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ADSORPTION AND REMOVAL OF *TEXTILE DYE* (METHYLENE BLUE MB) FROM AQUEOUS SOLUTION BY ACTIVATED CARBON AS A MODEL (APRICOT STONE SOURCE WASTE) OF PLANT ROLE IN ENVIRONMENTAL ENHANCEMENT

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Abstract

In this study susceptibility to remove textile dye (Methylene blue MB), from water solutions by means of Apricot stone as activated carbon. The adsorbent was characterized with (SEM) and (FT-IR). Study different factor like, contact time, primary concentration of MB dye, adsorbent mass of (AC), and Effect of solution temperature were studied in adsorption method. Result appeared the adsorption of MB neutral pH. The adsorption uptake was including increase with increase in primary concentration of MB dye range of 5-50 mg/L and equilibrium time but decreases with the mass of AC range of 0.01, 0.025, 0.05, 0.075 and 0.1 g/100 mL and different solution temperature (16, 35, and 55^{o}C). also study the equilibrium data estimate utilize Freundlich and Langmuir isotherms. Langmuir, model better appear the uptake of (MB) dye, reveal that the adsorption of textiles MB dye in this study on the Apricot stone (AC) is heterogeneous with multi-layers.

***Keywords*: **Methylene blue MB, textile dye, Adsorption, Apricot stone, activated carbon, Isotherm.

Introduction

The most serious environmental problems was water pollution, so the treatment and elimination of wastewater has revolutionary prevalent concern. Adsorption technology is concept as one of the most influential methods to remove contaminants from water, because it is easy, suitable and little cost through tall sorption capacity and wide adaptation. several adsorbents have been applied for the removal of dyes from aqueous water (Alkaim *et al*., 2012; Aseel, 2018). activated Carbon (AC), as substantial group of nano-material's, reign received increasing attentiveness in last year's (Simate, 2012). Thus activated carbon (AC) take to be among the adsorbents that have been utilize for the effective removal of dyes from aqueous effluents (Alyaa Kareem, 2016; Louis Lefebvre 2018). Activated carbon, also called, carob activates, activated coal, or activated charcoal, is a form of carbon processed to have minor, little-volume pores that increase the surface area obtainable for adsorption or chemical reactions. (Aljeboree, *et al*., 2012; Aseel, M.A. 2019). In this study, preparation activated carbon to removal/ adsorption of dye Methylene blue from an aqueous water. The effects of different factors, for example amount of the activated carbon, pH solution, solution of the temperature and concentration of the MB dye.

Materials and Methods

Apricot stone, acquired Hilla Souk in (Babylon/Iraq), crushed, washed with distilled water to remove Contaminated, after that activation by H_2SO_4 (20%) and dried via oven at 90ºC for 6 hr. Then, it is activated in air hot oven at 300ºC (3 hr). until pH reached 6.6–6.8 of activated carbon can be remove the free acid by washing the material with distilled water and dried at 102ºC. The clean bio-mass are mechanically ground and sieved to obtain a powder low particle size.

Preparation of dye Methylene blue MB dye solutions

Preparation the stock solution by means of dissolving 0.5 g Methylene blue MB dye in 500 mL of distilled water. Completely the data were approved at 35 ^{o}C temperature via a continual contact velocity of 200 rpm. at equilibrium time (24h.), through centrifugation processing separated solution of the dye MB immediately from dispersion solution .Also using UV–vis spectrophotometer was measured the concentration of dye MB solution residual .created on the variation the concentration dye in the water solution before and after adsorption, determination the removal of percentage (E%) and the adsorption capacity (qe) according to the following equations:

$$q_e = (C_o - C_e)\ V/W \quad ....(1)$$

$$E\% = (C_o - C_e)\ /C_o \times 100 \quad ....(2)$$

C_o (mg L^{-1}) the primary concentration of Methylene blue MB dye and C_e (mg L^{-1}) is the Methylene blue MB dye equilibrium concentration at time t (min), W (g) is the weight of adsorbent V (L) is volume of solution .

