



Removal of tetracycline from aqueous solution using Fe-doped zeolite

M. H. Jannat Abadi¹ · S. M. M. Nouri² · R. Zhiani^{3,4} · H. D. Heydarzadeh² · A. Motavalizadehkakhky⁵

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Abstract

Tetracycline is one of the most widely used antibiotics that causes contamination of aqueous environments and has raised serious concern during the past few years. In this work, adsorption of tetracycline on a modified zeolite was studied through a batch system. Synthetic zeolite 13X was modified using Fe(III). The results show that the removal efficiency of tetracycline by modified zeolite has considerably increased. Different experiments were carried out in order to analyze the effect of parameters such as pH, initial concentration of tetracycline, time, etc. The results indicate that tetracycline adsorption on the zeolite strongly depends on the pH of the solution due to amphoteric functional groups of tetracycline and maximum adsorption capacity of tetracycline by modified zeolite with a pH of approximately 6. The Langmuir isotherm shows good agreement with the experimental data suggesting monolayer adsorption. Maximum adsorption capacity of the modified zeolite reached at the experiments is almost 200 mg/g. XRD, XRF and FTIR results confirm the existence of the Fe phase in the zeolite texture. Amide groups of TC were responsible for the complexation with Fe³⁺. Also, tetracycline removal was studied in a continuous column to simulate an industrial waste water process.

Keywords Tetracycline removal · Adsorption · Modified zeolite · Fe-doped sorbent

Introduction

Tetracyclines (TC) are a broad spectrum class of antibiotics and are widely used for veterinary and human health purposes [1]. A large portion of antibiotics is transmitted from the body to excretion without modification. Excessive use of antibiotics, improper disposal, and lack of policy regulations pose a serious environmental and health concern [2].

Constant exposure to antibiotics in the environment not only disturbs natural ecological processes but can also be

fatal to humans in the form of multi-antibiotic resistant bacteria. These bacteria are present in environmental sources (e.g., water, soil, and sediments) and can readily transfer their resistance to pathogenic bacteria via horizontal gene transfer, resulting in a global antibiotic resistance problem [3].

In the last two decades, progress has been made to address the antibiotic contamination problems in many environmental sources using various remediation technologies. Several physical and chemical degradation methods such as chemical oxidation, adsorption, membrane filtration, ozonation, photo-fenton, and bio-degradation methods such as activated sludge, membrane reactor, and fixed bed reactor treatment have been applied to many antibiotics including TC with the purpose of degrading them in environmental sources. However, these remediation technologies are highly condition-based (e.g., pH, and molar ratio) and potentially expensive based on the concentration of the contaminant present in the environmental source (antibiotic) that needs to be degraded [4–9].

Removal of antibiotics by adsorption is one of the inexpensive methods with small technical difficulties. Many adsorbents have been widely used to remove tetracycline from wastewater such as carbon nanotubes [10], graphene

✉ S. M. M. Nouri
m.nouri@hsu.ac.ir

¹ Chemical Engineering Department, Islamic Azad University, Neyshabur Branch, Neyshabur, Iran

² Chemical Engineering Department, Hakim Sabzevari University, Sabzevar 9617976487, Iran

³ Young Researchers and Elite Club, Islamic Azad University, Neyshabur Branch, Neyshabur, Iran

⁴ Chemistry Department, New Materials Technology and Processing Research Center, Islamic Azad University, Neyshabur Branch, Neyshabur, Iran

⁵ Chemistry Department, Islamic Azad University, Neyshabur Branch, Neyshabur, Iran



oxide [11], activated carbon [12, 13], zeolites [14–16] and metal oxides [17]. Synthetic zeolite 13X is a common adsorbent which is composed of silicon-oxygen and aluminum-oxygen tetrahedron connected by oxygen atoms. The uniform pore structure and high surface area make it an ideal sorbent. The cation exchange capacity is relatively high, which enhances the effect of surface modification on the adsorbent capacity of the sorbent [18, 19]. Fe oxides are widely spread in ecosystems, and iron modified zeolites have been used for organic and heavy metal removal from wastewaters [20–23]. They show high affinity to TC compounds due to the surface complexation process [24, 25]. Iron ion could form a bridge between the zeolite and tetracycline molecule and enhance the adsorption process [26, 27].

The purpose of this work is to remove tetracycline using synthetic zeolite 13X. The synthetic zeolite has been modified with trivalent iron. The effect of different operating parameters such as pH, time, adsorbent dosage, etc. has been investigated.

Materials and methods

The zeolite used in this work is Na-13X which was purchased from IranZeolite. Tetracycline hydrochloride was purchased from Aldrich, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and NaOH from Merck Inc.

