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Adsorption of Methylene Blue Dye from Wastewater By Spent Tea Leaves

إمتزاز صبغة المثيلين الازرق من المياة الملوثة باستخدام ورق الشاي المستهلك

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Abstract:

The aim of present work was to investigate the ability adsorption of methylene blue (MB) dye from wastewater using low-cost adsorbent, spent tea leaves (STL), in batch isotherm adsorption technique. The adsorption experiments were carried out under different conditions of initial dye concentration (50-500) mg/l, STL dose (0.05-1) g, pH solution (2-11), and contact time (10-180) min under constant temperature of 30 ^{o}C. The results were indicated that the optimum conditions were adsorbent dose was 0.43 g per 100 ml dye solution, pH=7. The equilibrium isotherms have been analyzed using the Langmuir and Freundlich models. The experimental results were best described by the Freundlich isotherm model with maximum monolayer adsorption capacities found to be 62.2 mg/g with the high value of correlation coefficient. The results suggested that STL has high potential 98% to be used as effective adsorbent for MB dye removal.

Keywords: Adsorption, Spent tea leaves, Removal, Methylene blue dye, Wastewater.

الخلاصة :

يهف البحث الى التحقق من قابلية إمتزاز صبغة المثيلين الازرق من المياه الملوثة باستخدام مواد ممتزة واطئة الكلفة. ورق الشاي المستهلك تم اختبارهِ بتقنية امتزاز الوجبات. اجريت تجارب الامتزاز تحت ظروف مختلفة من تراكيز ابتدائية للصبغة (50-500 ملغم/ لتر)، كمية المادة الممتزة (0.05- 1 غم)، الدالة الحامضية للمحلول (2-11) وزمن خلط (10-180 دقيقة) وعند درجات حرارة ثابتة 30 ْم. اشارت النتائج ان الظروف المثلى كانت باستخدام 0.43 غم من المادة الممتزة لكل 100 مل من المحلول الصبغة وقيمة الدالة الحامضية 7. النتائج المختبرية حللت باستخدام موديلات لانكمير وفرندلش وكانت نتائج الامتزاز مطابقة الى حد كبير لموديل فرندلش حيث وجدت ان اقصى قيمة لمعدل الامتزاز كانت 62.2 ملغم/غم مع قيمة عالية لمعامل الارتباط. النتائج اشارت ان ورق الشاي المستهلك يمكن استخدامهِ بكفاءه (98 %) لامتزاز صبغة المثيلين الازرق.

Introduction:

Most of the industries like textile, leather, plastics, paper, food, cosmetics, etc., use dyes and pigments to color their products. The colored wastewaters of these industries are harmful to the aquatic life in rivers and lakes due to reduced light penetration and the presence of highly toxic metal complex dyes [1].

The color is the first contaminant to be recognized in wastewater. The presence of even very small amounts of dyes in water (less than 1ppm for some dyes) is highly visible and undesirable [2]. MB is the most commonly used substance for dying cotton, wood and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. Although MB is seen in some medical uses in large quantities, it can also be widely used in coloring paper, dyeing cottons, wools, coating for paper stocks, etc. Though MB is not strongly hazardous, it can cause some harmful effects. Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice and quadriplegia and tissue necrosis in humans [3].

Many treatment processes have been applied for the removal of dyes from wastewater such as: photocatalytic degradation [4], biological treatment [5], chemical coagulation [6], cation exchange membranes [7], electrochemical degradation [8] and adsorption/precipitation processes [9], integrated chemical–biological degradation [10] and adsorption on activated carbon [11, 12]. As

synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, the adsorption of synthetic dyes on inexpensive and efficient solid supports was considered as a simple and economical method for their removal from water and wastewater.

Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances [13].

Activated carbon has been popular choice as an adsorbent for the removal of MB from wastewater but its high cost poses an economical problem. Therefore, there is a need for the development of low cost and easily available materials, which can be used more economically on large scale. Due to the problems mentioned above, research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years [14].

The cost is actually an important parameter for the comparison and selection of adsorbents. Literature survey reveals that there has been numerous works reported using low cost adsorbents for dye removal, which are economical viable, easily available, highly effective in adsorption process [15].

Tea is consumed by the largest number of people in the world and considered the second most popular beverage in the world. Only water is rated higher in world consumption than tea. It is estimated that somewhere between 18 and 20 billion cups of tea are drunk daily on our planet. Canned or bottled tea drinks as well as instant tea drinks are produced on industrial scale by hot water extraction of tea leaves, and the producers face a problem in disposing of the spent tea leaves after the extraction. Hence, the utilization of such waste is most desirable [16].

