Kinetic Study of Adsorption of Azo Dye from Aqueous Solutions by Zeolite and Modified Synthetic Zeolite

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Abstract

Based on the porous structure of the Zeolite type Linde A, it was modified by the dimercaptothiadiazole lead compound (PbDMT). The detection of these changes on zeolite was characterization by using the techniques (FT-IR, XRD, AFM and SEM). The study of adsorption of the Congo red dye from its aqueous solutions on both surfaces adsorbents before and after modification (Zeolite , Zeolite - PbDMT) through Several factors (contact time, temperature and concentration of Congo red dye (CR). The kinetic results of the Congo red adsorption process showed that the equilibrium time at which the maximum value of adsorption of the Congo red dye was for each of the two surfaces adsorbents respectively. More than one kinetic model was applied to the experiments values. The results showed fit applied on pseudo second order equation for both surfaces adsorbents studied

1. Introduction

Waste disposal in the environment is a complex world problem focused on by various environmental organizations. These wastes are organic compounds which are used and widely used in various industries for coloring their products such as plastics, textiles, cosmetic, rubber, paper, etc.,. In these industries, their residues are left in the form of waste and dyes due to their chemical structures and as a result they are resistant to fading despite exposure to light, water and many chemicals. Thus, it is difficult to decolorize once released into the aquatic environment [1]. Most of these dyes represent acute problems of the ecosystem because they are toxic and have carcinogenic properties, making water inhibitory for aquatic life, due to chemical composition [2]. Synthetic dyes have many structural varieties, such as acidic, essential, dispersing, azo, diazo, anthroquinone-based and complex mineral dyes, which are located in either caustic, non-ionic or anionic type. Direct ionic dyes, the most problematic of acid-soluble water and interactive dyes [3].

The anionic dye, Congo red (Figure 1), the chemical formula of Congo red is $C_{33}H_{22}N_6Na_2O_6S_2$.Congo red is a diazo dye and is prepared by coupling tetrazotised benzidine with two molecules of napthionic acid. The IUPAC name of Congo red is [1-naphthalene sulfonic acid, 3,3′-(4,4′-biphenylenebis (azo))bis(4-amino-)disodium salt].Congo red contains NH_2 and SO_3 functional groups. The maximum absorbance of Congo red on a UV-vis spectrophotometer is recorded at 498nm [4,5]
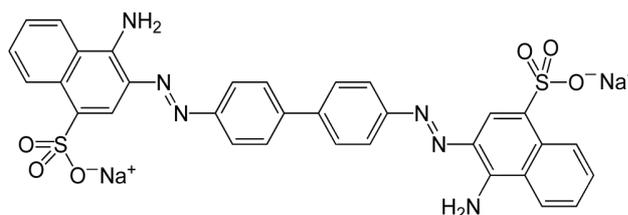

Figure 1: Structure of (CR) dye

There are various conventional methods of removing dyes including coagulation and flocculation, oxidation or ozonation and membrane separation [1] . However, these methods are not widely used due to their high cost and economic disadvantage.In contrast, an adsorption technique is by far the most versatile and widely used. The most common adsorbent materials are: zeolite metal hydroxides and activated carbon [6]. As proved by many researchers, removal of dyes by zeolite is economically favorable and technically easier. Zeolite is widely used as an adsorbent due to its high adsorption capacity, high surface area, microporous structure, and high degree of surface [6,7]. The aim of this work is to modify of zeolite and characterization applying for cong red adsorption under several conditions.Also, several kinatic models were aplied in order to specify the appropriate model that can describe the experimental data well.

2. Material and Methods
2.1 Materials
Hydrazine hydrate (Fluka / UK) (M.wt: 50.06 g mol^{-1}) , HCl (BDH/UK) (M.wt: 36.46 g mol^{-1}) , Potassium hydroxide (BDH/UK) (M.wt: 56.1g mol^{-1}), Carbon disulfide (Merck / UK) (M.wt: 76.139 g mol^{-1}) ,lead nitrate (BDH / UK) (M.wt: 331.2 g mol^{-1}) , congo red (BDH / UK) (M.wt: 696.66 g mol^{-1}), synthetic zeolite 5A (Petroleum Research & Development Center / Iraq) **.** The composition of Zeolite 5A mineral is: SiO$_2$ (32.52), Al$_2$O$_3$ (27.64) , Na$_2$O (4.20) , CaO (11.38) , L.O.I.(99.99).

