

Adsorption of Methyl Orange from Wastewater onto Cane Papyrus

Usama Akram Saed¹, Mohammed Hussein Ali², Ahmed Adnan Atshan¹

¹ Chemical Engineering Dept., College of Engineering, Nahrain University, Baghdad, Iraq.

² Chemistry Dept., College of Science, Nahrain University, Baghdad, Iraq.

¹ E-Mail: ¹ usama_alrawi79@yahoo.com, ² mo_chemical@yahoo.com, ³ almamory85@yahoo.com

Abstract:

The aim of the present work is the adsorption of the Methyl Orange dye from wastewater onto Cane Papyrus by using continuous system (fixed bed). Continuous adsorption experiments of fixed bed were carried out to study the effects of (flow rate Q, initial dye concentration C₀, bed depth Z, and PH) on the adsorption capacity and performance of fixed bed adsorber. Adsorption through Cane Papyrus was found to be effective for the removal of the Methyl Orange, where the percent dye removal was 50% and reach 70% for some cases. The equilibrium data were determined experimentally and the equilibrium isotherm was found to be of a favorable type and fit well by Langmuir and Freundlich isotherms. In the kinetics study, pseudo-first order and pseudo-second order were tested; the first equation showed the best represent the experimental data.

Keywords: Adsorption, Methyl Orange, Can Papyrus

Introduction

The total dye consumption of the textile industries alone is in excess of 107 kg/year and estimated 90% of this total end-up on fabric [1]. Consequently, approximately 10.7 kg/year of dyes are discharged into the waste streams by textile industries [2]. The most common uses of dye are in textile and paper making industries. The presence of dye, although small in amount, greatly affects the quality of the wastewater. The color of dye in wastewater makes it impossible to be used as drinking water after conventional waste treatment method. Due to the chemical characteristics of dye, they are stable and not easily degradable by conventional water treatment methods. Over the years, the characteristics of dyes have varied and the environmental impact of dyes has become increasingly worrying.

Adsorption onto solid can be defined as the phenomena that taking up the molecules from the fluid phase onto the solid surface [3]. Adsorption is probably one of the most common advanced wastewater treatment processes, and it finding increased used in the wastewater treatment for removal of refractory toxic substances [4].

Activated carbon is an effective adsorbent primarily due to its extensive porosity and very large available surface area for adsorption [5].

Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust buffing dust of leather industry, coir pith, crude oil residue tropical grass, olive stone and almond shells, pine bark, wool waste, coconut shell etc. [6].

The objective of the present study was to assess the ability of Cane Papyrus to remove methyl orange from waste water, after that the adsorption data was fitted to various equations.

Materials and Methods

Dye solution used in the present experiments was prepared by dissolving a weighed amount of the powder reactive Methyl Orange dye in distil water. Adsorbate is the reactive Methyl Orange dye with chemical structure as shown in figure (1), and molecular weight (304 g/mol).

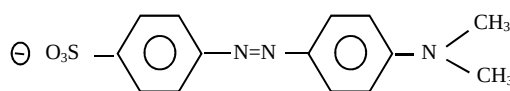


Figure 1: Molecular Structure of Methyl Orange Dye.

Adsorbent is Cane Papyrus taken from river, washed many times then dried at 120°C for 2hr, the taken amount was crashed using coffee machine. The Cane Papyrus was sieved at 300mm, the final sample was washed with many times to remove all dust and soil then dried again before it is used as adsorbent in the present work.

Experimental Set Up

Adsorption tests were carried out in a continuous system using Methyl Orange dye as the compound to be adsorbed by Cane Papyrus. figure 2 illustrates the schematic of apparatus for the study.

A vertical Glass column was used as fixed bed adsorber with inner diameter (1.5cm) and (80 cm) height. This column was packed with different heights of Cane Papyrus. The wastewater was introduced at the top of column and the samples were taken at interval time of (5min) from the bottom of the column.

