

The adsorption kinetics and removal of cationic dye, Toluidine Blue O, from aqueous solution with Turkish zeolite

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Abstract

Clinoptilolite, a natural zeolite, was investigated as an inexpensive and effective adsorbent for the adsorption of Toluidine Blue O (TBO) from its aqueous solution. The effect of parameters such as the initial concentration of TBO, the solution of pH, contact time, temperature and particle size on the TBO adsorption was examined. The adsorption rate data were analysed according to the first and second-order kinetic models. Kinetic studies show that adsorption of TBO on clinoptilolite was fitted to the second-order adsorption model with two-step diffusion process. The activation energies for TBO adsorption on clinoptilolite for the first and second diffusion processes were 8.72 kJ mol^{-1} and $19.02 \text{ kJ mol}^{-1}$, respectively. The adsorption isotherm was well fitted to both the Langmuir and Freundlich models. The maximum adsorption capacity of clinoptilolite for TBO was $2.1 \times 10^{-4} \text{ mol g}^{-1}$ at solution pH of 11.0.

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Keywords: Adsorption mechanism; Toluidine Blue O; Clinoptilolite; Adsorption kinetics; Dye

1. Introduction

Many industries have been widely used dyes and pigments for various purposes and their effluents can cause environmental pollution. In order to remove dyes from aqueous solutions, many chemical or biological treatments have been used either individually or together [1]. Among these removal methods, the adsorption process is a prominent method. Activated carbon is the most popular adsorbent and widely used [2,3]; on the other hand, due to its expensive cost and necessity of regeneration, many new approaches have been developed. In the recent years, for the removal of different type of substances from wastewaters, several materials have been evaluated as adsorbents like silicagel [4], clay [5], perlite [6–9], zeolite [10–18], hydroxyapatite [19], fly ash [20–23], unburned carbon [24,25], coir pith carbon [26,27], pulp fibers [28], shale oil ash [29], silkworm pupa [30], etc.

Synthetic and natural zeolites are important alternatives as adsorbents due to its high ion-exchange and adsorption capacities as well as thermal and mechanical stabilities. Clinoptilolite, a natural zeolite, has been used in several areas because of its sorptive and catalytic properties as well as its high ion-exchange capacity. The adsorption of ammonia [31–33] and heavy metals [34–46] through the use of natural zeolite has been investigated, and it has been realized that the application of zeolites in removing dye from wastewater has rarely been reported [10–18].

Toluidine Blue O, a phenothiazine type dye, has been widely used for different purposes in several fields such as medicine science, textile industry and biotechnology [47–50]. It can be used as a mediator for various chemical or biochemical reactions, colorant for cloths, photosensitizer for determining the actions of photoactivated microorganism and labelling agent for identifying organisms. The aim of this paper is to investigate the easy and economic removal method for Toluidine Blue O, a water soluble dye, from aqueous solution by adsorption on clinoptilolite. The effect of the initial concentration of Toluidine Blue O, the solution of pH, contact time, temperature, and particle size on the Toluidine Blue O adsorption was investigated. The adsorption kinetics and mechanism of Toluidine Blue O was also described.

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Table 1
The chemical composition of Gördes clinoptilolite

Constituent	Clinoptilolite (%)
SiO ₂	70.90
Al ₂ O ₃	12.40
Fe ₂ O ₃	1.21
CaO	2.54
MgO	0.83
Na ₂ O	0.28
K ₂ O	4.46
TiO ₂	0.089
MnO	<0.01
Cr ₂ O ₃	<0.01
LOI ^a	7.20

^a Loss on ignition.

2. Experimental

2.1. Materials

Clinoptilolite, used in the experiments was supplied by Enli Mining Corporation (Bornova-Izmir, Turkey) from the Manisa Gördes Region in Turkey. The chemical analysis of clinoptilolite involved was given in Table 1 [51]. Its cation exchange capacity, pore diameter, density, and surface area of Gördes clinoptilolite were 1.6–1.8 mequiv./g, 0.041 μm, 2.10 g/cm³, and 40.79 m²/g, respectively [52].

