Using Paper Waste as Adsorbent for Methyl Violet dye removal from waste water

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Abstract: This study has been conducted to examine the possibility of using waste paper as an adsorbent to remove methyl violet (MV) 2B dye from waste water. Initial dye concentration in the rang (20 to 80mg/L), pH of solution in the rang (4-10), adsorbent dose range (0.5-2.5 g) and contact time varying from (30 to 180)min, were studied. The experimental adsorption isotherms were fitted with the Langmuir and Freundlich models were found to be more represented to the experiments with high correlation coefficient ($R^2 = 0.8144$). The results showed that the highest (MV) dye removal efficiency was (97.63) at optimization condition pH 8, at room temperature for 120min, 2 g adsorbent dose and 20 mg/L dye concentration. The value of adsorption capacity was found to be 4.3 mg /g.

Keywords: *Adsorption, Waste paper, Methyl Violet, Isotherm Model.*

أستعمال المخلفات الورقية كمازة لأزالة صبغة المثيل البنفسجية من مياه الصرف الصحي

الخلاصة: أجريت هذه الدراسة لمعرفة أمكانية أستخدام المخلفات الورقية كمازة لأزالة صبغة المثيل البنفسجي (2ب)من فضلات المياه. التركيز الأولي للصبغة يتراوح بين (20-80) ملغم/لتر، درجة الحامضية للمحلول pH   تتراوح بين(4-10)، كتلة المازة تتراوح بين(5،0،5-2غم) ووقت الاتصال يتغير من (30الى180) دقيقة، تم أستخدام موديلين لانجمير وفروندليتش وجدت لتكون أكثر مطابقة للتجارب مع ارتفاع معامل التصحيح (R^2 0.8144 =). وأظهرت النتائج أن أعلى كفاءة إزالة لصبغة(MV) كانت (97.63%) عند أفضل ضروف الحامضية 8، في درجة حرارة الغرفة لمدة120min، 2 غم كتلة المازة وتركيز الصبغة 20 ملغم / لتر. وجد ان قيمة سعة الامتزاز 4.3.

1. Introduction

Water pollution has become serious environmental problem around the world and it is produced by the adding of chemical, physical, biological substances in certain concentration, either naturally or of manmade source [1].The basic sources of wastewater are the dyeing and finishing processes [2]. Wastewater can be from some manufacturing like dyestuff, textiles which can be difficult to treat leather, plastics, printing, etc. includes several types of synthetic dyes of [3], which are chemicals, and

on binding with a material will provide color to them [4], and primarily have complex aromatic structures which makes them biochemically constant[5].

 Due to high-scale production and broad application, as well as it can be consider as a source of huge environmental pollution and are serious health-risk; discharging even minor quantity colored wastewater is not only harmful the aesthetic nature of receiving streams, but as well it can influence aquatic life and food webs as a result of carcinogenic and mutagenic effects of dyes [6, 7].

    Dye removal from wastewater carried out by either biological methods or physicochemical methods. (e.g., adsorption, oxidation-reduction, chemical coagulation, ozone treatment, and membrane filtration) [8, 9, 10].
Adsorption technique is one of the best effective, inexpensive methods which used to produce high quality water [11].

    But the usage of expensive adsorbents can be reckoned a limiting factor [12, 13]. The cheaper and effective adsorbents from a variety of raw materials from waste to remove dyes have been used [14, 15]. Investigators have studied the feasibility of using low-cost substances, such as waste apricot [16], coconut shell [17], and dairy sludge [18], bamboo grass treated with concentrated sulfuric acid [19], peat [20], and bamboo [21] as adsorbents for the removal of dyes from waste water. These cheap adsorbents show good affinity towards dyes due to the presence of c
ellulose in these adsorbents [22].

    There is a large amount of paper waste in different forms produced daily. A lot of this cellulosic material is burned to create heat and only part of it is recycled for pulp and paper industries.
Putting this fact besides the sorption ability of cellulosic material, waste paper makes a potential green source to be used as low cost adsorbent for dye removal.
Adsorption isotherm models are applied (Langmuir & Freundlich) model, the Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites.

