

Determination of phenol in wastewater by using low cost modified Jordanian natural zeolite. Column and batch experiment

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Abstract

The ability of a modified Jordanian natural zeolite to remove phenol from wastewater has been studied as a function of contact time, initial phenol concentration, pH, and adsorbent calcining temperature. The phenol removal had been studied using column technique. The zeolite was modified using urea and thiourea after calcinations of this nature zeolite. Desorption was achieved with methanol solution (30%, v/v) using column technique. It was found that the treated natural zeolite was suitable for reuse without noticeable loss of adsorption capacity. Kinetic studies for phenol removal were performed using the batch experiment at different temperatures. The obtained experimental data were analyzed by various kinetic models such as: pseudo-second-order, intra-particle diffusion and Elovich models. It was found that the kinetics of phenol removal follows the pseudo-second-order equation. In the intra-particle diffusion, it was noticed that all curves were resolved in two portions and in two separate regions for all temperatures (25, 35, 45, 55 and 65 °C), which indicates multilinearity. The initial portion is attributed to the bulk diffusion ($k_{id, 1}$) while the linear portion is attributed to intra-particle diffusion ($k_{id, 2}$). The activation energy of sorption was calculated according to pseudo-second-order rate constant. Results showed that the treated calcinated zeolite with has lower activation energy than that for the untreated calcinated zeolite.

Keywords:

Phenol; removal; modified zeolite; wastewater; column

1. Introduction

Water pollution represents a real danger to the environment, and consequently to man. This pollution is primarily due to industrial wastes. The phenolic compounds are common pollutant substances, Which are a serious problem in many countries. The major sources of phenolic wastes are petroleum refineries, petrochemical, steel mills, coal gas, synthetic resins, pharmaceuticals, paints, and mine discharge. Phenolic waste imparts a carbolic odour 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 phenols have been classified as hazardous pollutants due of their potential toxicity to human health. There are several methods for the removal of phenol from aqueous solutions, such as adsorption, ion exchange, membrane processes, chemical oxidation, precipitation, distillation, gas-stripping, solvent extraction, complexation and bio-remediation. 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

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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 removal of a variety of organic compounds such as phenol [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 phenolic compound [4-9].

The total phenol concentration in wastewater of a typical Jordanian refinery processing three million tons of crude per year, which is around $\sim 85 \text{ mg L}^{-1}$. The concentration of phenolic compounds in wastewater from resin plants is typically in the range of 12 - 300 mg L^{-1} . The wastewater with the highest concentration of phenol ($> 1000 \text{ mg L}^{-1}$) is typically generated from coke processing [1].

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 phenolic compounds. Continuous column method and a conventional batch technique were 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, intra-particle diffusion and Elovich kinetic models.

1.1.1 pseudo-second-order model

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

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

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

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

If the second order kinetic equation is applicable, then a plot of t/q against t of 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, 10, 11].

Herein, the initial sorption rate h is given by

$$h = k_2 q_e^2 \quad \text{Eq (3)}$$

Intra-particle diffusion

The possibility of intra-particle diffusion resistance affecting adsorption was explored using the intra-particle diffusion model. The intra-particle diffusion model [6, 12, 13] is expressed as

$$R = k_{id}(t)^a \quad \text{Eq (4)}$$

A linearised form of this equation is given by

$$\log R = \log k_{id} + a \log(t) \quad \text{Eq (5)}$$

where: R is the percentage of phenol adsorbed, t is the contact time, a is the gradient of the linear plots, and k_{id} is the intra-particle diffusion rate constant.

1.1.2 Elovich model

The Elovich equation is given by

$$q_t = \beta \ln(\alpha) + \beta \ln t \quad \text{Eq (6)}$$

Where: q_t is the adsorbed amount at time t , α ($\text{mg g}^{-1} \text{min}^{-1}$), and β (g mg^{-1}) are the equilibrium rate constants for the Elovich model.

A plot of q_t versus $\ln t$ results in a straight line, α and β can be obtained from the slope and intercept respectively [6, 14, 15].

2. Experimental

2.1 Material

Zeolite samples used in this study were collected from Jebel Aritain in Jordan. Zeolitic tuff samples were thrice washed with distilled water to remove of impurities. Calcinations of the samples were done in the temperature range 100-900 °C for 8 hours, then stored in airtight desiccators until they were used. Phenol used in this study was obtained from Merk-schudardt (analytical grade) and was used without further purification. The stock solution was prepared by weighing out the pure crystalline solid in absolute ethanol. All solutions used in this study were diluted with distilled water as required. The concentrations of phenol solutions were determined by measuring absorbance of solution at 280 nm, using Diod Array spectrophotometer (S600).

2.2 Treatment of Zeolite

The zeolite samples of that were calcined to 800 °C (Z) were treated separately with saturated solution of urea (16.7 M) (ZU) and with saturated thiourea (1.18 M) (ZT). The mixtures were kept for 16 days, then, the supernatant was decanted and the wet samples were washed with distilled water several times then dried in an oven at 105 °C. The zeolitic tuff rock was crushed using mechanically agitated sieve banks then sorted into several size fractions in the average range 63-300 μm using standard sieve series [6]. The cation exchange capacity CEC was determined using methylene blue procedure [6]. It was estimated to be 40.6 mg/g.