Toluidine Blue O (TBO) (Aldrich Chem. Co., USA), phenothiazine type dye, was used in adsorption experiments. All of the TBO solutions were prepared with distilled water. The pH of the solution was adjusted with HNO₃ (Merck, Darmsdat, Germany) or NaOH (Merck, Darmsdat, Germany) solutions by using WTW 330 pH-meter with a combined pH electrode.

2.2. Method

Adsorption experiments were performed by shaking 0.05–0.3 g of clinoptilolite samples in a 20 mL of aqueous solutions of TBO (solid/liquid ratio of 2.5–15.0 g/L). After the adsorption period, the mixtures were centrifuged for 5 min at 4500 rpm and the phases were separated. The equilibrium concentration of TBO in the solution phase (C_e) was determined spectrophotometrically by measuring absorbance at maximum wavelength of 633 nm for TBO through a Shimadzu 1601 UV–vis spectrophotometer. The TBO amount in the adsorbent phase was calculated by the following formula:

$$q_t = \frac{(C_0 - C_e)V}{m}$$

where q_t was the amount of dye adsorbed per gram of adsorbent (mol/g) at time t , C_0 and C_e the initial and equilibrium concentrations (M), of TBO in solution, V the volume of the solution (L), and m was the weight of the adsorbent (g).

To determine the effect of experimental parameters onto adsorption process, this method was also applied at different concentrations, pHs and temperatures of TBO solutions. The initial concentration of TBO (C_0) was used in the range 1.0×10^{-3} M to 3.0×10^{-3} M. The pHs of TBO solutions were changed

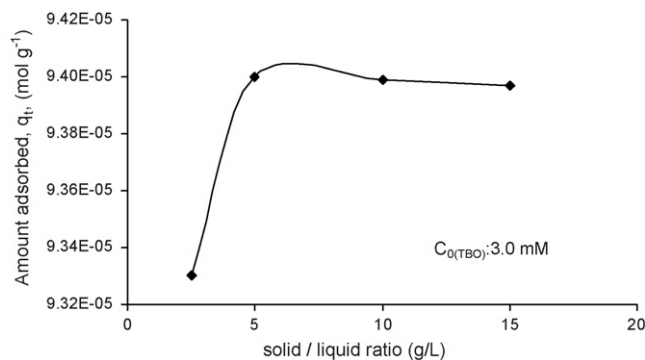


Fig. 1. Effect of solid/liquid ratio on the adsorption at 30 °C.

between 2.0 and 11.0. The Langmuir and Freundlich isotherms were evaluated at different temperatures.

3. Results and discussions

3.1. Preliminary experiments of TBO adsorption onto clinoptilolite

A series of experiments were performed with different solid/liquid ratios for varied times at 3.0×10^{-3} M initial TBO concentration to determine the optimum solid/liquid ratio and equilibrium time. When these solid/liquid ratios were compared to one another, the amount of adsorbed TBO at 5.0 g/L solid/liquid ratio was higher than that of 2.5 g/L solid/liquid ratio. The amount of adsorbed TBO at 5.0 g/L solid/liquid ratio was also higher than that of 10 g/L and 15 g/L solid/liquid ratio, but there were no significant differences between them (Fig. 1). Therefore, the optimum solid/liquid ratio was chosen as 5.0 g/L and it was used in the subsequent experiments.

The increasing time up to 30 min led to parallel increase in the amount of adsorbed TBO. The amount of adsorbed TBO increased sharply in 5 min then it showed slow increases up to 30 min (Fig. 2). The adsorption enhanced from 8.3×10^{-5} mol g⁻¹ to 9.4×10^{-5} mol g⁻¹ at a concentration of 3.0×10^{-3} M TBO when the contact time was increased from 5 min to 30 min. The adsorption process reached its equilibrium at 30 min. The amount of adsorbed TBO did not show significant change after 30 min. Consequently, the optimum equilibrium time was chosen as 30 min, and it was used in the further adsorption experiments.

