Adsorption Equilibrium and Thermodynamics of Diatomite (Çaldiran/Van) OnSome Textile Dyes

[1]Salih Alkan*, [1]Meliha Çalişkan, [1]İlhan Irende and [2]Ali Rıza Kul
[1]*Ordu University*, *Faculty of Arts and Sciences*, *Department of Chemistry*, *52200 Ordu*, *Turkey.*
[2]*Yüzüncüyıl University*, *Faculty of Sciences*, *Department of Chemistry*, *Van*, *Turkey.*
salihalkan@odu.edu.tr *

(Received on 5th June 2017, accepted in revised form 28th December 2017)

Summary: Together with increasing world population, developing technology and rapid industrialization process bring about environmental pollution. Nowadays, cleaning environment from industrial wastes and pollutants is of utmost importance. Some organic materials, produced by the majority of textile waste, cause environmental pollution. Many dyestuffs, which are hazardous for environment, can be released to environment by industrial organizations without having any precaution. Textile dyestuffs, being above certain concentrations, can cause poisoning of aquatic organisms. Dyestuffs can be classified as following: Anionic: Direct, acid and reactive dyes Cationic: Basic dyes Nonionic: Disperse dyes It can be said that most problematic group of dyes used in the textile industry is the group of reactive dyes. Analyzing performed studies shows that these views are supported. Today, adsorption techniques are gaining ground due to efficiency in removal of too stable pollutants. Adsorption is, economically, a reasonable method and we can say that it provides formation of high quality products. With the development of industry search for materials, to be used as adsorbent for removal of factory wastes and water-soluable dyestuffs from water, accelerates. In our study, from natural adsorbents diatomite(Çaldıran/VAN) is used as an adsorbent material. The removal of natural red and basic blue from aqueous solution using diatomite, was investigated with respect to the adsorbent dose (0,02 g), initial concentration (20-140 mg/L), temperature (between 25 and 45^{0}C), on batch adsorption were studied as a function of contact time. The lineer Langmuir, Freundlich and Temkin adsorption equations were applied to describe the equilibrium isotherms. In addition, the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to determine the kinetic data. The experimental data were well fitted by the pseudo-second-order kinetic model. Thermodynamic parameters such as the enthalpy (ΔH^0), Gibbs free energy (ΔG^0) and entropy (ΔS^0) shoved spontaneous and endothermic in nature of adsorption for both of adsorbents.

Keywords: Adsorption; Diatomite; Kinetics equilibrium; Thermodynamic; Basic blue; Natural red; Environment Pollution.

Introduction

Diatomite is suitable for industrial applications owing to its low density, high porosity, high melting point (1400^{o}C-1750^{o}C), low thermal conductivity, solubility in high alkaline and HCl solutions. Diatomite is employed as an insulation material in dye and agricultural protection medicines. In addition, diatomite has been used in cosmetics, pharmaceuticals and chemical industry. Similarly, diatomite is utilized as a catalyst carrier in metal, metal oxide, acid-salt contacts and as a catalyst in various processes ranging from sulfurization to free polymerization [1]. Diatomite ($SiO_2.nH_2O$) is a soft, light colored, slightly sedimentary rock formed by the accumulation of silica shells of diatoms and fossilized from algae in water [2]. It is known that diatomite is used in the sugar industry in our country because it is sterile and harmless to health, abundant in our country, convenient in terms of usage, also it provides clarity and filtration quality in world standards [3]. Usage area of Diatomite as an industrial raw material depends on not only its mineralogical structure but also physical properties such as adsorption capacity, surface area, pore volume, surface load. Great deals of modification methods are applied to improve the adsorption and physicochemical properties of diatomite [4]. The process of adsorption based on interactions between an adsorbate and an adsorbent at the surface-water interface. Therefore, surface properties of the adsorbent play an important role in the sorption process [5]. Adsorption is one of the methods used in removing heavy metals from aqueous solutions. Natural or modified diatomite has already been used for the adsorption of different elements from water and [6]. The equilibrium adsorption isotherm is very important in case of desing any adsorption process. Equilibrium studies give an indication about the relation between adsorbent and adsorbate [7]. On the other hand, the adsorption mechanisms could be well understood through kinetic models such as lagergren firs-order, pseudo second-order and intraparticle diffusion equations [8]. Batch adsorption technique was used in this study in order to determine the equilibrium data. Experimental results were applied

*To whom all correspondence should be addressed.

to Langmuir, Freundlich and Temkin isotherms. First order, pseudo second order and intraparticle diffusion kinetic models were calculated for determination of adsorption mechanism.

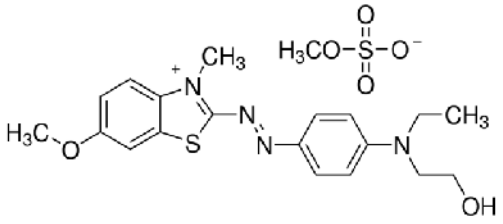
Experimental

The adsorbent. Diatomite used as an adsorbent was collected from Caldiran region in Van Basin Lake in Eastern Anotolia (Turkey). The powdered natural diatomite sample was washed by distilled water and dried in a drying oven at 110^0C.

X-ray fluoreresscence spectrometer (XRF, Philips 2400) was used for chemical analysis. The diatomite from Çaldıran-Van region consisted of the compounds of 69.70% SiO_2, 11.50% Al_2O_3, 4.40% Fe_2O_3, 0.65% TiO_2, 0.80% Na_2O, 1.40% K_2O. Loss on ignition was determined as 11.55% (8).

The moleculer structure of this basic blue is shown in Fig.

