Adsorption of Methylene Blue Dye From Aqueous Solution Using Can Papyrus

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Abstract

The use of low-cost, locally available, highly efficiencient and eco-friendly adsorbents has beeninvestigated as anideal alternative to the current expensive methods of removing dyes from wastewater. This study investigates the potentialuse of Can Papyrusfrom river for the removal of methylene blue (MB) dye from simulatedwastewater.The adsorption of (MB)cationic dye by Can Papyrus was firstly studied in a batchsystem at various dye concentrations. The results showed that the adsorption capacity ofthe dye increased by initial dye concentration.Laboratory column experiments were conducted to evaluate the performance of Can Papyrus for MB sorption under dynamic flow using continuous-flow column operation by varying the bed height (1, 1.5, 2.4 and 4cm) and the feed concentrations (5, 10 and 15mg/l).Three kinetic models (the pseudo-first-order, the pseudosecond-order and Elovichmodels) were used to calculate the adsorption rateconstants. The adsorption kinetics of the basic dye followedpseudo-first-order model. The experimental data isothermswere analyzed using the Langmuir, Freundlich, Tempkin and Sips equations.The adsorption was arapid with 90-99% of the dye removed within the first 10-20 min.The adsorption of MB followed the pseudo-first-order rate equation and fits the Langmuir, Freundlich, Tempkin and Sips equations well. Themaximum removal of MB was obtained at pH 8 as 100% for adsorbent dose of 1g and flow of 12.5ml/min in concentration of 15ppm at room temperature.

Keyword: Adsorption, Methylene Blue, Can Papyrus

الخلاصة

أستخدم سطح ماز متوفر ذو كفاءة عالية، غير ضار للبيئة لازالة الاصباغ والملوثات من مياه الانهار الملوثة صناعيا. الدراسة تتضمن استخدام قصب البردي من الانهار مباشرة لازالة الصبغة الزرقاء. تم دراسة الازالة بطريقتين، طريقة الامتزاز بواسطة (Batch System) في تراكيز مختلفة، أظهرت النتائج بان كفائة الامتزاز تزداد بزيادة التركيز الاولي. طريقة الامتزاز بواسطة سطح ثابت (Fixed Bed) بحشوة مختلفة الارتفاع (٤,٢.٤,١.٥,١) سم وتراكيز مختلفة (٥، ١٠ و ١٥ مغ/لتر)، تم تطبيق ثلاثة نماذج رياضية لحساب ثوابت الامتزاز هي(the pseudo–first–order, the pseudosecond–order and Elovichmodels) . اثبتت النتائج النظرية ان (pseudo–first–order) ينطبق مع النتائج العملية. النتائج العملية لطريقة (Batch System) تم تحليلها باستخدام اربع نماذج رياضية هي (Langmuir, Freundlich, Tempkin and Sips equations)، حيث وجد ان النتائج العملية تنطبق على المعادلات المذكورة انفا بصورة جيدة . تم حساب كفاءة الامتزاز حيث وجد ان معدل الازالة يتراوح بين ٩٠–٩٩% في وقت ١٠–٢٠ دقيقة. أعلى نسبة تم الحصول عليها لازالة الصبغة عند الاس الهايدروجيني ٨ (PH 8) ١٠٠% مع وزن السطع ١غم ومعدل التدفق ١٢.٥مل/دقيقة بتركيز ١٥ملغ/لتر في درجة حرارة الغرفة.

Introduction

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid [Baldez EE, 2008]. These materials are the complicated organic compounds and they resist against light, washing and microbial invasions. Thus, they cannot be decomposed easily [Barka N, 2009]. In effect, the discharge of contaminants in the environment is worrying for both toxicological and esthetical reasons as damage the quality of the receiving streams and is toxic to food chain organisms. The highest rates of toxicity were found amongst basic and diazo direct dyes [Bestani B, 2008]