2.2.Methods
2.2.1 Preparation of 2,5 – Dimercapto-1,3,4-thiadiazole (DMT) [8].
2, 5- Dimercapto-1,3,4-thiadiazole or (DMT) , M.wt (150) g/mole , M.P (162-164) and the chemical structure as shown in (Figure 2).
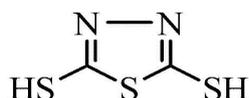
Figure 2: Chemical structure of DMT compound

This compound was prepared by the addition (5 g. 0.2 mol) hydrazine hydrate   to (11.2g .0.2 mol) of KOH dissolved in 25 ml. abs. ethanol,after that carbon disulphide (16 g) was added drop by drop. The resulting mixture was heated under reflux for 6 hours in order to relase of H$_2$S gas which was formed. The reaction mixture was allowed to cool down at room temperature and then filtered. The fitrate was added to ice-water and made acidification by adding HCl (10 %) dilute solution. The resulting solid was filtered and washed with hot ethanol to give pale yellow precipitate. The crude product was dried to give the desired product as yellow needles , yield (65%) , m.p(168-170)^{o} C.

2.2.2 Preparation of modified Zeolite by Lead Dimercapto-thiadiazole (PbDMT) complex
The synthetic zeolite was washed with excessive amounts of distilled water, dried at 160° C 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 a suspension solution of salt with continued stirring (Centrifuge tubes. Hettich (EBA-20) / UK) for half hr .The soloist was separated from the mixture by decantation, washed about seven times with distilled water, and dried in an oven (Labeich /Korea) at a temperature of 60 ^{o}C for 2 hours. Then the dry zeolite was added to (200 mL) of absolute ethanol with continuous stirring for 10 minute Then added a certain amount of DMT compound to suspension solution of zeolite + Pb with continuous stirring (QA9010X - Hot Plate Stirrer, Ceramic Surface) for half hrThe zeolite +PbDMT complex was separated from the mixture by filteration, and dried in an oven (Daihan Labtech Oven LDO - 060E/ Korea) at a temperature of 60 ^{o}C for 2 hours.

2.3 Adsorption experiments
2.3.1 Effect of adsorbent weight change
The effect of adsorbent weight change on adsorption was studied in this work by using a fixed concentration (40mg.L^{-1}) of (CR) dye with different weights for all adsorbents (0.01, 0.03, 0.05, 0.07, 0.10, 0.13and 0.15) g.

2.3.2 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, 180 min) at initial (CR) concentration of 40 mg/l. This was done by contacting 0.1g of each adsorbent with 10 ml of (CR) dye solution within range temperatures (288,298, 308, 318) K at pH 7 and uniform particle size ($\leq$ 150 μm)

Wavelength of maximum absorbency (λ_{max}) was found 498 nm for CR dye by using (Uv-Visible spectrophotometer double beam (shimadzu UV-1800)/ Japan)) .The contents were shaken (Labtech shaking water bath) by using shaker with a speed of (120 rmp) 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. The quantity of dye adsorbed can be calculated by using the following equation [9]:

$$q_e = \frac{(C\circ - C_e)V}{m} \qquad (1)$$

m: weight of adsorbent (g). C_o: initial concentration (mg.L^{-1}). C_e: equilibrium concentration (mg.L^{-1}). V : volume of solution (L). The percentage adsorption of dye on zeolite and modified zeolite was calculated using the equation :

$$Adsorption \% = \frac{(C\circ - C_e)}{C\circ} \times 100 \quad (2)$$

3. Results and discussion
3.1 Characterization of zeolite and modified zeolite
(Figure 3 – zeolite) XRD pattern (XRD-6000 shimadzu / Japan) of LTA zeolite before modified is shown high purity and a good crystallinity of zeolite. These results are in good agreement with those reported in the literature [10]. (Figure 3 –Zeolite-pbDMT) XRD pattern of LTA zeolite after modified showed that there are no changes in the positions of the diffraction peaks of zeolite A (Figure 3-pbDMT)after loading of lead Dimercapto thiadiazole cluster into the framework voids(Figure 3 – Zeolite-pbDMT). 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 Dimercapto thiadiazole cluster on the zeolite framework atoms (Al, Si, O) and compensating sodium and calcium ions[11].
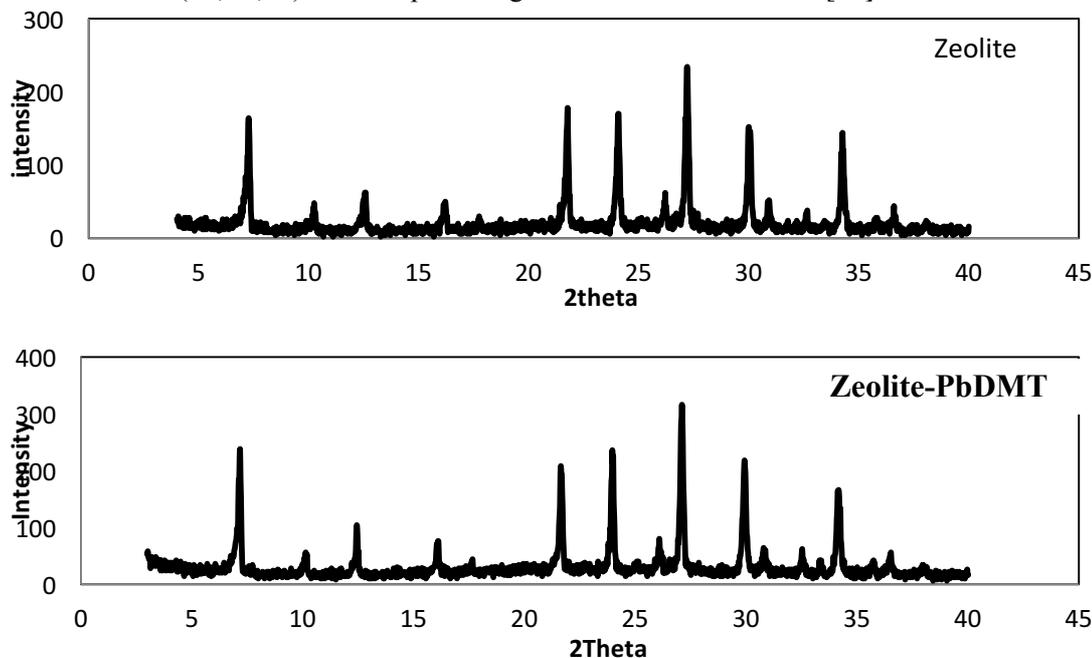

