Removal of Neutral Red Dye from Aqueous Solution by Adsorption onto Rice Bran

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Abstract

This work is concerned with the study of locally available rice bran **(*Oryza sativa L*)** as an adsorbent for the removal of neutral red dye from solution as low-cost adsorbent in wastewater treatment for the removal of color which comes from textile dyes or other industries.

Adsorption process were occurred at different acidity of solution (pH=3, 7, 11). 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).

Rice bran showed good adsorption capacity against neutral red dye and can extract the dye from aqueous solution. Adsorption isotherms of neutral red dye on bran from aqueous solution obeyed Freundlich adsorption isotherm indicating the heterogeneity of rice bran surface.

The thermodynamic parameter values are calculated as follow:

ΔH^o=-44.92 KJ.mol^{-1}, ΔG^o=-5.06 KJ.mol^{-1}, ΔS^o=-136.05 J.mol^{-1}.^{o}K^{-1}

In conclusion, adsorption of on rice bran is exothermic process with relatively high thermodynamic parameters values. The adsorption 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 neutral red dye on rice bran may be used effectively to remove the dye from aqueous medium.

الخلاصة

يعنى هذا البحث بدراسة مادة متوفرة محلياً (نخالة الرز) كمادة مازة لأزالة صبغة (N-R) من المحلول كمادة مازة رخيصة (أوقليلة الكلفة) في معالجة مياه الفضلات الصناعية من معامل الأنسجة والصناعات الأخرى لإزالة اللون.

أجريت عملية الأمتزاز عند درجات حامضية مختلفة (pH=3, 7, 11) كما وأعيدت التجربة عند أربعة درجات حرارية مختلفة (20, 30, 40, 50°C) لحساب الدوال الثرموديناميكية ($\Delta S^o, \Delta G^o, \Delta H^o$).

أظهرت نخالة الرز سعة أمتزاز جيدة لصبغة .N.R كما ونستطيع أستخلاصها من المحلول المائي .

درست أيزو ثرمات الأمتزاز ووجدت أنطباقية لمعادلة فرندلش عليها مشيرةالى عدم تجانس سطح نخالة الرز.

تم حساب القيم الثرموديناميكية وكالأتي :

ΔH^o=-44.92 KJ mol^{-1}, ΔG^o=-5.06 KJ mol^{-1}, ΔS^o=-136.05 J mol^{-1} $^oK^{-1}$

وبالنتيجة الامتزاز على نخالةالرز باعث للحرارة وذلك من قيم الدوال الثرموديناميكية العالية نسبيا.

أفضل امتزاز ظهر بنقصان درجه الحرارة مع زيادة حامضية الوسط .

ويمكن إن نستنتج من نتائج الدراسة الحالية بان عمليه امتزاز صبغه الأحمر المتعادل على نخالةالرز قد تستعمل عمليا لازاله الصبغة من الوسط المائي.

مفاتيح الكلمات: نخالة الرز-الأحمر المتعادل – الامتزاز

Introduction

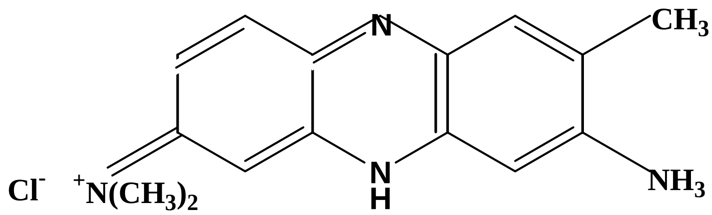
Any solid has some tendency to adsorb substances from aqueous medium onto their surface, however only some few solid materials have the selective adsorption capacity to adsorbate molecules. The adsorbate may be atoms, ions or molecules (adsorbate) of organic compound, color, odor, moisture etc.. [1, 2]. 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 [3, 4, 5].

Different adsorbents [6, 7, 8] were tested for their ability to remove and extract different dyes from aqueous solutions including activated charcoal [9], clays [10, 11, 12, 13, 14, 15], and agriculture products [16, 17] which used widely as adsorbents in the adsorption processes for different substances from solution including metal ions [18, 19, 20], and organic pollutants [21].

Some active surface materials have important applications in medicine arises from their high adsorption capability as physical antidotes in the treatment of acute poisoning by toxic substances and drug overdosage [22, 23] and as a drug carrier [24]. Dietary fibre 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 [25]. 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 that 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 [26].