Therefore, it is highly necessary to reduce dye concentration in the wastewater. The conventional methods for treating dye containing wastewaters are electrochemical treatment, coagulation and Flocculation, liquid–liquid extraction and adsorption [Bhattacharyya KG, 2005, Gunay A, 2007, Gupta VK, 2004]. Adsorption has been shown to be an effective way for removing organic matter from aqueous solutions in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances [Bhattacharyya KG, 2005]. A considerable amount of work has also been reported in the literature regarding the adsorption of MB on various adsorbent surfaces such as, activated carbon [Gurses A, 2002], rice husk [Gurses A, 2006], peanut hull [Karagoz S, 2008], glass fibers [Kumar KV, 2005], Indian rosewood sawdust [Lata H, 2007], neem leaf powder [Mohan D, 2002], perlite [Wang S, 2005a], fly ash [Wang S, 2005b], yellow passion fruit peel [Zhao M, 2008], and more.

In the present work, Can Papyrus, taken from river, were selected as an adsorbent to remove methylene blue from aqueous solution. Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood and silk. Although, MB is not strongly hazardous, but it can cause several harmful effects where acute exposure to MB will cause increased heart rate, nausea, vomiting, shock, cyanosis, jaundice, and quadriplegia and tissue necrosis in humans [Hamdaoui O, 2007]. The main objective of this research was to evaluate the adsorption aptitude of Can Papyrus for the removal of methylene blue as a model compound for basic dyes. The effects of pH, contact time, initial dye concentration and Can Papyrus dosage on adsorption capacity were investigated. Moreover, kinetic and equilibrium models were used to fit experimental data and the adsorption thermodynamic parameters were determined.

Experimental Setup

Material

Laboratory grade methylene blue (MB) with chemical structure as shown in figure (1), and molecular weight (319.85 g/mol) supplied by merck was use without further purification for the preparation of synthetic aqueous solution. The stock solution was prepared by dissolving a required amount in 1000 cm^3 of distilled water. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to required initial concentrations. Serial dilutions were made to obtain the required lower concentrations in the range of 5 to 15 ppm. The initial concentration was ascertained before each experimental run. The concentration of MB in the aqueous solution was determined at λmax of 660 nm using UV-visible spectrophotometer.

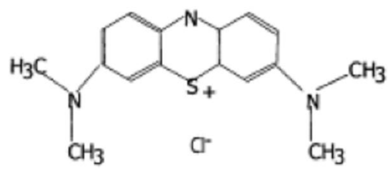

Figure 1. *The structure of methylene blue*

Preparation of Adsorbent

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

Batch and Continues Study

Two types of adsorption were study; the first one is batch process to calculate the adsorption equilibrium and the second one is the continuous operation to test the adsorbate with time. For batch experiment, 50ml of methylene blue solution of known initial concentration and a 0.04 g of Can Papyrus were taken in a 100 cm^{3} Erlenmeyer flasks with air tight stopper. This mixture was agitated in a room temperature using shaker, at a constant shaking speed. The flasks were agitated for a time 5min in order to study the kinetics of the adsorption process. The pH for the adsorbate adsorbent mixture before agitation was maintained at 7.0. An equilibrium study was also carried out at temperature of 30^{o}C.

Packed-bed sorption tests

Adsorption tests were carried out in a continuous system using Methylene Blue 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.

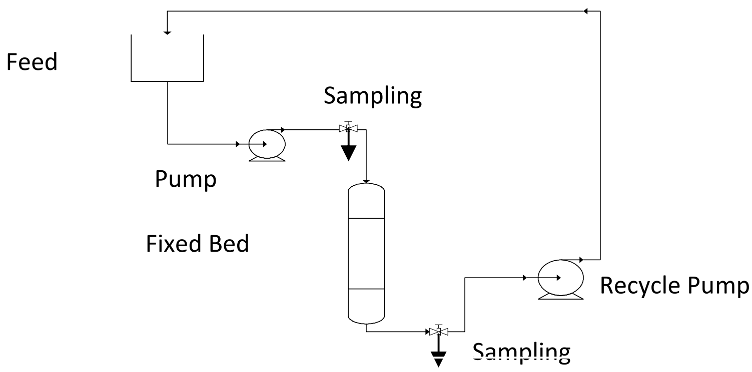

Figure 2: Schematic of continuous adsorption experimental rig.

