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REMOVAL OF DYESTUFF FROM WASTEWATER BY LEWATİT MONOPLUS M600

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ABSTRACT: *In this study, removal of dyestuff from wastewater by strong base anion exchange resin was investigated. The effects of parameters such as pH, contact time, temperature, resin dosage and initial concentration on dyestuff removal were studied. Kinetic test was performed to find out the mass transfer mechanism of the sorption process of dyestuff. The isotherm data could be well described by the Langmuir and Freundlich equations. The sorption capacity was found to be 26.11 mgg^{-1} by Langmuir isotherm. In the batch desorption process, various desorption solutions were tested. In the column study, the breakthrough curve was obtained and capacity value of the resin was calculated.*

Keywords: *Dyestuff; Ion-exchange; Lewatit MonoPlus M 600; Batch study; Column study.*

LEWATİT MONOPLUS M600 REÇİNESİ İLE ATIKSULARDAN BOYAR MADDE UZAKLAŞTIRILMASI

ÖZET: *Bu çalışmada, kuvvetli bazik anyon değiştirici reçine ile atıksulardan boyarmadde giderimi incelenmiştir. Boyarmadde giderimi üzerine pH, temas süresi, sıcaklık, reçine miktarı ve başlangıç derişimi gibi parametrelerin etkisi çalışılmıştır. Boyarmaddenin sorpsiyon sürecinin kütle aktarım mekanizmasını bulmak için kinetik testler yürütülmüştür. İzoterm verileri Langmuir ve Freunlich eşitlikleri ile iyi uyum sağlamıştır. Langmuir izotermi ile sorpsiyon kapasitesi 26,11 mgg^{-1} olarak bulunmuştur. Kesikli desorpsiyon sürecinde çeşitli desorpsiyon çözeltileri denenmiştir. Kolon çalışmasında ise kırılma eğrisi elde edilmiş ve reçinenin kapasite değeri hesaplanmıştır.*

Anahtar kelimeler: *Boyarmadde, İyon değişimi, Lewatit MonoPlus M 600, Kesikli çalışma, kolon çalışması*

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I. INTRODUCTION

Synthetic dyes and pigments are widely used in many industries such as textile, leather, tannery, food, paper, plastics, etc. Removal of dyes from industrial wastewaters is a very significant ecological concern since they may affect the photosynthetic activity in aquatic life by reducing sunlight penetration and they may also be toxic. In this context, color removal from textile effluents has been the target of great attention in the last few years.

Dyes are classified as follows: Anionic: direct, acid and reactive dyes; Cationic: basic dyes; Nonionic: disperse dyes [1]. Reactive dyes are a class of textile dyes having great commercial importance. The vinyl sulfone and chlorotriazine dyes are the most reactive and versatile of the fibre reactive dyes since these dye molecules actually react with fabric molecules [1-2].

Color can be removed from wastewater by chemical and biological methods including adsorption, ion exchange, coagulation – flocculation, oxidation, and electrochemical methods. Among these methods, adsorption is often considered as a simple and efficient technique.

Dyes are poorly biodegradable and generally resistant to environmental conditions. Therefore, there is no single process of adequate treatment for dye containing wastewaters. Recent work has explored applying adsorption/ion exchange/chemical or electrochemical techniques to water contaminated with a broad range of reactive dyes [3-5]. Different types of materials have been tested as sorbents for different types of dyestuffs. Among the studied alternative materials are coal, bentonite, clay, cotton waste, rice husk [6-7], perlite [8], sepiolite [9], hazelnut shells [10], wheat bran [11], sunflower seed shells [12], oil palm fibre activated carbon [13], agricultural residue anion exchanger [14], anion exchange membranes [3], and anion exchange resin [4].

In this study, batch sorption and column tests were performed using Lewatit MonoPlus M 600 for dyestuff removal from wastewater. Toward this aim, the effects of pH, contact time, temperature, resin dosage and initial concentration on the sorption of dyestuff were investigated. Five kinetic models were applied to fit the kinetic data obtained by using Lewatit MonoPlus M 600. The Langmuir and Freundlich isotherm models were tested for their applicability. In the column study, ion-exchange capacity of Lewatit MonoPlus M 600 was investigated.

II. EXPERIMENTAL METHODS

Lewatit MonoPlus M 600 is a strongly basic, gelular anion exchange resin with beads of uniform size based on a styrene-divinylbenzene copolymer. It was kindly supplied by *Ökotek Chem.*, Turkey. The characteristics of the resin are given in Table 1.

Table 1. *Typical chemical and physical characteristics of Lewatit MonoPlus M 600*

Ionic form	Cl^-
Functional group	Quaternary amine, type II
Structure	Gel type beads
Mean bead size (mm)	0.6 (+/- 0.05)
Bulk density (gL^{-1})	700
Density approx. (gml^{-1})	1.1
Total capacity ($eq(L\ resin)^{-1}$)	1.25
Maximum operating temperature (°C)	30
pH range	0-11

The reactive dyestuff was obtained from a textile factory in Turkey. The commercial name is *Remazol Black B*. It is an anionic dyestuff and has a vinyl sulfone group. The molecular structure of Black B in non-hydrolyzed form is illustrated in Fig. 1.

