Adsorption of the Eosin Dye from Aqueous Solution on the Surface of the β-zeolite Synthesis from Iraqi Rice Husk

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Abstract: ***In this study, the dye of the eosin was removed from the aqueous solutions byβ-zeolite synthesis from Iraqi rice husk as adsorbent material prepared from renewable source. The equilibrium time was determined for the adsorption process and it was found to be (90 min.) Using ultraviolet light spectroscopy. The results showed that the best weight of the adsorbent was 0.2 g. The study was also carried out in a range of acidic state (pH = 4-10), Isotherm been used (for Langmuir, Freundlich, Dubinin andTemkin) as it was found that the best Isotherm is Dubinin, moreover the amount of adsorption was calculated in a range of temperatures (20-40°C), The effect of adsorption was increased by increasing the temperature. This indicates that endothermic reaction was conducted. A kinetic study of adsorption was performed,the adsorption followed the false second orderequation, therate parameters and the thermodynamic functions were calculated for activation of the forward and backward interactions***.

Keywords: Eosin adsorption, Isothermate, kinetics, pigments, water treatment

1. Introduction

Pollution is one of the problems of the present age, which requires knowledge of how to get rid of it [(1)]. This problem is aggravated by the obvious role that man plays in exacerbating it. One type of environmental pollution is soil pollution due to chemicals or acid rain [(2)]. Groundwater and wastewater pollution also comes from public and commercial establishments of liquid industrial wastes [(3)], which have adverse and negative effects on human health. The problem of environmental pollution in the developing and advanced countries in the industries, especially the problem of wastewater pollution, and by international humanitarian and humanitarian organizations, is considered a source of concern [(4)]. These industries, which increase the problem of sewage pollution, are textile and leather dye industries. It is noted that many of these dyes are carcinogenic, toxic, [(5)]. There are several ways to treat water pollution including reverse osmosis, ion exchange, chemical oxidation, filtration and adsorption. Adsorption is one of the easiest, safe and effective ways to treat water pollution. The process of degreasing by adsorption using the adsorbed is the lowest cost of an economically successful operation. Examples of adsorbed are rice husks, fruit husks, date molasses and rubber [(6)]. There are two types of adsorption chemical and physical adsorption [(7)]. Several factors influence adsorption, including the weight of the adsorbed particles, the porosity of the surface, the temperature, the equilibrium time and the acid function.

2. Materials and Apparatus

ehT dye used in this study is the eosin dye (eosin yellowish). The adsorbent used in this study is β-zeolite synthesis from Iraqi rice husk prepared early by Muayed et al [(8)]. And then dried in the oven for sixhours at a temperature of 120 °C and then grinded with powder and sifted with a 75 μm sieve. The devices used are: UV-Visible spectroscopy to analyze and determine the concentration of the adsorbent material at equilibrium, centrifuge and magnetic stirrer with hotplate.

Experimental

The adsorption isomerized for the eosin dye by preparing 10 concentrations of (2-20 ppm) of the original concentration of the eosin dye, which is 25 ppm. 30ml of each concentration was withdrawn and placed in glass bottles (50ml) and (0.2 g) of the β-zeolite synthesis from Iraqi rice husk are well covered and placed inmagnetic stirrer a rotation speed (185 rpm) and controlling the temperature at 25 ° C and after reaching the specified equilibrium time is filtered and placed in a plastic test tube and placed in the centrifuge for (15 min) and strongly (3500 rpm) and then again filtered and measured for absorption and the amount of absorbent material was calculated (Qe mg/g) according to the following relationship[(9)]:

$$Q_e = \frac{C_o - C_e}{m} . V_{sol.} \;\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The adsorption kinetics of eosin was studied on the surface of β-zeolite synthesis from Iraqi rice huskby preparing 18 bottles of glass (50ml).30 ml of 10 ppm eosin dye and (0.2 g) of adsorbent were putting in each bottle then putted in magnetic stirrer with d temperature control at 25 ° C and five minutes later, the first bottle is withdrawn and filtered with filter papers and placed in the centrifuge for 15 min at 3500 rpm and then filtered again. Absorption is measured at the wavelength fixed by the spectroscopy - UV light and after 10 minutes sweep the second bottle, is returned to the same steps that followed the first with a bottle after every five minutes, and so pulls a bottle for (90 min). The process is repeated at 20, 25,30,35,40 ° C.

3. Results and Discussion

Determination of Equilibrium Time

This step is important for conducting a kinetic study aimed at following the change in the adsorption of the dye under study over time and determining the time required for the adsorption system to reach the equilibrium. The study was conducted with a fixed concentration of the (20ppm) eosin dyes and a constant acid function. The study showed that the process achieving equilibrium state at (90 minutes) forβ-zeolite synthesis from Iraqi rice husk and results is shown in Figure 1.