Figure 3: X-ray diffraction of zeolite and zeolite-PbDMT

(Figure 4-zeolite) FT-IR spectra (Shimadzu. iraffinity-1 (8400 s) / Japan) 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 (Al,Si)-O species [12] .due to porous anfd internal structure of zeolite the peaks at 403.cm^{-1} are assigned to the structure internal ((Al,Si)-O4) tetrahedral bending peaks of zeolite A . 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 [10]. (Figure 4- zeolite-pbDMT) FT-IR spectra of LTA zeolite modified by PbDMT shows agreement with XRD results.
The AFM images (SPM AA3000 Atomic force microscope / USA) (in two and three-dimensional) for the synthetic zeolite and pbDMT- Zeolite in (Figure 5) . it shows that the diameter of the particles for zeolite (95

nm) and for pbDMT – zeolite (79.27 nm) ,the average particle size for zeolite was (0.58 nm) and for the pbDMT – zeolite (2.64 nm) . This result indicates that average particle size for pbDMT - zeolite greater then zeolite
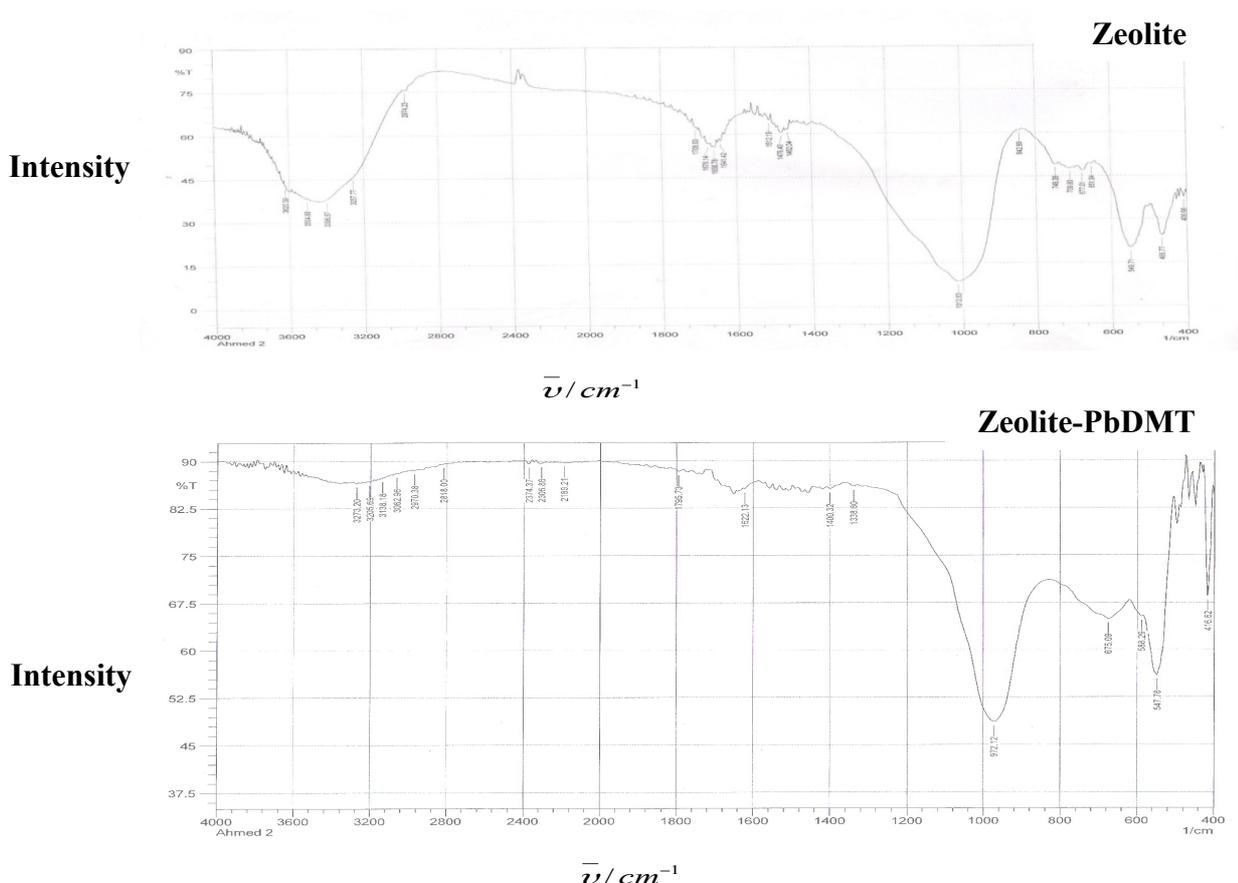