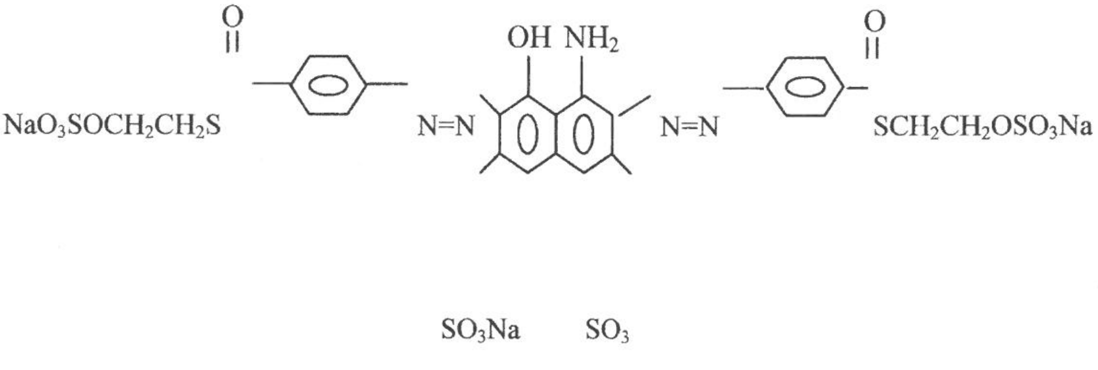

Figure 1. *The molecular structure of Black B in non-hydrolyzed form.*

The appropriate amounts of dye (100 mgL^{-1}), NaCl (30 gL^{-1}) and Na_2CO_3 (1.6 gL^{-1}) were placed in a beaker, and NaOH solution (10 M, 0.4 mlL^{-1}) and appropriate volumes of distilled water were added on the mixture. The solution was heated on a stirring plate at 50°C for 1 h. After cooling, pH of the solution was neutralized by adding HCl solution (12 M). A pH meter (Inolab) was used to follow the change in the pH value. The solution was transferred to a volumetric flask and diluted to 1 L with distilled water of the same neutral pH [15].

In batch sorption experiments, resin (0.25 g) was contacted with dyestuff solution (50 mgL^{-1}, 50 ml) at 25°C for 24 hours with continuous shaking (Memmert) at 140 rpm. After sorption, dyestuff concentration in the supernatant solution was analysed. All concentrations were measured at 593 nm that corresponds to maximum absorbance, using a spectrophotometer (Shimadzu UV-120-01).

In order to investigate the effect of pH on dyestuff sorption, pH values of the dyestuff solutions were adjusted to different values (2, 4, 7.2 (original pH), 9, 11) using either HCl or NaOH. Studies were conducted for various time intervals to determine when the sorption equilibrium was reached and the maximum dyestuff removal was attained. The amounts of dyestuff sorbed at various time intervals were fitted to different kinetic models. The experiments were carried out by using the resin at 25, 35, 45 and 55°C in order to investigate the effect of temperature. The sorption experiments of dyestuff solutions by different resin doses (0.01-0.35 g/50ml) were carried out at optimum pH and 25°C for 24 h shaking period. The effect of initial dyestuff concentration was investigated at 20, 40, 50, 60, 80 and 100 mgL^{-1} at 25°C and optimum pH for 24 h with continuous shaking. The Langmuir and Freundlich isotherms were employed to study the sorption capacity of the resin. Desorption experiments were carried out by immersing the resin loaded with dyestuff in desorption solutions (50 ml) for 24 h at 25°C. Different desorption solutions were tested, such as HCl (1N), NaOH (1N), HCl (1N) or NaOH (1N) in 60% methanol and NaCl (1N) in 60% methanol solutions.

The column experiments were performed in a glass column (0.7 cm internal diameter and 15 cm length). Glass wool was placed in the bottom of the column and then packed with a definite wet-settled volume of the resin (3 ml). The dyestuff solution (50 mgL^{-1}, original pH, 25°C) was delivered down flow to the column at 0.625 ml min^{-1} flow rates using a peristaltic pump (ATTOSJ 1211 Model). From the outlet of the column, each successive 4 ml fractions of the effluent were collected using a fraction collector (Spectral Chrom CF-1). Breakthrough curve was obtained by analysis of each fraction by the spectrophotometer. Column studies were terminated when the column reached exhaustion. The column experimental set up is shown in Fig.2.

