Adsorption Kinetic and Thermodynamic Study of Congo Red Dye on Synthetic Zeolite and Modified Synthetic Zeolite

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Abstract

Linde Type-A (LTA) zeolite was modified by adding lead sulfide into cavities of zeolite. The zeolite and zeolite –pbs were characterized by FTIR, XRD, AFM and SEM. The adsorption of congo red (CR) dye from aqueous solution by zeolite and zeolite – pbs were studied. Different parameters like contact time, temperature and concentration of (CR) dye were investigated. The results show that at contact time of 45, 30 min for maximum adsorption of (CR) dye onto zeolite and zeolite -pbs respectively were observed. The kinetic data was analyzed using pseudo-first-order and pseudo-second-order kinetic models. The adsorption kinetics of (CR) dye were fitted well with the pseudo-second-order kinetic model for both adsorbents. Experimental equilibrium data onto adsorption of C-R dye on zeolite and zeolite –pbs were analyzed by the Langmuir, Freundlich and temkin isotherm models .The calculated thermodynamic parameters, namely ΔG^o, ΔH^o, and ΔS^o for zeolite showed that adsorption of C-R dye onto zeolite was spontaneous , endothermic and increase in the randomness and for zeolite –pbs showed that adsorption of C-R dye onto zeolite -pbs was spontaneous and ,exothermic and decreasing randomness under examined conditions ,The results of analysis errors and R^2 values shows that the best fit was achieved with the Langmuir isotherm equation and were followed order:-

(Big R^2) langmuir > temkin > freundlich(small R^2)
(small error) Langmuir < temkin < freundlich(big error)

Key Words: adsorption, adsorption isotherms, modified adsorbent, thermodynamics, kinetics, Error Analysis.

Introduction

Synthetic dyestuffs can exist on the effluents of wastewater from different industries such textiles, paper, leather, plastics, etc.[1].Discharge of wastewater into natural streams and rivers from the industries using dyes poses severe environmental problems. Even small quantities of dyes can color large water bodies, which not only affect aesthetic merit but also reduce light penetration and photosynthesis. In addition, most of the dyes are either toxic or mutagenic and carcinogenic [2,3]. Azo dyes are the largest class of dyes with the greatest variety of colours - approximately 10–15 % of the dyes are released into the environment during dyeing of different substrates, such as synthetic and natural textile fibres, plastics, leather, paper, mineral oils, waxes, and even foodstuffs and cosmetics.

Congo Red (CR) serves as a model compound for common water-soluble azo dyes, which is used in paper, plastic, textile and dyes industries[4] For these reasons, Removal of these dyes from effluents in an economic way remains as a major problem for textile industries[5,6] . The most commonly used methods of color removal are biological and chemical precipitation However,. many physicochemical methods have been tested, but adsorption is considered to be superior to other techniques. This is attributed to its low cost, easy availability, simplicity of design, high efficiency, easy operation , biodegradability, and ability to treat dyes in more concentrated forms[7,8]. Sorption technology, including physical and chemical adsorption and ion exchange process technologies have the potential waters and industrial residues. In adsorption processes, atoms or ions (adsorbates) contained in a fluid phase diffuse to the surface of a solid (adsorbent), where they are chemically bound to the surface or held there by intermolecular forces[9].

Zeolite is used as adsorbent which has a large group of natural and synthetic hydrated aluminum silicates. They are natural, which offerd only a limited range of atomic structures and properties, and synthetic, with a wider range of properties and larger cavities than their natural counterparts [10] For their chemical, physical and structural individuality, zeolites are appropriate for various applications in different areas, like adsorption of cations, separation, ion exchange catalysis, due to their high sorption capacity and selectivity resulting from high porosity and sieving properties [11]. The present study is undertaken to evaluate the efficiency of a zeolite modified for the removal of dye in aqueous solution. in order to design adsorption treatment systems.

Materials and Methods

Materials

Thioacetamide (Hopkin and Williams chemicals .Ltd) , HCl (BDH) ,lead nitrate (BDH) , congo red (BDH) (m.wt: 696.66 g mol^{-1}figure1),synthetic zeolite 5A (Petroleum Research & Development Center) **.** The composition of Zeolite 5A mineral is: SiO_2 (32.52), Al_2O_3 (27.64) , Na_2O (4.20) , CaO (11.38) , L.O.I.(99.99).

Methods

Preparation of Modified PbS- Zeolite

The synthetic zeolite was washed with excessive amounts of distilled water, dried at 160 C^o for three hours for remove water molecules from zeolite cavities, The clay was ground and sieved to a particle size of 150 µm, The sieved zeolite (10 g) Suspended in aqueous solution(200 ml) then added (5ml) of lead nitrate (0.06 M) to suspension solution of zeolite with continues stirring for half hr .then thioacetamide (1g) dissolved in hot aqueous solution (20 ml) acidification with concentrated HCl (1 drop)and was added to Suspension aqueous solution of zeolite under stirring (QA9010X - Hot Plate Stirrer, Ceramic Surface) for one hr and heating ≤ 50 C^o.The zeolite was separated from the mixture by decantation, washed about seven times with distilled water, and dried in an oven (Daihan Labtech Oven LDO - 060E) at a temperature of 60 C for 2hr.

Adsorption Experiments

Wavelength of maximum absorbancy (λ_{max}) was found 498nm for congo red by using Uv-Visible spectro-photometer double beam (shimadzu UV-1800), This value were utilized for estimation of quantity of C-R dye adsorbed, Solutions of different concentrations for dye was prepared by serial dilution. Absorbance values of these solutions were measured_at the selected λ_{max} value for each dye and plotted against the concentration values. The calibration curves in the concentration range that falls in the region of applicability of Beer-Lambert's law were employed.

The quantity of dye adsorbed can be calculated by using the following equation[12]:

$$q_e = \frac{(C_\circ - C_e)V}{m} \text{ --------------(1)}$$

m: weight of adsorbent (g). C_o: initial concentration (mg/*l*). C_e: equilibrium concentration (mg/ *l*). V : volume of solution (L).

All batch adsorption kinetic and isothermal testes shaken using shaker (Labtech shaking water bath) at 120 rpm at different time and temperature, Adsorbent dose, contact time, temperature and were optimized by continuous variation method (studying one, while keeping the other parameters constant). After equilibrium, the solution was allowed to settle for 10 - 15 min, and separated by centrifuged (Centrifuge tubes. Hettich (EBA-20)) and volumes of 3ml supernatant were taken for spectro- photometrically measurements of dye content.by using Visible spectrophotometer single beam (CECIL,CE 1011).

Contact Time and Kinetic Study

Batch adsorption tests were carried out at different contact time intervals (1, 2, 4, 6, 10,15, 20, 25, 30, 45, 60, 90,120, 180min) at initial C-R concentration of 40 mg/l. This was done by contacting 0.1g of each adsorbent with 10 ml of C-R dye solution within range temperatures (288,298, 308, 318) K at pH 7 and uniform particle size (≤ 150 μm).

Result and Discussion

Characterization of Zeolite and Modified Zeolite

Figure(2 - zeolite) XRD pattern (XRD-6000 shimadzu) of LTA zeolite before modified showed high purity and a good crystallinity of zeolite. These results are in good agreement with those reported in the literature **[13]**. Figure (2 –zpbs) XRD pattern of LTA zeolite after modified showed that there are no changes in the positions of the diffraction peaks of zeolite A (figure 2-pbs) after loading of lead sulfide cluster into the framework voids (figure 2 - zpbs). This means that loading of lead sulfide cluster into the framework voids of zeolite A does not distort the zeolite framework. The change in the relative intensities of peaks is caused by higher stress by lead sulfide cluster on the zeolite framework atoms (Al, Si, O) and compensating sodium and calcium ions **[14]**.