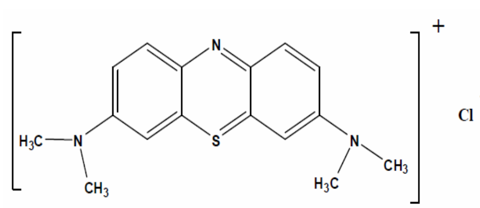

Fig. 1 : The Chemical structure of Methylene blue(MB).

Effect of several parameters on adsorption capacity

Effect of mass Apricot stone(AC) dosage

The effect of Apricot stone (AC) amount was studied by means of change the amount of Apricot stone (AC) in Adsorption of dye (Methylene blue MB) range 0.01, 0.025, 0.05, 0.075 and 0.1 gm /100 mL forasmuch the parameters like primary concentration of dye solution, contact time and temperature were all kept constant throughout adsorption process. Apricot stone (AC) amount was studied employ a chains of conical flasks having 100 mL of solutions Methylene blue(MB) dye solutions with the primary of dye concentration of 30 mg/L. The dye solution put in shaker at 35°C through over night

Effect of primary concentration of methylene blue dye

The effect of primary concentration MB dye its study via of shaking the chains of conical flasks having 100 mL of solution dye MB by various concentrations kind (5, 10, 20, 30, 40 and 50 mg/L) at 35ºC. All experiments was show at pH (6) normal and the Apricot stone (AC) dosage (0.075gm /100mL).

Effect of solution temperature

Study effect the temperatures solution by means of shaking the chains of conical flasks having 100 mL of solution dye MB (30 mg/L) with various temperature solution (16, 35, and 55°C). All the experiments were shown at the best pH (6) and the Apricot stone (AC) dosage (0.075gm/100mL).

Results and Discussion

FT-IR characterization for adsorbent/adsorbate

To check the surface groups accountable for methylene blue MB adsorption through utilize FT-IR technique. surfaces adsorbent (Apricot stone) and dye Methylene blue (MB)-loaded adsorbent sample after adsorption wear put in oven at 75 ºC for 3 h. Samples were made as pellet and then (FT-IR) of MB dye on adsorbent after the adsorption operation were registered in the extent 4000–400 cm^{-1} on a Bio Rad FTS 175C spectrophotometer Fig. 2.

The stretching adsorption band of O–H in the crystal structure of the adsorbent is observed at 3445 cm^{-1} determine to free OH and minify after adsorption with the adsorbent Methylene blue . All these findings propose the attachment of MB dye on Apricot stone. (Acemioglu, 2004; Hameed, 2008; Dizge, 2008; Guerra, 2011).

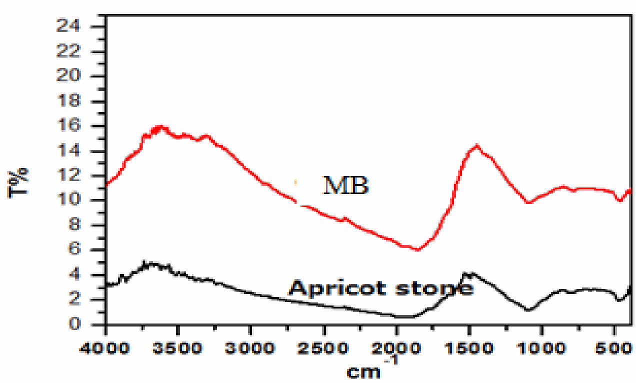

Fig. 2: FT-IR spectra for adsorption of MB on the surface of Apricot stone.

SEM characterization for adsorbent/adsorbate

Scanning electron microscopy (SEM) be necessary a fundamental tool for describe the morphology of the surface and essential physical particulars onto Apricot stone (AC). SEM of adsorbent substance were possessed after MB dye adsorption on Apricot stone (AC). surfaces appear obviously on the (MB)dye -loaded adsorbent plated via molecules of MB dye overall the surface at the normal pH The molecules of the methylene blue dye appear to need created a void-free film disappear particles of reliefs and porosity of the aggregates (Gupta 2011; Kismir, 2011). On the opposite the Apricot stone (AC) after adsorption exhibit well distinguishable particles and a structure porous show in (Fig. 3).

