (mg/g).

The adsorption intensity, n, indicates the adsorption nature. Adsorption process is favorable in range of n 1 to 10. If plotting log q_e versus log C_e a straight line can be obtained (Figure 6). From the slope of the line n was found to be 5.9 and the intercept gave the K_F value as 19 and r^2= 0.993 indicated that the equilibrium data are more compatible with Freundlich isotherm model.

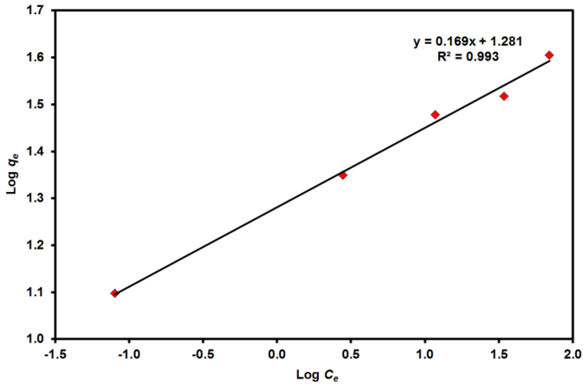


Figure 6. Freundlich isotherm of BR 18 adsorption by KF/sepiolite (pH = 8, C_o = 50 mg/L and contact time of 60 min).

The adsorption value 5.9 calculated for n indicates a favorable adsorption process. All parameters obtained from Langmuir and Freundlich isotherms were depicted in Table 2.

Table 2. Adsorption isotherm constant for BR 18 onto KF/sepiolite at pH=8 and temperature 20 °C.

Langmuir				Freundlich		
q_m (mg/g)	b (L/g)	R_L	r^2	K_F (mg/g)	n_f	r^2
41.6	0.3	0.6	0.988	3.6	5.90	0.993

3.6. Kinetics of adsorption

Adsorption is one of the most popular methods used in pollution treatment. To identify the underlying mechanism through adsorption and to understand the performance of adsorbent used in adsorption are significant. There are several kinetic approaches to define the adsorption mechanism. In the present study, the conformity of experimental data were searched for pseudo-first order, pseudo-second order and intraparticle diffusion kinetics model. All kinetic studies were at pH=8, 50 mg/L dye concentration, temperature of 20 °C and 60 min adsorption time.

The pseudo-first order kinetic is described as [30]:

$$\frac{1}{q} = \frac{k_1}{q_e t} + \frac{1}{q_e} \tag{6}$$

where q is the adsorbed dye quantity (mg/g) at t (min) time, q_e represent adsorbed dye at equilibrium (mg/g) and k_1 is the rate constant of pseudo-first order (1/min). If the values of $1/q_e$ plot against to $1/t$ a straight line can be obtained. From the linear plot q_e and k_1 can be found.

The pseudo-second order model is expressed as [31]:

$$\frac{t}{q} = \frac{1}{k_2 {q^2}_e} + \frac{t}{q_e} \tag{7}$$

where k_2 is the rate constant of pseudo-second order (g/mg.min). The plot of t/q versus t gives a straight line (Figure 7). From the slope and intercept q_e and k_2 can be determined.

Finally, intraparticle diffusion model is given as [14]:

$$q = k_p t^{1/2} + C \tag{8}$$

where k_p represents the intraparticle diffusion rate constant (mg/g. min) and C is about boundary layer (mg/g). Plotting the values of q versus $t^{1/2}$ yielded two regions. The first region may the boundary layer effect and the second region indicates the diffusion of dye molecules into adsorbent pores. Similar results were reported in previous studies [18,30,32-34]. The two observed regions in the intraparticle model indicate that at least two steps take place in the adsorption process.

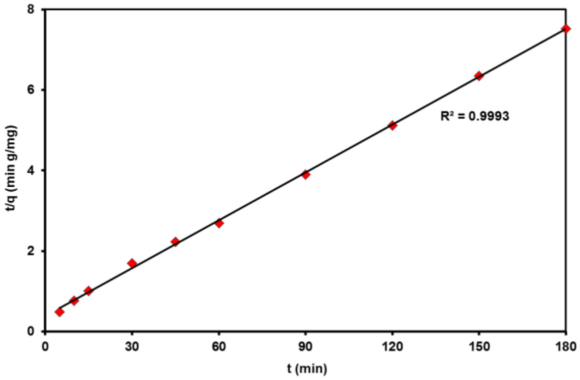


Figure 7. Plot of pseudo-second order kinetic model of BR 18 onto KF/sepiolite (pH = 8, Temperature = 20 °C).

