Adsorption Study of Methylene Blue Dye on Rice Bran in Aqueous Solution

دراسة امتزاز صبغة ازرق المثيلين على نخالة الرز في المحلول المائي

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Abstract :

The extraction of certain pollutant substances from solution on solids is one of the cheapest and easiest separation methods. Furthermore, some of the extracted substances are economically important. In this work, an attempt was done to obtain cheap adsorbent, rice bran, for adsorption and extraction of methylene blue dye (MB) from aqueous solution. Study of some practical parameters affecting adsorption process such as initial dye concentration, acidity, and compute the thermodynamic parameters (ΔH^o, ΔG^o, ΔS^o) for the adsorption process. The extent of the MB removal by rice bran increased with increase in the initial concentration of the dye and temperature. Thermodynamic parameters, such as ΔH^o, ΔG^o, and ΔS^o have been calculated by using the thermodynamic equilibrium coefficient obtained at different temperatures and concentrations were: ΔH^o=10.28KJ.mol^{-1}, ΔG^o=-5.08KJ.mol^{-1}, ΔS^o=52.39J.mol^{-1}.^{o}K^{-1}. It can be concluded from the results of the present study that the process of adsorption of MB on rice bran may be used effectively to remove the dye from aqueous medium as acidity is increased. The dye removal increased with increase in the initial concentration of the dye and temperature indicating that the process is endothermic and spontaneous. MB can be used to remove the dye even the solution is hot with good efficiency.***Keywords***: Rice bran, adsorption, methylene blue.

الخلاصة :

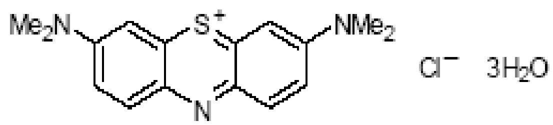
يشكل استخلاص بعض المواد الملوثة من المحلول على سطح المواد الصلبة واحد من اسهل وابسط طرق الفصل كما ان بعض المواد المستخلصه تكون ذات اهمية اقتصادية . في هذا البحث اجريت محاولة للحصول على ماده مازة رخيصه ومتوفرة (نخالة الرز) لامتزاز واستخلاص صبغة ازرق المثلين من المحلول المائي. كما تم حساب بعض الدوال الثرموديناميكية (ΔH^o, ΔG^o, ΔS^o) وتاثير تركيز الصبغه الابتدائي وحامضية المحلول على كمية الماده الممتزه او عمليه الامتزاز.ان سعة ازالة صبغة بواسطة نخالة الرز تزداد بزيادة التركيز الابتدائي للصبغة ودرجة الحرارة . تم حساب القيم الثرموديناميكية باستعمال ثابت التوازن المحسوب عنددرجات حرارية مختلفة وتراكيز مختلفة وكانت النتائج كالاتي :-

ΔH^o=10.28KJ.mol^{-1}, ΔG^o=-5.08KJ.mol^{-1}, ΔS^o=52.39J.mol^{-1}.^{o}K^{-1}.

يستنتج من هذا البحث امكانية امتزاز صبغة (m.b) على نخالة الرز هي عملية كفوءة لازالة الصبغة من المحلول الحامضي عند زيادة الحامضية للمحلول،كما تزداد كمية المادة الممتزة بزيادة التركيز الاولي ودرجة الحرارة مشيرة الى كون العملية ماصة للحرارة وتلقائية .ان ازالة الصبغة من المحلول باستعمال نخالة الرز بالامكان اجراؤها في المحاليل الساخنة وبكفاءة عالية . مفاتيح الكلمات: نخالة الرز-ازرق المثيلين –الامتزاز.

