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Research Article

ADSORPTION AND REMOVAL OF TETRACYCLIN ANTIBIOTIC FROM WATER BY ZEOLITE ADSORBENT

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ABSTRACT
The antibiotics have been widely used to treat diseases. Most antibiotics are changing undergo metabolic pathways in human body are excreted. Also, the presence of antibiotics in streams, lakes and water supplies encourages the growth of resistant bacteria in humans and environment. In fact, they may damage as the parent compounds or secondary metabolites into the environment through the discharge of wastewater. Therefore, the aim of this research is removal of tetracyclin antibiotic from water by zeolite adsorbent and to determine the mechanism and predominant factors controlling the adsorption of tetracycline on zeolite. For this purpose, firstly, a sorption kinetics experiment was conducted to understand the characteristics of the process. So, the zeolite adsorbent was added to a solution that had the tetracycline in pH 2 to 9 and temperature of 25° C for about 3.5 hr. Thus, sample was collected at the different time for the analysis of tetracycline concentration onto the zeolite adsorbent by UV/VIS spectrophotometer. Also, FTIR and X-ray diffraction were employed to probe the interaction of zeolite and tetracycline. Then, the sorption kinetics with Langmuir and Freundlich isotherm were studied through a kinetics experiment and a modeling simulation. The results showed that adsorption capacity of tetracycline onto zeolite increased when pH was increased from 2.0 to 5.0, and then, decreased significantly. So, it can be said, the effect of pH was associated with the pH-dependent speciation of tetracycline and surface charge property of zeolite. Also, 90% of adsorption of tetracycline onto the zeolite occurred rapidly in the first 45 minutes and the adsorption equilibrium was reached about 3 hr. An analysis of fourier transform infrared spectroscopy showed that surface complexation between tetracycline and the aluminum atoms in zeolite was responsible for the adsorption of tetracycline on the zeolite. Also, the results showed that tetracycline adsorption kinetics onto the zeolite is the similar to Langmuir.

Keywords: *Tetracycline, Zeolite, Adsorption Antibiotic, Langmuir Isotherm*

INTRODUCTION

The antibiotics have been widely used to treat diseases for several decades. Most antibiotics are changing undergo metabolic pathways in human body and are excreted in urine (about 90%) (Halling-Sørensen, 2001). In the description should be said, firstly, antibiotics are used for resistant bacteria in patients. Secondly, the presence of antibiotics in streams, lakes and water supplies encourages the growth of resistant bacteria in humans and environment. Therefore, they may damage as the parent compounds and/or secondary metabolites into the environment through the discharge of wastewater (Chen *et al.*, 2016).

Nowadays, the occurrence and fate of pharmaceutically active compounds in the water have been recognized as one of important problems in environmental (Garcia-Ivars *et al.*, 2017) so that, their potential impact on human health and ecosystem are unavoidably.

In fact, the occurrence of antibiotics in hospital effluents and waste or surface waters can be dangerous for environment (He *et al.*, 2016).

An investigation on three antibiotics from the sulfonamide, tetracycline, and macrolide groups have been shown that tetracycline plays the most significant role in environmental pollution, because tetracycline was found in both surface water and groundwater (Kay *et al.*, 2005; Batt and Aga, 2005; Lindsey *et al.*, 2001). So, wastewater treatment technology is needed for removing antibiotics.

Adsorption is one of used effective methods for treatment of low-concentration antibiotics. To date, studies and applications have been reported on organic pollutant and antibiotics for adsorption in adsorbents materials (Shu *et al.*, 1997; Franklin *et al.,* 1988). Recently, adsorption of tetracycline have been studied on soils, clays, humic acids, and metal oxides adsorbents that they may be effective (Pils JRV and Laird, 2005). However, the preparation procedures of some adsorbents are complicated and costly, which hinders their industrial applications.

