THERMODYNAMIC AND ISOTHERM STUDIES OF RHODAMINE B REMOVAL FROM WASTE WATER USING VAN PUMICE

Ali Rıza KUL

Science Faculty of Yuzuncu Yıl University,65300,Van,Turkey, alirizakul@yyu.edu.tr

Hasan ELİK

Science Faculty of Yuzuncu Yıl University,65300,Van,Turkey

Veysel BENEK

Science Faculty of Yuzuncu Yıl University,65300,Van,Turkey

ABSTRACT

Coloring Materials are among the pollutants that must be removed from the waste water due to their carcinogenic effects. With adsorption, we can effectively and cheaply remove such contaminants. Adsorption is carried out using porous materials such as pumice, clay or activated carbon.In this study, it is aimed to remove Rhodamine B dye from waste water by using Van pumice. The samples were taken and applied to Freundlich and Langmuir isotherm models and the process was found to be compatible with the Freundlich isotherm model. In addition, thermodynamic parameters were calculated and it was calculated that the adsorption process was spontaneous and endothermic.

Keywords: Thermodynamics, Isotherm, Rhodamine B, Dyestuff, Van Pumice, Adsorption

INTRODUCTION

Environmental pollution has become a major problem for humanity as a result of the rapidly developing industry. As a result, increasing pollution pollutes environment, groundwater and all living things are affected negatively. The material used to make the surface of the objects look more beautiful is called paint. The materials applied to make the materials such as fabric and fiber colored are called the dye. The dye' structure may be inorganic or inorganic, undissolved, crystalline or perticular. They can be separated by scouring from the surface they are applied to. However, since the dyestuffs are organic and interact with the surface,they do not separate from the surface by washing or scouring (Yağız, 2016).

Rhodamine B is a dyestuff used for industrial dyeing.

1. Rhodamine B

Rhodamine B (RB) is defined as rhodamine basic violet 10, rhodamine 610. Rhodamine B is highly soluble in water. It is generally found in the group of dye substances with basic properties but at the same time Rhodamine B has amphoteric properties. Rhodamine B is commonly used as a coloring agent in the textile industry, food industry, pharmaceutical industry and microbiological studies. However, due to the fluorescent effect, it is used for hydrogeological studies in order to follow the waterways (Baran, 2012).

2.- Adsorption

Adsorption is divided into different sub-parts in the form of physical adsorption, chemical adsorption, displacement adsorption. Physical adsorption occurs by adhesion of the substance to be adsorbed to the solid surface as a result of weak Van der Waals forces. During chemical adsorption, a chemical bond is formed between the substance adsorbed and the surface. This requires high energy for this and it is usually irreversible. Displacement adsorption is the phenomenon of the dissociation of solute ions in the solution by electrostatic forces into the surface-charged regions. For equally charged ions, molecular size determines the choice of adsorption, usually smaller ions are preferred (Tantekin, 2006).

3. Pumice

Pumice is a light, porous and heat insulated rock type which is formed as a result of the lava emerging to the earth and then suddenly cooling down and the gases leaving the structure. As in many places, pumice is often used as building material in our country. Pumice named with more than one name; Also known as pumice, heel stone, tuff or pumice stone. Turkey ranks second in the world in terms of total reserves of pumice. The significant seams are located in Tatvan and Ahlat, Niğde-Nevşehir vicinity, Iğdır and Kars, Mollakasım (Van), Erciş (Van), Güdül (Ankara), Doğubeyazıt (Ağrı) and Cumaovası (İzmir). The pores in the pumice are smaller than 1 mm. The pores are irregular and spherical, oval, elongated tubular (Benek, 2015). Pumice is also used in adsorption processes due to its porous structure. In this study, we used Van Pumice which is found in the Van area.

MATERIAL AND METHOD

1. The milling process: Pumice was primarily pulverized into powder and then sieved through a 230 mesh screen. After being stirred for 3 hours in 1 liter of water, pumice was placed in storage containers for use in experiments after it was dried by oven drying method at 45 ° C.

2. Preparation of the solution: 1 g of Rhodamine B was taken and it was completed to 1 liter in volumetric flask thus 1000 ppm stock solution was prepared. In adsorption equilibrium studies 2 g of pumice were treated with 1000 L Rhodamine B solutions. In 30 ppm, 40 ppm, 50 ppm and 60 ppm concentrations, Rhodamine B solutions prepared at pH 5, were shaken at 298 K, 308 K and 318 K temperatures and at different times (5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 200, 240, 300 minutes). Concentration was studied depending on temperature and time by keeping the Rhodamine B adsorption pH constant at 5 inside the pumice sample. All adsorption measurements were made with T80 + UV / VIS model spectrophotometer.