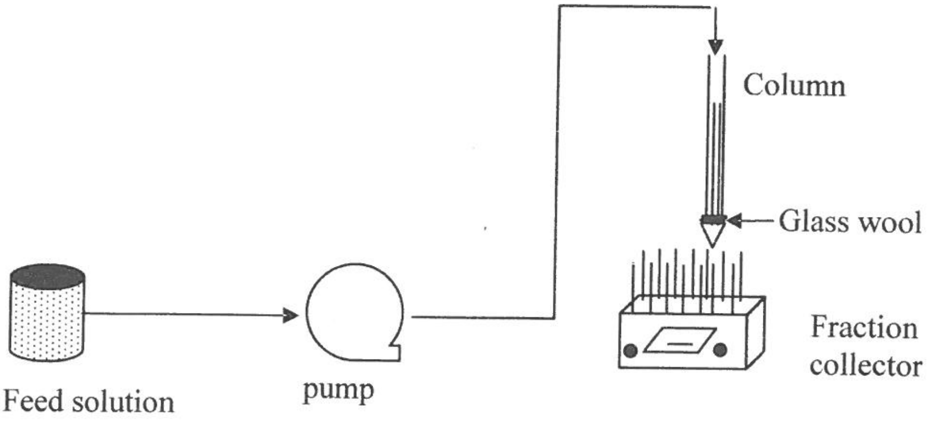

Figure 2. *The column experimental set up.*

III. RESULTS AND DISCUSSION

III.1. Effect of pH

The effect of pH on the removal of dyestuff is shown in Fig. 3. Initial pH of the dyestuff solution has essentially no effect on the dyestuff removal by resin. High dyestuff removal values were obtained by the use of resin. More than 98% removal values were reached at all pH values.

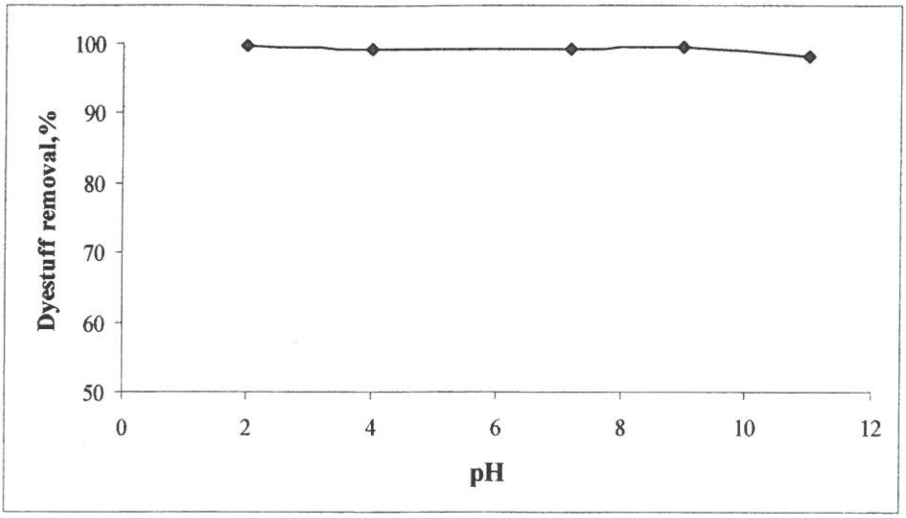

Figure 3. Effect of pH on dyestuff removal.

III.2. Effect of Contact Time

Effect of contact time on the removal of dyestuff by resin is shown in Fig. 4. The value of equilibrium time was found to be 15 hours. The amount of dyestuff sorbed increased with increase in contact time.

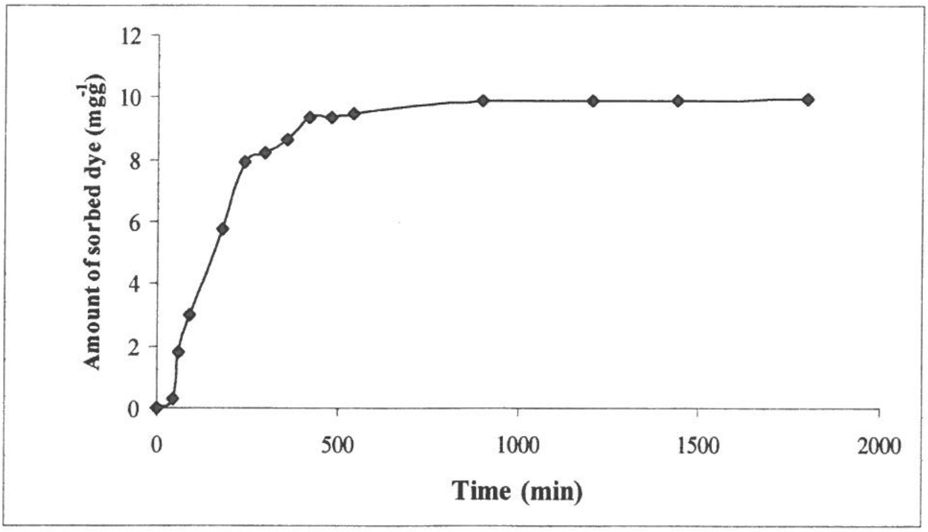

Figure 4. Effect of contact time on dyestuff removal.

