REMOVAL OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTIONS BY USING ACTIVATED CARBON/UREA-FORMALDEHYDE COMPOSITE RESIN AS AN ADSORBENT

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ABSTRACT

Activated carbon/urea formaldehyde resin (AC/UF) may be used as a sorbent for textile dyes removal from industrial wastewaters such as methylene blue (MB). In order to obtain the adsorption mechanism of adsorption processes were studied by (FTIR) spectroscopy. The effect of various parameters like initial concentration, amount of AC composite doping, and mass dosage has been studied. Increasing the concentration of the adsorbent promoted an increase in the percentage of removal until saturation of the adsorbent. The experimental isotherm data were analyzed using Langmuir, Freundlich and Temkin models. Within the studied range of dye concentrations, the adsorption equilibrium was found to follow the Freundlich isotherm model well, with $R^2 > 0.985$. The present adsorption studies of MB dye from aqueous solution revealed the potential of AC/UF to be utilized as an alternative, inexpensive, and environmentally benign adsorbent for water purification.

Key words: Methylene blue, Adsorption, Adsorption isotherms, Urea formaldehyde resin.

INTRODUCTION

Dye wastewater is obtained mainly from textile, leather, paper, rubber, plastics, cosmetics, pharmaceutical, and food industries. Because dye wastewater always comes as large quantities, complex composition, color depth, and is of high toxicity. It causes severe environmental pollution and human health hazards if it is not treated properly before

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discharging into the natural water[1]. Some of the dyes also inhibit the growth of biota and importantly they can be mutagenic and carcinogenic compounds[2]. The cationic dye of methylene blue (MB) is mostly used for dying of cotton, silk and wood[3]. MB can disturb human health as it cause the injury of eyes, breathing difficult, worming, profuse sweating, mental confusion and methemoglobinemia[3]. Therefore, an increased interest has been focused to find economic and effective methods for removing of such dyes from the contaminated water[4,5].

Current treatment methods for dye wastewater include physical, chemical, and biological methods, and so on. Various removal methods have been studied by photocatalytic degradation[6-16], adsorption[17-24], chemical coagulation,[25] liquid membrane separation[26], electrolysis[27], biological treatments[28], and oxidation[29]. However, these processes vary in their effectiveness, costs, and environmental impacts[30]. Among these processes, the adsorption process is much more competitive than other methods for its ready availability, lower cost, and wider range of applications[1]. In adsorption processes a porous solid (adsorbent) is used to capture soluble substances present in aqueous solution (dyes for instance). Adsorption studies are generally focused on adsorbent selection, and articles, which evaluate its performance for dye removal can be commonly found on the literature: agro-industrial byproducts,[31,32] chitosan,[33,34] bacterial and fungal biomass,[35,36] activated carbon,[20,37,38] industrial waste[39,40] and minerals,[41-43] among others has already been considered. The studies involving this material showed that it could be a more efficient and low-cost material for dye uptake.

This study is yet another attempt to explore the possibility of utilizing AC/UF resin composite for the removal of hazardous methylene blue dye (MB) from aqueous solution by performing batch studies. The effect of factors such as adsorbent dose, initial concentration and amount of composite doping was investigated. The equilibrium sorption behavior of the adsorbents has been studied using the adsorption isotherm technique. Experimental data have been fitted to various isotherm equations to determine the best isotherm to correlate the experimental data.

EXPERIMENTAL

Materials

Analytical grade MB supplied by Sigma-Aldrich, is used as adsorbate without further purification. The concentration of this dye is determined by a UV/spectrophotometer (Shimadzu 1650, Japan) at 663 nm wavelength.
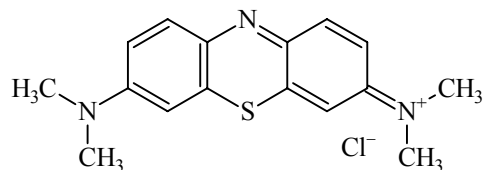
Fig. 1: Chemical structure of methylene blue

AC/UF powder preparation

AC/UF was prepared as: Some amount of urea was dissolved in aqueous solution acidified, then an amount of formaldehyde was added to the solution, with heating magnetinc stirrer for 24 hr at 60-80°C, then dried in oven for 24 hr to get a white powder of Urea/Formaldehyde (UF), the same lat step repeat again with different amounts of activated carbon prepared in our previous work[19] to get get AC/UF. For preservation, they kept in glass stopper bottles (containers) and to minimize contact with humidity all these bottles were preserved in oven (60°C) before the time of use.

