Local wheat chaff as an adsorbent for removal of Azure B dye from aqueous solution:Equilibrium and thermodynamic studies

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Abstract

This study is concerned with the adsorption of Azure B (AB) dye from solution on the surface of wheat chaff. UV-spectrophotometric technique has been used to produce quantitative adsorption data at different conditions of contact time, ionic strength, pH and temperature.

The calculated data were in accordance with Freundlich equation and the adsorption isotherms are of ***H-curve*** type according to Giles classification. The results obtained show that adsorption process follows the second order rate expression.

The adsorption phenomenon was examined as a function of temperature ***(25, 35, 50 ^oC)***. The extent of adsorption of Azure B on the surface was found to increase with increasing temperature (***endothermic process***). The basic thermodynamic functions have also been calculated.

The amount of dye adsorbed on the chaff at different pH values showed an increase in the following order: pH 5.2< 6 < 7 < 8 <9.3

The adsorption process is affected by the electrolyte concentration. The results indicated a decrease in adsorption capacity of Azure B in the presence of sodium chloride salt.

Keywords: wheat chaff, Azure B, adsorption equilibrium, thermodynamics.

قشور الحنطة المحلية سطح ماز لازالة صبغة الازور B من محلولها المائي:دراسة التوازن والثرموديناميك

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الخلاصة:

يعنى هذا البحث بدراسة أمتزاز صبغة الازور B من محلولها المائي على سطح قشور الحنطة ، وكان الغرض من الدراسة هو البحث عن أفضل الظروف الواجب توفرها في عملية تنقية المياه .وقد تم استخدام تقنية مطيافية الأشعة فوق البنفسجية لمعرفة كميات الامتزاز عند ظروف متباينة من الأس الهيدروجيني ودرجة الحرارة والقوة الأيونية لمحلول الامتزاز.

أظهرت النتائج أن ايزوثيرم الامتزاز من نوع (***H***) طبقا لتصنيف ***Giles*** والذي يتفق مع معادلة فرندلش للامتزاز، كما بينت النتائج بان أمتزاز صبغة الازور B يزداد بزيادة تركيز المادة الممتزة وان عملية الامتزاز تتبع قانون السرعة من المرتبة الثانية.

بينت الدراسة إن أمتزاز الصبغة على سطح قشور الحنطة عند ثلاث درجات حرارية ***(25, 35, 50 ^oC)*** يزداد مع زيادة درجة الحرارة\(أمتزاز ماص للحرارة) كما حسبت القيم الثرموديناميكية الأساسية لعملية الامتزاز.

وجد ان كمية أمتزاز الصبغة على سطح قشور الحنطة عند قيم مختلفة من الأس الهيدروجيني يزداد وفقاً للترتيب الآتي:

5.2<6<7<8<9.3

إن أمتزاز صبغة الازور B يتأثر بالقوة الأيونية للمحلول .فقد قلت كمية الصبغة الممتزة في المحلول بوجود ملح كلوريد الصوديوم.

Introduction

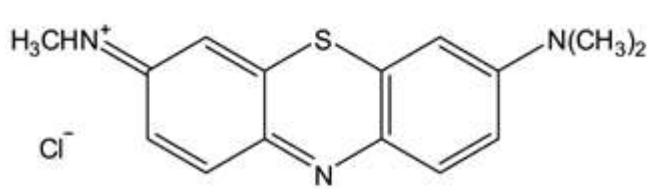
Water contamination can be defined as any physical, chemical and biological changes in water quality that negatively affect living organisms. Water contamination can be occurs when energy and other materials are released, degrading the quality and purity of water for different users. It's implicate all of the pollutant materials that cannot be naturally destroyed by water(1). Several physical and chemical methods were used for the treatment contamination of water, such as phase change, gravity separation, oxidation or reduction processes , ion exchange and adsorption(2).Adsorption is a phenomenon in which the atoms, ions and molecules accumulate on the solid surface by different types of forces, it's often used as a method for treating aqueous solution to remove highly toxic dissolved contaminating organic compounds and toxic heavy metals(3). Dyes are one of the most common organic contaminants, which are widely used in paper, textiles, wool and cotton dyeing, plastic industries(4,5). "Textile effluents are highly colored and their discharge into rivers makes water inadequate for agricultural, domestic, and industrial purposes"(6). Most textile dyes are highly cytotoxic to mammalian cells and may be causes carcinogenic, mutagenic and teratogenic effects on human health(4,7). A wide variety of reports using adsorption technique for treatment of textile wastewater by activated charcoal(8),clays(9) and different types of agricultural wastes such as , rice husk(10), saw dust(11), bean peal(12), groundnut shell(13),etc.