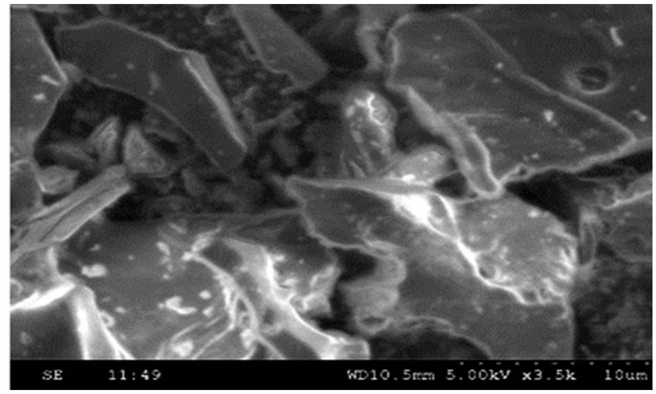

Fig. 3: SEM image for Apricot stone surface after adsorption.

Effect of Adsorbent Dose

Effect of the mass Apricot stone (AC) was needful in arranging to the minutest probable quantity, which appear the maximum adsorption stoichiometric. The different quantity from 0.001 to 0.1 gm /100 ml of Apricot stone (AC). The results show in Fig. 4.

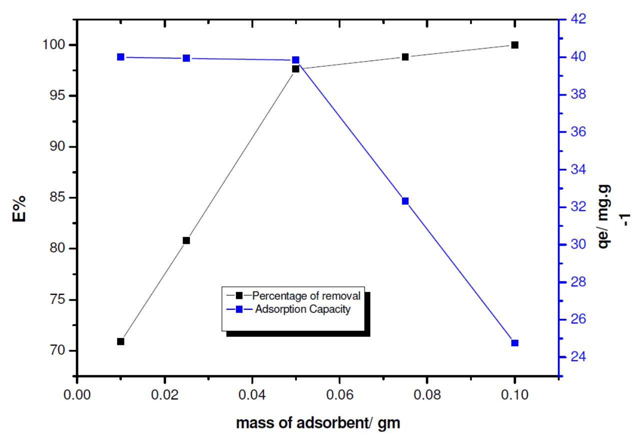

Fig. 4: Effect of amounts Apricot stone(AC) on adsorption MB dye : experimental conditions: Temp. 35 °C , dye conc. 30 mg/L, pH 6, and particle size 75 µm

Increase the surface area related with adsorbent mass enhancement the percentage of the dye removal and increase the number of adsorption sites obtainable from adsorption as reported previously (Zhu, 2007; Vimonses, 2009; Hua, 2010; Xia, 2011). The increase of methylene blue dye removal with Apricot stone (AC) mass due to the more binding active sites for adsorption and decrease adsorption capacity cases the adsorption active places stay unsaturated through reaction of the adsorption active site increases by means of increasing the mass Apricot stone (AC) (Yener, 2006; Malik, 2007; Aljeboree, 2016).

Effect of Temperature

To locate whether the continuing adsorption operation was exothermic or endothermic. Isotherms of the adsorption were estimation for several dye MB-Apricot stone (AC). in the study removal of MB dye at a temperature of (288.15, 303.15, and 333.15 K) at different primary concentrations of MB dye (10-50 $mg.L^{-1}$) results presented in Figures (5to7).