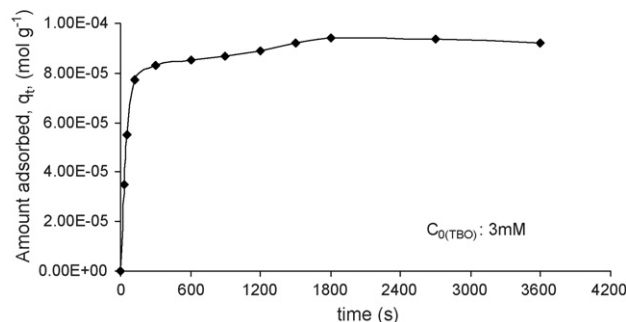


Fig. 2. Effect of contact time on the adsorption at 30 °C.

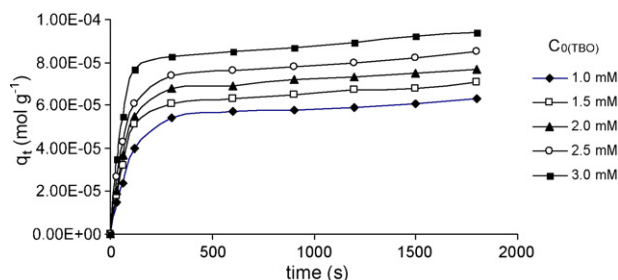


Fig. 3. Effect of the initial concentration on TBO adsorption onto clinoptilolite at 30 °C.

The effect of particle size of clinoptilolite was also investigated. For this purpose, three different particles (<45 μm , 63–100 μm , 200–300 μm) were examined. The results showed that the adsorption of TBO increased as the particle size decreased. This is probably because decreasing particle size brought about an increase in the surface area. This result can be compared with other studies [22,24]. Therefore, a clinoptilolite particle size of <45 μm was employed for other experiments.

3.2. The effect of the contact time and the initial concentration of TBO

Fig. 3 depicts the effect of initial concentration on TBO adsorption onto clinoptilolite. The amount of TBO adsorption increased with increasing both initial concentration of TBO and reaction times. The adsorption of TBO onto clinoptilolite reached equilibrium at 30 min. The amount of TBO adsorption was found $9.4 \times 10^{-5} \text{ mol g}^{-1}$ at a concentration of $3.0 \times 10^{-3} \text{ M}$ and pH of 7.0. The adsorption capacity of clinoptilolite for TBO is greater than the previous report [23], and approximately similar to another report [28].

3.3. The effect of pH of the solution

It is known that the adsorption of dyes onto the adsorbent surface is primarily influenced by the solution pH. Fig. 4 shows the TBO adsorption onto clinoptilolite at different pHs as a function of reaction time. As shown, the adsorption of TBO increased with the increasing pH and reached at a maximum level of pH 11.0. The adsorption increased from $6.4 \times 10^{-5} \text{ mol g}^{-1}$ to $2.1 \times 10^{-4} \text{ mol g}^{-1}$ at a concentration of $3.0 \times 10^{-3} \text{ M}$ TBO when the pH was enhanced from 2.0 to 11.0 at 30 °C. The increase of TBO adsorption onto clinoptilolite with increas-

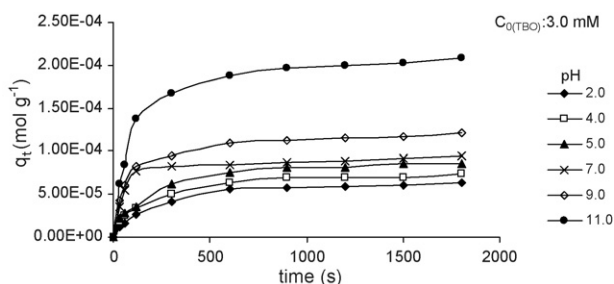


Fig. 4. Effect of pH on TBO adsorption onto clinoptilolite at 30 °C.