All the kinetic data are summarized in Table 3. From Table 3, experimental data of adsorption BR 18 were best fitted by the pseudo-second order kinetics model.

Table 3. Kinetic parameter obtained for adsorption of BR 18 on KF/sepiolite (pH=8, Temperature=20 °C, 50 mg/L initial dye concentration).

Pseudo-first order			**Pseudo-second order**		
q_e (mg/g)	k_1 (1/min)	r^2	q_e (mg/g)	k_1 (1/min)	r^2
25	9.5	0.974	25.6	0.005	0.999

3.7. Thermodynamic parameter

Thermodynamic data give a great of knowledge about adsorption nature. The parameter such as enthalpy ($\Delta H°$), Gibbs free energy ($\Delta G°$) and entropy ($\Delta S°$) can be evaluated by following equations [32]:

$$\Delta G^0 = -RT\ln K_c \tag{9}$$

where $\Delta G°$ represents the free energy (kJ/mol), R and T are gas constant (8.314 J/mol.K) and temperature (K), respectively. K_c is the equilibrium constant in form of (q_e/C_e). Enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) can be estimated as:

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

The plot ln K_c versus $1/T$ gives a straight line (Figure 8). From the slope and intercept of the line $\Delta H°$ and $\Delta S°$can be determined, respectively. Here, $\Delta H°$ and $\Delta S°$ at 20℃ were calculated as -50.20 kJ/mol and -0.15 kJ/mol, respectively. $\Delta G°$ value was found to be -6.90 kJ/mol. The negative value of $\Delta G°$ means that the adsorption process occurs spontaneously in nature. The negative value of $\Delta S°$ indicates a decreased randomness at the solid/solution interface. Similar behavior was reported previously [30,35]. The calculated thermodynamic parameters are presented in Table 4.

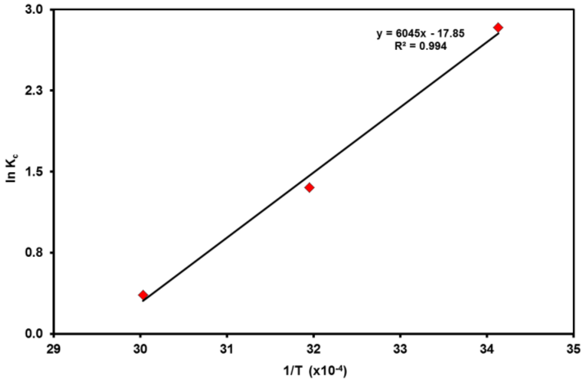


Figure 8. Plot of lnK_c versus 1/T (pH = 8, C_o = 50 mg/L and contact time of 60 min.).

Table 4. Thermodynamic parameters for adsorption of BR 18 onto KF/sepiolite.

T (K)	$\Delta H°$ (kJ/mol)	$\Delta G°$ (kJ/mol)	$\Delta S°$ (kJ/mol. K)
293	-50.02	-6.90	-0.15

4. Conclusion

In this work, the removal of BR 18 was investigated on KF/sepiolite adsorbent as a function of pH, initial dye concentration, contact time and temperature. The optimum conditions for pH, initial dye concentration, contact time and temperature were found to be 8, 50 mg/L, 20 °C and 60 min, respectively. Adsorption isotherm studies showed that equilibrium results complied with Freundlich isotherm model best. Kinetic analysis proved that the adsorption of BR 18 followed pseudo-second order. As a result of thermodynamic investigation for BR 18 on KF/sepiolite, $\Delta H°$, $\Delta G°$ and $\Delta S°$ were found to be -50.02 kJ/mol, -6.90 kJ/mol and-0.15 kJ/mol.K, respectively. The negative values of $\Delta H°$ and $\Delta G°$ indicated the adsorption of BR 18 onto KF/sepiolite system was exothermic and spontaneous in nature.