The aim of present work was to investigate the adsorption of MB dye from wastewater by STL in order to study the effect of various operating parameters such as initial dye concentration, adsorbent dose, pH and contact time for determine the optimum conditions for this removal. Also, evaluate experimental data with the equilibrium isotherm for Langmuir and Freundlich models.

Materials and Methods

Materials:

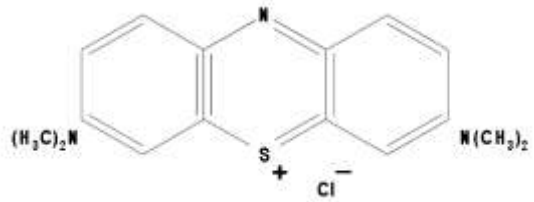
The adsorbent spent tea leaves was collected from the local shop making tea. The tea leaves was washed several times in distillate water to remove any adhering dirt and repeatedly boiled with water until the filtered water was cleared. Then it was oven dried at 80 ◦C for 24 h. Finally, the dried sample was ground and sieved to obtain a particle size range of 5–8 mm [13,14] and stored in plastic bottle for further use. No other chemical or physical treatments were used prior to adsorption experiments.

Chemicals:

The adsorbate MB is a basic dyestuff, 99.8% purity, was supplied by (Merk, Germany). The properties and characteristics of the dye are listed in Table (1). A stock solution of MB dye (1000 mg/l) was prepared by dissolving an accurate weight quantity of dye in double-distillate water. The stock solution was then properly wrapped with aluminum foil and stored in a dark place to prevent direct sunlight, which may cause decolorization. Experimental solutions of desired concentrations were obtained successive dilutions. The range in concentration of MB dye prepared from standard solution varied between (50–500) mg/l based on most common MB dye concentrations range in industrial effluents [16, 17],. The concentrations of residual MB dye were measured using UV spectrophotometer equipment (Shimadzu UV/Vis 1601 Spectrophotometer, Japan). The maximum wavelength of this dye is 668 nm.

The pH of each test solution was adjusted to the required value with diluted 0.1 N HCl or 0.1 N NaOH solutions using digital pH meter to perform the measurements.

Table (1) Properties and characteristics of MB dye [17]

Generic name	Methylene Blue
Chemical formula	$C_{16}H_{18}ClN_3S.3H_2O$
Molecular weight (g/mol)	373.9
Molecular volume (cm^3/mol)	241.9
Molecular diameter (nm)	0.8
λ_{max} (nm)	668
Color index	52.015
Chemical structure	

Batch Experiments:

Batch adsorption experiments were performed for the study of MB dye adsorption from solutions. The effects of initial concentration (50 - 500) mg/l, Adsorbent dosage (0.05-1) g, pH (2-11) and contact time (10-180) min were studied. Adsorption experiments were carried out by adding a fixed amount of adsorbent (0.5 g) contacted with 100 ml dye solution into a number of 250 ml conical flask containing of different initial concentrations (50–500) mg/l of dye solution without changing the solution pH (7) at temperature of 30 ℃ ± 1 ℃. The flasks were placed in a thermostatic water bath shaker and agitation was provided at 130 rpm for 180 min to ensure equilibrium was reached as shown in Fig. 1. At different intervals of time, samples were drawn out of the adsorber using syringe (2ml). Dye concentration was measured using a spectrophotometer in the visible range at maximum wave length. The amount of adsorption at equilibrium, qe (mg/g), was calculated by:

$$q_e = \frac{V\,(C_o - C_e)}{W} \qquad \ldots(1)$$

where C_o and C_e (mg/l) are the concentrations of MB dye at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of dry sorbent used. The percentage removal of dye was calculated as follows:

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \qquad \ldots(2)$$

Fig. (1) Experimental Equipment

Results and Discussion

Effect of Initial Dye Concentration and Contact Time:

Figure 2 shows the effect of the initial dye concentration (50-500 mg/l) on the adsorption of MB at constant adsorbent dose, 0.5 g and neutral pH solution. It was observed that amount of MB adsorbed was rapid in the first 40 min for all initial concentrations, and thereafter adsorption rate decreases gradually till it reaches equilibrium.