RESULTS AND DISCUSSION

1. Isometric studies of pumice on Rhodamine B

Adsorption studies were conducted on the Langmuir and Freundlich isotherm model.

1.1. Freundlich isotherm model

The Freundlich isotherm model is used to describe the heterogeneous surface of the adsorbent (Köylü et al., 2015). The linear shape of the Freundlich isotherm model is as follows. (Khan et al., 2011):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (1)$$

Here KF represents the power of the relationship between adsorbed and adsorbent. High values of KF show that the proximity of the adsorbent material to the adsorbed material is very high for each other. qe is the amount of adsorbed material on the unit adsorbent (mg/g), Ce is the heavy metal concentration remaining in solution after adsorption (mg/L) and n is the expression of the adsorption intensity. Generally, n values between 1 and 10 is a good indication that it is a good adsorption. The 1/n value is the heterogeneity factor and takes values in the range 0-1.When the n value is close to zero, it shows that the surface heterogeneity is high. The KF and n constants are found with graphical casting of the alteration of logqe against logCe. The y-axis cut point of the line obtained from the graph gives Log KF and its slope gives 1/n.

1.2. Langmuir isotherm model

Langmuir isotherms are based on assumptions that molecules adsorbed on the surface are in a single layer and that there is no covering on all sides of the surface but the holding energy is the same throughout the surface. Langmuir isotherm model is shown below.

$$q_e = \frac{q_m x K_L x C_e}{1 + K_L x C_e} \quad (2)$$

Here, qm shows the maximum adsorption capacity of adsorbent (mg/g), KL shows the Langmuir adsorption constant and Ce shows the amount of the substance remaining after the solution is adsorbed (mg/L). If necessary corrections are made in the equation;

$$\frac{C_e}{q_e} = \frac{1}{q_m x K_L} + \frac{C_e}{q_m} \quad (3)$$

is obtained. If the C_e/q_e value is plotted against the C_e value, then the slope will be 1/qm.; The shift will give a value of 1/qmKL. Table 1 gives the Langmuir and Freundlich isotherm data calculated using the above links.

T (K)	Langmuir			Freundlich		
	b (L/mg)	q_m (mg/g)	R^2	n	K_F (mg/g)	R^2
298	-22,59	1,5105	0,886	0,1272	$7,5x10^{-10}$	0,9730
303	24,005	-3,5580	0,870	0,2366	0,000056	0,9500
308	-0,0405	-5,000	0,583	0,2930	0,00074	0,8000

Table 1. *Calculated Freundlich and Langmuir parameters*

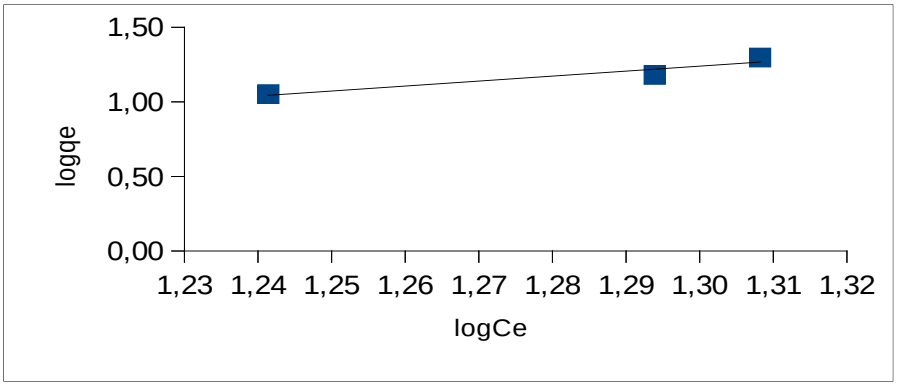

Figure 1: *Freundlich graph (308 K) drawn for the adsorption of Van Pumice on Rhodamine B*