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References

[1]. Tabak, A.; Eren, E.; Afsin, B.; Caglar, B. *J. Hazard. Mat.* **2009**, *161*, 1087-1089.
[2]. Han, Z. X.; Zhu, Z.; Wu, D. D.; Wu, J.; Liu, Y. R. *Synt. React. Inorg. Metal-Org. Nano-Metal Chem*. **2014**, *44*, 140-147.
[3]. Wang, S.; Ariyanto, E. *J. Coll. Int. Sci*. **2007**, *314*, 25-31.
[4]. Qui, M.; Qian, C.; Wu, J. X. J.; Wang, G. *Desalination* **2009**, *243*, 286-292.
[5]. Belala, Z.; Jeguirim, M.; Belhachemi, M.; Addoun, F.; Trouve, G. *Desalination* **2011**, *271*, 80-87.
[6]. Ozer, A.; Akkaya, G.; Turabik, M. *J. Hazard. Mat*. **2006**, *135*, 355-364.
[7]. Szygula, A.; Guibal, E.; Ruiz, M.; Sastre A. M. *Coll. Surf. A: Physochem. Eng. Asp*. **2010**, *54*, 283-290.
[8]. Lee, Y. C.; Kim, E. J.; Yang, J. W.; Shin H. J. *J. Hazard. Mat*. **2011**, *192*, 62-70.
[9]. Kim, T. H.; Park, C.; Yang, J.; Kim, S. *J. Hazard. Mat*. **2004**, *112*, 95-100.
[10]. AbdurRahman, F. B.; Akter, M.; Abedin, M. Z. *Int. J. Sci. Tech. Res*. **2013**, *2*, 47-50.
[11]. Eren, E.; Afsin, B *Dyes Pigments* **2007**, *73*, 162-167.
[12]. Mahmoodi, N. M.; Salehi, R.; Arami, M. *Desalination* **2011**, *272*, 187-195.
[13]. Gomez, V.; Larrechi, M. S.; Callao, M. P. *Chemosphere* **2007**, *69*, 1151-1158.
[14]. Deniz, F.; Saygıdeger, S. D. *Desalination* **2010**, *262*, 161-165.
[15]. Bulut, Y.; Aydın, H. *Desalination* **2006**, *194*, 119-124.

[16]. Rauf, M. A.; Qadri, S. M.; Ashraf, S.; Al-Mansoori, K. M. *Chem. Eng. J.* **2009**, *150*, 90-95.

[17]. Wang, S.; Li, H.; Xu, L. *J. Coll. Inter. Sci.* **2006**, *291*, 71-78.

[18]. Atar, N.; Olgun, A. *J. Hazard. Mat.* **2007**, *146*, 171-179.

[19]. Turabik, M. *J. Hazard. Mat.* **2008**, *158*, 52-64.

[20]. Sun, Q.; Yang, L. *Water Res.* **2003**, *3*, 1535-1544.

[21]. Fernandes, A. N.; Almeida, C. A. P.; Menezes, C. T. B.; Debacher, N. A.; Sierra, M. M. D. *J. Hazard. Mat.* **2007**, *144*, 412-419.

[22]. Demirbas, E.; Nas, M. Z. *Desalination* **2009**, *243*, 8-21.

[23]. Rao, V. V. B.; Rao, S. R. M. *Chem. Eng. J.* **2006**, *116*, 77-84.

[24]. Kuncek, I.; Şener, S. *Ultrason. Sonochem.* **2010**, *17*, 250-257.

[25]. Alkan, M.; Demirbas, O.; Celikcapa, S.; Dogan, M. *J. Hazard. Mat.* **2004**, *B116*, 135-145.

[26]. Ozcan, A. S.; Tetik, S.; Ozcan, A. *Seperation Sci. Techn.* **2004**, *39*, 301-320.

[27]. Tekbas, M.; Bektas, N.; Yatmaz, H. C. *Desalination* **2009**, *249*, 205-211.

[28]. Ozdemir, Y.; Dogan, M.; Alkan, M. *Micropor. Mesopor. Mat.* **2006**, *96*, 419-427.

[29]. Algoufi, Y. T.; Akpan, U. G.; Asif, M.; Hameed, B. H. *App. Cat. A: General* **2014**, *487*, 181-188.

[30]. Ozcan, A.; Oncu, E. M.; Ozcan, A. S.; *Coll. Surf. A: Physicochem. Eng. Asp.* **2006**, *277*, 90-97.

[31]. Dada, A. O.; Olalekan, A. P.; Olatunya, A.; Dada, O. *J. App. Chem.* **2012**, *3*, 38-45.

[32]. Alver, E.; Metin, A. U. *Chem. Eng. J.* **2012**, *200-202*, 59-67.

[33]. Doğan, M.; Ozdemir, Y.; Alkan, M. *Dyes and Pigments* **2007**, *75*, 701-713.

[34]. Derakhshan, Z.; Baghapour, M. A.; Ranjbar, M.; Faramarzian, M. *Health Scope* **2013**, *2*, 136-44.

[35]. Ugurlu, M. *Micropor. Mesopor. Mat.* **2009**, *119*, 276-283.