III.3. Kinetic Models of Ion-Exchange

Various empirical models have been given for dyestuff removal from wastewater by ion exchange. The ion exchange between the counter ion in solution and the exchangeable ion on the resin is well described as a heterogeneous process. In this study, noncatalytic fluid-solid reaction models were applied for dyestuff removal by ion exchange. For the noncatalytic reaction of particles surrounded with fluid, we consider two simple idealized models, the progressive-conversion model (infinite solution volume) and the unreacted core model [16].

In the progressive-conversion model, the species originally in the solution phase enters and reacts throughout the particle at all times, most likely at different rates at different locations within the particle [16]. The ion exchange rates are controlled by diffusion. The chemical exchange reaction at the fixed charge of the resin is usually assumed to be too fast to affect the overall exchange rate [17].

Particle diffusion control is given by the following equation [18-19]:

$$-\ln(1-x^2)=2kt \quad \text{where } k=D_r\Pi^2/r_o^2 \tag{1}$$

Film diffusion control is given as follows [18-19]:

$$-\ln(1-x) = K_{li}t \quad \text{where } K_{li}=3DC/r_oC_r \tag{2}$$

In the unreacted core model, the reaction occurs at the outer skin of the particle, and then the reaction zone moves into the particle through the unreacted core. For spherical particles, the relationship between time (*t*) and fractional conversion (*x*) are as follows [16, 18-20]:

When the fluid film controls the rate:

$$x=3C_{Ao}K_{mA}t/ar_oC_{so} \tag{3}$$

When the reacted layer controls the rate:

$$[3-3(1-x)^{(2/3)}-2x]=6D_{e,r}C_{Ao}t/ar_o^2C_{so} \tag{4}$$

When the chemical reaction controls the rate:

$$[1-(1-x)^{(1/3)}]=k_sC_{Ao}t/r_o \tag{5}$$

Five kinetic models were applied to fit the kinetic data of the resin. Fig. 5 and 6 show the functions of these kinetic models versus time.

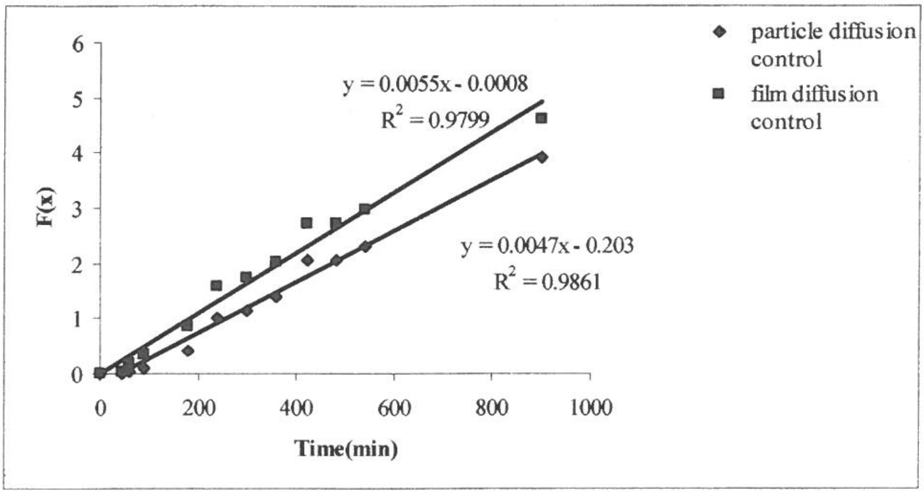

Figure 5. *Kinetic behavior of resin based on progressive-conversion models.*

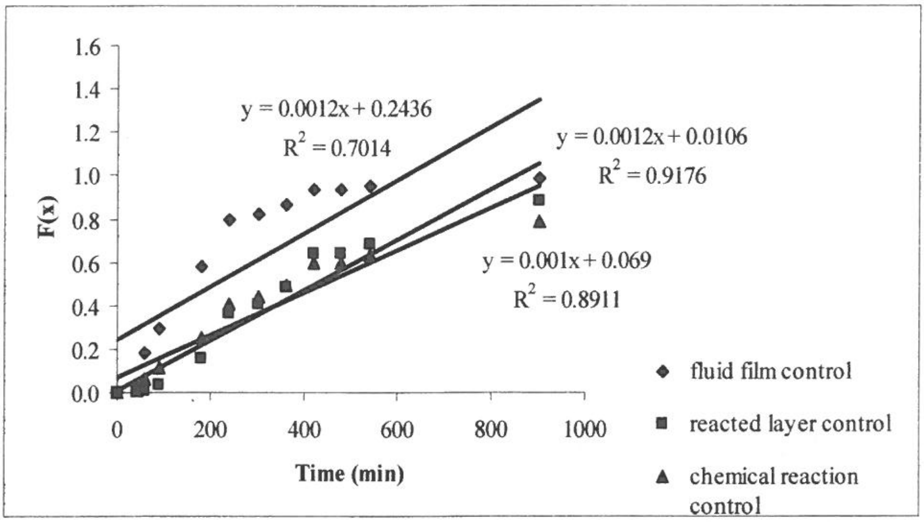

Figure 6. *Kinetic behavior of resin based on unreacted core models (fluid film control, y=0.0012x+0.2436; reacted layer control, y= 0.0012x+0.0106; chemical reaction control,*

$$y = 0.001x + 0.069$$

Since the resin reached equilibrium after about 15 hours, the data obtained at contact times larger than 15 hours were neglected. The results of the linear regression analysis for kinetic models are summarized in Table 2. The linear correlations for the linear models indicate that the reaction is particle diffusion controlled.

