



REMOVAL OF TEXTILE DYE (METHYLENE BLUE MB) FROM AQUEOUS SOLUTION BY ACTIVATED CARBON AS A MODEL (CORN-COB SOURCE WASTE OF PLANT): AS A MODEL OF ENVIRONMENTAL ENHANCEMENT

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Abstract

Activated carbon corn-cob may be used as a sorbent for textile dyes removal from industrial wastewaters such as methylene blue (MB). The adsorbent was characterized with Fourier transform infrared spectrophotometer (FT-IR), and scanning electron microscope (SEM). Various physiochemical parameters such as, contact time, initial dye concentration MB "5-30 mg L⁻¹", adsorbent dosage (0.001-0.1) g, and temperature (17, 35, 50) °C were investigated in a batch-adsorption technique. Result showed that the adsorption of MB was favorable at basic pH. The amount of dye removed was dependent on initial dye concentration, mass dosage pH of solution and solution temperature. Experimental data were analyzed using two model equations: Langmuir and Freundlich, isotherms and it was found that the Freundlich isotherm model fitted the adsorption data most with the highest correlation (R² ≥ 0.93879). The present adsorption studies of MB dye from aqueous solution revealed the potential of AC to be utilized as an alternative, inexpensive, and environmentally benign adsorbent for water purification.

Key words: Activated carbon, Methylene blue, Textiles dye, Adsorption isotherm.

Introduction

Synthetic dyes are used widely in dyeing and printing processes; among them many dye wastes are harmful and carcinogenic (Vandevivere 1998), causing a serious hazard to aquatic living organisms. Many conventional treatment technologies such as the tricking filter, activated sludge, chemical coagulation, carbon adsorption and photo-degradation processes for the dye removal have been investigated extensively (S.H. Lin 1993). Waste waters containing dyes are difficult to remove because of their inert properties. Another difficulty arises during the removal of dyes by the presence of minimum quantity of dye molecules in wastewater. The high costs involved in removing trace amounts of impurities make the conventional methods of removing dyes unpopular to be applied at a large scale (Crini 2007). Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials (Derbyshire, Andrews *et al.*, 2001). Many studies have been made on the possibility of adsorbents using activated carbon, peat, chitin, silica, fly ash, clay and others (Crini 2006). However, the adsorption capacity is not very large; to improve adsorption performance new adsorbents are still under development. Activated carbon has been established as an effective adsorbent due to its large surface area, low density and chemical stability, adsorption onto activated carbon has been found to be superior for wastewater treatment compared to other physical and chemical techniques, such as flocculation, coagulation, precipitation and zonation (Aljeboree 2015; Aljeboree 2016; Aljeboree, Alshirifi *et al.*, 2017). Activated carbon, also called activated charcoal, activated coal, or carbo activates, is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions (Aljeboree, Alshirifi *et al.*, 2017; Aljeboree, Alkaim *et al.*, 2019).

Due to its high degree of microporosity, just one gram of activated carbon has a surface area in excess of 500 m², as determined by gas adsorption. An activation level sufficient for useful application may be attained solely from high surface area; however, further chemical treatment often enhances adsorption properties.

Materials and Methods

Methylene blue (MB) dye, which has the chemical structure shown in Fig. 1, presents decentralizing positive charge on the organic skeletal structure, which could play a major role in keeping the species on the surface of the AC. The concentration of this dye is determined by a UV/spectrophotometer (Shimadzu 1650, Japan) at 663 nm wavelength.

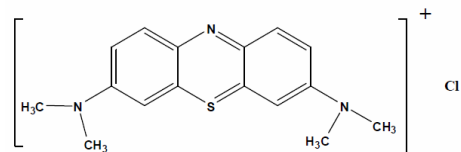


Fig. 1: The chemical structure of MB

All solutions used were prepared with deionized water and all reagents were of analytical grade. Working solutions of MB were prepared from a stock solution of 1000 mg L⁻¹ to give the required initial concentrations (C₀ = 5 to 30 mg L⁻¹) for each experimental run.

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:

$$q_e = (C_0 - C_e) V / W \quad \dots(1)$$

$$E\% = (C_0 - C_e) / C_0 * 100 \quad \dots(2)$$

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 sorbent.

Preparation of (corn-cob) activated carbon surface :

The activated carbon (corn-cob) was produced by impregnating 30g of dried raw (or demineralized) corn-cob powder with 100 ml of 40% H_3PO_4 at room temperature for 12h. followed by carbonization at 5000 OC for 60 mins in air. The sample was then cooled at room temperature and was thoroughly washed with distilled water to a neutral pH. This was then dried overnight at 110 °C in air. The clean biomass are mechanically ground and sifted to get a powder with particle size <50 μm .

Effect of Different Parameters on Adsorption Process

Initial Dye Concentration

Dye (MB) Initial tested concentrations were 5, 10, 15, 20, 25 and 30mg/L of dye onto (AC) with shaking in water-bath at 35 °C. The experiment was conducted at pH 6. Agitation was provided for 60 min contact time at a constant agitation speed of 120 rpm.