2.3 Column experiments

Continuous column method was used to study the adsorption of phenol onto different zeolitic samples. Experiments were carried out using column reactor. The glass tube (0.5cm \times 10 cm) columns used in this experiment, were filled with zeolite bed. The bottom of each column contains a plug glass wool to support the modified zeolite bed. A slurry packing technique was used to obtain homogenous bed in the column. Prior to each experiment, the treated zeolitic packed in the column was conditioned at the working pH with a buffer solution. Solutions were driven through the columns aided by peristaltic pump at constant flow rate of 0.15 mL/minute. Two replicates of each experiment were performed and the blanks were simultaneously run in order to take into account the possible contaminations, and eventual, releases the investigated phenol from the zeolite. The amounts of the adsorbed

phenol were determined and related to several variables such as; calcinations, contact time, pH and initial concentration of phenol.

Effect of calcinations: an accurate amount of 1 gm of each Z, ZT and ZU, which was previously calcined in the range of 100-900 °C, were applied using 10 ppm of 25 ml of phenol. The effects of contact time, initial phenol concentration and the pH were studied. All experiments were done at room temperature using an accurate amount of 1 gm of adsorbent for each type of the modified zeolite, with particle size of 125-250 µm. The accurate amounts of adsorbent were placed in glass columns separately, and the uptake of phenol of 10 ppm by the adsorbent as a function of contact time was measured. Removal of phenol was also studied at different initial concentrations in the range of 10-200 ppm. The added volume of the phenol solution was 25 mL of pH 4.

Other experiments were carried out to study the effect of pH in the range of 1.00-10.00. Buffer solutions in the pH range of 1.00-2.50 were prepared using KCl and HCl, sodium acetate with acetic acid were used to prepare buffer with pH in the range of 3.00-6.00 and diethanolamine with HCl to prepare buffer with pH in the range 7.00-10.00. To check pH, the stationary phase was treated with the desired buffer solution and the phenol solutions were also buffered to the desired pH.

For all experiments, the treated calcinated zeolite (Z) at 800 °C was chosen since it gives the best removal results. The adsorbed amount of phenol was calculated from the difference between influent and effluent concentrations. The removal efficiency (R) of these species amount can be calculated from the relation,

$$R = \frac{C_o - C_e}{C_o} \times 100 \quad \text{Eq (7)}$$

Where C_o and C_e (mg/L) are the initial and final concentrations of adsorbate, respectively, and q_e (mg/g)

2.4 Regeneration experiment.

Several experiments were carried out to estimate the adsorption and desorption of phenol onto the three types of the modified zeolite. For adsorption studies, separate columns filled with 1.0000 g of modified zeolite and 105.0 ml of separate solutions of 10 ppm of phenol were added individually to these columns, the effluent was collected at 2-minute intervals for the first 30 minute, then at 15-minute intervals afterward. For the desorption experiments, the loaded modified zeolite samples used in previous part were reused via addition of methanol solution (30%, v/v), then, effluent was collected at the same time intervals as of the adsorption process. Other conditions were maintained constant: (i.e., the calcinations temperature equal 800°C, pH equal 1.00, particle size 125-250 µm, flow rate 1mL/minute).

2.5 Kinetic Equilibrium and temperature effect

Batch adsorption experiments for kinetic studies were performed. The batch technique was selected due to its simplicity. Accurately weighted one gram of the modified zeolite was added to 50.00 mL of solution, thermostated to a specific temperature, then placed in a shaker water bath (GFL 1083) runs at 180 rpm. A portion of a solution was taken out after five minutes, and the solution was separated by centrifugation at 5000 rpm using centrifuge (CN180). The supernatant was analyzed, spectrophotometrically, to monitor the change of absorbance of phenol during the adsorption process. The analysis is continued for half an hour at 5 minutes intervals. The interval of analysis was expanded to half an hour, an hour, two hrs, four hrs, six hrs, eight hrs and 24 hrs. Three forms of the zeolite samples were used: Z, ZT

and ZU (mentioned earlier). Experiments were performed at several other different temperatures, 25, 35, 45, 55 and 65 °C.

3. Results and discussion

Experimental observation showed that removal of phenol by the treated zeolite was found to be rapid during the initial 80 minute and remain constant afterwards.

3.1 Effect of calcination.

Information on temperature effect, morphology of materials and physical properties of surface area and pore size distribution, are limited in literature. The surface area and pore size distribution as well as the morphology of the synthesized materials are important factors when applied as adsorbents or catalytic supports [16].

Heat treatment has been shown to play a role in the dispersion of the adsorbed guest in the zeolite [17]. The calcination leads to get rid of impurities exist in the pores. Calcination of zeolite in temperature range of 100 -900 C° was used as a modified method to optimize adsorption capacity. Results are shown in Figure, 1 (A), which that the percentage of removal of phenol increases with temperature in the range 100 to 700 °C. After that, the percentage of removal of phenol nearly was constant. All experiments were done using zeolite calcinated at 800 °C.

3.2 Effect of contact time

The adsorption data for the uptake of phenol versus contact time at different initial concentrations is illustrated in Fig.1 (B). The rate of phenol removal was found to be very rapid during the initial 80 minutes, and then remains nearly constant thereafter. The phenol removal efficiencies reached up to 79.70% , 91.10% and 95.10% for Z, ZT and ZU, respectively. The higher sorption rate at the initial period may be due to higher number of vacant sites on the adsorbent available at the initial stage [11, 18].

3.3 Effect of initial concentration

Removal of phenol by the treated zeolite as a function of its initial concentration was investigated. It was found that an increase in initial concentration resulted in an increased of phenol uptake, as shown in Table (1, a) and illustrated in Figure. 1 (C). Initially, the number of adsorption sites available is higher and the driving force for mass transfer is greater, which makes the adsorbate reaches the adsorption site with ease. The percent removal of phenolic compound has the following order using these three types ZU > ZT > Z for all concentrations [19].

