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Evaluation of Jordanian treated natural zeolite for the uptake of p-nitrophenol from wastewater by continuous column method

Hutaf M. Baker

Faculty of Science, Department of Chemistry, Al al-Bayt University, P.O. BOX 130091, Mafraq 25113, Jordan
Tel. +962 2 6297000; email: hutafb@aabu.edu.jo
Faculty of Art and Science, Department of Chemistry, Petra University, Amman, Jordan

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ABSTRACT

In this study, removal of p-nitrophenol (PNP) onto Jordanian zeolite was investigated. The surface of the calcinated zeolite (CZ) was modified using urea (CZU) and thiourea (CZT). The experiments of the removal were carried out under different operating conditions in column reactor. A pseudo-second-order, intraparticle diffusion, and Elovich kinetic models were investigated to predict the rate constants and equilibrium capacities for this process. The results showed that the removal of PNP highly fitted the pseudo-second-order for the three adsorbents which provides the best correlation of the experimental data. The activation energies were calculated using the rate constants of the pseudo-second-order kinetic model, the Ea values for CZU, and CZT were found to be small, since the process is an exothermic one, which may be as physical and chemisorptions.

Keywords: p-Nitrophenol; Zeolite; Column; Kinetics

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1. Introduction

Water pollution represents a real danger to the environment and consequently to man. This pollution is primarily due to industrial wastes. The p-nitrophenolic compounds are common pollutant substances, which are a serious problem in many countries. The major sources of p-nitrophenolic wastes are petroleum refineries, petrochemical, steel mills, coal gas, synthetic resins, pharmaceuticals, paints, and mine discharge. p-nitrophenolic waste imparts a carbolic odor to river water and it is toxic to fish and human. They are considered as one of the main pollutants in wastewater, because they are harmful to organisms even at low concentrations. Many p-nitrophenols have been classified as hazardous pollutants due to their potential toxicity to human health. There are several methods for the removal of p-nitrophenol from aqueous solutions, such as adsorption, ion exchange, membrane processes, chemical oxidation, precipitation, distillation, gas-stripping, solvent extraction, complexation, and bioremediation. Adsorption is the most popular method in which activated carbon or ion exchange resins are usually applied. This method has been recommended by the USEPA as one of the best available technologies for the removal of organic compounds, however it is highly expensive and many in which developing countries like Jordan can not afford. In recent years, there has been a continuous search for locally available and cheaper adsorbents to replace activated carbon for the removal of a variety of organic compounds such as p-nitrophenol [1–3]. In wastewater treatment, zeolite is commonly applied as an adsorbent, ion exchanger, or molecular sieve medium. Due to its abundance and inexpensive cost, a great deal of research has been performed on this species of natural zeolite which is known as clinoptilolite. Several studies reported that zeolites are good adsorbent for p-nitrophenolic compound [4–9]. It was reported that the concentration of p-nitrophenolic compounds in wastewater from resin plants is typically in the range of 12–300 mg/L and the highest concentration of p-nitrophenol (>1,000 mg/L) in wastewater is typically generated from coke processing [1].

The total p-nitrophenol concentration in the wastewater of a typical Jordanian refinery processing three million tons of crude per year is around ~85 mg/L.

In this study, the Jordanian zeolite was used after modification by calcinations at high temperature then treating with urea and thiourea, which is known to have a strong affinity towards p-nitrophenolic compounds. The characterization of Jordanian zeolite such as XRD, XRF, SEM, and the cation exchange capacity were done previously [6,8,10]. Continuous column technique was used to study the effect of many variables. Obtained data were treated using different kinetic models.

1.1. Adsorption kinetics

Several kinetic models are used to examine the rate of the adsorption process and the potential rate-controlling step. In the present work, kinetic data obtained from batch studies have been analyzed using pseudo-second-order, intraparticle diffusion, and Elovich kinetic models.

1.1.1. Pseudo-second-order model

The pseudo-second-order rate equation is expressed as follows:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \qquad (1)$$

where k_2 is the rate constant of pseudo-second-order sorption ($g\,mg^{-1}\,min^{-1}$), q and q_e are the amounts of solute sorbed at a given time and at equilibrium time ($mg\,g^{-1}$), respectively. Integration of Eq. (1) gives

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (2)$$

If the second-order kinetic equation is applicable, then a plot of t/q against t should give a linear relationship. The quantities q_e and k_2 can be determined from the slope and the intercept of the plot [6,11,12].

Herein, the initial sorption rate h is given by

$$h = k_2 q_e^2 \qquad (3)$$

1.1.2. Intraparticle diffusion

The possibility of intraparticle diffusion resistance affecting adsorption was explored using the intraparticle diffusion model. The intraparticle diffusion model [6,13,14] is expressed as

$$R = k_{id}(t)^a \qquad (4)$$

A linearized form of this equation is given by

$$\log R = \log k_{id} + \alpha \log(t) \qquad (5)$$

where R is the percentage of p-nitrophenol adsorbed, t is the contact time, α is the gradient of the linear plots, and k_{id} is the intraparticle diffusion rate constant.