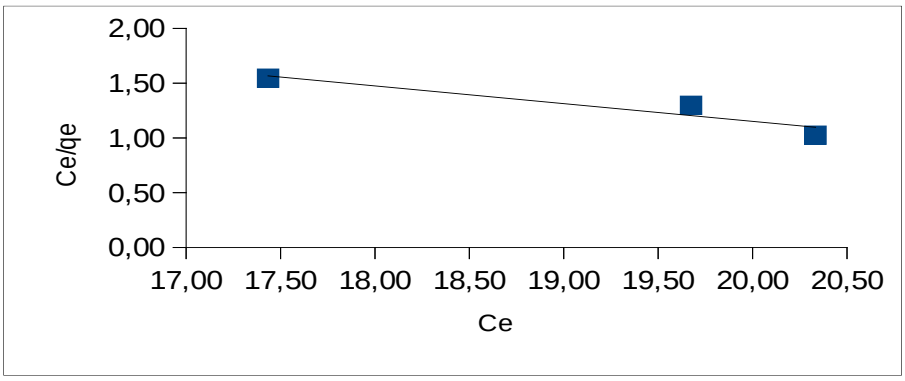

Figure 2: *Langmuir graph (308 K) drawn for the adsorption of Van Pumice on Rhodamine B,*

When we look at the isothermal data of Van pumice calculated on Rhodamine B it was observed that adsorption is more appropriate to Freundlich isotherm and the best result was found to be at 303 K with R2 = 0.9156.

3.2. Thermodynamic studies of Pumice over Rhodamine B

The enthalpy, entropy and free energy changes for the adsorption process can be determined using the equilibrium constant. These thermodynamic parameters are shown in the following equations.

$$\Delta G = -RT\ln K_c \quad (4)$$

$$\ln K_C = -\Delta H/RT + \Delta S/R \quad (5)$$

Here, ΔG is the standard Gibbs release energy, ΔH is the standard enthalpy, and ΔS is the standard entropy. ΔH and ΔS, respectively, is calculated from the slope and cut-off point of 1/T graph against lnKc. Adsorption equilibrium constant is expressed as:

$$K_c = C_{ads}/C_e \quad (6)$$

Here, C_{ads} is the concentration of adsorbed dye at the moment of equilibrium (mg/L), C_e is the concentration of the residual dye in solution at the time of equilibrium (mg/L). The thermodynamic parameters calculated using the above equations are given below.

T (K)	K_c	ΔG°, J/mol	ΔH°, J/mol	ΔS°, J/mol.K
298	1,4492	-154,2237		
308	1,5414	-179,8765	0,0113	0,0320
318	1,6890	-217,8933		

Table 2. *Thermodynamic calculations of pumice on Rhodamine B*

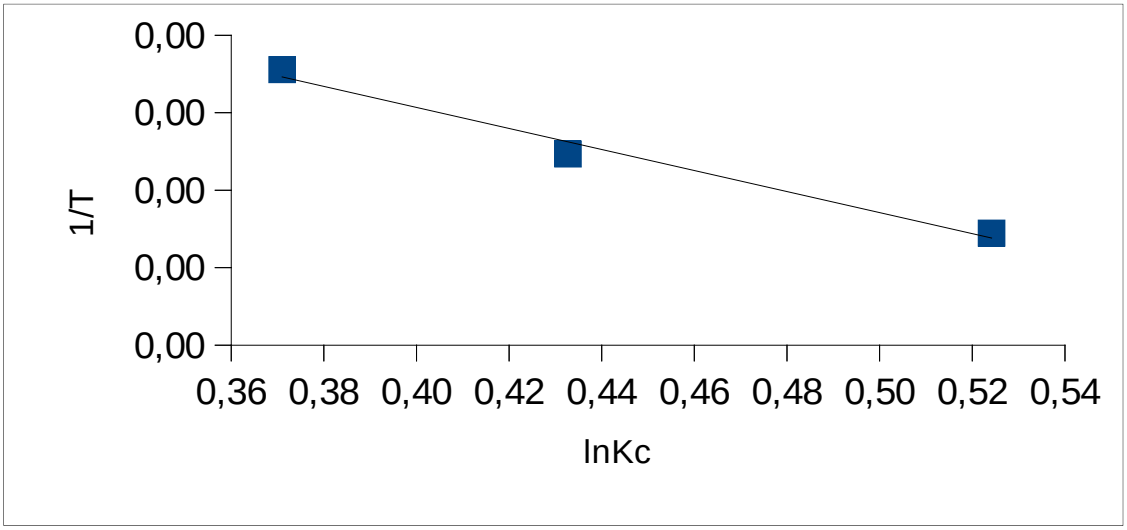

Figure 3: *Thermodynamic graph of the pumice calculated on Rhodamine B (50 mg / L)*

The positive value of ΔS indicates that the entropy increases so that the process is spontaneous. The ΔG value is negative for all temperature values and tends to decrease as the temperature increases. This is another finding indicating that the process is spontaneous. We can see the positive value of ΔH and say that the adsorption process is endothermic.