Table 2. *Evaluation of kinetic models for Lewatit MonoPlus M 600*

Model	Slope	R^2
$-\ln(1-x^2)$	0.0047	0.9861
$-\ln(1-x)$	0.0055	0.9799
x	0.0012	0.7014
$3-3(1-x)^{(2/3)}-2x]$	0.0012	0.9176
$1-(1-x)^{(1/3)}$	0.001	0.8911

III.4. Effect of Temperature

The temperature of the dyestuff solution has essentially no effect on the dyestuff removal by resin. More than 99% removal values were reached at all temperature values. The effect of temperature on removal of dyestuff is shown in Fig. 7.

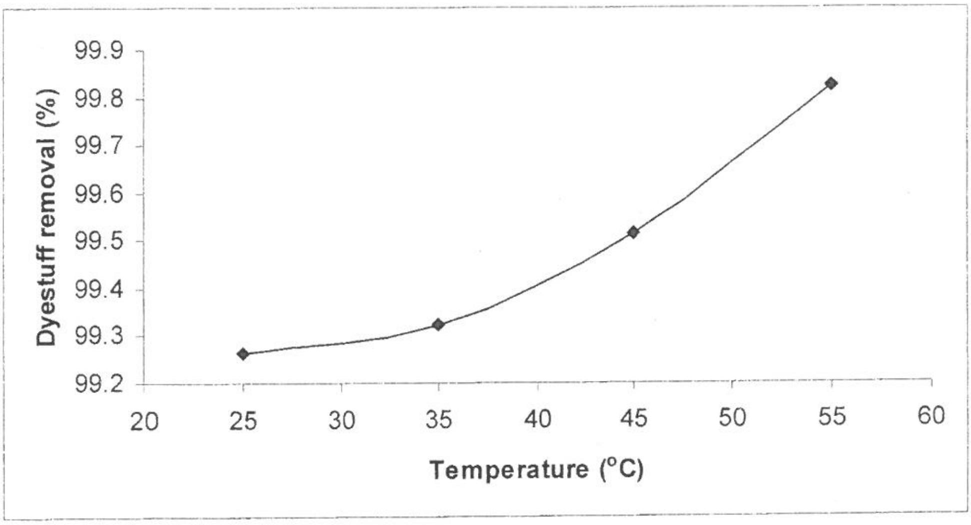

Figure 7. *Effect of temperature on dyestuff removal.*

Thermodynamic parameters such as change in free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were calculated using the following equations, respectively:

$$\Delta G^{o} = -RT\ln K \tag{6}$$

where *R* is the gas constant and *K* is the sorption equilibrium constant (concentration of sorbed dyestuff/concentration of dyestuff remained at solution) and *T* is the temperature in *K*.
According to the Van't Hoff equation:

$$\ln K = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT} \tag{7}$$

The values of ΔH^o and ΔS^o were obtained from the slope and intercept of the Van't Hoff equation from the Fig. 8.

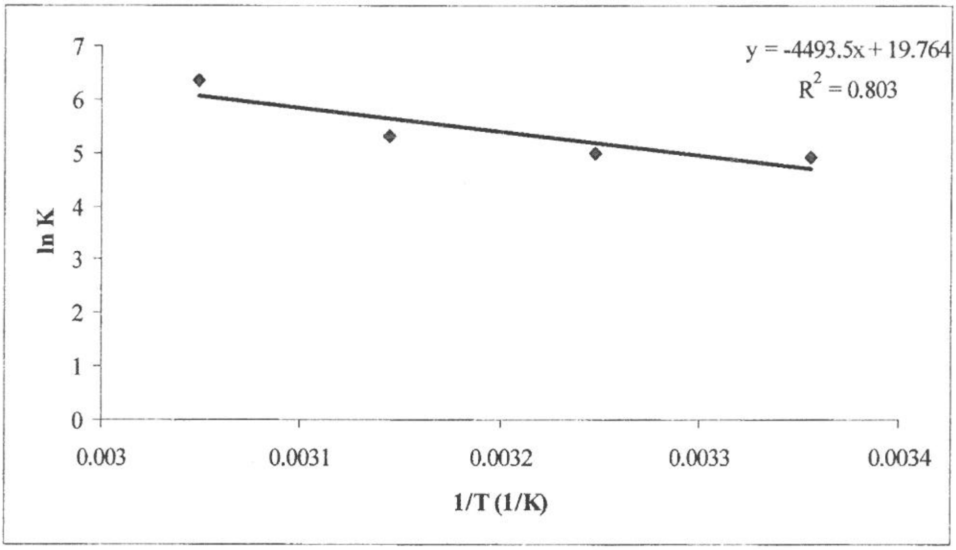

***Figure 8**. Van't Hoff plot for the removal of dyestuff.*

The positive value of ΔH^o indicated that the process was endothermic in nature. The positive value of ΔS^o indicated the increased randomness at the solid-solution interface during the sorption of dyestuff on resin. The negative value of ΔG^o indicated that the sorption process was favorable and spontaneous in nature. The values of the thermodynamic parameters are shown in Table 3.

