Removal and Recovery of Methylene Blue Dye from Aqueous Solution using Avena Fatua Seed Husk

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Received in: 31/May/2016, Accepted in: 29/June/2016

Abstract

In present investigation, removal mechanism of methylene blue (MB) dye from aqueous solution by using Avena fatua seed husk was investigated at 308K by batch method. Effect of float/dry time, contact time, adsorbent dose, MB initial concentration, pH and temperature was achieved to get the adsorption optimum condition. Equilibrium data were tested by Langmuir and Freundlich isotherms and the data fitting well with Freundlich model . Kinetic data analysis by pseudo-first order, pseudo-second order and intraparticle diffusion model and the result shows better fit with pseudo-second order. Arrhenius equation at 298, 308, 318 and 328K was used to get the activation energy and found to be 23.57kJ.mol^{-1}. The thermodynamic values of standard free energy, enthalpy and entropy show negative sign exhibit spontaneous, exothermic and decrease the randomness respectively. The pH at point of zero charge, specific surface area and FTIR spectra was measured for adsorbent and the desorption process which achieved to regenerate the adsorbent after adsorption process.

Keywords: Methylene blue, Avena fatua, Adsorption, specific surface area, Langmuir, Freundlich, Isotherm, Thermodynamic

Introduction

About 110,000 tones of more than 100,000 types of commercially available dyes are lost during the dyeing process per year as liquid effluents [1]. Most of this dye carcinogenic, mutagenic and toxic to aquatic organisms [2] furthermore, the color effluent alter the light penetration and reduces the photosynthetic action even at low concentration. Due to most of the dyes are designed to resist light and biodegradable the conventional biological, physical, chemical and combination of these treatment techniques such as coagulation, filtration, floatation, ion exchange, chemical oxidation, photo degradation, solvent extraction, membrane separation are inefficient for removal of dyes[3]. Adsorption is economic as well as effective method for removal of dyes from waste water by different adsorbents such as zeolites, activated carbon, clay and agricultural by-products. Activated carbon is wide used as adsorbent with high efficiency but the major drawback is high cost of commercially activated carbon therefore, the derived of activated carbon from low cost agricultural waste economically as compared to commercial activated carbon but this is limited by cost of carbonization process, method of activation, regeneration process and efficiency of prepared activated carbon [1]. The economic, efficiency and abundance of agricultural by-products enhance many researchers to investigate different biomass such as, Parthenium hystrophorous weed [4], cork bark and stalks grape [5], ginger waste [6], perlite [7], barley husk [8], lemana minor [9], peanut hull [10], wheat bran [11], rice husk [12], sargassum muticum [13], and so on. The adsorption process removes the dyes molecule and also the other water pollutants includes; heavy metals and other chemical compounds[6].

The goal of present investigation is introducing locally abundant, low cost adsorbent and evaluate its removal efficiency by modal adsorbate MB (cationic) dye also known as basic blue 9. MB dye has wide range of application in medical[14], dying of wood, cotton and silk even it is not considered as toxic material but also have some harmful affect[15]. The adsorbent used in this study is seed husk of Avena fatua one of weeds grows normally in different types of soil among the barley, wheat and with other winter crops in Iraq. The adsorption parameter was achieved by batch mode and kinetic, equilibrium, thermodynamic and desorption studies predict the mechanism influence the adsorption reaction.

Materials and Methods

Adsorbate

Methylene Blue dye supplied by CDH(Central Drug House) New Delhi, was used to prepare the stock solution without prier purification. All the preparation and dilution achieved by double distilled water. Molecular formula of the dye is: $C_{16}H_{18}ClN_3S.xH_2O$ where x=2,3; Molecular weight: 319.86g.mol^{-1}, λ max=665nm and chemical structure were shown in Figure (1).

Adsorbent

Collection and Preparation

The Avena fatua seed husk was collected from Tuwaitha, Baghdad, Iraq. The husk was washed with distilled water to remove the dirt and dried at room temperature for 48hours, finally crushed and sieved.

Characterization

In order to characterize the surface of adsorbent pH at zero point charge was determined by adjusting the pH of nine 25mL 0.1M KNO_3 solution in the range from 2 to 10 by using 0.1M NaOH and HCl, after that 0.1g of Avena fatua seed husk were added for each solution and left for more than 1hour. Finally the pH was measured by (Hanna pH-meter, China)

before and after the addition of adsorbent then, pH_i-pH_f plotted against pH_i[16]. To find the characterized groups affect the adsorption, FTIR spectra were measured by (Shimadzu 8400S, Japan) spectrophotometer in the range 400 to 4000cm^{-1}. The specific surface area Ss (m^2/g) of Avena fatua seed husk by MB dye adsorption were calculated by using the following equation [13]

$$S_S = \frac{q_m \times N_A \times A_{MB}}{M.Wt} \quad (1)$$

Where q_m(g/g) maximum adsorption capacity (q_m(mg/g) calculated from Langmuir isotherm plot multiply by10^{-3}), N_A Avogadro's number (6.023× $10^{23} mol^{-1}$), $A_{MB}$is occupied surface area of single MB molecule (197.2× $10^{-20} m^2$) [17] and $M.Wt$ is molecular weight of MB dye (319.86g.mol^{-1}).

Equilibrium Experiments

The adsorption process achieved by batch experiments in series of conical flask (250mL) where solution of MB dye (50mL) with different initial concentrations (5-50) mg/L. The pH adjusted by 0.1M of HCl and NaOH. 0.1g of Avena fatua seed husk were added to MB solution and maintained in constant stirring by(Lab stirrer 78-1,China) for 40min at 308K to reach equilibrium. The mixture was then centrifuged by(Lab centrifuge 80-2,China) and the supernatant concentration determines using spectrophotometer (APEL-303, Japan) at 665nm. The removal efficiency and the amount of MB dye adsorbed at equilibrium q_e were calculated using the following equations [3]:

$$\%\text{Removal} = \frac{C_o - C_e}{C_o} 100 \quad (2)$$

$$q_e = \frac{C_o - C_e}{m} \text{ x V} \quad (3)$$

Where, C_o is initial concentration (mg/L), C_e is equilibrium concentration (mg/L), m (g) adsorbent weight and V solution volume in liter.