   The Langmuir isotherm equation is the first theoretically developed adsorption isotherm and it is still retains an important position in physisorption as well as chemisorption theories. The equation has also been derived using thermodynamic and statistical approaches.
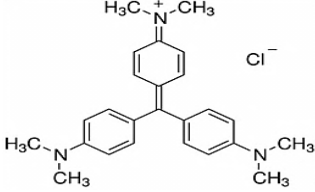

2. Materials and Methods

2.1. Dye

    MV (2B) dye was used in this work with the specifications according to the supplier, as illustrated in Table (1), Germany origin (Riedel-de Haen) purchased from chemical bureaus in Iraq.

2.2. Adsorbent

  paper waste (A4) was taken from office which was smooth, flat, multi-purpose paper, elemental chlorine free fiber, acid free and moisture retention capacity according to the

label on the pack. It was cut into suitable small pieces (5*2)mm by using suitable paper shredder and then kept in dry place.

Table.1. Specifications of MV Dye

Item	MV dye
Molecular Weight	393.96
Composition	Dye content, 75%
Melting point (MP)	137 °C (dec.)(lit.)
Molecular structure of MV (2B)	
Empirical Formula	$C_{24}H_{28}N_3Cl$
Wave length (nm)	584

3. Batch Adsorption Experiments

The experiments were done in (300) mL Erlenmeyer flasks where 2g of the adsorbent and 50mL of the MV solutions of (20–80 mg/L) concentration be added. The pH of each solutions in interaction with adsorbents was found to be in the range of 4–10, and then the prepared solution agitated by using ultrasonic wave device (which were available in Lab.) with an agitating speed of 300 rpm and for 180 min. After agitating the samples were withdrawn from the device, to get rid from the present suspended adsorbent, the mixtures were filtered through filters papers. By using UV- Visible spectrophotometer (UV-160 A Shimadzu). Final concentrations of (MV) were obtained. The percentages of dye removal or the amount of dye adsorbed were calculated from the following equation:

$$R\% = \frac{C_o - C_e}{C_o} * 100 \qquad (1)$$

$$q_e = \frac{V}{M}\left(C_o - C_e\right) \qquad (2)$$

Where R is the removal efficiency, Co, C_e represent the initial and final dye concentrations, V is the volume of the solution and m is the mass of adsorbent.

4. Effect of pH on Dye Adsorption

pH of solution usually plays a major role in the adsorption process and it affects the Solution chemistry of dyes and the activity of the functional groups of the adsorbent. In cases of dyes, different dye classes require different pH ranges. For instance, basic dyes require alkaline medium while reactive dyes demand strong acidic conditions for optimum dye adsorption. The effect of initial pH on adsorption of MV was examined over a range of pH values from (4-10) adjusted by using 0.5N HCl or 0.5N NaOH through taking 50ml of 20 mg/l MV dye solutions with 2 g of paper waste for 180 min

shaking at room temperature. (Normality was used for titration calculation, which is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of an identified analyte, unlike the Molarity use when the temperature of experiment change)

5. Effect of Dye Concentration

The initial concentration of MV solution in the range of (20, 40, 60, 80) mg/L and batch experiments were carried out with 2 g of paper waste at solution pH 8 for 180 min.

6. Effect of Adsorbent Dose

To determine the effect of adsorbent dose different weights of paper waste (0.5, 1, 1.5, 2, 2.5) g adding to the 50 ml MV solution of 20mg/l concentration and pH 8 that obtained from prior experiments.

7. Effect of Contact Time on Dye Adsorption

To find the effect of contact time (2) g of paper waste sample was mixed with 50ml of the aqueous solutions with initial concentrations 20mg/l of MV. The flasks with their contents were shaken for the different adsorption times (30-180) min at pH 8.