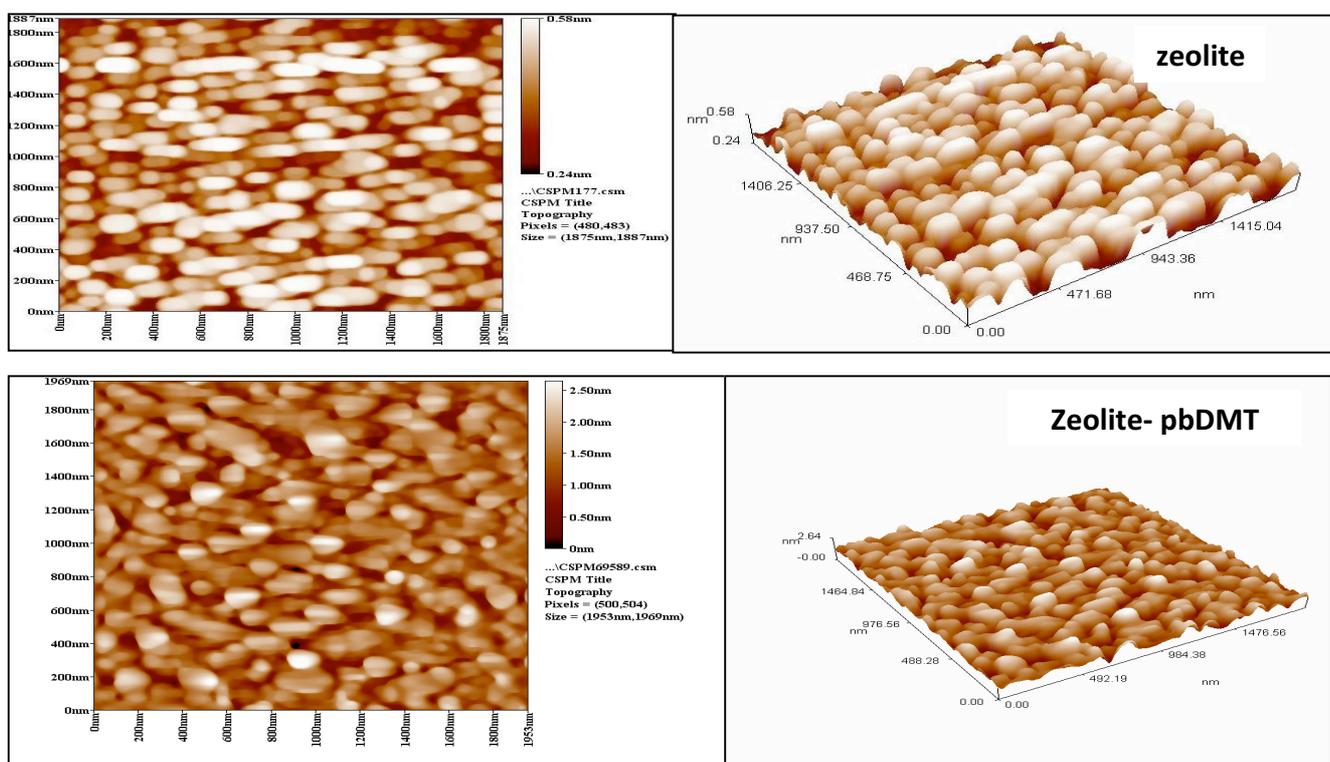**Figure 4:** FT-IR spectra of zeolite and zeolite-PbDMT