1.1.3. Elovich model

The Elovich equation is another rate equation in which the absorbing surface is heterogeneous. It is given in the linearzed form by

$$q_t = \frac{1}{\beta}\ln(\delta\beta) + \frac{1}{\beta}\ln t \qquad (6)$$

where q_t is the adsorbed amount at time t, δ is the initial adsorption rate (mg/g min), and β is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg).

A plot of q_t vs. ln t gives straight line with slope of $(\frac{1}{\beta})$ and the intercept of $\frac{1}{\beta}\ln(\delta\beta)$ [6,15,16].

2. Experimental

2.1. Preparation of sorbent

The tuff samples of zeolite were supplied by the Jordanian Natural Resources Authority (JNRA). They were treated by washing them with deionized distilled water many times; the washed samples were air dried, these samples were calcinated in the range of 100–900°C for 8 h. Part of calcinated samples were treated with saturated solutions of urea and thiourea separately, that means three kinds of samples were prepared. Finally the different sorbents were crushed, then they were grounded and sieved to different particle size in average range of 63–350 μm.

2.2. Preparation of reactor column

The three sorbents CZ, CZT, and CZU were packed into separate glass columns of (20 cm × 1.4 cm id) were filled with 1,000 mg of selected sorbent, for all experiments buffer solutions were used in order to adjust the suitable pH, containers which contain the PNP solutions were placed at the top of the columns, the solution were passed through the column by gravity with flow rate 1 mL/ min using peristaltic pump. The eluates were collected by washing the sorbents with 30% of methanol; the absorbance of eluates was recorded at 403 nm. The following parameters were optimized during the study: contact time for time intervals of 5, 10, 15, 20, 25, 30,……1,440 min, solution pH in the range of 1–8, calcinations, particle size, solution temperature in the range of 25–65°C, and initial concentration of PNP in the range of 10–200 mg/L.