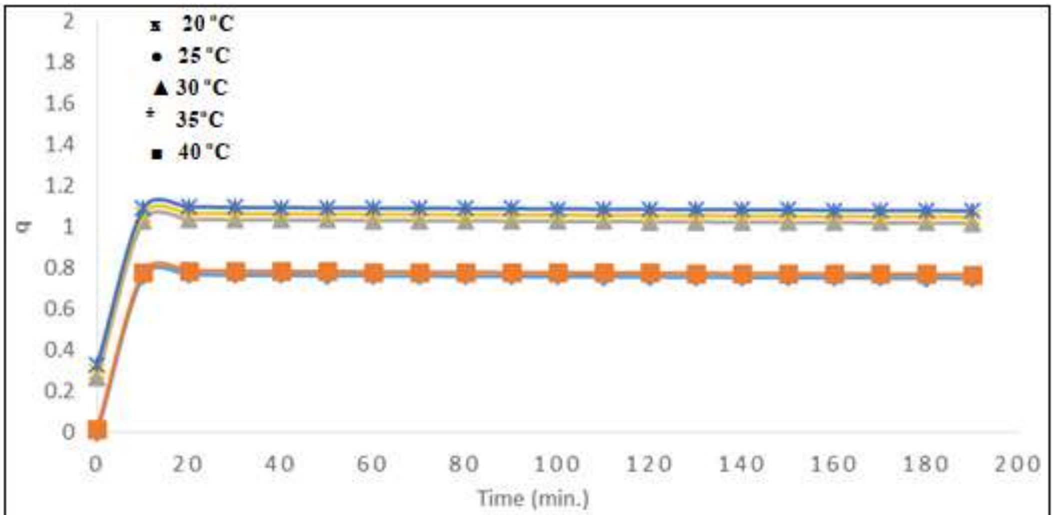

Figure 1 Effect of time on adorption and determine of equilibrium time

The results shown above show that the amount of material absorbed after 10 minutes increases and continues to increase to a certain time and then starts gradually decreasing or stabilizing [10]. The time at which the amount of absorbent material begins to decrease or stabilize is called the equilibrium time, i.e., the time when the absorbent material reaches equilibrium with the solvent surface. The reason that the amount of the adsorbent material is established is that at the beginning of adsorption, the dye molecules begin to enter the surface pores the surface is very active and has a high attraction towards the dye molecules until the surface is saturated with the dye molecules. After that, the amount of the absorbent material gradually decreases or stabilizes due to the resistance of the dispersion of these particles. It can thus be concluded that the spread of the dye molecules inside the surface pores is the dominant step on for adsorption.

Effect of Adsorbent Weight

The effect of the weight of the adsorbent on the adsorption of the eosin dye was studied by changing the weight of the β-zeolite synthesis from Iraqi rice husk (within 0.05-0.5g range), with the original concentration of the constant eosin (10ppm) and the acidic constant and temperature constant at 25 ° C And a fixed time (90 min) for the, as the results are shown in Figure 2. The percentage of adsorption can be calculated from the following relationship:

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

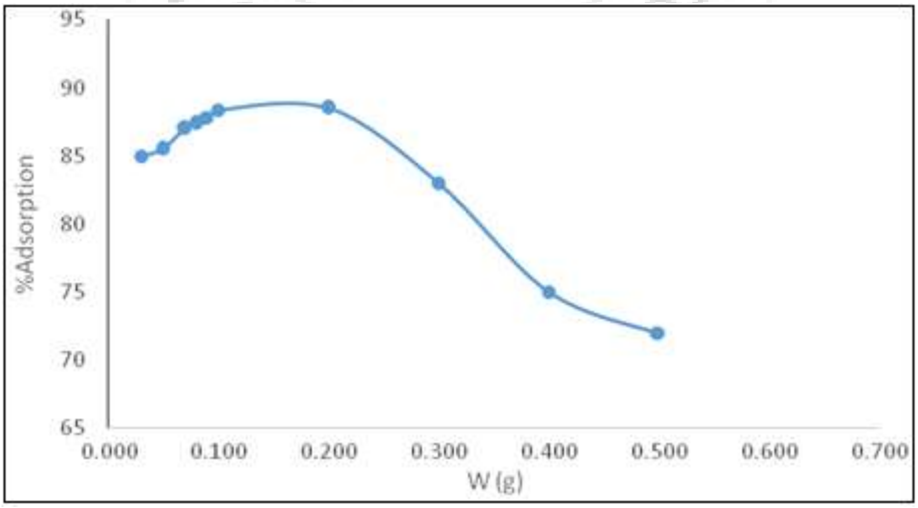

Figure 2: The weight of the adsorbed surface and percentage of adsorption of the eosin dye on the surface of β-zeolite synthesis from Iraqi rice husk at Temp. =25 ^{o}C.

The percentage of adsorption found to increase with the weight of the surface up to a weight of 0.2g has the maximum ratio after this weight is lowering, it is likely due to the availability of large exchange sites or increase the surface area [11], the arrival of saturation.

Effect of pH

The effect of the acidic function on the adsorption of the eosin dye on the surface of β-zeolite synthesis from Iraqi rice husk was studied by changing the acid function within the 4-7-10 range and in different concentrations of the eosin dye within the range (2-20ppm) while maintaining constant temperature at 25 ^{O}C and equilibrium time (90min) as the results are shown in Figure 3.

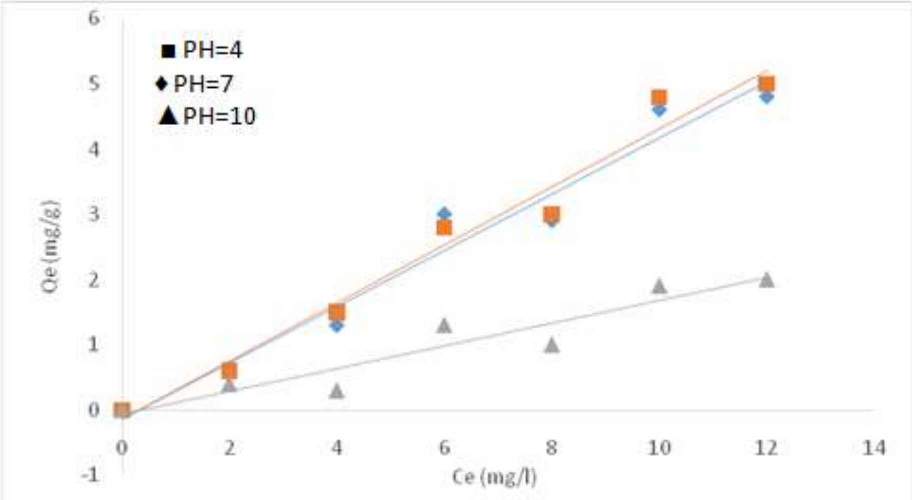

Figure 3: Effect of the acidic function on adsorption of the eosin dye on the surface of β-zeolite synthesis from Iraqi rice husk at 25 ° C