Kinetic Experiments

The 25mg/L of dye solution under the optimum conditions were taken. The concentration of unadsorbed dye measured with time interval 5min and the amount of dye adsorbed at time t were calculated by following equation [1]:

$$q_t = \frac{C_o - C_t}{m} \text{ x V} \quad (4)$$

Where, $C_o$is initial concentration (mg/L), $C_t$is concentration at time t (mg/L), m (g) adsorbent weight and V (L) solution volume.

Recovery Experiments

0.5g of adsorbent was added to 50mL of 25mg/L dye solution and the concentration at equilibrium time were measured. The supernatant was discarded and the adsorbent was dried at room temperature. The 50mL of 0.01M of HCl, was added to adsorbent and the desorbed dye was measured. This procedure was repeated with different concentrations of HCl from 0.01 to 0.1M as well as acetone and distilled water and the recovery percentage was calculated using following equation [18]:

$$\%\text{Recovery} = \frac{C_d}{C_a} 100 \quad (5)$$

Where C_d (mg/L) concentration of desorbed MB dye and C_a (mg/L) is concentration of adsorbed MB. The adsorbent after desorption process was washed to remove the acidity and then dried at room temperature finally crushed and heated at 378K for 1hour.

Result and Discussion

Characteristics of Adsorbent Surface

The pH_{pzc} is the pH where net electric charge present on the Avena fatua seed husk surface is zero (Fig.2), shows pH_{pzc} is 4. The MB (cationic) dye adsorbed at pH above 4 that conformed by measuring effect of pH as described later. FTIR spectrum before adsorption (Fig. 3a) shows broad band from 3467.77 to 3215.11cm^{-1} this refers to O-H alcohol and phenol groups that conformed by absence N-H (EDS from literature) [19] and C-O stretch at 1080.06 and 1026.06cm^{-1}. The intense band 2927.74 $cm^{-1}$and medium bands at 2788.88 and 2763.80 cm^{-1} indicate O-H carboxylic acid supported by C=O at 1730.03 and 1649.02 cm^{-1} and C-O at 1240 and 1425.30 cm^{-1} [6]. Fig.3b shows disappear bands at 2788.88 and 2763.80 cm^{-1} and shift the 1730.03 and 1649.02 to 1722.31 and 1652.88 cm^{-1}respectively, that proved carboxylic groups affect the adsorption. The specific surface area of adsorbent was found 119.01m^2/g

Factors Influence the Adsorption

Effect of Float/Dry Time

The presence of water molecule decreases the adsorption percentage due to blocking the adsorbent site. Fig.4 indicates that as the floating time increases the removal percentage decreases and heating the adsorbent at 333K increases the adsorbent capacity till the surface free from water molecule at this point no further affect of heating on percentage removal.

Effect of Adsorbent Dose

The increase of adsorbent dosage leads to increase removal percentage due to more surface area and adsorption sites will interact with adsorbate in known volume of dye solution [1]. Fig.5 shows that 0.15g is the optimum dose and above this amount no significant increase of adsorption percentage.

Effect of PH

Figure (6) indicates the adsorption of MB increase significantly as the pH is raised from 2 to 8 and above 8 kept constant. hence, the optimum pH for adsorption of MB is 8. This increase in adsorption percentage is due to electrostatic attraction between MB (cation) molecule and anionic groups present on the adsorbent surface and that is conformed by point of zero charge where the surface have anionic nature at pH above 4 [7].

Effect of Contact Time

The contact time required to reach the equilibrium is important factor to site the adsorption optimum condition. Fig.7 illustrates that the adsorption of MB on the Aven fatua seed hush is equate rapid 40min at different temperatures and the percentage removal decreases by the increase temperature and that exhibits exothermic process[1].

Effect of Initial Concentration

The influence of MB dye initial concentration on the percentage removal was achieved at 308K using 0.15g of adsorbent with different initial dye concentration in the range (10, 20, 30, 40 and 50mg/L) at optimum conditions. Figure(8), shows decrease in the removal percentage with increasing initial concentration that is because the adsorption sites saturated and no more sites on the adsorbent surface [10]

Equilibrium Studies

To understand how the adsorbate particle distributes between the liquid phase and solid surface of adsorbent at the equilibrium. The data fitted to well-known isotherms Langmuir and Fruendlich. The Langmuir assumes the adsorbent surface is uniform with limit number of adsorption site and no more adsorption takes place after formation monolayer[4]. Freundlich assumes heterogeneous surface and the concentration of adsorbate affect the adsorption capacity [16,20]. The linear form of Langmuir equation and separation factor defined by Weber and Chakkravorti are given by following equations [4]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (6)$$

$$R_L = \frac{1}{1+K_L C_o} \qquad (7)$$

Where C_e (mg/L) unadsorbed MB dye concentration at equilibrium, q_e (mg/g) amount of MB dye adsorbed on the 0.15g of adsorbent at equilibrium, q_m is maximum adsorption capacity and K_L is Langmuir constant obtained from plot of $\frac{C_e}{q_e}$ versus C_e (Fig.9). The K_L value and the initial concentration C_o used to calculate the separation factor R_L and the value ranged from 0.4640 to 0.1476 this confirmed the adsorption process favorable at the optimum condition used in this study.

The Freundlich isotherm in the logarithmic form is represented by following equation [6]:

$$\text{Log } q_e = \log K_F + \frac{1}{n} \log C_e \qquad (8)$$

Where C_e (mg/L) unadsorbed MB dye concentration at equilibrium, q_e (mg/g) amount of MB dye adsorbed on the 0.15g of adsorbent at equilibrium. K_F and $\frac{1}{n}$ are Freundlich constants, K_F is adsorption coefficient and indicate the amount of adsorbate adsorbed onto adsorbent for unit equilibrium concentration. The $\frac{1}{n}$ value ranges from zero to one is a function of adsorption intensity or surface heterogeneity [16]. The surface becoming more heterogeneity as the $\frac{1}{n}$ value comes near to zero. A value of $\frac{1}{n}$ less than one indicates chemisorptions process, while the unity implies partition between the liquid phase and solid phase are independent of concentration [20]. On the other hand, above unity exhibit cooperative adsorption [21]. The linear plots of log q_e against log C_e(Figure (10), gives slope value below unity and this implies that adsorption process follows chemisorptions process. The values of correlation coefficient and constants of Langmuir and Freundlich model are summarized in (Table 1), shows the adsorption of MB dye on to Avena fatua seed husk follows Langmuir as well as Freundlich model and the Freundlich adsorption model appears better fit (R^2=0.987) than the Langmuir model (R^2=0.973).