In the meantime, zeolites a group of silicate minerals, are low-cost and easily available materials that can be a good adsorbent to remove organic compounds and hospital pollutants such as tetracycline from the environment. In fact, zeolites are crystalline alumino-silicates, characterized by three-dimensional networks containing channels and cavities whose dimensions are comparable with small organic molecules. Such networks of well-defined micro-pores may act as adsorption and reaction sites whose selectivity and activity can be modulated by acting on their structure and chemical composition. The three-dimensional framework, consisting of nanometre-sized channels and cages, imparts high porosity and a large surface area to these materials (**11,** Koohsaryan and Anbia, 2016). One of their defining features is that the shape of their internal pore structure can strongly affect their adsorption selectivity with respect to host molecules (Kowalska-Kus *et al.*, 2017; Emdadi *et al.*, 2017; Bergamasco *et al.*, 2017). Zeolites are commonly used in areas as diverse as laundry detergents, gas separation, oil refining and the petrochemical industries, agriculture, wastewater and sewage treatment (**11,** Faruque Hasan *et al.*, 2017). The aim of this research is the using zeolite adsorbent as a sorbent for the removal of tetracycline from water.

The aim of this research is to investigate the adsorption of tetracycline onto the zeolite and to determine the mechanism and predominant factors controlling the adsorption of tetracycline on zeolite. In the following, fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were employed to probe the interaction of zeolite and tetracycline. Then, the sorption kinetics with Langmuir and Freundlich isotherm were studied through a kinetics experiment and a modeling simulation.

MATERIALS AND METHODS

Materials

Zeolite (a micro-porous, aluminosilicate mineral with particle size <µm) was used in the study that was purchased from Sigma-Aldrich. Then, FTIR and X-ray diffraction (XRD) (X'Pert PRO, PANalytical, Netherlands) were used to confirm that no drastic structural change occurred.

Tetracycline with purity of 98% with Molecular Weiht of 444.43 g mol^{-1} and solubility of 95% ethanol:soluble 12.5 mg/ml (Figure 1) purchased from Sigma-Aldrich.

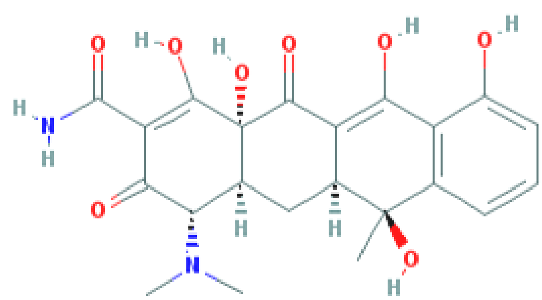

Figure 1: Molecular Structure of Tetracycline (Pils and Laird, 2005)

Methods

Determination of Adsorbent and Adsorbate Properties

1- *Adsorbent*

The specific surface, average pore sizes, and pore volumes of the adsorbents were determined by nitrogen adsorption/desorption isotherm method at liquid nitrogen temperature using the Accelerated Surface Area and Porosimetry (ASAP 2000, Micromeritics Co., USA). Prior to the analysis, the samples were degassed overnight at 105°C. The Brunauere Emmette Teller (BET) model was applied to calculate the apparent surface area. The point of zero charge (PZC) of the zeolite adsorbent was measured, which was similar to the method described by the literatures (Pils and Laird, 2005). So, 0.042 gr zeolite was added into a 40 mL NaCl solution (0.01 M) and the initial pH (pH_i) ranging from 2 to 9 was adjusted (by adding HCl or NaOH solution). The mixtures with various pHi values were shaken for 48 hr to allow them to reach the equilibrium. The final pH (pHf) versus pHi was plotted to determine the PZC.

2- Adsorbate

The equilibrium tetracycline concentrations were analyzed by a UV/VIS spectrophotometer (SmartSpec 3000, Bio-Rad Corp.) at a wavelength of 254 nm.

Adsorption onto Adsorbent

Firstly, a sorption kinetics experiment was conducted to understand the characteristics of the process. Therefore, the zeolite adsorbent (1 g/L) was added to a solution that had the 0.05 mM tetracycline, 0.01 M NaCl (as ionic strength background), pH 5.0 with the temperature of 25° C and about 3.5 hr. The sample was collected at the different time for the analysis of tetracycline concentration onto the zeolite adsorbent by UV/VIS spectrophotometer (figure 2).