The equilibrium adsorption increases from 9.6 to 62.2 mg/g with increase in the initial MB concentration from (50-500) mg/l. It was also found that the equilibrium removal of MB decreased from 95.2% to 62.1% as the initial MB concentration increased from (50-500) mg/l. The findings are because as the initial concentration increases, the mass transfer driving force becomes larger, hence resulting in higher MB adsorption. The initial concentration provides an important driving force to overcome all mass transfer resistances of the MB between the aqueous and solid phase. A similar phenomenon was observed for the adsorption of MB onto banana stalk waste [18].

The adsorption of MB was also studies as a function of contact time in order to find out the equilibrium time for maximum adsorption. Figure 3 illustrated that the equilibrium time required for the adsorption of MB in 60 min for solutions with initial dye concentrations of (50-100) mg/l. However, for initial dye solution concentrations in the range of (200-500) mg/l was needed 90 min to reach equilibrium. However, the experimental data were measured at 180 min to be sure that full equilibrium was attained. An equilibrium adsorption time of 135 min was reported for the adsorption of MB onto wheat sheel [19] and 150 min for the adsorption of MB on fallen phoenix tree's leaves [20].

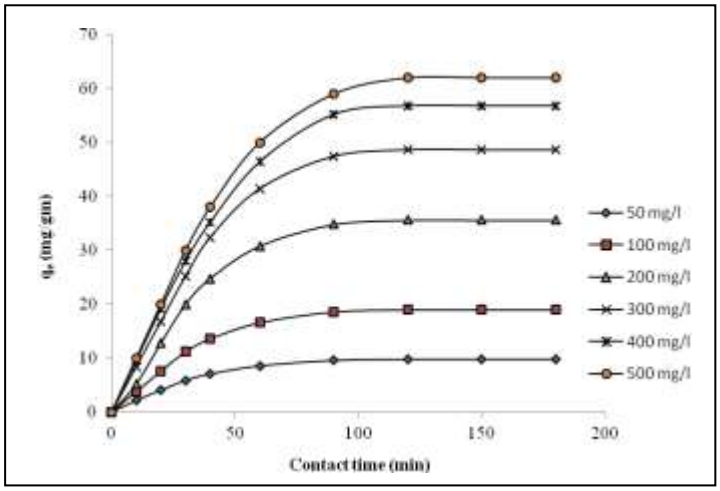


Fig. (2) Effect of initial concentration and contact time on amount of dye adsorbed at constant adsorbent dose of 0.5 g and neutral pH

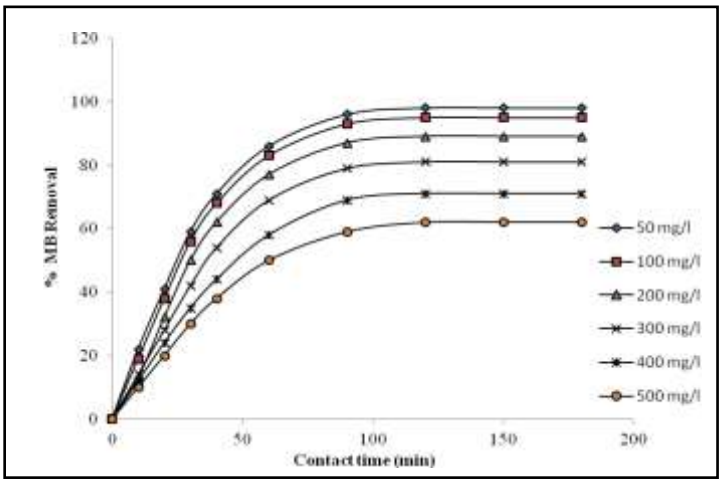


Fig. (3) Effect of initial concentration and contact time on percentage removal of MB at constant adsorbent dose of 0.5 g and neutral pH

Effect of Adsorbent Dosage:

Adsorbent dose is the one of the important parameter of adsorption. The effect of adsorption dosage was determined at fixed initial dye concentration of 100 mg/l and neutral pH solution. Figure 4 and Figure 5 shows the effect of STL dose on the percentage removal of MB at equilibrium time. It was observed that the percentage removal increased from 36.4% to 95.2 % with increase in adsorbent dose from 0.05 to 0.43g and thereafter remained constant. Also, the amount of MB dye adsorbed increase from 7.2 to 19 mg/g for an increase in STL from 0.05 to 0.43 g. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase dosage of the adsorbent. The optimum of STL dose was found to be 0.43 g per 100 ml of dye solution. A similar observation was reported for removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon [21] and removal of Brilliant green on treated saw dust [22].