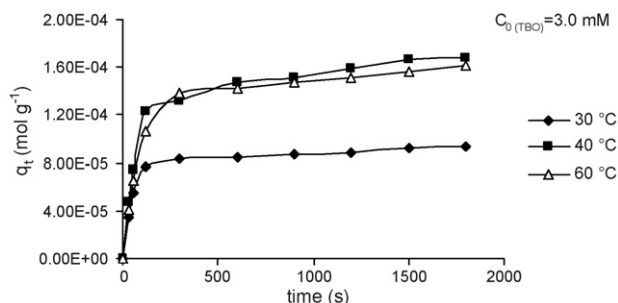


Fig. 5. Effect of temperature on TBO adsorption onto clinoptilolite.

ing pH values can be explained by the electrostatic interaction between cationic dye and negatively charged clinoptilolite surface. Doğan et al. [9] and Wang et al. [24] obtained similar enhancement in the adsorption of methylene blue with increasing pH.

3.4. The effect of the solution temperature

The effect of the solution temperature on TBO adsorption was investigated at various temperatures, 30 °C, 40 °C, and 60 °C. Compared to the 30 °C, the adsorption of TBO onto clinoptilolite increased at 40 °C (Fig. 5). The adsorption increased from $9.4 \times 10^{-5} \text{ mol g}^{-1}$ to $1.68 \times 10^{-4} \text{ mol g}^{-1}$ at a concentration of $3.0 \times 10^{-3} \text{ M}$ TBO when the temperature was increased from 30 °C to 40 °C. The increases of dye adsorption with an increasing temperature have been widely observed in many studies [8,9,24,25].

3.5. Adsorption kinetics and mechanism

The rate constants of TBO adsorption onto clinoptilolite were evaluated by using different kinetic models. According to Lagergren and Svenska Equation (1), the first-order rate constants were calculated:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

where q_e and q_t were the amounts of TBO adsorbed (mol g^{-1}) at equilibrium and at time t (s), respectively. The rate constants, k_1 , were calculated from the plots of $\ln(q_e - q_t)$ versus t for different concentrations, temperatures and pHs of TBO. The adsorption of TBO onto clinoptilolite was not fitted to a first-order reaction, for the correlation coefficients were lower than 0.99 and experimental and calculated values of equilibrium adsorption capacities (q_e) differ from each other.

The second-order kinetic model based on adsorption equilibrium capacity may be expressed as the following equation:

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

where k_2 was the rate constant of second-order TBO adsorption ($\text{g mol}^{-1} \text{ s}^{-1}$). Figs. 6–8 exhibit the linear plots of t/q_t versus t . The results show the experimental and calculated values of q_e agree with each other. The correlation coefficients for the second-order kinetic model were higher than 0.999 indicating

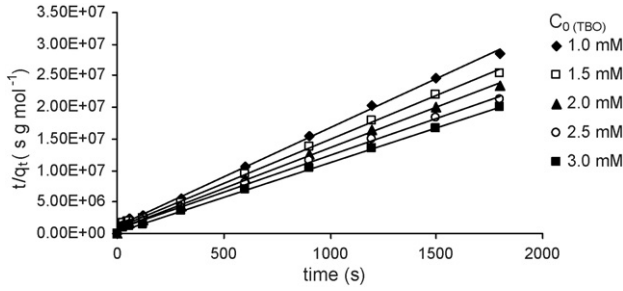


Fig. 6. Second-order kinetic model at different concentrations ($T: 30\text{ }^{\circ}\text{C}$).

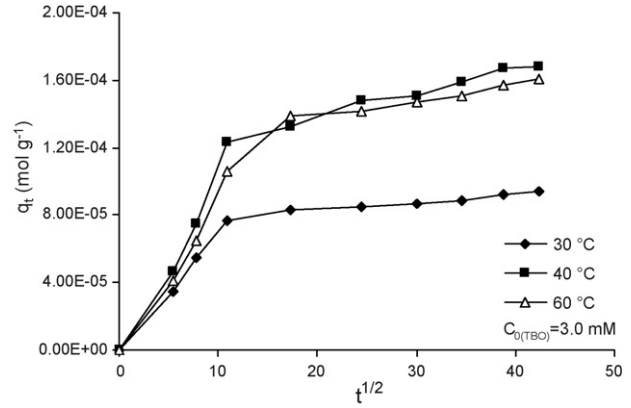


Fig. 9. Intra-particle diffusion plots for adsorption of TBO onto clinoptilolite at different temperatures.