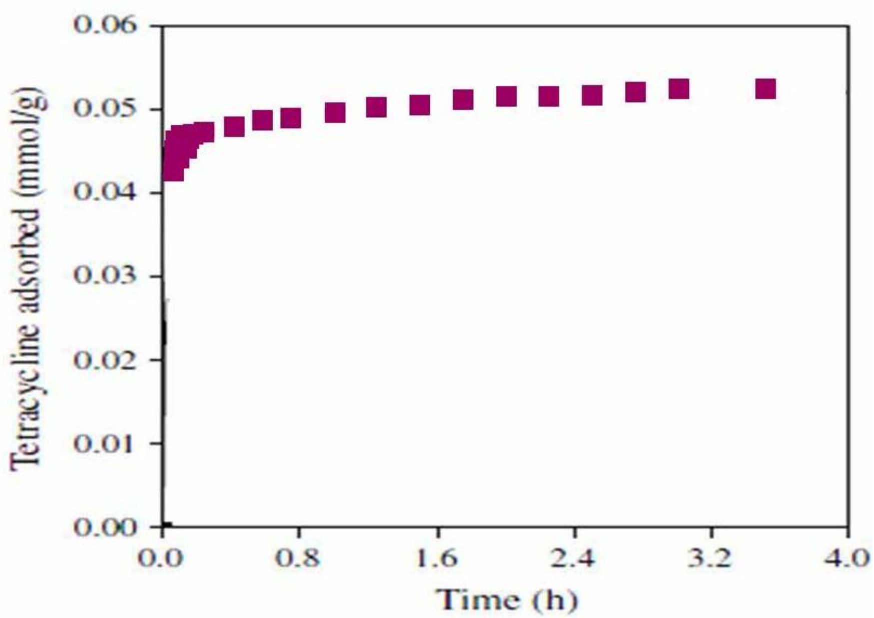

Figure 2: Adsorption Kinetics of Tetracycline on Zeolite

Also, in order to evaluate the pH effect (ranging from 2 to 9), 40 mL solution containing 0.1 mM tetracycline and 0.01 M NaCl was added into a tube containing 0.042 gr of sorbent and pH of the solution was adjusted by HCl solution and the mixtures were shaken at 25 °C for 3.5 hr. The samples were collected at the different pH for the analysis of tetracycline concentration onto the zeolite adsorbent by UV/VIS spectrophotometer (figure 3).

pH Effect Study

The adsorption of tetracycline onto zeolite adsorbent at different pH is shown in Figure 3. In accordance with the mentioned figure, the adsorption initially increased when the (2.0 to 5.0), and then, decreased. The adsorptive behavior may be associated with the pH of tetracycline and surface charge characteristics of zeolite. Tetracycline (TC_{H2L}) is an amphoteric molecule with multiple ionizable functional groups, and may exist as cation (TC_{H3L}^{+}), anions (TC_{HL}^{-} and $_{L}^{-2}$), zwitterions (TC_{H2L}^{0}), or at different pH. The following reactions may occur between tetracycline species and the zeolite (Ze_{SOH}) surface (Kang *et al.*, 2010).

$Ze_{SOH} + H^{+} = Ze_{SOH2}^{+}$ pH<PZC (1)
$Ze_{SOH} = Ze_{SO}^{-} + H^{+}$ pH> PZC (2)
$Ze_{SOH} + mH^{+} + TC_{HnL}^{n-2} = Ze_{SOH(m=n+1)L}^{m+n-2}$ [n= 0,1,2,3 and m+n=2] (3)

At a lower pH, the tetracycline mainly exists as positively charged species. So, it can be adsorbed onto zeolite through Equation (3) and electrostatic attraction between tetracycline and zeolite.