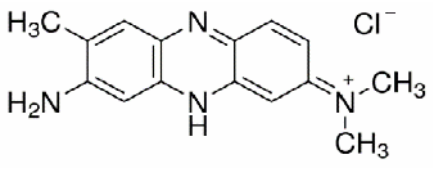
Basic Blue ($C_{20}H_{16}N_4O_6S_2$)



Dye Name:	Metylene Blue
Molecular Formula:	$C_{20}H_{16}N_4O_6S_2$
Molecular weight, g/mol:	482.57
λ max. (nm):	617

The moleculer structure of this naturel red is shown in Fig.

Natural Red ($C_{15}H_{17}ClN_4$)



Dye Name:	Neutral Red
Molecular Formula:	$C_{15}H_{17}ClN_4$
Molecular weight, g/mol:	288.78
λ max. (nm) :	533

Material

In this study, the characterization and adsorption properties of some dyes (natural red and basic blue) on the diatomite obtained from Çaldıran district of Van province were studied. Natural red and basic blue dyes used in the experiments purchased from Sigma-Aldrich (St. Louis, MO, USA). The collected samples from the Van-Çaldiran area were powdered by a grinder. 100 g of diatomite were stirred in 2 L of distilled water for 12 hours at room temperature. Then let it be precipitated. The solution was separated by filtration and it was dried in an oven at 110^oC. It was sieved with 400 mesh (LOYKA ESM 200) sieve and stored in polyethylene bags for future.

Preparation of dye solutions

The stock solutions of 500-1000 mg/L (ppm) natural red and basic blue were prepared with ditilled water, and then they were diluted to the desired concentrations (20, 40, 80, 100, 140 mg/L). The pH of the dye solutions was adjusted with 0.1N NaOH (Merk) and 0.1 N HCl (Merk) solutions using a pH meter. The measurement was performed by a WTN pH meter (Series ISOLAB, Laborgerate GmbH).

Effect of initial dye concentration on adsorption

20, 40, 80, 100 and 140 mg/L dyestuff solutions were used to investigate the effect of the initial dye concentration on adsorption. Adsorption experiments were carried out by shaxing 20 mg of sorbent with 50 mL aqueous solution of natural red and basic blue in 250 mL-Erlenmayer flasks placed in a temperature controlled shaxing water bathat different concentrations, pH and temperatures as a function of time. The adsorption of natural red and basic blue on the diatomite was carried out at 25^oC, 35^oC and 45^oC for each concentration. Natural pH values for natural red and basic blue were 6.9 and 6.0, respectively. The amount of natural red and basic blue, q_e were calculated using the folloving equation

$$q_e=(C_0-C_e)V/m \quad (1)$$

where, q_e is the amount of dye natural red and basic blue (mg/g). C_0 and Ce are the initial equilibrium liquid phase concentration of dye (mg/L), respectively. V is the volume dye solution (L), and m adsorbent mass (g).

Bath adsorption studies

Adsorption experiments were carried out in a temperature-controlled shaking water bath at a

stirring speed of 120 rpm by adding 10 ml of dye solutions onto 2 mg of diatomite. After that, 10 ml samples were taken from these mixtures at the specified time intervals (1, 5, 10, 15, 20, 30, 60, 90, 120, 150 and 180 min) and they were centrifuged at 3.500 rpm for 3 min. After centrifuged supernatants were analyzed for the determination of the final concentration of natural red and basic blue by using an UV-vis spectrophotometer. The maximum absorbance values of these samples were measured at 533 nm for natural red and at 617 nm for basic blue at the maximum wavelength in a UV-visible spectrophotometer. The amounts of adsorbed dye on the diatomite were calculated by subtracting from the initial dye concentration.

Equilibrium adsorption isotherm models

The adsorption equilibrium data on the diatomite of the dye were fitted to the Langmuir, Freundlich and Temkin isotherms used commonly.

Lanqmuir isotherm: The adsorbent surface is a single layer on the adsorption where the Langmuir isotherm is valid. This isotherm also increases linearly along with adsorption and adsorbent initial concentration.

$$C_e/q_e=1/K_Lq_m+C_e/q_m \quad (2)$$

The mathematical expression of the Langmuir isotherm is calculated via the dimensionless separation R_L constant defined by Webber and Chakkravorti to find the suitability of adsorption [9].

$$R_L=1/(1+K_LC_0) \quad (3)$$

R_L > Unfavorable adsorption
$0 < R_L < 1$ Favorable adsorption
$R_L = 0$ Irreversible adsorption
$R_L = 1$ Lineer adsorption

R_L: the dimensionless separation factor constant, K_L:Langmuir isotherm constant (L/mg) related to the adsorption energy, C_0: initial concentration (mg/L). The value of R_L constant from 0 to 1 indicates the adsorption nature to be unfavorable, favorable or irreversible [10].

Freundlich isotherm

The Freundlich isotherm is used to describe the adsorption of various adsorbent molecules from solution phase. The lineer form of Freundlich isotherm is representent by the equation

$$q_e=K_F.C_e^{1/n} \quad (4)$$

$$\log q_e=\log K_F+(1/n)\log C_e \quad (5)$$

where q_e is the amount of diatomit adsorbed per unit weight the sorbent (mg/L), K_F is (mg/g) the measure of adsorption capacity and 1/n is the intercept and slope of the plot of log q_e , log C_e respectively. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption.

In this equation K_F $[(mg.g^{-1})\ (mg.L^{-1})]^n$ and n are the Freundlich constants related to adsorption capacity and adsorption intensity.

Temkin isotherm

The heat of adsorption and the adsorbate-adsorbent interaction on adsorption isotherms were studied by Temkin and Pyzhov, who assumed that because of the adsorbate-adsorbent interactions, the energy of the molecules adsorption will decrease linearly with coverage [11].

$$q_e=RT/b_T\ \ln A_TC_e \quad (6)$$

and can be linearized as:

$$q_e= B\ln A_t+B\ln C_e$$

where $B=RT/b_t$ .B is the Temkin constant related to heat of sorption (j/mol), A_t is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature (K). Therefore, by plotting q_e versus ln C_e enables one to determine the constants A_t and B.