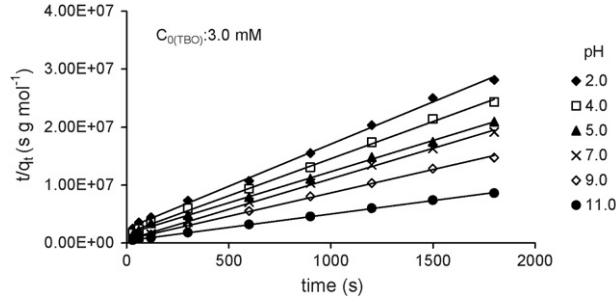


Fig. 7. Second-order kinetic model at different pHs ($T: 30\text{ }^{\circ}\text{C}$).

the applicability of this kinetic model of the adsorption process of TBO onto clinoptilolite. Similar results have been found in the adsorption of methylene blue [9,24], 2-chlorophenol [26] and congo red [27].

The intra-particle diffusion model was also examined by using the intra-particle diffusion from the following equation:

$$q_t = k_{dif}\sqrt{t} + C \quad (3)$$

where k_{dif} was the intra-particle diffusion rate constant ($\text{mol s}^{-1/2} \text{g}^{-1}$) and C was the intercept of the plot of q_t versus \sqrt{t} .

Fig. 9 shows the intra-particle diffusion model of TBO adsorption onto clinoptilolite. The plot presents a multilinearity, which indicates that two steps occur in the adsorption process. The diffusion rate constant for the second step was much smaller than that of the first step. The first sharper step was the external surface adsorption and the second step was the gradual adsorp-

tion. The adsorption of methylene blue onto fly ash, zeolite and unburned carbon showed similar a diffusion model [24].

The results using various kinetic models of TBO adsorption onto clinoptilolite was given in Table 2. The results showed that second-order model fitted to the experiments. The diffusion model for TBO adsorption onto clinoptilolite showed a two-stage adsorption process.

3.6. The analysis of the adsorption isotherms

In order to clarify the adsorption isotherms, Langmuir and Freundlich equations were used. The Langmuir equation is valid for the monolayer sorption onto surfaces with a finite number of identical sites and it can be expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

where q_e was the equilibrium concentration of TBO on clinoptilolite (mol g^{-1}), q_m the monolayer capacity of clinoptilolite (mol g^{-1}), K_L the adsorption constant (L mol^{-1}), and C_e was the equilibrium concentration of TBO in solution (M).

The Freundlich equation is employed to describe heterogeneous systems, and the equation in logarithmic form (5) can be given as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where K_F and n were the empirical Freundlich constants and indicative of adsorption capacity and adsorption intensity, respectively, q_e and C_e were as described above the Langmuir equation. The value of $1/n$ is generally between 0 and 1. When $1/n$ value closes to zero, the surface has become more heterogenic. A value for $1/n$ below one depicts a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [53].

The shape and favourability of the adsorption process can be identified in terms of a dimensionless separation factor (R_L). R_L is calculated as follows

$$R_L = \frac{1}{1 + K_L C_e} \quad (6)$$

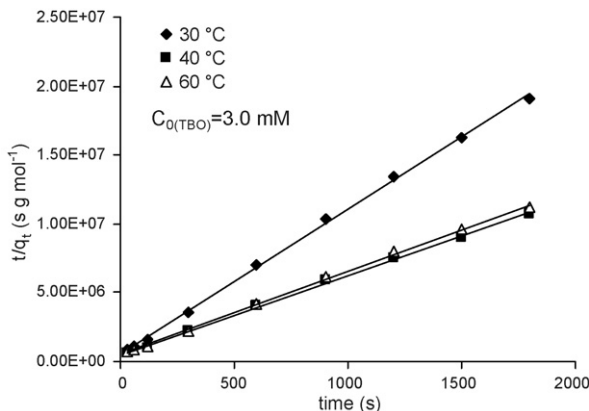


Fig. 8. Second-order kinetic model at different temperatures.