Figure(3-zeolite) FTI R spectra of LTA zeolite is shown in Figure 1. The bands at 450 to 1200 cm^{-1} are known to assignable to Si-O-Al, Si-O-Si, Si-O, Si-Al and T-O species **[15]**.The peaks at 403.cm^{-1} are assigned to the structure insensitive internal (TO_4) tetrahedral bending peaks of zeolite A in literature. Peaks 1633 cm^{-1} and 3033 cm^{-1} are assigned to the external linkage asymmetrical stretching and internal tetrahedral symmetrical stretching respectively. In the other hand, the broad bands at 3350 to 3700 cm^{-1} are attributed to Si-OH, Si-OH-Al and -OH hydroxyl groups. The band at 668 cm^{-1} is known to assignable to Si-O-M where M is the exchangeable Na^+ ion metal species. The absorption band at 677 cm^{-1} in LTA is visible which is in corporate with Na atoms in the zeolite framework **[13]**. Figure (3- zeolite-pbs) FTI R spectra of LTA zeolite modified by PbS shows agreement with XRD results. The AFM images (SPM AA3000 Atomic force microscope-USA 2008) (in two and three-dimensional) and granularity distribution charts for the synthetic zeolite and PbS- Zeolite in Figure (4) . it shows that the diameter of the particles for zeolite (95 nm) and for pbs – zeolite (81 nm) ,the average particle size for zeolite was (0.58 nm) and for the pbs – zeolite (0.84 nm) . This result indicates that average particle size for pbs - zeolite less then zeolite. Figure (5-zeolite) shows the SEM image (SEM-- T-Scan ,Vega-111,Czech), of zeolite and pbs - zeolite particles with magnification of 25000, Scanning electronic micrographs show uniform morphology and cubic shape of particles for LTA zeolite. The average diameter of the particle observed from SEM analysis is ≥ 1 μm, Figure (5-zeolite-pbs) shows the changes on the surface of the pbs - zeolite up to 500 nm and this indicates on pbs cluster from pores to zeolite surface**.**

Kinetic Studies of Adsorption

Effect Contact Time

The adsorption of congo red dye on zeolite and modified zeolite was studied as a function of contact time, and draw q_e versus t in Figure (6) at different temperatures . from Figures (6) are shown The adsorption rates of congo red dye onto zeolite and modified zeolite are observed to be very fast within the first few minutes and gradually decrease and become almost constant after a period of 45 and 30 min respectively. and shows a very fast increase in q_e with time in both adsorbents, The initial uptake is attributed to surface adsorption. When the dye adsorption at the exterior surface reached the saturation level, the dye begins to enter the pores of the zeolite and modified zeolite surface and is adsorbed by the interior surface of the adsorbent particles. The interior surface seems to be very active and have a very high affinity toward dye molecules. Hence, a high dye uptake by is observed **[16]**, and these results are similar with result of the percentage adsorption of dye on zeolite and modified zeolite were calculated using the equation :

$$Adsorption\,\% = \frac{(C_{\circ} - C_e)}{C_{\circ}} \times 100 \text{ --------(2)}$$

Figure(7) shows nearly 40-52%, 50-69% The percentage adsorption of congo red on zeolite and modified zeolite at 45 and 30 min respectively within range (288, 298 ,308 .318) K.

Kinetic of Adsorption

Kinetic of adsorption describes the solute uptake rate, which in turn governs the residence time of adsorption reaction. Batch experiment were conducted to study the rate of congo red (40 mg/L) adsorption by the zeolite and modified zeolite (0.1g) at pH 7 .

1-Pseudo- First Order Model

The pseudo first order model was described by lagergren **[17]**,

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \text{-------- (3)}$$

The linear form is

$$\ln(q_e - q_t) = \ln q_e - (K_1)t \text{-------------(4)}$$

Where q_e and q_t are the amount of (CR) dye adsorbed mg /g at equilibrium and at any time t respectively and k_1 (min^{-1}) is the equilibrium rate constant of pseudo first order adsorption . The plot of ln (q_e- q_t) vs. t should give linear relationship from which the value of k_1 , equilibrium adsorption q_e and correlation coefficient R^2 were calculated . The pseudo first order kinetic model for adsorption of (CR) dye on the zeolite and modified zeolite are less applicable due to the low correlation coefficients(R^2 >0.88) at different temperatures table (1), Figure (8) .

2-Pseudo -Second Order Model

The pseudo-second order model is represented by the following differential equation **[18]**

$\frac{dq_t}{dt} = K_1(q_e - q_t)^2$--------- (5)

Where k_2 is the equilibrium rate constant of pseudo- second order adsorption (g/ mg.min)
The linear form is :

$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}(t)$-------- (6)

The initial adsorption rate , h (mg/ g.min) is expressed by the following equation:

$h = K_2 q_e^2$------------- (7)

The slope and intercept of plot t/q_t versus t were used to calculate the second order rate constant k_2 .The correlation coefficients were found ($R^2 > 0.98$) for both adsobent different temperatures ,and the calculated q_e values agree very well with experimental data (table2,figure 9). This model confirms that the adsorption of (CR) dye on the zeolite and modified zeolite follows the pseudo second order model .
The adsorption rate constant may be expressed as a function of temperature by following the relationship of Arrhenius equation **[19]**:

$-\ln k_a = \ln A - Ea / RT$ --------- (8)

Where k_a is the rate constant of sorption (min^{-1}), Ea is the activation energy of sorption ($kJ.mol^{-1}$), R is the gas constant (0.008314 kJ K^{-1} mol^{-1}), T is solution temperature(K).The ln k_{ad} values for the pseudo second order were plotted as a function of reciprocal of the Kelvin temperature. Linear variation were observed as shown in figure (10) .

From figure (10) The value of activation energy of adsorption obtained is(5.92kJ.mol^{-1}) for adsorption (CR) dye on zeolite and , (27.70 kJ.mol^{-1}) for adsorption (CR) dye on zeolite-pbs which activation energy of adsorption on zeolite –pbs larger than zeolite which indicates that the process occurs in favor of adsorption direction.

Adsorption Isotherms

Adsorption of congo red dye from an aqueous solution on zeolite and modified zeolite was studied first at different temperatures(288, 298, 308,318)K keeping pH of the solution (pH≈7) unchanged.
The results of this study were represented as the initial concentration of congo red (C_o), the equilibrium concentration (C_e) measured at equilibrium time and the quantity adsorbed (q_e) and the quantities adsorbed (q_e) were plotted versus equilibrium concentration (C_e) to obtain the general case of the adsorption isotherms as shown in Figures (11) which represent the isotherms of (CR) dye on the zeolite and zeolite- pbs at different temperatures,and as shown the (CR) equilibrium isotherm for both adsorbents are a L-type isotherm. L-shaped adsorption isotherm indicate the adsorbed solute molecules are most likely being adsorbed in a flat geometry, which is based on the assumption of high adsorption affinity between the dye and the surface [20,21].