Preparation of dye solutions

The stock solution was prepared by dissolving 1 g of analytical grade dye MB in 1000 mL of distilled water. All experiments were carried out at room temperature (25 ± 1°C) using a constant agitation speed of 100 rpm.

At predetermined time (60 min), the dispersion was drawn and separated immediately by centrifugation processing. Residual MB concentration in the supernatant was measured using a UV–vis spectrophotometer. The adsorption amount (q$_e$) and percentage removal (E%) are calculated based on the difference in the MB concentration in the aqueous solution before and after adsorption, according to the following equations:

$$q = \frac{(C_o - C_e)\,V}{W} \qquad \ldots(1)$$

$$E\% = \frac{(C_o - C_e)}{C_o} \times 100 \qquad \ldots(2)$$

where C_0 (mg L^{-1}) is the initial MB concentration and C_e (mg L^{-1}) is the MB equilibrium concentration at time t (min), V (L) is volume of solution, and W (g) is the weight of AC/UF sorbent.

RESULTS AND DISCUSSION

FT-IR Analysis

The FT-IR spectra of UF, different composite of AC/UF, performed before and after MB adsorption showed characteristic bands corresponding to various functional groups.

It is clear from the Fig. 2 that UF have a little bit shift in spectra when compared with AC/UF and the same behavior after adsorption of MB, a significant change in intensity or shift of the present function groups has been observed. Fig. 2 shows new interactions formed between the functional groups of main composite of AC/UF and the positively charged dye molecules.
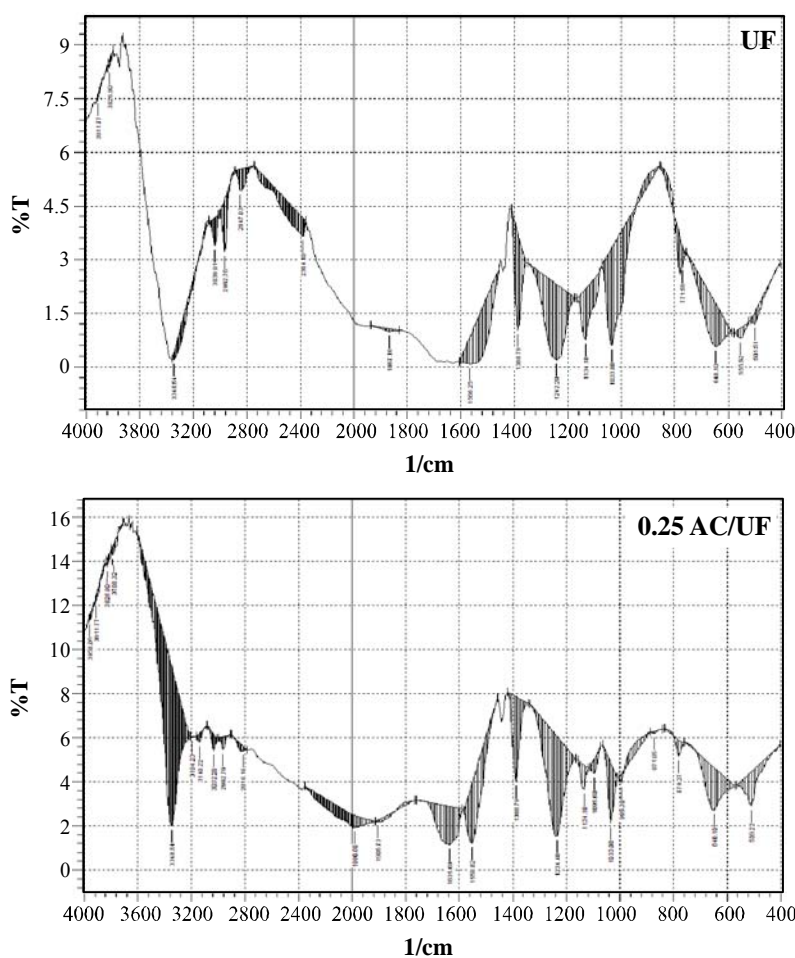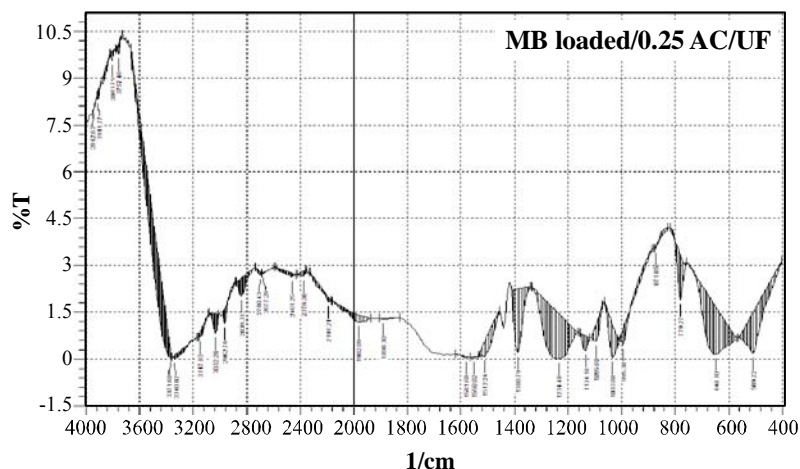
**Fig. 2: FT-IR spectrum of UF, 0.25 AC/UF, and MB loaded on 0.25 AC/UF
(Adsorbent dosage = 0.5 g, Contact time = 60 min, Temperature = 298 K,
Shaking rate = 100 rpm and pH = 6.4, and Contact time 1 hr)**