Table 3. *Thermodynamic parameters for the removal of dyestuff*

Temperature (°C)	K	ΔG^o (kcalmol^{-1})	ΔH^o (kcalmol^{-1})	ΔS^o (kcalmol^{-1}K^{-1})
25	134.59	-2.9	8.93	0.039
35	134.59	-3.0		
45	204.13	-3.4		
55	570.43	-4.1		

III.5. Effect of Resin Dosage

The effect of resin dosage on the removal of dyestuff is shown in Fig.9.

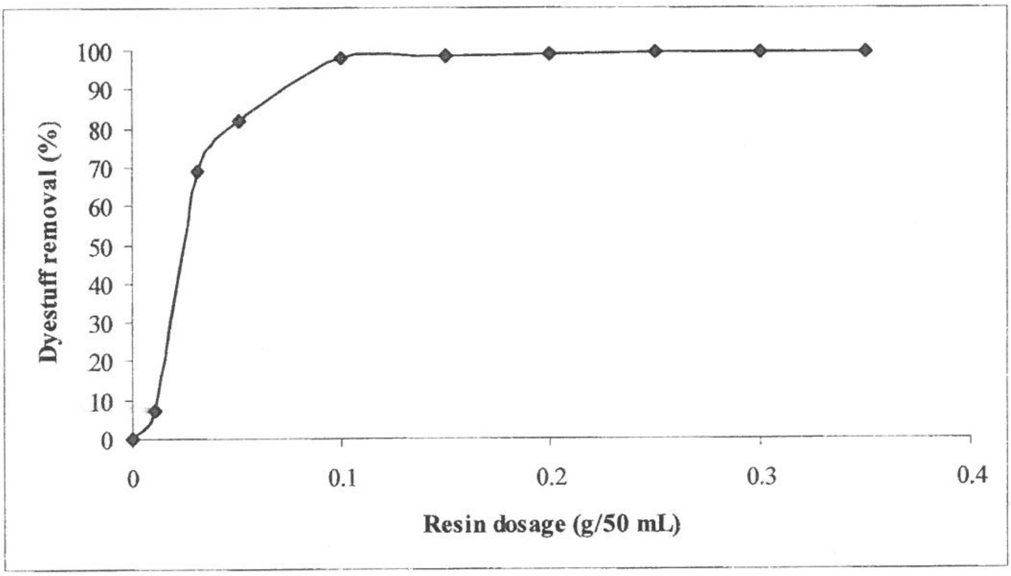

Figure 9. *Effect of resin dosage on the removal of dyestuff.*

It was observed that the dyestuff uptake increased with increasing dosage of the resin. The results also indicate that the removal efficiency increases up to the optimum dosage beyond which the removal efficiency is negligible.

III.6. Effect of Initial Concentration

Dyestuff solutions of different initial concentrations were used to investigate the effect of concentrations on the removal of dyestuff at 25°C. At concentrations of 20, 40, 50, 60, 80 and 100 mgL^{-1}, the decolourisation values were 99.41%, 99.16%, 99.26%, 99.07%, 98.52% and 98.07%, respectively. The percentage uptake of dyestuff decreased by increasing initial concentration. This was due to the saturation of the sorption sites in the resin as the concentration of the solution increased.

III.7. Sorption Isotherms

The Langmuir and the Freundlich isotherm equations were tested at 25°C in this study. The linear form of the Langmuir isotherm equation is given by Eq. (8) [21]:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{8}$$

where C_e is the equilibrium concentration (mgL^{-1}), q_e is the amount of dyestuff sorbed at equilibrium (mgg^{-1}), Q_o and b are the Langmuir constants related to sorption capacity and energy of sorption, respectively. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L , which is defined below [21]:

$$R_L = \frac{1}{1 + bC_o} \tag{9}$$

where b is the Langmuir constant (Lmg^{-1}). The calculated R_L values (Table 4) were between 0 and 1, indicating favorable sorption of dyestuff by resin.

Table 4. *R_L values for Lewatit MonoPlus M 600*

C_o(mgL^{-1})	R_L
20	0.0332
40	0.0168
50	0.0135
60	0.0113
80	0.008
100	0.007

The linearised Freundlich equation is represented by the equation [21]

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{10}$$

where K and n are the Freundlich constants, being indicative of the sorption capacity and intensity of sorption. According to Treybal [22], it has been shown using mathematical calculations that n was between 1 and 10, representing beneficial sorption.

The plot of linear Langmuir and Freundlich equations are shown in Fig. 10 and 11.