8. Adsorption Isotherm

Adsorption is usually described through an isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [23]. Several models describe the process of adsorption from which Langmuir and Freundlich isotherm models were can be represented respectively as follows [24]

K_L (Langmuir constant) were found by linearizing equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

The linear equation of Freundlich isotherm is as follows:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{4}$$

Where: K_f and n: Freundlich constants, of n between 2 and 10 shows good adsorption. The numerical value of 1/n less than 1 indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations

The Freundlich isotherm is more extensively used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. This model is based on adsorption on a heterogeneous surface.

It can be predicted whether an adsorption system is favourable or unfavourable using the essential characteristic of the Langmuir isotherm expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter defined by (5):

$$R_L = \frac{1}{1 + K_L\, C_o} \qquad\qquad (5)$$

Where C_o is the highest initial concentration. This parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$) or unfavourable ($R_L > 1$).

9. Results and Discussion

9.1. Effect of pH

The effects of solution pH on the adsorption of (MV) within paper waste was determined and the results are shown in Figure (1) that the removal efficiency increase with increase pH until it reached the maximum, at pH 8 and found that further increase in pH is unfavourable. Higher removal percentages of MV from solution were observed (96.45%, 96.55.3%, 99.18%, 95.75%) at pH (4, 6, 8, 10) respectively. As cellulose present in paper has negative value surface charged at wide range of pH, strong electrostatic attraction exist between it and the cationic MV dye, which leads to adsorption [25]. At high solution pH, the positive charge at the solution interface will decrease while the adsorbent surface appears negatively charged [26].
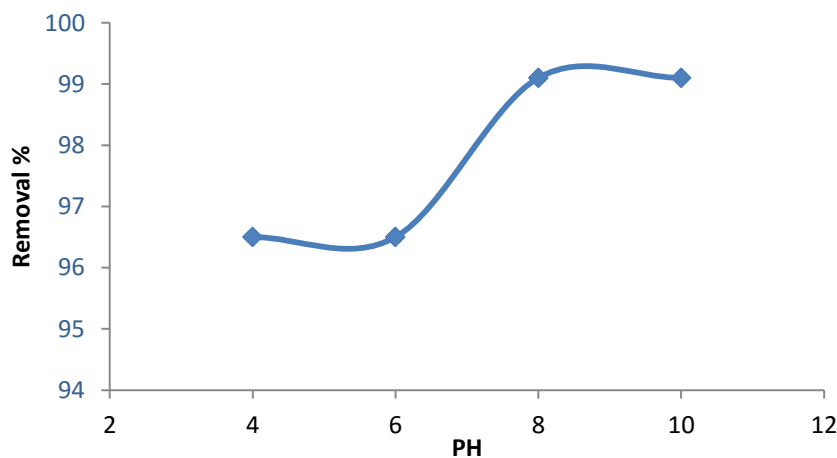

Figure1. Effect of pH solution on (MV) removal efficiency.

9.2. Effect of Initial Dye Concentration

The effects of dye concentration on removal efficiency of (MV) dye by paper waste shown in Figure 2. When pH fixed at 8.The results show that with increasing the initial dye concentration from (20 to 80) mg/L the removal efficiency was increased slightly from (95.3% to 96.5%).This slight effect associated with increase dye concentration is related to the saturation the vacant sites on the adsorbent surface in higher dye concentrations [27]. In other words, with the decrease of the pollutant concentration in