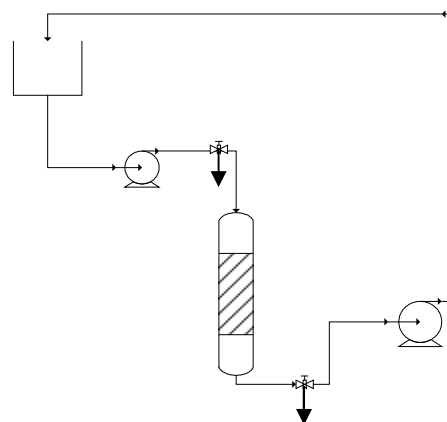


Figure 2: Schematic of continuous adsorption experimental rig.

Column Studies

A 300 mm Cane Papyrus was placed inside a fixed-bed column. The column dimension was 15mm I.D. and 80 mm height. Prior to each experiment, distilled water was passed through the column to rid the column impurities and air bubbles of. Different concentrations were pumped through the column at various flow rates. Effluent samples were collected from the bottom of the column at different intervals and the concentration of Methyl Orange was analyzed by measuring the absorbance at 464 nm with a UV/VIS spectrophotometer. All tests were carried out at room temperature, 25°C.

Results and Discussion

1- Effect of contact time and initial dye concentration

The experimental results of adsorptions of Methyl Orange dye on the Cane Papyrus at various concentrations (10, 20, 30, and 40)mg/L with contact time are shown in figure 3 and 4. The equilibrium

data were collected in table 1 which reveals that percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of cane papyrus increased with increase in dye concentration. This means that the adsorption is highly dependent on initial concentration of the dye. It is because this that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low; subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration. Equilibrium was established at 20 minutes for all concentrations. Figure 3 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dye on the cane papyrus surface [7].

Table 1: Equilibrium parameters for the adsorption of Dyes onto Cane Papyrus

t(min)	C _e (mg/l)				q _e (mg/g)			
	1.5g of Adsorbate							
	ppm							
0 (C ₀)	10	20	30	40	10	20	30	40
5	8.371	17.898	26.351	27.746	0.054	0.07	0.121	0.41
10	8.002	16.071	25.506	26.042	0.067	0.131	0.149	0.46
15	6.033	14.097	22.247	24.515	0.13	0.197	0.258	0.516
20	6.66	10.719	20.716	24.098	0.11	0.31	0.309	0.53
30	6.37	10.55	20.678	24.098	0.121	0.315	0.31	0.53
40	5.97	10.11	20.301	23.572	0.134	0.33	0.323	0.55