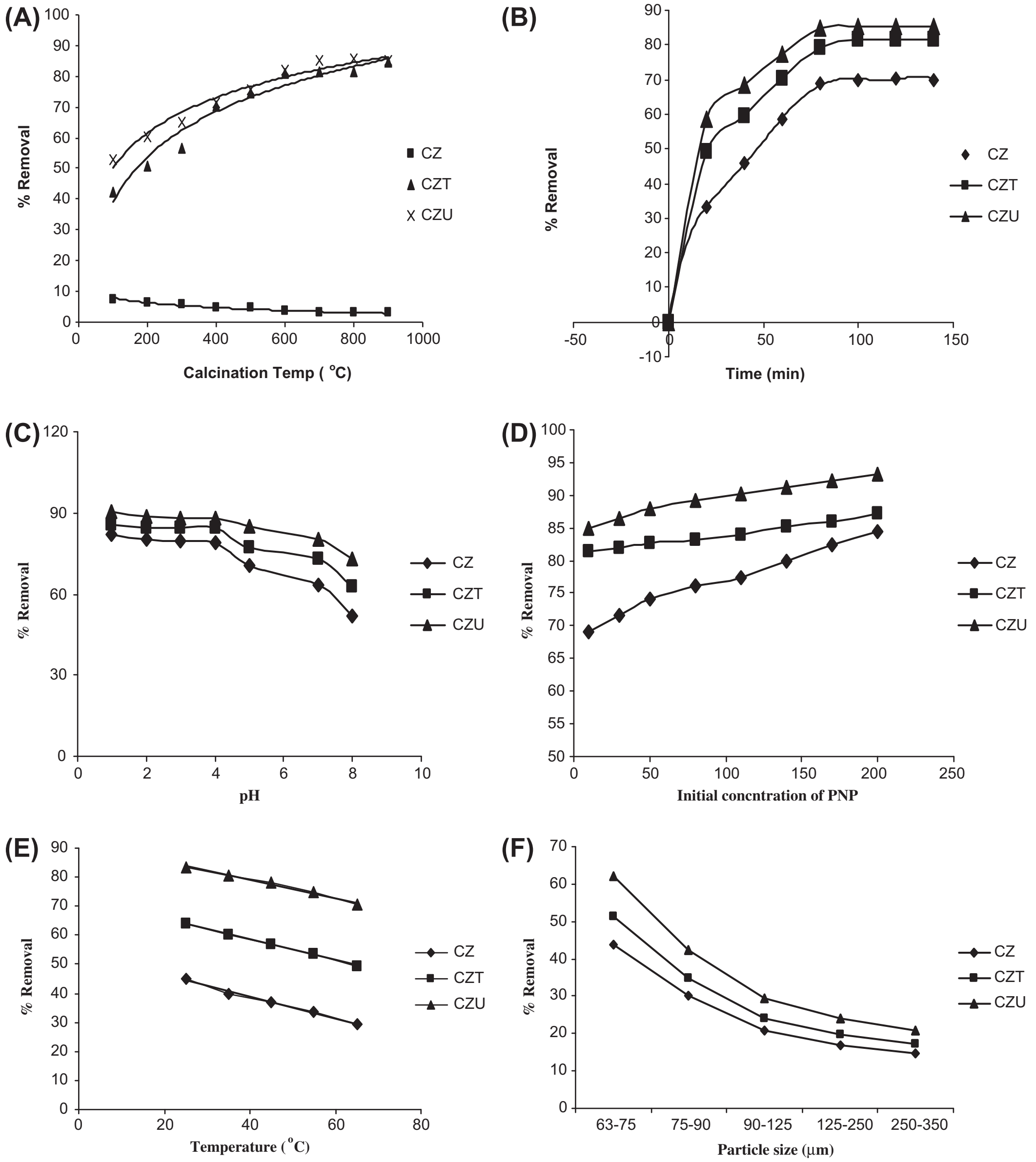

Fig. 1. Effect of different variables on the removal of phenol onto using CZ, CZT, and CZU. Conditions: particle size 63–75 μm, $C_0 = 10$ ppm, pH = 3.00, adsorbent dose 1 g/25 ml, and flow rate = 1 ml/minute. (A): Effect calcinations. (B): Effect of contact time. (C): Effect of pH. (D): Effect of initial concentration. (E): Effect of temperature, and (F): Effect of particle size.

2.3. Removal kinetics

Evaluation of adsorption kinetic of PNP by using the different sorbents was investigated; the same procedure in Section 2.2 was applied to study the kinetic of these reactions. The collection of eluates was done at different time intervals and different solution temperature by keeping the other variables of pH, calcinated temperature, particle size, and initial concentration of PNP constant, the optimum values of these parameters were used.

3. Results and discussion

3.1. p-nitrophenol removal in column

Experimental studies were conducted in column reactor to evaluate the effect of calcinations, contact time, solution pH, initial concentration, temperature, and particle size on the removal of PNP.

3.1.1. Effect of calcinations

From Fig. 1(A) it was seen that the removal of PNP increased by increasing the temperature of calcinations for CZT and CZU, but for CZ it seems that there is little effect of this parameter. The increasing of removal may be due to the change of the surface area, pore size distribution as well as the morphology of these materials. The calcinations lead to get of impurities which exist in the pores. It was noticed that the removal of PNP increases in the range of 100–600℃, after that the% removal remain constant [6]. All the other experiments were done at the optimum temperature which is 600℃.

3.1.2. Effect of contact time

The effect of contact time on PNP uptake using the three adsorbents was studied. As seen from Fig. 1(B), it is apparent that PNP uptake reached very rapid saturation after the initial 20 min for the three adsorbents, indicating fast kinetics, and fast diffusion into the intraparticle system to reach this rapid equilibrium, which may due to the availability of more rapid adsorption vacant sites at the initial stage. Also, it was noticed that there is no significant change for the removal after about 80 min for all adsorbents. It can be seen from Fig. 1(B), that the curves are single, smooth, and continuous leading to saturation, for that the possibility of the formation of monolayer coverage of PNP on the outer surfaces of the adsorbents [17] can be achieved.

3.1.3. Effect of pH

The effect of pH on the adsorption process is an important factor. It determines the charge of the adsorbent and degree of ionization of the adsorbate. The adsorption isotherms of PNP at different pH values are shown in Fig. 1(C). Fig. 1(C) shows that the amount of PNP adsorbed from aqueous solution is significantly high at pH values of 1–4 when compared to pH 8, pH 7, and pH 6, respectively. At low pH 1–4, the adsorption of PNP on CZ, CZT, and CZU increases rapidly, this may be attributed to substitution of nitro (NO_2) group, an electron-withdrawing group in the benzene ring. This NO_2 group substitution will enable the ring to withdraw more electrons from the oxygen atom thereby increasing the acid strength of PNP. In view of the increase in acidic strength of PNP, the PNP will rapidly adsorb on the negatively charged surface of adsorbent. At intermediate pH 5, there was a gradual decrease in the removal of PNP from aqueous solution onto zeolites [18]. This reduction of adsorption of PNP onto zeolites at intermediate pH 5 may be attributed to the reduction in acidic strength of PNP when compared to pH 3; the pKa of PNP is 7.12. All the other experiments were done at the optimum pH which is 3.