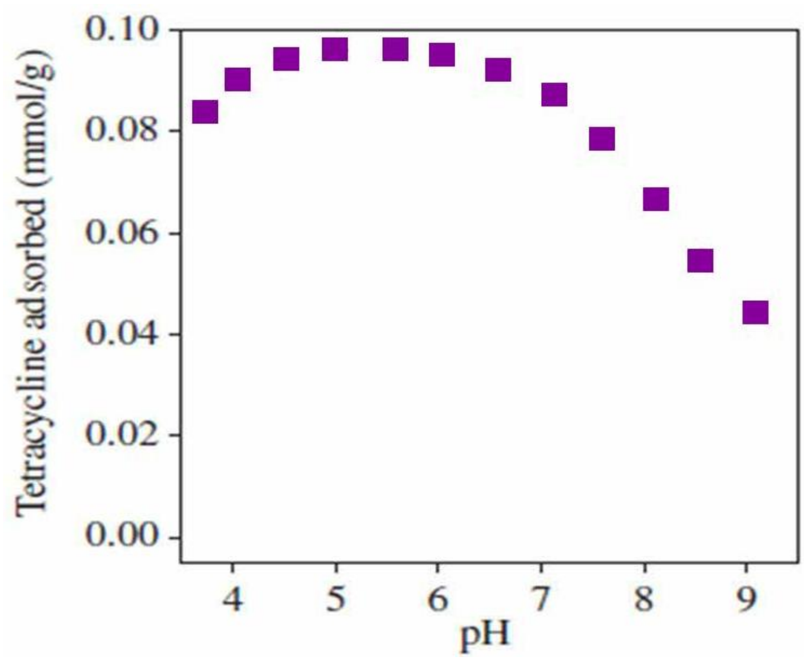

Figure 3: pH Effect on the Adsorption of Tetracycline on Zeolite

Adsorption Equilibrium

In the adsorption isotherm experiments, 40 mL tetracycline solutions with different concentrations were added into tubes containing 0.042 gr of sorbent and the solution pH was maintained at 5.0.

Adsorption Kinetics

Adsorption kinetic was found that about 90% of the uptake of tetracycline by the zeolite quickly occurred in the first 45 minutes, followed by a relative slow process. The adsorption equilibrium can be established about 3 h. The kinetics experimental result is shown in Figure 4. Simulation of tetracycline adsorption kinetics on zeolite (in figure 3) and was conducted by the intraparticle diffusion model with an assumption of a ‘‘two-step mass transport mechanism’’. Constant physical properties were assumed. The mathematical equation and its corresponding initial and boundary conditions are given as follows (Paul Chen and Lin, 2001):

$$\frac{1}{D_s}\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial q}{\partial r}\right] \quad 0 \le r \le a_p, t \ge 0 \quad (5)$$

$$q = 0 \quad 0 \le r \le a_p, t < 0 \quad (6)$$

$$\frac{\partial q}{\partial r} = 0 \quad r = 0 \quad (7)$$

$$D_s\rho_p\frac{\partial q}{\partial r} = k_f(C - C^*)r = a_p \quad (8)$$

In where (C) and (q) respectively are the concentrations of tetracycline in the bulk and solid phases. (C^*) is the aqueous phase concentration at the particle surface in equilibrium with the corresponding concentration in the solid phase (q^*).

D_s: Surface diffusion coefficient
ρ_p: Apparent particle density
r: Radius distance measured from the center of particle

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a_p: Particle radius
k_f: External mass transfer coefficient
t: Time

This model well describes the experimental data. The external mass transfer coefficient and the pore diffusion diffusivity were 7.1 $\times 10^{-3}$ m/s and 4.1×10^{-8} m^2/s, respectively. The values of both parameters were within the range of those in the literatures (Chang *et al.*, 2003).