INTRODUCTION :

Many substances used as adsorbents for different dyes in order to obtain cheep, available, non toxic adsorbents for removing dyes from aqueous solutions in different industries [1, 2, 3]. Any solid has some tendency to adsorb substances from fluid medium onto their surface, however only some few solid materials have the selective adsorption capacity to adsorbate molecules. The adsorbate may be atoms, ions or molecules (adsorbate) of organic compound, color, odor, moisture etc [4]. Many factors can influence the process of adsorption; the concentration of adsorbate (substance being adsorbed), surface area of the adsorbent; temperature, pH, ionic strength, solubility, chemical state of both adsorbent and adsorbate molecules and the kinetic effect (5). Different adsorbents (6) were tested for their ability to remove and extract different dyes from aqueous solutions including activated charcoal (7), clays (8), and agriculture products (9) which used widely as adsorbents in the adsorption processes for different substances from solution including metal ions (10), and organic pollutants (11). Dietary fiber is mainly composed of plant cell walls which vary in composition and properties according cell type and plant species. In addition to polysaccharides, the walls of some plant cell types contain the hydrophobic polymers lignin or suberin that may produce surface activity (12). One of these important dietary fibers is rice bran from rice (*Oryza sativa L.*). It is a by-product of making polished rice from brown rice. Therefore, rice bran is very inexpensive, costing 1/50–1/40 than of activated carbon, which would lower the cost of wastewater treatment significantly. Additionally, the use of rice bran is significant from the aspect of effective utilization of waste matter (13).Rice bran has a good adsorptive activity against different substances including different pesticides from an aqueous solution (13), metal ions (14), and several organic compounds, such as dichloromethane, chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, and benzene (15).



Methylene Blue (3,7-Bis(dimethylamino)phenothiazin-5-ium chloride trihydrate)

The term adsorption isotherm refers to the relation between the extent of adsorption (Qe) or (X/M) with the equilibrium concentration of the adsorbate in solution (Ce) at constant temperature. (X) is the amount of dye adsorbed in milligrams by (M) grams of the adsorbent (16). The process of adsorption from solution is more complicated than the corresponding process of gas adsorption on solid surface. The solvent effect and the complicated interaction between solvent molecules and dye molecules to be adsorbed have to be taken into account.This work is concerned with the study of locally available rice bran as an adsorbent for the removal of methylene blue dye from solution as low-cost adsorbent in wastewater treatment for the removal of color which comes from textile dyes or other industries.

Experimental:

A- Adsorption process:

Commercial rice bran (Oryza sativa L.) was obtained from locally markets. It was cleaned, washed with excessive amounts of water, and dried at 50˚C for two hours and kept in an airtight container. A volume of 10 milliliters of eight different concentrations of MB solutions (2, 4, 6, 8, 10, 12, 14, and 16mg/L) was shaken with 0.05g of dried rice bran adsorbent at a certain temperature in a thermostated shaker bath at shaking speed 60cycle/minute for 30minutes which is measured experimentally as a time needed for reaching the equilibrium state. After the equilibrium time is elapsed, the mixtures were centrifuged at a speed of 3000Xg for 10 minutes. Acidity of the solutions were adjusted using few drops of 0.1N HCl or 0.1N NaOH solutions. Absorbencies were measured at the maximum wave length (λmax) of methylene blue dye solutions depending on the pHs used in the experiment. The maxima used were λmax=661nm at pH=7, λmax=658nm at pH=3, λmax=659nm at pH=11 using UV-Visible spectrophotometer (Apple®) and then converted into absolute concentration readings through the calibration curve. The experiments were repeated at different temperatures (20, 30, 40, 50°C) in order to measure the thermodynamic parameters (ΔH^o, ΔG^o, ΔS^o).

B-Adsorption Isotherms Calculations:

Two main theories have been adopted to describe adsorption isotherms. The first, Langmuir adsorption isotherms which represented by the linear equation:

$$\frac{Ce}{Qe} = \frac{1}{ab} + \frac{Ce}{a} \qquad \text{------------------------------ (1)}$$

Where (a) represents a practical limiting adsorption capacity when the surface is fully covered with a monolayer of adsorbate. The constant b is the equilibrium adsorption constant which related to the affinity of the binding sites [17].The applicability of these equations on the adsorbent-adsorbate (solute) system assume the formation of one layer of adsorbate molecules on the surface while the Freundlich adsorption isotherm (equation) consider heterogeneity of the surface and the formation of more than one layer is probable. The linear form of Freundlich isotherm is:

$$\log Q_e = \log k + \frac{1}{n} \log C_e \qquad \text{------------------ (2)}$$

Where k and n are Freundlich constants characteristics of the system, including the adsorption capacity and the adsorption intensity, respectively [2,16].