Table 1.a: Effect of pH on phenol removal by modified zeolite (particle size 125-250 μm, calcinations at 800°C, flow rate 0.15 mL min⁻¹, modified zeolite (Z) dose 1g/25 mL, C₀=10 ppm).

pH	% Removal		
	phenol/Z	phenol/ZT	phenol/ZU
1.00	7.00	72.50	76.80
2.00	67.00	69.4	73.10
3.00	65.90	69.10	72.30
4.00	64.60	69.10	72.10
5.00	51.00	56.00	64.90
7.00	42.20	44.40	50.00
8.00	39.00	47.50	52.60
9.00	20.00	28.00	36.70

3.4 Effect of pH

The pH of an aqueous medium is an important factor which influences the uptake of the adsorbate. The chemical characteristics of both adsorbate and adsorbent vary with pH. Table (1, b) and Figure.1 (D) showed the effect of pH on the adsorption of phenol in the range of 1.00-10.00. It was observed that the highest value of uptake of phenol by the modified treated zeolites was in the range of 1.00-5.00, which is almost constant in this range. However, the uptake capacity decreased considerably when the pH of the initial solution is 5.00- 10.00. It is known that phenol has high affinity towards urea and thiourea via hydrogen bonding. At low pH, phenol does not get ionized and it can interact easily with urea and thiourea. The reduction in adsorption at higher pH is possibly due to increased solubility of phenol. Urea and thiourea did not show any dissociation in the pH range 1.00-10.00, because the pKa for urea and thiourea is 26.00 and 21.00, respectively [11, 18-21]. Results indicate that the maximum removal for phenol occurred at pH = 1.00 and takes the order: ZU > ZT > Z.

Table1.b Effect of initial concentration on phenol removal by modified zeolite. (calcined temperature 800 °C, pH = 4.00, flow rate 0.15 mL min⁻¹, modified zeolite (Z) dose 1g/25mL).

C _o (ppm)	% Removal		
	phenol/Z	phenol/ZT	phenol/ZU
10	62.80	70.70	76.00
30	66.00	72.90	79.40
50	69.00	76.00	84.00
80	71.30	78.10	87.20
110	73.00	79.90	87.10
140	76.00	82.80	89.90
170	79.00	86.10	91.80
200	81.40	88.60	94.90

3.5 Effect of temperature

Information on the effect of temperature on the morphology of materials and their physical properties (surface area and pore size distribution) is limited in the literature. These physical properties are important factors when they are applied as adsorbents or catalytic supports. Heat treatment has been shown to play a role in the dispersion of the adsorbed guest in the zeolite [22]. Calcinations of zeolite in temperature range of 100 -900 °C was used as a modified method to optimize adsorption capacity, as shown in Figure.1 (A). It was noticed that the percentage of removal of phenol increases with temperature of the calcinations in range 100 to 700 °C. After that, the percentage of removal of phenolic compounds is nearly constant up to 900 °C. Calcinations may lead to get rid of impurities that exist in the pores and at the surface beyond 700 °C. The maximum removal was investigated in the range 700-900 °C for the three types of zeolite (Z, ZU, ZT). Because of this, all experiments were done using zeolite calcined at 800 °C. Using different particle size of the treated zeolite did not affect the percentage of removal. Most of the adsorption capacity for the modified treated zeolite is in the micropores, therefore, once the adsorbate molecule is given enough time to diffuse into the micropores, the capacity is controlled by the structure of the adsorbent, no matter what the particle size is [19].