In order to prepare the treated zeolite, 3 g of zeolite was impregnated in 50 cc solution of 40 mmol FeCl_3 . The solution was stirred at room temperature for 24 h, separated and washed several times with deionized water and dried at 105 °C overnight. The obtained samples were powdered and used for the adsorption experiments.

For the adsorption experiments, 50 ml of tetracycline solution with different concentrations and specified amounts of sorbent were mixed using a shaker for 24 h to make sure it reaches the equilibrium state. After separation by centrifuge, the supernatant solution was collected for concentration measurement using UV–Vis spectroscopy at 357 nm wavelength. The pH of the solutions was adjusted using 0.1 M NaOH and HCl. To investigate the effect of pH, experiments were carried out in the pH range of 2–9. For all the experiments, temperature was set to 30 °C. For the kinetic experiments, 75 mg of modified zeolite was added to 50 ml of tetracycline solution (200 ppm). Each 15 min, 1 ml of the solution was separated using a 0.22 μm membrane filter and the tetracycline concentration was measured.

FESEM (TESCAN MIRA III), XRD (Philips PW 1730), XRF (Philips PW 1410), BET (BELSORP MINI II) and FTIR (Thermo AVATAR) analyses were performed for characterization of the sorbents. The XRD analysis was performed using the Philips PW 1730 instrument at an angle between 10 and 80 degrees. A glass tube with 20 mm diameter and 130 mm height was used for removal of tetracycline at continuous conditions. The tetracycline solution (200 ppm) was delivered using a peristaltic pump at a flow rate of 1 ml/min. The breakthrough curves were used to study the adsorption capacity of the sorbents.

Results and discussion

Adsorbent characterization

Table 1 shows the XRF results for raw and modified zeolites. An increase in Fe content of the modified zeolite is noticeable. In addition, the Na content decreases which may be due the exchange of the Na^+ ion with Fe^{3+} ion. It seems that part of Fe^{3+} is exchanged with Na^+ in the zeolite texture and other parts were precipitated in the form of Fe_2O_3 .

To investigate the crystallinity of the sorbents and phase study, XRD analysis was carried out. Figure 1 shows the patterns for raw and modified zeolites. The characteristic peaks attributed to zeolite 13X can be seen at 2θ values of 12.5, 17.7, 21.7, 27.2 and 33.5. For the modified zeolite, no sharp and clear peaks attributed to iron oxide can be detected. The large difference in the concentration of zeolite to Fe is one of the main reasons that decreases the intensity of Fe oxide peaks in comparison to the zeolite peaks [28].

Figure 2 presents the FESEM graphs for raw and modified zeolites. No considerable changes can be observed in the morphology of the two samples.

BET results showed that the specific surface area of the zeolite significantly increases after modification, from 25.72 to 98.82 m^2/g . Total pore volume also increases from 0.1811 to 0.2716 cm^3/g .

Infrared spectrum analysis was carried out on the 13X zeolite sample before and after modification and also after tetracycline adsorption to investigate the mechanism of adsorption (Fig. 3). After modification of zeolite, a new band around 597 cm^{-1} appeared which is related to the Fe–O bond. In addition, some of the existing bands of 13X zeolite shifted such as the band of 439 cm^{-1} assigned to Si–O bond that shifted to 431 cm^{-1} and the band of 609

Table 1 XRF results for raw and modified zeolites

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	Cl	LOI
Raw zeolite	40.847	27.351	0.458	0.039	23	–	7
M-zeolite	40.969	27.036	8.445	0.073	8.349	2.3	12

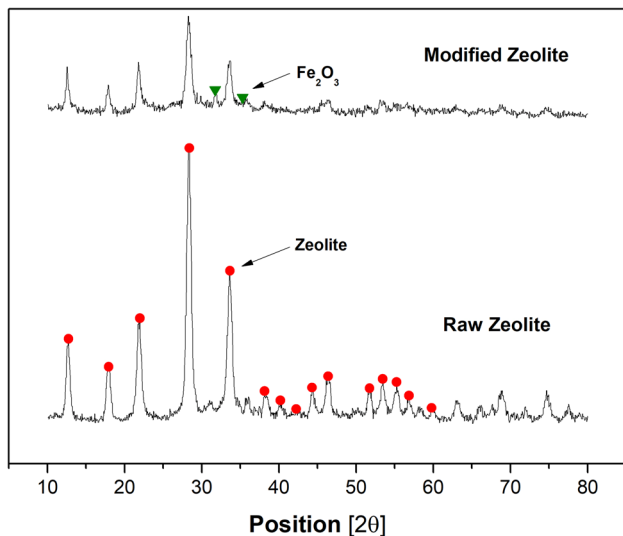


Fig. 1 XRD patterns of raw and modified zeolites

assigned to the Al–O bond that shifted to 605 cm^{-1} . These changes indicate the formation of the Fe–O bond on the zeolite through the interaction between the Fe ion and the O^{2-} anion of Si–O–Al. IR spectra of Fe-13X zeolite after TC adsorption change as a new band around 1462 cm^{-1} assigned to vibration of the aromatic ring of TC appeared. The band of 1675 cm^{-1} assigned to the C=O amid group shifted to 1720 cm^{-1} . It can be concluded that iron ion has interaction with the nitrogen atom of the amide group of TC.