C-Adsorption Thermodynamics:

In order to obtain a thermodynamical state of the adsorption process, the adsorption experiments were repeated at different temperatures (20, 30, 40, 50°C) to measure the thermodynamic parameters (ΔHº, ΔGº, ΔSº). The equilibrium constant (K) for the adsorption process at each temperature is calculated from division of the quantity of dye adsorbed on the rice bran surface on the quantity of dye still present in solution:-

$$K = \frac{Qe * 0.05}{Ce * 0.01} \qquad \text{---(3)}$$

Where (0.05g) represent the weight of the rice bran that has been used and (0.01) represents the volume of the dye solution used in the adsorption process.

The change in free energy (ΔGº) could be determined form the equation:-

$$\Delta G^\circ = -RT \ln K \qquad \text{--(4)}$$

Where R is the gas constant (8.314 J.mole-1.ºK-1) and T is the absolute temperature.

The heat of adsorption (ΔHº) may be obtained from the vant Hoff's equation:-

$$\ln K = \frac{-\Delta H^\circ}{RT} + cons\tan t \qquad \text{-------------------------------------(5)}$$

Where K is the equilibrium constant when Ce approaches zero at certain temperature. It obtained from plotting (Ln K) of each concentration against corresponding Ce. Plotting (In K) versus (1/T) should produce a straight line with a slope =(-ΔHº/R) from which the enthalpy (ΔHº) of the adsorption process is obtained. The change in entropy (ΔSº) was calculated from Gibbs equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \text{-- (6)}$$

Results and Discussion:

Adsorption isotherms of methylene blue dye on rice bran from aqueous solution obeyed Freundlich adsorption isotherm (Figure (1)). This fact obtained from the applicability of the linear form of Freundlich equation with high correlation coefficient values (Figure (2)). Table (1) showed the Freundlich constants that indicated the adsorption capacity (k) and the intensity of adsorption (n) at four different temperatures. In general, the results of Table (1) indicated that the increases in adsorption capacities and the decrease in adsorption intensities as temperature increases. Adsorption isotherms of different dyes on different surfaces including rice bran [15,18] were also obeyed Freundlich isotherm indicating heterogeneity of these surfaces [16, 19].The study of the adsorption process of MB dye on rice bran requires taking the nature of the surface and the chemical composition of rice bran into consideration. Rice bran contains lectin, chitin [20], and myo-inositol derivatives [21]. It has shown that

different types of plant cell walls adsorbed a range of substances including carcinogens including heterocyclic aromatic amines which are like the chemical structure of MB dye [12]. The removal by rice bran was examined using 22 different pesticides. The removal efficiencies varied from 22.2% to 98.8%. The variation in the removal efficiency of different pesticides was studied, and the pesticides with high lipophilicity were found to be easily removed by rice bran [13]. Rice bran was the most effective of the adsorbents among different adsorbent including charcoal and different natural and modified clays in removal of organochlorine compounds from environment [22]. According to the Giles interpretation [23] for the adsorption isotherm shapes, the adsorption isotherm of neutral red dye molecules on the rice bran surface was follow S4 type indicating the heterogeneity of the surface and the presence of different types of forces between the dye molecules and the surface active sites.
The removal of these organochlorine compounds and benzene by rice bran was attributed to the uptake by intracellular particles called spherosomes [15]. Figure (3) showed the natural logarithm of equilibrium constants (LnK) against equilibrium concentration (Ce) of adsorption of MB on rice bran surface. The intercepts of the straight lines with Y axis (LnK) give the natural logarithm of equilibrium constants (LnK) from which the equilibrium constants will calculated when Ce approaches zero and used for vant Hoff's equation plotted in Figure (4).

