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Adsorption Properties of Basic Dyes (Maxilon Red GRL and Maxilon Yellow GRL) onto Bentonite

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In this study, adsorption kinetics, thermodynamics and adsorption stability parameters of maxilon red GRL and maxilon yelow GRL which are used in textile industry especially in dyeing of acrylic fibers on to bentonite were studied. The adsorption of the dyes onto bentonite was investigated during a series of batch adsorption experiments to determine the effect of initial dye concentration and contact time. The Langmuir and Freundlich isotherm models were tested for their applicability. Adsorption capacities, adsorption stability constants and Langmuir and Freundlich constants were calculated. Kinetic studies have been made at two different temperatures Adsorption equilibrium studies have been studied using 5 different dye solutions at 37 ºC, pH 4.5-5.0 and in 10 h. The experimental data were analyzed using the pseudo first-order adsorption kinetic model. According to this model, the rate constants were evaluated at two different temperatures.

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

INTRODUCTION

Bentonite is a soft, 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 applications 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 carcinogens and toxic. These are important sources of water pollution and their treatment becomes a major problem for environmental point of view. 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]. Some other studies have been conducted on physico-chemical methods of removing colour from dye wastewater. They included the use of coagulants, oxidizing agents and membrane, electrochemical and adsorption techniques[3]. The advantages and disadvantages of such techniques have been extensively reviewed. Of these methods, adsorption has been found to be an efficient and economical process to remove dyes and also to control biochemical oxygen demand[4]. Many studies have been made on the possibility of using different adsorbents for dye removal such as activated carbon[5,6], fly ash[7], chitin[8], silica[9], clay[10], chitosan[11] and others[12-17]. However, the adsorption capacity of the adsorbents was not large and to improve adsorption performance new adsorbents are still under development.

In recent years, clay has been accepted as one of the appropriate low-cost adsorbents for the removal of dyes from dye wastewater. Among the studied clays, expandable layered silicates (*e.g.*, montmorillonite) as adsorbents have received considerable recognition[2]. Hence, this tempted us to choose bentonite which is abundant and in low-cost in Turkey. In this article, the adsorption equilibrium and kinetics of maxilon red GRL and maxilon yellow GRL on bentonite are reported.

EXPERIMENTAL

The dyes used in this study are maxilon yellow GRL and maxilon red GRL (basic dyes), obtained from a textile firm in Turkey. Bentonite was obtained from Çankiri bentonite firm. The chemical composition of Çankiri bentonite are given in Table-1.

TABLE-1
CHEMICAL COMPOSITION OF BENTONITE [Ref. 18]

Constituents	Weight (%)	Constituents	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 (LOI)	10.90

0.5 g of bentonite was weighed into each of two 50 mL glass bottles with lids using electronic scale. On one of them, 20 mL of 10 ppm red GRL and on the other, 20 mL of 10 ppm yellow GRL solutions were added and each solution was agitated in a magnetic mixer for 5 min. pH's were brought to pH 4.5-5.0 range by adding 0.1 M HNO_3 slowly. Then these solutions were kept in incubator adjusted to 37 ºC for 5 different time periods which are 15, 30, 60, 120 and 180 min. There after, the solutions were taken and poured into centrifugal tubes and centrifuged at 1000 rpm for 0.5 h. These were filtered and poured into glass bottles with lids to measure their dye concentrations. Their absorbance values were measured using Shimadzu UV-1201 spectrophotometer. The maximum wavelength (λ_{max}) for maxilon yellow GRL dye was taken as 480 nm and for maxilon red GRL dye as 538 nm.

The same procedure was repeated at 48 ºC and time period 15, 30, 60, 120 and 180 min. The following equation were used for determination of 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 *versus* log t graph of the linear equation above, from the gradient, reaction rate n and from the y-intercept, the reaction rate constant k was calculated[19].

Adsorption equilibrium studies: Half-gram of bentonite was weighed into each of 5 bottles. By using separate 10, 20, 50, 100 and 200 ppm maxilon red GRL and maxilon yellow GRL dye solutions on it, 10 h stability period was carried out at 37 ºC and pH 4.5-5.0. The solutions were carefully filtered. The dye concentration in the supernatant was measured spectrophometerically.

RESULTS AND DISCUSSION

Initial adsorption tests: Initial concentrations of both dyes were adsorbed fast during the first 15 min of the processs and the dyeing elements were removed with the same rate. It has been reported previously that basic dyes could integrate easily with both living or non-living activated sludge[3]. This is mainly because of the positive structure of basic dyes. They are also known as cationic dyes because of the positive structure of the chromophore group. The initial batch sorption studies showed that bentonite would absorb maxilon red and maxilon yellow GRL to an appreciable degree (Fig. 1). The data also showed that a contact time of 1 h was sufficient to achieve equilibrium.