Rice bran has a good adsorptive activity against different substances including different pesticides from an aqueous solution [26] , metal ions [27, 28, 29], several organic compounds, such as dichloromethane, chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, and benzene [30].

Neutral red used in the measurement of cytotoxicity [31, 32], cell apoptosis measurement [33] , and photosynthesis inhibitor in different light dependent species [34]. Neutral red stains both normal and cancer mitotic cells, but uptake by living mitotic cancer cells is distinctly higher than in normal cells [35].



Neutral Red: 3-amino-7(dimethylamino)-2-methyl-hydrochloride.

Rice bran, among anothers, adsorb in vitro the hydrophobic, environmental mutagen 1,8-dinitropyrene and other mutagens. Direct mechanisms of protection of cancer by fibers include the adsorption of carcinogens onto undegraded dietary fibres which pass out of the intestinal tract in the faeces [25, 36].

In one research, dietary fibers have the ability to nonspecific adsorption of T4 [37]. Adsorption of the vital dye, neutral red was previously studied on the matrix of the calcium-binding "vesicles" from the green alga [38].

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 [23].

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 neutral red 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 and dried at 50˚C for two hours and kept in an airtight container. A volume of 10 milliliters of eight different concentrations of neutral red 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 30 minutes 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 neutral red solutions depending on the pHs used in the experiment. The maxima used were λmax=539 nm for pH=7, λmax=543 nm for pH=3, λmax=428 nm for 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:

$$\frac{Ce}{Qe} = \frac{1}{ab} + \frac{Ce}{a} \quad ....(1)$$

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 [24].

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:

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

Where k and n are Freundlich constants characteristics of the system, including the adsorption capacity and the adsorption intensity, respectively [4, 23].

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 (ΔH^o, ΔG^o, ΔS^o). The equilibrium constant (K) for the adsorption process at each temperature is calculated from division of the quantity of dye adsorbed on the bentonite surface on the quantity of dye still present in solution:-

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

Where (0.05g) represent the weight of the clay 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:-

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

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:-

$$\ln K = \frac{-\Delta H^\circ}{RT} + constant \quad \text{---(5)}$$

Where K is the equilibrium constant when Ce approaches to 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:

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

Results and Discussion

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 [39, 40, 41].

Adsorption isotherms of neutral red dye on 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 the decrease in adsorption capacities and intensities as temperature increases. Adsorption isotherms of different dyes on different surfaces including rice bran [29, 30, 31, 42] were also obeyed Freundlich isotherm indicating heterogeneity of these surfaces [4, 23].

Table (1): Freundlich constants (k and n) of adsorption of methylene blue on bentonite clay surface at three temperatures. Where k refers to the adsorption capacity and n refers to the adsorption intensity.

T	logk	K	1/n	n
293	0.313	2.058	1.142	0.876
313	-0.262	0.548	1.349	0.741
323	-0.365	0.432	1.398	0.716
333	-0.615	0.243	1.868	0.535