Kinetic Studies

To comprehend the mechanism of adsorption reaction, the kinetics experimental observation data was fitted to pseudo-first order (Lagergren equation), pseudo-second order as well as intraparticle diffusion model. The linear form of pseudo-first order formulated as the following [8]:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (9)$$

Where $q_e$and q_t the adsorption capacity at equilibrium and time t respectively. From the plots of log (q_e-q_t) against the time t for 25mg/L concentration of MB dye at 298,308,318 and 328K respectively (Fig.11), the value of $k_1(min^{-1})$ rate constant, calculated equilibrium

uptake q_e and correlation coefficient obtained and listed in table 2. Although the correlation coefficient shows 0.97 with pseudo-first order but the experimental equilibrium uptake q_e value far away from calculated q_e value this conformed the adsorption of MB onto Avena fatua seed husk does not agree with pseudo-first order model.

The (Ho and McKay 1999) pseudo-second order model represented by following equation [22]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \text{t} \qquad (10)$$

A linear plot of $\frac{t}{q_t}$ against time t at 298,308,318 and 328K respectively Figure (12) gives the straight line and from the slope and intercept value of k_2(g.$mg^{-1}.min^{-1}$) and q_e can be calculated. The initial adsorption rate h_o at various initial concentrations is related in the following equation [16]:

$$h_o = k_2 q_e^2 \qquad (11)$$

The adsorption of MB onto Avena fatua seed husk obeyed pseudo-second order model as the correlation coefficient close to 1 and the calculated adsorption capacity agree with the experimental adsorption capacity. Furthermore, the small value of sum of error squares calculated by using following equation [12]:

$$\text{SSE (\%)} = \sqrt{\frac{\sum(q_{e,exp} - q_{e,cal})^2}{N}} \qquad (12)$$

Where SSE is sum of error squares and N number of data point.

The Weber and Marris intraparticle diffusion model is given by following equation [8]:

$$q_t = k_{id} t^{0.5} + \text{C} \qquad (13)$$

Where k_{id}(mg/g.$min^{1/2}$) is the intraparticle diffusion rate constant and C is constant obtained from the intercept of plot q_t versus $t^{0.5}$(Fig.13), the plot does not pass through the origin at 298, 308, 318 and 328K for 25mg/L initial concentration of MB dye therefore, the intraparticle diffusion not the rate controlling step[7].

Activation Parameter

To indicate the type of adsorption process the pseudo-second order rate constant k_2 at different temperatures substituted in Arrhenius equation [7]:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad (14)$$

Where A (mg. mol^{-1} . min^{-1}) Arrhenius factor, E_a (J. mol^{-1}) activation energy, R (J. K^{-1} . mol^{-1}) gas constant and T (K) absolute temperature. The higher value (40-800kJ.mol^{-1}) of E_a predict the chemisorptions while lower value (5-40 kJ.mol^{-1}) predict physical adsorption [1]. The E_a of MB dye onto Avena fatua seed husk obtained from slope of (Fig.14) was 23.57 kJ.mol^{-1} this value indicates physical adsorption.

Thermodynamic Parameters

Thermodynamic parameters are calculated by following equations [10]:

$$K_c = \frac{C_{ads}}{C_e} = \frac{C_o - C_e}{C_e} = \frac{C_o}{C_e} - 1 \qquad (15)$$

$$\Delta G^o = -\text{RT} \ln K_c \qquad (16)$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (17)$$

Where, K_c equilibrium constant, C_o(mg/L), C_{ads}(mg/L), and C_e(mg/L) represent the dye initial concentration, concentration of adsorbed dye and remaining concentration in solution at equilibrium, respectively. The ΔG^o, ΔH^o and ΔS^o are change in free energy, enthalpy and entropy respectively. R gas constant (8.314J.$mol^{-1}.K^{-1}$) and T (K) solution absolute temperature. The ΔG^o obtained have negative sign that indicates the adsorption process was spontaneous and from slope and intercept of van't Hoff plot (Fig.15), ΔH^o and ΔS^o are calculated. The thermodynamic results summarized in table.3.shows negative value of enthalpy indicates exothermic adsorption reaction and negative value of entropy indicate decrease in randomness.

Desorption Studies

The desorption of MB dye from adsorbent surface achieved by adding different concentrations of HCl and as the acidity increases the desorption increases(Figure16) and that conformed electrostatic attraction between cationic MB dye and anionic groups present on adsorbent surface[2].

Conclusion

The Avena fatua seed husk is a locally available and low-cost material that can be used as adsorbent for removal the cationic dye MB from aqueous solutions, without any pre-treatment. The adsorbent was characterized by FTIR spectroscopy indicating the presence of –COOH, C-O, and O–H groups. The optimum pH for the adsorption of MB was 8 and the contact time necessary for equilibrium was 40min. There are several indicatives that the mechanism of adsorption of methylene blue by Avena fatua seed husk should be an electrostatic attraction of negatively charged adsorbent at pH=8.0 (since the carboxylic acids of the adsorbentt should lose a proton at this pH value) with positively charged methylene blue. The pseudo-second order kinetic model was properly fitted when compared with other kinetic models. The negative sign of thermodynamic parameter refers to spontaneous, exothermic and decrease of randomness. The equilibrium data described by Langmuir as well as Freundlich model and the maximum adsorption capacity is 30.05mg/g at 308K.