The acidity function affects the surface and the absorbed material and the interactions that occur between them. In this study it was found that the percentage of adsorption on the surface of the β-zeolite synthesis from Iraqi rice huskdecreases with the increase of the acidic function. The surface contains the (OH) groups. In the pH solution, the positive charge on the surface increases due to the abundance of protons. On the other hand, Hydrogen ions displace Na^+ from CO_2 and ONa^- in the dye of the eosin and replace it without changing the color or the maximum wavelength so the interference ratio increases between the dye and the surface through the bond between the oxygen atoms to the dye of the eosin and the surface. The tendency of the dye to bind to a surface is more than its tendency to correlate with the particles The amount of adsorption in the acid medium is increased, either in the base medium of pH=10 and the percentage of adsorption is attributed to the transformation of this formula into salt as the hydroxyl group changes to the ion of the phenoxide, producing a negative charge on the oxygen atom and thereby increasing its solubility Because of their ability to molecular interventions in the center of adsorption, thus weakening the adsorption ratio, the surface will acquire a negative charge through the solution, and the hydroxyl groups act to pull Na^+ from the dye of the Eocene from CO_2 and ONa^- Without color change or great wavelength. Therefore, there will be a severe repulsion of identical shipments of dye and surfaces, reducing the amount of material absorbed on the surface due to the electrostatic repulsion between them. Either in the study of the best acidic function of the surface and found at pH = 1 where the acidic center increases the percentage of adsorption on the surface and results are shown in Figure 4.

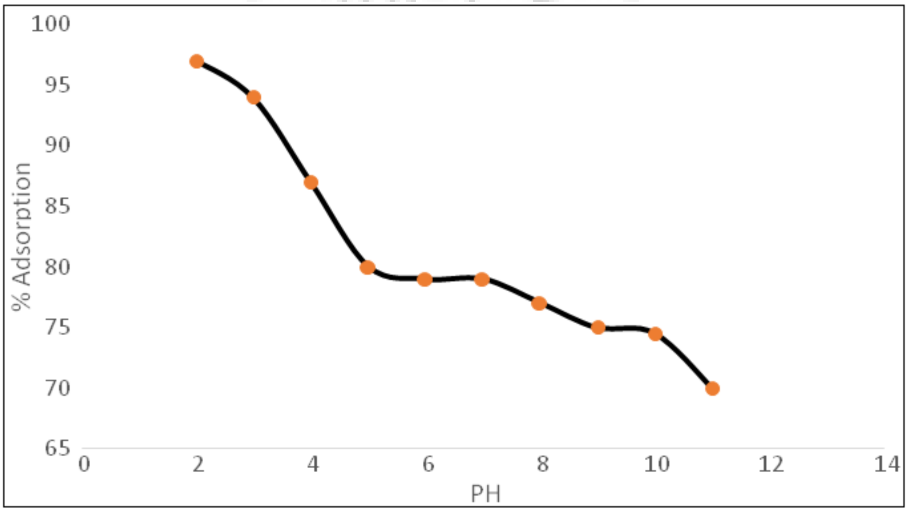

Figure 4: Effect of acid function change on the percentage of adsorption of the ionic dye on the surface of the β-zeolite synthesis from Iraqi rice husk

Effect of temperature on Adsorption

The effect of temperature on the adsorption of the eosin dye in the range (20-40)^{o}C was studied on the surface of β-zeolite synthesis from Iraqi rice husk. The results are illustrated in Figure 5. The results indicate that the amount of adsorption of the eosin dye decrease with increasing temperature. This decrease in quantity can be explained by the fact that increasing the temperature causes less rapid particle spread on the surface and thus weakens the interplay between the solvent surface and the molecules of the absorbing material(12).This corresponds to the thermodynamic functions, ΔH is negative because the adsorption process is heat-induced

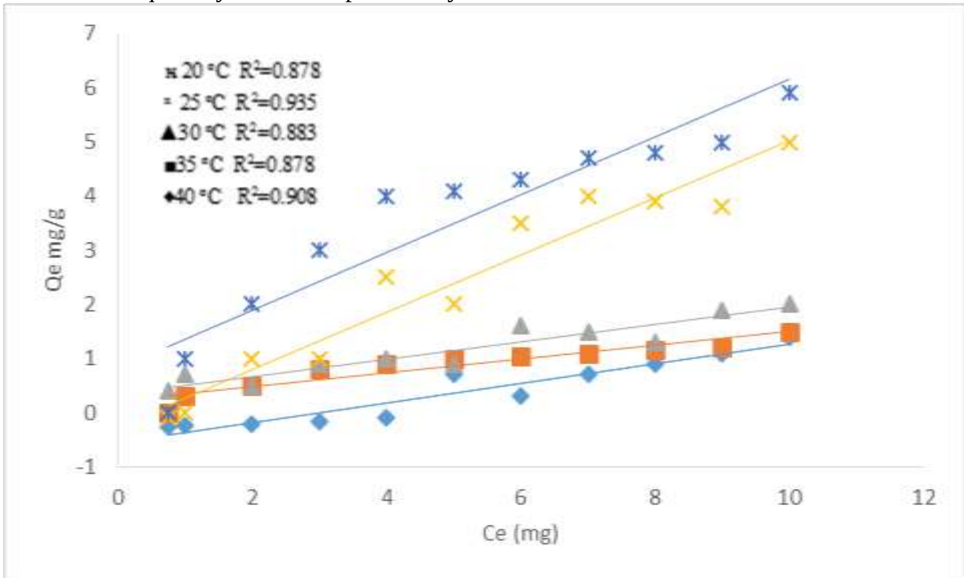

Figure 5: Effect of temperature change on the adsorption of the eosin dye on the surface of β-zeolite synthesis from Iraqi rice husk