Continuous Process

A 2, 4, and 6cm of 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. The 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 Methylene Blue was analyzed by measuring the absorbance at 660 nm with a UV/VIS spectrophotometer. All tests were carried out at room temperature, 25^{o}C.

The percentage of methylene blue adsorbed and the amount adsorbed were calculated as [Baldez EE, 2008]:

$$\% \text{ adsorbed} = 100\,(Co - Ce) / Co \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where Co is the initial concentration of the adsorbate (ppm) and Ce is the equilibrium concentration (ppm).

Amount adsorbed, qe = V (Co – Ce)/ m………………2

Where m (g) is the weight of Can Papyrus used for the adsorption studies and V (cm^3) is the volume of the adsorbate.

Kinetic Models and Adsorption Isotherms

Kinetic Models

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. The following models areused to describe the adsorption kinetics behavior:

1-Pseudo-First Order Model [Hamdaoui O, 2007]

The adsorption kinetics can be described by a pseudo-first orderequation as suggested by Lagergren.

$$\frac{dq}{dt} = k_1\left(q_e - q_t\right) \qquad .....3$$

Where:k_1(min-1) is the rate constant of the pseudo-first ordermodel,q_t(mg /g) denotes the amount of adsorption at time t(min), and q_e(mg /g) is the amount of adsorption at equilibrium.

After definite integration by application of the conditions t = 0 to t = tand q = 0 to q = q_e, Equation (3) becomes

$$\ln\left(q_e - q_t\right) = \ln q_e - \ln k_1 t \qquad .....4$$

The adsorption rate constant, k_1, can be experimentallydetermined by the slope of linear plots $\ln\left(q_e - q_t\right)$ vs. t.

2-Pseudo-Second Order Model [Hamdaoui O, 2007]

Thepseudo-second order equation developed by [*Hamdaoui O, 2007*] can be written as

$$\frac{dq}{dt} = k_2\left(q_e - q_t\right)^2 \qquad .....5$$

Where:k_2(g/mg.min) is the rate constant of the pseudo second order. Integrating Equation (5) for the boundary conditions t= 0 to t = t and q = 0 to q = q_e gives:

$$\frac{1}{\left(q_e - q_t\right)} = \frac{1}{q_e} + k_2 t \qquad .....6$$

Which has a linear form of

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad .....7$$

Where $k_2$and $q_e$can be obtained from the intercept and slope of plotting $\frac{t}{q_t}$ v.s. t.

3- Elovich Model (Wang S, 2005a)

In reactions involving chemisorption of adsorbate on a solid surface without desorption of products, adsorption rate decreases with time due to an increased surface coverage. One of the most useful models for describing such ‘activated’ chemisorption is the Elovich equation. The Elovich equation can be written as (Hamdaoui , 2007):

$$q = \frac{1}{\alpha}\ln\left(\alpha\beta\right) + \frac{1}{\alpha}\ln t \qquad .....8$$

Where: α is the initial adsorption rate, and β is the desorption constant during each experiment.

Adsorption Isotherms

Adsorption isotherms are important for the description of how adsorbates will interact with an adsorbent and are critical in optimizing the use of adsorbent [Longhinotti E, 1998]. Thus, the correlation of equilibrium data using either a theoretical or empirical equation is essential for adsorption data interpretation and prediction. Several mathematical models can be used to describe experimental data of adsorption isotherms. Foure famous isotherm equations, the Langmuir, Freundlich, Temkin, and Sips Isotherm, were employed for further interpretation of the obtained adsorption data.

1- Langmuir Isotherm

The theoretical Langmuir isotherm [Longhinotti E, 1998] is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identicalsites. The Langmuir nonlinear equation is commonly expressed as followed:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad .....9$$

Where; $q_m$and $K_L$are Langmuir constants related to theadsorption capacity and energy of adsorption, respectively.