The thermodynamical parameters values are:

ΔH^o=10.28kJ mol^{-1}, ΔG^o=-5.08kJ mol^{-1}, ΔS^o=52.39J mol-1$^o K^{-1}$.

Free energy change and entropy values were measured at 298ºK. These values are high and indicated a spontaneous adsorption process as seen in the adsorption of other substances [24]. It is supposed from the thermodynamic values that, moderate and nonspecific interaction occurs between dye molecules and the active sites of rice bran surface. Endothermic process for the adsorption of MB on rice bran is consistent with other adsorption processes [25] and differs from other which was endothermic processes[24]. The negative value of free energy change indicates a spontaneous adsorption process although it was endothermic deu to the ΔH^o was low among the range of physical adsorption heat . Adsorption is a natural process and usually accompanied by a decrease in free energy change and entropy of the system [26]. Adsorption of methylene blue dye on rice bran showed a decrease in basic solution and mildly good adsorption capacity in neutral and acidic solution (Figure (5) and(6)). This may be due to the complex interaction among solvent, solute, and surface in response to the changing in acidity. The adsorption results can be explained by considering the textural properties of the rice bran and the interactions between the surfaces and the dyes, which include hydrogen bonding, electrostatic, and hydrophobic interactions. These forces affected by the changing in acidity because the net charge on each species will change as acidity changes. The mechanism of adsorption was best described with a model that included cation exchange, surface complexation of ion forms of the compounds, solution speciation, the presence of other competitor ions in rice bran surface, and the exchangeable pore waters may also affect [27]. The adsorption amounts may explained by dependency of adsorption on the relative energies of adsorbent-adsorbate, adsorbate-solvent, and adsorbate-adsorbate interactions [28]. These findings may be applied for the adsorption of dye on rice bran surface in our study.

Conclusion:

The rice bran has activity to adsorb MB from solution. Adsorption of MB from solution on rice bran is endothermic process with negative free energy change. The adsorption process enhanced by decreasing temperature and with increasing acidity of the medium. It can be concluded from the results of the present study that the process of adsorption of MB on rice bran may be used effectively to remove the dye from aqueous medium.

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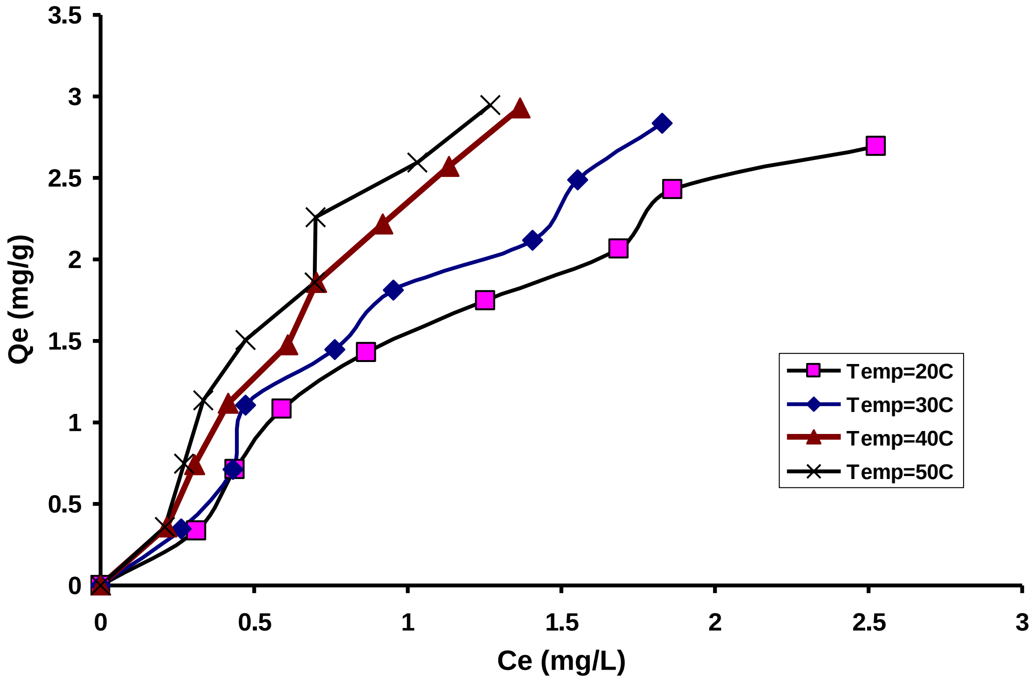

