

# Adsorptive Removal of Methylene Blue from Simulated Dyeing Wastewater with Melamine-Formaldehyde-Urea Resin

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**ABSTRACT:** A melamine-formaldehyde-urea (MFU) resin was used as adsorbent to clean wastewater containing a basic dye (methylene blue) used to simulate leather and textile processing dyes. Dye removal was followed by measuring the initial and final dye concentration in solution by UV-Vis spectroscopy using the analytical wavelength of  $\lambda = 665$  nm and the molar absorptivity of  $\epsilon = (8.43 \pm 0.05) \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>. The concentration range of methylene blue in solution for adsorption experiments was between  $10^{-7}$  and  $10^{-5}$  M so as to avoid dye polymerization reactions in solution that would give rise to apparent deviations from Beer's law. Batch and column methods were used for investigating adsorptive removal of dye. Parameters such as pH

and contact time were optimized. The capacity of the sorbent for the dye was found by classical adsorption modeling ( $15.0$  mg g<sup>-1</sup>) with the aid of a Langmuir isotherm. The optimal pH for adsorption was 7–8. Adsorption is thought to proceed mainly through cation exchange of methylene blue (MB<sup>+</sup>) with the R–COO<sup>-</sup> exchange groups of the sorbent. Adsorption was fast, and reached an equilibrium within 30 min. Color removal of simulated leather dyeing wastewater was shown to be feasible under optimal conditions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3442–3448, 2009

**Key words:** methylene blue; melamine-formaldehyde-urea resin; dye adsorption; leather dyeing wastewater treatment

## INTRODUCTION

Leather industry is one of the most important and widespread industries in the world, but liquid and solid wastes produced by this industry are difficult to treat. It is estimated that 10–15% of the dyes are lost in dye effluents during dyeing processes.<sup>1</sup> Textile industry produces relatively large volumes of wastewater, e.g., at the order of 1 cubic meter of dye-contaminated water per ton of clothes processed. Dye contamination in water prevents the penetration of light required for photosynthetic activity, inhibits the growth of biota, and may form chelates with metal ions present in water that may be more toxic to aquatic organisms than the parent metal ions alone.<sup>2</sup>

Removing dyes from leather and textile wastewaters is rather difficult because of their high resistance to degradation and oxidation by conventional methods.<sup>3</sup> At the present time, there is no single process capable of adequate treatment, mainly due to the complex nature of the effluents.<sup>4</sup>

Wastewaters can be treated as biologically, chemically and physically. By biological methods many organic molecules existing in the wastewaters are

degraded using microbial degradation, fungal decolorization or adsorption by microbial biomass and bioremediation systems.<sup>5</sup>

Coagulation, chlorination, flocculation, conventional oxidation and electrochemical processes are introduced as the chemical methods. These techniques reveal efficiency for the treatment of wastewaters. The major disadvantages of the chemical processes are their high cost and accumulation of the concentrated sludge after the removal of dye.

Adsorption and membrane-filtration processes are widely used as physical methods. Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications.<sup>6</sup> Adsorptive removal of dyeing waste color is advantageous, because of its low cost, simplicity of process design, ease of operation, and insensitivity to toxic substances.<sup>2</sup> Among potential sorbent materials, activated carbon is the most important one for its high surface area and porous morphology, but its re-use is limited by the material loss during recovery.<sup>7–10</sup>

This study investigates the possibility of melamine-formaldehyde-urea (MFU) resin as an adsorbent for the removal of dye from leather industry wastewaters. Methylene blue which is also known as tetramethyl thionine was used as a model dye to obtain the optimal conditions for the adsorptive treatment process. Parameters as granule size, pH, contact time,

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column flow rate were studied by batch and column processes, respectively.

## EXPERIMENTAL

### Reagents and chemicals

All chemicals used were of analytical grade (E. Merck), and distilled water was used throughout.

The melamine-formaldehyde-urea resin was synthesized in the mole ratio of 1 : 3 : 1, respectively, using the procedure of Wohnsiedler<sup>11</sup>; the pH for synthesis was maintained by NaOH addition. The synthesized resin was then washed with 1M HCl, 1M NaOH and sufficient water to obtain neutral pH in the filtrate, dried, grounded and screened to the desired particle size. The resin was characterized by IR spectroscopy as described elsewhere.<sup>12</sup>

A methylene blue stock solution at 20 mg/L concentration was prepared by dissolving solid methylene blue in distilled water in an ultrasonic bath (more concentrated solutions of the dye may partly dimerize and further polymerize in aqueous medium,<sup>1</sup> giving rise to apparent deviations from Beer's law). Because methylene blue is difficult to dissolve in water, the dye was allowed to stand for 2 days in a dark cabinet (UV component of daylight enhances photodegradation of the dye) at room temperature until the absorbance of the solutions remained unchanged.