2- The Freundlich Isotherm

The Freundlich isotherm model [Temkin MJ, 1940] is the earliest known equation describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involvesheterogeneous adsorption. The Freundlich isotherm can bed erived assuming a logarithmic decrease in the enthalpy ofadsorption with the increase in the fraction of occupied sitesand is commonly given by the following non-linear equation:

$$q_e = K_F C_e^{1/n} \qquad ......10$$

Where $K_F$is a constant indicative of the adsorption capacity of theAdsorbent and n is an empirical constant related to the magnitude of the adsorption driving force.

3- The Tempkin Isotherm

Temkin and Pyzhev considered the effects of some indirect sorbate /adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly withcoverage [Jain R, 2008].The Temkin isotherm has been used in the following form

$$q_e = \frac{RT}{b} \ln\left(K_T C_e\right) \qquad ......11$$

Where; $K_T$is the equilibrium binding constant (L /g), b is related to heat of adsorption (J/mol), R is the universal gas constant (8.314J/mol K) and T is the absolute temperature (K).

4- Sips Isotherm

Sips isotherm is a combination of the Langmuir and Freundlich isotherm type models and expected to describe heterogeneous surfaces much better. At low adsorbate concentrations it reduces toa Freundlich isotherm, while at high adsorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm [Wang S, 2005] The model canbe written as:

$$q_e = \frac{q_m a_s C_e^{1/n}}{1 + a_s C_e^{1/n}} \qquad .....12$$

Where a_s is Sips constant related to energy of adsorption.

Results and Discussion

1- Effect of contact time and initial dye concentration

Figure 3 shows the effect of initial dye concentration onthe adsorption rate of the dye at pH=7 and 293 KAn increase in initial dye concentration for 0.4g of Can Papyrus leads to a decrease in the adsorption capacity. As the initial dye concentration increases from 5 to 15 mg/L, the adsorption efficiency of dye for 40min changes from 83.25 to 41.54%. This indicates that the initial dye concentration plays an important role in the adsorption capacity of dye [Wang S, 2005].

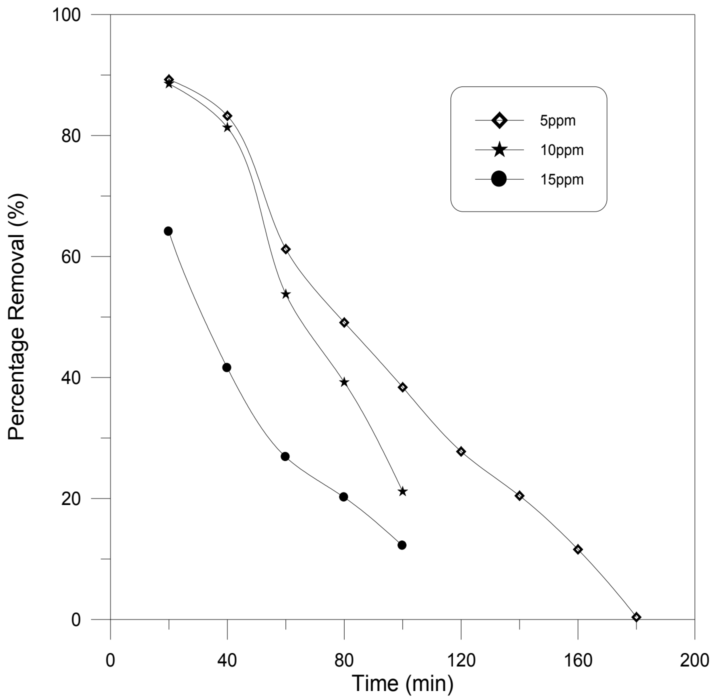

Figure 3:Effect of residence time and initial conc on adsorption of MB Onto 0.4gCan Papyrus

2- Effect of PH

The pH of the dye solution plays an important role in the whole adsorption process, particularly on the adsorption capacity [Vadivelan V, 2005]. As shown in Figure 4, a consistent increase in adsorption capacity of the MB was noticed as the pH increased from 2 - 8, whereas in the range 8 - 12, the adsorption amount was decreased affected by pH. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively chargedsurface sites increased, which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion [Baldez EE, 2008]. In addition, lower adsorption of methylene blueat acidic pH might be due to the presence of excess H^+ ions competing with dye cations for the available adsorption sites [Vadivelan V, 2005].