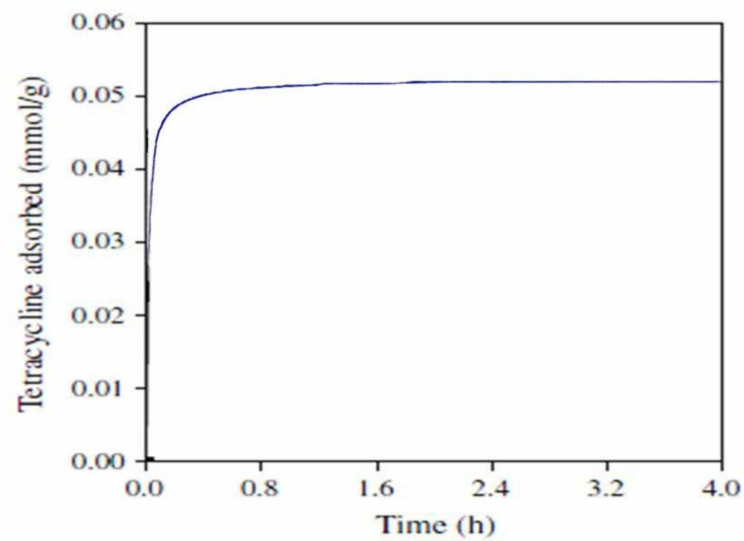

Figure 4: The Adsorption Kinetics Experimental of Tetracycline on Zeolite

Adsorption Isotherm

Adsorption isotherms of tetracycline on zeolite (with m=1.0gr/L) at different temperatures (10–40° C) with 0.01M NaCl and pH=5.0 have been showed in Figure 5. It shows that the adsorption is an endothermic process. It should be noted, tetracycline adsorption on zeolite is favored at a higher temperature.

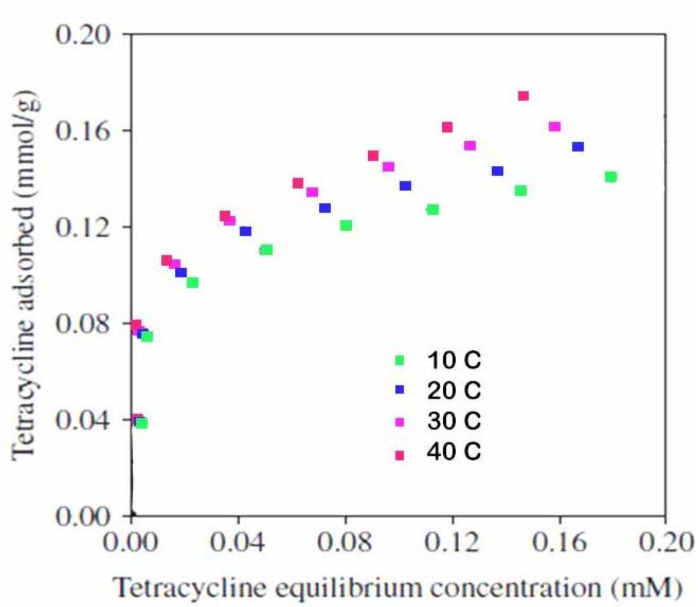

Figure 5: Adsorption Isotherms of Tetracycline on Zeolite at Different Temperatures

Freundlich and Langmuir isotherms are commonly used in the description of adsorption behavior.
Freundlich isotherm is given by the following equation.

$$q_e = k_f C_e^n \qquad (9)$$

q_e (mmol/g): Equilibrium adsorbed tetracycline concentration.
C_e (mM): Equilibrium aqueous tetracycline concentration.
k_f ($mmol^{1-n}/(L^n.g)$) and n: Respectively, the adsorptive capacity and intensity; Freundlich constants in the mentioned isotherm.
Also, the Langmuir isotherm is given by the following equation.

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \qquad (10)$$

q_{max} (mmol/g): Langmuir constant (representing maximum monolayer sorption capacity).
b (M^{-1}): Langmuir constant (related to the binding energy of adsorption).
The Langmuir and Freundlich isotherm parameters together with the regression coefficients are listed in Table 1. Correlation coefficient (r^2) is about 0.99. Also, figure 6 is showed adsorption kinetics with the mentioned isotherms.

Table 1: The Langmuir and Freundlich Isotherm Parameters

(T)°C	Freundlich Constants			Langmuir		
	K_f	N	r^2	q_{max}	B	r^2
10	0.20	0.22	0.996	0.14	118336.2	0.996
20	0.22	0.198	0.995	0.15	133877.8	0.995
30	0.23	0.199	0.995	0.16	147058.6	0.995
40	0.25	0.205	0.998	0.17	145478.7	0.999

* The Freundlich constants (n) of 0.198–0.205 ($0 < n < 1$) show the favorability of tetracycline adsorption onto the zeolite.