Real industrial wastewater containing an azodye (a composite NC-dyestuff used in leather dyeing, of which the exact chemical composition is patented) was obtained from Karakoc Kimya (located in Tuzla Organized leather processing industrial region) at the final stage of the leather dyeing operation. The synthetic leather-dyeing wastewater was produced in the laboratory according to the recipe given by the leather factory. The synthetic wastewater contained ammonium lignosulfonate, ammonia, ammonium formate, and formic acid in addition to the azodye supplied by the factory.

### Instruments

All spectrophotometric measurements were made with a UV-Visible PG T80+ spectrophotometer. The pH measurements were made with 766 Knick pH-meter equipped with a glass electrode. Edmind Buhler 7400 Tubingen shaker was used for batch contact experiments. The IR spectrum of the synthesized resin was taken with a Perkin-Elmer 1310 IR spectrometer.

### Methods

#### Batch adsorption

The data for adsorption isotherms were recorded at room temperature. A definite amount of adsorbent

with a particle size of 16–18 mesh was introduced to 10 mL aqueous solutions of methylene blue of desired concentrations. The initial concentrations of methylene blue solutes were varied in the range 1.5–15.0 mg/L. All adsorption experiments were performed at pH 7–8 for 20 min in the rate of 325 rpm except those in which the effects of pH and contact time were investigated. The pH of the solutions was adjusted with dilute NaOH or HCl solutions. At the end of the adsorption process, the concentration of residual methylene blue remaining in solution ( $C_e$ ) was determined spectrophotometrically. The measurements were made at the wavelength  $\lambda = 665$  nm which corresponds to maximum absorbance. Solutions containing no methylene blue were used as blank. The amounts of methylene blue adsorbed and the resin capacity were calculated with the aid of the concentrations of the solutions before and after the adsorption process.

The dependence of adsorption on particle size was investigated by batchwise adsorption experiments. To four different 50-mL-flasks were placed 0.2 g amounts of resin having particle sizes between 16 and 70 mesh; 10 mL-aliquots of 2.0 mg/L methylene blue solution were added. Batchwise contact of solute-sorbent and absorbance measurement after equilibration were practiced as stated above.

#### Column adsorption

A mass of 1.5 g of resin in the particle range of 16–18 mesh suspended in water were slurry packed in a glass column at a height of 3 cm. After rinsing the column with water thoroughly, 2.0 mg/L methylene blue solution was passed through the column with a flow rate of 1 mL/min (except in cases when the effect of flow rate was investigated). The column eluates in successive 2.5 mL-fractions were monitored with a spectrophotometer. Solutions containing no methylene blue were used as blank. The resin capacity was calculated with the aid of the concentrations of solutions before and after the adsorption process (i.e., at conditions when column breakthrough occurred).