Effect of operational factors on adsorption

Effect of amount AC doping on UF resin

Fig. 3 shows the effect of AC amount doping ion the UF polymer. It is clear from Fig. 3, when the composite amount increased the adsorption capacity and the percentage of removal increased, this is due to increased of surface are of the adsorbent by increased of AC amount.
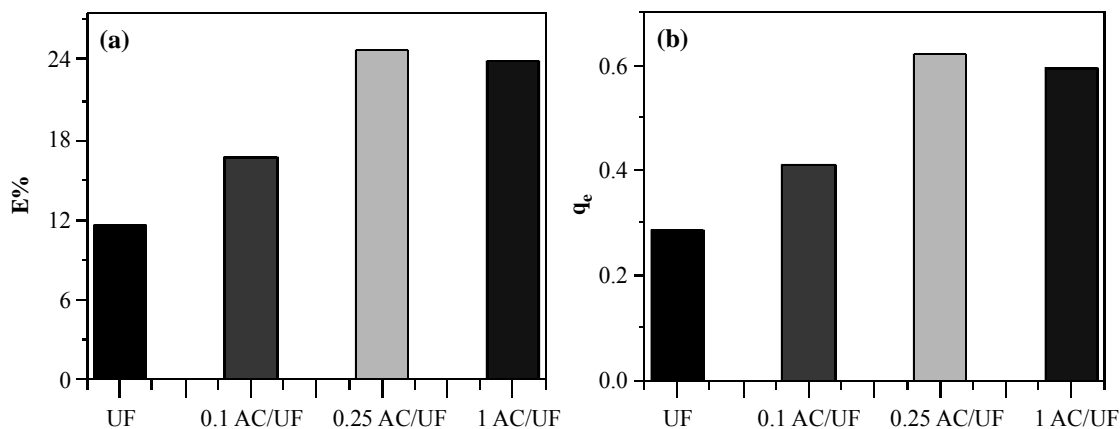
**Fig. 3: Effect of AC amount doping on the surface of UF for enhancement
(a) Percentage of removal, (b) Adsorption capacity**