Table 2
Kinetic values calculated according to the second-order and diffusion kinetic models

Parameters			Second-order model				Diffusion model		
Temperature (°C)	Concentration ($\times 10^{-3}$ M)	pH	q_e (mol g $^{-1}$)	k_2 (g mol $^{-1}$ s $^{-1}$)	R^2	k_{diff} (mol s $^{-1/2}$ g $^{-1}$)	R^2	k_{diff} (mol s $^{-1/2}$ g $^{-1}$)	R^2
30	3.0	7.0	9.49×10^{-5}	205.05	0.9989	7.0×10^{-6}	0.9967	4.0×10^{-7}	0.9685
40	3.0	7.0	1.74×10^{-4}	66.40	0.9982	1.0×10^{-5}	0.9778	1.0×10^{-6}	0.9691
60	3.0	7.0	1.66×10^{-4}	68.84	0.9988	9.0×10^{-6}	0.9874	9.0×10^{-7}	0.9639
30	1.0	7.0	6.41×10^{-5}	243.3	0.9975	4.0×10^{-6}	0.9744	3.0×10^{-7}	0.9709
30	1.5	7.0	7.15×10^{-5}	231.17	0.9977	5.0×10^{-6}	0.9718	4.0×10^{-7}	0.9734
30	2.5	7.0	8.52×10^{-5}	227.26	0.9981	6.0×10^{-6}	0.9955	4.0×10^{-7}	0.9664

where K_L signifies the Langmuir constant and C_e is the equilibrium concentration. According to the value of R_L , the isotherm shape can be expressed as unfavourable ($R_L > 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values for the adsorption of TBO onto the clinoptilolite in the range 0.17–0.33, 0.14–0.45, and 0.13–0.40 at 30 °C, 40 °C, and 60 °C depict that the adsorption process is favourable at all temperatures.

Figs. 10 and 11 show the linearized Langmuir and Freundlich adsorption isotherms of TBO on clinoptilolite at different temperatures. The parameters for two isotherms obtained from experimental data and the related correlation coefficients are also presented in Table 3. As seen from Table 3, the Langmuir model yields a better fit ($R^2 = 0.9926$ and 0.9983) than the Freundlich model ($R^2 = 0.9830$ and 0.9488) at 40 °C and 60 °C. At 30 °C, adsorption process is well fitted to both Langmuir ($R^2 = 0.9922$) and Freundlich ($R^2 = 0.9901$) models. As also showed in Table 3, the values of $1/n$ are 0.2722, 0.2234, and 0.2472, which depict a favourable adsorption.

3.7. Activation parameter

The activation energy of TBO adsorption was calculated from the Arrhenius plot using Arrhenius equation:

$$\ln k_{\text{diff}} = \ln k_0 - \frac{E_a}{R_g T} \quad (7)$$

where k_{diff} was the intra-particle diffusion rate constant of TBO adsorption (g mol $^{-1}$ s $^{-1}$), k_0 the temperature independent factor (g mol $^{-1}$ s $^{-1}$), E_a the activation energy of TBO adsorption (kJ mol $^{-1}$), R_g the gas constant (J K $^{-1}$ mol $^{-1}$), and T was the solution temperature (K).

According to the slope of Arrhenius plots, the activation energies were calculated as 8.72 kJ mol $^{-1}$ and 19.02 kJ mol $^{-1}$ for two-stage intra-particle diffusion of TBO from its solution. The methylene blue adsorption onto perlite showed one-stage intra-particle diffusion, and activation energy was found 13.96 kJ mol $^{-1}$ [9]. The other investigation for methylene blue adsorption onto unburned carbon exhibited two-stage

