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Adsorption of Maxilon Blue GRL from an Aqueous Solution: Equilibrium and Kinetic Studies

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Removal of a basic dye, maxilon blue GRL by bentonite, from an aqueous solution was studied. The adsorption of the dye on to bentonite was investigated during batch adsorption experiments carried out to determine the effect of initial dye concentration and contact time. The Langmuir and Freundlich isotherm models were tested for their applicability. Kinetic studies were conducted in two different temperatures and five different reaction periods. Adsorption stability studies were done with five different dye solutions at 37 ºC, pH 4.5-5.0 and in 10 h stability periods and adsorption capacities, adsorption stability constants and Langmuir and Freundlich constants were calculated. The experimental data were analysed using the pseudo-first-order adsorption kinetic model. According to this model, the rate constants were evaluated for two different temperatures. The experimental data fit the first-order kinetic model.

Key Words: Dye adsorption, Basic dyes, Langmuir model, Bentonite, Kinetics.

INTRODUCTION

Bentonite is a soft, moldable, light coloured clay stone formed by chemical decomposition of glassy volcanic material such as volcanic clay and tufa and composed primarily of minerals of smektite group and partially of collodial silica. Bentonite has many areas of use such as dyeing industry, oil refinery, bleaching process in cleaning of textile waste waters, filling material in pharmaceutical, paper, rubber industry and this makes bentonite a very interesting material[1].

In modern industrial society, dyes are widely used for textiles, printing, dyeing and food. In dye wastewater, the colour produced by minute amounts of organic dyes in water is of great concern because colour in water is aesthetically unpleasant. Moreover, some dyes and their degradation products may be carcinogenic and toxic. They are important sources of water pollution and their treatment becomes a major problem for environmental managers. Some investigations have focused on the development of a treatment process for dye wastewater, such as biological and advanced oxidation processes. Some other studies have been conducted on physico-chemical methods for removing colour from dye wastewater[2]. In various researches, coagulants, oxidizing agents and membrane, electrochemical and adsorption technique have been extensively reviewed. Among these methods, adsorption comes at the top of the methods that have high performance in treatment of waste water containing dyeing elements. It was found that methylene blue dye was adsorbed faster than safranin dye in colour removel and adsorption in discrete and filled colon system of methylene blue and safranin dyes using active clay passed through active carbon, chemical activation and prolysis[3]. Many studies have been conducted on the possility of adsorbents using HCl-activated montmorillonite[4], novel polymer[5], zeolite[6], silica[7], clay[8], organomineral[9] and others[10-15]. However, the adsorption capacity of the adsorbents is not very large and to improve adsorption performance new adsorbents are still under development.

Several researchers have tested various affordable and widely available adsorbents for using them in removal of colour from dye waste waters[4]. Bentonite, which is abundant in Turkey was chosen as adsorbent. The chemical composition of Çankiri bentonite is given in Table-1.

TABLE 1
CHEMICAL COMPOSITION OF ÇANKIRI BENTONITE [Ref. 16]

Constituent	Weight (%)	Constituent	Weight (%)
SiO_2	57.52	Na_2O	2.67
Al_2O_3	14.51	K_2O	1.80
Fe_2O_3	5.65	SO_3^-	0.00
CaO	4.36	Cl^-	0.00
MgO	2.05	Loss of ignition	10.90

EXPERIMENTAL

Kinetic tests: 0.5 g of bentonite was weighed in 50 mL glass bottles with lids using electronic scale. 20 mL of 10 ppm blue GRL solution was added and they were mixed in a magnetic mixer (rotations/min) for 5 min. pH was measured using Hanna brand pH meter. pH's were brought to 4.5-5.0 interval by adding 0.1 M HNO_3 slowly. Then this solution was kept in incubator adjusted to 37 ºC in five different time periods *viz.*, 0.25, 0.5, 1.0, 2.0 and 3.0 h. Then the solution was shaken and poured into centrifugal tubes and centrifuged for 0.5 h at 1000 rpm. They were filtered by removing the clear portions and poured into glass bottles with lids to measure their dye concentrations. Their absorbance values were measured with Shimadzu

UV-1201 spectrophotometer. In measurements, the maximum wavelength (λ_{max}) for maxilon blue GRL dye was taken as 450 nm. The same steps of this process were repeated at 48 ºC constant temperature by keeping in 0.25, 0.5, 1.0, 2.0 and 3.0 h time intervals.