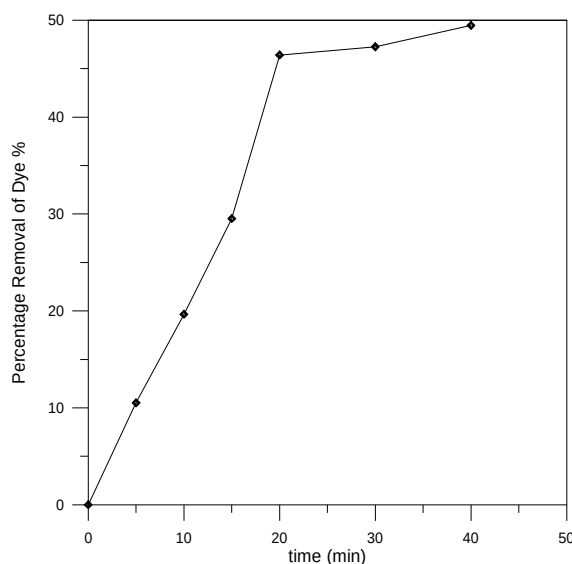


Figure 3: Effect of contact time on the removal of dye (20ppm) by Cane Papyrus

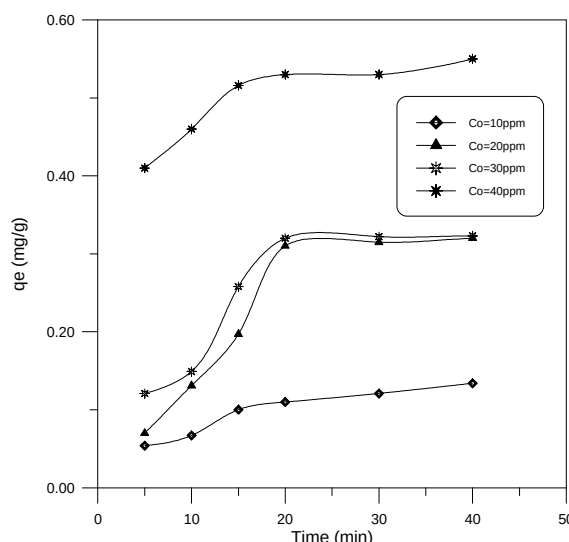


Figure 4: Adsorption capacity (mg/g of Cane Papyrus) as function of time for different concentrations

2. Effect of pH

The effect of pH on adsorption of methyl orange on cane papyrus was shown on figure 5, and can be observed as follows: pH=1.5>pH=4.5>pH=6.5>pH=9.5>pH=13.5

This is indicating that when the acidity of solution increased the amount of adsorption of (Methyl Orange) on the adsorbent surface Cane Papyrus was

increased. It means that the adsorbent has good partial negative charge by hydroxyl groups (-OH), and (Methyl Orange) also has negative charge as shown in Figure 1. That made repulsion between surface and methyl orange in solution.

When the acidity increase due to concentration of H^+ that will decrease the negative charge for Methyl Orange (MO^-), then adsorption increases.
 $H^+ + ^-MO \rightarrow H^+ ^-MO$

But, when the basicity of solution was increased, the amount of adsorption is decreased due to the increase of concentration of (OH^-), as shown in FTIR (figure 6).

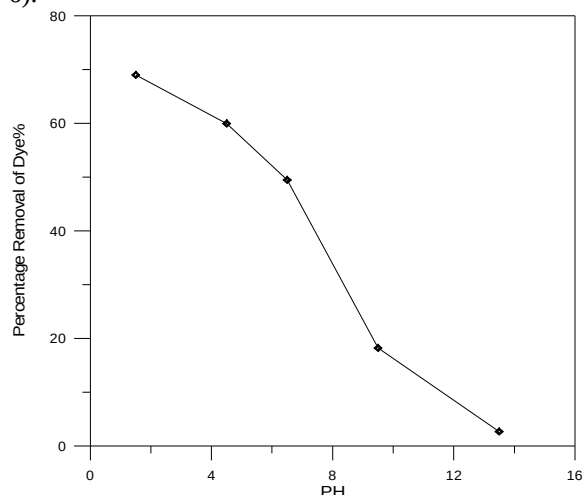


Figure 5: Effect of PH on the removal of dye (10ppm) by Cane Papyrus

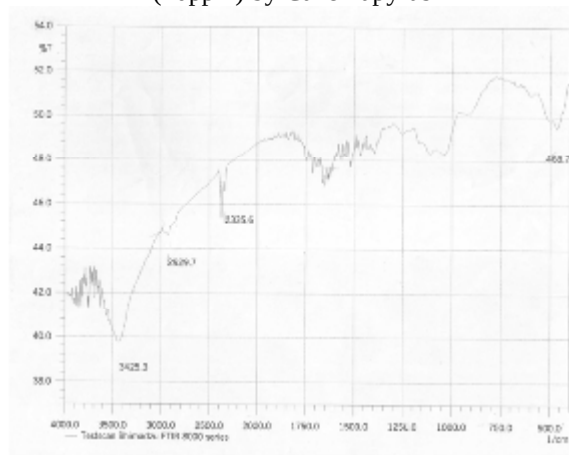


Figure 6: FTIR for Cane Papyrus

3. Effect of Depth of Cane Papyrus

The influences of three bed heights of 4cm, 6cm, and 8cm at dye concentration of 10 ppm and at the hydraulic loading rate of 2.5 ml/min were studied. Figure 7 show the abrupt curve obtained for Methyl Orange (MO) adsorption on the Cane Papyrus. As expected, the abrupt point decreases with decreasing the bed height and increasing bed height increases the breakthrough time. The mass transfer zone in a fixed bed travels from the entrance of the bed and progresses towards the end of the column. Hence, an increase in the bed height results in a longer distance for the mass transfer zone to reach the end of the