Results of kinetic test: The dye concentrations of maxilon yellow GRL and maxilon red GRL dyes measured at 37 and 48 ºC in 15, 30, 60, 120 and 180 min time in solution during sorption on to bentonite, are graphed as log t *versus* log C. These are shown in Figs. 2-5, respectively.

Linear plots of log C *versus* log t are shown in Figs. 2-5. The values which were derived for the reaction rate constants each equation are shown at Tables 2 and 3.

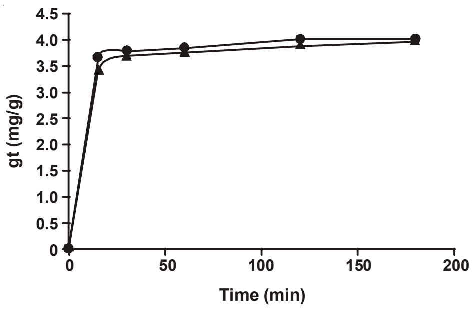

Fig. 1. Basic adsorption curves for maxilon red (●) and maxilon yellow (▲)

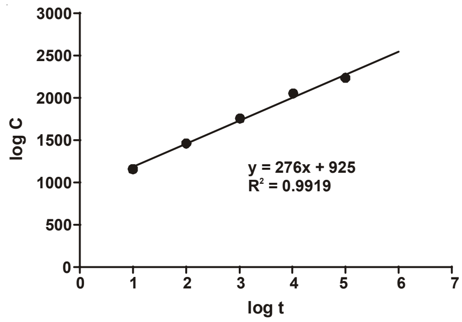

Fig. 2. Plot log C *vs.* log t for maxilon yellow GRL at 37 ºC

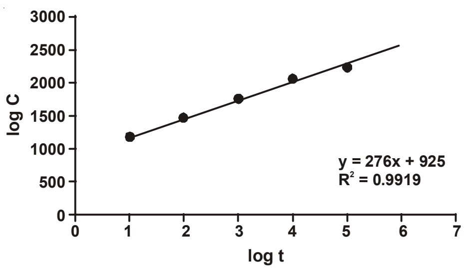

Fig. 3. Plot log C *vs.* log t for maxilon yellow GRL at 48 ºC

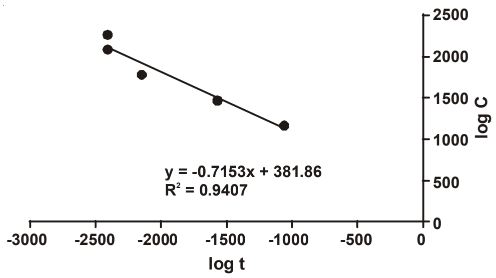

Fig. 4. Plot log C *vs.* log t for maxilon red GRL at 37 ºC

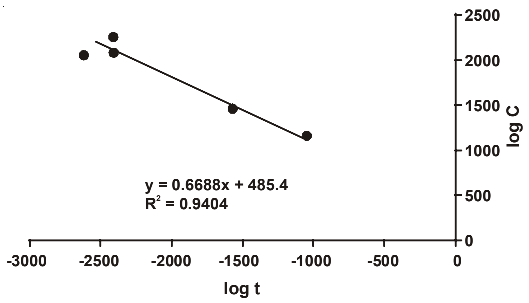

Fig. 5. Plot log C *vs.* log t for maxilon red GRL at 48 ºC

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

Reaction rate	Rate constant	Correlation coefficient
First order Lagergren (per min)	5.3730×10^{-2} (k_{37} ºC)	0.99
First order Lagergren (per min)	2.0453×10^{-1} (k_{48} ºC)	0.99

TABLE-3
FIRST DEGREE REACTION SPEED CONSTANTS AND CORRELATION COEFFICIENTS RELATED TO ADSORPTION OF MAXILON RED GRL ON TO BENTONITE AT 37 AND 48 ºC

Reaction rate	Rate constant	Correlation coefficient
First order Lagergren (per min)	1.004×10^{-2} (k_{37} ºC)	0.94
First order Lagergren (per min)	1.533×10^{-1} (k_{48} ºC)	0.94

Adsorption isotherms: Concordance of adsorption stability test results with Freundlich and Langmuir models are described[19]. Equation 5 can be written as:

$$C/X = 1/K_2M + C/M \quad (5)$$

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 adsorption stability constant and M monolayer adsorption capacity respectively. By using linear form of this equation C/X *versus* C were graphed.

Concordance of adsorption stability with Langmuir adsorption isotherm has been shown by using the equilibrium above. C/X was graphed against C's. 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.

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

$$X = K_1C^{1/n} \quad (6)$$

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

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

where K_1 and n are Freundlich constants. From the slope and the y-intercept of the line values, K_1 can be calculated.