3. Kinetic Study Of Rhodamine B From Waste Water Using Van Pumice

It is very important to clarify the mechanism of an event and depending on this elucidation the interpretation of the experimental data for the processes to be designed. For this, it is essential to find the speed determination station of the event. With the understanding of adsorption kinetics effective adsorbent - adsorbent contact time /the retention period is found. Kinetic is an important step in understanding the adsorption steps that affect the speed of the adsorption process. The equations used to determine the adsorption speed are:

• First-order pseudo Reaction speed equilibrium, Lagergren equality:

$$\text{Log}(q_e - q_t) = \log q_e - (k_1/2.303)\, t \qquad (7)$$

To use this equation in the results obtained from experiments, qe (adsorption capacity in balance) value must be found in advance by extrapolating the experimental data for t = ∞.

• Second-order pseudo Reaction speed equilibrium, Ho equality:

$$t/q_t = [1/k_2 q_e^2] + (1/q_e)\, t \qquad (8)$$

here,

k_1 Lagergren, Second-order pseudo, Adsorption speed constant (dk^{-1})

k_2 Ho Second-order pseudo Adsorption speed constant (g/mg.dk)

q_e Amount of adsorbed material on the unit adsorbent(mg/g)

q_t The amount of dye adsorbed in time t (mg/g)

Log (qe - qt) values are plotted separately against t value of t and t/qt values and then k1 and k2 values are calculated. (Kayacan, 2007).

T (K)	k_2	Theoric q_e (mg/g)	Experimental q_e (mg/g)	R^2
298	0,0013	17,9179	14,7925	0,9624
308	0,0023	17,1229	15,1630	0,9829
318	0,0034	17,1020	15,7030	0,9939

Table 3. *Second order kinetic calculations (50 mg/L)*

T (K)	k_1	Teorik q_e (mg/g)	Deneysel q_e (mg/g)	R^2
298	0,0258	17,7807	14,7925	0,9691
308	0,0477	25,4731	15,1630	0,8590
318	0,0396	19,4911	15,7030	0,9608

Table 4. *First order kinetic calculations (50 mg / L)*

DISCUSSION AND CONCLUSION

In this study, the adsorption study of Rhodamine B on Van pumice was examined. The resultant was applied to the Langmuir and Freundlich isotherms and adsorption was found to conform to the Freundlich isotherm. As a result of adsorption, when ΔH is greater than zero it indicates that the process is endothermic, and when ΔS is also greater than zero it indicates that the irregularity in adsorption increases. The process is spontaneous and this can be explained by the fact that ΔG is negative. All these results show that the Rhodamine B adsorption process on Van pumice is a appropriate method. Our work has been directed towards the removal of Rhodamine B from waste water using Van pumice. The resulting samples were centrifuged at the end of the study. These were then read in a spectrophotometer. And values have been applied to first-order pseudo-and second-order pseudo-kinetic equations. When we look at the data, because the correlation value of the process is large, it is concluded that it is appropriate to second order kinetic model.

REFERENCES

Baran, E. (2012). Investigation of Adsorption of Malachite Green and Rhodamine B on Zeolite Surface in Single and Dual Systems (Master Thesis). Kilis 7 Aralık University Institute of Science, Kilis.

Benek, V. (2015). The Use of Some Natural Pumice Stone in the Van Region for the Adsorption of Some Heavy Metals(Master Thesis). Yüzüncü Yıl University, Van.

Kayacan, S. (2007). Removal of dyes from coal and odors from aqueous solutions (Master thesis). Ankara University, Institute Of Science, Ankara.

Khan, T. A., Sharma, S., & Imran, A. (2011). Adsorption of Rhodamine B dye from aqueous solution onto acid activated mango (Magnifera indica) leaf powder: Equilibrium, kinetic and thermodynamic studies, (3), 286–297.

Köylü, E., Gonen, F., & Nalan, F. (2015). Color Removal from Waste Water of Textile Industry Containing Acidic Dyestuffs by Adsorption Method Anadolu University Journal of Science and

Technology-A Applied Sciences and Engineering, 16(2), 145. https://doi.org/10.18038/btd-a.48423

Tantekin, T. (2006). Investigation of Adsorption of Activated Carbon from Waste Apricots of Various Dyes Used in Malatya Textile Factories (Master Thesis). İnönü University, Institute of Science, Malatya.

Yağız, A. (2016). Adsorption of Textile Dyestuffs from Aqueous Solutions Using Kiwi Shell (ORDU) (Master Thesis). Ordu University, Army.