Table 1
Pseudo-second-order model for the removal of PNP aqueous solutions on CZ, CZT, and CZU at various temperatures

Samples	$q_{e,exp}$	K_2	R^2	q_{cal}	SSE%
25℃					
CZ	0.132	0.250	0.9988	0.137	2.678
CZT	0.228	0.250	0.9999	0.232	1.241
CZU	0.348	0.250	0.9999	0.351	0.610
35℃					
CZ	0.116	0.170	0.9949	0.122	3.657
CZT	0.214	0.390	0.9999	0.220	1.983
CZU	0.335	0.320	0.9999	0.340	1.055
45℃					
CZ	0.110	0.100	0.9848	0.120	6.428
CZT	0.200	0.230	0.9998	0.210	3.536
CZU	0.326	0.250	0.9999	0.330	0.868
55℃					
CZ	0.099	0.210	0.9927	0.103	3.209
CZT	0.191	0.210	0.9997	0.195	1.589
CZU	0.311	0.240	0.9999	0.311	0.057
65℃					
CZ	0.087	0.340	0.9994	0.089	1.626
CZT	0.176	0.180	0.9994	0.182	2.411
CZU	0.295	0.230	0.9999	0.300	1.198

3.1.4. Effect of initial PNP concentration

The initial concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases. It was seen from Fig. 1(D), which represents the results of initial concentration of PNP within the range of 10–200 mg/L that an increase in initial PNP solution concentrations resulted in increased of this

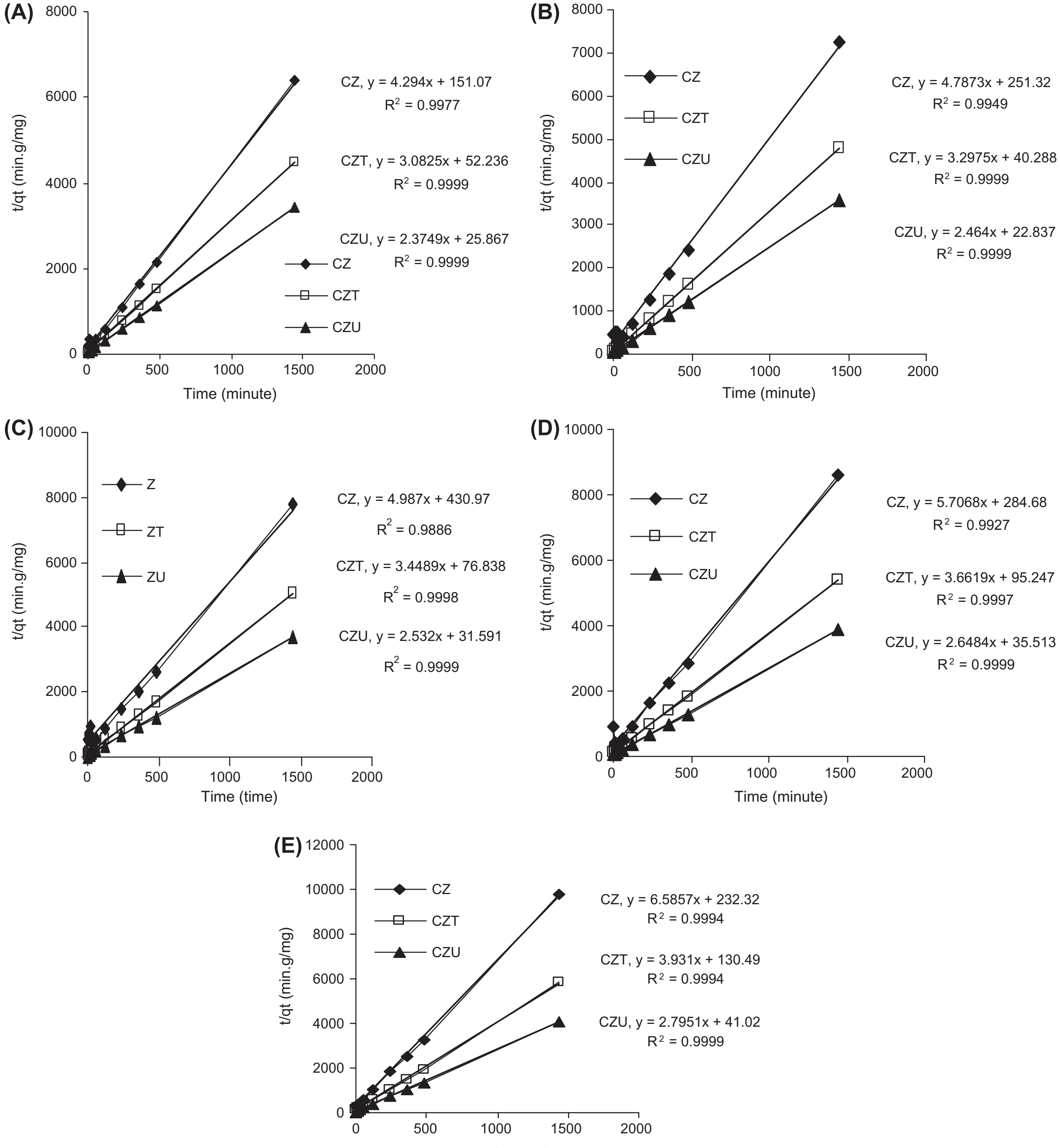

Fig. 2. Pseudo-second-order model for the removal of PNP aqueous solutions on CZ, CZT, and CZU. Conditions: pH = 3, particle size 63–75 μm, C_0 = 10 ppm adsorbent dose 1 g and flow rate = 1 ml/minute. A = 25°C, B = 35°C, C = 45°C, D = 55°C, and **E** = 65°C.