Kinetics models

Several kinetic models have been proposed to express the adsorption mechanism of solute molecules onto an adsorbent.

Pseudo-first-order kinetic equation

The linear form of pseudo-first-order model was described by Lagergren

$$dq_t/dt=k_1(q_1-q_t) \quad (7)$$

where q_e and q_t are the amount of solute adsorbed at equilibrium and at a time, t, $(mg.g^{-1})$ respectively, and k_1 is the pseudo-first-order rate constant (min^{-1}). Integration Eq (7) for the initial and conditions t=t, $q_t=q_t$, a linear plot is obtained [12].

$$\log(q_e-q_t)=\log q_e-k_1/2.303.t \quad (8)$$

Pseudo-second-order kinetic

The pseudo-second-order model can express as

$$dq_t/d_t=k_2(q_e-q_t) \quad (9)$$

$$t/q_t=1/k_2q_e^2+t/q_e \quad (10)$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t ($mg.g^{-1}$), k_2 ($g.mg^{-1}.min^{-1}$).

Intraparticle Diffusion Model

This model describes about the diffusion of the adsorbate from the outer surface into the pores of the composite [13-15]. It is also known as Weber and Morris equation is given as

$$q_t=K_p.t^{1/2}+C \quad (11)$$

where K_p is the particle diffusion rate constant ($mg.g^{-1}.min^{-1}$), C characterizes the extent of diffusion. The value of K_p can is obtained by plotting q_t against $t^{1/2}$.

Adsorption thermodynamic study

By evaluating these parameters, it is possible to decide whether the process is spontaneous or not. Reactions happen spontaneously at a given temperature ΔG^0 is a negative value. With the slope and intercept giving the values of ΔH^0 and ΔS^0 respectively. The free energy of an adsorption process is associated with the equilibrium constant by the following.

Thermodynamic parameters such as standard free energy change (ΔG^0), Standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) can be calculated as [16].

$$\Delta G^0=-RT\ln K_d \quad (12)$$

where, ΔG^0 is the free energy exchange (kj/mol), T is the absolute temperature in Kelvin (K), R is the ideal gas constant (8.314 J/mol.K), K_d (L/g) is a thermodynamic equilibrium constant obtained with the Eg.

$$\ln K_d=\Delta S^0/R-\Delta H^0/RT \quad (13)$$

A plot of ln K_d versus 1/T.

Result and Discussions

The diatomite sample was taken from the Van-Çaldıran region in Turkey. The analyses revealed that the diatomic particles are present in a clay-bearing environment and these particles are circular and platelets with a size range of 0.005-0.025 mm. It is seen that diatomite collected from the region consists of SiO_2 in a ratio of 69.70% and a small amount of various oxide compounds based on the analysis performed [17].
(Table-1)

Table-1: Chemical analysis of original diatomite.

Component	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	K_2O	K.K
Massive %	69.70	11.50	4.40	0.65	0.80	1.40	11.55

Effect of initial material concentration on adsorption

Concentrations of 20, 40, 80, 100 and 140 mg/L of natural red and basic blue were studied to determine the effect of initial dye concentrations. The maximum adsorption values at 20 minute for concentrations of 20 and 40 mg/L for natural red was 19.49 mg/g and 39.83 mg/g and for concentrations of 80 mg/L, 100 mg/L and 140 mg/L, the maximum adsorption values at 150 minute were determined to be 39.94 mg/g, 79.88 mg/g, and 99.72 mg/g, respectively. The maximum adsorption values at 20 minute for concentrations of 20 and 40 mg/L for basic blue was 19.65 mg/g and 39.60 mg/g and for concentrations of 80 mg/L, 100 mg/L and 140 mg/L, the maximum adsorption values at 150 minute were determined to be 79.67 mg/g, 99.22 mg/g, and 139.05 mg/g, respectively. These results showed that at low concentrations, the adsorption has similar trends and at a very early point of times, adsorption reaches the equilibrium. After this point, there is no significant change in the amount of adsorbed material. It has been also observed that an increase in the concentration led to an increase in the adsorption.

Adsorption isotherms

Freundlich isotherm

The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process and the smaller 1/n, the greater the expected heterogeneity. The Freundlich isotherms plotted on diatomite at different temperatures in the adsorption of natural red and basic blue is shown in Fig. 2. Using the Freundlich isotherm, the value of n found natural red 1.2921 and basic blue 1.6326 denotes spontaneous adsorption. Values of n in the range $1<n<0$ indicate favorable bio sorption [18]. As the amount of the adsorbed substance is quite low in the solution, the results were calculated as negative values.

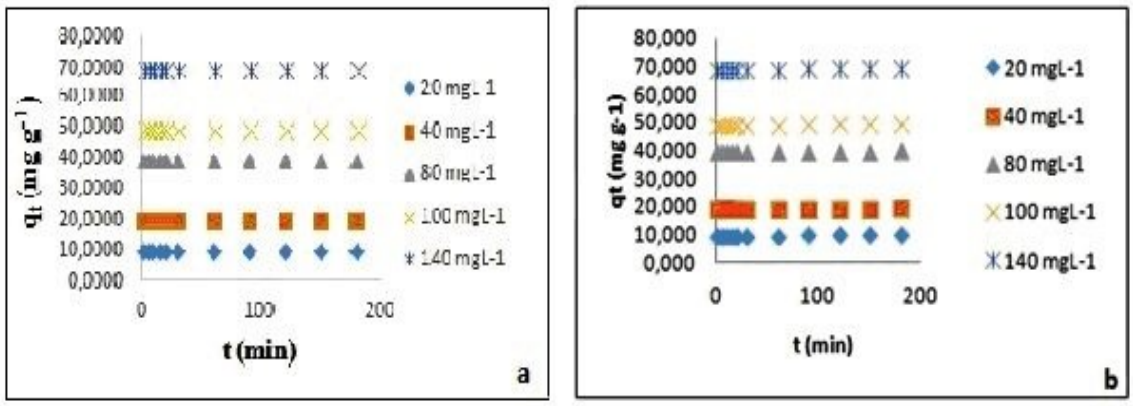


Fig. 1: (a). Effect of initial concentration on adsorption of Natural red on diatomite surface (R=25^{0}C,pH=6.9, w/v=20mg) (b). Effect of initial concentration on adsorption of Basic blue on diatomite surface(R=25^{0}C, pH=6.0, w/v=20mg).