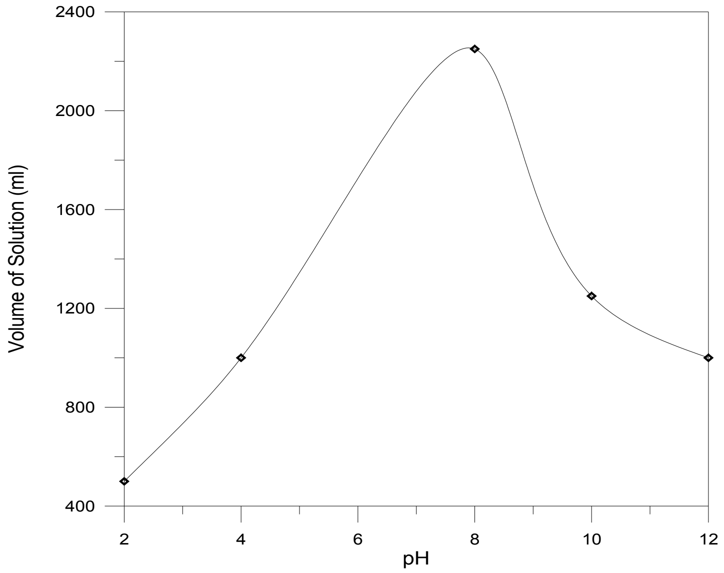

Figure 4: pH v.s volume of solution used until deactivate the adsorbent for 1g, 4cm and 15ppm MB

3- Effect of depth of can papyrus

The adsorption of MB onto Can Papyrus was studied by changing the amount of adsorbent (0.4, 0.6, and 1g) in the test solution while keeping the initial dye concentration (15 mg/l) constant, at different contact time sduring 180 min. The results are shown in figures. 5 and 6.In the MB removal, it is seen that the adsorption efficiency increases as the Can Papyrus amount increases. The increase in the efficiency can be explained by the increasing surface area where the adsorption takes place [Wang S, 2005].

Figure 5 can be showed that the amount of MB removed from the solution using a certain height of Can Papyrus, for example, the 1750 ml of solution (concentration of 15ppm) can be permanently adsorbed in 2.4 cm height (0.6 g). As for figure 6, it represents the removal efficiency with contact time using different weighting of Can Papyrus, where we note that the amount of removal of MB up to 100% at 1 g of adsorbat in time not to exceed 20 minutes as shown in figure 7, while the efficiency falling decrease during time due to decrease the surface area of adsorbate as shown in figure 8, the Can Papyrus was filled with blue color during the contact time.

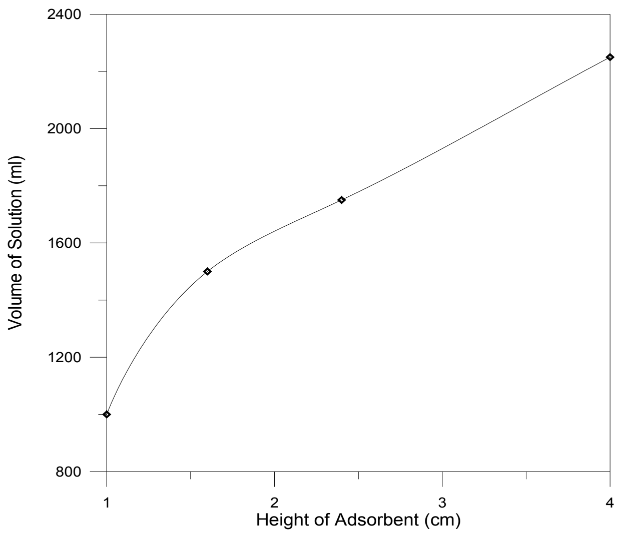

Figure 5: Height of can Papyrus v.s Volume of solution used until deactivate the adsorbent for 1g, 4cm and