4. Calculation of Thermodynamic Parameters of Adsorption

The values of thermodynamic functions are very important in the interpretation of many interactions (especially the process of adsorption) in terms of their direction and the nature of the forces controlling them, as well as they give a good description of the nature of the regularity of molecules in different systems resulting from molecular interventions of all kinds. The enthalpy value (ΔH) is a direct measure of the interference forces between the emitted molecule and the surface of adsorbent. The enthalpy value is calculated using the Van't Hoff equation, which is:

$$\boldsymbol{K_C = Ae^{-\frac{\Delta H}{RT}}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 3$$

$$\ln X_m = -\frac{\Delta H}{RT} + k \dots\dots\dots\dots\dots\dots\dots\dots 4$$

As follows:

$\ln X_m$ = greatest amount of adsorption (mg/g). K = Constant Van't Hoff equation. R = General constant of gases (8.314 J / mol.K). By drawing the relationship between $\ln X_m$ and the inverse temperature (1 / T) we obtain the slope on △H as in Figure 6. The results of the thermodynamic functions are shown in Table 1. The change in free energy (△G) Automatic or non-automatic interaction is recognized through the following relationship:

$$\Delta G = -RT\ln K \dots\dots\dots\dots\dots\dots\dots 5$$

It was found that the adsorption of the eosin dye on the surfaceof β-zeolite synthesis from Iraqi rice husk isspontaneous and through a Gibbs relationship, the change in the entropy (△S) can be determined from the following relationship:

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots\dots\dots\dots 6$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \dots\dots\dots\dots\dots\dots 7$$

A change in the entropy to the dye of the eosin on the surface of the of β-zeolite synthesis from Iraqi rice husk is negative. This indicates that the molecules of eosin dye that are adsorbed are still in continuous movement on the surfaceof β-zeolite synthesis from Iraqi rice husk rather than the solution.

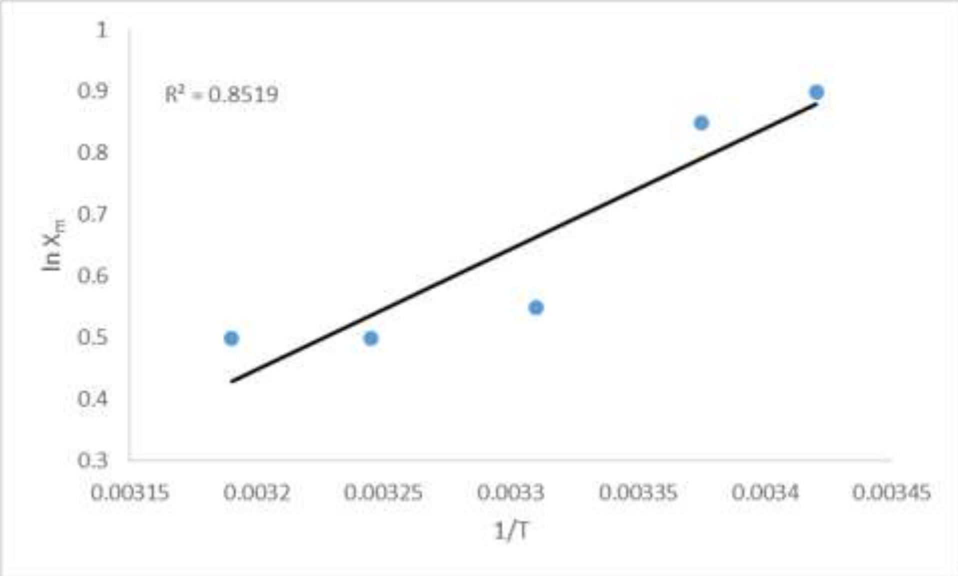

Figure 6: The maximum adsorption amounts ($\ln X_m$) at the different temperatures (T) in K for the dye of the eosin on the surface of β-zeolite synthesis from Iraqi rice husk

Table 1: Values of the thermodynamic functions of the eosin dye on the surface of β-zeolite synthesis from Iraqi rice huskand five degrees of temperature (20, 25,30,35,40°C).

C_o (mg/L)	Thermodynamic Function	20 °C	25°C	°C30	°C35	40°C
25ppm	ΔH kJ.mol^{-1}	+17.037				
	ΔG kJ.mol^{-1}	-0.282	-0.364	-0.596	-2.35	-2.98
	ΔS J.mol^{-1} K^{-1}	+0.0527	+0.0521	0.0547+	0.0597+	0.0608+

5. Adsorption Kinetics

The kinetic study was performed on adsorption of the eosin dye using the batch method at 20ppm concentration and in a range of thermal degrees (293-313K). The following equation was applied:

$$\ln(a-x) = \ln a - k_1 t \ldots\ldots .8$$

Or

$$\ln(C_{o-}\, q_t) = \ln C_o - k_1 t \ldots\ldots 9$$

We obtain rate constant (K_1) from the slope of equations and ($\ln q_e$) from the intersection. This equation represents the first stage interaction as the kinetic of reaction passes through two phases and the correlative coefficient (n = 0.99, 0.967, 0.965, 0.963, 0.965) and in the following degrees of temperature (20, 25,30,35,40°C), respectively, as shown in Figure 7. The results were analyzed by adsorption of the eosin dye according to the false first order equations of the Largergreen for reverse reaction.

$$\ln(q_e - q_t) = \ln q_e - (K_1 + K_{-1})t$$

In the graph between ln (q_e-q_t) and the time from slope, we obtain the constant rate of the forward reaction and the constant rate of the inverse reaction. Correlation coefficients (0.742, 0.761, 0.823, 0.867, 0.891)and the following thermal degrees (20, 25,30,35,40°C), respectively, as in Figure 8.