Figure 4 presents a comparison between the raw and modified zeolites for tetracycline removal. The adsorption efficiency increases considerably after modification. The absorption percentage is obtained using the following equation:

$$\text{Ad\%} = \frac{C_0 - C_f}{C_0} \times 100. \quad (1)$$

The amount of tetracycline adsorbed per unit mass of zeolite is calculated as follows:

$$q_e = \frac{(C_0 - C_f) \times V}{m}. \quad (2)$$

C_0 and C_f are the initial and final concentration of the solution in ppm, V is the volume of solution in liters and m is the weight of the adsorbent in grams.

Effect of sorbent dosage

The effect of adsorbent weight on the adsorption capacity is shown in Fig. 4. It can be seen that for the adsorbent weight of 75 mg, the removal efficiency is nearly optimum (high enough and does not change considerably with increasing the sorbent weight). However, the adsorption capacity of sorbent decreases with increasing the sorbent dosage. This may be due to the fact that the ratio of the number of TC molecules in the solution to vacant sites of the sorbent decreases with increasing the sorbent weight. Thus, the probability of interaction between vacant sites and TC molecules decreases.

Effect of pH

The effect of pH on the efficiency of tetracycline removal by zeolite 13X is shown in Fig. 5.

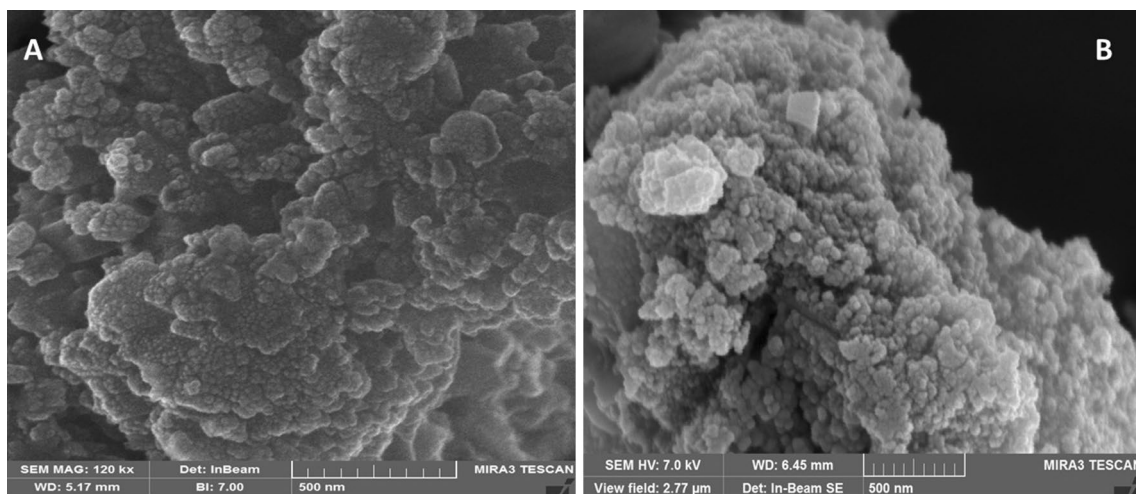


Fig. 2 FESEM images of raw (a) and modified (b) zeolites



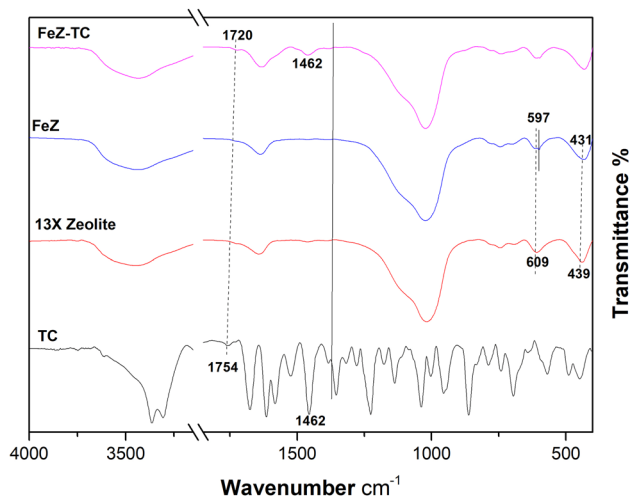


Fig. 3 IR spectra of TC, raw zeolite, modified zeolite, and modified zeolite after TC adsorption