Figure 5: AFM image of zeolite and zeolite-PbDMT

(Figure 6-zeolite) shows the SEM image (SEM-- T-Scan ,Vega-111/ Czech), of zeolite and pbDMT - 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 6-zeolite- pbDMT) shows the changes on the surface of the pbDMT - zeolite up to 500 nm and this indicates on pbDMT cluster from pores to zeolite surface**.**
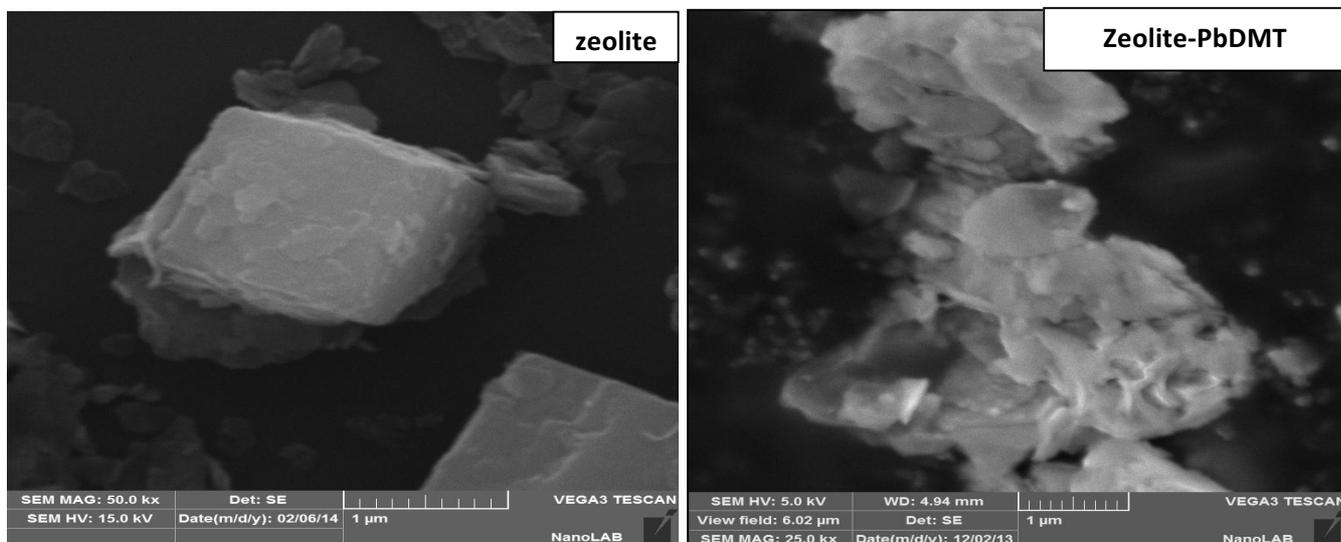

Figure 6: SEM image of zeolite and zeolite-DMT

3.2 Effect of the adsorbent weight change

The study aimed to find adsorbent amount which is required to attain surface saturation at certain conditions. The experiments were carried out as in (3-a) and the results are presented in (Figure 7).

Figure 7 shows the plateau region at (0.1g) which represents the amount of the zeolite and modified zeolite adsorbents at the saturation stage. As seen in (Figure 7) ,the curves approach the plateau region with the increase of the adsorbent weight,due to the increase of adsorption sites available when more adsorbent is used which in other words is due to the greater availability of the exchangeable sites or surface area of the adsorbent [13]. As the concentration of the (CR) dye is constant, the increase of the dose of the adsorbent increases the surface area for adsorption. Since the adsorbent particle size is almost constant, the surface area will be directly proportional to the dose of the adsorbent in the system[14].This valueof plateau represents the amount of the adsorbents at saturation stage. The plateau values for all adsorbents in this study were (0.1g) .
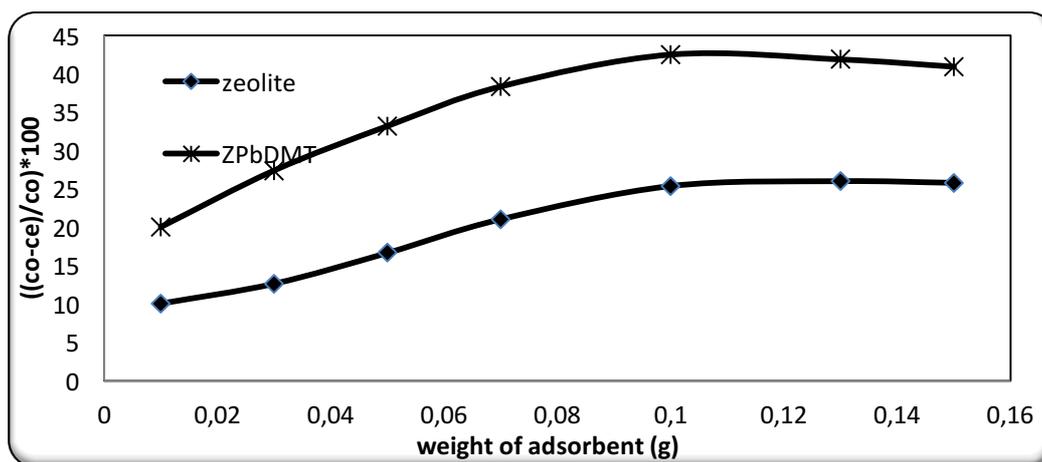

Figure 7. Effect of the adsorbent weight on adsorption of (CR) dye on the zeolite and modified zeolite on different weights at 298 K.