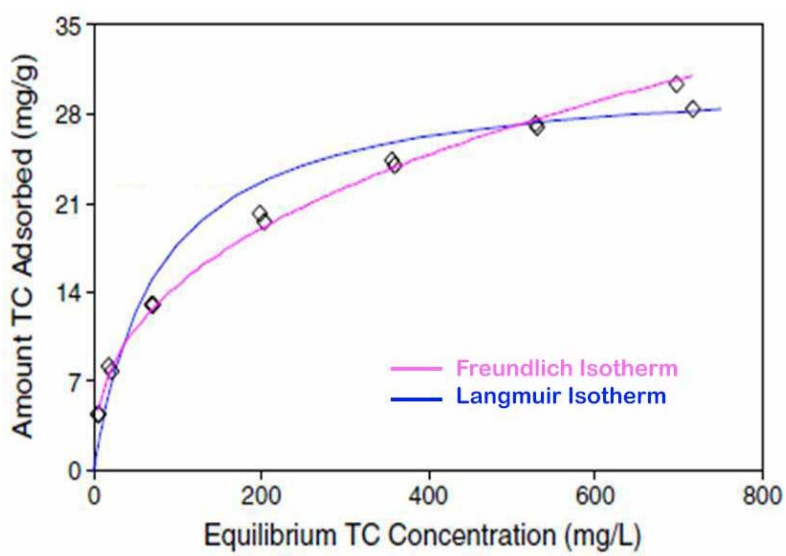

Figure 6: Tetracycline Adsorption Kinetics onto Zeolite with Langmuir and Freundlich Isotherm

To further evaluate the thermodynamic feasibility of the process and to study the nature of the sorption process, the thermodynamic constants, standard free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) were calculated using the following equations.

$$\Delta G = \Delta H - T\Delta S \qquad (11)$$

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (12)$$

T (°K): Temperature
R: Universal gas constant (8.314 J/ (mol K))
K: Equilibrium constant related to the Langmuir constant (b) that can be determined according to following equation (55.5 corresponds to the molar concentration of the solvent or water)
$K = b \times 55.5$
Table 2 shows ∆G (kJ/mol) in the temperature varies. The positive ∆H value (5.32 kJ/mol) suggests that the sorption in our study is an endothermic process.

Table 2: ∆G (kJ/mol) in the Temperature Varies

(T)°C	∆H (kJ/mol)	∆S (J/mol K)	∆G (kJ/mol)
10	5.32	149.5	-37.0
20			-38.5
30			-40.0
40			-41.5