column and therefore an increase in the breakthrough time [8]. A higher removal of MO uptake was also observed at a higher bed height due to the increase in the specific surface of the Cane Papyrus which provided more fixation binding sites for the dye to be adsorbed. The increase in the adsorbent mass in a higher bed provided a greater surface area which would lead to an increase in the volume of the solution treated [9].

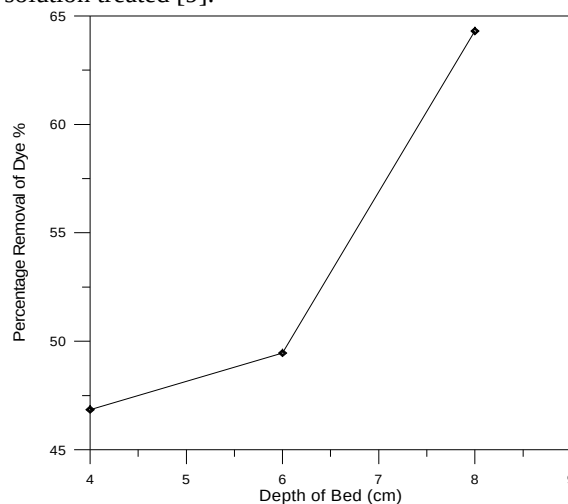


Figure 7: Effect of Depth on the removal of dye by Cane Papyrus

(1gm=4cm, 1.5g=6cm and 2gm=8cm)

4- Effect of Flow rate

The effect of flow rate was investigated and shown in figure (8), It is clear that the flow rate increases the break point time of the curve decreases and adsorption capacity decreases. This is due to increase the linear velocity and also decreases the contact time between the MO solution and cane papyrus.

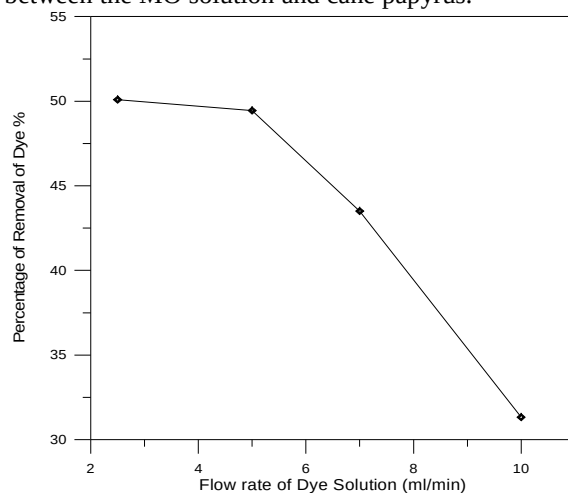


Figure 8: Effect of Flow rate on the removal of dye by Cane Papyrus

Adsorption Isotherm

Adsorption isotherms were investigated to evaluate the applicability of the adsorption process for the removal of the organic dyes from industrial waste water. The interactions between the adsorbate and adsorbent have been described by several models for

the adsorption isotherm [10 and 11]. These adsorption models are used to evaluate the performance of the adsorption process, as they represented the surface properties and affinity of the adsorbent. For the case where the adsorbent solute particles is negligible, Langmuir isotherm is used. This model is valid for monolayer adsorption on a homogenous surface. The Langmuir isotherm is expressed as Equation (1):

$$q_e = \frac{k_L C_e}{1 + a_L C_e} \quad \dots 1$$

Where, q_e (mg/g) is the amount of adsorption at equilibrium, C_e are the final dye concentrations (mg/L), K_L is the constant related to overall solute adsorptivity (l/g), and a_L is the constant related to the energy of adsorption (l/mg).