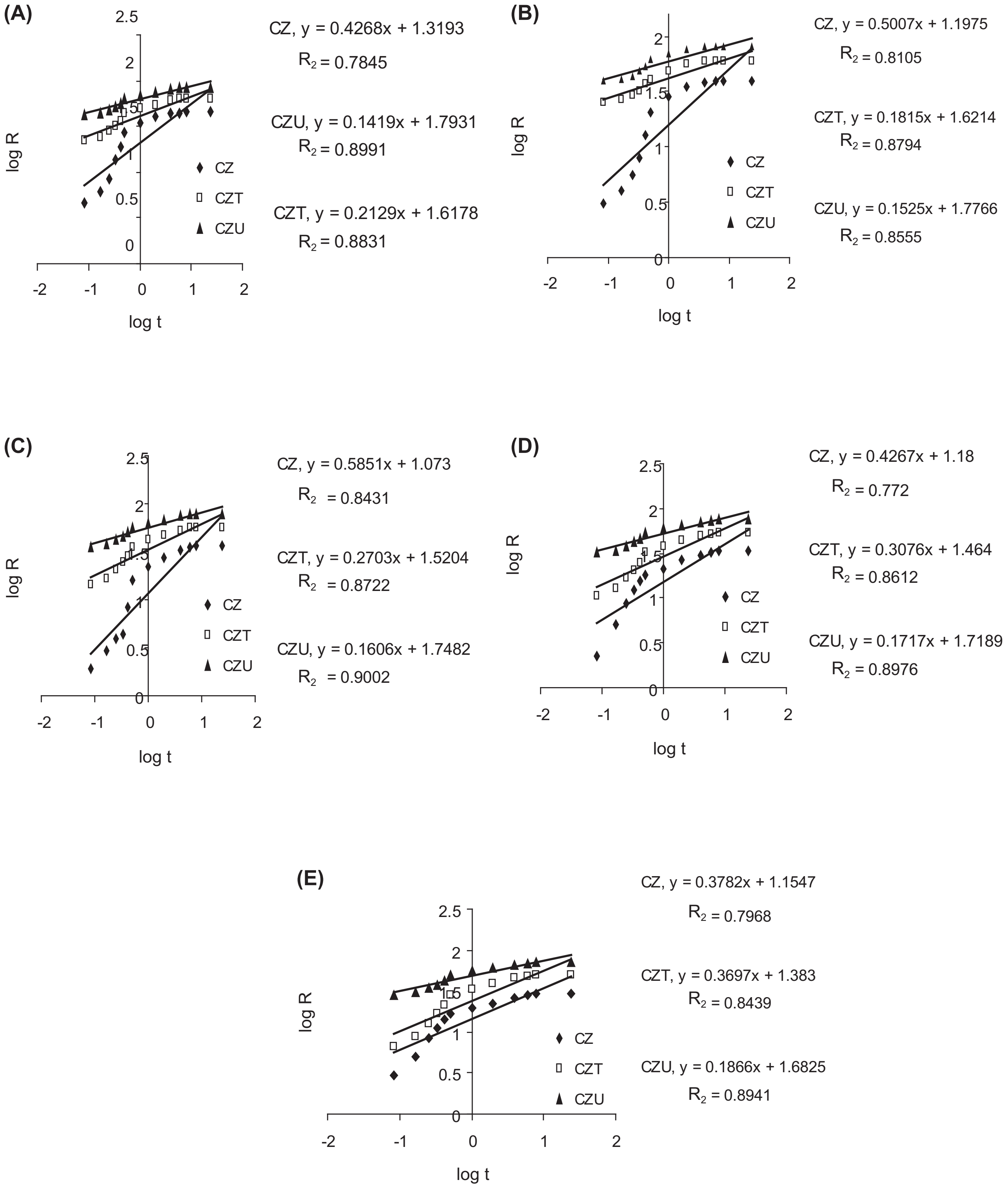

Fig. 3. Intraparticle diffusion model for the removal of PNP aqueous solutions by CZ, CZT, and CZU. Conditions: pH = 3, particle size 63–75 μm, C_0 = 10 ppm adsorbent dose 1 g and flow rate = 1 ml/minute. A = 25°C, B = 35°C, C = 45°C, D = 55°C, and E = 65°C.