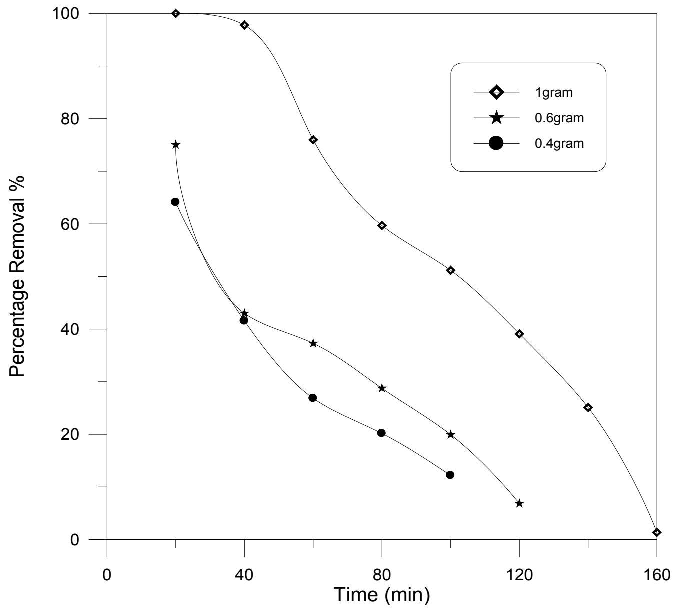

Figure 6: Percentage Removal of Methylene Blue on can Papyrus at 15ppm and 12.5ml/min

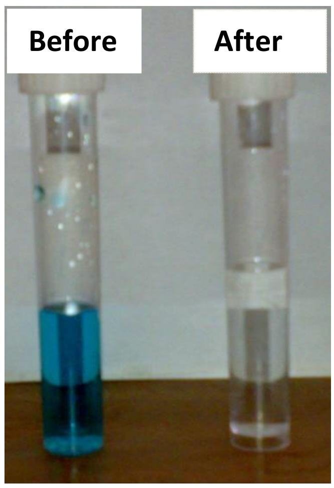

Figure 7: Picture show the efficiency of removal of MB on Can Papyrus before and after adsorption for 0.6g (2.4cm), 15ppm and 12.5ml/min

Figure 8: Picture show the efficiency of removal of MB on Can Papyrus for 0.6g (2.4cm), 15ppm and 12.5ml/min

Mechanism of Adsorption

It is important to be able to predict the rate at which contamination is removed from aqueous solutions in order to design an adsorption treatment plant. In order to investigate the mechanism of adsorption and potential rate controlling steps such as mass transfer and chemical reaction [Vadivelan V, 2005], the kinetics of MB sorption onto Can Papyrus was investigated using three different models: the pseudo-first-order, the pseudo second-order kinetic models, and the Elovich Model. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2, values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of MB adsorption.

The plot of log ($qe - qt$) vs. t should give a linear relationship from which $K1$ and qecan be determined from the slope and intercept of the plot, respectively.

The plot of (t/qt) vs. t should give a linear relationship from which $qe$and $K2$ can bede termined from the slope and intercept of the plot, respectively. The plot of equation 8 between q and (lnt) give α and B respectively.

Table 1 lists the calculated adsorption constants at 15ppm initial dye concentration by the pseudo first-order, pseudo second-order and Elovich models. The correlation coefficients,R^2, of the pseudo second-order model did not exceed the values of 0.872. The calculated qe values are too low compared with experimental q_{exp}values. This shows that the adsorption of MB by Can Papyrus did not follow the pseudo second-order. The correlation coefficient $R^2$for the pseudo first-order and Elovicha dsorption models have an extremely high value (greater than 0.98), and the calculated qevalues also agree very well with the experimental data.

Table1: Equilibrium Kinetic constants for MO adsorption on Cane Papyrus

Equation	Q_e (mg/g)	k1 (min^{-1})	k2 (g mg^{-1} min^{-1})	α	β	R^2
Pseudo-First Order	0.1737	0.001556				0.995
Pseudo-Second Order	837.2		0.053			0.872
Elovich Model				0.254	818.973	0.983

Adsorption Isotherm

Adsorption isotherms describe qualitative information on the nature of the solute-surface interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. Adsorption isotherms are critical in optimizing the use of adsorbents, and the analysis of the isotherm data by fitting them to different isotherm models is an important stepto find the suitable model that can be used for design purposes [Mohan D, 2002].