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Table (1): Isotherms constants and correlation coefficient of MB dye onto Avena fatua seed husk

Langmuir isotherm			Freundlich isotherm		
K_L (L/mg)	q_m (mg/g)	R^2	K_F (mg/g$(\frac{L}{mg})^{1/n}$)	1/n	R^2
0.1155	32.05	0.973	3.758	0.6685	0.987

Table (2): Comparison of kinetic results of 25mg/L MB dye onto Avena fatua seed husk at different temperatures

T(K)	$q_{e,exp}$ mg/g	Pseudo-first order			
		$k_1(min^{-1})$	$q_{e,cal}$	R^2	%SSE
298	11.25	0.07208	2.47	0.970	8.78
308	10.6	0.07393	2.35	0.971	8.25
318	10.85	0.0569	2.47	0.926	8.38
328	10.55	0.04974	3.6	0.973	6.95

T(K)	$q_{e,exp}$ mg/g	Pseudo-second order				
		k_2 g.$mg^{-1}.min^{-1}$	$q_{e,cal}$	R^2	h_o	%SSE
298	11.25	0.06793	11.47	0.999	8.937	1.22
308	10.6	0.06479	10.85	1	7.628	0.25
318	10.85	0.05146	11.06	0.999	6.297	0.21
328	10.55	0.02755	10.94	0.997	3.297	0.39

Table (3): Values of thermodynamic parameters for the adsorption of MB on the Avena fatua seed husk at different temperatures

T(K)	ΔG(kJ.mol^{-1})	ΔH(kJ.mol^{-1})	ΔS(J.$mol^{-1}.K^{-1}$)
298	-5.161	-12.22	-20.33
308	-4.958		
318	-4.755		
328	-4.551		