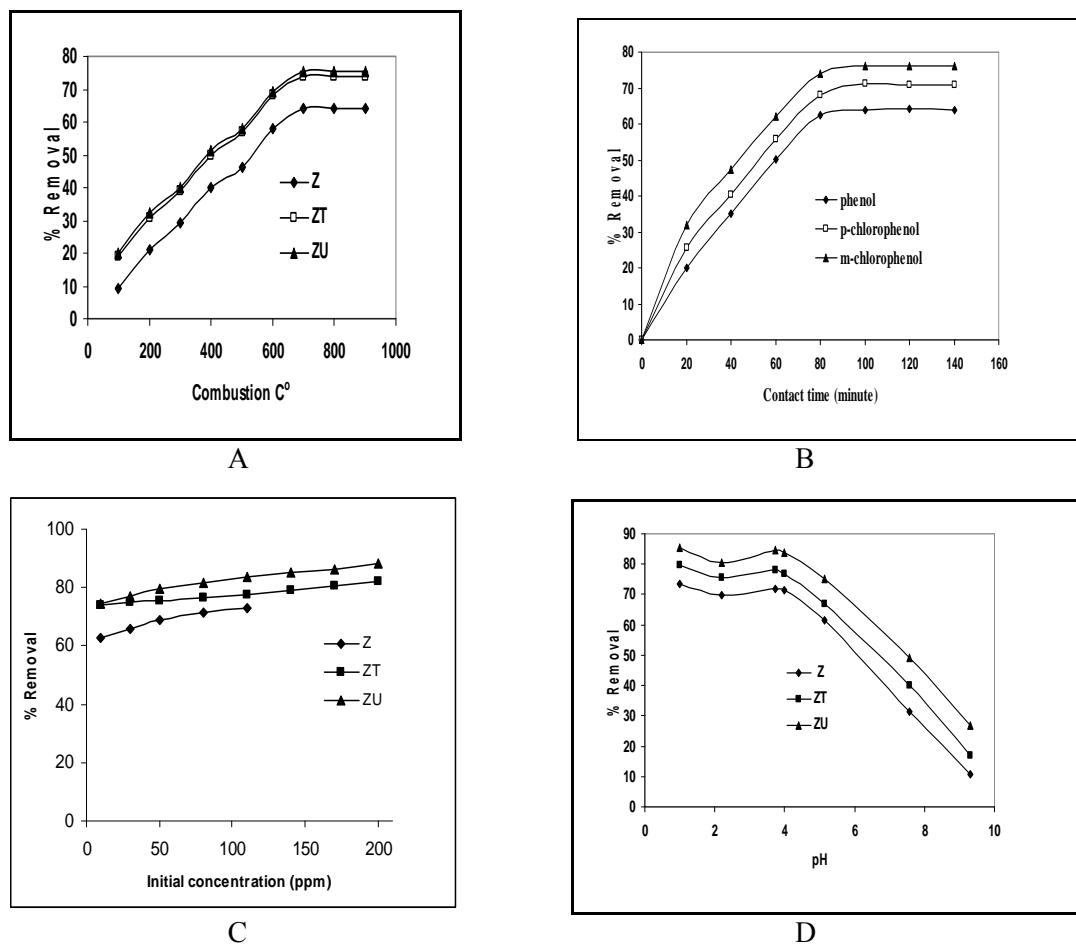
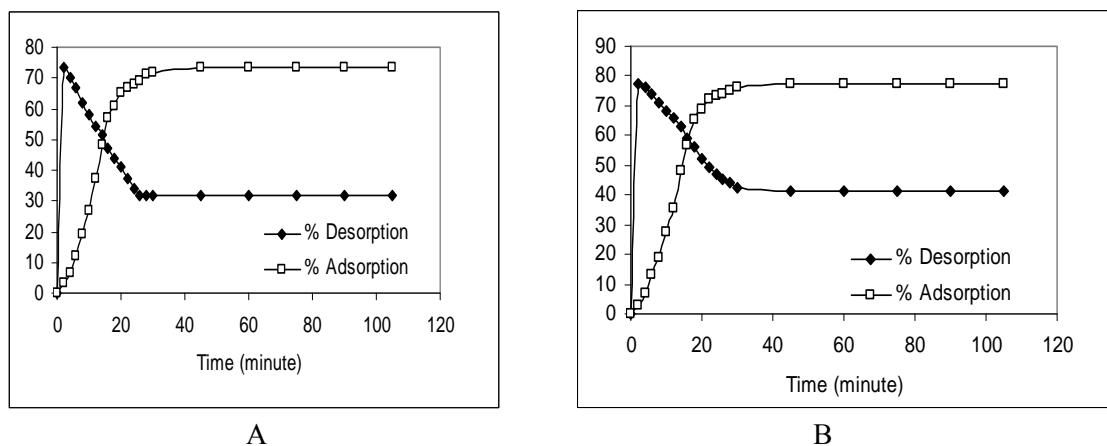
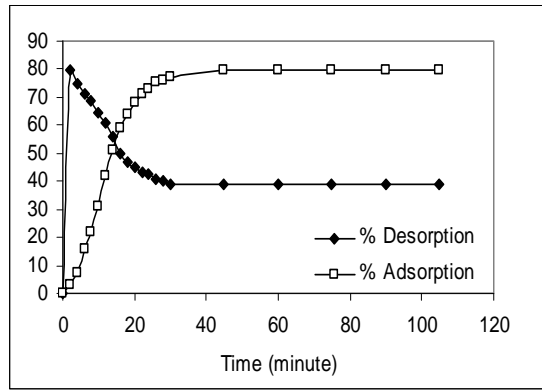


Fig. 1. Effect of different variables on the removal of phenol onto using Z, ZT, and ZU. Conditions: particle size 125-250 μm , $C_0 = 10$ ppm, $\text{pH} = 4.00$, adsorbent dose 1g/25ml and flow rate= 0.15 ml/minute. **A:** Effect calcination. **B:** Effect of contact time. **C:** Effect of initial concentration. **D:** Effect of pH.

3.6 Regeneration of adsorbent.

To be useful in separation and removal processes, adsorbed species should easily desorbed under suitable conditions and adsorbents should be reused many times to lower material costs. Methanol solution (30%, v/v) as desorption agent was used for regeneration. More than 80% of the adsorbed chlorophenol was desorbed within 20 minutes for the three types of adsorbent, as shown at Fig. 2. This means that methanol breaks down the interaction forces between chlorophenol and binding sites onto the adsorbent [17, 16].





C

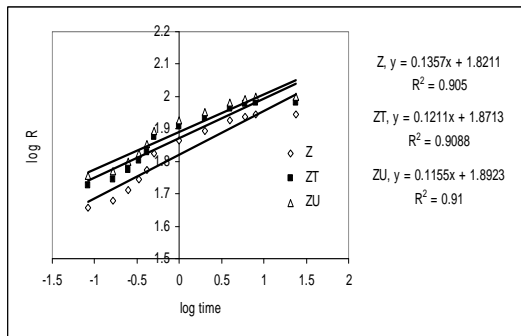
Fig. 2. The regeneration of (A: Z, B: ZT, C: ZU) using methanol (30%, v/v) from phenol at different time.

Conditions the calcination temperature equal 800 C°, pH equal 1.00, particle size 125-250 μm, Flow rate 1mL/minute.