The results were analyzed according to the second false equation [13]:

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^{\,2}} + \frac{1}{q_e} t \ldots\ldots\ldots\ldots 11$$

$$h = K_2 q_e^{\,2} \ldots\ldots\ldots\ldots .12$$

Correlation coefficients (1.000, 1.000, 1.000, 1.000 and 1.000) were found in the following temperatures (20, 25, 30, 35, 40 °C) respectively, asshown in figure 9, from the values Correlation coefficient is shown to be suitable for adsorption of the eosin dye on the surface β-zeolite synthesis from Iraqi rice huskthrough the results.

The process of adsorption passes through two phases. First phase, the process of adsorption is very fast and the process of adsorption is so high that it is difficult to track the study. It is not possible to calculate the activation energy. It is followed by a slow phase. After that, the adsorption system reaches the state of equilibrium. Like the opposite reactions. . In the study of the adsorption process at different temperatures and using the Arrhenius equation, which describes the relationship between the value of the constant rate and the interaction with temperature

$$\ln K = \ln A - \frac{E}{RT} \ldots\ldots\ldots\ldots 13$$

By plotting the relationship between $\ln k_1$ versus the inverted temperature in Kelvin we obtain the slopewhich is represent the activation energy value of the front reaction and draw the relationship between ($\ln k_{-1}$) versus the inverted temperature in Kelvin. We obtain the activation energy value of the reverse reaction. The equilibrium constant is equal to the sum of the individual constants rate (forward and reversible). The front reaction rate constant and the inverse reaction Shown as in Figure10 and Figure 11 respectively. Thermodynamic functions can be calculated to activate both directions using the following equations:

$$\Delta H^{*} = E - RT \ldots\ldots\ldots\ldots 14$$

The value of ΔS^* can be calculated from the knowledge of the value of the frequency factor i.e.:

$$A = \frac{KT}{h} e^{\left(1+\frac{\Delta S^*}{R}\right)} \dots\dots\dots\dots\dots\dots\dots\dots 15$$

K is Boltzmann constant (1.38 * 10^{-23} $J.K^{-1}$) and h-Planck constant (6.626 * 10-34 $J.S^{-1}$) and A is the frequency factor in the second unit, taken ln to the latter equation with rearrangement, becomes as follows:

$$\Delta S^* = R\left[\ln A . \ln\left[\frac{KT}{h}\right] - 1\right] \dots .. 16$$

(△S*) resulting in the unit ($J.K^{-1}.mol^{-1}$). The free energy of activation can be calculated by unit ($J.mol^{-1}$) from the following equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \dots\dots\dots\dots\dots\dots .17$$

The positive values (△H*) indicate the high energy of the effective complex (mean state) compared with the initial state and the end of the adsorption process. The value of the adsorption can be calculated from the difference between adsorption in the front and back direction. In both directions increases with increasing temperature.

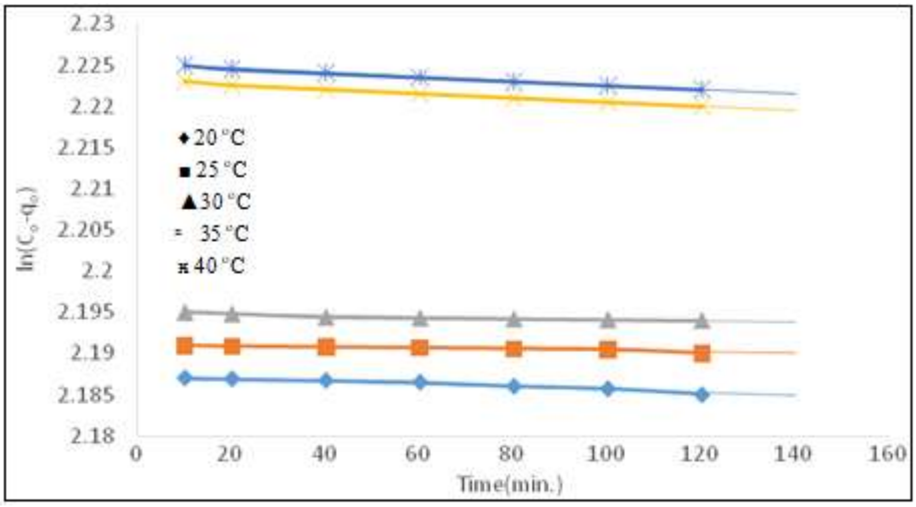

Figure 7: is the first order for adsorption of the eosin dye on the surface of the of β-zeolite synthesis from Iraqi rice huskand five degrees of temperatures at a concentration of 20ppm.