Effect of mass dosage

The effect of mass dosage was studied by agitating of different masses (0.01, 0.025, 0.05, 0.075, and 0.1) g, particle size 50 μm of AC and 100 mL of (MB) dye concentration (20 mg.L^{-1}) using shaker water-bath at 35 °C. The experiment was conducted at pH 6. Agitation was provided for 60 min contact time at a constant agitation speed of 120 rpm.

Effect of solution temperature

The effect of solution temperature was studied by agitating of variants solution temperatures (17, 35, and 50 °C), mass dosage 50 mg of AC and 100 mL of (MB) dye concentration (20 mg.L^{-1}) using water-bath shaker. The experiment was conducted at pH 6. Agitation was provided for 60 min contact time at a constant agitation speed of 120 rpm.

Result and Discussion

Adsorbent dosage

One of the parameters that strongly affect sorption capacity is the quantity of the contacting sorbent in the liquid phase because it determines the capacity of adsorbent for a given initial concentration of dye solution .The effect of AC dosages on the amount of dye adsorbed was investigated by contacting 100 mL of dye solution with an initial dye concentration of 50 mg/L for the adsorbent, for a contact time of 60 min at a temperature of $25 \pm 0.5^\circ\text{C}$, a shaking speed of 120 rpm and optimum pH of 6.0. Different amounts of adsorbents (0.005, 0.01, 0.05, and 0.1 g), results are shown in Fig. 2. The increase in surface area of AC may be the reason of elevation in the drug removal as a more effective site were be obtainable for adsorption The efficiency of drug abstraction was 97% at the optimum dose of AC nanoparticles, Also the results of increment of adsorbed drug quantity. The adsorption concentration reduction with adsorbent amount elevation is mostly because through reaction sites number was available for elevated adsorption

site by adsorbent amount increment while adsorption sites remain unsaturated (Aljeboree, Al-Gubury *et al.*, 2019).

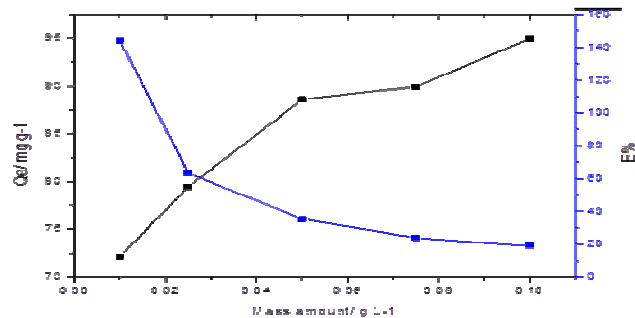


Fig. 2: Effect of mass dosage on the adsorption of methylene blue (MB) by the surface of AC. (pH of solution 6.1, Temp. 35 C, dye concentration 20 ppm, agitation rate 120 rpm, time of agitation 24 hr.)

Effect of initial MB concentration and Temperature

Figure 3 to 5 shows the effects of different initial MB concentrations on the adsorption capacity and removal efficiency of AC. as shown, the adsorption capacity (Q_e) increase with increasing initial MB concentration, while the percentage of removal decreasing with initial dye concentrations. The removal of dye by adsorption on AC was found to be rapid low concentrations of dye and then to slow down with increasing in dye concentration (Aljeboree, 2016). The color removal of MB dye solution onto AC 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 (Fabryanty, Valencia *et al.*, 2017; Aljeboree 2019; Aljeboree, Al-Gubury *et al.*, 2019). To determine whether the ongoing adsorption process was endothermic or exothermic in nature. The adsorption isotherms were determined for various dye-adsorbent systems. The removal of methylene blue MB has been studied at a temperature of (290, 308, and 313 K). Temperature has a pronounced effect on the adsorption process from the change in temperature will cause changes in the equilibrium capacity of the adsorbent for adsorption of particular adsorbate. The uptake of dye decrease with the increase in temperature, indicating the exothermic nature of the adsorption reaction (Alqaragully 2014). It was explained that as the temperature increased, the physical bonding between the organic compounds (including dyes) and the active sites of the adsorbent weakened. Besides, a decrease in the degree of freedom of adsorbed species and a decrease in available adsorption active sites (Tan 2008; Aljeboree and Abbas 2019; Liu, Li *et al.*, 2019).

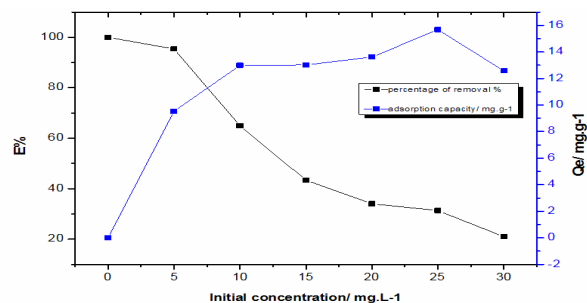


Fig. 3: Effect of initial concentration on the percent removal and amount of adsorbed MB dye onto AC (Exp. Condition: Temp. = 17°C, contact time 24 h, and pH of solution 6).