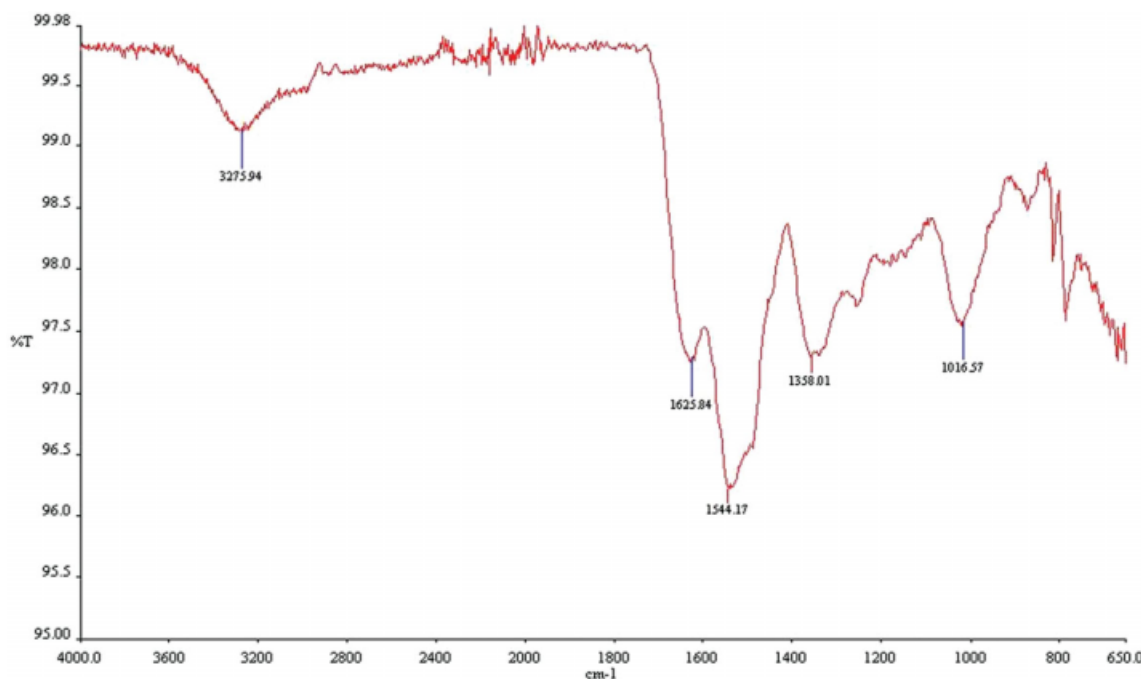
## RESULTS AND DISCUSSION

### IR spectrum of resin

The IR spectrum of the synthesized melamine-formaldehyde-urea (MFU) resin (Fig. 1) showed bands at 3275.94, 1625.84, and 1358.01  $\text{cm}^{-1}$ , attributable to NH, C=O, and CN group vibrations, respectively.

### Effect of contact time

Methylene Blue solutions at different concentrations as 0.2, 2.0, and 10.0 mg/L were prepared by diluting



**Figure 1** IR spectrum of the synthesized melamine-formaldehyde-urea resin. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

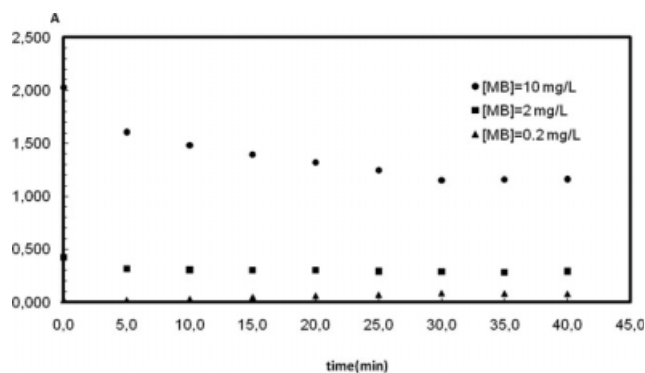
the stock solution. The concentration range was selected in geometric order so as to cover all possibilities of monomer and dimer of the dye<sup>1</sup> that would result in a more realistic description of the adsorption process as a function of concentration. The adsorption of methylene blue on 0.2 g resin (liquid/solid ratio = 50) was followed for 40 min. Figure 2 shows the absorbance of methylene blue remaining in solution decreases with increasing contact time.

The adsorption of methylene blue on the resin showed a fast increase with time at the initial stage of adsorption, and after 25 min, the absorbance of the dye remaining in solution practically stayed constant. Dogan et al. showed that the dye adsorption onto perlite is fast, and basically physical in nature.<sup>13</sup> Similarly, maximum dye was sequestered within 30 min in contact experiments using sawdust sor-

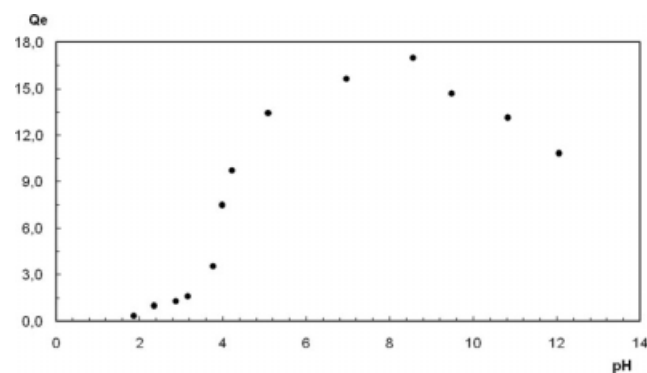
bent for methylene blue-containing simulated wastewater, and adsorption was shown to follow a first order rate equation.<sup>2</sup>