Figure (1): Adsorption isotherms of methylene blue on rice bran at different temperatures (20, 30, 40, and 50ºC).

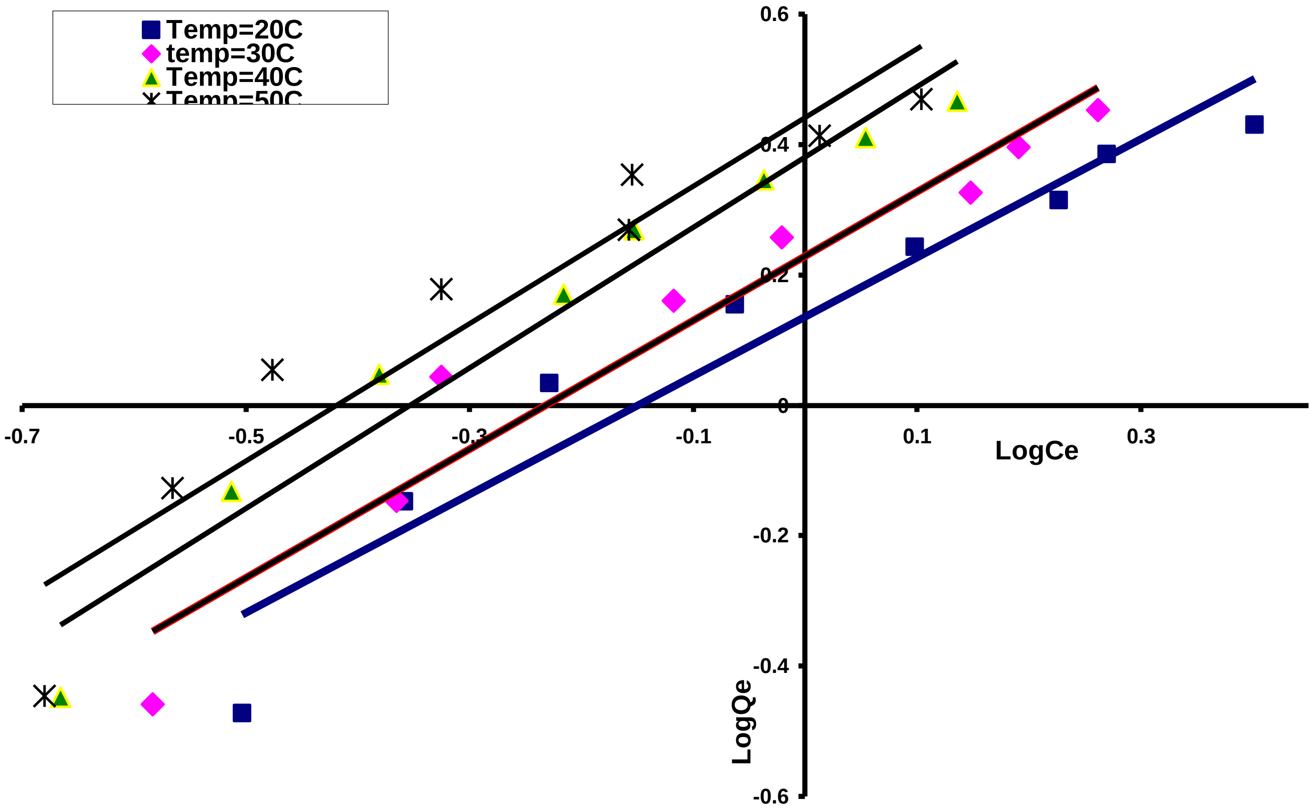

Figure (2): Linear form of Freundlich equation of adsorption of methylene blue on rice bran at different temperatures (20, 30, 40, and 50ºC).