On the other hand we note increasing quantity with increasing temperature of the zeolites and it was due to the likelihood of absorption of the dye inside the zeolite as well as the occurrence of adsorption and decreases with increasing temperature for zeolite -pbs and that of an adsorption process only [22].
Several models were published to describe the experimental data of the adsorption isotherms, The Freundlich equation is an empirical model that considers heterogeneous adsorptive

energies on the adsorbent surface and the equation expressed as follows The linear form of Freundlich isotherm **[23]** is:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \text{------------- (9)}$$

Where K_F is a constant, indicating the relative adsorption capacity of the adsorbent (l/g^{-1}) and n is a the heterogeneity factor, representing the intensity of adsorption, Plotting ln q_e versus ln(C_e) (Equation (9)) figure (12-a) results in a straight line of slope 1/n and intercept ln (k_F).
Langmuir model is the most widely used isotherm equation, which has the linear form as follows **[**24,25]

$$\frac{C_e}{q_e} = \frac{1}{k_L} + \frac{a}{k_L} C_e \text{------------- (10)}$$

where a and K_L are Langmuir isotherm parameters, representing the maximum uptake capacity per unit mass of adsorbent (mg/g), and the Langmuir constant (l/mg) respectively.
Plotting C_e /q_e versus C_e (Equation (10))figure (12-b) results in a straight line of slope a/k_L and intercept 1/ k_L.
The Temkin isotherm model assumes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface, and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy. The Temkin isotherm can be described by Equation **[**26**]:**

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \text{-------------(11)}$$

where K_T is the equilibrium binding constant (L mol^{-1}) corresponding to the maximum binding energy, b is related to the adsorption heat, R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature (K). Plotting q_e versus ln(C_e) (Equation (11)) figure (12-c) results in a straight line of slope RT/b and intercept (RT ln K_T)/b. constants of isotherms were mentioned previously recorded in Table(3) shows the values of the constants of the Freundlich isotherm at different temperature, for zeolite where ($n > 3$) for all temperatures indicates that the adsorption of C-R dye on zeolite is easily achieved. The value of K_f increases with increasing temperature ,and it is obvious that high temperature is helpful for adsorption and the mechanism of the adsorption is chemical adsorption_but for zeolite- pbs that ($n > 6$) for all temperatures indicates that the adsorption of C-R dye on zeolite- pbs is more easily achieved than adsorption on zeolite and The value of K_f decreases with increasing temperature indicates that process is a favourable physical adsorption.
Table(3) shows the values of the constants of the Langmuir isotherm at different temperatures, for zeolite the maximum adsorption capacity (a_L) of C-R dye on zeolite increased with an increase in temperatures , showing that (a_L) is enhanced at high temperatures on the other hand The energy of adsorption (k_L) is enhanced at high temperatures on zeolite surface, because it was increased with a increase in temperatures, while for zeolite - pbs the maximum adsorption capacity (a_L) of C-R dye on zeolite decreased with an increase in temperatures , showing that (a_L) is enhanced at lower temperatures on the other hand The energy of adsorption(k_L) is enhanced at lower temperatures on zeolite -pbs surface, because it was decreased with an increase in temperatures **[**27].
Table(3) shows the values of the constants of the temkin isotherm at different temperatures, for zeolite which have heat of adsorption b_T within(13-23) kJ.mol^{-1} and zeolite – pbs have b_T within(10-18) kJ.mol^{-1} and K_T of zeolite –pbs Greater than K_T of zeolite This means that the values of b_T zeolite – pbs are smaller than zeolite and that indicates that zeolite-pbs. More favorable for the physical adsorption from zeolite at all different temperatures.

Thermodynamic Studies

The batch adsorption process was studied at different temperatures of 15, 25, 35, 45 °C in order to investigate the effect of temperature on the adsorption process using modified pbs-zeolite. This was done by contacting 0.1g of adsorbents with 10 ml of different concentrations (10,15,20,25,30, 40 ,50mg/l) C-R dye solution at pH 7 for 45 and 30 min respectively. The results were used to investigate the thermodynamics of the adsorption process. thermodynamic parameters including the change in free energy (ΔG_), enthalpy (ΔH_) and entropy (ΔS_) were used to describe thermodynamic behavior of the congo red adsorption onto zeolite and zeolite - pbs. The equilibrium constant (K_e) for the adsorption process at each temperature is calculated from division of the quantity of dye adsorbed on the zeolite and zeolite – pbs form the equation [28,29]:

$$K = \frac{Q_e * 1000}{C_e} \quad \text{-------------} \ (12)$$

Where (0.1g) represents the weight of the clay that has been used and (0.01 L) represents the volume of the dye solution used in the adsorption process, The change in free energy (ΔG°) could be determined from the equation **[30]**:-

$$\Delta G^\circ = -RT \ln K \qquad \text{------------} \ \mathbf{(13)}$$

Where R is the gas constant (8.314 J.mole^{-1}. K^{-1}) and T is the absolute temperature. The heat of adsorption (ΔH°) may be obtained from the vant Hoff's equation:-

$$\ln K = \frac{-\Delta H^\circ}{RT} + cons \ \tan \ t \qquad \text{-------------}(14)$$

Where K is the equilibrium constant when Ce approaches to zero at certain temperature. Figure (13) 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 =(-ΔH°/R) from which the enthalpy (ΔH°) of the adsorption process is obtained .The change in entropy (ΔS°) was calculated from Gibbs equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \text{----------------} \ (15)$$

the equilibrium constant (K_e), free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°)were recorded in table (4) from Table (4) For zeolite The negative ΔG° values indicate thermodynamically spontaneous nature of the adsorption. The decrease in ΔG values with increasing temperature shows an increase in feasibility of adsorption at higher temperatures. The positive ΔH° is an indicator of endothermic nature of the adsorption, The positive ΔS° value suggests an increase in the randomness at sorbate - solution interface during the adsorption process. while_for zeolite- pbs The negative value of ΔG° confirms the feasibility of the process and the spontaneous nature . The increase in ΔG° values with increasing temperature shows an increase in feasibility of adsorption at lower temperatures The value of ΔH° was negative, indicating that the nature of the adsorption is exothermic. The negative value of ΔS° shows the decreasing randomness at sorbate-solution interface during the adsorption process [31].

Error Analysis

Determination of the best isotherm model is only possible through analysis of the correlation coefficient (R^2). Although efficient, this indicator is limited to solving isotherm models that present linear forms . Therefore, in this work, three different error functions were employed in order to discover the isotherm model most suitable for representing the experimental data.

The Sum of Squared Errors (SSE) (Equation (16)) is the most commonly utilized error function. However, it has the disadvantage of providing isotherm parameters that present better adjustment to the final portion of the isotherm. This is due to the magnitude of the errors, which causes an increase in squared errors as the adsorbate concentration increases.

$$SSE = \sum_{i=1}^{n} (q_{cal} - q_{exp})^2 \quad -------- (16)$$

The sum of absolute errors (SAE) (Equation (17)) also provides better adjustments for higher concentrations. This occurs because an increase of the concentration range causes an increase in error.

$$SAE = \sum_{i=1}^{n} \left| q_{cal} - q_{exp} \right| --------- (\mathbf{17})$$

The average relative error (ARE) (Equation (18)) function attempts to minimize the fractional error distribution across the entire concentration range.