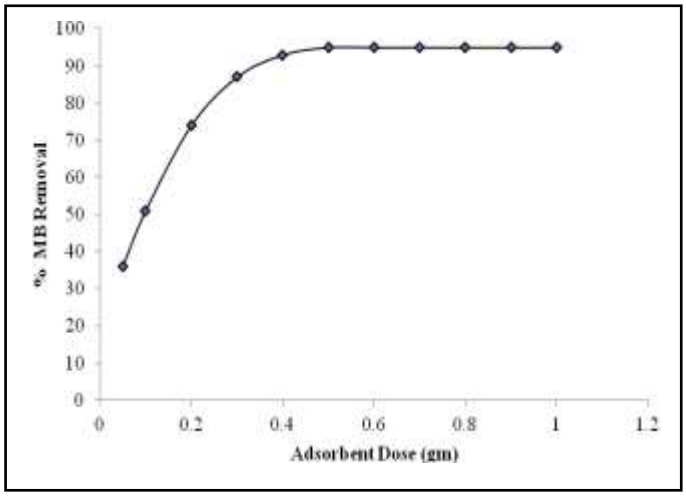


Fig. (4) Effect of adsorbent dose on the removal percentage at (Co=100 mg/l, pH=7 and equilibrium time of 180 min)

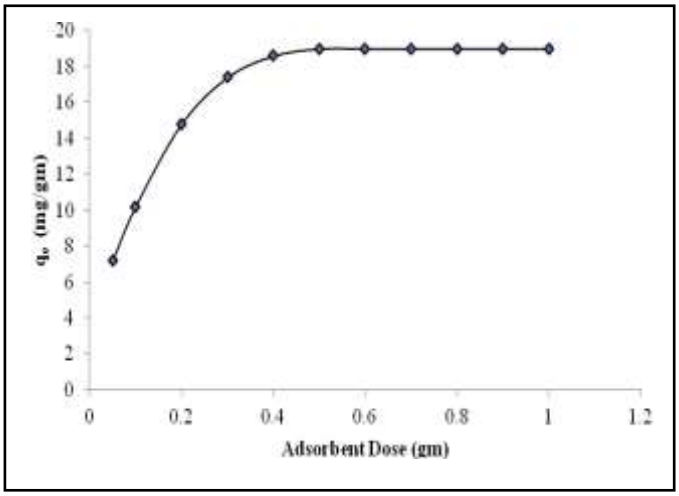


Fig. (5) Effect of adsorbent dose on the amount dye adsorbed at (Co=100 mg/l, pH=7 and equilibrium time of 180 min)

Effect of pH Value:

The effect of pH on the adsorption of MB was studied. The experiments were conducted at 100 mg/l initial MB concentration and optimum adsorbent STL dose of 0.43 g. It was observed that the pH a significant influence to the adsorption process. MB is a cationic dye, which exists in aqueous solution in the form of positively charged ions. Figure 6 and 7 shows that the maximum uptake of MB dye was observed at pH 7. At pH between range 2-7 the removal was increased from 85.1% to 95.2%. Also, equilibrium adsorption (q_e) was found to increase from 17.05 to 19.06 mg/g. The low adsorption of MB at acidic pH was suggested to be due to the presence of excess H^+ ions that complete with the dye cation for adsorption site, the number of positively charged sites decreases while the number of the negatively charged sites increases that favour the adsorption of MB due to electrostatic attraction. As the pH value increased from 7-11, the efficiency of the dyes removal is slightly became lesser. Also, the equilibrium adsorbed (q_e) decreased from 19.06 to 18.1 mg/g. At higher solution pH, decrease in adsorption rate is due to the formation of soluble hydroxyl complex between the adsorbent and the dye. A similar result was reported for the adsorption of MB onto wood shavings [23] and onto sunflower seed hull [24].