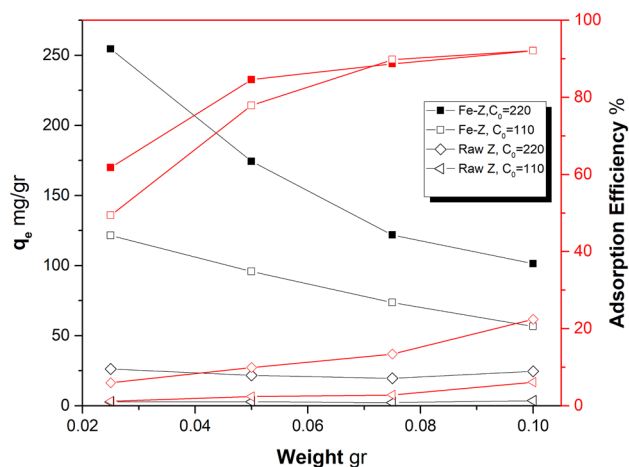


Fig. 4 Effect of sorbent dosage on the removal efficiency of tetracycline for raw and modified zeolites (pH 6, $T=25\text{ }^{\circ}\text{C}$, time=24 h)

The effect of pH on the absorption capacity depends on the structure of tetracycline and the functional groups of the zeolite-iron composite surface. The results show that the removal of tetracycline strongly depends on the pH of the solution. This is due to the fact that tetracycline charges considerably change with pH as shown in Fig. 6. For pH below 3.3, the dimethylammonium group is protonated, which results in tetracycline in $+00$ form. Between 3.3 and 7.7, it is in the form of zwitterion $+0$. Above 7.7, it is present as monovalent anion, $+--$, or a divalent anion, $0--$.

On the other hand, deprotonation and protonation reactions of iron hydroxide coated on zeolite change the

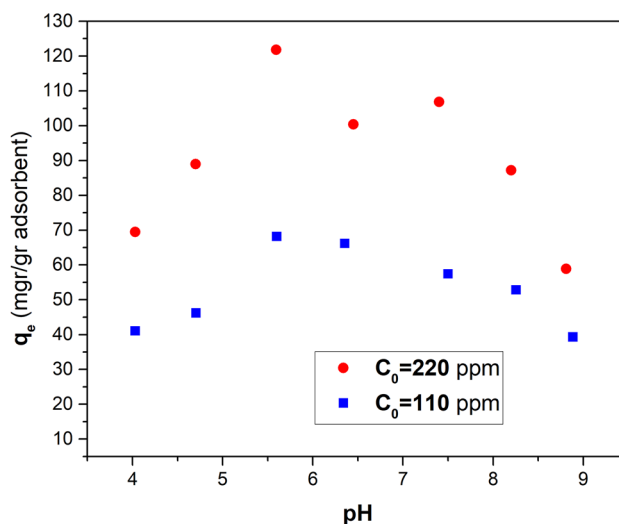


Fig. 5 Effect of pH on the removal efficiency of tetracycline by modified zeolite (sorbent weight=0.075 g, $T=25\text{ }^{\circ}\text{C}$, time=24 h)

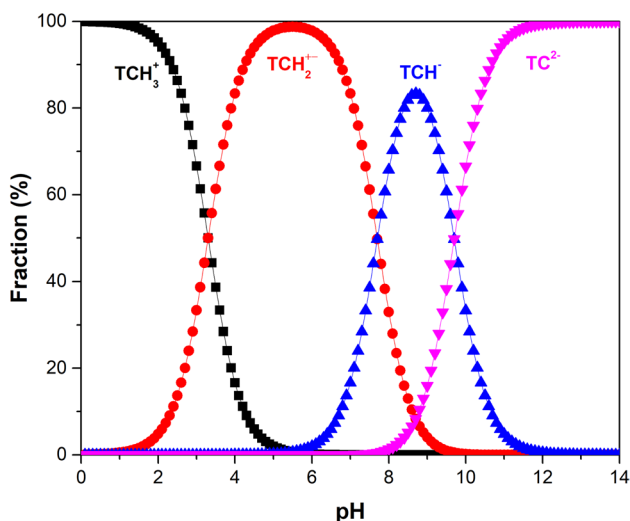


Fig. 6 Tetracycline dissociation under different pH values in aqueous solution

surface charge of the modified zeolite. Under the acidic condition, the surface charge is more positive and at alkaline condition, it becomes negatively charged [21]. This is in agreement with the fact that the pH_{zpc} of modified zeolite was measured as 6.35.

So, at acidic and alkaline conditions, electrostatic repulsion between tetracycline molecules and modified zeolite decreases the adsorption capacity. It seems that the best efficiency of modified sorbent for tetracycline removal is in the pH range of 5.5–6.