#### Effect of pH and possible reaction mechanism

Thirteen methylene blue solutions at different pH values were prepared by diluting the stock solution. Methylene blue solution was contacted with 0.2 g melamine-formaldehyde-urea resin (liquid/solid ratio = 50) for 20 min at 325 rpm. The parameter  $C_{ads}$  (Fig. 3) as the amount of adsorbed methylene blue was calculated with the aid of the difference of absorbance values. At a pH of about 7–8, the adsorption by the resin was found to be maximum (Fig. 3). This is in accordance with the reported pH range of maximal methylene blue adsorption onto various

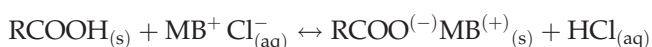


**Figure 2** Effect of batchwise contact time on adsorption process.



**Figure 3** Effect of pH on methylene blue adsorption by MFU resin.

noncommercial activated carbons prepared from plant wastes.<sup>14</sup> Al-Ghouti et al.<sup>1</sup> showed that at low pH when both the adsorbent (diatomaceous earth) and dye (methylene blue) are positively charged, there is significant decline in the observed adsorption. Here, the  $-NH$  groups of the resin should be positively charged at low pH, enhancing repulsion of the similarly charged methylene blue cation ( $MB^+$ ). Moreover, excessive  $H^+$  ions compete with the dye cations for effective adsorption sites at low pH, thereby decreasing adsorption. Because the tendency of the dye to polymerize at high pH increases,<sup>1</sup> the effective cationic charge of the dye may decline at high pH so as to decrease adsorption onto the negatively-charged sorbent (possibly having effective  $-COO^-$  groups). Inspection of the work of Gaffar<sup>15</sup> reveals that the principal dye adsorption reaction by the carboxylic groups of the resin at neutral pH can probably be represented by the equation:

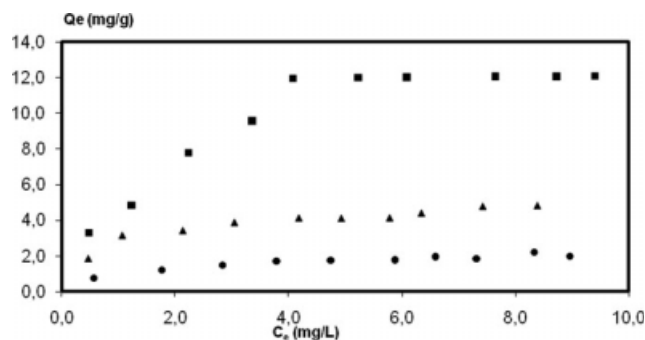


Because weak acidic surface groups function better at a pH slightly above their acidity constant ( $pK_a$ ) near neutrality to enable a stronger electrostatic attraction with the dye cation (i.e., of the type  $RCOO^- + MB^+$ ), dye adsorption on the resin was maximal at neutral pH. Although the basic character of adsorption is electrostatic, additional intermolecular forces such as hydrogen (H)—bonding interaction between the dye nitrogen atoms and surface hydroxyls of the sorbent may play additional roles in dye uptake.<sup>1,14</sup>

Self-aggregation of methylene blue (MB) in aqueous medium is a well-established fact. The interaction energy giving rise to self-aggregation basically comes from van der Waals and dispersion forces, in addition to short-range forces involving multipores.<sup>16</sup> In their comprehensive review of ionic self-assembly of supramolecular systems, Faul and Antonietti<sup>17</sup> summarized the diverse combinations between polyelectrolytes, dye clusters, and similar systems, and stated that H—bonding is one of the key forces determining the strength and directionality of secondary interactions used for higher levels of integration in such systems. Thus, hydrogen-bonding interactions are relatively weak between MB and solvent ( $H_2O$ ) molecules,<sup>16</sup> but

**TABLE I**  
The Effect of Resin Grain Size on Methylene Blue Uptake

Grain Size (mesh)	$A_{(\lambda=665 \text{ nm})}$	Adsorption, %
16–18	0.113	67.150
18–30	0.065	81.100
30–35	0.052	84.880
35–70	0.041	88.080



**Figure 4** Adsorption Isotherm of Methylene Blue on MFU Resin and fits of Langmuir Model (■: 20°C (293.15°K) ▲: 30°C (303.15°K) ●: 40°C (313.15°K)).