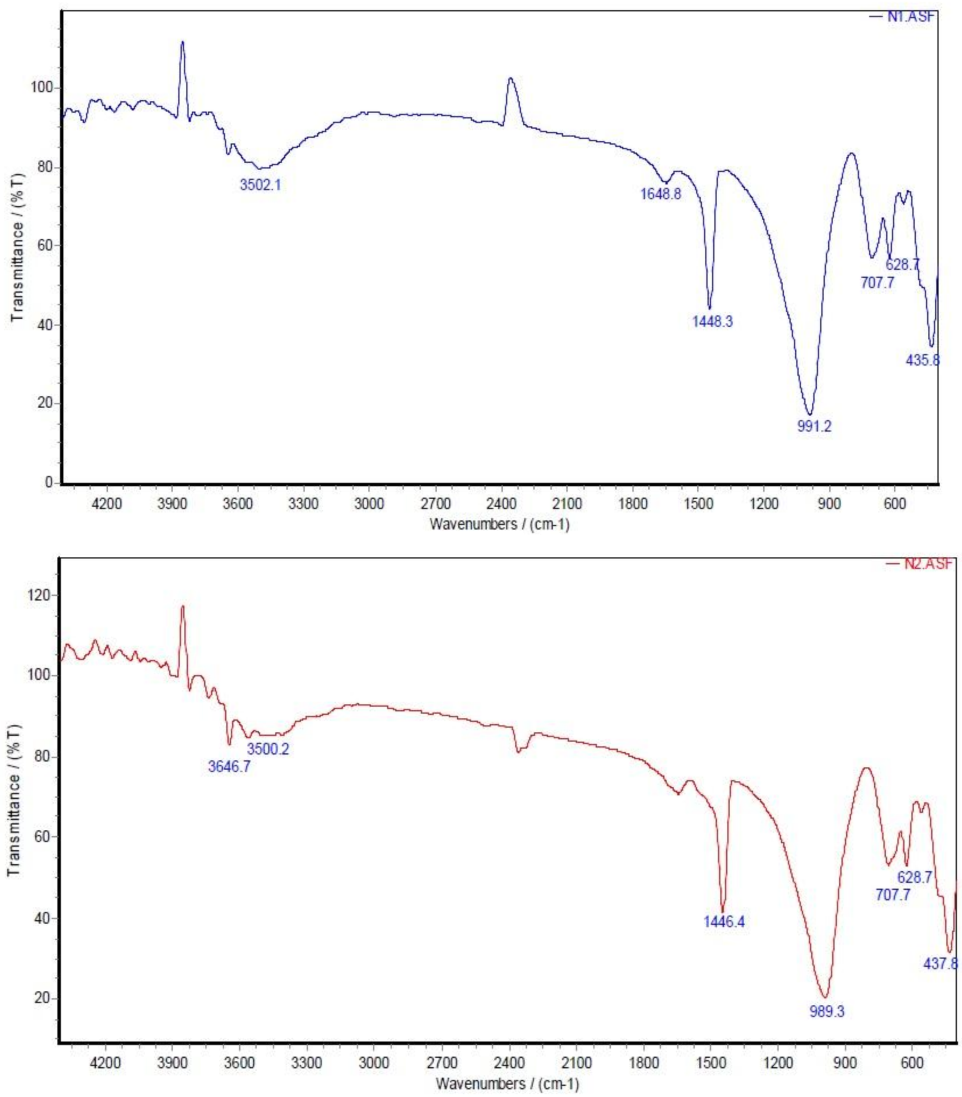

Figure 7: FTIR Spectra for Zeolite: before (the Spectra Blue) and after (the Spectrared) Tetracycline Adsorption

Fourier Transform Infrared Spectroscopy

FTIR spectra for adsorbents before and after tetracycline adsorption are shown in figure 7. Absorption bands at 3502.1 and 1648.8 cm^{-1} are ascribed to the ν(O–H) and δ(O–H) (Chen and Yang, 2005).

No apparent shift is observed in the spectra of the zeolite before and after the tetracycline adsorption, which indicates that the zeolite structure is not change during the adsorption. This conclusion can further be confirmed by the XRD patterns of zeolite before and after the adsorption of tetracycline (Figure 8).

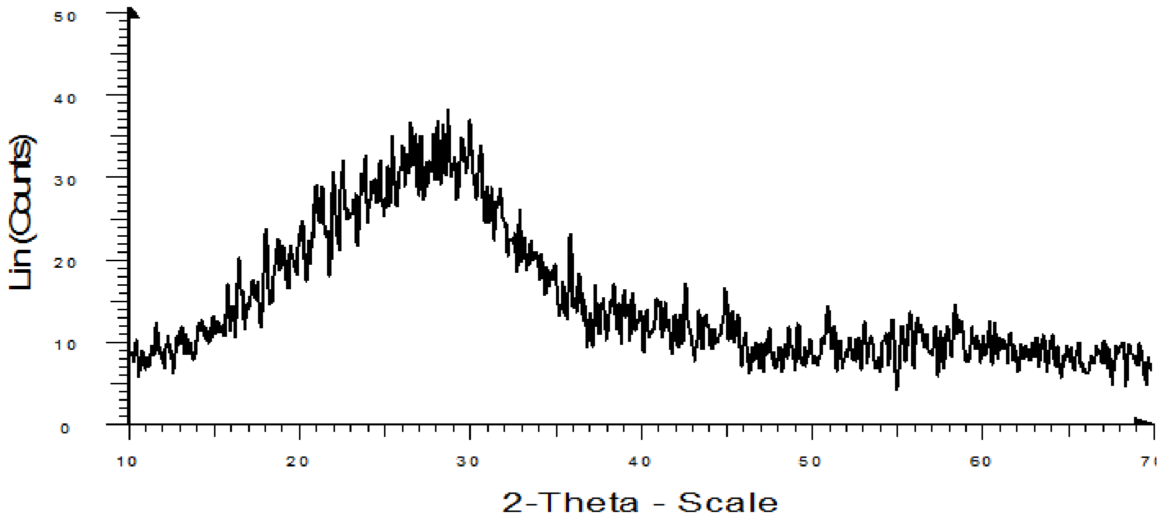

Figure 8: XRD Patterns of Zeolite

The Study of Morphology of Adsorbent

Scanning electron microscope (SEM) images were made to investigate the surface morphology of zeolite before and after tetracycline adsorption are shown in Figure 9.