Kinetic experiments

The rate of tetracycline adsorption on the modified zeolite was analyzed using different kinetic models (Lagergren, pseudo-second order, Elovich and diffusion model).

Figure 7a presents the effect of contact time on the adsorption efficiency. First order and second order equations were used to investigate the kinetics of adsorption. The pseudo first order rate equation is as follows:

$$\frac{dq}{dt} = k_1(q_e - q). \tag{3}$$

Integrating Eq. (3) results in:

$$\frac{\ln q_e - q}{q_e} = -k_1 t. \tag{4}$$

The pseudo-second order equation can be expressed as:

$$\frac{dq}{dt} = k_2(q_e - q)^2. \tag{5}$$

Integrating Eq. (5) gives:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t. \tag{6}$$

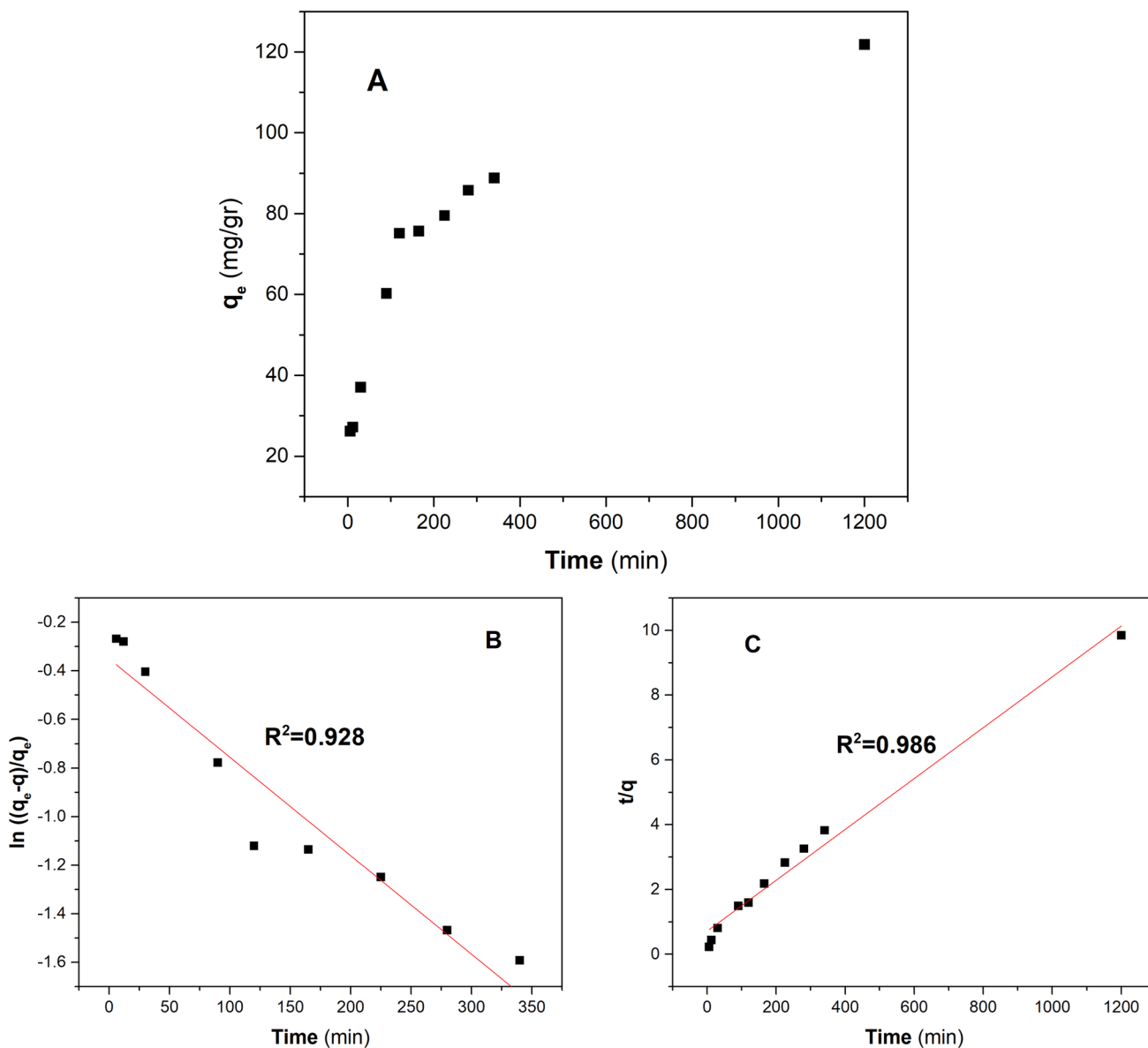


Fig. 7 a tetracycline concentration in the solution versus time, b linear form of first-order kinetic, c linear form for second-order kinetic (sorbent weight = 0.075 g, $T = 25\text{ }^\circ\text{C}$, time = 24 h)

By plotting $\frac{\ln q_e - q}{q_e}$ for the first order and $\frac{t}{q}$ for second order versus t , the lines with slopes of $-k_1$ and $\frac{1}{q_e}$ are obtained.