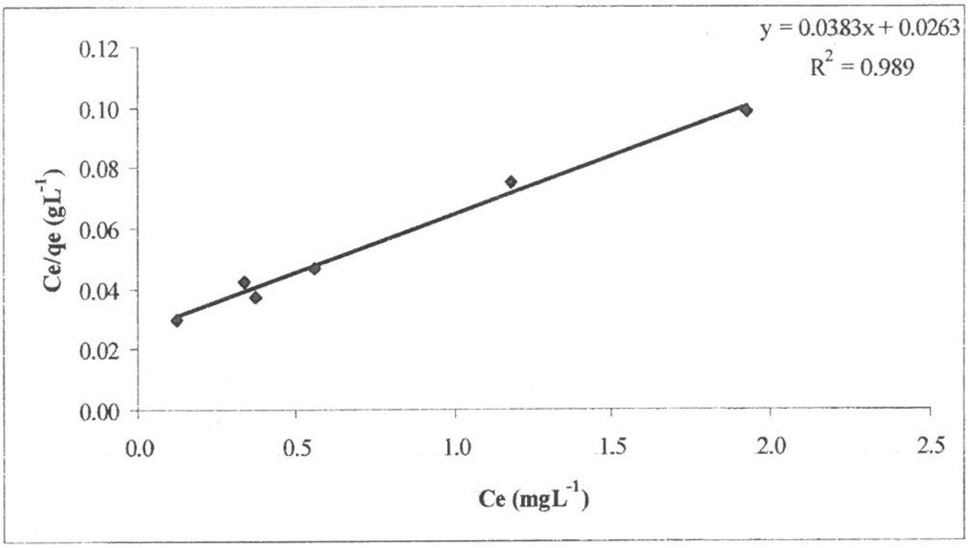

Figure 10. *Langmuir plots for the removal of dyestuff.*

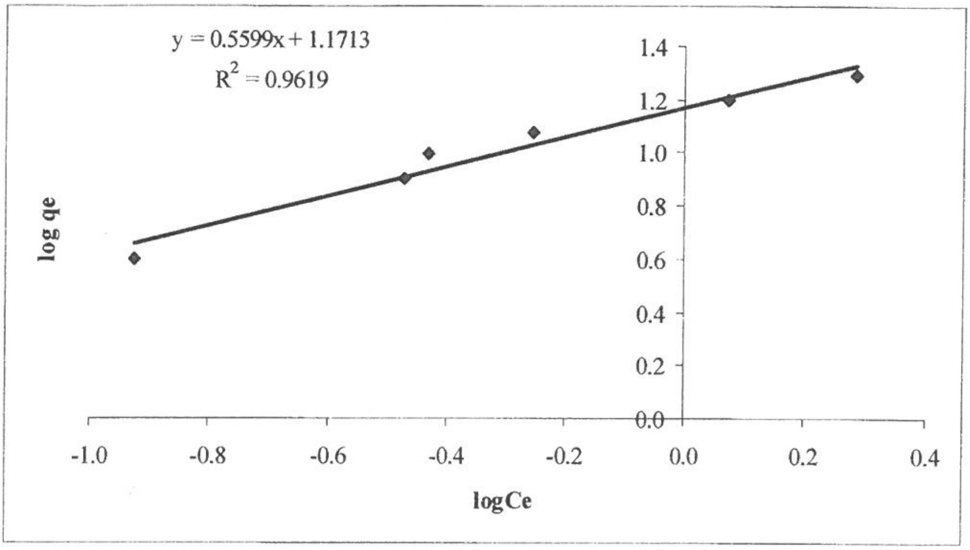

Figure 11. Freundlich plots for the removal of dyestuff.

The constants of Langmuir and Freundlich equation were given in Table 5. Experimental data fitted both the Langmuir and Freundlich isotherm models. The applicability of the Langmuir and Freundlich isotherms signifies mono layer sorption and heterogeneous surface binding [21].

Table 5. Langmuir and Freundlich constants for Lewatit MonoPlus M 600

Langmuir isotherm			Freundlich isotherm		
$Q_o(mgg^{-1})$	$b(Lmg^{-1})$	R^2	$K(mgg^{-1})(Lmg^{-1})^{1/n}$	n	R^2
26.11	1.456	0.989	14.83	1.786	0.962

III.8. Desorption of Dyestuff

The desorption experiments in various solutions in the batch system were carried out in order to find a suitable desorbent for dyestuff recovery from the resin. Desorption tests performed with HCl (1N), NaOH (1N), HCl (1N) in 60% methanol, NaOH (1N) in 60% methanol and NaCl (1N) in 60% methanol solutions gave 1.49%, 0.3%, 4.42%, 0.24% and 5.56% desorption values, respectively. Dyestuff desorption values were very low so the regeneration of the resin was not investigated.

III.9. Column Study

The performance of packed beds is described through the concept of the breakthrough curve. The breakthrough curve of dyestuff removal by Lewatit MonoPlus M 600 was obtained and shown in Fig.12.