The aim of this work into investigates the capability of using the waste of agricultural ,wheat chaff, as a biosorbent for removal of Azure B dye from wastewaters in different conditions of temperature, ionic strength, and pH to determine the thermodynamic functions at equilibrium conditions.

2-Materials and Methods

2.1. Preparation of Dye Solutions

Azure B was supplied by sigma; the chemical structure of this dye was shown in Scheme (1).



Scheme (1). The chemical structure of Azure B

Wavelength of maximum absorbency (λ_{max}) was recorded for Azure B and found 646 nm. This value was utilized for estimation of quantity of dye adsorbed. Solutions of different concentrations were prepared by serial dilution and the absorbance values of these solutions at 646 nm plotted against concentration values. The straight line obtained verifying the applicability of Beer- Lambert's law.

2.2. Preparation of surface

Wheat chaff was washed several times with distilled water; to remove all dust, contaminants and soluble materials. Washed surface was then dried under sunlight and in an oven at 120^{o}C for 1.5 hr. and kept in airtight container until using. The powder surface was sieved to particle size of 150 µm and this particle size was used in all experiments.

2.3. Effect of Contact Time

Adsorption kinetic study was carried out by adding known amount of surface into 10 ml dye solutions (60 ppm). The solutions were centrifuged at a desired time intervals and the residual dye concentration was determined by spectrophotometer (Shimadzu.PC1650,Japan).

2.4. Adsorption Isotherm

10 ml of AB dye Solutions of known concentrations were added to stopper flasks containing 0.1g of wheat chaff surface. The flasks were shaken in a thermostatic controlled water bath (using shaker water bath, K&K, Scientific, Korea) until equilibrium is attained (90 min). This time is sufficient for the adsorption process to reach equilibrium. After the equilibrium time elapsed, the suspensions were centrifuged twice at 3000 rpm for 10 min. The clear supernatants were assayed for AB dye. The concentrations at equilibrium were obtained by comparing the experimental data with the calibration curve of dye.

The quantity of dye adsorbed was calculated according to the following equation[14]:-

$$Q_e \text{ or } \frac{x}{m} = \frac{V\,(C_o - C_e)}{m}$$

Where:

x : the quantity adsorbed

m : weight of adsorbent (g).

C_o : initial concentration (mg/L).

C_e : equilibrium concentration (mg/ L).

V : volume of solution (L).

2.5. Effect of Temperature

Adsorption experiment was repeated in the same manner at temperatures of 25, 35 and 50^{0}C to calculate the basic thermodynamic functions.

2.6. Effect of Ionic Strength

Fixed concentration of AB dye solutions and different weight of sodium chloride (0.05-0.3g) were added to flasks containing 0.1 gm of surface. The procedure described for the adsorption experiment was followed as mentioned above.

2.7. Effect of pH

The effect of different pH on the adsorption process of dye was studied by using solutions of fixed concentration of dye with different pH values (5.2-9.3).

3. Results and Discussion

The adsorption of AB from aqueous solution on wheat chaff has been studied at temperature (25˚C) and at other two temperatures (35 and 50˚C) at pH ≈6.

The general shape of dye adsorption isotherm is shown in Figure (1), where the quantities adsorbed on surface are plotted as a function of equilibrium concentration at the constant temperature.

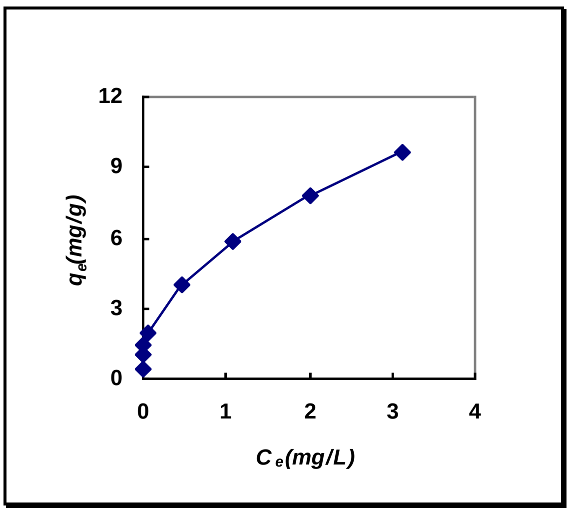


Figure (1). Adsorption isotherm of AB on chaff at 25 ºC

The results showed an increase in adsorption capacity of wheat chaff as the concentration of AB dye increased. The physicochemical characterization of wheat chaff as a type of agricultural materials contains functional groups, abundant floristic fiber, and proteins which make adsorption process possible(15).