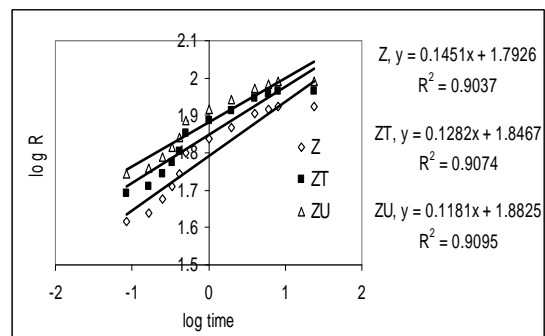
3.7 Kinetics studies

3.7.1 pseudo-second-order model

Figure (3) shows the linearized form of the pseudo-second-order kinetic model. The pseudo-second-order rate constant k_2 , amount of phenol adsorbed at equilibrium q_e , initial sorption rate h , (which were calculated using Eq(2) and Eq(3)), and the corresponding correlation coefficient values are shown in Table (2) for all temperatures. High values of R^2 were observed at all temperatures, for the three types, indicating that removal of phenol onto the adsorbents has a good fitting with this model. The values of k_2 , q_e and h were found to followed the order (ZU) > (ZT) > (Z), as shown in Table (2). This means that urea has the best result for removal of phenol using this kinetics model. Also, results indicated that q_e , k_2 , and h decreased as temperature increased, as shown in Table (2). This means that adsorption is an exothermic process for the all three types studied [23, 24].



A



B

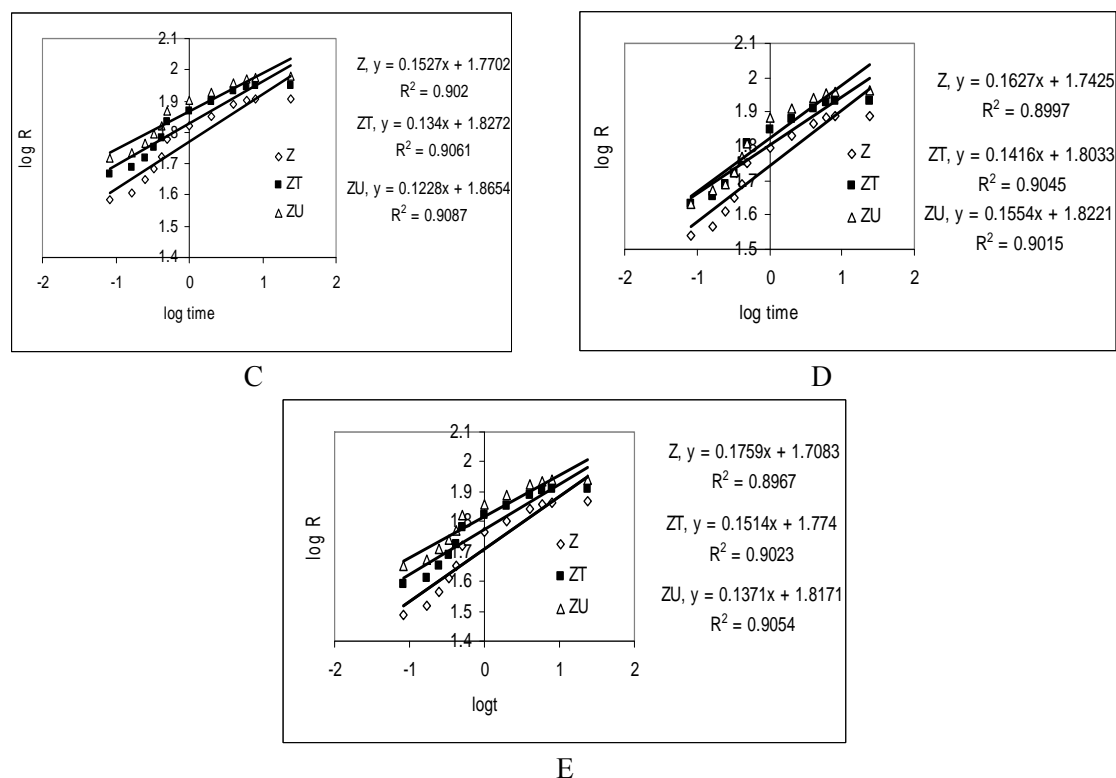


Fig. 3. Second-order kinetics plots for the removal of phenol using Z, ZT, ZU, particle size. 63-75 μm , calcination at 800 °C, $C_0 = 10$ ppm, adsorbent dose = 1g/50 ml, pH = 1.00, (A- 25 °C, B- 35 °C, C- 45 °C, D- 55 °C, E - 65 °C).

3.7.2 Intra-particle diffusion

If a straight line passing through the origin is obtained when Eq (5) is applied, then, we can be assumed that the mechanism involves diffusion of the species. In this case, the slope of the linear curve equals the rate constant of intra-particle transport (k_{id}). In the present study, no plot for the intra-particle diffusion model is found to pass through the origin. This deviation from the origin may be due to the difference in the mass transfer rate in the initial and final stages of adsorption. Further more, such deviation of straight lines from the origin indicates that the pore diffusion is not the sole rate-controlling step.

From Fig. 4, it was found that all curves resolved in two portions in two separate regions for all temperatures (25, 35, 45, 55 and 65 °C). This indicates that the initial portion is attributed to bulk diffusion ($k_{id,1}$) while and the linear portion is attributed to intra-particle diffusion ($k_{id,2}$) [25]. The values of $k_{id,1}$ and $k_{id,2}$ were obtained from the slopes of the two straight lines and they are shown in Table (2).