$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{q_{cal} - q_{exp}}{q_{cal}} \right| -------- (\mathbf{18})$$

where q_{calc} is the calculated value, q_{exp} is the experimental value and n is the number of data points **[32,33]** . Table (5) According values of R^2 and types errors the isotherm models for zeolite and zeolite –pbs at all temperatures are following order:-

(Big R^2) langmuir > temkin > freundlich(small R^2)
(small error) Langmuir < temkin < freundlich(big error)

shows that the Langmuir, Temkin, Freudlich models have smaller errors in almost all of the cases and that the Langmuir model shows high accuracy. In this case, the Langmuir isotherm model can be more useful for describing the adsorption process of congo Red by both adsorbents **.**

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Table No. (1): Adsorption kinetics parameters of pseudo-first order of (CR) dye on zeolite and zeolite – PbS

adsorbent	288 K			298 K		
	Pseudo-first order			Pseudo-first order		
	k_1(min^{-1})	q_e(mg/g)	R^2	k_1(min^{-1})	q_e(mg/g)	R^2
Zeolite	-0.094	0.786	0.941	-0.128	0.762	0.942
Zeolite - pbS	-0.070	0.787	0.915	-0.140	0.638	0.953
adsorbent	308 K			318 K		
	Pseudo-first order			Pseudo-first order		
	k_1(min^{-1})	q_e(mg/g)	R^2	k_1(min^{-1})	q_e(mg/g)	R^2
Zeolite	-0.121	0.692	0.976	-0.115	0.685	0.995
Zeolite - pbS	-0.130	0.639	0.947	-0.120	0.374	0.883

Table No. (2): Adsorption kinetics parameters of pseudo-second order of (CR) dye on zeolite and zeolite – PbS

Adsorbent	**288 K**				**298 K**			
	Pseudo-second order				**Pseudo-second order**			
	k_2 (g. mg^{-1} .min^{-1})	**q_e (mg/g)**	**R^2**	**h (mg. g^{-1} .min^{-1})**	**k_2 (g. mg^{-1} .min^{-1})in**	**q_e (mg/g)**	**R^2**	**h (mg. g^{-1} .min^{-1-1})**
Zeolite	**0.382**	**1.912**	**0.988**	**5.102**	**0.428**	**2.033**	**0.999**	**7.315**
Zeolite + pbS	**0.318**	**2.410**	**0.994**	**10.733**	**0.619**	**2.488**	**0.999**	**23.714**
Adsorbent	**308 K**				**318 K**			
	Pseudo-second order				**Pseudo-second order**			
	k_2 (g. mg^{-1} .min^{-1})in^{-1})	**q_e (mg/g)**	**R^2**	**h (mg. g^{-1} .min^{-1-1})**	**k_2 (g. mg^{-1} .min^{-1})$^{-1}$**	**q_e (mg/g)**	**R^2**	**h (mg. g^{-1} .min^{-1-1})**
Zeolite	**0.481**	**2.083**	**0.999**	**9.058**	**0.475**	**2.132**	**0.998**	**9.817**
Zeolite + pbS	**0.605**	**2.747**	**0.999**	**34.455**	**1.077**	**2.513**	**0.999**	**42.961**

Table No. (3): Freundlich, Langmuir and Temkin isotherm constants for dyes uptake by Zeolite and zeolite - pbs

zeolite						
T/K	Freundlich isotherm		Langmuir isotherm		Temkin isotherm	
	K_F	**n**	**K_L**	**a**	**K_T**	**b**
288	0.208	3.001	0.126	0.819	1.384	13.812
298	0.321	3.880	0.220	0.879	4.026	15.478
308	0.424	4.520	0.333	0.969	8.823	15.972
318	0.628	7.668	0.598	1.024	231.27	23.981
Zeolite +PbS						
T/K	Freundlich isotherm		Langmuir isotherm		Temkin isotherm	
	K_F	**n**	**K_L**	**a**	**K_T**	**b**
288	1.269	6.578	0.941	2.108	222.0	10.254
298	1.160	6.869	2.038	1.785	302.1	12.165
308	0.979	7.511	1.079	1.522	790.4	16.969
318	0.764	6.094	0.489	1.402	247.8	18.004

Table No.(4): Thermodynamic parameters of adsorption process of (CR) dye on the adsorbents at different temperatures

T/K	Zeolite				Zeolite - PbS			
	ΔG (J mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	K_e	ΔG (J mol^{-1})	ΔH (kJ mol^{-1}	ΔS (J mol^{-1} K	K_e
288	-8391.1	15.297	82.25	33.3	-13151.9	-24.626	-39.84	242.9
298	-9223.5	15.297	82.28	41.4	-13128.5	-24.626	-38.58	200.1
308	-10157.4	15.297	82.64	52.8	-12519.5	-24.626	-39.31	132.8
318	-10816.7	15.297	82.12	59.8	-12021.7	-24.626	-39.64	94.4

Table No. (5). correlation coefficient, R^2 and errors function for different isotherm models at different temperatures

T/K	**Zeolite**					**Zeolite –pbs**			
	isothermTypes	ARE	SAE	SSE	R^2	ARE	SAE	SSE	R^2
288	Freundlich	0.100	0.681	0.167	0.955	0.498	2.043	1.454	0.834
	Langmuir	0.047	0.001	0.001	0.996	8.197	0.638	0.504	0.996
	Temkin	0.158	0.000	0.002	0.977	0.779	0.164	0.098	0.800
298	Freundlich	0.175	0.004	0.010	0.893	0.488	0.032	0.120	0.794
	Langmuir	0.296	0.000	0.002	0.997	1.479	0.080	0.027	0.999
	Temkin	0.330	0.000	0.006	0.932	0.153	0.071	0.086	0.796
308	Freundlich	0.184	0.006	0.015	0.871	0.573	0.039	0.101	0.656
	Langmuir	0.682	0.014	0.004	0.996	0.739	0.113	0.052	0.996
	Temkin	0.355	0.000	0.010	0.899	1.876	0.060	0.088	0.775
318	Freundlich	0.024	0.001	0.003	0.962	0.170	0.009	0.025	0.874
	Langmuir	0.557	0.023	0.003	1.000	1.894	0.111	0.029	0.994
	Temkin	0.044	0.000	0.002	0.975	2.116	0.110	0.026	0.958