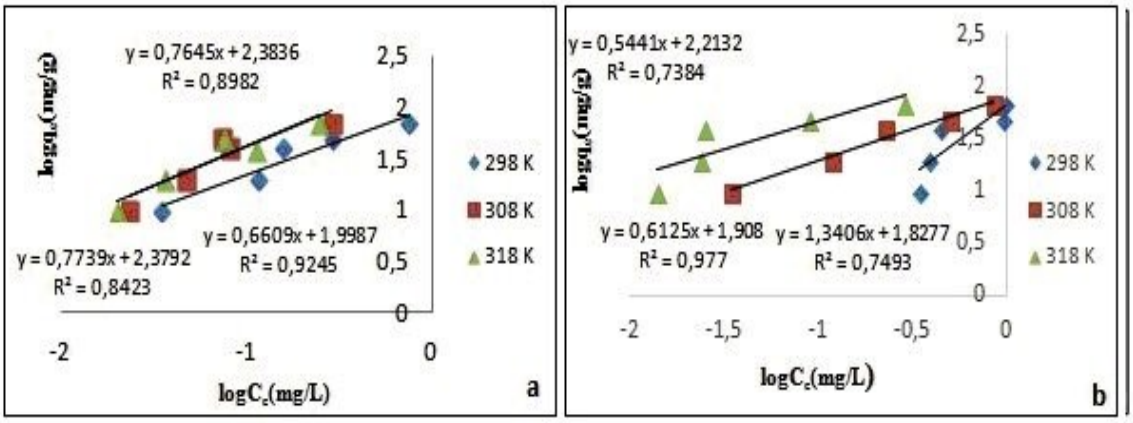


Fig. 2: (a). Freundlich isotherm of adsorption of natural red of diatomite (pH:6.9, w/v:20 mg) (b). Freundlich isotherm of adsorption basic blue of diatomite (pH: 6.0, w/v:20 mg).

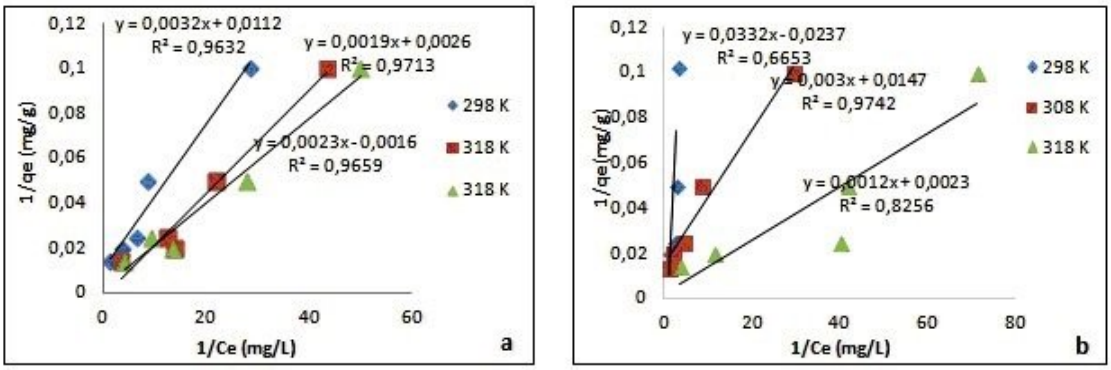


Fig. 3: (a) Langmuir isotherm of adsorption natural red onto diatomite at various temperatures (pH:6.9, w/v:20 mg) and (b). Langmuir isotherm of adsorption of basic blue onto diatomite at various temperatures(pH:6.0, w/v:20 mg).

Freundlich constants and the correlation values of lines plotted using n values of these two dyes are given in Table-2.

It was seen that the correlation values obtained for the natural red shows compatible trends with Freundlich isotherm. The Freundlich isotherm is compatible with basic blue at 308K. n value greater than 1 indicates that the diatomite is favorable for adsorption of natural red and basic blue. It is known that when the correlation coefficient approaches 1, the favorability increases [19].

Table-2: Freundlich isotherm constant in the adsorption of natural red and basic blue on diatomite at different temperatures.

	Natural red			Basic blue		
T(K)	298	308	318	298	308	318
K_F (mg/g)	0.3007	0.3764	0.3772	0.2850	0.2805	0.3450
n	1.5130	1.2921	1.3080	0.7459	1.6326	1.8378
R^2	0.9245	0.8423	0.8982	0.7493	0.9770	0.7384

Langmuir isotherm

The Langmuir constants, the correlation values of lines plotted using q_m and K_L values of two dyes at different temperatures are given in Table-3. As seen from Table-3, The Langmuir isotherm constant, q_m and K_L increased with increasing the temperature, indicating that the sorption density was higher at higher temperatures [20].

Table-3: Langmuir isotherm constants in adsorption on natural red and basic blue on diatomite at different temperatures.