The shapes of AB dye adsorption isotherms were found to coincide with the H-type isotherm reported by Giles et al.(16). The H-type isotherm refer to high affinity between the dye and surface of adsorbent.

The equilibrium adsorption of AB on chaff can be mathematically expressed in terms of adsorption isotherm. Adsorption isotherm data are best represented by applying the Freundlich equation[17]:

$$\frac{x}{m} = kC_e^{1/n}$$

Where: $\frac{x}{m}$ is the quantity adsorbed in mg/g. C_e is the equilibrium concentration in mg/*l*, *n* and *k* are constants for the given adsorbent and solute.

The applicability of Freundlich isotherm is indicated by using the linear from of Freundlich equation:

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C_e$$

Figure (2) shows the linear relationship of *log Qe* versus *log Ce*. The values of Freundlich constants as well as the correlation coefficient was also calculated ($r^2 = 0.985$, $n=2.681$, $k=10^{0.77}$). The fit of data to the Freundlich model indicate that the binding of AB dye by chaff surface are governed by physical forces. The high magnitude of the exponent, n, gives an indication of the favourability and capacity of the adsorbent-adsorbate system.

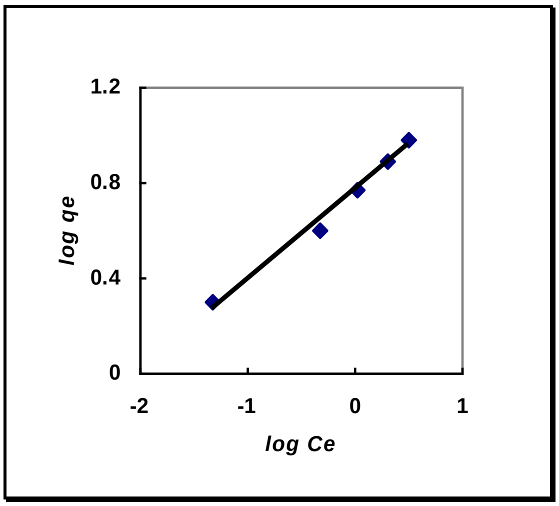


Figure (2): Linear form of Freundlich isotherm of AB on wheat chaff

The general shapes of AB dye adsorption isotherms at three different temperatures are given in Figure (3).

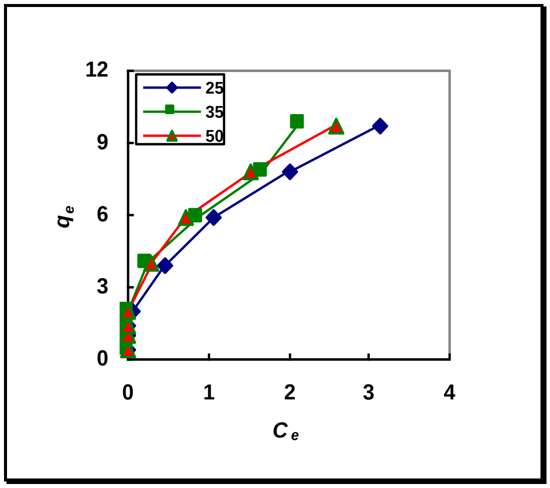


Figure (3): Adsorption isotherms of AB at different temperatures

The results showed a slight increase in the amount of dye adsorbed on surface with increasing temperature from 25ºC to 50ºC; hence the adsorption process was thermodynamically endothermic in nature. The extent of adsorption of some dyes was found to increase with increasing temperature. Endothermic dye uptake may be attributed to the possibility of occurring absorption by the surface in addition to adsorption process [18].

The thermodynamic quantities of adsorption process were estimated through calculating Xm values at different temperatures. The heat of adsorption (ΔH) may be obtained from Van't Hoff equation: $\ln X_m = \frac{-\Delta H}{RT} +$ constant, the change in free energy (ΔG) could be determined from equation: (ΔG = - RTlnK) and the change in entropy (ΔS) was calculated from Gibbs equation:

$$\Delta G = \Delta H - T.\Delta S$$

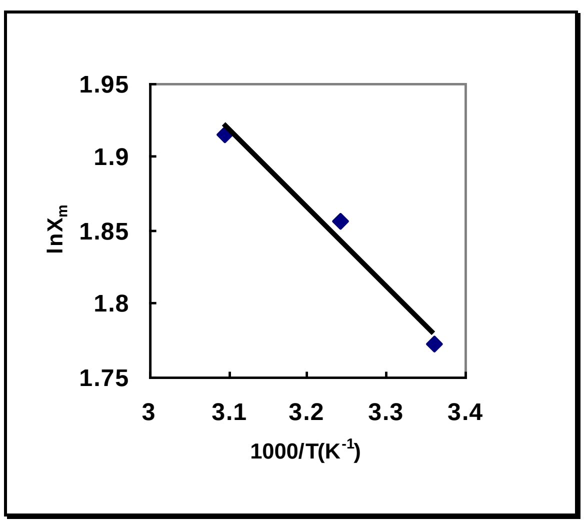


Figure (4): Plot of ln X_m against reciprocal absolute temperature

Table (1) shows the thermodynamic values of adsorption process of dye. These values suggested van der Waals type of adsorption.

Table (1): Values of thermodynamic functions of adsorption process

ΔH ***kJ.mol^{-1}***	***ΔS*** ***J.mol^{-1}.k^{-1}***	***ΔG*** ***kJ.mol^{-1}***
+4.447	+48.270	-9.937

The adsorption of AB dye on wheat chaff is endothermic and spontaneous as indicated by the positive value of enthalpy (ΔH) and negative value of free energy change (ΔG). The adsorption of dye is in conjunction with an increase in entropy.

Figure (5) showed that adsorption of dye on wheat chaff was slightly affected by pH solution.

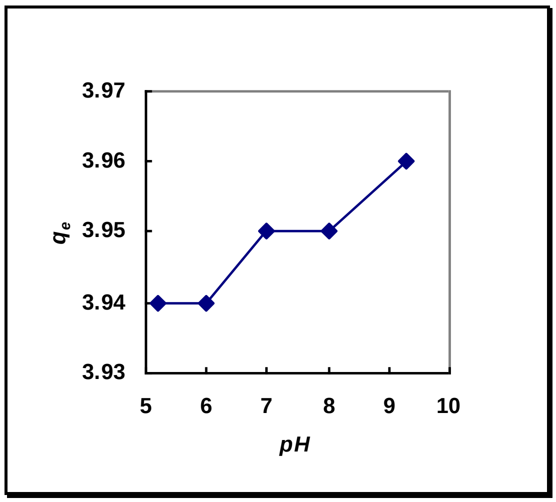


Figure (5): Effect of pH in adsorption uptake of dye at 25^{o}C

AB dye appeared in the cationic form when it dissolved in aqueous solution, so in low pH medium the repulsion forces between the positive charge of chaff surface and the cationic form of dye may be predominant.

The effect of ionic strength on adsorption uptake of dye on wheat chaff was studied at different weights of sodium chloride salt (0.05-0.3 g). Figure (6) shows the effect of electrolyte concentration on the adsorption uptake of AB on adsorbent surface.

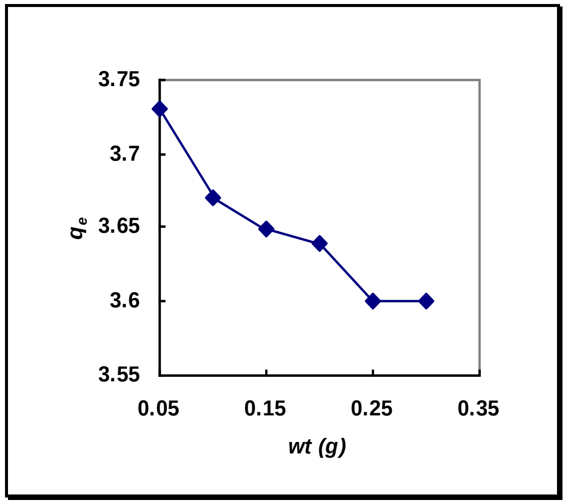
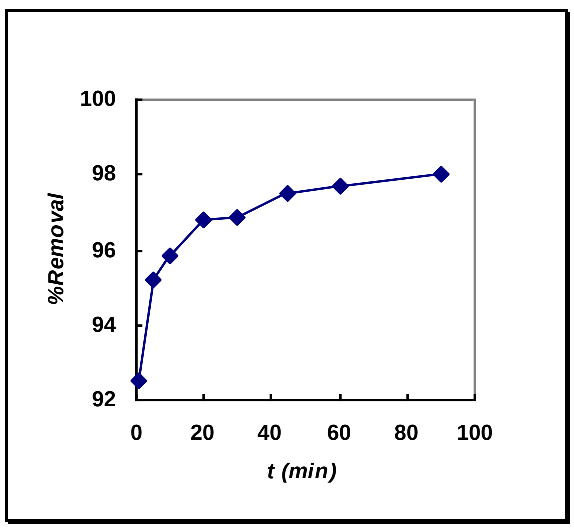


Figure (6):Effect of ionic strength on adsorption uptake of AB on wheat chaff

The adsorption extent has decreased in the presence of electrolyte. This result may attributed to the competition between the hydrated cations (sodium ion and cationic form of dye) on the adsorption sites of surface[19].