The aquatic environment, molecules of the adsorbate have more chance to react with the available active sites on paper waste and, as a result, the adsorption rate is increased [28].
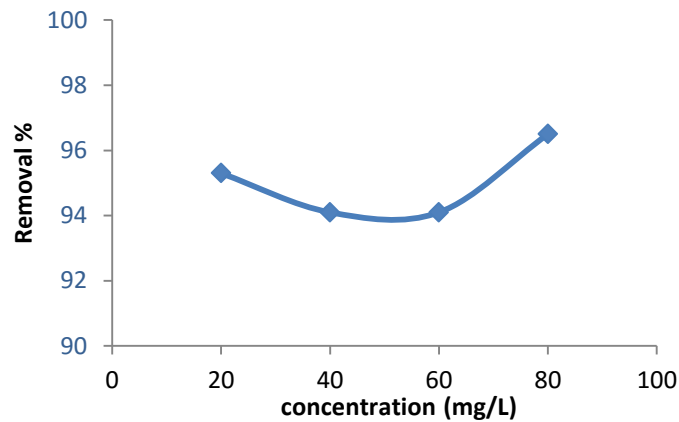

Figure 2. Effect of concentration on (MV) removal

9.3. Effect of Adsorbent Dose

Figure 3. Shows the removal of (MV) by waste paper at different adsorbent doses (0.5- 2.5 g) for the dye concentrations of 20 mg/L at pH 8. The results showed that, the increase in adsorbent dose lead to increase in the percentages of dye removal efficiency gradually in the range of (83.3%, 95.4%, 96.25%, 98.3%, 98.86%) respectively. This higher removal efficiency of MV as adsorbent dose increased, is due to the increase in adsorbent surface and availability of more adsorption site area of the adsorbent. Therefore the quantity of dye adsorbs increases [29].
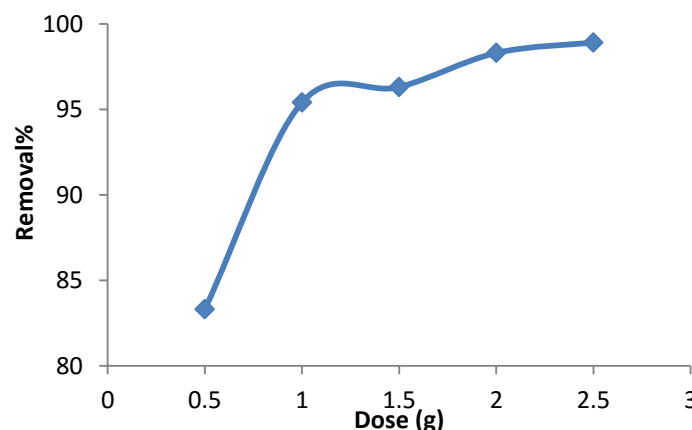

Figure 3. Effect of dose on (MV) removal

9.4 . Effect of Contact Time

The effect of contact time on the adsorption of MV dye by the waste paper is shows in figure 4. Based on the results, by increasing the contact time, the percentage of dye

6

removal efficiency increased, The results show that, as contact time increased, the percentage of dye removal efficiency increased (91.9%, 94.5%, 95.2%, 97.6%, 97%) respectively at varying time (30, 60, 90, 120, 180) min , and the best removal obtained at 120 min [30].
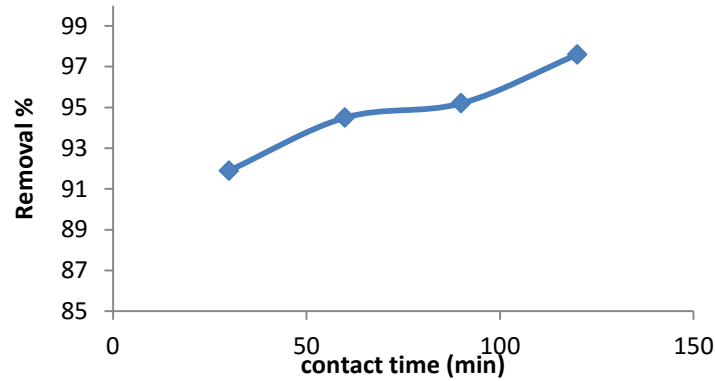