At all temperatures, it was found that $k_{id,2}$ values are higher than the $k_{id,1}$ values and both of them decrease by increasing temperature. For phenol as the adsorbent, it takes the following order:

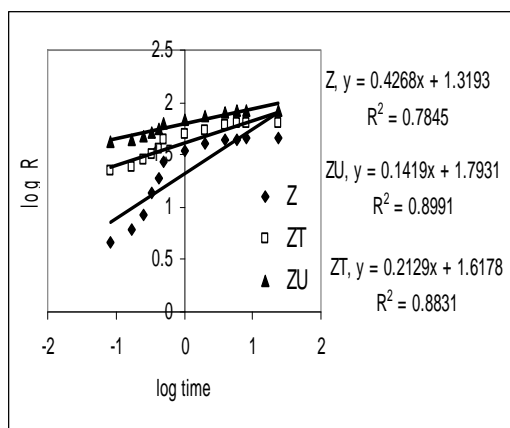
$$\text{Phenol: } k_{id,1} (\text{ZU}) > k_{id,1} (\text{ZT}) > k_{id,1} (\text{Z}) .$$

$$\text{Phenol: } k_{id,2} (\text{ZU}) > k_{id,2} (\text{ZT}) > k_{id,2} (\text{Z}) .$$

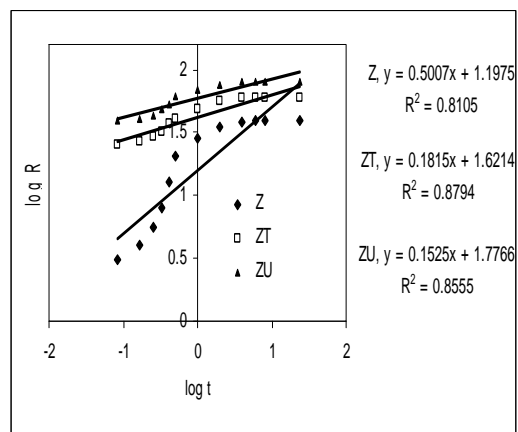
For $k_{id,1}$, we can assume that the thickness of boundary layer decrease by modification [12, 23]. This model indicates that the adsorption of phenol onto the modified zeolite is followed by an intraparticle diffusion model up to 120 minute. That means although intraparticle diffusion was involved in the adsorption process, it was not the only rate-controlling step [25]. The values of R^2 obtained from the plots of intraparticle diffusion kinetics are lower than those obtained from that of pseudo-second order model.

Table. 2 The adsorption kinetic model constants for the removal phenol using Z, ZT and ZU.

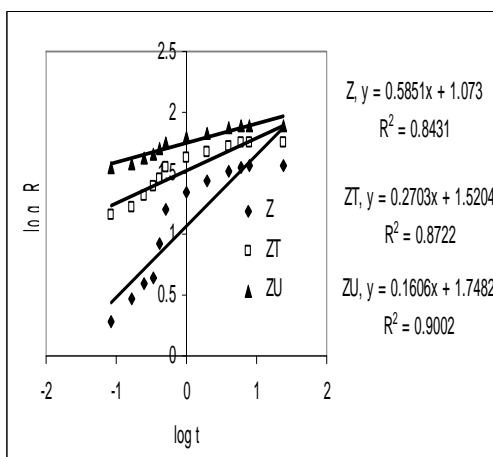
Adsorbent	Temperature °C	Pseudo second-order				Intraparticle diffusion			Elovich model			
		K ₂ (g/mg.min)	h (mg/g.min)	q _e (mg/g)	R ²	α	K _{id1}	K _{id2}	R ²	β (g/mg)	α (mg/g. min)	R ²
Z	25	0.0061	0.1324	4.6577	0.9977	0.4268	29.2954	37.5960	0.7845	0.8839	0.3601	0.8788
ZT		0.0091	0.3829	6.4893	0.9999	0.2129	49.9157	51.6817	0.8831	0.8896	2.4564	0.9281
ZU		0.0109	0.7732	8.4246	0.9999	0.1419	68.0193	71.3562	0.8991	0.8856	23.0392	0.9274
Z	35	0.0912	0.0040	0.2089	0.9949	0.5007	33.3000	31.5606	0.8105	0.0421	0.2326	0.8885
ZT		0.2699	0.0248	0.3033	0.9999	0.1815	44.9406	52.0399	0.8794	0.0383	5.2213	0.9056
ZU		0.2658	0.0438	0.4058	0.9999	0.1525	65.3631	72.5657	0.8555	0.0454	15.4203	0.8829
Z	45	0.0577	0.0023	0.2005	0.9886	0.5851	20.7946	24.1406	0.8431	0.0399	0.1704	0.9289
ZT		0.1548	0.0130	0.2899	0.9998	0.2703	44.1610	44.0696	0.8722	0.0453	0.9825	0.9310
ZU		0.2029	0.0316	0.3949	0.9999	0.1606	62.2348	65.3782	0.9002	0.0453	10.3123	0.9310
Z	55	0.1144	0.0035	0.1752	0.9927	0.4267	44.0757	23.1073	0.7720	0.0317	0.3531	0.9412
ZT		0.1408	0.0105	0.2731	0.9997	0.3076	42.3000	40.5640	0.8612	0.0453	0.6677	0.9310
ZU		0.1975	0.0282	0.3776	0.9999	0.1717	58.9840	61.8776	0.8976	0.0453	0.6677	0.9310
Z	65	0.1867	0.0043	0.1518	0.9994	0.3782	33.5076	20.6658	0.7968	0.0263	0.4604	0.9413
ZT		0.1184	0.0077	0.2544	0.9994	0.3697	41.9798	35.9784	0.8439	0.0453	0.4246	0.9338
ZU		0.1904	0.0244	0.3578	0.9999	0.1866	55.3395	57.8808	0.8941	0.0453	4.5065	0.9310