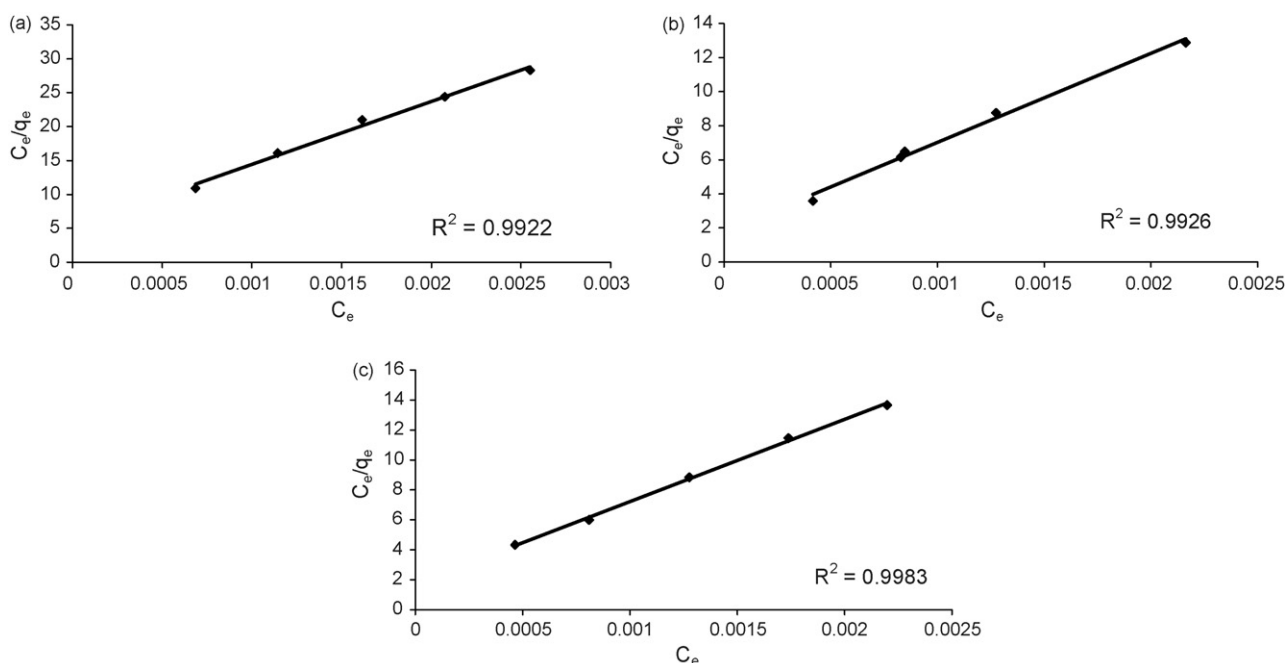


Fig. 10. Langmuir plots for adsorption of TBO onto clinoptilolite at different temperatures (a) 30 °C; (b) 40 °C; (c) 60 °C.