Figure 4. Effect of contact time on (MV) removal

9.5. Adsorption Isotherm

The typical graphical representations of the linearized plots are shown in figures (5) and (6) for adsorption of methyl violet on paper waste. The results show that the adsorption isotherms experimental equilibrium data (Table 2) were fitted to both the Freundlich and Langmuir isotherm equations, but Freundlich isotherm model provide better satisfactory than Langmuir isotherm model. This can be proved by investigating at the coefficient of determination for both models, R^2 straight line. Increasingly large K_f value indicates greater adsorption capacity. 1/n is a function of the strength of the used absorbent material shows a graph of adsorption isotherms for paper waste where the graph is showing the removal of (MV) is quite good. The value of R_L is less 1 which suggests that the adsorption is favorable. This well accordance to the Freundlich isotherm equilibrium data propose multilayer coverage of MV onto the site presence on surface of paper waste [31]. And assumes that the energy adsorbed on the adsorbent is non-homogeneous [32, 33].

Table 2. Isotherm constants for (MV) removal by waste paper

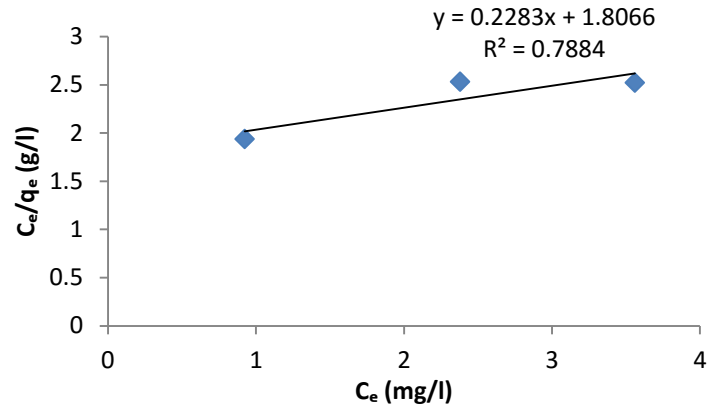| Material	Freundlich isotherm				Langmuir isotherm		
Material	K_f	n	R^2	R_L	R^2	K_L	qmax (mg/g)
Waste paper	0.516	1.08	0.814	0.022	0.788	0.55	4.6

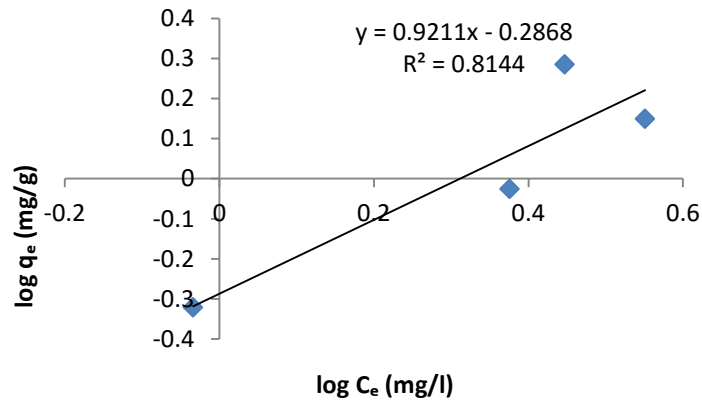Figure 5. Langmuir adsorption isotherm model

Figure 6. Freundlich adsorption isotherm model

10. Conclusions

Paper waste used as low cost adsorbent was successful for MV removal. Decolonization of dye waste water using paper waste was found to be the best method regarding cost-effective and environmental concerns. The results gained from this study were extremely well described by the theoretical Freundlich isotherm. Best removal effeciency was 97.63 at the conditions (pH 8, concentration 20 mg/L, dose 2g, contact time 120 min).

11. Abbreviations

C_o	Initial dye concentration
C_e	final dye concentration
K_L	Langmuir constant
K_F	Freundlich constant
MV	Methyl violet
m	Mass of adsorbent
n	Freundlich constant

q_e	Amount of dye adsorbed
q_m	Maximum adsorption capacity
R%	Percentage of dye removal
R_L	Separation factor
R^2	Correlation coefficient
V	Volume of the solution

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