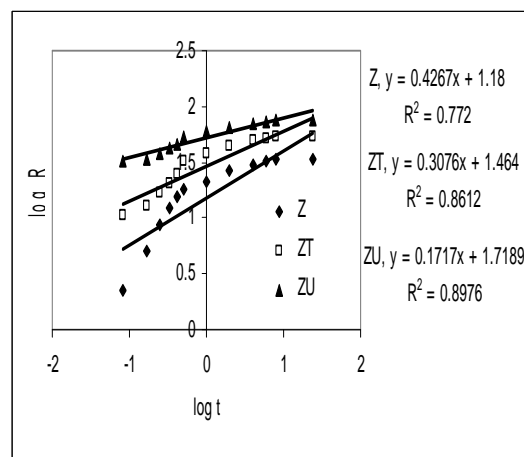
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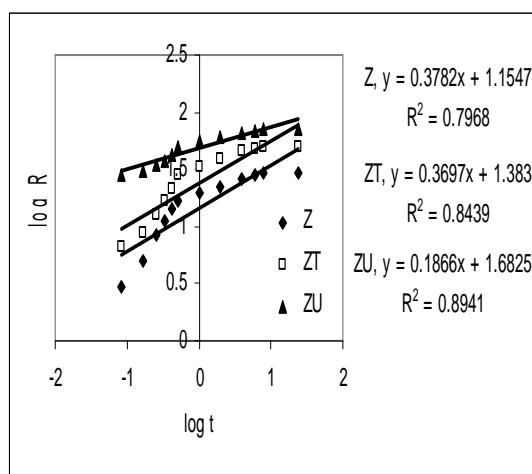
B



C



D



E

Fig. 4. Intraparticle diffusion plots for the removal of phenol using Z, ZT, ZU, P.S. 63-75 μ m, Combustion at 800 °C, $C_0 = 10$ ppm, adsorbent dose = 1g/50 ml, pH = 1.00, (A- 25 °C, B- 35 °C, C- 45 °C, D- 55 °C, E - 65 °C).

3.7.3 Elovich model

Applying the Elovich model using Eq (6) for (α) and (β), it was found that the values of (α) were nearly constant while the values of (β) increase by modification but decrease by increasing the temperature, as illustrated in Figure (5) and shown in Table (2). The values of $R^2 \approx 0.93$, is lower than that for pseudo-second order and the Intra-particle diffusion models. The values of all R^2 for all models suggested that the pseudo-second order model mechanism is the predominant mechanism. This means that the uptake process follows pseudo-second order expression has a correlation coefficients higher than 0.99.

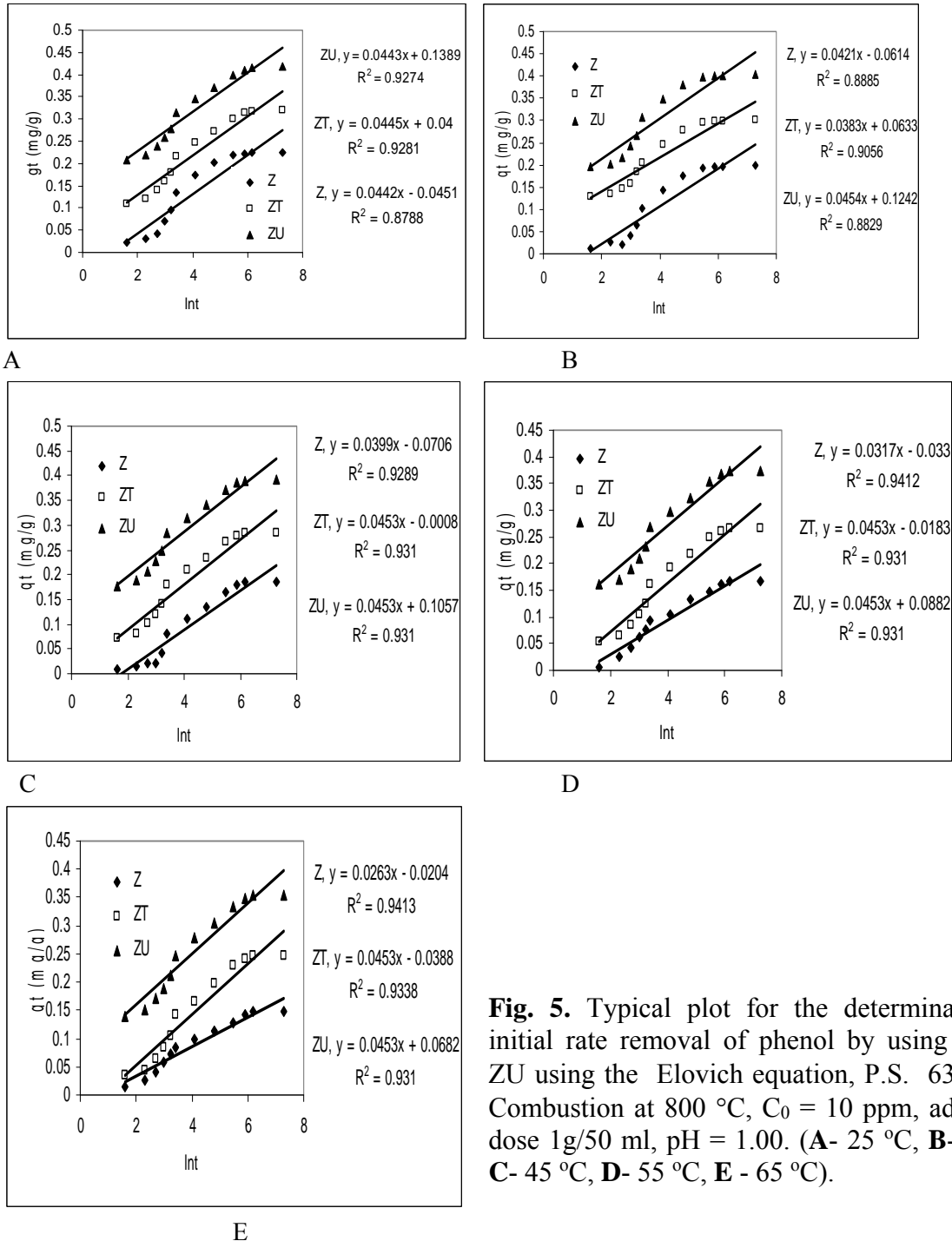


Fig. 5. Typical plot for the determination of initial rate removal of phenol by using Z, ZT, ZU using the Elovich equation, P.S. 63-75 μ m, Combustion at 800 °C, $C_0 = 10$ ppm, adsorbent dose 1g/50 ml, pH = 1.00. (A- 25 °C, B- 35 °C, C- 45 °C, D- 55 °C, E - 65 °C).