Table 2
Intraparticle diffusion model of the removal of PNP from aqueous solution by CZ, CZT, and CZU at various temperatures

Temperatures (°C)																				
Samples	25				35				45				55				65			
	$k_{id,1}$	$k_{id,2}$	α_1	α_2	$k_{id,1}$	$k_{id,2}$	α_1	α_2	$k_{id,1}$	$k_{id,2}$	α_1	α_2	$k_{id,1}$	$k_{id,2}$	α_1	α_2	$k_{id,1}$	$k_{id,2}$	α_1	α_2
CZ	14.90	1.23	2.00	1.89	16.04	1.30	1.76	1.80	18.37	1.61	1.61	1.65	27.32	1.51	1.97	1.64	15.72	1.47	1.83	1.58
CZT	3.24	1.32	2.38	2.40	2.29	1.21	2.31	2.40	5.00	1.40	2.30	2.300	7.00	1.43	2.28	2.25	22.11	1.65	2.76	2.65
CZU	2.37	1.28	3.12	3.15	2.53	1.18	3.10	3.20	2.67	1.32	3.10	3.10	2.90	1.34	3.01	3.05	3.30	1.37	2.96	3.00

phenolic compound uptake for all adsorbents, it can be noticed also that from the curves for all adsorbents the uptake increased even at 200 mg/L, which may due to the presence of more available sites on all of the adsorbents than the number of PNP species. The removal curves are single, smooth, and continuous, indicating the formation of monolayer coverage of the PNP molecules onto the outer surface of the adsorbent [19]. The initial concentration of PNP used for other experiment was 10 mg/L.

3.1.5. Effect of particle size

The sorption is surface phenomenon. From Fig. 1 (F), it can be observed the smaller particle size shows higher removal for PNP than the larger one for all the three adsorbents, because the smaller one has larger surface area, the effective surface area increases as particle size decreases, and the sorption capacity increases because the number of available sits is more [6]. All the other experiments were done at the optimum particle size which is in the range of 63–75 μm.

3.1.6. Effect of temperature

The removal of PNP is temperature dependent. Fig. 1(E) shows the amount of PNP removed from aqueous solution as a function of temperature at PNP concentrations of 10 mg/L. There was a gradual decrease on the uptake of PNP by the calcinated zeolite and its modified forms as the temperature increased at the range of 25–65°C, the percent removal of PNP was (45.0–29.5%) to (64–49.5%), and (83.5–70.7%), for CZ, CZT, and CZU, respectively. It can be seen that the PNP removal follows a similar pattern in the three adsorbents studied, but the amount adsorbed at a particular temperature differs. These results indicate that the uptake of PNP increases at lower temperature. The decrease on the uptake of PNP with the increase in temperature may be explained as a result of the increase in the average kinetic energy of the PNP. The increase in temperature may be associated with the decrease in the stability of PNP-adsorbent complex, for that it can be said that the process is an exothermic one [20]. For the other variables, 25°C was chosen as the optimal temperature.

3.2. Removal kinetic studies

The rate of PNP removal on all sorbents was determined by studying the removal kinetics at different temperatures and at the optimum variables.

3.2.1. Pseudo-second-order

It was found from the results belonging to this model, which are given in Table 1 and shown in Fig. 2 at different temperatures that there are good-fit straight lines for all of the experimental data at all temperatures for all kinds of adsorbents with high correlation coefficients (R^2).

Moreover, there is a good agreement between the experimental adsorption capacity and the calculated one at different temperature values for CZ, CZU, and CZT as shown in Table 1, indicating the applicability of this model to describe the kinetics of the adsorption process of PNP onto sorbents [21].

3.2.2. The intraparticle diffusion

Plots are shown in Fig. 3; the plots are not linear over the whole time range which means that more than one process affected the adsorption. From these plots it was found that, the first sharper region is the