The Freundlich isotherm is commonly used to describe adsorption characteristics for heterogeneous surface. Derived empirically in 1912 [12]. Freundlich isotherm can be expressed as Equation 2:

$$q_e = K_f C_e^{1/n} \quad \dots 2$$

Where; K_f is the constant related to overall adsorption capacity (mg/g); $1/n$ is the constant related to surface heterogeneity (dimensionless).

The constant from equation 1 and 2 were estimated using statistical software package (SPSS and Statistica) as shown in table 2.

Figure 9 show the experimental and calculated data of q_e for Methyl Orange over Cane Papyrus using Langmuir and Freundlich Isotherms.

Table 2: The values of parameters and correlation coefficient (R^2) for each isotherm model

Langmuir	K_L	$\square_L$	R^2
	0.3512	0.0456	0.983
Freundlich	K_f	n	
	0.6451	0.3491	0.971

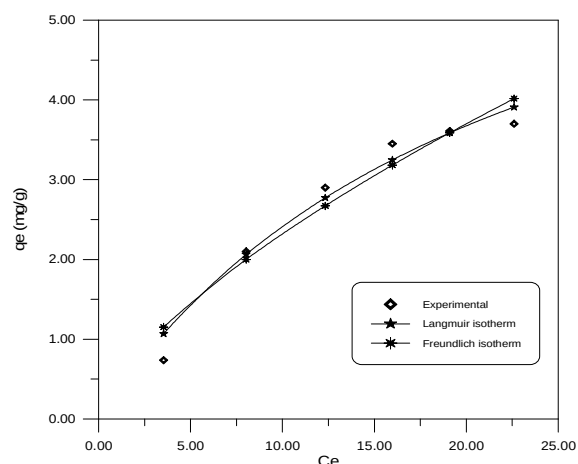


Figure 9: Experimental and theoretical data were obtained from the Langmuir and Freundlich equations for the adsorption quantity

Kinetic studies

Kinetic studies are carried out to determine the efficiency of dye onto the adsorbent. The experiments were carried out at pH 7, flow rate 5 mL/min, influent concentration 20mg/L and bed height 4cm. There are

several different kinetic models available to describe adsorption kinetics [13]. The experimental data in this investigation was applied into the pseudo-first order and pseudo-second order equations. Figures 9 and 10 represents the data for pseudo-first order and pseudo-second order models, respectively. A plot of $1/q$ versus $1/t$ yields a linear plot where the pseudo-first order reaction rate constant, k_1 (min^{-1}) is determined from the slope of the plot. The intercept of the plot is used to determine the amount of dye adsorbed at equilibrium q_e (mg g^{-1}). Kinetic constants q_e and k_2 for pseudo-second order reaction is calculated from the slope and intercept, respectively of the t/q versus t plot.

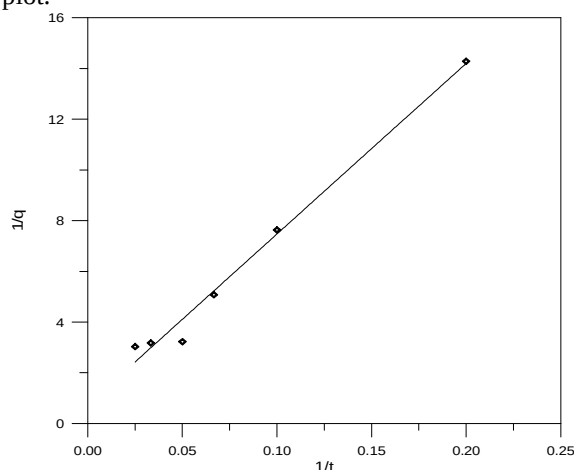


Figure 9: Plot of pseudo-first order kinetic model for the adsorption of MO on Cane Papyrus