Table (1): Freundlich constants (k and n) of adsorption of methylene blue on rice bran surface at four temperatures. Where k refers to the adsorption capacity and n refers to the adsorption *intensity.*

T	logk	K (mg/g)	1/n	n(g/L)
293	0.1354	1.36584054	0.909	1.10011001
303	0.229	1.6943378	0.986	1.01419878
313	0.381	2.4043628	1.078	0.92764378
323	0.441	2.76057786	1.054	0.9487666

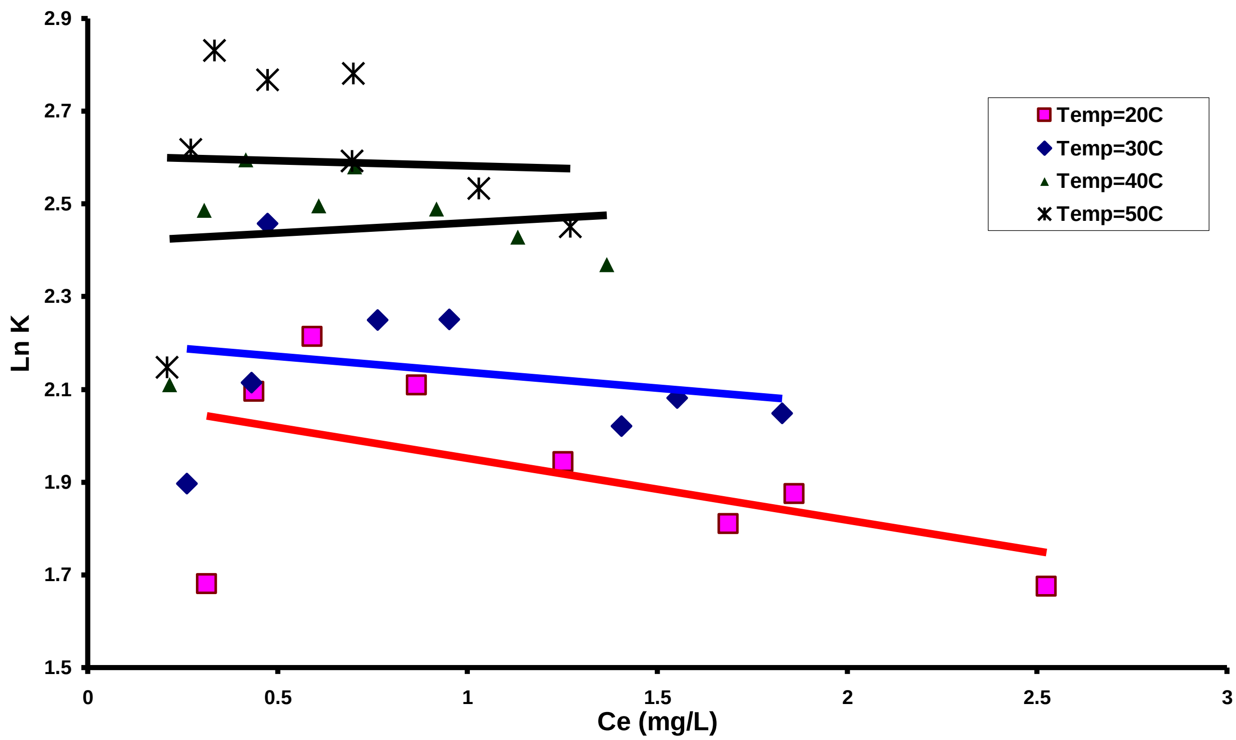

Figure (3): Natural logarithm of equilibrium constants (LnK) against equilibrium concentration (Ce) of adsorption of methylene blue on rice bran surface. The intercept represent the (LnK) when Ce approaches to zero at certain temperature.