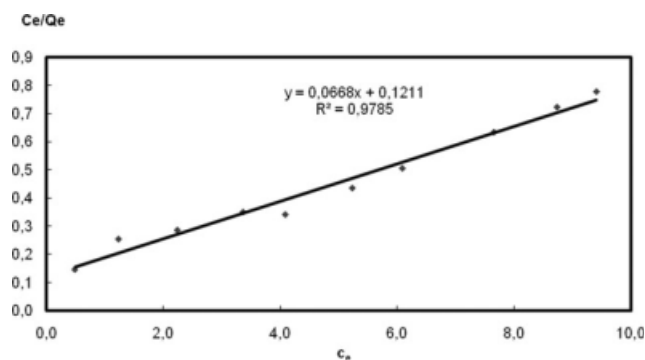
they should be much stronger between the *N*-containing aromatic ring of MB and melamine moieties of resin<sup>18</sup> resulting in dye adsorption. Additionally, it may be hypothesized that water structural effects and hydrophobic interactions (e.g.,  $\pi$ - $\pi$  interactions between the aromatic rings of sorbent and dye) are thought to play part in MB adsorption onto the resin. All these interactions may be classified as noncovalent (semichemical or physical) interactions considering the strength of associated intermolecular forces.

### Effect of particle size

Decreasing the grain size of resin particles had a positive effect on dye adsorption, as reflected in Table I. This observation also gives a clue on the physical nature of adsorption due to the favorability of increased surface area of the sorbent.

### Adsorption isotherms

Understanding adsorption equilibria are required for the analysis and design of adsorption processes. Adsorption equilibrium data of methylene blue was fitted to both Langmuir and Freundlich models. The constant parameters of the Langmuir equation have



**Figure 5** Linearized adsorption isotherm of Langmuir model at 293.15 K.

TABLE II  
Parameters of Langmuir and Freundlich Isotherms

Adsorption isotherm	Isotherm Equation	Slope <sup>-1</sup>	K <sub>L</sub> or K <sub>f</sub>	R <sup>2</sup>
Langmuir Isotherm	$Q_e = 8.250C_e/(1+1.551 C_e)$	Q <sub>max</sub> = 15.0 mg/g resin	K <sub>L</sub> = 0.552 L/mg	0.978
Freundlich Isotherm	$Q_e = 4.898 C_e^{0.47}$	n = 2.128	K <sub>f</sub> = 4.898 mg/g	0.900

a strictly defined physical meaning in contrast to the parameters of the empirical Freundlich equation.<sup>6</sup>

The simplest theoretical model for the monolayer adsorption is the Langmuir isotherm equation having the following form;

$$Q_e = Q_{\max}k_L C_e(1 + k_L C_e) \quad (1)$$

$$C_e/Q_e = (Q_{\max}K_L)^{-1} + Q_{\max}^{-1}C_e \quad (2)$$

$$Q_e = (C_0 - C_e)V/m \quad (3)$$

where Q<sub>max</sub> and K<sub>L</sub> are Langmuir isotherm parameters representing the maximum adsorption capacity for the resin and equilibrium constant related to the Gibbs free energy change of adsorption.<sup>19</sup> C<sub>e</sub> and Q<sub>e</sub> represent the equilibrium concentrations of the adsorbed dye in solution and on the sorbent resin, respectively; V and m denote the solution volume and resin mass, respectively. Figures 4 and 5 show the main adsorption isotherm [represented by eq. (1)] and its linearized form [represented by eq. (2)], respectively, regarding methylene blue adsorption on MFU resin.

With the aid of the linearized isotherm (correlation coefficient: r = 0.98) shown in Figure 5, the original Langmuir isotherm equation for batch adsorption data was derived as follows:

$$Q_e = 8.25C_e/(1 + 0.551C_e) \quad (4)$$

The Freundlich isotherm may be linearized with a similar algorithm: the logarithmic version of the Freundlich equation represents a line with a slope of 1/n and an intercept of K<sub>f</sub> in accordance with eq. (5) (figure not shown).

$$Q_e = 4.898C_e^{0.47} \quad (5)$$

All the parameters calculated for Langmuir and Freundlich adsorption modeling of dye uptake data are collectively summarized in Table II.