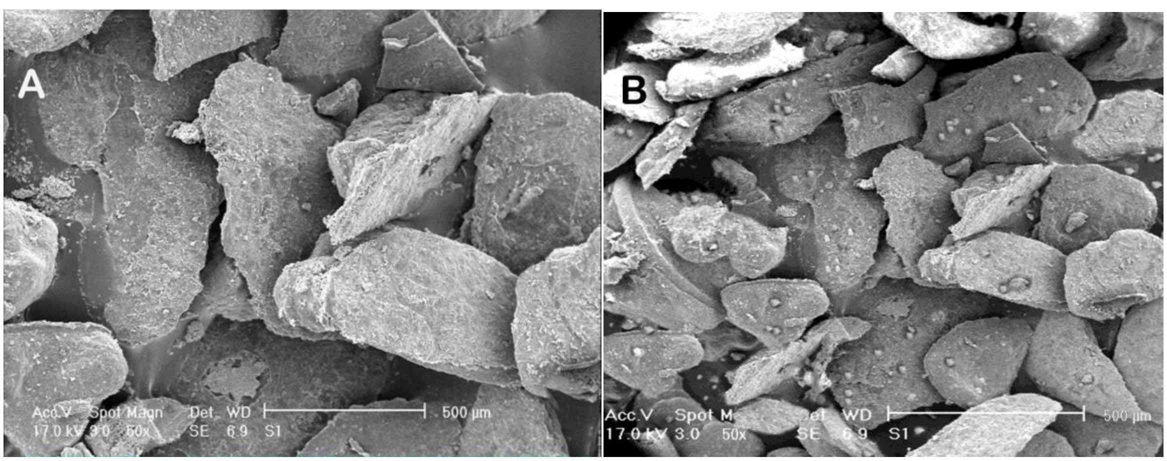

Figure 9: SEM Images of Zeolite Adsorbent before (A) and after (B) Tetracycline Adsorption

Also, the study of the basic properties of the zeolite adsorbent showed that the specific surface areas of the zeolite were ideal for adsorption of tetracycline. This high specific area of the zeolite adsorbent was appropriate for the adsorption of tetracycline from water solution.

The average pore sizes of the adsorbent were found to be 3.6 nm, which indicated the adsorbent used were porous. The pore volume of the zeolite was 0.55cm^3/g. Moreover, the PZC of the zeolite was 3.16, which indicated that the surfaces of the zeolite were negatively charged over the experimental pH ranging from 2 to 9.

RESULTS AND DISCUSSION

The presence of tetracycline together with other antibiotics even at micrograms per liter concentrations in natural aqueous environments may induce chronic toxic effects in aquatic plants and microorganisms. For instance, chronic exposure of bacteria and other microorganism to antibiotics may cause the development of antibiotic resistance in the environment, which may threaten our ecosystem. Therefore, it is of great importance to develop cost-effective treatment technologies to remove such compound from aqueous solutions (Paul Chen *et al.*, 2002; Keykhah and Dahanzadeh, 2017).

This study showed the adsorption capacity of tetracycline onto zeolite increased when pH was increased from 2.0 to 5.0, and then decreased significantly. So, it can be said, the effect of pH was associated with the pH-dependent speciation of tetracycline and surface charge property of zeolite. Also, results showed, followed by a relative slow process. 90% of adsorption of tetracycline onto the zeolite occurred rapidly in the first 45 minutes and the adsorption equilibrium was reached about 3 hr. Moreover, Freundlich and Langmuir equations were well used to describe the adsorption isotherm and thermodynamic analyses showed that the adsorption process was spontaneous and endothermic, and increasing temperature facilitated the adsorption. A analysis of fourier transform infrared spectroscopy showed that surface complexation between tetracycline and the aluminum atoms in zeolite was responsible for the adsorption of tetracycline on the zeolite. Also, the results showed that tetracycline adsorption kinetics onto the zeolite is the similar to Langmuir.

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