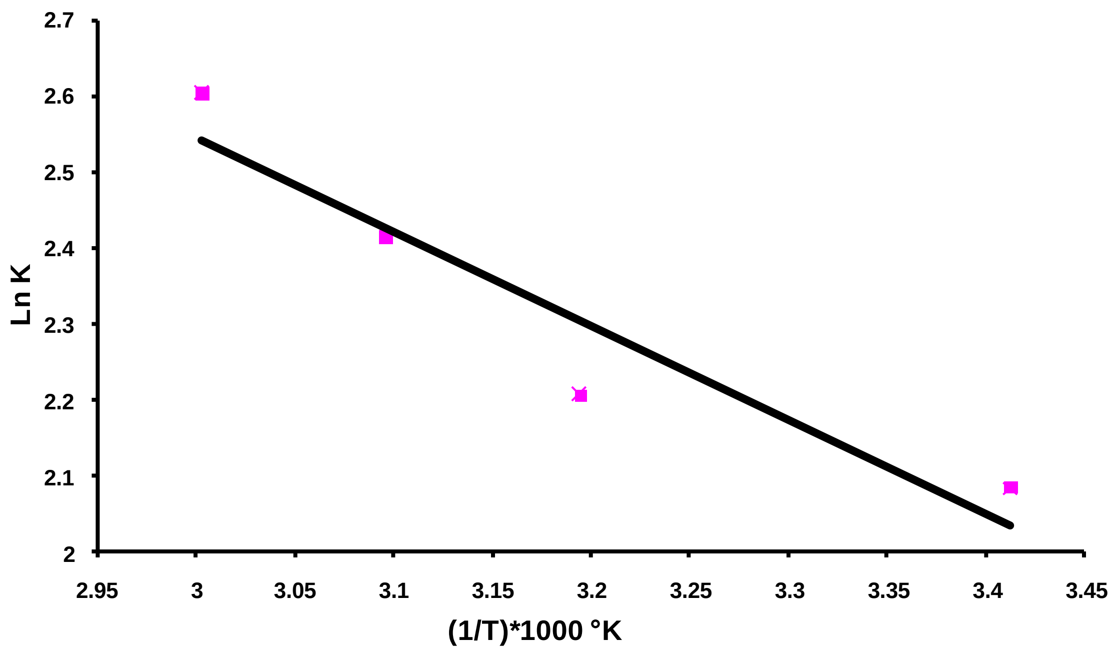

Figure (4): Correlation of equilibrium constants, when Ce approaches to zero of adsorption of methylene blue on rice bran surface at (20, 30,40, and 50°C) according to the vant Hoff's equation.