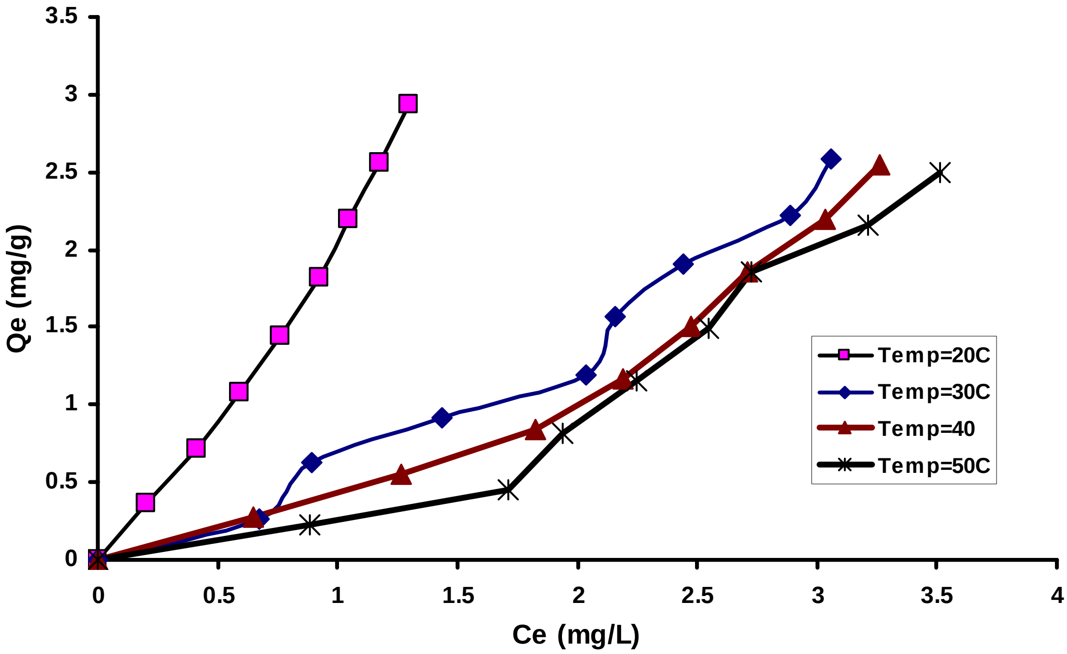


***Figure (1): Adsorption isotherms of neutral red on rice bran at different temperatures* (20, 30, 40, *and* 50°C).**

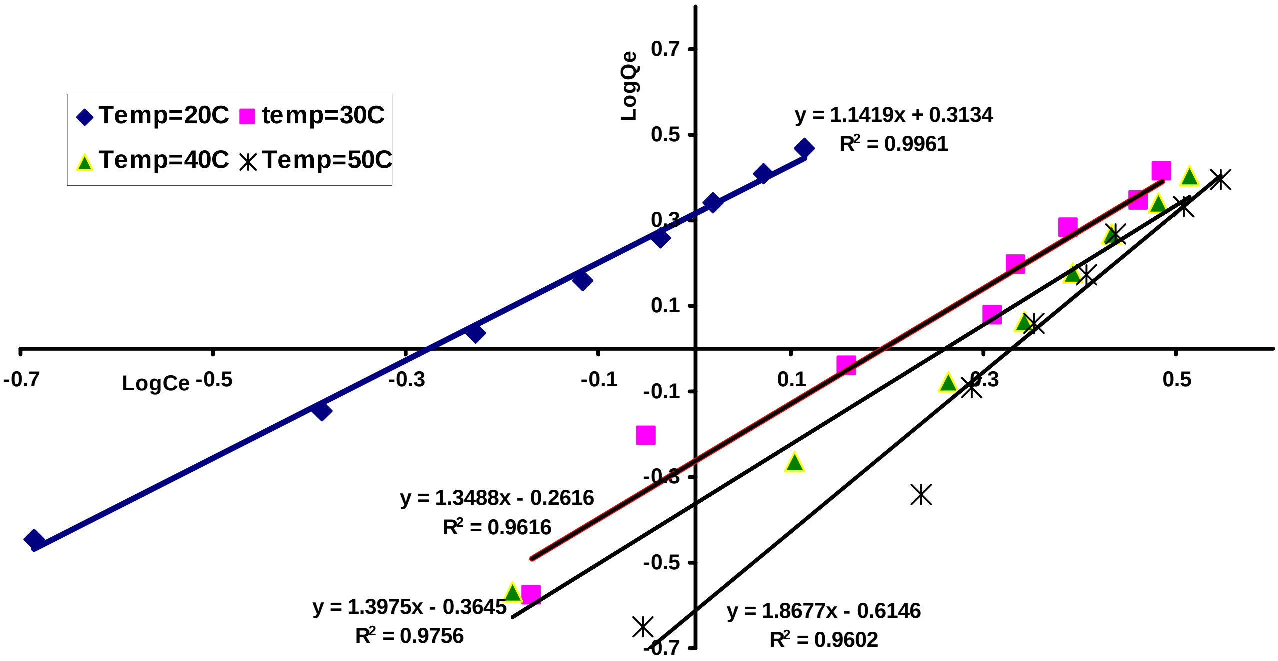


Figure (2): Linear form of Freundlich equation of adsorption of neutral red on rice bran at different temperatures (20, 30, 40, and 50°C).