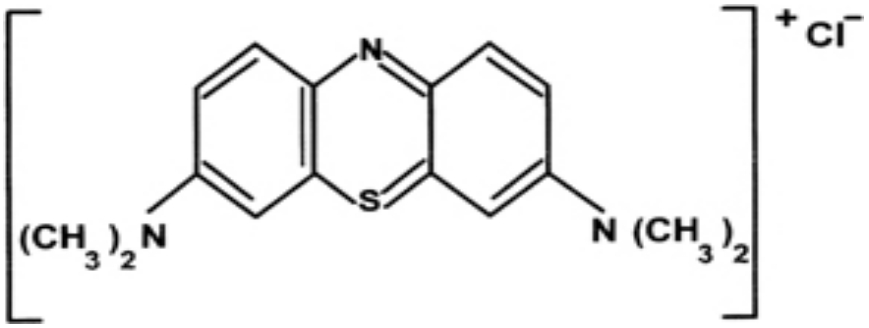

Figure (1): The chemical structure of Methylene Blue

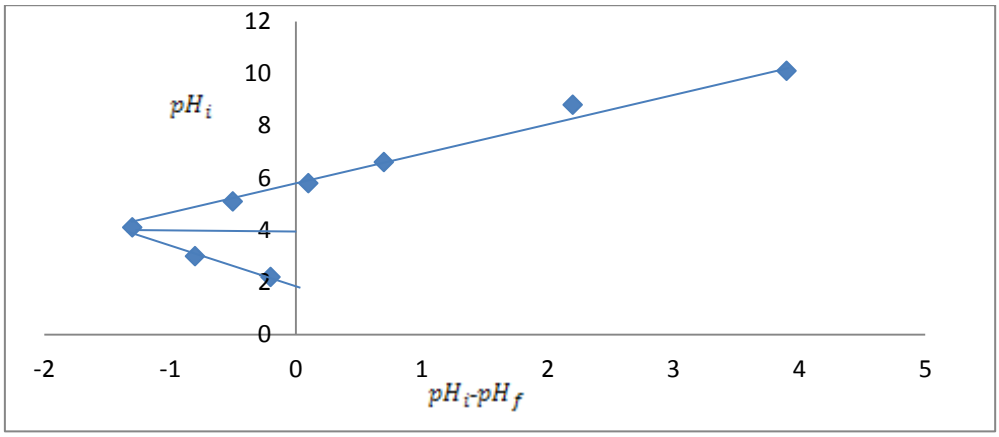

Figure (2): Point of zero charge of adsorbent surface

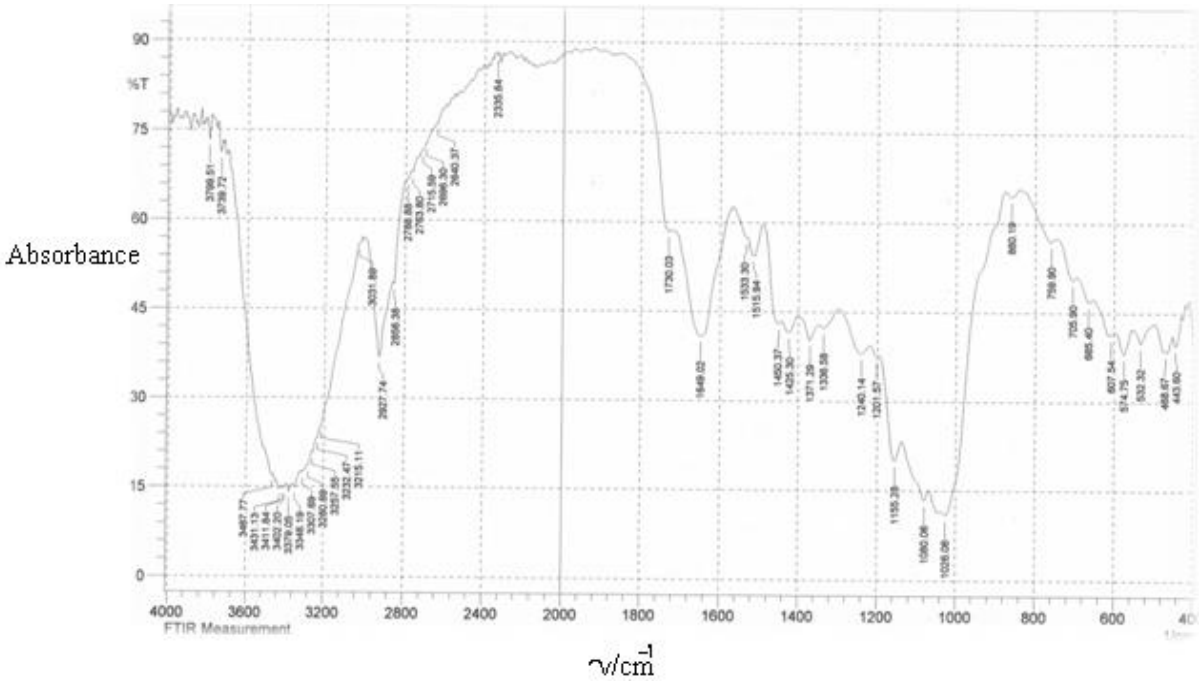

Figure (3a): FTIR spectrum of Avena fatua seed husk surface before adsorption

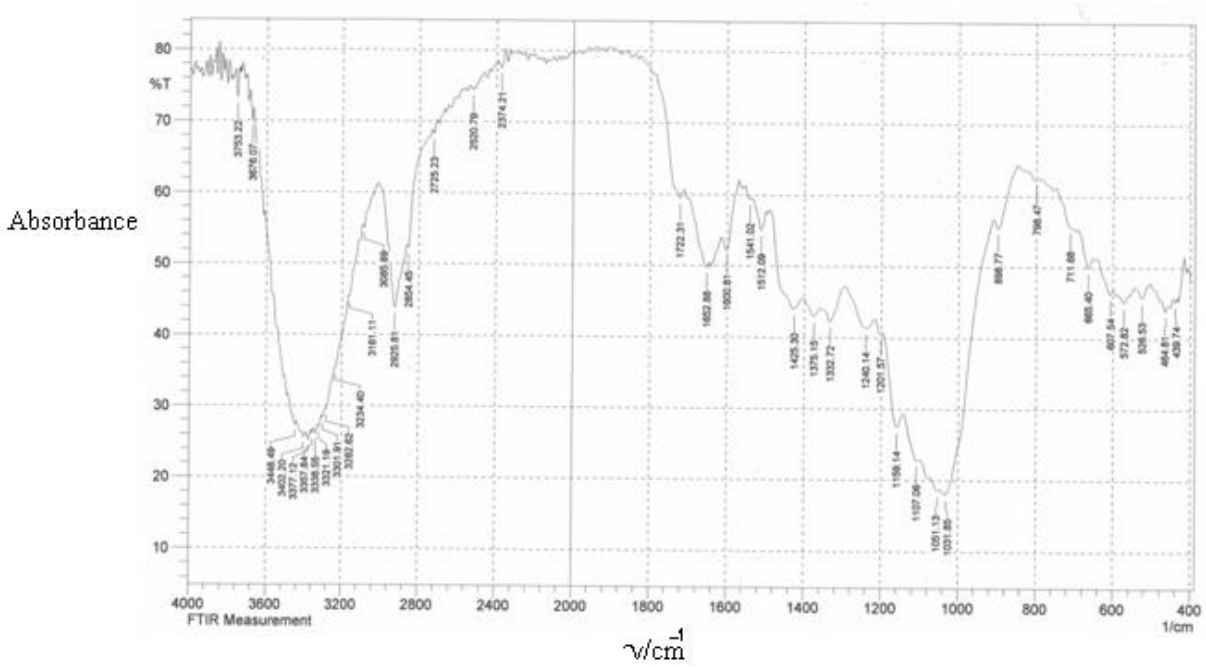

Figure (3b): FTIR spectrum of Avena fatua seed husk surface after adsorption

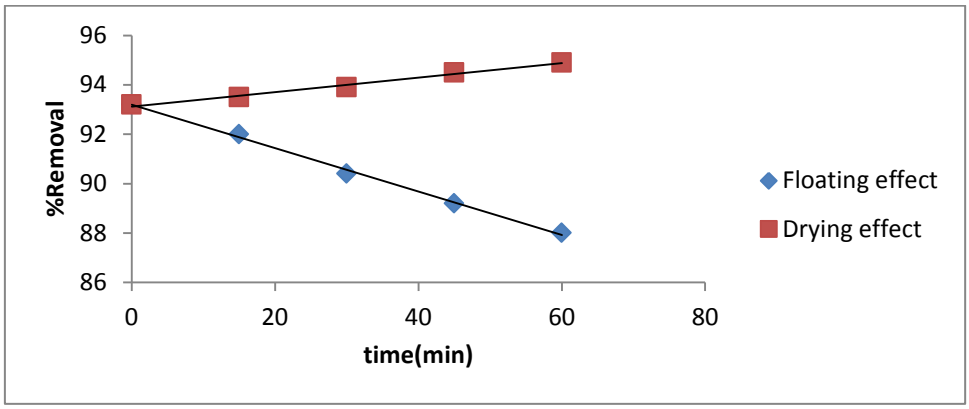

Figure (4): Effect of float/dry time on the removal percentage

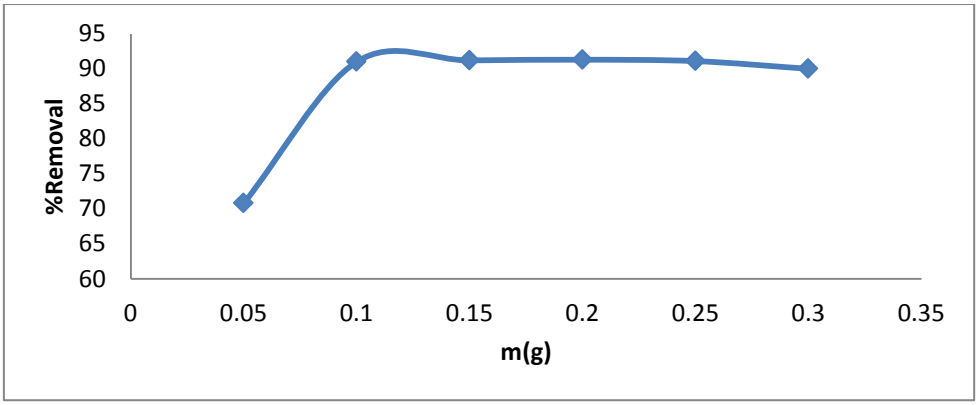

Figure (5): Effect of adsorbent dosage on percentage removal of 25mg/L initial concentration of MB dye at 308K