	Natural red			Basic blue		
T (K)	298	308	318	298	308	318
K_L(L/mg)	0.2856	1.5174	0.7307	1.4009	0.2040	0.5231
q_m(mg/g)	312.5	434.7	526.3	30.1	333.3	833.3
R_L	0.1489	0.0318	0.0640	0.1492	0.0297	0.0264

As can be seen from the table, since the correlation coefficient values of natural red at different temperatures is high, it can be said that it is compatible Langmuir adsorption model. The value of R_L found natural red (0.1489, 0.0318, 0.0640) and basic blue (0.1492, 0.0297, 0.0264) is between 0 and 1. It can also be seen that the Langmuir isotherm is compatible with basic blue at 308 K. Based on these results, adsorption for natural red occurred in homogeneous regions on diatomite and it can partially occur for basic blue. Langmuir isotherm constant on diatomite of natural red q_m (312.5, 434.7, 526.3) and basic blue q_m (30.1, 333.3, 833.3). K_f natural red (0.3007, 0.3764, 0.3772) and basic blue (0.2850, 0.2805, 0.3450). As can be seen from the values, the adsorption capacity for each dyestuff is reduced due to competition from the dyes. [21-23].

Temkin isotherm

Temkin isotherm for natural red and basic blue is given in Fig. 4. Temkin isotherms for natural red and basic blue are shown in Fig 4(a) and Fig 4(b). Temkin isotherm equilibrium binding constant A_T and constant related to heat of adsorption.

$q_e = (RT/b_T)\ \ln K_T + (RT/b_T)\ \ln C_e$

$B = RT / b_T$ and correlation values for the two dyes are given in Table-4. It can be said that the correlation values obtained for natural red are compatible with Temkin and it is compatible at 308K for basic blue [24-26].

Table-4: Temkin isotherm constant on diatomite of natural red and basic blue at different temperatures.

	Natural red			Basic blue		
Temp.(K)	298	308	318	298	308	318
b_T	121.94	108.69	107.05	57.74	139.75	144.75
A_T	4.80	4.68	3.20	3.75	2.90	2.90
R^2	0.9384	0.9111	0.9172	0.8358	0.9452	0.8890

Kinetic models

For the interpretation of the kinetic batch experimental data three different kinetic models were used: (1) the pseudo-first order kinetic model, (2) the pseudo-second order kinetic model and (3) the intra-particle diffusion model.

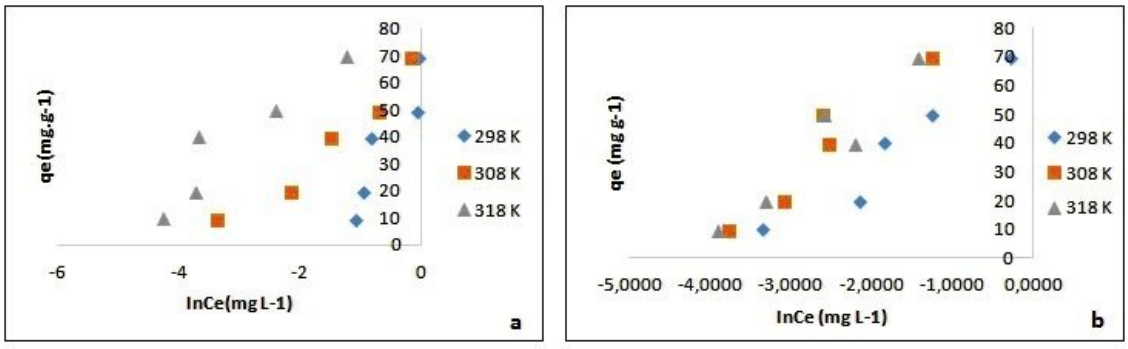


Fig. 4: (a) Temkin isotherm in the adsorption of Natural red onto diatomite (pH:6.9, w/v:20 mg) and (b). Temkin isotherm in the adsorption of basic blue on diatomite (pH:6.0, w/v:20 mg).

Table-5: Intra-particle diffusion, pseudo-first and-second order kinetic parameters of natural red adsorption onto diatomite and basic blue concentrations (T=298 K).

Adsorbent	Concentration ($mg.L^{-1}$)	q_e, experimental ($mg.g^{-1}$)	pseudo-first order			pseudo-second order			intraparticle diffusion model	
			k_1 (min^{-1})	q_e, calculated	R^2	k_2($g.mg^{-1}min^{-1}$)	q_e, calculated	R^2	k_i	R^2
Natural red diatomite	20	9.98	0.0603	0.0246	0.8135	1.022	9.99	1	0.029	0.6204
	40	19.97	0.0439	0.0455	0.9627	0.011	20.449	0.9794	0.089	0.9166
	80	39.96	0.0508	0.0817	0.9356	0.892	40.00	1	0.075	0.9312
	100	49.96	0.0377	0.0768	0.9846	2.020	49.75	1	0.042	0.9399
	140	99.79	0.0112	0.0499	0.4619	0.964	69.44	1	0.097	0.9825
Basic blue diatomite	20	9.98	0.0377	5.142	0.5648	3.44	9.83	1	0.0007	0.5147
	40	19.94	0.0865	0.088	0.8554	0.94	19.84	1	0.0965	0.7420
	80	39.88	0.0255	0.133	0.7401	0.371	39.84	1	0.0243	0.8541
	100	49.75	0.0366	0.201	0.7777	0.340	49.50	1	0.0208	0.9408
	140	69.58	0.0251	0.188	0.8411	0.414	69.44	1	0.0207	0.9395