The study of the adsorption process of 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 [(43)], and myo-inositol derivatives [(44)]. It has shown that different types of plant cell walls adsorbed a range of carcinogens including heterocyclic aromatic amines which are like the chemical structure of neutral red dye. Cell walls that contained lignin or suberin adsorbed hydrophobic carcinogens particularly well. [(25)]. 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 [(26)].

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 [(45)].

According to the Giles interpretation [46] for the adsorption isotherm shapes, the adsorption isotherm of neutral red dye molecules on the rice bran surface is of S2 type indicating the heterogeneity of the surface and the presence of different types of forces between the dye molecules and the surface active sites.

Rice bran among different among different lees materials is effective in adsorbing organochlorine compounds. There was a high correlation between the removal efficiency in adsorbing organochlorine compounds such as chloroform, dichloromethane, or benzene by lees materials and the number of spherosomes from different lees materials[47]. The removal of these organochlorine compounds and benzene by rice bran was conformed to the Freundlich type and attributed to the uptake by intracellular particles called spherosomes [30].

Figure (3) showed the natural logarithm of equilibrium constants (LnK) against equilibrium concentration (Ce) of adsorption of neutral red on rice bran surface. The intercepts of the straight lines give the natural logarithm of equilibrium constants (LnK) from which the equilibrium constants, when Ce approaches zero, could be obtained and used for vant Hoff's equation plotted (Figure (4)).

The thermodynamical parameters values are:

(ΔH^o=-44.92 KJ.mol-1, ΔG^o=-5.06 KJ.mol-1, ΔS^o=-136.05 J.mol-1.^{o}K-1).

Free energy change and entropy values were measured at 298^{o}K. These values are high and indicated a spontaneous adsorption process as seen in the adsorption of other substances [40]. It is supposed from the thermodynamic values that, moderate and nonspecific interaction occurs between dye molecules and the active sites of rice bran surface.

Exothermic process for the adsorption of neutral red on rice bran is consistent with other adsorption processes [48] and differs from other which was endothermic processes [49].

In one study; adsorption of industrially important dyes including methylene blue from aqueous media on activated charcoal has been investigated. The calculated values for the heat of adsorption and the free energy indicated that adsorption of dyes is favored at low temperatures. These results are differ from the result of our research indicating the ability of bentonite as a better adsorbent when the adsorption occurs at high temperature as it happen really in different industries [50].

The results of this work can be compared with other papers related to the adsorption of different dyes on different adsorbents in order to treat the waste water from different industries and laboratories [51, 52].

The adsorption of dichloromethane and chloroform by rice bran was observed over the range of pH 1-11. Therefore, rice bran is applicable for treatment of wastewater over a wide pH range. Dichloromethane was successfully removed from water samples with an average removal efficiency of 70% after 60 minutes when rice bran was added to water samples containing from 0.006 to 100 mg/L dichloromethane [30].

Adsorption of neutral dye on rice bran showed a decrease in basic solution and mildly good adsorption capacity in neutral and acidic solution (Figures (5 & 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.

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 [53]. The adsorption amounts may explained by dependency of adsorption on the relative energies of adsorbent-adsorbate, adsorbate-solvent, and adsorbate-adsorbate interactions [54]. These findings may be applied for the adsorption of dye on rice bran surface in our study.

Conclusion:

Adsorption of on rice bran is exothermic process with relatively high thermodynamic parameters values. The adsorption 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 neutral red dye on rice bran may be used effectively to remove the dye from aqueous medium.