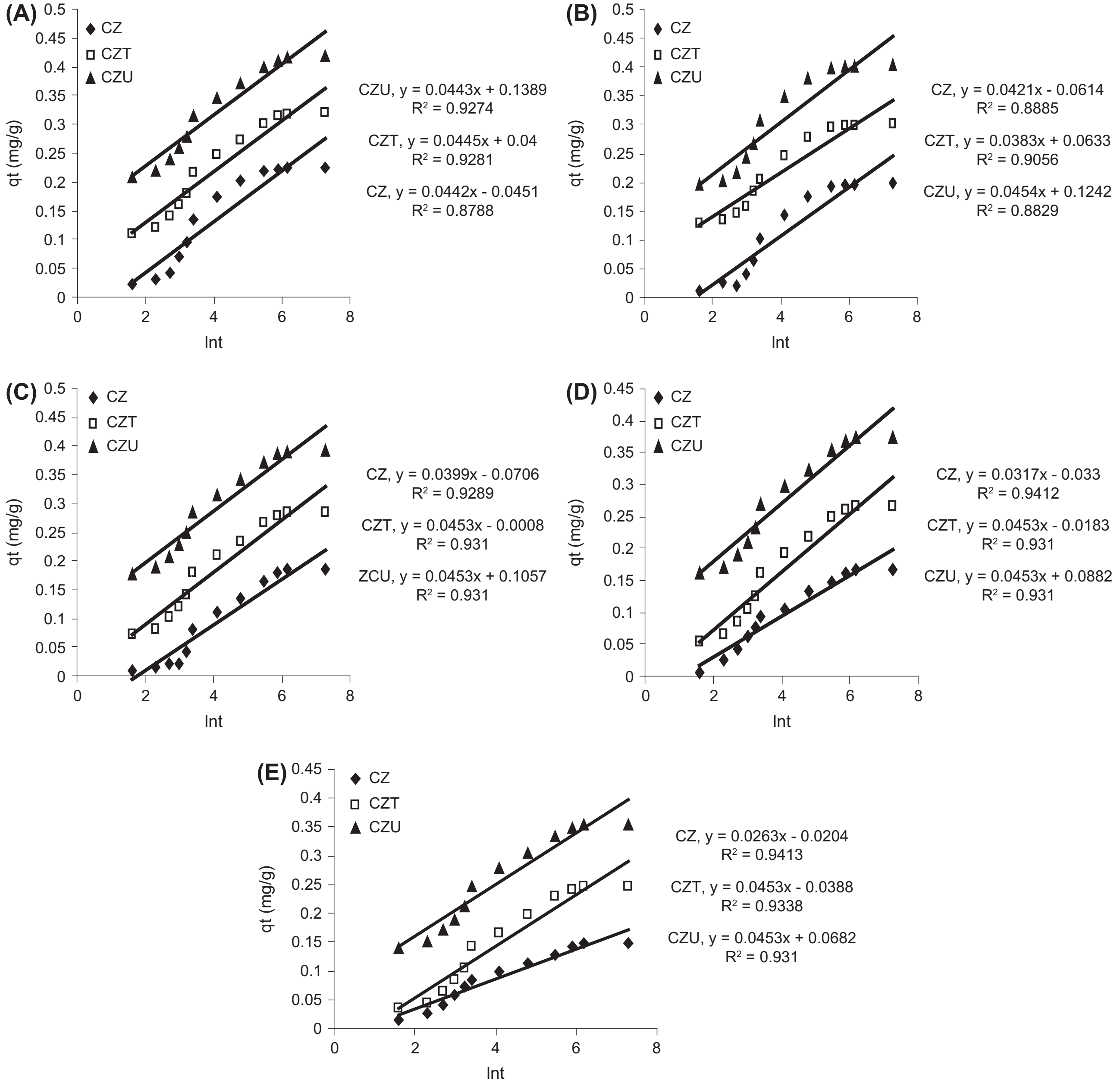

Fig. 4. Elovich kinetic model for the removal of PNP aqueous solutions by CZ, CZT, and CZU. Conditions: pH = 3, particle size 63–75 μm, C_0 = 10 ppm adsorbent dose 1 g and flow rate = 1 ml/minute. A = 25℃, B = 35℃, C = 45℃, D = 55℃, and E = 65℃.

instantaneous adsorption or external surface adsorption. The second region is the gradual adsorption stage where intraparticle diffusion is rate limiting. When intraparticle diffusion starts to slow down the low p-nitrophenol concentration left in the solution at all different temperatures.

Table 2 presents intraparticle diffusion constants ($k_{\mathrm{id},\ 1}$ and $k_{\mathrm{id},\ 2}$), it seen that the order of adsorption rate was first stage ($k_{\mathrm{id},\ 1}$) > ($k_{\mathrm{id},\ 2}$) for all different temperatures for the removal of p-nitro phenol using CZ, CZT, and CZU. When p-nitrophenol species diffused in the pore of the particle, the diffusion resistance increased, which caused the diffusion rate to decrease at all different temperatures.

The intercept α provides information about the thickness of the boundary layer, the resistance to the external mass transfer increases as the intercept increases [22]. From Table 2, the values of α at different temperature were found to be followed this order according to adsorbents CZU > CZT > CZ, which indicates an increase in the thickness of the boundary layer and a decrease in the chance of external mass transfer, therefore the chance of the internal mass transfer will increase.

The XRF and the SEM for this Jordanian zeolite show that this zeolite is rich with SiO_2, Al_2O_3 which gives good selectivity, large number of pores, high surface area with layers, and sheets allow water to diffuse through these pores and the ion exchange may take place [8].