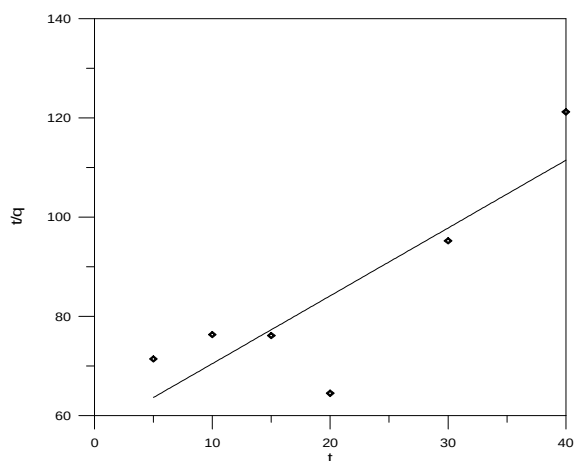


Figure 10: Plot of pseudo-second order kinetic model for the adsorption of MO on Cane Papyrus

The correlation coefficient (R^2) values for both plots were determined and the adsorption process is found to abide by the pseudo-first order kinetic model. In batch adsorption, the stirring and shaking allows both the sorbate and adsorbent to move freely, exposing the adsorbate to the full surface area of the adsorbent. However, in column adsorption, the adsorbate is only in contact with a fraction of the surface area of the adsorbent. Table 2 tabulates the constants calculated for pseudo-first order and pseudo-second order

models. The results indicate best fit obtained with pseudo-first order model, with the value of k_1 was $0.0495 \text{ g mg}^{-1} \text{ min}^{-1}$.

Table 2: Equilibrium Kinetic constants for MO adsorption on Cane Papyrus

pseudo-first order			pseudo-second order		
q _e (mg/g)	k ₁ (min ⁻¹)	R ²	q _e (mg/g)	k ₂ (g mg ⁻¹ min ⁻¹)	R ²
0.4036	0.0495	0.987	0.7321	0.0328	0.731

Conclusion

The results of this study indicate that Cane Papyrus can be successfully used for the adsorption of Methyl Orange from aqueous solutions. The maximum adsorption capacity was shown when the PH of the solution taken in the acid region. The equilibrium isotherm for the system of adsorbed Methyl Orange dye was a favorable type, and was well represented by Langmuir and Freundlich equations. Two simplified kinetic models, pseudo-first order, and pseudo-second-order were tested to investigate the adsorption mechanism. The pseudo first- order kinetic model fits very well with the dynamical adsorption behavior of MO dye.

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الامتزاز للصبغة البرتقالية من المياه الملوثة بها باستخدام وسط ماز متكون من قصب البردي

أسامة أكرم سعيد¹ ، محمد حسين علي² ، أحمد عدنان عطشان¹

¹ قسم الهندسة الكيميائية ، كلية الهندسة ، جامعة النهرين ، بغداد ، العراق

² قسم علوم الكيمياء ، كلية العلوم ، جامعة النهرين ، بغداد ، العراق

الملخص:

الهدف من البحث هو امتزاز الصبغة البرتقالية (مثيل برتقالي) من مياه الصرف الصحي على قصب البردي باستخدام نظام مستمر (الحشوة ثابتة) وقد اجريت عدة تجارب لدراسة تأثير معدل التدفق، تركيز الصبغة، ارتفاع القصب، الاس الهيدروجيني على الامتزاز ومن خلال التجارب وجد بأن قصب البردي فعال في ازالة الصبغة البرتقالية من المياه حيث بلغت نسبة الازالة 50% واحيانا تصل الى 70%.
لقد تم معاملة النتائج رياضيا ووجدت بأنها تتطابق مع الموديل الرياضي ذو المرتبة الاولى الكاذبة اكثر من الموديل الرياضي ذو المرتبة الثانية الكاذبة .