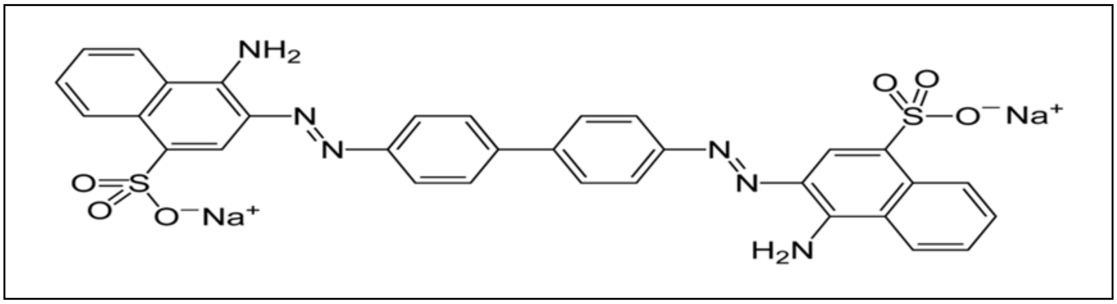

Figure No.(1) :The chemical structure of Congo Red

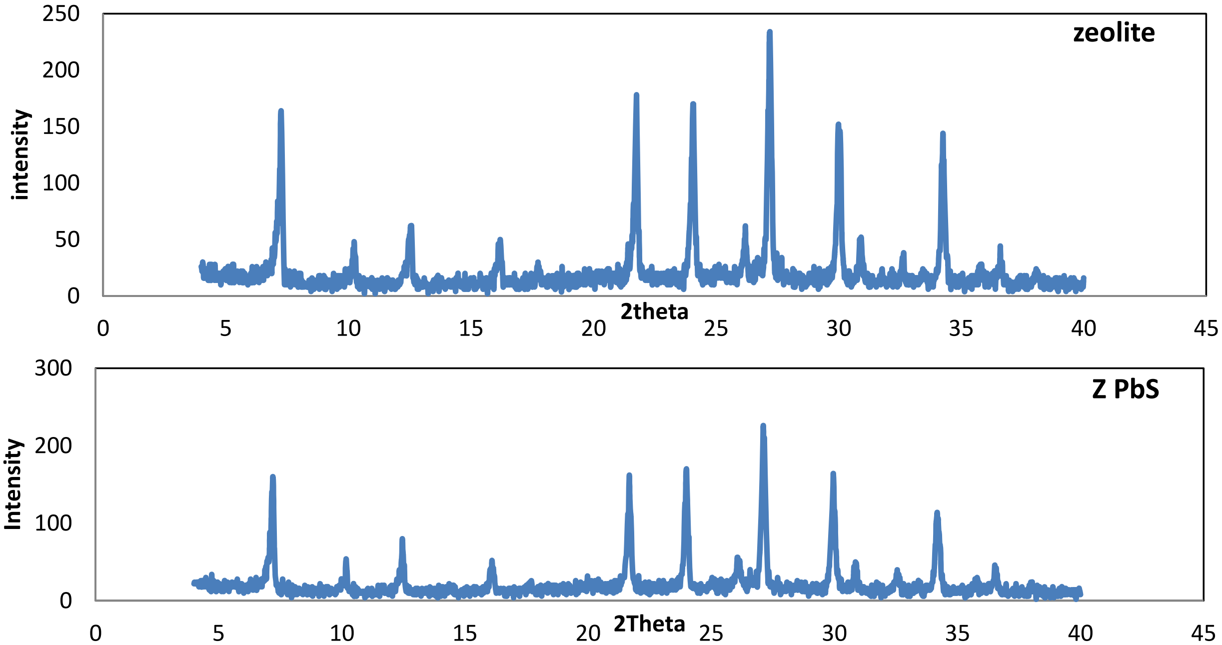

Figure No. (2): X-ray diffraction of zeolite ,zeolite-PbS

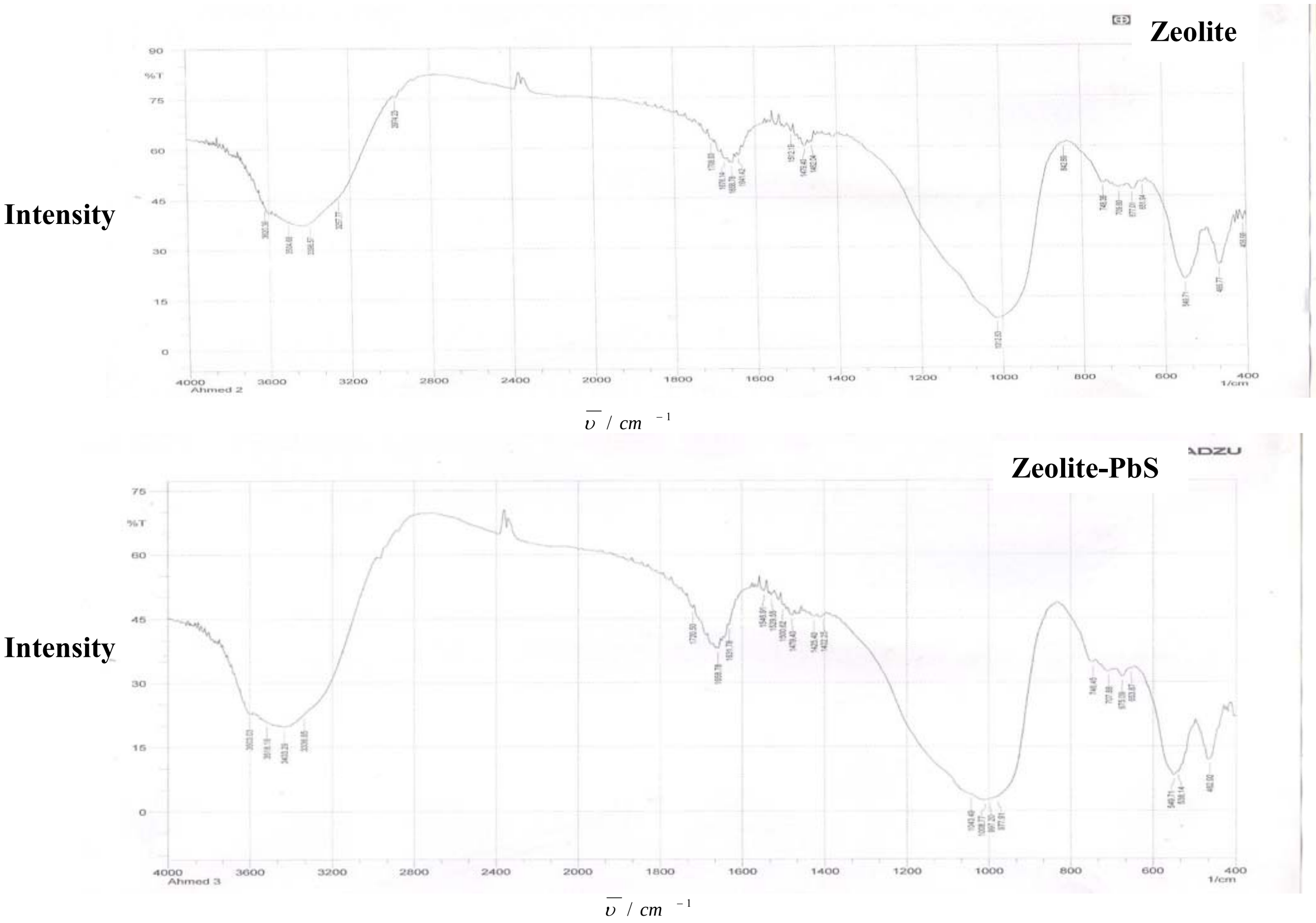

Figure No. (3): FTI R spectra of zeolite ,zeolite-PbS

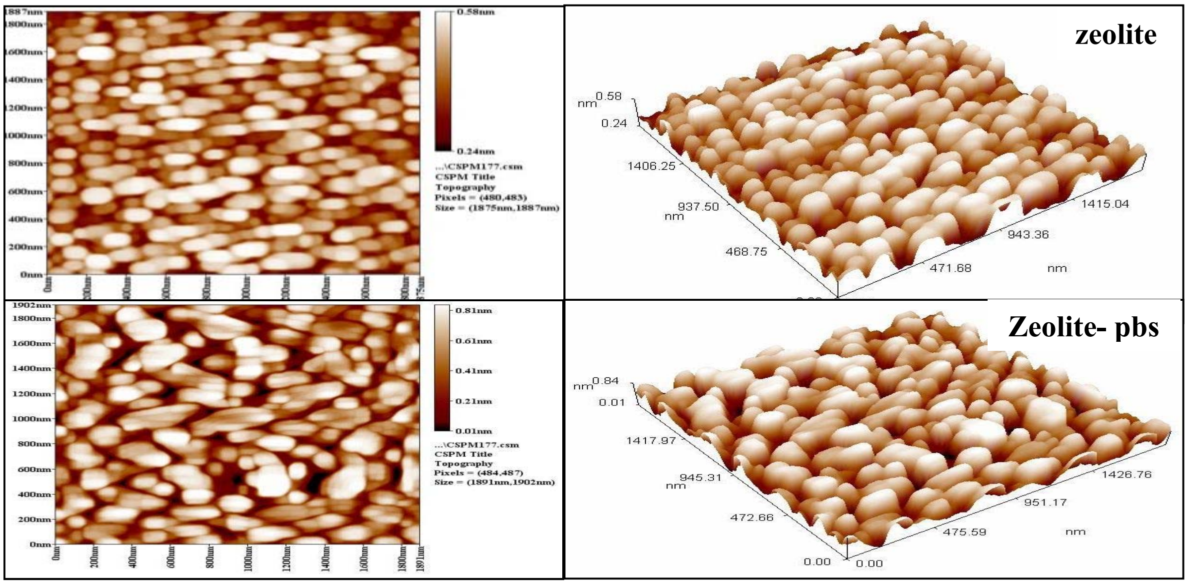

Figure No. (4): AFM image of zeolite ,zeolite-PbS

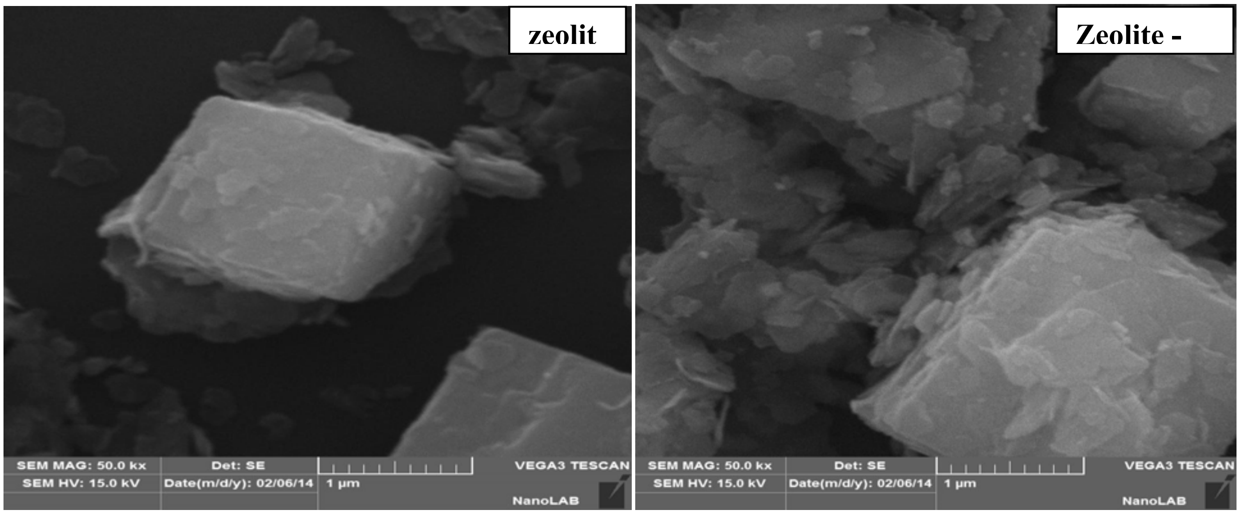

Figure No. (5): SEM image of zeolite, zeolite-PbS