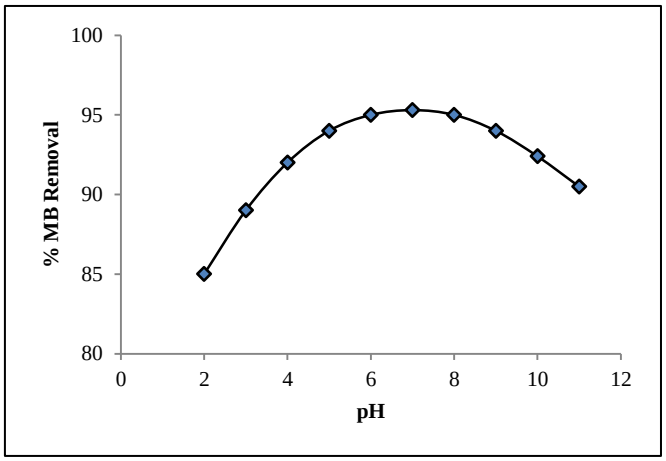


Fig.(6) Effect of pH value on the % removal dye efficiency at (Co=100 mg/l, Dose = 0.43 g and equilibrium time of 180 min)

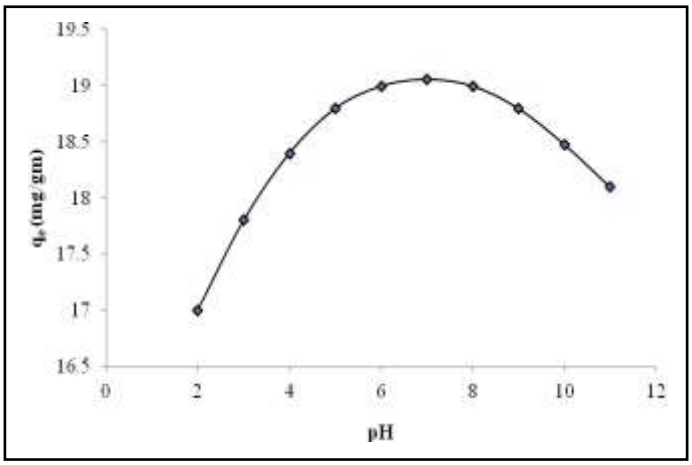


Fig.(7) Effect of pH value on the amount dye adsorbed at (Co=100 mg/l, Dose = 0.43 g and equilibrium time of 180 min)

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Classical adsorption models, Langmuir and Freundlich, were used to describe the equilibrium adsorbed dye (C_e) at constant temperature. The Langmuir equation which is valid for monolayer sorption onto the surface a finite number of identical sites and is given by equation (3):

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{q_o K_l} \cdot \frac{1}{C_e} \qquad \ldots(3)$$

Where q_o and K_l are Langmuir parameters related to maximum adsorption capacity (mg of solute per g of adsorbent) and free energy of adsorption, respectively. C_e is the equilibrium concentration in the solution (mg/l) and q_e is the equilibrium adsorption capacity of adsorbent (mg of adsorbate per g of adsorbent). The value of q_o and K_l can be evaluated from both intercept and slope, respectively, of the linear plot of the experimental data of $1/ q_e$ versus $1/ C_e$ as illustrated in Fig.8 and tabulated in Table (2). The correlation coefficient (R^2) was (0.9742).

The essential characteristics of the Langmuir isotherm can be expressed in term of a dimensionless constant separation factor for equilibrium parameter, R_L which defined by eq. (4):

$$R_L = \frac{1}{1 + K_l C_o} \qquad \ldots(4)$$

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Values of R_L were found to be confirmed that the STL is favorable for adsorption of MB dye under conditions studied as shown in Fig.10. The linear form of Freundlich model can be written as eq. (5):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad \ldots(5)$$

The value of K_f and n can be evaluated from both intercept and slope, respectively, of the linear plot of the experimental data of $\ln q_e$ versus $\ln C_e$ as illustrated in Fig. (9) and tabulated in Table (2). The Freundlich isotherm model yielded the best fit with the highest correlation coefficient (R^2) value (0.9931). From Fig. 7 and 8 can be seen that Freundlich model showed a better fit of the data than the Langmuir model.

Table (2) Parameters of Langmuir and Freundlich isotherm models

Langmuir Constants			Freundlich Constants		
q_o	K_l	R^2	K_f	n	R^2
45.7792	0.26311	0.9742	10.5147	2.784	0.9913

Table (4) lists the comparison of maximum adsorption capacity of MB onto various agricultural adsorbents. It is clear that STL used in the present work had relatively suitable adsorption capacity of 62.2 mg/g if compared to other adsorbents found in the literature.