Figures 7b and 7c show the results of first and second order kinetics for tetracycline removal by the modified zeolite. As can be seen, the second order kinetics is more consistent with the experimental data. The Elovich model was usually applied to systems in which the solid surface is heterogeneous. The equation is formulated as [29, 30]:

$$\frac{dq}{dt} = a \exp(-bq_t). \quad (7)$$

It can be linearized and simplified as:

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t. \quad (8)$$

Figure 8a shows the linear form of the Elovich equation. According to the dimensionless form of the Elovich equation (Eq. 9) developed by Wu et al. [30], R_E is defined as the approaching equilibrium factor ranging between 0.02 and 0.3:

$$\frac{q_t}{q_{ref}} = R_E \ln\left(\frac{t}{t_{ref}}\right) + 1. \quad (9)$$

Using Eq. 9, R_E was calculated as 0.15. This value indicates that the kinetic of tetracycline adsorption on zeolite is in zone II and the curve rises mildly.

The overall rate of adsorption in a solid–liquid system could be described by three steps in series: (1) transport of adsorbent from the bulk of liquid to the solid surface; (2) diffusion of adsorbate from the surface through the pores of adsorbent; (3) adsorption on the vacant sites of the adsorbent.

Generally, the last step is very rapid and the mass transfer steps are the rate controlling stages [31]. The equation used for studying the diffusion regime is as follows:

$$q = k_d t^{1/2} + C. \quad (10)$$

k_d is the rate constant for intra-particle diffusion. C is a constant that represents the effect of external mass transfer. The higher the intercept (C), the bigger the effect of boundary layer resistance.

Figure 8b presents the diffusion stages of adsorption. The first section of the plot is related to the external mass transfer resistance and the latter linear portion represents the intraparticle diffusion.

Adsorption isotherms

Isotherm graphs examine the equilibrium absorbance at different concentrations and test their compatibility with the adsorption theories.

The Langmuir theory in the linear form is usually expressed as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b c_e}, \quad (11)$$

where q_m is the maximum single-layer absorption capacity in mg g^{-1} , C_e is the equilibrium concentration of TC in the solution (mg L^{-1}) and b is the Langmuir constant.

Another well-known model is the Freundlich isotherm, which assumes that the surface energy of the various active points are different and expressed as follows:

$$q_e = k c_e^{1/n}. \quad (12)$$

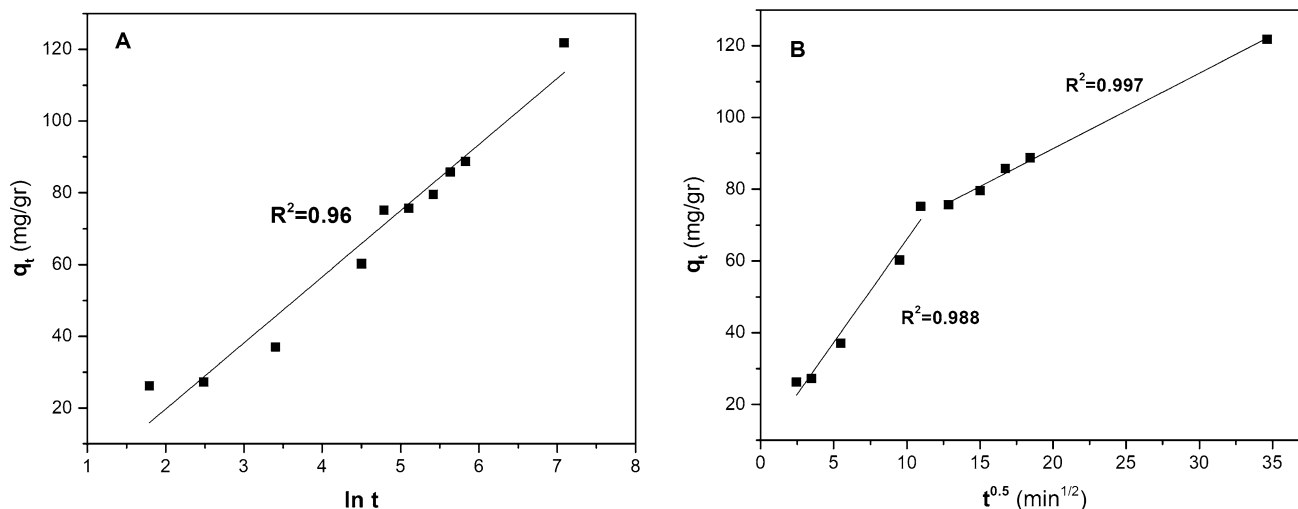


Fig. 8 a Elovich model and b intraparticle diffusion plot for adsorption of tetracycline on the modified zeolite