Among the Freundlich parameters, K<sub>f</sub> are related to adsorption capacity and n characterizes the heterogeneity of the system. As can be seen from Table II, the Langmuir model can represent the actual adsorption data better than the Freundlich isotherm. It is apparent from Figure 4 that adsorption (Q<sub>e</sub>) reaches a plateau region (possibly corresponding to monolayer coverage) with respect to equilibrium concentration of the aqueous phase (C<sub>e</sub>) beyond a limiting concentration, which is a characteristic property of the Langmuir isotherm. The observed Langmuir capacity of the MFU resin for methylene blue is higher than that of some unconventional sorbents (e.g., perlite: 5.8–7.7 mg/g,<sup>13</sup>) and slightly lower than that of sulfuric acid-treated sawdust.<sup>2</sup>

#### Effect of temperature

Temperature is an important parameter to determine and understand the mechanism of adsorption. In this study we used three different temperatures to predict the mechanism of adsorption of MB on MFU resin. The observed capacity was maximal at 20°C (Fig. 4).

All the parameters calculated for Langmuir adsorption modeling of dye uptake for different temperatures are collectively summarized in Table III.

The graph of ln K<sub>L</sub> versus 1/T (Fig. 6) obtained from Table IV gave the following linear (r<sup>2</sup> = 0.916) equation:

$$\ln K_L = 0.833 - 421(1/T) \quad (6)$$

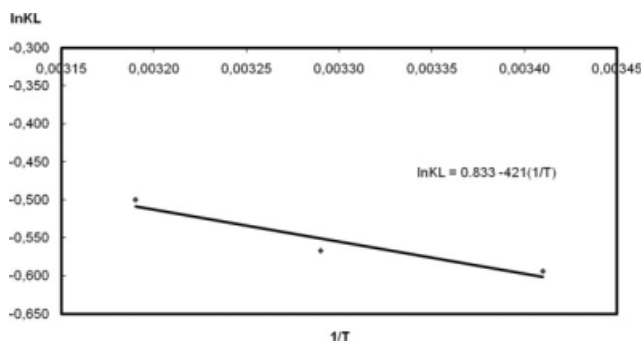
which is similar to the following theoretical equation;

$$\ln K_L = \Delta S^0/R - \Delta H^0/RT \quad (7)$$

Solving the above equations (i.e., using the slope-intercept of Ln K<sub>L</sub> versus (1/T) curve), the thermodynamic parameters such as ΔS<sup>0</sup>, ΔH<sup>0</sup>, ΔG<sup>0</sup> values were

TABLE III  
Parameters of Langmuir Isotherm at Different Temperatures

Isotherms	Parameters	T <sub>1</sub> = 293.15 °K	T <sub>2</sub> = 303.15 °K	T <sub>3</sub> = 313.15 °K
Langmuir	K <sub>L</sub> (L/Mg)	0.552	0.567	0.606
	Q <sub>max</sub> (Mg/g)	15.0	5.6	2.4
	R <sup>2</sup>	0.978	0.943	0.981



**Figure 6**  $\ln K_L$  versus  $1/T$  graph for the determination of  $\Delta H^0$  value.

calculated.

$$0.833 = \Delta S^0 / 8.31$$

$$\Delta S^0 = 6.92 \text{ J/mole K} = 0.00692 \text{ kJ/mole K} \quad (8)$$

$$\Delta H^0 / RT = 421 / 8.31T$$

$$\Delta H^0 = 3496 \text{ J/mole} = 3.5 \text{ kJ/mole} \quad (9)$$

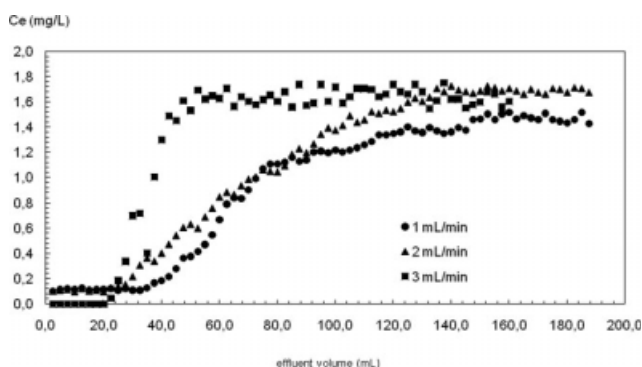
$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{for } 293.15^{\circ}\text{K}, \Delta G^0 = 1.47 \text{ kJ/mole} \quad (10)$$

For the relatively low magnitude of  $\Delta H^0 = 3.5$  kJ/mol, the adsorption mechanism is accepted to be basically physical.<sup>13</sup>

### Optimal flow rate and column capacity

Flow rates of 1, 2, and 3 mL/min were tested to determine the optimum flow rate for methylene blue adsorption by the dynamic column method. A mass of 1.5 g of MFU resin was slurry-packed at a height of 3 cm into a glass column. Figure 7 shows the optimum flow rate as 1 mL/min, as it provides a higher dynamic capacity for dye sorption (i.e., area above the curve).