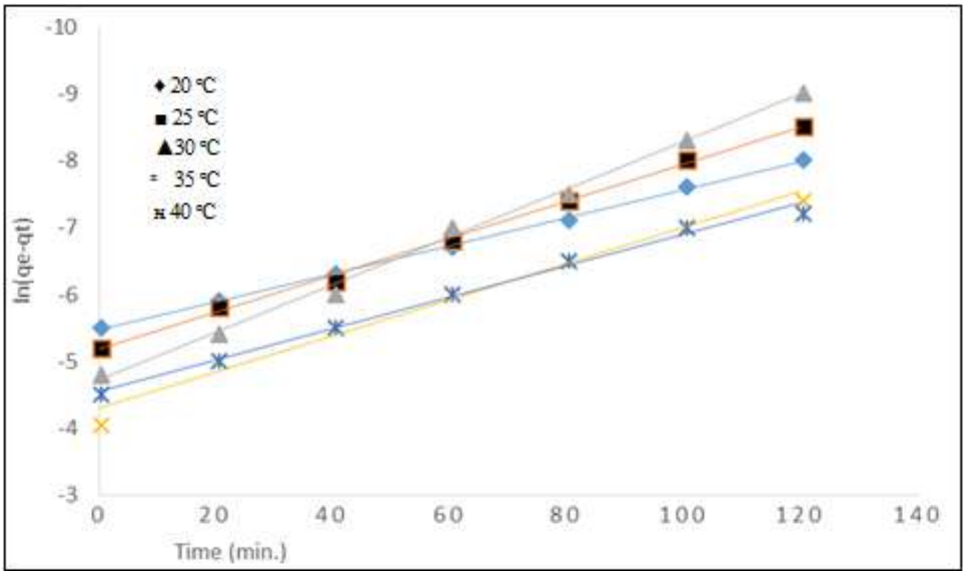

Figure 8: is the first false order for adsorption of the eosin dye on the surface of the β-zeolite from Iraqi rice husk and five degrees of temperatures at a concentration of 20ppm.

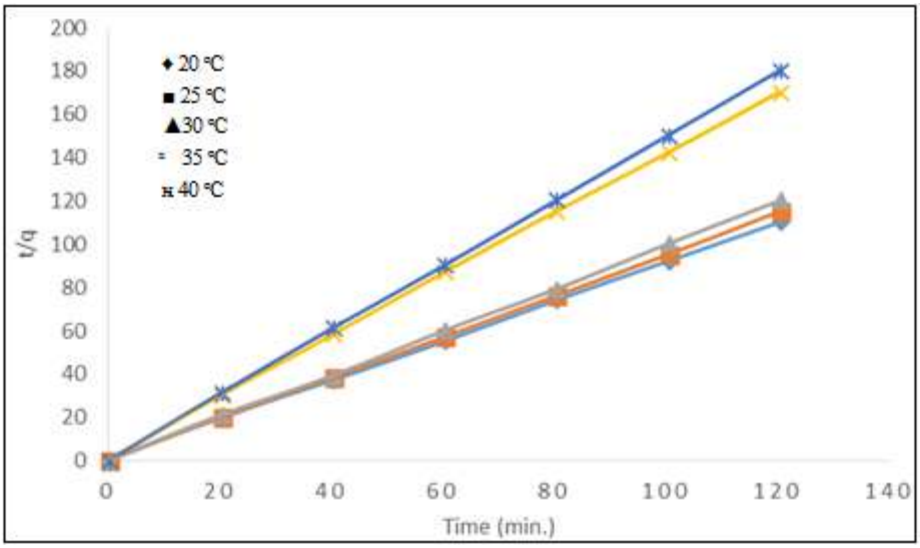

Figure 9: second false order of adsorptioneosindye on the surface of β-zeolite from Iraqi rice husk for five temperatures and at a concentration of 20ppm

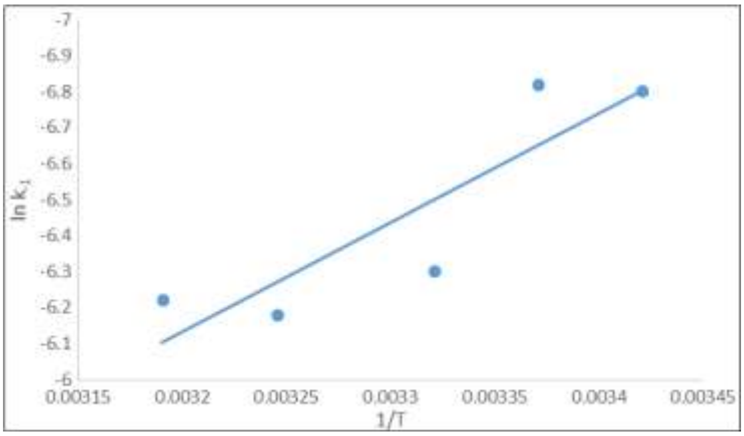

Figure 10: Arrhenius equation for the forward-direction reaction of adsorption of the ionic dye on the surface of the β-zeolite from Iraqi rice husk

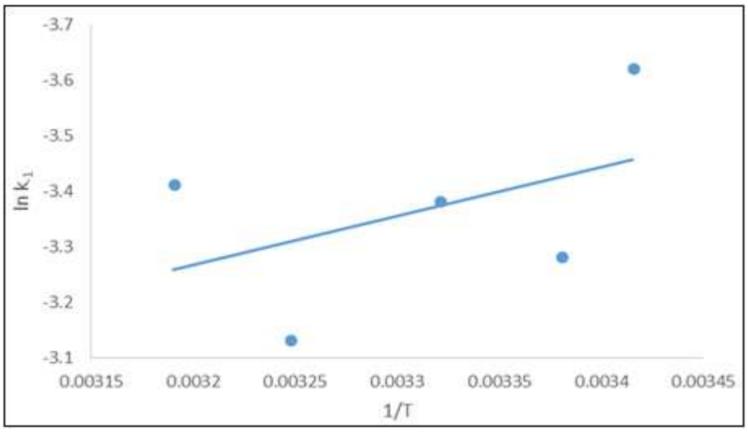

Figure 11: Arrhenius equation for reverse-reaction of adsorption of the ionic dye on the surface of the β-zeolite from Iraqi rice husk