Effect of AC/UF mass dosage

From an economic point of view, the study of adsorbent mass is useful for selecting the appropriate amount of adsorbent for industrial applications. The effect of adsorbent dose on the MB removal was studied by varying dosage of AC/UF from (0.5 to 10 g L^{-1}) at dye initial concentration of 5 mg L^{-1}. The results are shown in Fig. 4.
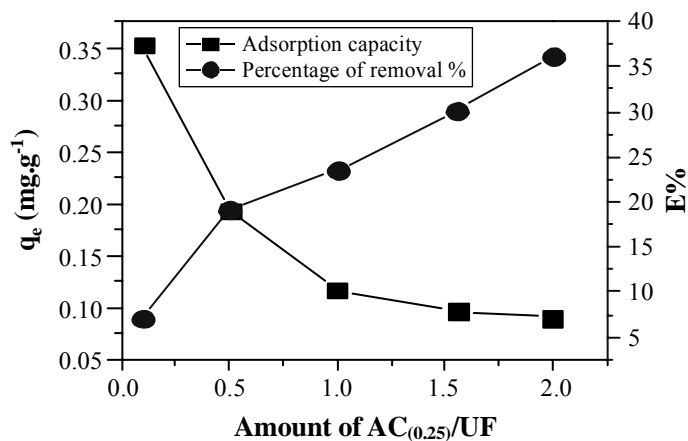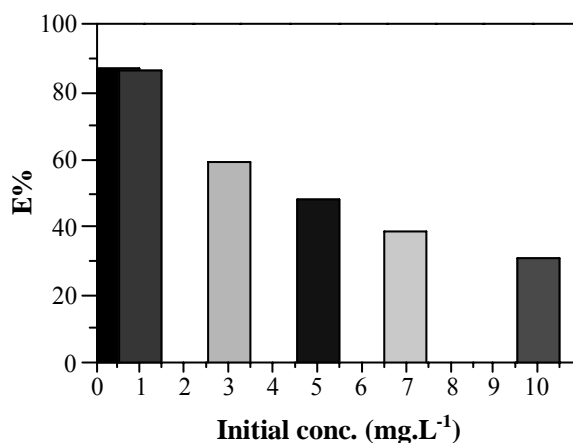

Fig. 4: Effect of adsorbent dosage on the removal of MB onto AC/UF (T = 298 K; Initial MB concentration = 5.0 mg L^{-1}; Shaking speed = 100 rpm; Natural pH = 6.4)

The increase percentage removal E% of MB was due to an increase in surface area and adsorption sites for a fixed initial dye concentration.[44,45] While, the adsorption capacity (mg g^{-1}) decreased with increasing adsorbent mass. This may be attributed to aggregation or overlapping of sorption sites. Therefore, the total number of binding sites and effective surface area of AC/UF decreases and the diffusion path length increased, resulting in adsorption capacity decrease.[1]

Effect of initial MB concentration

The initial concentration of the MB dye solution has a significant effect on color removal. It can be seen from Fig. 5 that the color removal of MB dye solution onto AC/UF by adsorption rose rapidly at the beginning and then gradually slowed down until equilibrium was reached. It might be explained that a large number of vacant surface sites were available for adsorption during the initial stage. However, with a lapse of adsorption time, the remaining vacant surface sites were difficult to be occupied due to steric barrier between MB adsorbed on the surface of AC/UF and solution phase.[1,46] The results can be

attributed to an increase in the driving force of concentration gradient with the increase in the initial concentration.[1]

Fig. 5: Effect of initial MB dye concentration on the removal of MB onto AC/UF
(T = 298 K; Adsorbent dosage = 5 g L^{-1}; Shaking speed = 100 rpm; Natural pH = 6.4)

Adsorption isotherm

Equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems for practical applications, as the isotherms can be used to interpret the specific relationship between the concentration of adsorbate and its extent of adsorption onto the adsorbent surface at a constant temperature.

Adsorption data are most commonly represented by the equilibrium isotherm value, which is a plot of the quantity of the sorbate removed per unit sorbent (q_e) as the solid phase concentration of the sorbent against the concentration of the sorbate in the liquid phase (C_e). Several isotherm models have been used to predict validity of the experimental data. In the present study, three of the most commonly used models, namely the Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption equilibrium.

The non-linear form of the Langmuir isotherm model[47] is given as:

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \qquad \ldots(3)$$

where K_L (L/mg) is the Langmuir adsorption constant related to the energy of adsorption, q_{max} and q_e (mg/g) are the maximum and equilibrium adsorption capacity,

respectively. Langmuir constants generated from adsorption data plot of q_e against C_e shown in Fig. 6 are summarized in Table 1.