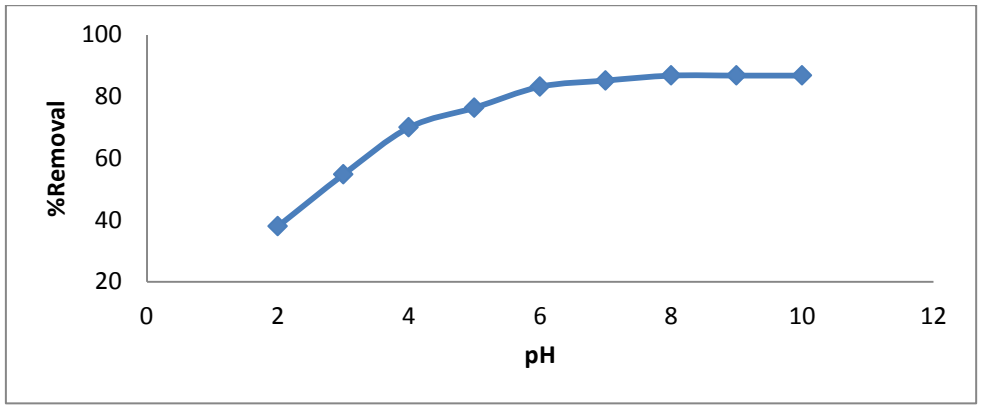

Figure (6): Effect of pH on percentage removal of 25mg/L initial concentration of MB dye at 308K

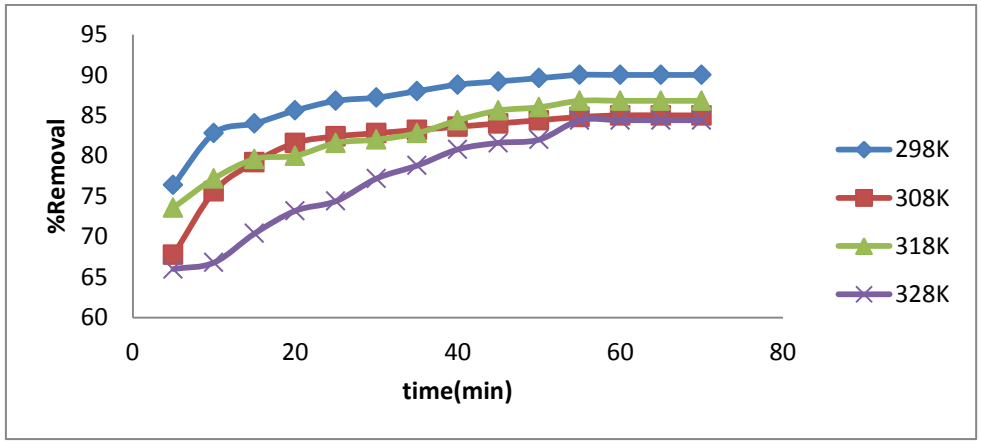

Figure (7): Effect of contact time on percentage removal of 25mg/L initial concentration of MB dye at different temperature

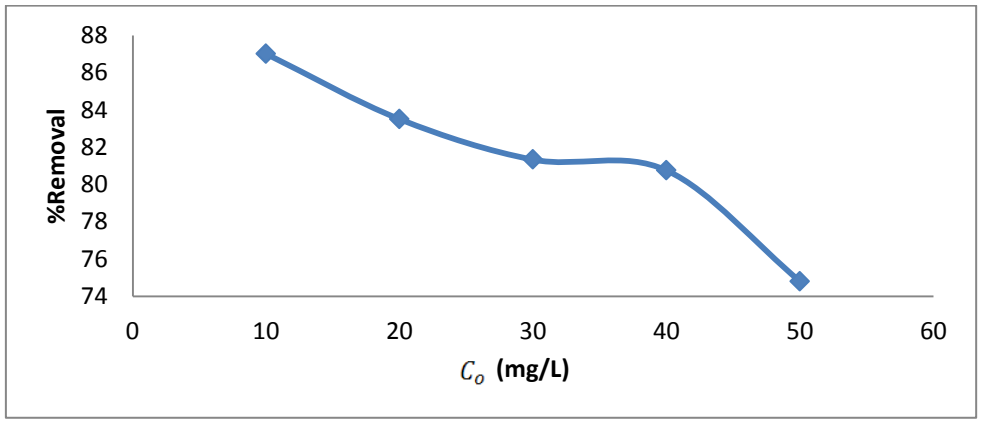

Figure (8): Effect of initial concentration of MB dye on percentage removal at 308K

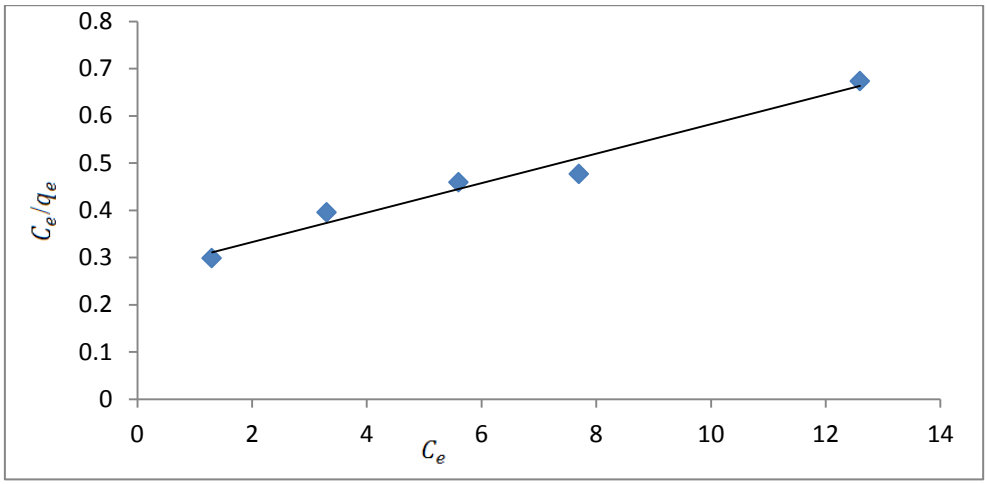

Figure (9): Langmuir isotherm for adsorption of MB onto Avena fatua seed husk at 308K