The following kinetic equilibriums were used in determination of dye adsorption reaction speed.

$$\frac{dC}{dt} = -kC^n \tag{1}$$

where C = dye concentration in solution, t = reaction time, k = reaction rate constant, n = reaction degree. By integration of equilibrium (1), the following equilibriums are obtained.

$$\frac{1}{C^{n-1}} = \frac{1}{C_o^{n-1}} + (n-1)kt \tag{2}$$

$$\log\frac{1}{C^{n-1}} = \log A + \log[1 + (n-1)kt / A] \tag{3}$$

where $A = 1/C_o^{n-1}$. At time t, when [(n-1)kt/A]>>1, eqn. 3 can be simplified as:

$$\log C = \frac{1}{1-n}\log(n-1)k + \frac{1}{1-n}\log t \tag{4}$$

In the log C *vs*. log t graph of the linear equation above, from the gradient, reaction rate n and from the y-intercept, the reaction rate constant k were calculated[17,19].

Stability tests: 5 g each were weighed from 0.5 g bentonite adsorbent. By using separate 10, 20, 50, 100 and 200 ppm maxilon blue GRL dye solution on it, 10 h stability period was carried out at 37 ºC constant temperature and pH = 4.5-5.0 interval. By using 5 different dye solutions on total of 5 samples, the clear portion was filtered by centrifuge after the stability period. Dye concentrations in the filtered portions were measured with spectrophotometer.

RESULTS AND DISCUSSION

Initial adsorption tests: Initial dye concentrations of maxilon blue GRL was adsorbed fast in first 15 min of the adsorption and the dyeing elements were removed with the same speed. In the study about adsorption of basic dyes on to bentonite, it is seen in literature studies that these kinds of dyes are adsorbed easily. The initial batch adsorption studies showed that bentonite would adsorb maxilon blue GRL to an appreciable degree (Fig. 1). The data also showed that a contact time of 100 min was sufficient to achieve equilibrium. In the study made by Norozi *et al*. about equilibrium and kinetic adsorption study of a cationic dye by a natural adsorbent silkworm pupa. They have shown that process was uniform and rapid adsorption of dye reached equilibrium[3] in 2 h.

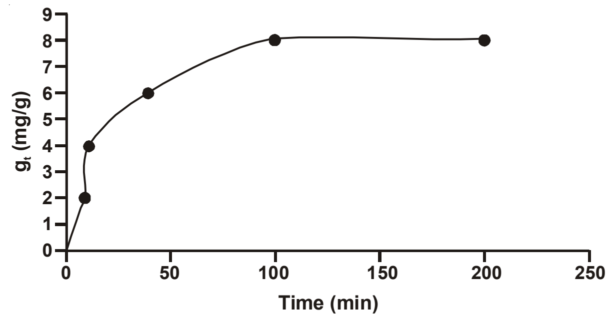

Fig. 1. Basic adsorption curve for maxilon blue GRL

Results of kinetic test:

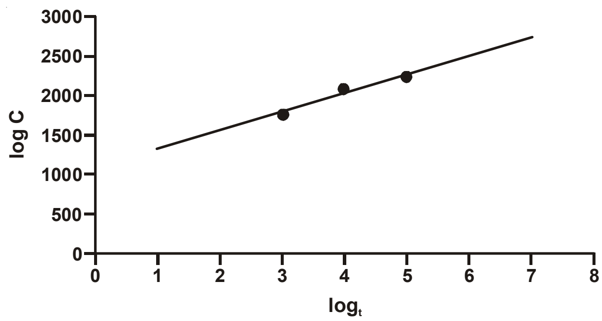

Fig 2. Reaction speed graph of maxilon blue GRL at 37 ºC

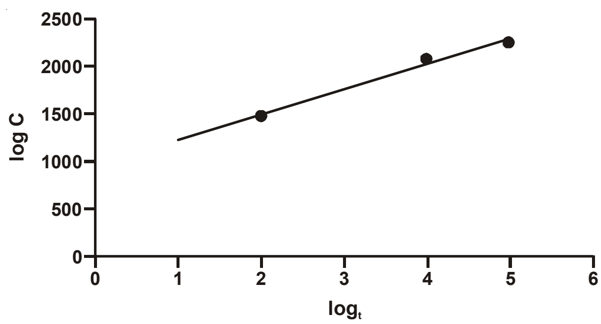

Fig. 3. Reaction speed graph of maxilon blue GRL at 48 ºC

Linear plots of log C *vs.* log t are shown in Figs. 2 and 3. The values which were derived for the reaction rate constants for each equation are shown in Table-2.