Integrating the upper portion of the curve (shown in Fig. 7) for 1 mL/min flow rate under the same con-



**Figure 7** -Effect of flow rate on dynamic column adsorption of methylene blue.

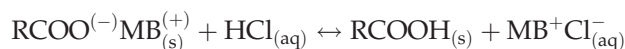
**TABLE IV**  
InKL Versus  $1/T$  Values for the Determination of  $\Delta H$

$1/T$	$\ln K_L$
0.00341	-0.594
0.00329	-0.567
0.00319	-0.500

ditions yielded a dynamic resin capacity of 81.4 mg/g. The dynamic capacity was greater than the batch capacity of dye sorption, because a column consists of several theoretical plates of multistage adsorption<sup>20</sup> in contrast to the single stage batch adsorption.

### Regeneration of the resin

The column regeneration experiments were performed at 25°C with 10 mL of 3M HCl solution. The spectra of methylene blue in the infiltrate and eluate (column effluent) were taken in neutral solution (pH 7–8) so as to compensate for any deviations from Beer's law due to pH changes. Absorbance spectral data showed that approximately 77% of the retained methylene blue could be easily regenerated with 3M HCl. The plausible reaction equation for regeneration is as follows:



### Performing optimal conditions for the treatment of leather industry wastewater

The optimal conditions of adsorption predetermined for methylene blue model dye were applied to synthetic and real wastewaters of a leather dyeing plant. The synthetic wastewater was obtained in the laboratory by dyeing leathers according to the recipe given by the leather plant. Aside from the conditions optimized for methylene blue removal, the single parameter tested was the column flow rate. Tables V and VI represent the transmittance percentages at selected wavelengths of the wastewater before and after the column treatment processes.

As can be seen from Tables V and VI, dye removal could be achieved with the proposed adsorptive treatment so as to increase the transmittance at

**TABLE V**  
Transmittance Percentages ( $T$ , %) of Real Leather Wastewaters (Collected from a Leather Dyeing Plant) Before and After the Adsorptive Treatment Process

Column flow rate (mL/min)	$(T, \%)$ of wastewater before adsorption		$(T, \%)$ of wastewater after adsorption	
	$\lambda: 290 \text{ nm}$	$\lambda: 600 \text{ nm}$	$\lambda: 290 \text{ nm}$	$\lambda: 600 \text{ nm}$
1	1	12.9	49.3	70.5
2	1	12.9	30.0	22.8
3	1	12.9	13.0	15.7

**TABLE VI**  
**Transmittance Percentages (*T*, %) of Synthetic Leather Wastewaters (Prepared in the Laboratory According to the Plants Recipe) Before and After the Adsorptive Treatment Process**

Column flow rate (mL/min)	<i>(T</i> , %) of wastewater before adsorption		<i>(T</i> , %) of wastewater after adsorption	
	$\lambda$ : 290 nm	$\lambda$ : 600 nm	$\lambda$ : 290 nm	$\lambda$ : 600 nm
1	4.3	13.6	87.3	99.5
2	4.3	13.6	72.0	97.2
3	4.3	13.6	32.4	60.9

600 nm from 13.6 to 99.5%, and from 12.9 to 70.5%, respectively, for simulated and real wastewaters.

### CONCLUSIONS

This study has proven that melamine-formaldehyde-urea (MFU) resin is an important adsorbent for dye removal because of its low cost, considerable adsorption capacity, and dilute acid regenerability. The isotherm of adsorption of methylene blue -as a model dye- on melamine formaldehyde resin basically fits the Langmuir model in preference to the Freundlich model. The optimal removal pH is in the neutral region (pH 7–8), and the adsorption capacity of the resin for methylene blue is greater than those of most unconventional sorbents. The adsorption mechanism is basically of physical character (noncovalent interaction) as demonstrated by the low value

of  $\Delta H^0$ . The column capacity is greater than the batch capacity.

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