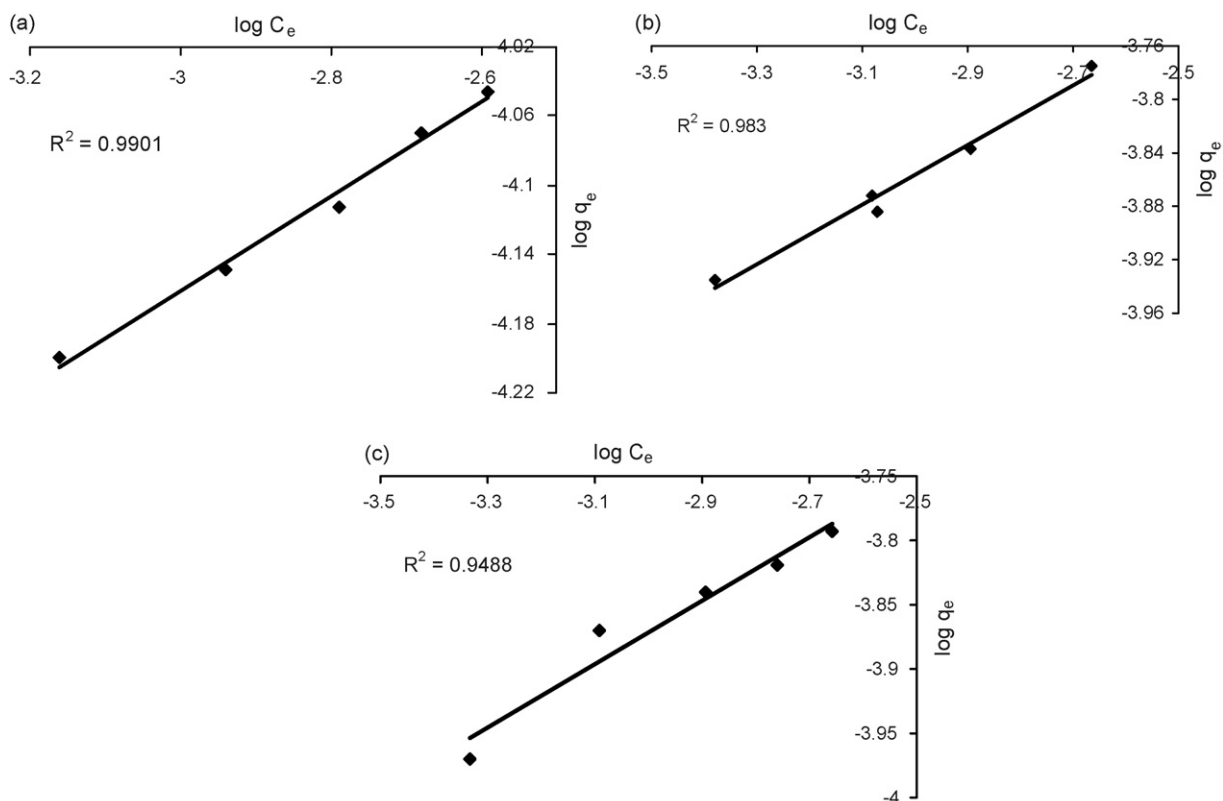


Fig. 11. Freundlich plots for adsorption of TBO onto clinoptilolite at different temperatures (a) 30 °C; (b) 40 °C; (c) 60 °C.

Table 3
Parameters of Langmuir and Freundlich isotherms

Temperature (°C)	pH	Langmuir isotherm			Freundlich isotherm		
		K_L (L/mol)	q_m ($\times 10^{-4}$ mol g $^{-1}$)	R^2	K_F ($\times 10^{-4}$)	$1/n$	R^2
30	7.0	1786	1.08	0.9922	4.52	0.2722	0.9901
40	7.0	2903	1.92	0.9926	6.51	0.2234	0.9830
60	7.0	3163	1.82	0.9983	7.42	0.2472	0.9488

intra-particle diffusion, and activation energies for both stages were obtained as 12.4 kJ mol $^{-1}$ and 39.3 kJ mol $^{-1}$ [24].

4. Conclusion

Clinoptilolite, a natural zeolite, was firstly reported for the adsorption of TBO. It was a highly efficient adsorbent for TBO adsorption in the aqueous solution. The adsorption of TBO was found to be dependent on concentration, temperature, pH, contact time and adsorbent amount. The adsorbed amount of TBO increased with increasing concentration, pH and temperature. The kinetics of TBO adsorption show that a contact time of 30 min was needed to reach equilibrium values within the experimental system used. The optimum amount of clinoptilolite was found to be 5.0 g/L. The results obtained in batch adsorption of TBO onto clinoptilolite showed that the adsorption kinetics can be explained by a second-order equation better than Lagergren's first-order. The adsorption process could be well described by two-stage diffusion. The data obtained from adsorption isotherms were well fitted to Langmuir model at

all temperatures and well fitted to Freundlich model at 30 °C. Compared to the other investigations related to adsorption of some dyes, our results were in good agreement [9,23,24,28]. The cost and adsorption characteristics favour clinoptilolite to be used as an effective adsorbent for the removal of TBO. The adsorption of TBO onto clinoptilolite was successively achieved, and these results are also promising for the use of TBO-adsorbed clinoptilolite to prepare a sensor in our further investigations.

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