Adsorption Isotherms

Information given by Isotherm adsorption is important. It gives an idea of how molecules are distributed between the liquid phase and the solid phase when adsorption reaches equilibrium. The adsorption isotherms of the eosin dye were studied at concentrations (2-20 ppm) and different teperatures (20, 25,30,35,40^{o}C) and the results are shown in Figure 12. All adsorbents of adsorption to the eosin dye indicate that they are S type by Giles classification. The S-type isotherm is based on the assumptions of Isotherm Freunndlich, which include that the adsorbent surface is not homogeneous. This property is general due to the different locations of adsorption are unsaturated and energy differences. The results of adsorption were analyzed according to Lagmuir linearization as shown in Figure 12 which are:

$$\frac{C_e}{Q_e} = \frac{1}{K_1 q_{max}} + \frac{1}{q_{max}} \ldots\ldots\ldots\ldots\ldots\ldots 18$$

The correlation coefficient (R^2) values between 0.061-0.332 indicate that this equation is not suitable for the results of adsorption of the ionic dye on the surface of the β-zeolite from Iraqi rice husk.

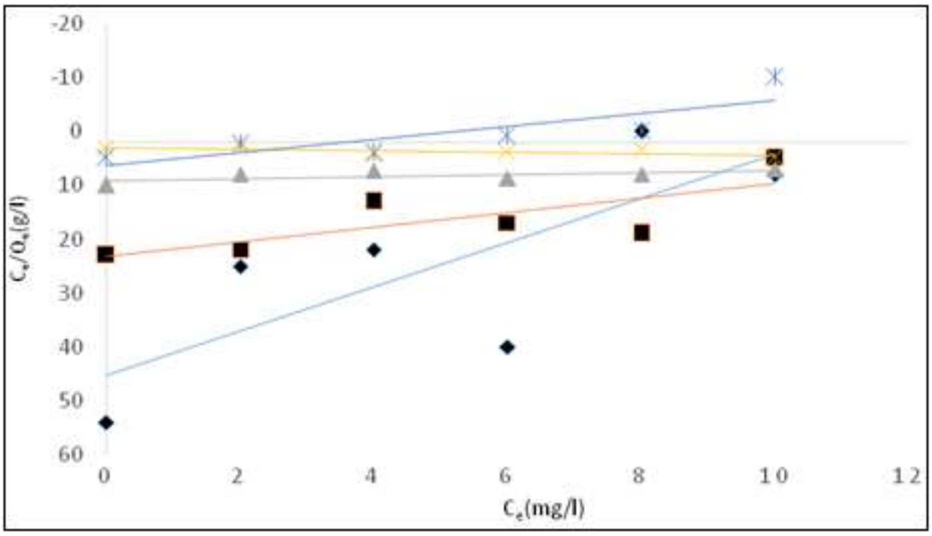

Figure 12: Isotherm Langmuir for the dye of eosin on the surface of the β-zeolite from Iraqi rice husk

The results of the adsorption of the ionic dye on the surface of the β-zeolite from Iraqi rice husk were analyzed according to the linear isotherm of Freundlich(14) which are:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \ldots\ldots\ldots 19$$

The results are shown in figure (13) .

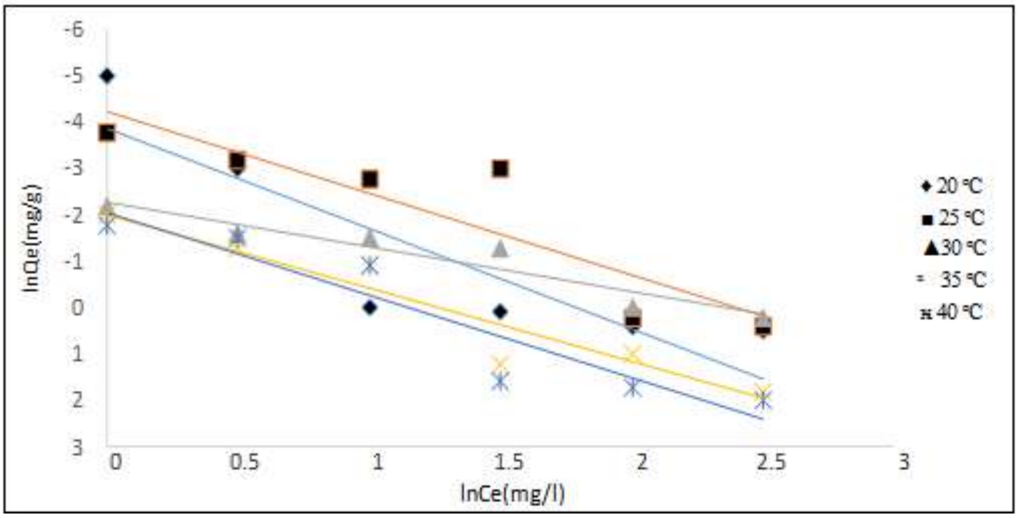

Figure 13: Isotherm Freundlich for the dye of the eosen on the surface of the β-zeolite from Iraqi rice husk