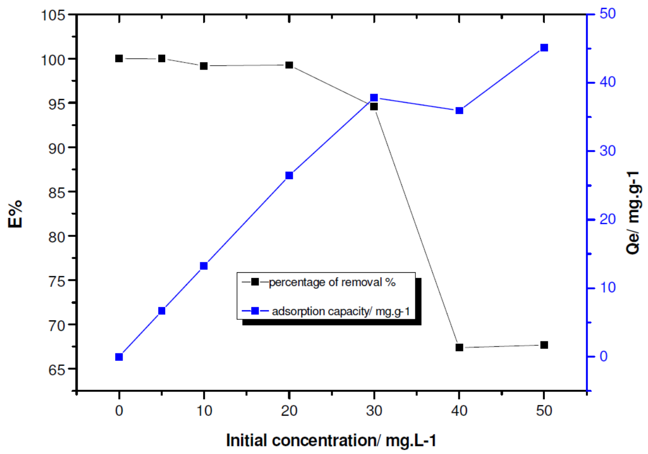

Fig. 5: Effect of primary concentration on the removal percentage and adsorption capacity MB dye onto *Apricot stone* (Exp. Condition: Temp. = 35°C equilibrium time 24 h, and of solution of pH 6).

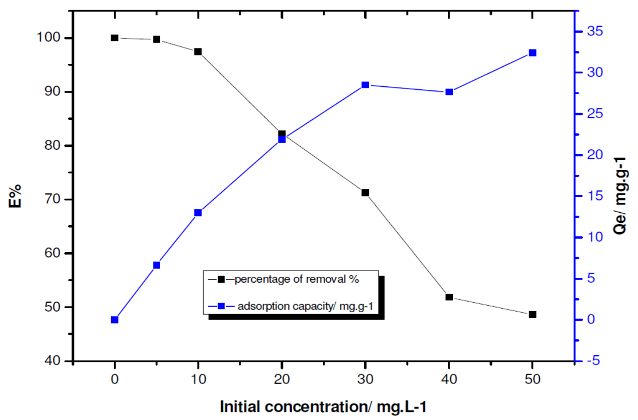

Fig. 6 : Effect of primary concentration on the removal percentage and adsorption capacity MB dye onto *Apricot stone* (Exp. Condition: Temp. = 50 °C equilibrium time 24 h, and of solution of pH 6).

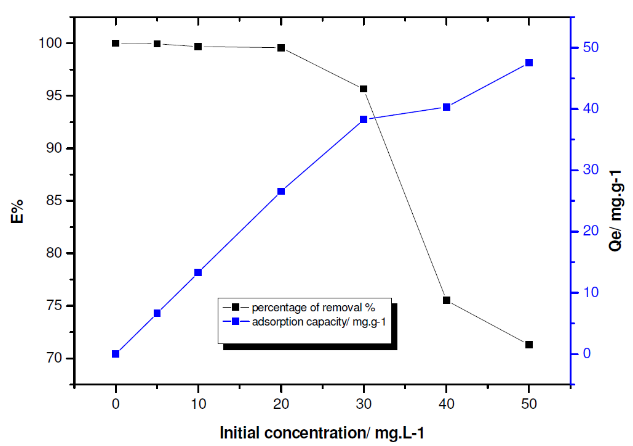

Fig. 7 : Effect of primary concentration on the removal percentage and adsorption capacity MB dye onto *Apricot stone* (Exp. Condition: Temp. = 15°C equilibrium time 24 h, and of solution of pH 6).

The result appear with increasing the solution temperature decreased the adsorption capacity of MB dye was while the percentage removal (E%) MB dye decreased with increasing the temperature of the solution for all primary concentrations of Methylene blue dye (Aljeboree 2012).

From Figures. (5-7), with increasing temperature the adsorption capacity of Apricot stone (AC) decreases, This is probably because effect of the exothermic through the adsorption process (Rattanaphani 2007; El-Sayed, 2011). Though, the adsorption phenomenon is generally affected via many factors, particularly temperature (El-Sayed, 2011). The percentage removal (E%) of Methylene blue dye with temperatures solution possibly will increase the mobility of the ions of MB dye and yields a swelling effect in the internal structure of adsorbent, therefore allowing the great molecules of MB dye to penetrate further (Xie, 2011).