Table 2 Fitting parameters for the adsorption isotherms

Langmuir			Freundlich			D–R			Temkin	
q_m (mg g ⁻¹)	b	R^2	k	n	R^2	q_m	B	R^2	k_T	R^2
204	0.053	0.9958	48.32	3.85	0.9273	167	2×10^{-5}	0.83	35.7	0.975

By linearizing the equation above, the following equation is obtained:

$$\ln q_e = \ln k + \frac{1}{n} \ln c_e, \quad (13)$$

where k and n are the constants of the Freundlich equation, and C_e and q_e are the equilibrium concentrations of TC and the adsorption capacity.

The Dubinin–Radushkevich (DR) isotherm is another equation which has been widely used to correlate the experimental data of different microporous adsorbents [32, 33]. The linear form of D–R equation is as follows:

$$\ln q_e = \ln q_m - \beta \varepsilon^2, \quad \varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (14)$$

where q_e is the amount of tetracycline adsorbed at equilibrium state, q_m is the maximum adsorption capacity, β is the activity coefficient and ε is the Polanyi potential.

The Temkin isotherm assumes the linear decrease of the heat of adsorption of all molecules in a layer with increasing the surface coverage [34, 35]. The linear form is expressed as:

$$q_e = k_T \ln f + k_T \ln C_e. \quad (15)$$

where k_T and f are constant. Table 2 presents the fitting parameters calculated by different equations. Although the results of models can be used to explain the results, the Langmuir model best fits the experimental data (Fig. 9).

The results show that the experimental data matched the Langmuir equation well and R^2 is close to 1. Thus, the adsorption of TC on the modified zeolite is a selective monolayer adsorption due to the formation of a chemical bond. The maximum adsorption capacity of modified zeolite for tetracycline is 204 mg g⁻¹ which is about four times greater than unmodified zeolite. Table 3 presents a comparison between the adsorption capacities of different adsorbents for the removal of antibiotics reported in the literature.

Column study

Figure 10 shows the result of column experiments for the raw and modified zeolites. The breakthrough curves have a typical ‘S’ shape. The raw zeolite shows small retention for tetracycline (about 10%). Fe-modified zeolite, however, shows 100% removal of tetracycline for the first 10 bed volumes, despite the high concentration of tetracycline, which makes it possible for use in pharmaceutical wastewater treatment.

Conclusion

The following conclusions can be drawn from the results of this work:

1. Adsorption of TC on the modified zeolite is strongly pH dependent and the best results can be reached at a pH range of 5.5–6.
2. The Langmuir isotherm can be best fitted with the experimental data with an adsorption capacity as high as 200 mg g⁻¹, which is in agreement with the experimental results.
3. Modification of zeolite 13X with Fe³⁺ significantly increases the adsorption capacity of tetracycline.
4. The kinetics of adsorption follows the second order model. Also, the diffusion model is well fitted with the experimental data showing that external mass transfer and intra-particle diffusion play an important role on the overall rate of adsorption.
5. The modified zeolite shows good performance for the removal of tetracycline in the fixed bed column.