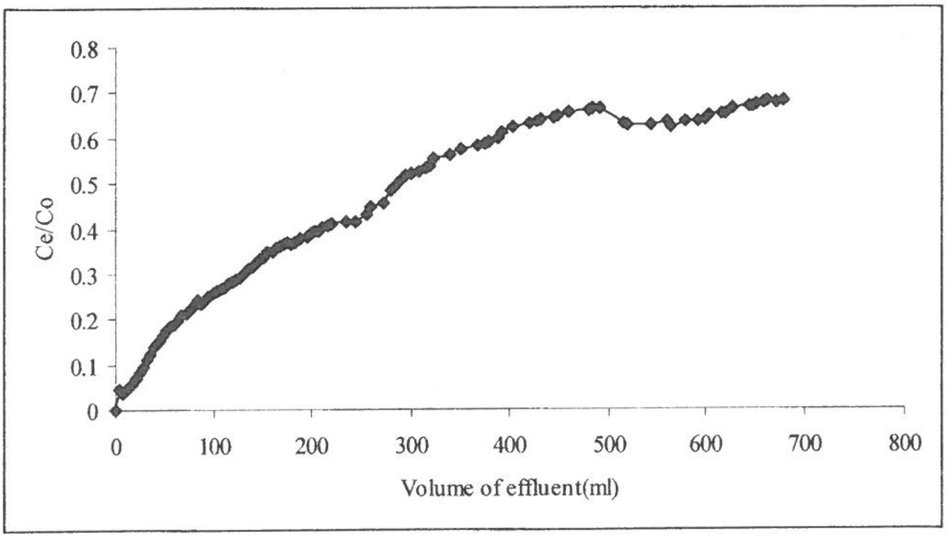

Figure 12. *Breakthrough curve for the removal of dyestuff.*

The breakthrough curve is usually expressed in terms of sorbed dyestuff concentration (C_{sor}=inlet dyestuff concentration (C_o)-effluent dyestuff concentration (C)) or normalized concentration defined as the ratio of effluent dyestuff concentration to inlet dyestuff concentration (C/C_o) as a function of time (t) or volume of effluent (V) for a given bed height. Total sorbed dyestuff quantity (maximum column capacity, q_o; mgg^{-1}) in the column was calculated from Eq.11 [23]:

$$q_o = \int_0^{V_T} \frac{(C_o - C\ )dV}{m} \tag{11}$$

where m is the mass of the resin (g). The capacity value q_o was obtained by graphical integration as 3.5 mgg^{-1}.

IV. CONCLUSIONS

The removal of dyestuff from wastewater was investigated with Lewatit MonoPlus M 600. The following results were obtained:

1) pH value did not affect dyestuff removal significantly for Lewatit MonoPlus M 600. Resin exhibited high removals for dyestuff at all pHs.
2) The sorbed amount of dyestuff from wastewater increased with time. The equilibrium was reached within 15 hours.
3) The particle diffusion model is the best kinetic model to describe the sorption process.
4) The removal of dyestuff was found to be an endothermic process. Hence, the sorption of dyestuff increased as temperature increased.
5) The increase in resin dosage increased the percent removal of dyestuff.
6) The sorption yield decreased by increasing the initial dyestuff concentration.
7) Equilibrium sorption data followed both Langmuir and Freundlich isotherm models. The sorption capacity was found to be 26.11 mgg^{-1} (28.7 $mg(cm^3)^{-1}$)by Langmuir isotherm. This result is in agreement with the observations of Liu et al. [3]. They reported that the Langmuir adsorption capacity of Cibacron Blue 3GA is 31.5 $mg(cm^3)^{-1}$ for strong basic and 25.5 $mg(cm^3)^{-1}$ for weak basic anion exchange membranes and the capacity of Cibacron Red 3BA is 24.5 $mg(cm^3)^{-1}$ for strong basic and 18.5 $mg(cm^3)^{-1}$ for weak basic anion exchange membranes.
8) The column capacity value calculated by graphical integration of the area above the breakthrough curve was 3.5 mgg^{-1}.

V. ACKNOWLEDGEMENT

We would like to thanks Prof. O. Sermet Kabasakal and Assoc. Prof. Neşe Öztürk for their supports.

VI. LIST OF SYMBOLS

a	stochiometric coefficient
C	total concentration of both exchanging species, M
C_{Ao}	concentration of species A in bulk solution, M
C_r	total concentration of both exchanging species in the ion exchanger, M
C_{So}	concentration of solid reactant at the bead's unreacted core, M
D	diffusion coefficient in solution phase, m^2s^{-1}
$D_{e,r}$	diffusion coefficient in solid phase, m^2s^{-1}
D_r	diffusion coefficient in solution phase, m^2s^{-1}
k_s	reaction constant based on surface,ms^{-1}
K_{li}	rate constant for film diffusion (infinite solution volume condition), Ls^{-1}
K_{mA}	mass transfer coefficient of species A through the liquid film, ms^{-1}
x	fractional attainment of equilibrium or extent of resin conversion

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