The values of the Langmuir (Figs. 6 and 7) and Freundlich parameters (Figs. 8 and 9) were obtained, respectively, from the linear correlations between the values of log X and log C, The adsorption isotherm parameters along with the correlation coefficients are presented in Table-4. The linear relationships were evidenced by the R^2 values for the Langmuir model 0.90 and 0.88 maxilon red and maxilon yellow, respectively; Freundlich model, 0.99 and 0.89 for maxilon red and maxilon yellow, respectively. The maximum amount of dye per unit weight of adsorbent were found 33.784 and 25.258 mg/g for maxilon red and maxilon yellow, respectively.

The essential characteristic of the Langmuir isotherm can be expressed by a separation or equilibrum parameter, a dimensionless constant, which is defined by eqn. 8:

$$R_L = 1/(1 + k_2C_0) \quad (8)$$

where C_0 = initial concentration of dye (mg/L) and k_2 = 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).

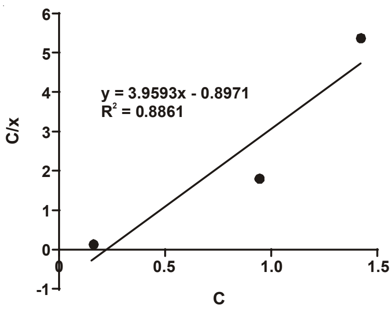

Fig. 6. Langmuir adsorption isotherm for maxilon yellow GRL (37 ºC, pH 4.5-5.0, stability period 10 h)

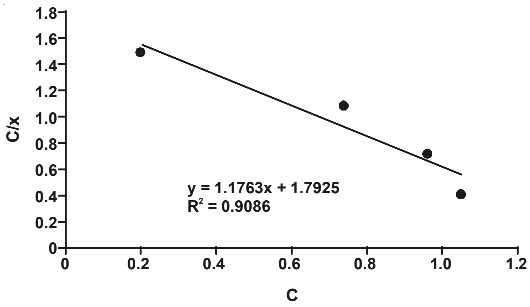

Fig. 7. Langmuir adsorption isotherm for maxilon red GRL (37 ºC, pH 4.5-5.0, stability period 10 h)

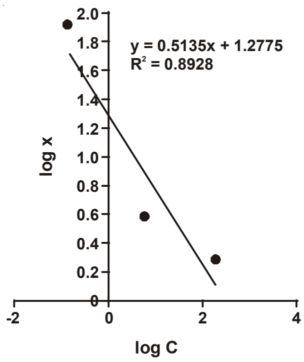

Fig. 8. Freundlich adsorption isotherm for maxilon yellow GRL (37 ºC, pH 4.5-5.0, stability period 10 h)

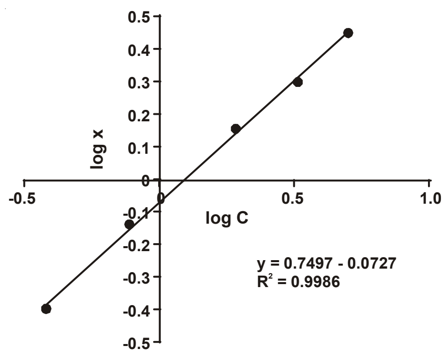

Fig. 9. Freundlich adsorption isotherm for maxilon red GRL (37 ºC, pH 4.5-5.0, stability period 10 h)

TABLE-4
LANGMUIR AND FREUNDLICH MODEL CONSTANTS

	Langmuir model				Freundlich model			
	M (mg/g)	$K_{2,\ L/mg}$	R^2	R_L	$C_{o,\ mg/L}$	n	$K_{F,}$ L/g	R^2
				0.211	10			
				0.118	20			
Maxilon red GRL	33.784	0.374	0.90	0.051	50	1.333	1.727	0.99
				0.026	100			
				0.013	200			
				0.185	10			
				0.102	20			
Maxilon yellow GRL	25.258	0.441	0.88	0.043	50	1.947	1.278	0.89
				0.022	100			
				0.011	200			

The values of R_L were found to be in the range of 0-1, indicating that the adsorption process is favourable for adsorbent. In addition, the Freundlich adsorption constant, n, should be among 1-10 for beneficial adsorption[21]. When the correlation coefficient of both dyes are considered (Table-3), it is seen that they are favourable with Freundlich and Langmuir isotherms and maxilon red GRL is more favourable with Freundlich model than maxilon yellow GRL.

Conclusion

In the test studies, it was demonstrated that bentonite can be used effectively for removal of maxilon red GRL and maxilon yellow GRL dyes. In addition, because bentonite adsorbent is abundant and low-cost in Turkey, it was concluded that it is one of the important adsorbent in removing dyes from water solutions. The results of adsorption stability tests for both dyes have been evaluated with respect to Langmuir and Freundlich adsorption isotherms. The Monolayer adsorption capacities of maxilon red GRL and maxilon yellow GRL were found to be 33.78 and 25.25 mg/g, respectively.

The suitability of first-order kinetic model for the sorption of maxilon red and maxilon yellow GRL onto adsorbent was also discussed. It was observed that the adsorption kinetics of adsorbent obeyed the first-order adsorption model.

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