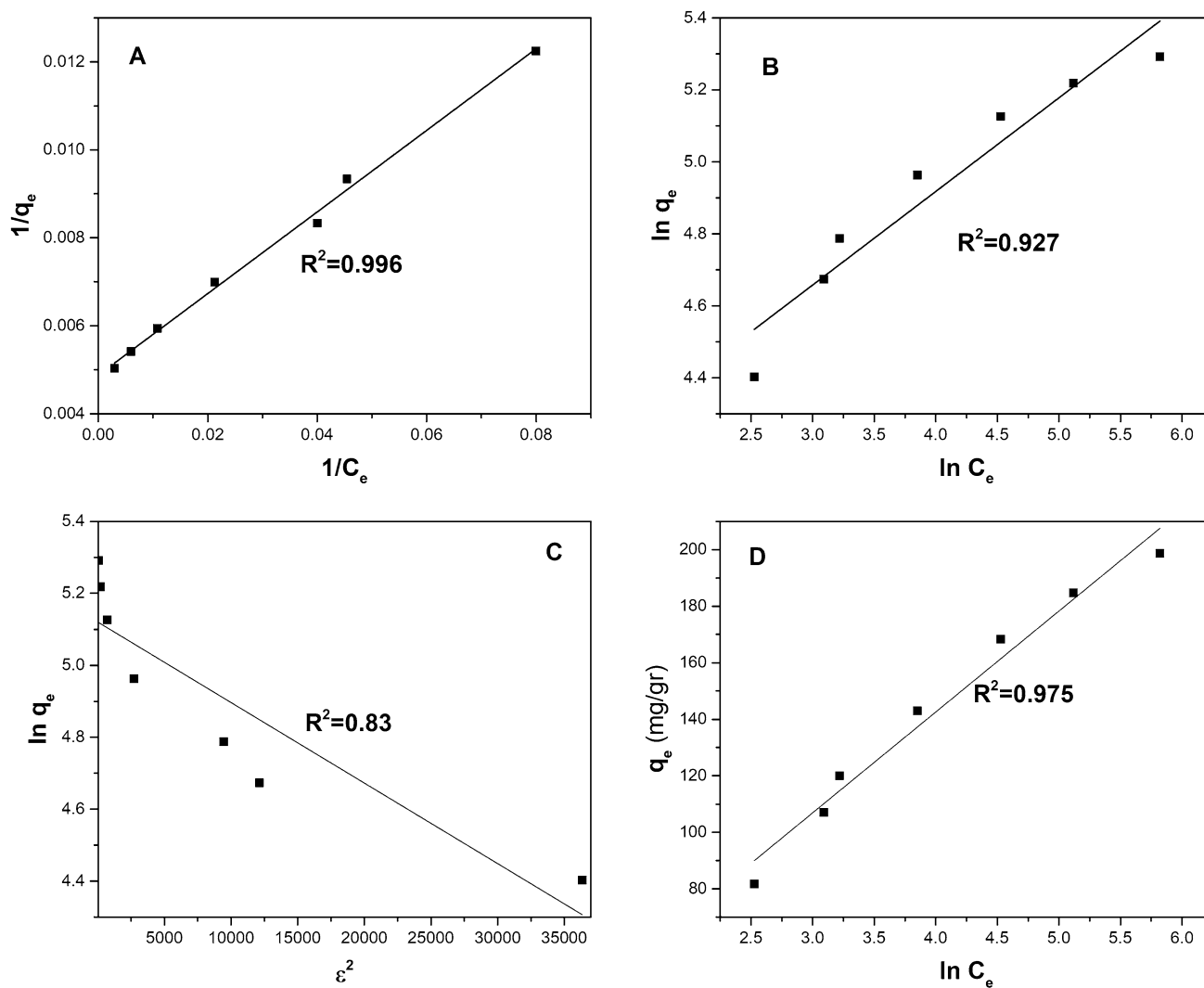


Fig. 9 Correlation of experimental data with **a** Langmuir isotherm and **b** Freundlich isotherm, **c** D–R isotherms and **d** Temkin isotherm

Table 3 Comparison between different adsorbents for tetracycline removal from solutions

Adsorbent	Contaminant	C_0 (ppm)	Time (min)	q_{\max} (mg/g)	References
Fe modified zeolite	Tetracycline	100–600	400	200	Current work
MWCNT	Tetracycline	50	20	150	[10]
Graphene oxide	Tetracycline	8–333	90	313	[11]
AC (beet pulp)	Tetracycline	200	720	280	[36]
AC (macadamia nut shell)	Tetracycline	500	180	410	[37]
GO functionalized magnetic particle	Tetracycline	10–50	10	39.1	[38]
Fe–Mn oxide	Tetracycline	44.4–222.2	840	90	[17]

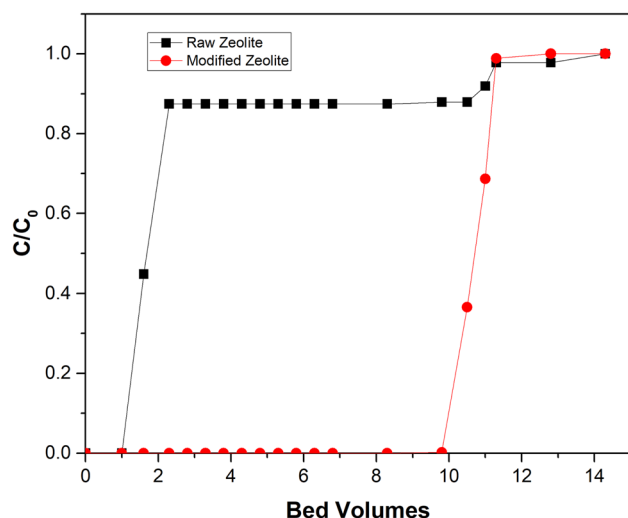


Fig. 10 Breakthrough curves for raw and modified zeolites ($T=25\text{ }^{\circ}\text{C}$, $C_0=220\text{ ppm}$)

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