The equilibrium adsorption studies were conducted using various initial MB concentrations of 5-30mg/ l. Isotherm parameters of the four models obtained by using non-linear regression are listed in Table 2.

Table 2: Langmuir, Freundlich and Tempkin and Sipspara meters for MB dye

Equation / constant	Langmuir	Freundlich	Tempkin	Sips
R^2	0.933	0.925	0.924	0.985
q_m	0.021257			
K_L	0.979076			
K_f		1.0055		
n		939.244		
b			1336.197	
K			167.913	
q_m				0.2044
a_s				0.0545
n				2.8456

Among the tested four-parameter equations, the better and perfect representation of the experimental results of the adsorption isotherms is obtained using the Sips model. According to Table 3 and figure 9, the coefficients of correlation are very good (R^2=0.985).

The value of the maximum adsorption capacity obtained using the Sips equation are higher than these calculated by the Langmuir, Freundlich and Tempkin models and the mean value of the average percentage error for the studied compounds is for the Sips model than for other models. It can be also seen that the values of n at equilibrium is 2.845. It is noted that the values of n are bigger than 1, reflecting the favorable adsorption [Lata H, 2007].

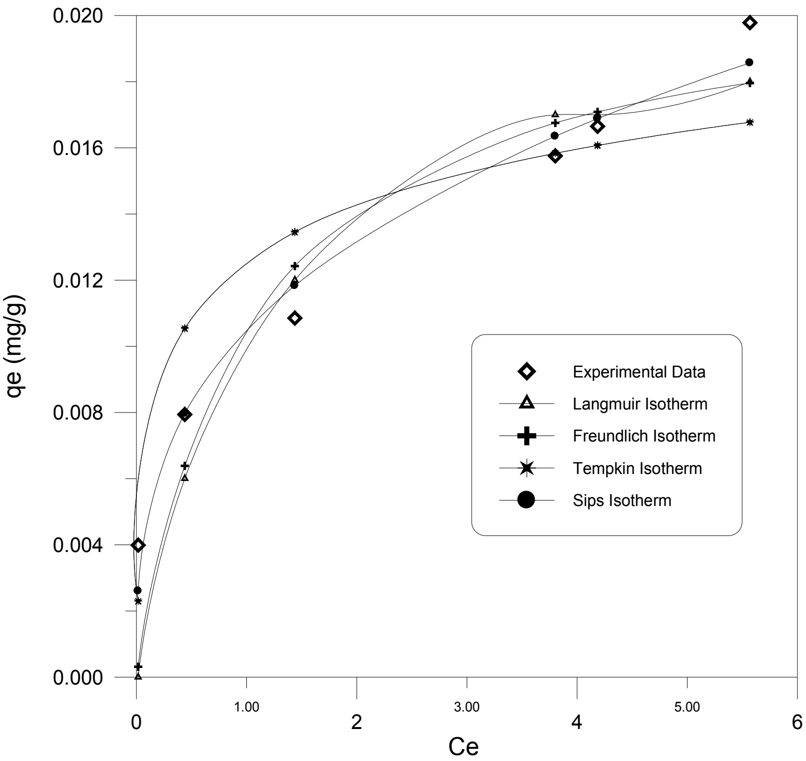

Figure 9: Experimental and theoretical data were obtained from different isotherm equations for the adsorption quantity (0.04g, 50ml, 5min stirring)

Concolution

The results of presented this investigation show that, Can Papyrus has a suitable adsorption capacity for the removal of MB from aqueous solutions. The equilibrium adsorption is practically achieved in 20 min. The experimental results were analyzed by using Langmuir, Freundlich, Tempkin and Sips isotherm models and the correlation coefficients for Langmuir, Freundlich, Tempkin and Sips equations are well fitted. The data indicate that the adsorption kinetics follow the pseudo-first-order rate. The present study concludes that the Can Papyrus could be employed as low-cost adsorbents as alternatives to commercial activated carbon for the removal of color and dyes from water and wastewater.

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