TABLE-2
FIRST DEGREE REACTION SPEED CONSTANTS AND CORRELATION COEFFICIENTS RELATED TO ADSORPTION OF MAXILON BLUE GRL ON TO BENTONITE AT 37 AND 48 ºC

Reaction rate	Rate constant	Correlation coefficient
First order Lagergren (min^{-1})	k_{37} ^{0}C 9.595×10^{-3}	0.97
First order Lagergren (min^{-1})	k_{48} ^{0}C 2.167×10^{-2}	0.98

Adsorption isotherms: Concordance of adsorption stability test results with Freundlich and Langmuir models are described (eqn. 5) as[19]:

$$C/X = 1/K_2M + C/M \tag{5}$$

where C (mg/L) and X (mg/g) are the amounts of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium, K_2 is adsorption stability constant and M is monolayer adsorption capacity, respectively.

Concordance of adsorption stability with Langmuir adsorption isotherm has been shown by using the equilibrium above. By using linear form of this equation C/X *vs.* C were graphed (Fig. 4). From the slope of line, monolayer adsorption capacity (M) and from the y-intercept of the line, adsorption stability constant (K_2) have been calculated.

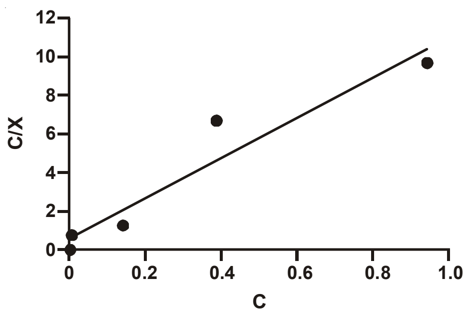

Fig. 4. Langmuir adsorption isotherm drawn for maxilon blue GRL (37 ºC, pH 4.5-5.0, stability period 10 h)

The equilibrium (eqn. 6) that provides Freundlich adsorption isotherm can be written as[19]:

$$X = K_1C^{1/n} \tag{6}$$

Concordance of adsorption equation with the Freundlich adsorption isotherm is analyzed by using the linear form of the adsorption eqn. 6:

$$\log X = K_1 + 1/n \log C \quad (7)$$

where K_1 and n are Freundlich constants. From the slope of the line, n and from the y-intercept values, K_1 constants have been calculated.

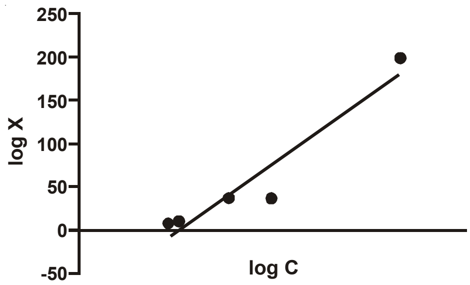

Fig. 5. Freundlich adsorption isotherm drawn for maxilon blue GRL (37 ºC, pH 4.5-5.0, stability period 10 h)

Linear plots of C/X *vs.* C and log X *vs.* log C are shown in Figs. 4 and 5. The values which were derived for the Langmuir model constants and Freundlich model constants for each equation are shown in Table-3.

TABLE-3
LANGMUIR AND FREUNDLICH MODEL CONSTANTS

	Langmuir model				Freundlich model			
	M (mg/g)	$K_{2\,(L/g)}$	R^2	R_L	$C_{o,\ mg/L}$	n	$K_{1,}$ L/g	R^2
Maxilon blue GLR	95.82	0.174	0.96	0.365	10	1.25	8.73	0.90
				0.223	20			
				0.103	50			
				0.054	100			
				0.028	200			

Equilibrum parameter, a dimensionless constant, is defined by eqn. 8:

$$R_L = 1/(1+K_2C_0) \quad (8)$$

where C_0 is the initial concentration of dye (mg/L) and K_2 is the Langmuir constant (L/mg). R_L indicates the nature of the adsorption process as given below[20]:

$R_L > 1$ Unfavourable; $R_L = 1$ Linear;
$0 < R_L < 1$ Favourable; $R_L = 0$ Irreversible

The values of R_L were found to be in the range of 0-1, indicating that the adsoprtion process is favourable for adsorbent. In addition, the Freundlich adsorption constant, n, should be between 1-10 for beneficial adsorption[21,22]. When the correlation coefficient of maxilon blue dye is considered (Table-3), it is seen that this is favourable with Freundlich and Langmuir isotherms.

Conclusion

In kinetic and stability test studies, it was demonstrated that bentonite can be used effectively for removal of maxilon blue GRL dye. In addition, because bentonite adsorbent is abundant and low-cost in Turkey, it was concluded that it was one of the important adsorbent in removing dyes from water solutions.

The results of adsorption stability test for maxilon blue have been evaluated with respect to Langmuir and Freundlich adsorption isothrems. The monolayer adsorption capacity of maxilon blue was found to be 95.82 mg/g.

The suitability of first-order kinetic model for the adsorption of maxilon blue onto adsorbent was also discussed. It was decided that the adsorption kinetics of adsorbent obeyed the first-order adsorption model.

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