Table (4) Adsorption capacity of different adsorbent for MB adsorption

Adsorbent	*q_m(mg/g)*	*References*
Spend Tea Leaves	62.2	Present Work
Cedar sawdust	142.36	[25]
Sawdust	133.87	[26]
Coconut husk	99	[27]
Coffee husk	90.1	[28]
Tea waste	85.16	[29]
Rice husk	40.59	[30]
Cotton waste	24	[31]
Banana peel	20.8	[32]
Orange peel	18.6	[32]
Wheat shells	16.56	[19]
Glass fibers	2.24	[33]

Conclusions:

1- STL has been proven to be an effective low-cost adsorbent for the removal of MB via adsorption from wastewater.
2- The amount of dye adsorbed was found to vary with initial dye concentration, pH solution, adsorption dose and contact time.
3- The equilibrium data were analyzed according to Langmuir and Freundlich models. The adsorption equilibrium was best fitted to the Freundlich isotherm model with maximum monolayer adsorption capacities found to be 62.2 mg/g, with good correlation coefficient.
4- The STL used in this work are freely and abundantly available, do not require an additional pretreatment step such as activation before applications and possess high adsorption capacity for MB. Therefore, the adsorbent is expected to be economically feasible for removal of MB dye from wastewater.

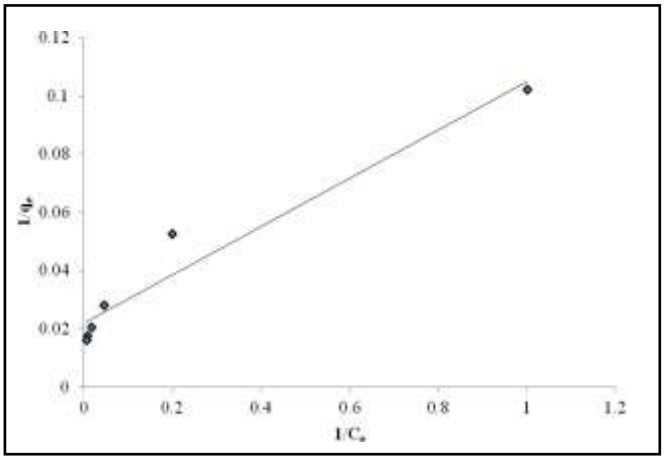


Fig (8) Langmuir Isotherm for Adsorption of MB Dye

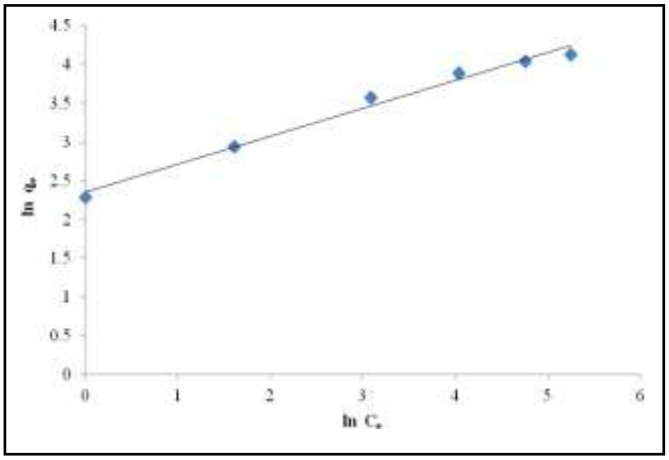


Fig (9) Freundlich Isotherm for Adsorption of MB Dye

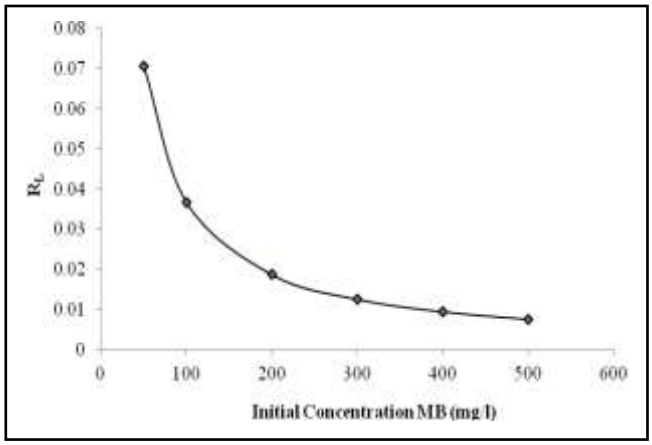


Fig (10) The separation factor for MB adsorption

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