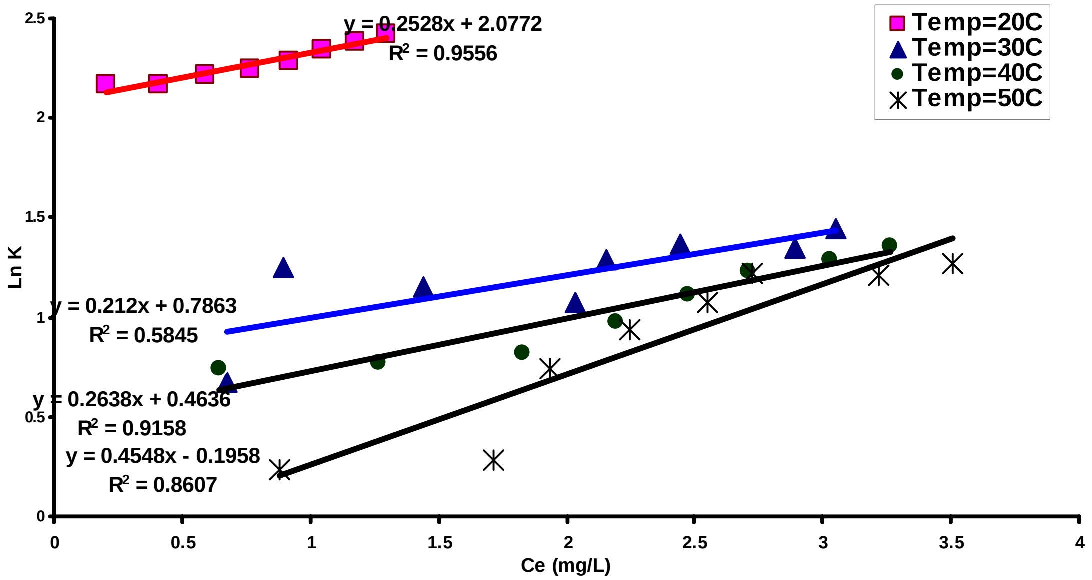


Figure (3): Natural logarithm of equilibrium constants (LnK) against equilibrium concentration (Ce) of adsorption of neutral red on bentonite clay surface. The intercept represent the (LnK) when Ce approaches to zero at certain temperature.

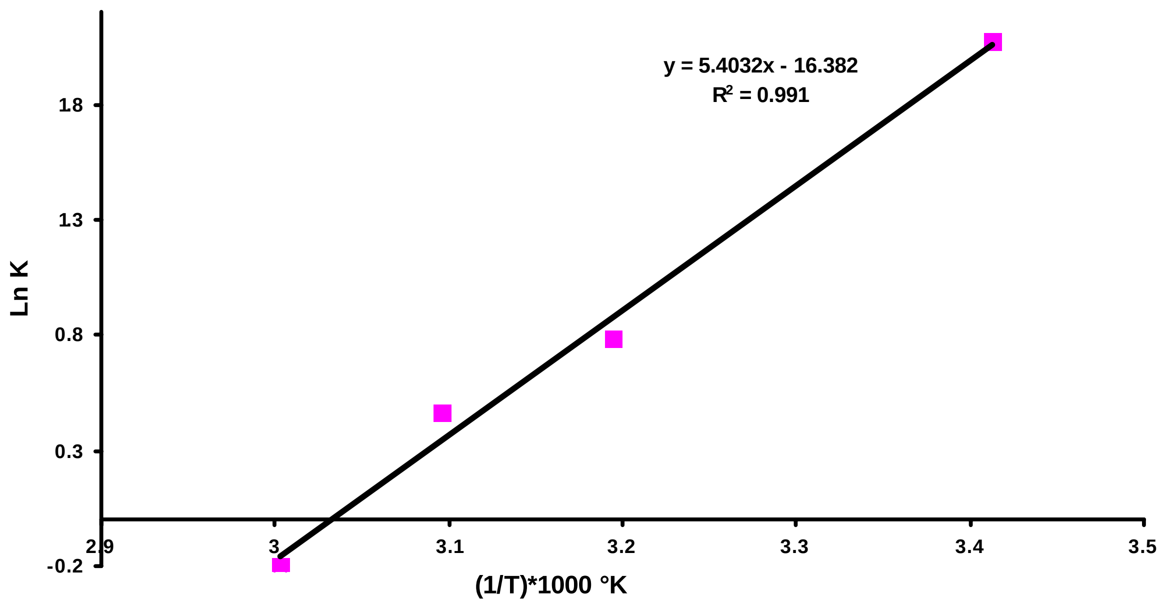


Figure (4): Correlation of equilibrium constants ,when Ce approaches to zero of adsorption of neutral red on rice bran at (20, 30, 40, and 50°C) according to the vant Hoff's equation.