3.3 Effect contact time

The adsorption of (CR) dye on zeolite and modified zeolite was studied as a function of contact time, and draw $q_e$versus t in (Figure 8) at different temperatures. from (Figure 8) is 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 20 min respectively which 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 (CR) dye uptake by is observed [15], result of the percentage adsorption of dye on zeolite and modified zeolite were calculated using the equation (2), (Figure 9) shows nearly 40-52%, 50-65% of This percentages adsorption of congo red on zeolite and modified zeolite at 45 and 20 min respectively within range of temperatures (288, 298, 308, 318) K.
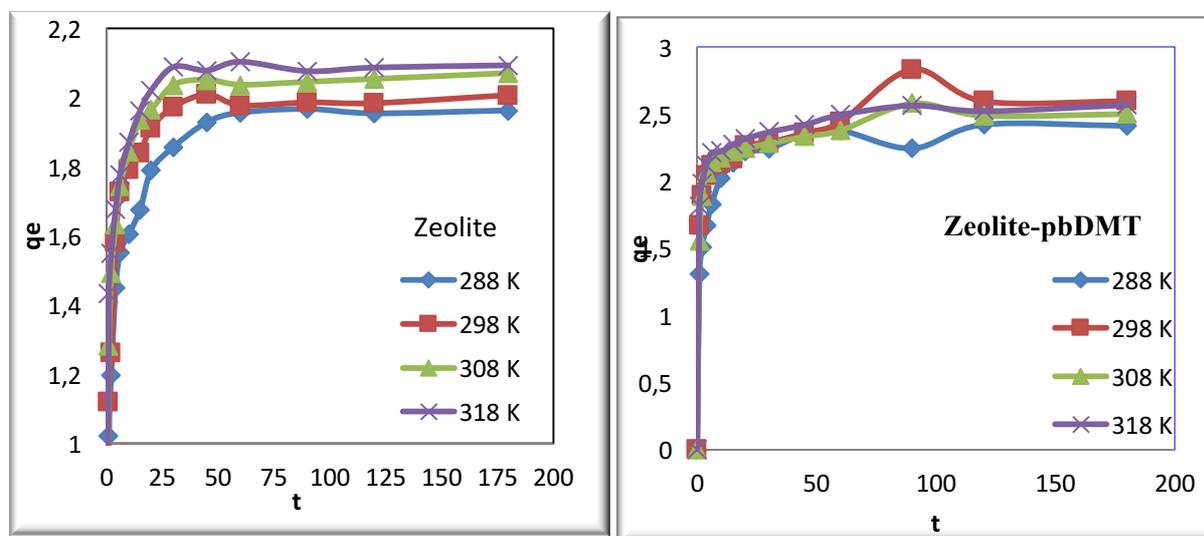

Figure 8 : Effect of contact time on the removal of (CR) by zeolite and zeolite - PbDMT at different temperatures
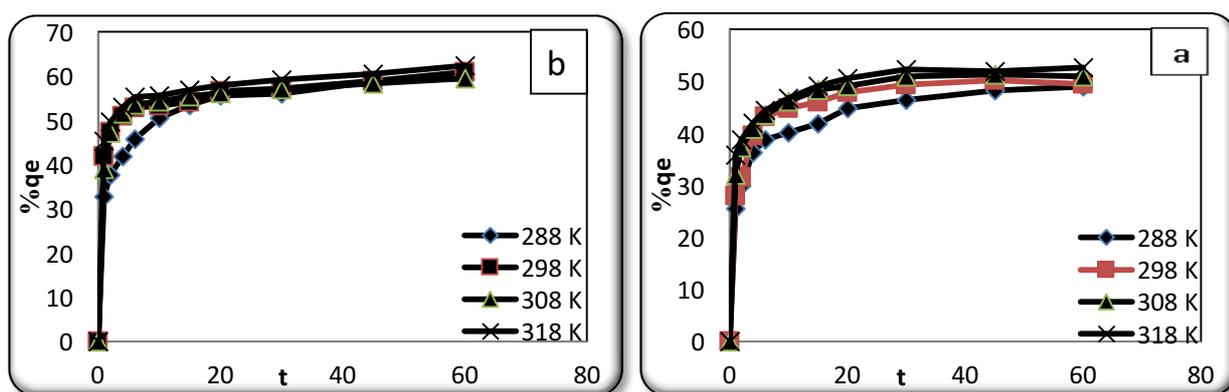

Figure 9: Effect of contact time on the removal of (CR) dye by: a- zeolite b- Zeolite-PbDMT at different temperatures

3.4 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.