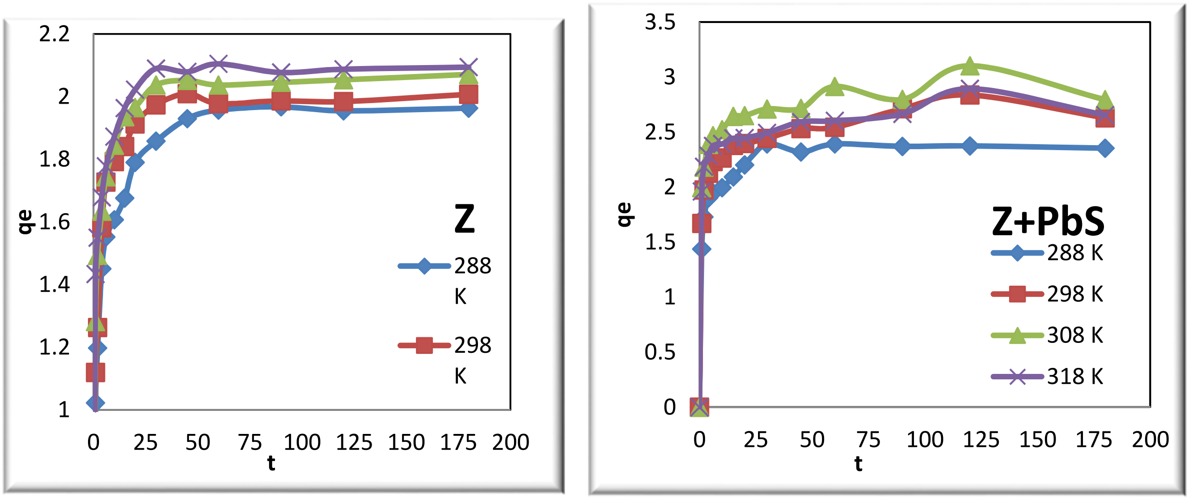

Figure No. (6): Effect of contact time on the removal of (CR) by zeolite and zeolite - PbS at different temperatures

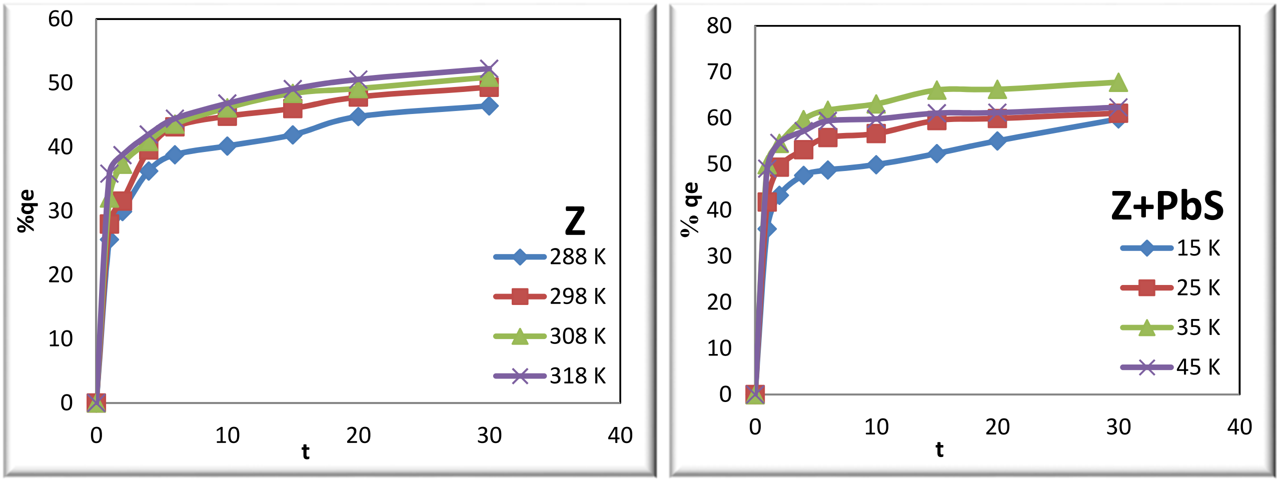

Figure No.(7): Effect of contact time on the percentage removal of (CR) by zeolite and zeolite – PbSat different temperatures

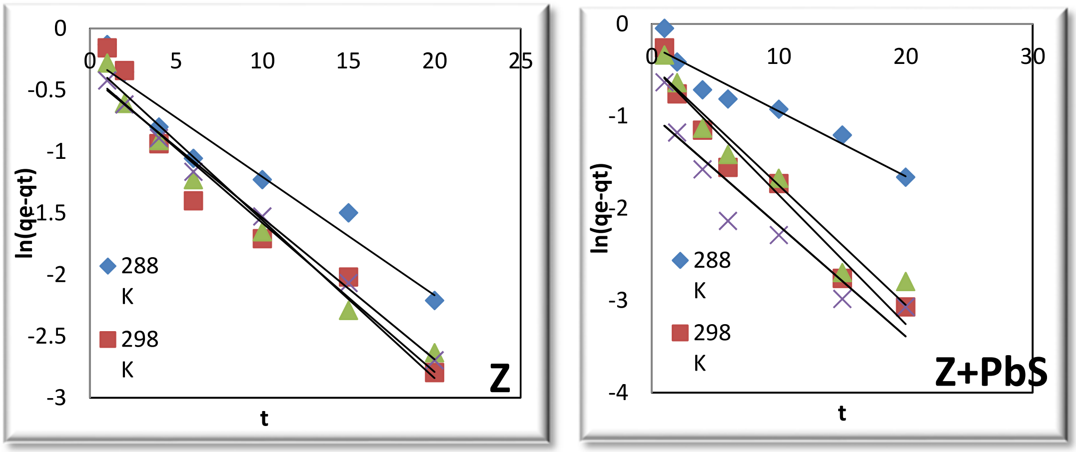

Figure No. (8): the applicability of the first order kinetic model to (CR) dye adsorption on zeolite , zeolite – PbS