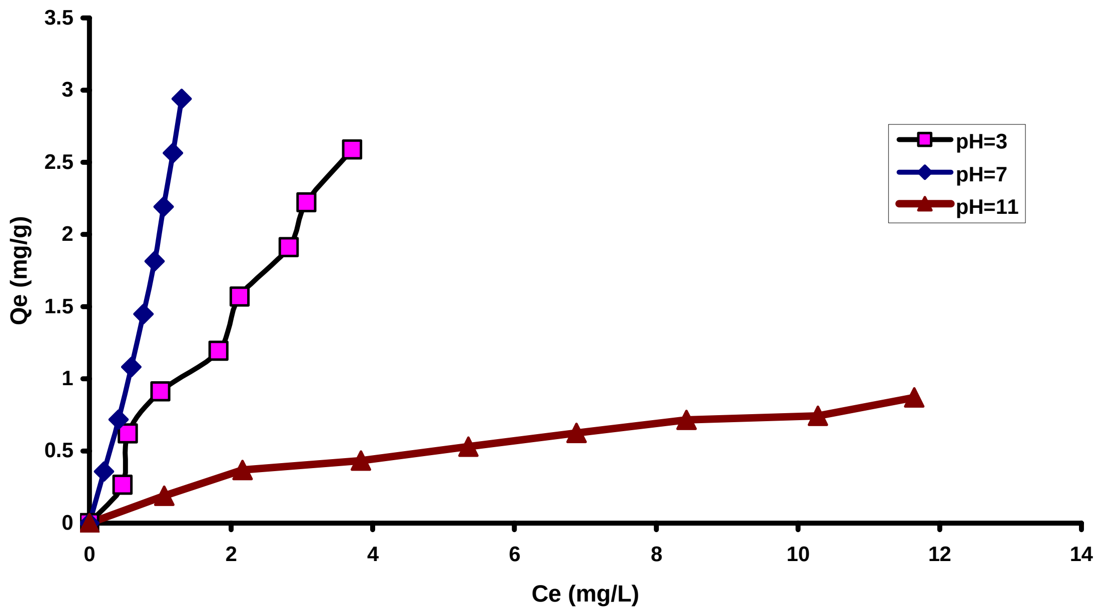


Figure (5): Adsorption isotherms of neutral red on rice bran at different pHs (3, 7, 11) at 20°C.

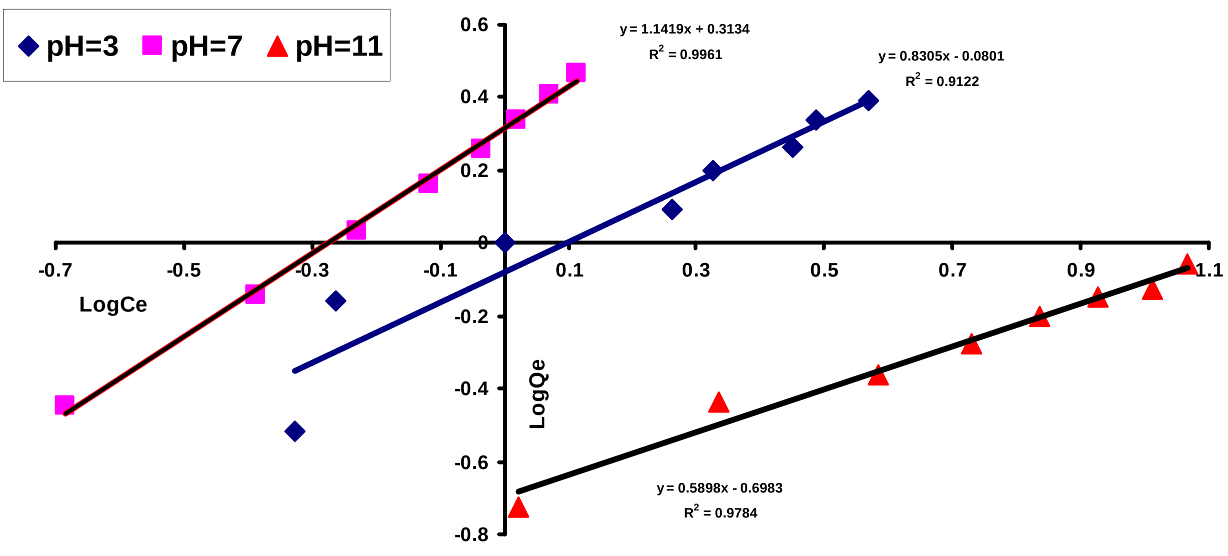


Figure (6): Linear form of Freundlich equation of adsorption of neutral red on rice bran on three different pHs at 20°C.

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