3.2.3. Elovich model

Fig. 4 shows the plots of Elovich model, the values of kinetic constants of β and δ are listed in Table 3 for all adsorbents at different temperature values. From Table 3, it can be seen that in general the values of β decrease when zeolite modified by urea and thiourea, and the constants δ was observed to increase sharply when modification of zeolite taken place at temperature values in the range of (25–65℃). That means when zeolite is modified the rate of chemisorptions and available adsorption sites on surface increase. At 65℃, it was observed that the values of δ decrease. The explanations for this form of kinetic equation involves a variation of the energetic of chemisorptions with the active sites are heterogeneous in all of the adsorbents [23].

4. Validity of kinetic models

The validity of the three models pseudo-second-order model, intraparticle diffusion, and Elovich models was investigated in order to compare the applicability of the models; a normalized standard deviation Δq (%) is calculated:

$$\Delta q(\%) = \mathrm{SSE}\% = \sqrt{\frac{\sum\left[(q_\mathrm{e}, \exp - q_\mathrm{e}, \mathrm{cal})/qe, \exp\right]^2}{(n-1)}} \times 100 \tag{7}$$

where n is the number of data points [24], the calculated values of SSE% for intraparticle diffusion and Elovich models were found in the range of 32.49 to 36.12%. Table 1 lists the calculated values of SSE% which have the highest values of 6.3% for the pseudo-second-order model which improved the best fitting for this model rather than the other models which have also R^2 lower than the second-order model.

5. Activation energy

The activation energy, E_a, can be calculated by the Arrhenius equation:

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{(E_\mathrm{a}/R)(T_2 - T_1)}{(T_1 T_2)}\right) \tag{8}$$

where E_a is the activation energy ($\mathrm{J\,mol^{-1}}$), k_1 and k_2 are the rate constants of removal ($\mathrm{g\,mg^{-1}\,s^{-1}}$), R is the gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$), and T is the removal temperature (K).

Table 3
Elovich kinetic model of the removal of PNP from aqueous solution by CZ, CZT, and CZU at various temperatures

Temperatures (℃)															
Samples	25			35			45			55			65		
	β	δ	R^2	β	δ	R^2	β	δ	R^2	β	δ	R^2	β	δ	R^2
CZ	17.89	0.019	0.9762	23.75	0.010	0.8885	20.88	0.0082	0.9289	26.32	0.013	0.9412	22.08	0.204	0.931
CZT	14.68	0.12	0.9692	26.11	0.20	0.9056	15.77	0.0622	0.931	15.77	0.042	0.931	31.65	0.015	0.9413
CZU	12.02	1.16	0.9823	22.03	0.70	0.8829	12.99	0.7934	0.931	12.99	0.539	0.931	15.75	0.027	0.9338

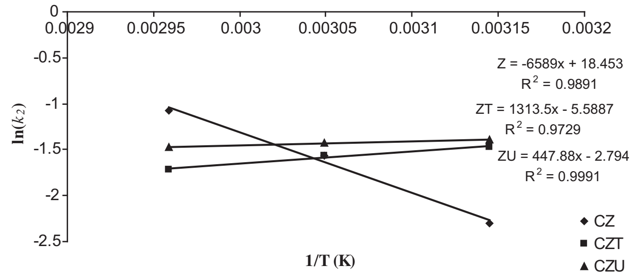

Fig. 5. The activation energy for the removal of PNP from aqueous solutions using CZ, CZT, and CZU.

The activation energy was investigated using k_2 as shown in Fig. 5, it was found from the figure that the E_a values for CZU and CZT are similar to each other with small negative values of activation energy because the equilibrium rate constants decrease by increasing temperature for both adsorbents that means the process is an exothermic one with a little physical nature. For CZ, the E_a was found with positive value that means the process is an endothermic one with physical nature [24].

6. Conclusion

- The removal of PNP was investigated using the modified Jordanian zeolite with urea and thiourea regarding with calcinations, contact time, solution pH, initial concentration, temperature, and particle size. The removal of PNP was dependent on all the previous parameters for all adsorbents CZ, CZT, and CZU.
- Generally, it was found that the efficiency of the calcinated modified zeolites for the removal of PNP was higher than the calcinated zeolite only.
- The ability of CZ, CZT, and CZU for removing PNP from aqueous solutions is possible along wide range of pH 1–8, which explain the high affinity of adsorbents for binding PNP as un- dissociated or partially dissociated forms.
- The pseudo-second-order, intraparticle diffusion, and Elovich kinetic models were developed to predict the rate constants and the equilibrium capacities.
- The analysis of the kinetics and rate data revealed that pseudo-second-order sorption is predominant for removal of PNP; the correlation coefficients for this kinetic model are much higher than the other models which are intraparticle model and Elovich model for all adsorbents.
- The calculated activation energy using pseudo-second-order rate constant for CZ found to be positive but for CZT and CZU the activation energies found to be negative but in small values which indicate that the process is an exothermic one with chemical nature.

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