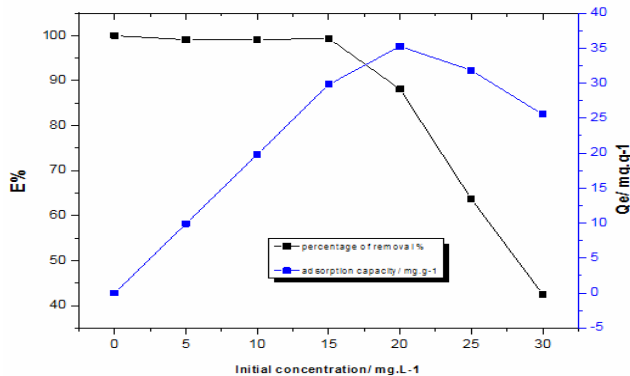


Fig. 4 : Effect of initial concentration on the percent removal and amount of adsorbed MB dye onto AC(Exp. Condition: Temp. = 50°C, contact time 24 h, and pH of solution 6).

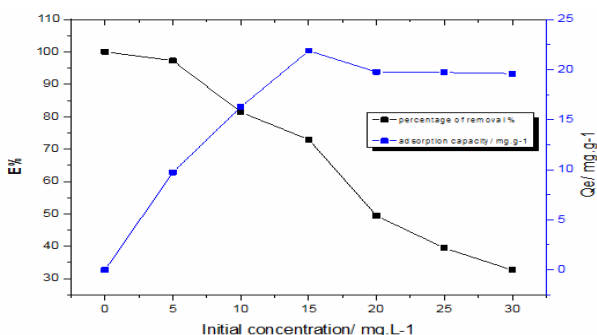


Fig.5: Effect of initial concentration on the percent removal and amount of adsorbed MB dye onto AC(Exp. Condition: Temp. =35°C, contact time 24 h, and pH of solution 6).

Models of Adsorption Isotherm

To investigate the parameters dependency of the adsorption capacity, two equilibrium models were analyzed, including Langmuir and Freundlich. All the isotherms were simulated using an iterative procedure based on a non-linear least-squares algorithm. The Langmuir adsorption isotherm equation (Langmuir, 1918 and Freundlich, 1939).

$$q_e = \frac{q_0 k_L C_e}{1 + K_L C_e}$$

expressed as follows requires for its applicability a monolayered coverage on the surface of adsorbent:

where q_e , K_L , q_{max} and C_e are uptake at equilibrium ($mg\ g^{-1}$), the Langmuir constant ($L\ mg^{-1}$), the monolayer adsorption capacity ($mg\ g^{-1}$) and the solution concentration at equilibrium ($mg\ L^{-1}$), respectively. The Freundlich equation is applicable for multi component adsorption. The Freundlich isotherm is expressed by (Ho, 2002 and Özacar, 2003):

$$q_e = K_f C_e^{1/n}$$

where K_f : Empirical Freundlich constant or capacity factor ($L.g^{-1}$) and n is the Freundlich exponent.

The Results of this model are shown in Figures (6), and the Langmuir constants are illustrated in Tables (1).

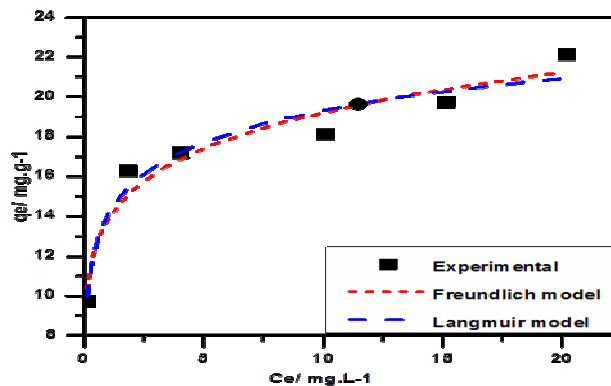


Fig. 7: Methylene blue dye adsorption model of Different adsorption isotherm nonlinear fit . on AC at pH 6, mass dosage 0.5 g/L, 35 °C initial conc. 20mg/L

Table 1: Model of Langmuir and Freundlich, isotherms parameters for Paracetamol drug adsorbed on the surface of at 35 °C.

Isotherm models	Parameters	MB dye
Langmuir	$q_m (mg.g^{-1})$	37.4496 ± 3.556
	$K_L (L.mg^{-1})$	0.59908 ± 0.9422
	R^2	0.92554
Freundlich	K_F	13.80408 ± 0.6174
	$1/n$	0.1434 ± 0.0198
	R^2	0.93879

Conclusion

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 waste water Encouraging results were obtained with AC tested as adsorbent of MB dye, currently used in papermaking and textile industries. The obtained results indicate that whole AC can be successfully used as adsorbent of MB dye in aqueous solution, also determined, the equilibrium data were fitted to the Langmuir and Freundlich isotherm models. The adsorbent dose inversely affected the adsorption capacity of AC, whereas the adsorption capacity increased with increasing initial dye concentration.

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