The correlation coefficients (R^2), which are between (0.777 - 0.921), where we observe the non-suitability of the Freundlich equation for the results of the adsorption of the eosin dye on the surface of the β-zeolite from Iraqi rice husk. (n = 1) indicates that adsorption is linear and if (n> 1) indicates that adsorption is physical and if (n<1) indicates that adsorption is chemical, the n values range from 0.377-0.708. Less than one indicates that adsorption is chemical (i.e., bound by chemical forces). The value of n ranging from (1-10) indicates that adsorption is good. The results were analyzed according to the linear Isotherm of Dubinin, which is more general than Langmuir and Freundlich on the heterogeneous surface and its linear equivalent [13]

$$\ln Q_e = \ln q_{max} - \beta\varepsilon^2 \ldots\ldots\ldots\ldots\ldots\ldots 20$$

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots 21$$

(R) Is the general constant of gases and its value here is ($8.314.10^{-3}$ $KJmol^{-1}K^{-1}$). Either adsorption energy (E) is calculated by the following equation: $E = (-2\beta)^{-0.5}$ and the results are shown in Figure 14.

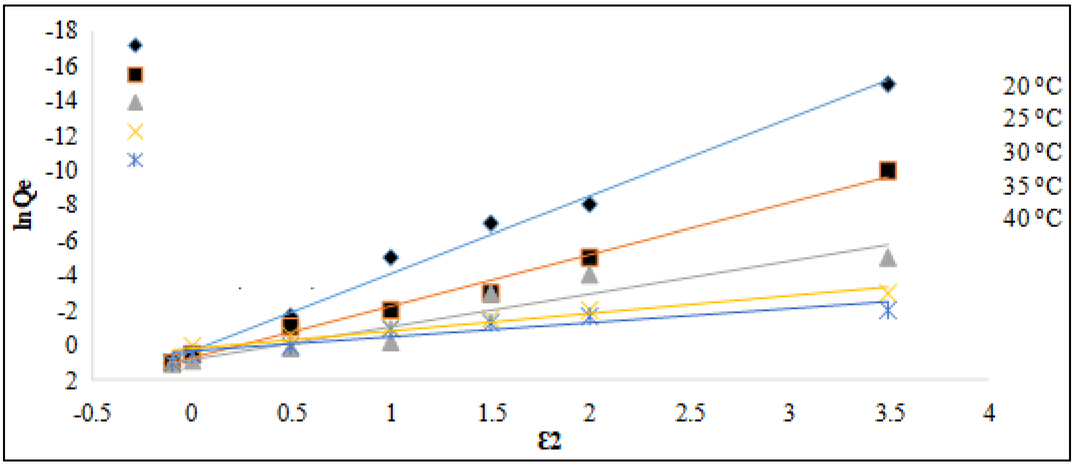

Figure 14: Isothermin Dupinin model for the dye of eosin on the surface of β-zeolite from Iraqi rice husk

The energy equation gives us a perception of the adsorption mechanism. E <8KJ / mol indicates that the physical forces influence adsorption and that E> 16 indicates the spread of the molecules and when E is between (8-16) indicates that adsorption is directed by ion exchange In the chemical adsorption, the energy results listed in Table (4) range from (10.987-23.750) i.e. the chemical adsorption. Also, the energy increases with this temperature increase and is consistent with the thermodynamic function values, which indicate that the value of the change in the enthalpy is positive, i.e., a heat absorber. The values of the correlation coefficient (R^2) range from 0.943 to 0.981. We observe from high values that this equation is suitable for isothermadsorption representation of the eosin dye on the surface of the β-zeolite from Iraqi rice husk. Also, the value of the maximum adsorption capacity (q_{max}) which are increased with increasing temperature and values ranging (0.339-0.752).

The results were analyzed according to isothermtemkin as in figure (15) the linear equation is:

$$Q_e = B \ln K_T + B \ln C_e \ldots\ldots\ldots\ldots 22$$

According to the correlation coefficient value of 0.860-0.971 for adsorption of the eosin dye on the surface of the β-zeolite from Iraqi rice husk. The most suitable formula for Isotherm adsorption representation of the eosin dye on the surface of theb-zeolite from Iraqi rice husk isisotherm Dubinin.

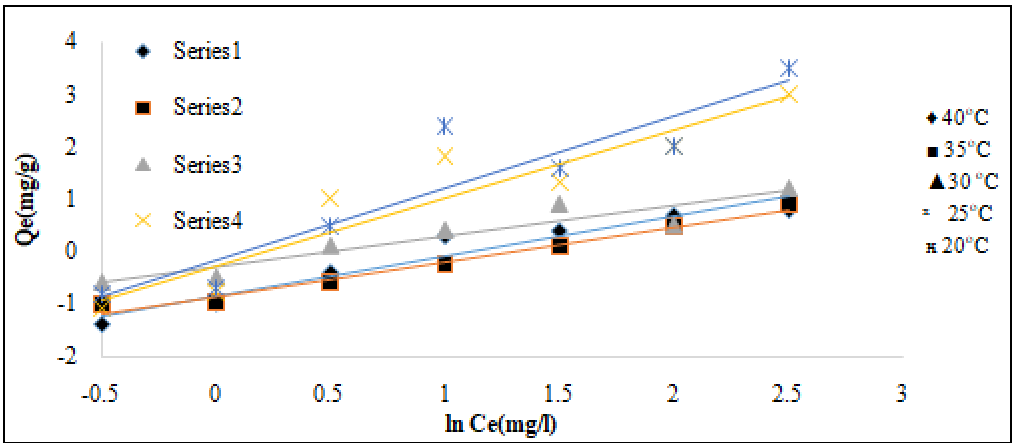

Figure 15: IsothermTemkin of the eosin dye on the surface of the β-zeolite synthesis from Iraq rice husk

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