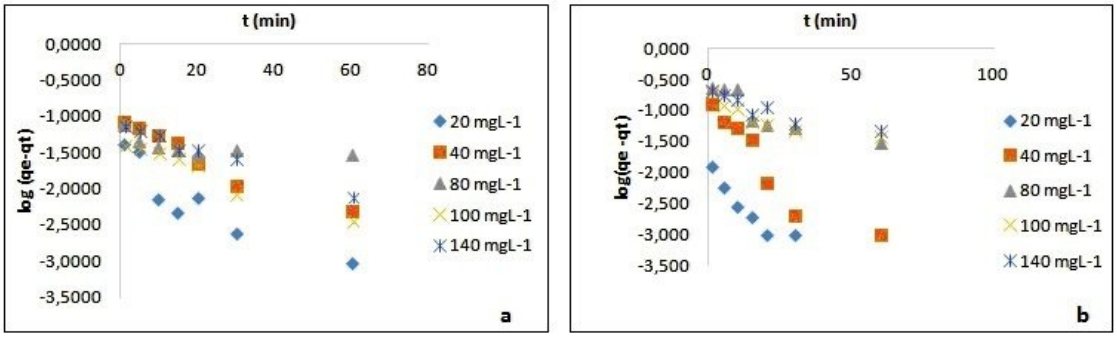


Fig. 5: (a). Pseudo-first orders kinetics of natural red adsorption on diatomite different concentrations at 298 K (b). pseudo-first order kinetics of basic blue adsorption on diatomite different concentrations at 298 K.

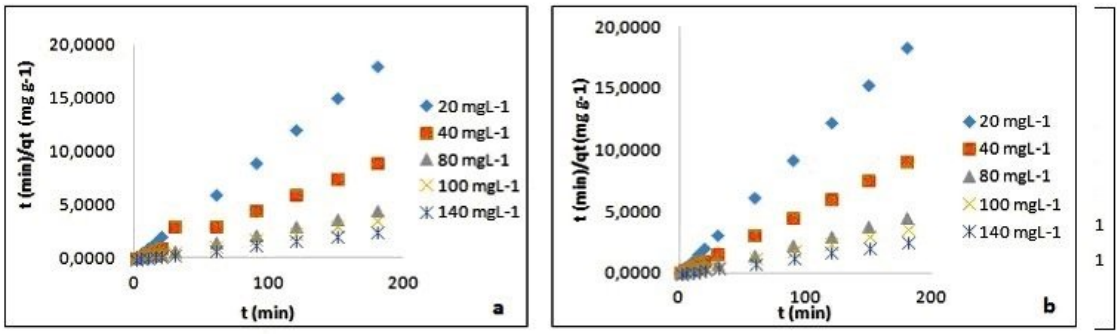


Fig. 6: (a). Pseudo-second order adsorption kinetics of natural red onto diatomite different concentrations and at 298K (b). pseudo-second order adsorption kinetics of basic blue onto diatomite different concentrations at 298 K.

It can be said that the correlation values on the chart are low as the adsorption does not fit the kinetic model of the pseudo- first order. The q_e values obtained from the equations should be the same or similar to the experimental q_e values [27-29]. It was observed that the kinetic truths and correlation values (R^2=1) obtained for natural red and basic blue. As the q_e values obtained from the equations are close to the experimental q_e values, it can be said that the adsorption is compatible with kinetic modeling from the pseudo-second order. This suggests that both dyes may have a chemical interaction with the diatomite [30-32].

When the intra-particulate diffusion line was examined, it was observed that the intra-particle velocity constant values increased in concentration residue [33].

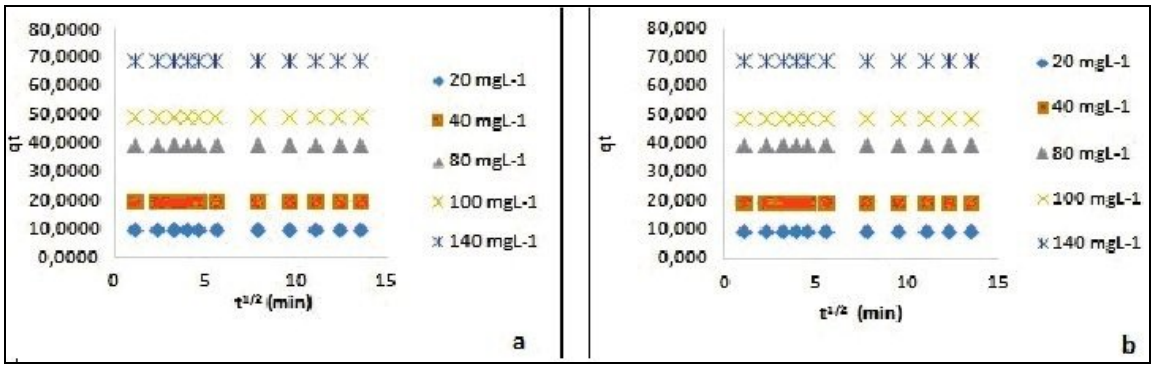


Fig. 7: (a) intraparticle diffusion drawings for natural red and diatomite adsorption different concentration at 298 K and (b). intraparticle diffusion drawings of basic blue and diatomite adsorption different concentration at 298 K.