Adsorption Isotherms

Freundlich Isotherm:

The empirically derived isotherm Freundlich is well-defined as shadows equation (3) (Ho, 2002; Özacar, 2003)

$$q_e = K_f C_e^{1/n} \qquad ....(3)$$

qe : Quantity adsorbed per unit mass of adsorbent at equilibrium (mg/g), (mol/g)

Ce : concentration of the equilibrium of adsorbate in solution after adsorption (mg/L), (mol/L)

K_f : capacity factor ($L.g^{-1}$), or Empirical Freundlich constant

1/n : Freundlich exponent

Kf defined as the distribution coefficient or adsorption and appear the amount of MB dye adsorbed on the adsorbent for unit concentration equilibrium. 1/n is the heterogeneity agent and n is a gauge of the deviation from adsorption of the linearity. Its value indicates the degree of nonlinearity between concentration solution and adsorption as follows: if the value of n is equivalent to unity, is linear of the adsorption; if the value is overhead unity adsorption is a favorable adsorption process physical, if the value is lower unity, this implies that chemical process (Senthil Kumar, 2010).

Langmuir Isotherm

The Langmuir isotherm is most widely used for the adsorption of pollutants from liquid solutions (Langmuir, 1916; Langmuir, 1918). An another equation was derived by way of Langmuir on the base of a definite case of the nature adsorption process from solution. The Langmuir adsorption isotherm is defined in equation 4 (Langmuir, 1916 and Langmuir 1918).

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \qquad ....(4)$$

where

qe : quantity adsorbed per unit mass of adsorbent at equilibrium (mg/g).

Ce : concentration of the equilibrium of adsorbent in solution after adsorption (mg/L).

q_o: Empiricial Langmuir constant which represents maximum adsorption capacity (mg/g).

K_L: empiricial Langmuir constant (L/mg)

The q_0 represents the whole number of surface places per weight of adsorbent. q_0 could be alike for all adsorbates. Though, q_0 may vary somewhat among several complexes because of several in adsorbate sizes. Thus, it generally represents the maximum achievable surface concentration of a given compound.

A plot of qe versus Ce (Fig.8) where the values of 1/n and KF are attained from the slope ad intercept of the linear regressions (Table 1).

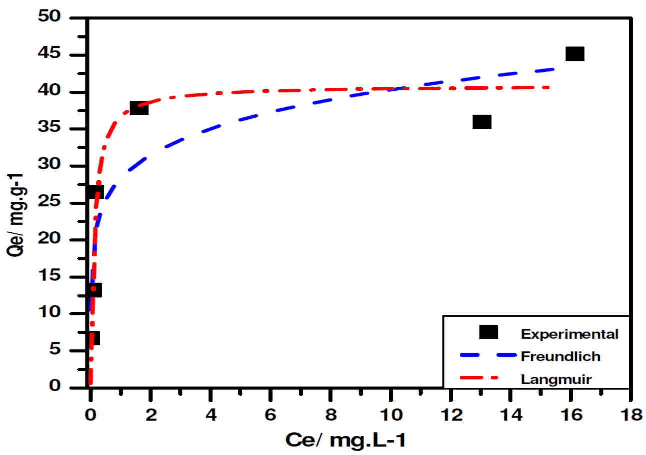

Fig. 8 : Paracetamol CRL dye adsorption model of Different adsorption isotherm nonlinear fit . *Apricot stone* (Exp. Condition: Temp. = 35°C, contact time 24 h, and pH of solution 6)

Table 1: model of Langmuir and Freundlich, isotherms factors for MB dye on the of *Apricot stone* (AC) at 35 °C.

Isotherm models	Parameters	MB dye
Langmuir	qm (mg.g^{-1})	40.91706 ± 3.22175
	K_L(L.mg^{-1})	8.7094 ± 3.5575
	R^2	0.88304
Freundlich	K_F	28.3018 ±3.02855
	1/n	0.15368 ±0.04244
	R^2	0.8072

Conclusions

- The adsorption efficiency and percentage of color removed increase with increasing equilibrium time, and surface area, and decreasing with increasing of temperature of the dye solution and the adsorption efficiency decreasing with increasing of adsorbent dosage
- For MB dye on adsorbent surfaces maximum adsorption found to be at T = 15. In fact adsorption found to decrease with increase in temperature of the solution.
- All effective parameters give good fitting of Langmuir model better than Freundlich models because suggests that adsorption is heterogeneous in nature.

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