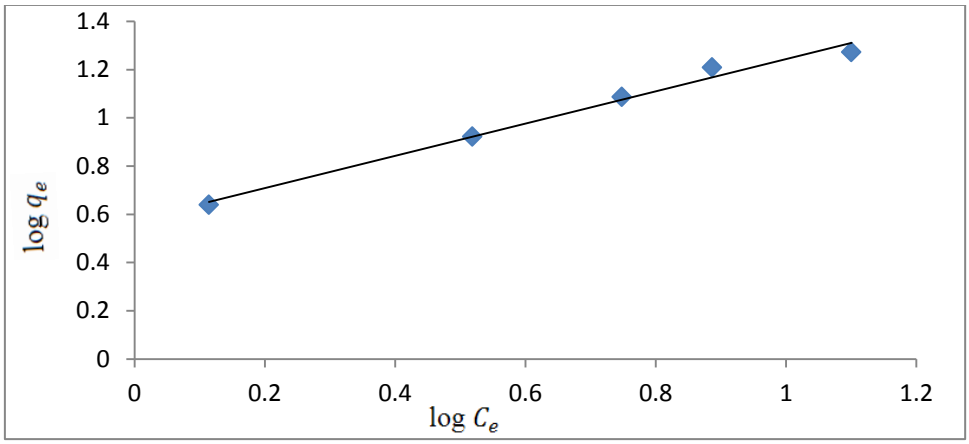

Figure (10): Freundlich isotherm for adsorption of MB onto Avena fatua seed husk at 308K

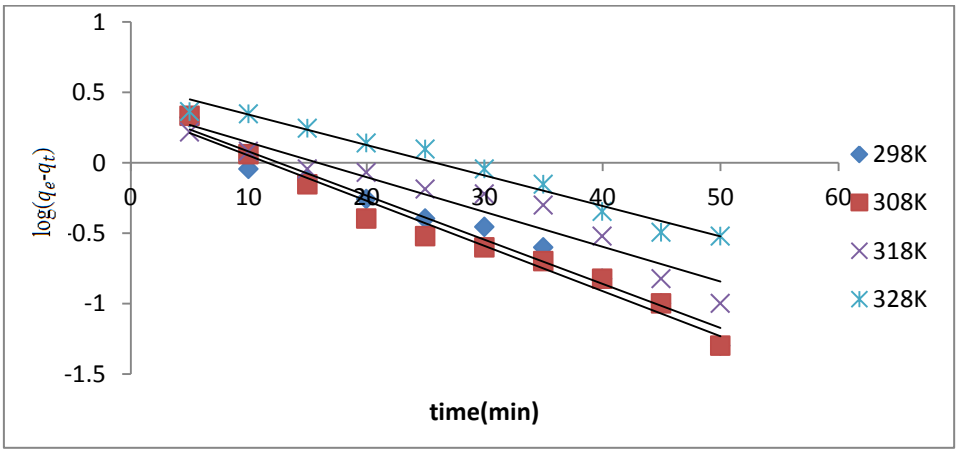

Figure (11): Pseudo-first order for adsorption of 25mg/L MB dye onto Avena fatua seed husk at different temperature.

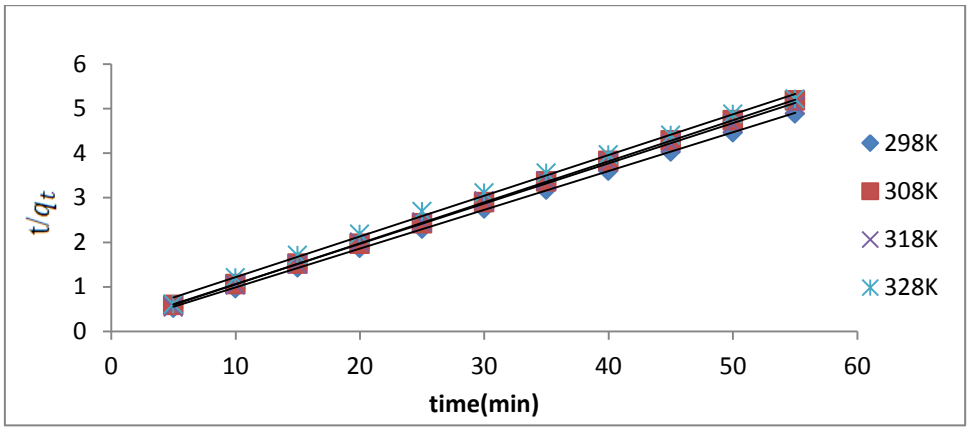

Figure (12): Pseudo-second order for adsorption of 25mg/L MB dye onto Avena fatua seed husk at different temperature

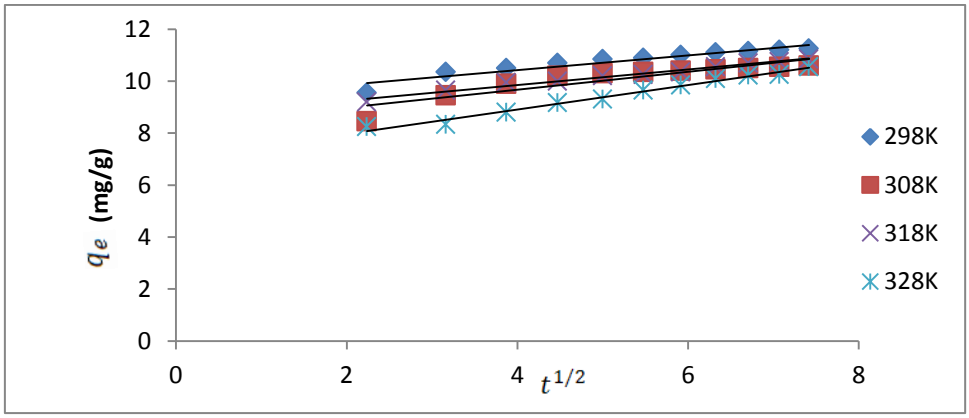

Figure (13): Weber and Marris plot for adsorption of 25mg/L MB dye onto the Avena fatua at different temperature