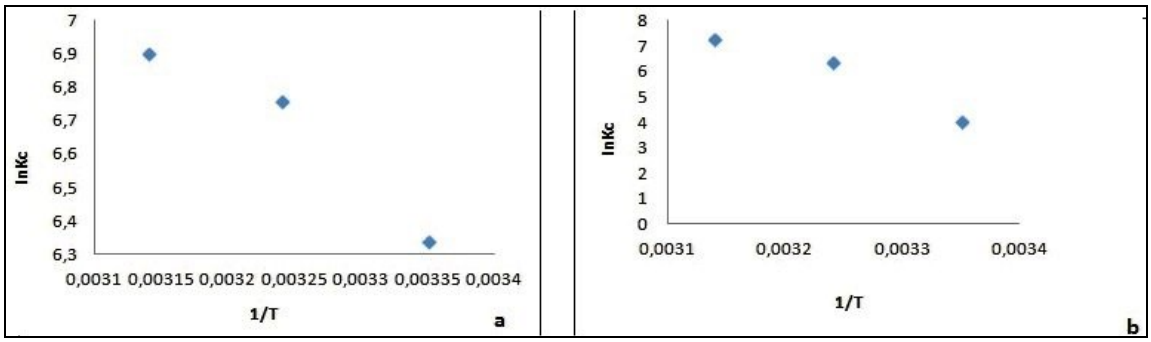


Fig. 8: (a). Clausius-Clapeyron equation for the adsorption of natural red with diatomite (C_o =20mg/L, pH=6.9) and (b). Clausius-Clapeyron equation for basic blue adsorption with diatomite (C_o=20 mg/L, pH=6.0) .

Table-6: Themodynamic parameters of natural red (C_0:20 mg.L^{-1}, pH:6.9) and basic blue (C_0:20 mg.L^{-1}, pH:6.0) of different temperatures.

Natural red					Basic blue				
Temperature (^{0}C)	K_c	ΔG^0 (j.mol^{-1})	ΔH^0 (J.mol^{-1})	ΔS^0 (j.mol^{-1}.K^{-1})	Temperature (^{0}C)	K_c	ΔG^0 (j.mol^{-1})	ΔH^0 (j.mol^{-1})	ΔS^0 (j.mol^{-1}.K^{-1})
25	6.34	-15707.8			25	4.05	-10034.1		
35	6.76	-17029.3	22323.4	127.2	35	6.37	-16311.7	126904.8	461.2
45	6.90	-18242.5			45	7.26	-19194.3		

The standard Gibb's free energy (ΔG^0) values for natural red and basic blue were observed as negative. Accordingly, it can be said that the adsorption process by diatomite of both dyes is a spontaneous process. Regarding these dyes, ΔG^0 decreases with increasing temperature. This indicates that a higher adsorption is actually occurred at higher temperatures. At higher temperature, ions are readily desolvated and thereby their adsorption becomes more favorable [34-36]. Standard enthalpy (ΔH^0) and standard entropy (ΔS^0) values of natural red and basic blue are found. Positive enthalpy indicates that adsorption is endothermic, while positive values of ΔS^0 indicate changes in adsorbent surface [37].

Conclusions

In this paper, concentration on adsorption seems to be high. With increasing concentration, the adsorption was completed longer. With increasing concentration, the amount of dyestuff per gram of adsorbent increased, while adsorption of the face decreased. It has been found to be compatible with Langmuir isotherm model for natural red, and 308K for basic blue. The adsorption for natural red is partly performed in homogeneous regions on the diatomite and this was performed partly for basic blue. Both dyes have shown that the pseudo second-order kinetic model looks better for the Freundlich isotherm model for natural red. As the amount of the adsorbed substance is quite low in the solution, the results were

calculated as negative values. The negative ΔG^0 values obtained at all contact temperatures of the biosorption process were found to be a spontaneous process of adsorption by diatomite from both dyes. Adsorption has been found to be more suitable at higher temperatures. Diatomite can be classified as a highly effective adsorbant compared to other low-cost adsorbents.

References

1. P. Miretezyk and A. F. Cirelli, Fluoride removal from water by Chitosan derivatives and composites, A review, *J. of Fluorine Chem.* **132**, 231 (2011).
2. J. F. Lemonas, *Am. Ceram. Soc. Bull*, **76**, 92 (1997).
3. B. Taş and M. Çetin, Biyolojik orijinal tek doğal mineral; Diyatomit, Tübay Bilim Dergisi, **512**, 28 (2012).
4. N. Çalışkan, A. R. Kul, S. Alkan, E. G. Söğüt and İ. Alacabey, Adsorption of Zinc (II) on diatomite and manganase-oxide-modified diatomite: A kinetic and equilibrium study, *J. of Haz. Mat*., **193**, 27 (2011).
5. Y. Bulut, N. Güzelbenli, and H. Aydın, Equilibrium and kinetics studies for adsorption of direct blue 71 from aqueous solution by wheat shells, *J. of Haz. Mat*., **144**, 300 (2007).
6. L. Rozic, T. Novakovic, S. Petrovic, Z. Vukovic and Z. Cupic, Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution, *Chem. Ind. Eng*. **14**, 4 (2008).
7. K. Palmer, An overview of potential environmental impact from industrial activity, Industrial Pollution Handbook. H. M. Freeman (Ed), Mc Graw Hil, Industrial Pollution Handbook, (1995).
8. M. A. M. Khraisheh, Y. S. All-Degs and W. A. M. The use of Acacia tortilis leaves as a low-cost adsorbent environment, *Chem. Eng*., **99**, 177 (2004).
9. M. Ackacha and L. Elsharif, The use of Acacia tortilis leaves as a low-cost adsorbent environment, Conf. a Geo and Env. Sci. Jeju Island, South Korea, (2012).
10. R. K. Prasod and S. N. Srivastova, of distillery spent wash onto fly ash: Kinetics and Mass Transfer Studies, *Chem. Eng. J*., **146**, 90 (2009).
11. J. M. Smith and H. C. Van Ness, Introduction to chemical engineering thermodynamics, Mc Graw-Hill Publishing Company, New York, (1987).
12. Y. S. Ho, Mc. Kay, J. Waseda and J. C. F. Foster, Study of the sorption of divalent metal ions on to peat, Sci.&Tech., **18**, 639 (2000).
13. W. I. Weber and J. C. Morris, Kinetics of adsorption on carbon from solution, *J. of the Sant. Eng. Div. American Soc. of Civil Eng*., **89**, 31 (1963).
14. A. A. Alshaheri, M. İ. M. Tahir, M. B. A. Raman, T. B. S. A. Ravoof and T. A. Saleh, Catalytic oxidation of cyclohexane using transition metal complexes of dithiocarbazate Schiff base, *Chem. Eng. J.*, **327**, 423 (2017).
15. G. I. Danmaliki and T. A. Saleh, Effect of bimetallic Ce/Fe nanoparticles on the desulfurization of thiophones using activated carbon, , *Chem. Eng. J*, **307**, 914 (2017).
16. M. Ackacha and L. Elsherif, The use of Acacia Tortilis leaves as low-cost adsorbent to reduce the lead cations from an aquatic environment, Int. Con. On Geo. And En. Sci. Jeju Island, South Korea, 80 (2012).
17. S. Eda and N. K. Çalışkan, Çaldıran-Van diatomiti: Modifikasyonu ve fizikokimyasal özellikleri, Fen-Bil.Ens, Universty of Y.Y.Ü Van, (2015).
18. L. Shifera, K. Siraj and A. Yifru, Adsorption of lead (II) and chromium (VI) onto activated carbon prepared from pineapple peel: Kinetics and themodynamic study. *Ind. J. Chem. Tech.*, **24**, 145 (2016).
19. S. Çoruh, H. E. Gürkan, E. Kılıç and F. Geyikli, Rediction of Adsorption efficiency for the removal malachite green and acid blue 616 dyes by waste marble dust using ann. *Global Nest J*, **16** (2014).
20. F. Güzel, H. Saygılı, G. A. Saygılı, F. Koyuncu and C. Yılmaz, Optimal oxidation with nitric acid of biochar derived from pyrolysis of weeds and its application in removal of hazardous dye methlene blue from aqueous solution. *J. Cle. Pro* **144**, 260 (2017).
21. D. Liu, S. Dong, A. Maimaiti, B. Wang, J. Huang, Y. Wang, G. Yu, As (III) and As (V) adsorption on nanocomposite of hydrated zirconium oxide coated carbon nanotubes, *J. Colloid Interface Sci.,* **511**, 277 (2018).
22. S. Wang and E. Ariyonto, Competitive adsorption of malachite gren and Pb^{+2} ions on natural zeolite, *J. of Col. and Int. Sci*., **314**, 25 (2007).
23. B. P. Han, Y. Wang, Q. Sun, L. Wang, J. Song, X. He and C. Dou, Malachite green adsorption onto natural zeolite and reuse by microwave irradiation, *J. of Haz. Mat.*, **175**, 1056 (2010).