Pseudo- first order model

The pseudo first order model was described by lagergren [16],

$$\ln(q_e - q_t) = ln \, q_e - (K_1)t \quad (3)$$

where q_e and q_t are the amount of (CR) dye adsorbed mg.g^{-1} at equilibrium and at any time t respectively and k_1 (min^{-1}) is the adsorption rate constant of pseudo first order equation. The plot of ln (q_e- q_t) against t should give linear relationship from which the value of k_1, 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 10).
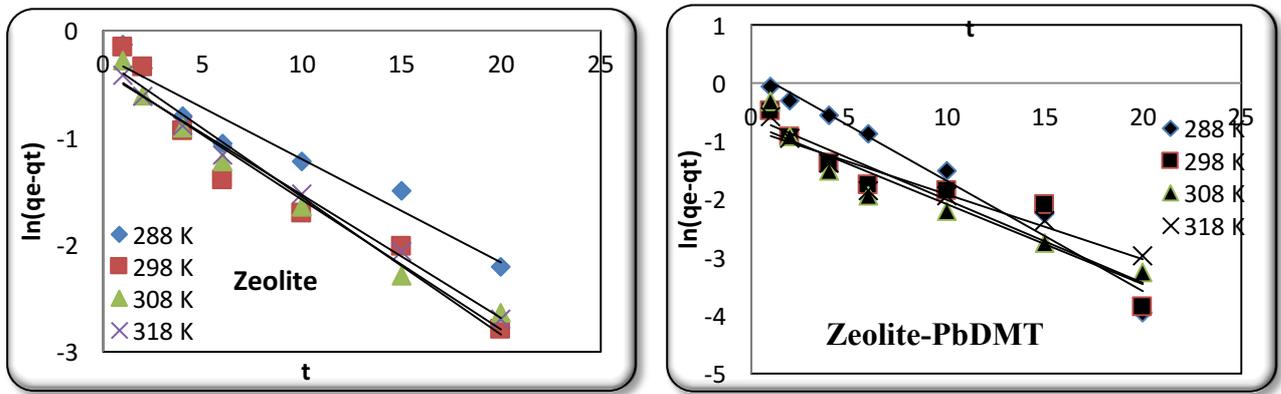
Figure 10. The applicability of the first order kinetic model to (CR) dye adsorption on zeolite and zeolite – PbDMT

Table 1. Adsorption kinetics parameters of pseudo-first order of (CR) dye on zeolite and zeolite – PbDMT

adsorbent	288 K			298 K		
	Pseudo-first order			*Pseudo-first order*		
	$k_1(min^{-1})$	$q_e(mg.g^{-1})$	R^2	$k_1(min^{-1})$	$q_e(mg.g^{-1})$	R^2
Zeolite	0.094	0.786	0.941	0.128	0.762	0.942
Zeolite - pbDMT	0.189	1.231	0.968	0.143	0.558	0.884
adsorbent	308 K			318 K		
	Pseudo-first order			*Pseudo-first order*		
	$k_1(min^{-1})$	$q_e(mg.g^{-1})$	R^2	$k_1(min^{-1})$	$q_e(mg.g^{-1})$	R^2
Zeolite	0.121	0.692	0.976	0.115	0.685	0.995
Zeolite - pbDMT	0.137	0.493	0.910	0.112	0.450	0.927

Pseudo -second order model

The pseudo-second order model is represented by the following differential equation **[17]**

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}(t)(4)$$

Where k_2 is the equilibrium rate constant of pseudo- second order adsorption (g/ mg.min), The initial adsorption rate, h (mg/ g.min) is expressed,by the following equation:

$$h = K_2 q_e^2 (5)$$

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 (Table 2, Figure 11).
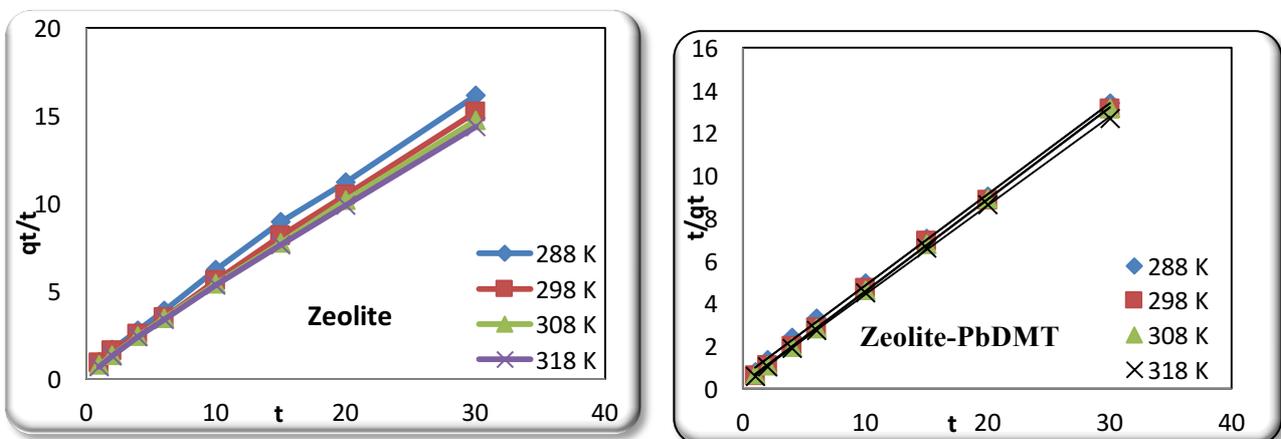

Figure 11: The applicability of the second order kinetic model to (CR) dye adsorption on zeolite and zeolite – PbDMT

Table 2: Adsorption kinetics parameters of pseudo-second order of (CR) dyeon zeolite and zeolite – PbDMT

| 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} .$min^{-1})in^{-1}$)	q_e (mg/g)	R^2	h (mg. g^{-1} .min^{-1-1})
Zeolite	0.382	1.912	0.988	1.397	0.428	2.033	0.999	1.770
Zeolite -pbDMT	0.330	2.336	0.999	1.802	0.734	2.320	0.999	3.953
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	0.847	1.569	0.999	2.088	1.361	1.259	0.998	2.160
Zeolite -pbDMT	0.829	2.315	0.999	4.444	0.820	2.392	0.999	4.695

This model confirms that the adsorption of (CR) dye on the zeolite and modified zeolite follows the pseudo second order model.

Conclusion

From this study we concluded main two points :
1- The modified zeolite have a high ability for CR dye adsorption from aqueous solutions larger than unmodified zeolite .
2- Adsorption of CR dye on zeolite and modified zeolite using batch method obey pseudo - second order equation with good correlation.

References
1- C. R. B.Tharcila, C. I. Juliana, P. M. Carina, A. F. Denise, *J .Orbital: Electron. Chem.* 5 (2013) 179-191.
2- R. V. Kandisa, N. Saibaba, K. B. Shaik , R .Gopinath, *J .Bioremediat .Biodegrad* , 7 (2016) 1-4.
3- T.Robinson, G.McMullan, R. Marchant , P. Nigam, *J. Biores*. Tech., 77 (2001) 247-255.
4- V. Vimonses, S .Lei, B. Jin, C . W. K. Chow, C. Saint , *J. Chem. Eng.,* 148 (2009) 354-364.
5- M. K .Purkait, A .Maiti , S .DasGupta , S .De , *J. Hazard. Mater.*, 145 (2007) 289-295 .
6- Z .Asku, S .Tezar, *Pro. Biochemistry*, 40 (2005) 1349-1361.
7- C. F. Iscen, I .Kiran, S .Ilhan, *J. Hazard. Mater.*, 143(2002) 335-338 .
8- O. S. Amodu, T. V. Ojumu1, S.K. Ntwampe, O. S. Ayanda, *J. Encapsulation. Adsorption Sciences*, 5 (2015) 191-203.
9- M. Belhachemi, F. Addoun , *Desalination and Water Treatment* ., 37(2012) 122-129.
10- J. Kugbe, N .Matsue, T .Henmi, *J. Hazard. Mater.*, 164 (2009) 929-935.
11. M.M.J .Treacy, J.B. Higgins, Collection of simulated XRD powder patterns for zeolites, Elsevier, Amsterdam (2001) 212.
12- M. Lamia, D. Fatiha, B. kara , D.Ayada, *J. Orient. Chem.,* 32 (2016)171-180.
13- T. A. Waly, A. M. Dakroury, G .O. El-sayed, S. A. El-salam, *J. American Sci.*, 6 (2010) 910-917.
14- M .Mincea, V. Patrulea, A .Negrulescu, R. Szabo, V. Ostafe, *J. Water Resource. Protection*, 5 (2013) 446-457.
15- A.M. Abbas, Y. I. Mohammed, T. A.Himdan, *J. Ibn Al-Haitham for Pure & Appl. Sci*, 28 (2015) 52-68.
16- C. Namasivayama, N. Kanchana., *Chemosphere*, 25 (1992) 1691.
17- Y.S. Ho, G. Mckay, *J. Chem. Eng.*, 70 (1998) 115.

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