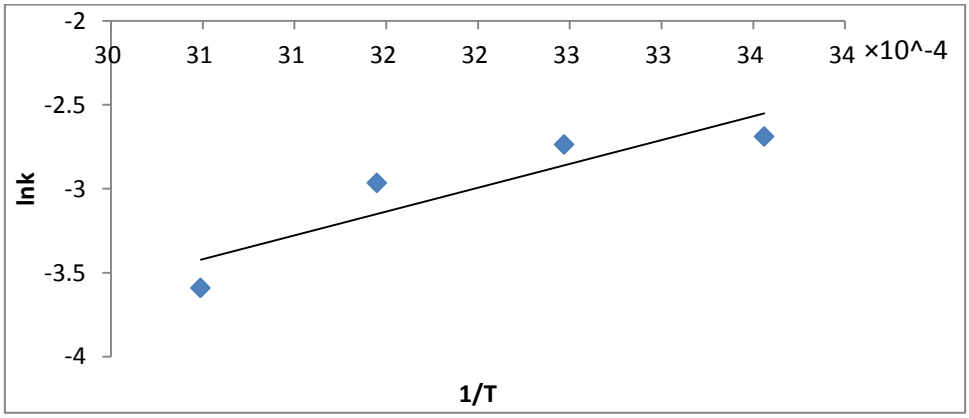

Figure (14): Arrhenius plot of MB dye onto Avena fatua seed husk

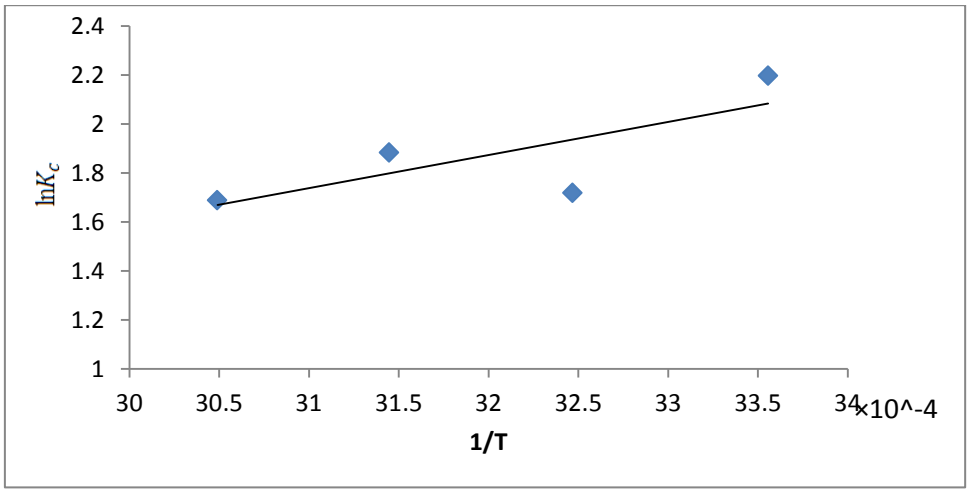

Figure (15): Van't Hoff plot of MB dye onto Avena fatua seed husk.

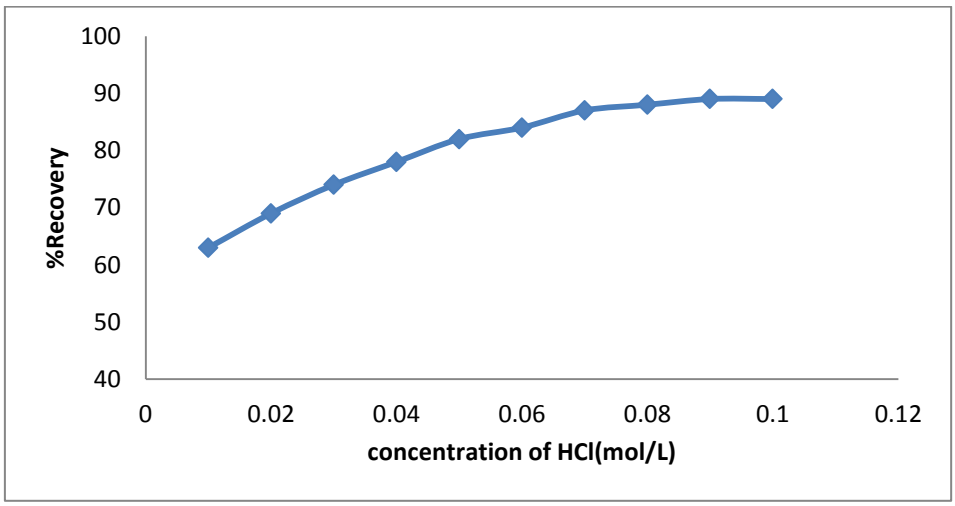

Figure (16): Desorption of 25mg/L MB dye from adsorbent surface at 308K

ازالة واسترداد صبغة المثيلين الازرق من المحلول المائي باستعمال قشور بذور الدوسر

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استلم في:31/أيار/2016، قبل في:29/حزيران/2016

الخلاصة

تم دراسة ميكانيكية ازالة صبغة المثيلين الازرق من المحلول المائي باستعمال قشور بذور الدوسر عند درجة حرارة 308 كلفن بطريقة الوجبة. كما وتم دراسة تأثير كل من زمن النقع، زمن التماس، التركيز الابتدائي للمادة الممتزة، كمية المادة المازة، درجة الحرارة و الدالة الحامضية للوصول الى الظروف المثلى للامتزاز. تم اختبار القياسات عند الاتزان باستعمال معادلة لانكماير و فروندليج واظهرت النتائج انطباقا مع معادلة فروندليج اما القياسات الحركية فقد اختبرت بمعادلة المرتبة الاولى ألكاذبة، المرتبة الثانية ألكاذبة و معادلة الانتشار و وأظهرت النتائج ان تفاعل الامتزاز من المرتبة الثانية الكاذبة. معادلة ارينيوس عند 318،308،298 و 328 كلفن استخدمت للحصول على طاقة التنشيط و وجد انها تساوي $23.57 kJ.mol^{-1}$. المتغيرات الثرموديناميكية مثل الطاقة الحرة، الانثالبي والانتروبي اظهرت قيمة سالبة مما يدل على ان التفاعل تلقائي، باعث للحرارة و مصحوب بنقصان العشوائية على التوالي. المادة المازة شخصت من خلال قياس طيف الاشعة تحت الحمراء والدالة الحامضية عند الشحنة صفر اضافة الى حساب المساحة السطحية و تم اعادة تنشيط السطح الماز من خلال ابتزاز الصبغة من السطح كي يمكن اعادة استعماله.

الكلمات المفتاحية: المثيلين الازرق، الدوسر، امتزاز، المساحة السطحية ،لانكماير ، فروندليج، ايزوثيرم، ثرموديمكية .