24. M. J. Temkin and V. Pyzhev, Recent Modifications to Langmuir isotherms, *Acta Phsiol. Chem*. USSR, **12**, 271 (1940).
25. E. Hosienzadeh, A. R. Rahmanie, G. Asgari, G. McKay, A. R. Dehghanian, Adsorption of acid black 1 using activated carbon prepared from scrap tires: kinetic and equilibrium studies, *JSIR*, **71**, 682 (2012).
26. A. Tawfik K. O. Saleh, S. A. Sulaiman, S. A. Al-Hammadi, H. Dafalla, G. I. Danmaliki, Adsorptivite desulfurization of thiophene, benzothiophene and dibenzothiophene over activated carbon manganese axide nanocomposite: with column system evaluation. *J. Cle. Pro*, **154**, 401 (2017).
27. F. Güzel, H. Saygılı, G. Akkaya, F. Koyuncu, C. Yılmaz, Optimal oxidation with nitric acid of brochar derived from pyrolysis of weeds and its application in removal of hazardous dye methylene blue from aqueous solution. *J. Cle. Pro*, **144**, 260 (2017).
28. G. I. Danmaliki, T. A. Saleh, Influence of conversion parameters of waste tires to activated carbon on adsorption of dibenzothiophene from model fuels. *J. Cle. Pro*, **117**, 50 (2016).
29. T. A. Saleh, G. I. Danmaliki, Adsorptivi desulfurization of dibenzothiophene from fuels by rubber tyres-derived cabons: Kinetics and isotherms evaluation. Process Safety and Environmental Protection, **102**, 9 (2016).
30. S. Wang, H. Li and L. Xu, Application of zeolite MCM-22 for basic dye revomal wastewater, *J. of Col. and Int. Sci.*, **295**, 71 (2005).
31. M. Uğurlu and M. H. Karoğlu, Adsorption of amonium from an aqueous solution by fty ash and sepiolite, *Micr. and Mes. Mat*., **139**, 173 (2011).
32. N. Dizadji, N. Aboatalebi and N. Nouri N, Adsorption of chromium and copper in aqueous solutions using tea resudi, *Int. J. Env. Sci. Tec*., **8**, 3 (2011).
33. S. M. Re and P. D. Allen, Removal of Cu(II) and Cd(II) from aqueous solution by seafood processing waste sludge, *Water Research*, **35**, 534 (2001).
34. F. Y. Wang, H. Wang and J. W. Ma, Adsorption of Cd(II) ions from aqueous solution by a new low cost adsorbent-Bamboo charcool, *J.of Haz. Mat.*, **177**, 300 (2009).
35. L. Xiao-ming, W. Zheng, D. Wang, Q. Yang, J. CaO, X. Yue, T. Shen and G. Zeng, Removal of Pb(II) from aqueous solutions by adsorption onto modified areca waste: Kinetic and thermodynamic studies, Desalination, **258**, 148 (2010).
36. M. Delaver, A. A. Ghoreyshi, M. Jahanshahı, S. Khalili and N. Nabian, *Chem. Ind. Eng.Q*, **18**, 2 (2012).
37. A. J. Habish, S. Lazarevic, I. J.Castvan, B. Konvonjak, D. Janockovic and R. Petrovic, *Chem. Ind. Eng. Q*, **21**, 2 (2015).