Figure (7) shows the percent of dye removal by surface as a function of time. The saturation curve rise sharply in the initial stage of adsorption process, which refer to the presence of more vacancy sites on the surface.



Figure(7): Effect of contact time on the removal of dye at 25°C

The kinetic analysis of adsorption process was performed by applying Lagergren pseudo-first order and pseudo-second order models, the linear form of first order model[20] is:

$$\ln (q_e - q_t) = \ln q_e - k_{ad}\, t$$

Where q_e and q_t are adsorption amounts (mg dye/gm of adsorbent) at saturation and at time t (min), respectively. Value of k_{ad} was obtained from the slope of the plot of $\ln (q_e - q_t)$ vs t (Figure (8)).

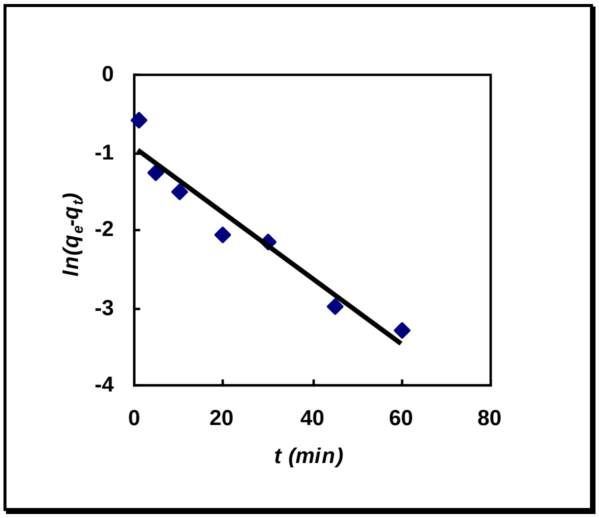


Figure (8): Applicability of first order model to dye adsorption

The linear form of pseudo second order model [21] is:

$t/q_t = 1/h + (1/q_e)\, t$

Where h is the initial adsorption rate and is equal to: $h = k_2\, q_e^2$, k_2 is the pseudo-second order rate constant. The plot t/q_t vs. t (Figure (9)) give a straight line and the values of pseudo-second order constants can be obtained.

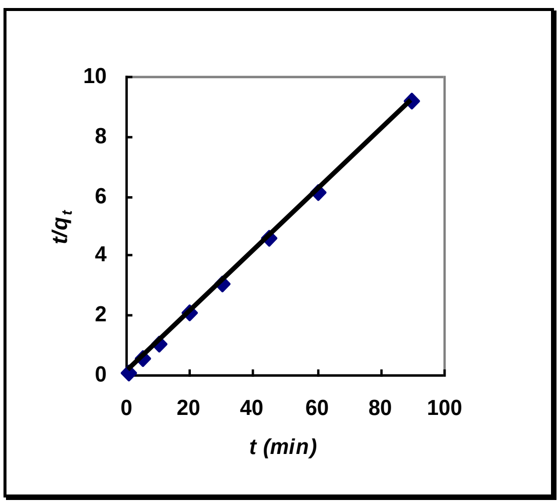


Figure (9):Applicability of pseudo-second order kinetic model to dye adsorption

The kinetic parameters for dye adsorption are shown in Table (3). As indicated from the correlation coefficient and theoretical qe values, the pseudo-second order model fitted the experimental data better than the pseudo-first order kinetic model.

Table(2): Kinetic parameters for adsorption of AB on wheat chaff

Pseudo-first order			***Pseudo-second order***			
k_1 (min^{-1})	q_e (mg/g)	r^2	k_2 ($g.\ mg^{-1}.min^{-1}$)	q_e (mg/g)	h ($mg.\ g^{-1}.min^{-1}$)	r^2
0.042	0.389	0.940	0.465	9.813	44.84	1.000

4.Conclusions

-chaff surface appeared of high activity in the adsorption from solution of Azure B dye.

-The adsorption isotherms of AB dye obeyed Freundlich isotherm.

-Azure B-chaff interaction exhibited low enthalpy value (endothermic).

-Adsorption of dye on the surface is pH dependent.

-There was a negative correlation between the amounts of AB adsorbed and the ionic strength of solution.

-The adsorption of Azure B follows pseudo second-order kinetic model.

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