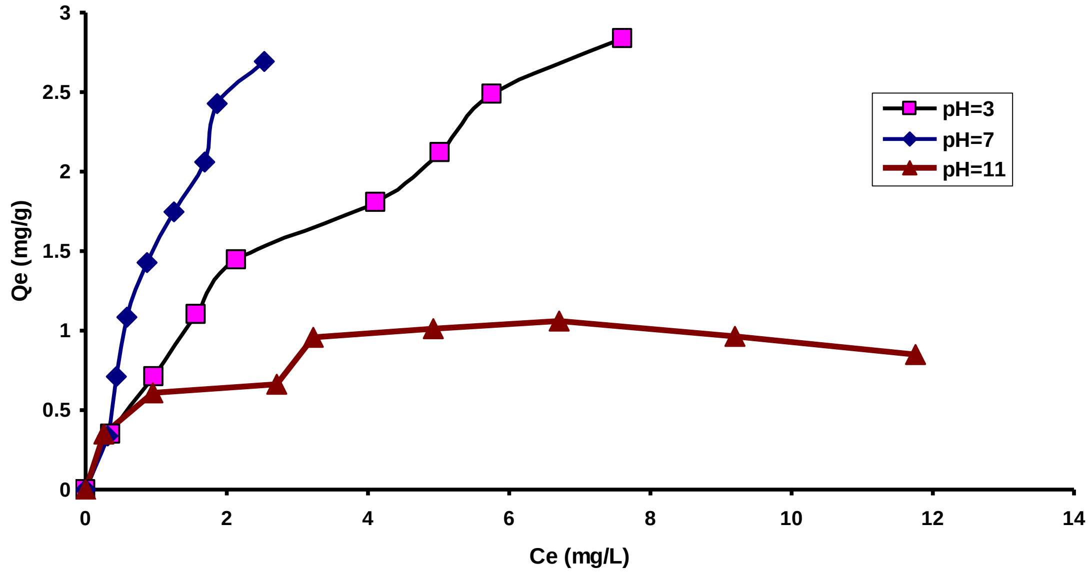

Figure (5): Freundlich isotherms of adsorption of methylene blue on rice bran at different pH (3, 7, 11).at tempreture 20 ºC

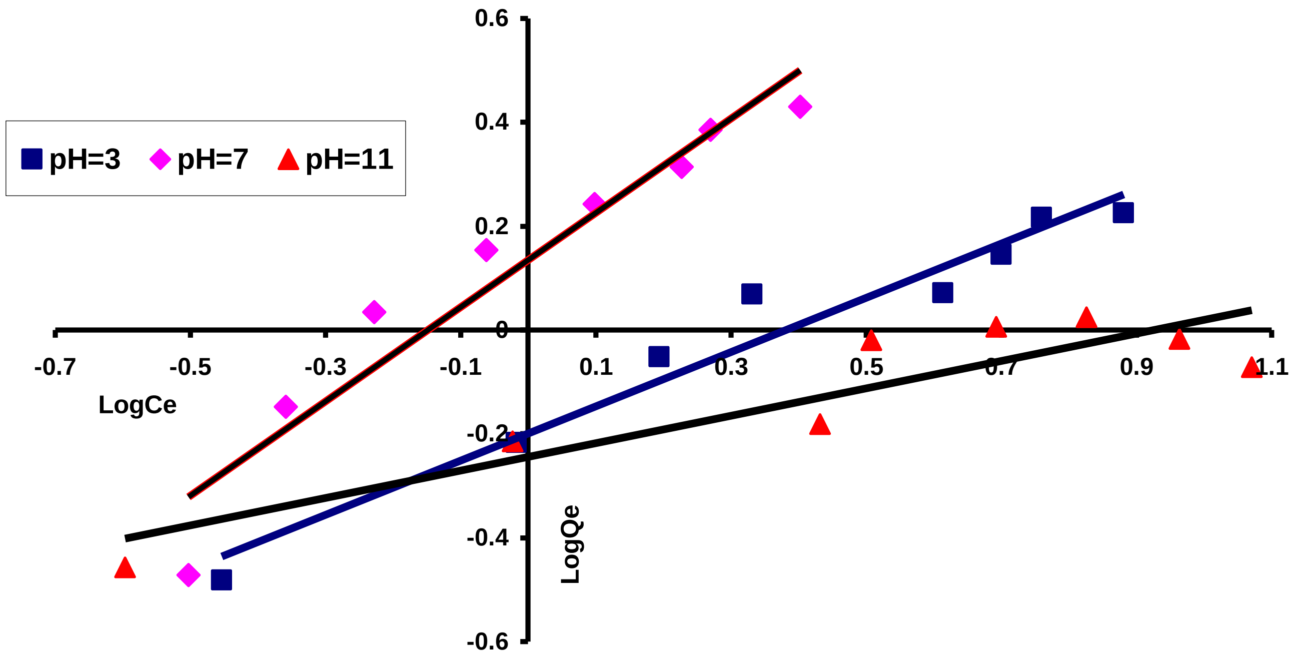

Figure (6): Linear form of Freundlich equation of adsorption of methylene blue on rice bran at different pH (3, 7, 11). at tempreture20 ºC