The Freundlich isotherm is based on the premise that adsorption occurs on rare heterogeneous surfaces sites with different energy of adsorption and are also non-identical. The non-linear form of the Freundlich isotherm was used to investigate the adsorption process adherence to the model [48]:

$$q_e = K_f C_e^{1/n} \qquad \qquad \dots(4)$$

K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n$ is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n is equal to unity, the adsorption is linear; if the value is below to unity, this implies that adsorption process is chemical; if the value is above unity adsorption is a favorable physical process.[49] The values of the model parameters obtained from the plot of q_e against C_e shown in Fig. 6 are presented in Table 1.

Table 1: Langmuir, Freundlich and Temkin model isotherms parameters for MB adsorbed on the surface of AC/UF

Isotherm models	Parameters	Value	SE
Langmuir	q_m (mg.g^{-1})	1.4146	0.57
	K_L(L.mg^{-1})	0.6396	0.057
	R^2	0.94455	
Freundlich	K_F	0.32608	0.0132
	$1/n$	0.34934	0.0271
	R^2	0.98512	
Temkin	B/J.mole^{-1}	31.23	6.9231
	K_T	0.11049	0.00638
	R^2	0.9836	

q_{max} = Maximum adsorption capacity; K_L = Langmuir constant; K_F, $1/n$ = Freundlich constants; b, k_T = Temkin constants; R = Universal gas constant 8.314 J.K^{-1}.mol^{-1}
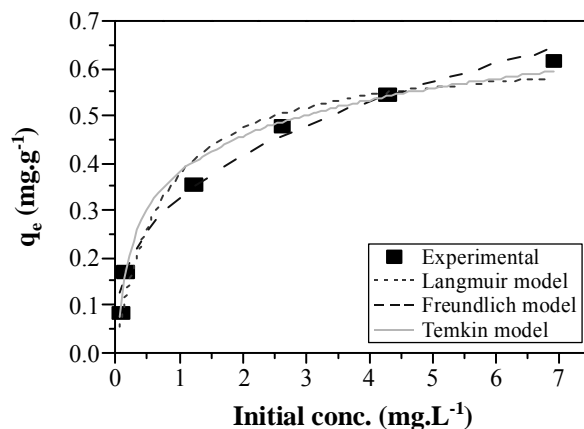
**Fig. 6: Langmuir, Freundlich and Temkin isotherms plot
(pH 6.4, agitation speed 100 rpm, mass dosage 5 g/L)**

The non-linearized form of Temkin isotherm[50] is represented by Eq. (5):

$$q_e = \frac{RT}{b} \log(K_T C_e) \qquad \qquad \dots(5)$$

where b Temkin constant related to the heat of adsorption (kJ/mol), R : Gas constant (8.314 J/mol.K), T : Temperature (K), and KT : Empirical Temkin constant related to the equilibrium binding constant related to the maximum binding energy (L/mg), (L/mol).

The adsorption data can be analyzed according to the Eq. (5), results are shown in Fig. 6, the isotherm constants K_T and b shown in Table 1. The best fit of isotherm was selected based on the highest correlation coefficient (R^2) value (closest to unity), which described the fitness of the isotherm to the experimental data.

CONCLUSION

Encouraging results were obtained with AC/UF tested as adsorbent of MB dye, currently used in papermaking and textile industries. The obtained results indicate that whole AC/UF can be successfully used as adsorbent of MB dye in aqueous solution, results show the AC/UF activity higher than UF resin. The adsorption isotherms from aqueous solutions onto AC/UF were also determined, the equilibrium data were fitted to the Langmuir, Freundlich and Temkin isotherm models. The adsorbent dose inversely affected the adsorption capacity of AC/UF, whereas the adsorption capacity increased with increasing initial dye concentration. The adsorption equilibrium data were fitted very well by the Freundlich isotherm model, with $R^2 > 0.9855$. Thus, the present investigation has provided a

new efficient, low-cost, economical, and environmentally safe adsorbent with potential for practical application in the treatment of dye-contaminated wastewater.

ACKOWLEDGMENT

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