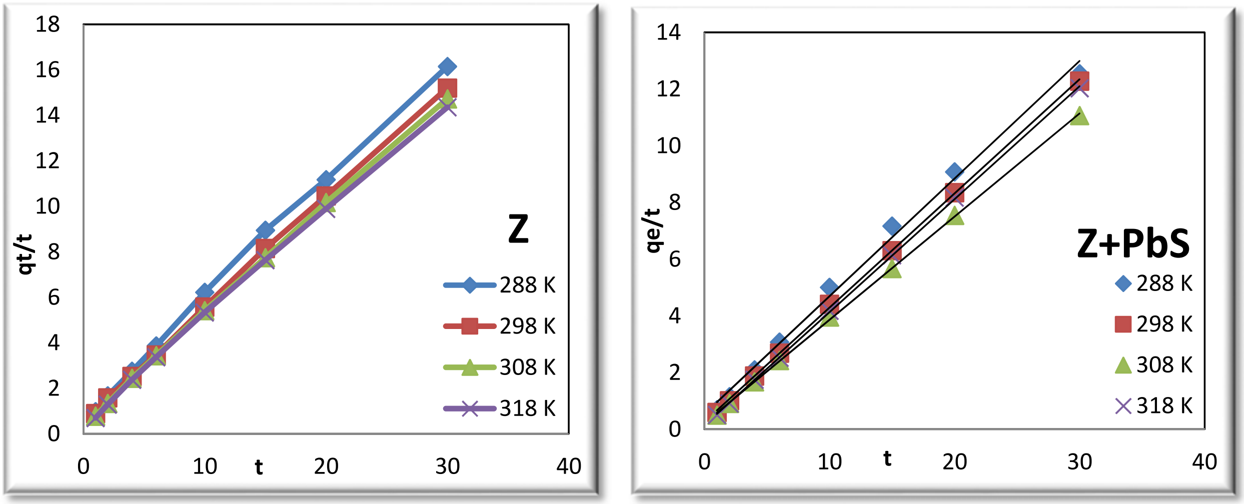

Figure No .(9): The applicability of the second order kinetic model to (CR) dye adsorption on zeolite and zeolite – PbS

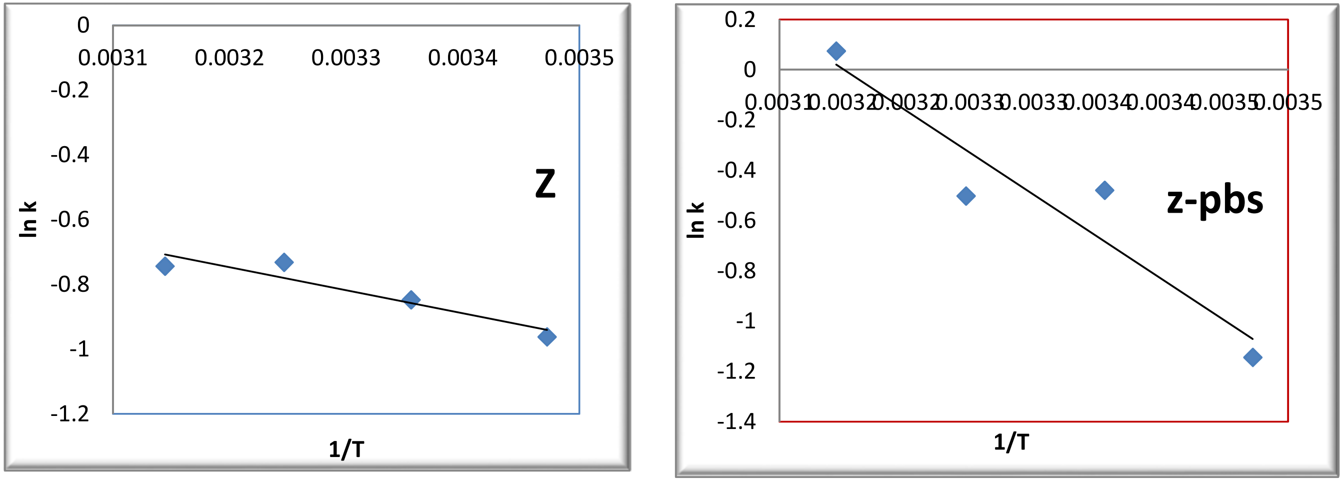

Figure No.(10): Relationship for Arrhenius equation to calculate the activation energy for pseudo second order reaction by effect of temperature at pH of 7

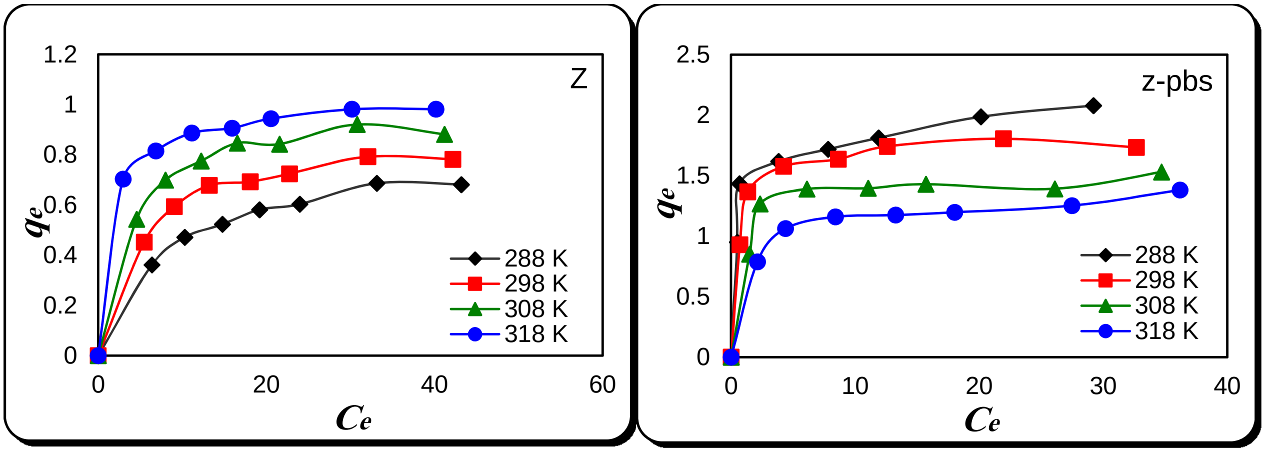

Figure No.(11): Adsorption isotherms of (CR) dye on zeolite and zeolite-pbs at different temperatures