3.7.4 Effect of temperature

Temperature has a pronounced effect on the adsorption capacity of the adsorbents. Since sorption is an exothermic process, it is expected that an increase in temperature of the adsorbate-adsorbent system results in decrease of sorption capacity, as shown for all results. Results confirm the exothermic nature of adsorption process. However, if the adsorption process is controlled by the diffusion process (intra-particle transport-pore diffusion), then the sorption capacity will increase by increasing temperature.

3.7.5 Activation energy

Generally, reaction rate is temperature dependent. The activation energy for removal of phenol onto this modified zeolite can be estimated by Arrhenius equation,

$$k = Ae^{(-E_a/RT)} \quad \text{Eq (8)}$$

Where, k is the rate constant for removal (g min^{-1}), A is the Arrhenius constant which is temperature independent factor (g min^{-1}), E_a is the activation energy (kJ mol^{-1}), R is a universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the solution temperature. In this study, activation energy of sorption process was calculated using the values of the rate constant from a pseudo-second-order kinetic equation at five different temperatures [26]. An Arrhenius plots of $\ln k$ versus $1/T$ is illustrated in Fig. 6 and the values of activation energy are shown in Table 3.

It was found that the E_a follows this order for the three modified types $ZT < ZU < Z$. This shows that that the ZT has a greater affinity (lower activation energy) for removal of phenol than ZU . This indicates that thiourea enhances the adsorption capability of the zeolite while the treated urea sample has shown less effect. However, both treated samples have a greater affinity phenol removal than the Z sample.

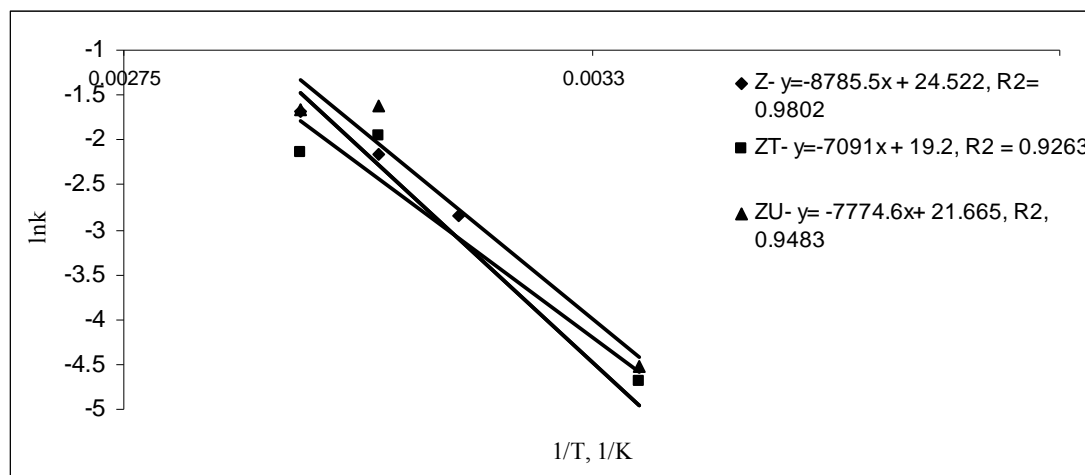


Fig. 6. Plot of $\ln(k_2)$ against reciprocal temperature for phenol onto Z , ZT , and ZU . Conditions: particle size. $63\text{-}75\mu\text{m}$, calcination temperature $800\text{ }^\circ\text{C}$, $C_o = 10\text{ ppm}$, adsorbent dose = $1\text{g}/50\text{ ml}$ and $\text{pH} = 1.0$

Table. 3 The activation energies for removal of phenol using Z , ZT , and ZU .

Adsorbent	E_a (kJ mol^{-1})	R^2
Z	73.04	0.9898
ZT	58.95	0.9912
ZU	64.64	0.9262

Conclusions

A modified surface of Jordanian zeolite was studied as an adsorbent for phenol, removal from aqueous solution. Modification of zeolite was done by calcination followed by treatment with urea and thiourea. Results obtained from column experiments indicate that adsorption capacity of the adsorbent was considerably affected by initial pH, initial phenol concentration, contact time and temperature. Also it was found that the amount of phenol adsorbed increases with initial phenol concentration. The rate of phenol removal was found to be very rapid during the initial 80 minutes then remains nearly constant thereafter. Results also indicate that the optimal uptake of phenol took place at a pH in the range of 1-5, and then the adsorption of phenol decreased with increasing pH. Also, removal capacity was found to decrease by increasing temperature, which means that the process is an exothermic.

The pseudo-second-order, intra-particle diffusion and Elovich kinetic models were used to analyze the data obtained using batch experiments. Results indicate that the pseudo-second-order equation provided the best correlation for the adsorption data.

The activation energy of sorption was calculated using the pseudo-second-order rate constant. The values were found to be for Z, ZT, and ZU 73.04, 58.95, and 64.64 kJ mol⁻¹ respectively. ZT and ZU showed higher ability for removing phenol from aqueous solution than Z. This can be attributed to the ability of urea and thiourea to hydrogen bonding with phenol, either directly or through the adsorbed water.

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