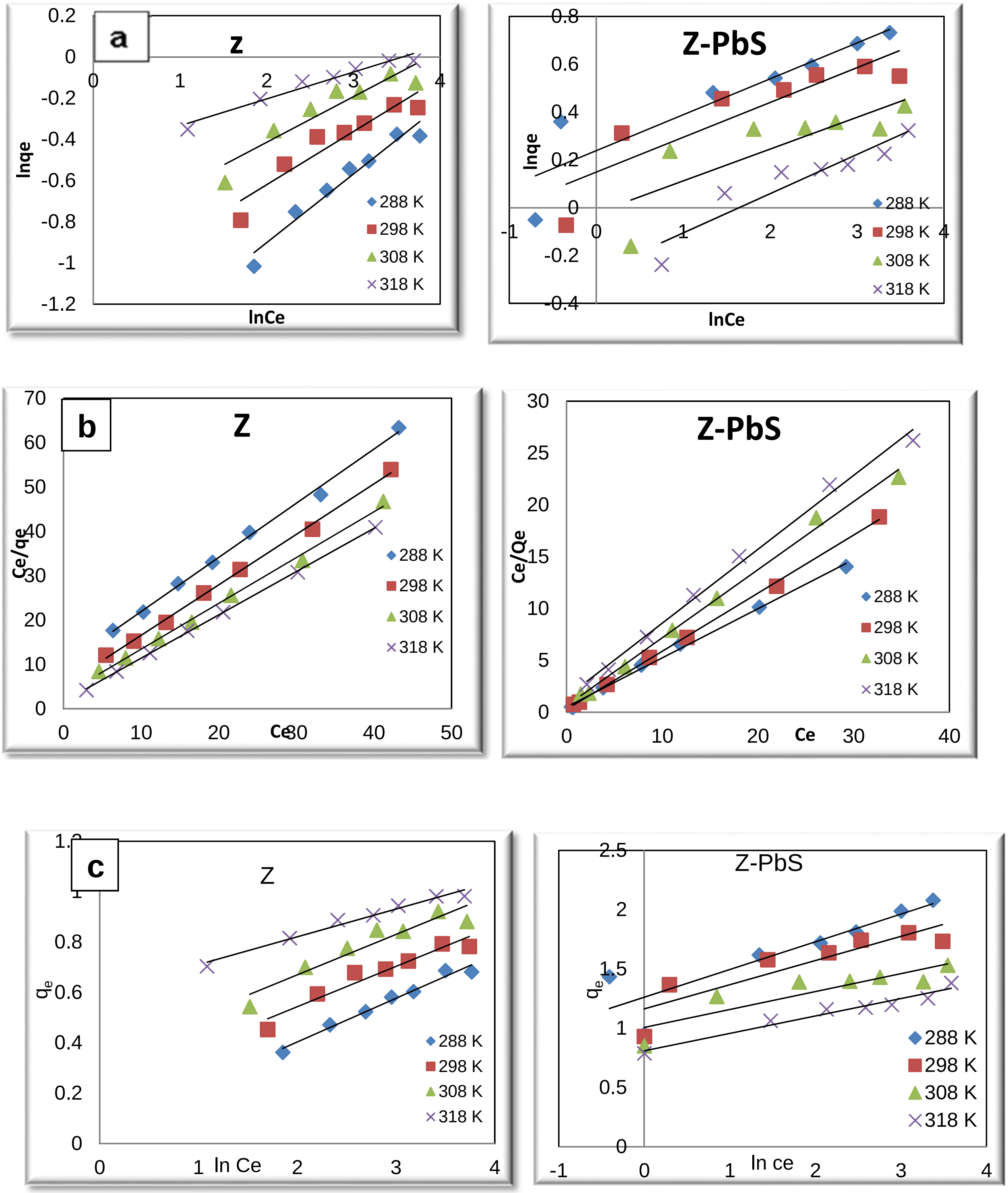

Figure No.(12): isotherm models of (CR) adsorption on zeolite ,zeolite –pbs : a- Freundlich model, b- Langmuir model, c- Temkin model at different temperatures

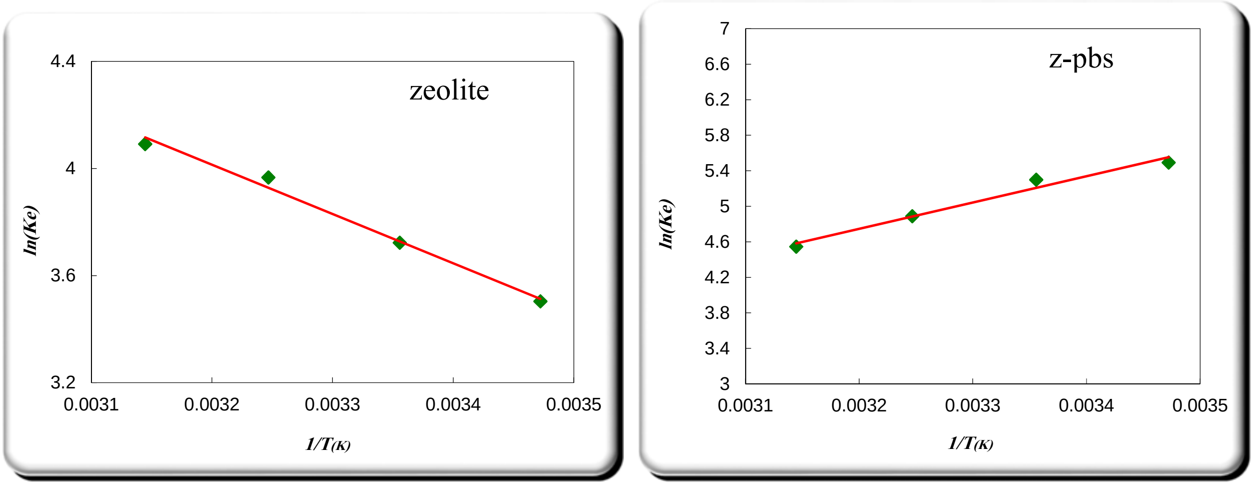

Figure No. (13): Plot of ln K_e against reciprocal absolute temperature for adsorption of (CR) dye on zeolite and zeolite-pbs

دراسة حركية وثرموديناميكية امتزاز صبغة الكونغو الأحمر على الزيولايت الصناعي والزيولايت الصناعي المعدل

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الخلاصة

عدل الزيولايت من نوع ليندا A من خلال اضافة كبريتيد الرصاص الى فجوات الزيولايت وتم تشخيص كل من الزيولايت والزيولايت المعدل بواسطة مطيافية الاشعة تحت الحمراء FTIR والاشعة السينية XRD ومجهر الماسح الالكتروني SEM ومجهر القوى الذرية AFM. درس في هذا البحث امتزاز صبغة الكونغو الاحمر من محلولها المائي بواسطة الزيولايت والزيولايت المعدل بكبريتيد الرصاص درست عن طريق عدة عوامل مثل زمن الاتزان , درجة الحرارة و التركيز الابتدائي لصبغة الكونعو الاحمر . وبينت النتائج ان زمن الاتزان هو 45 و30 دقيقة لاعظم امتزاز للكونغو الاحمر على الزيولايت والزيولايت المعدل تواليا . حللت البيانات الحركية بواسطة انماط حركية من المرتبة الاولى الوهمية والمرتبة الثانية الوهمية أذ بينت حركية امتزاز الكونغو الاحمر تتبع المرتبة الثاتية الوهمية على كلا السطحين المازين .حللت بيانات التوازن لامتزاز الكونغو الاحمر لكلا السطحين حللت بواسطة موديلات فريندليش و لانكماير وتمكين , الدوال الثرموديناميكة المحسوبة (ΔS, ΔH, ΔG) للامتزاز على الزيولايت تبين انه تلقائي وماص وغير منتظم تحت ظروف الدراسة والامتزاز على الزيولايت المعدل تبين انه تلقائي وباعث واكثر انتظاما .بينت نتائج معامل الارتباط R^2 وتحليل الاخطاء ان موديل لانكماير هو افضل ايزوثيرم مطبق لهذه الدراسة وذلك بحسب الترتيب الأتي:
لانكماير > تمكين > فريندليش.

الكلمات المفتاحية :الامتزاز , ايزوثيرمات الامتزاز , المازات المعد لة , ثرموديناميكية , حركيات , تحليل الاخطاء .