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Removal of tetracycline from aqueous solution using nano zeolite modified by Al and Fe

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ABSTRACT

Due to its widespread use in medicine and veterinary medicine, tetracycline has a high percentage of release in the environment and enters the drinking water ecosystem more than others, and on the other hand, its persistence in water causes an increase in antibiotic resistance and genotoxicity. It occurs in humans and aquatic animals, so their removal is one of the important challenges for researchers. Due to its special structure, including uniform pores and a very high specific surface area, zeolites are of great interest in the process of removing toxic and dangerous substances. However, the structure the uniqueness of zeolite, and the different applications that have been investigated. In this research, zeolite was modified with iron and aluminum and characterized by different techniques such as X-ray diffraction, transmission electron microscopy, scanning electron microscopy, atomic force microscopy and Fourier-transform infrared spectroscopy, then its ability to remove tetracycline was studied (pH 2–11), tetracycline concentration (10–60 mg/L), time (30–100 min), mL/mg of zeolite modified/Al/Fe. One of the advantages of this method is that the structure is synthesized at 1,000°C, which causes a heat-resistant structure, and also the ability to recycle the adsorbent after five steps have been studied and the removal ability does not change much at each stage and can be negligible.

Keywords: Nano adsorbent; Zeolite/Al/Fe; Water purifier; Modified of zeolite

1. Introduction

In 1990, the antibiotic that was discovered at that time had a special place in animal and human medicine and its use has increased a lot [1,2]. Antibiotics are generally different in terms of mechanism of action in terms of antimicrobial pharmacology, and after being absorbed in human and animal bodies, they are excreted from the body in the form of a series of insufficient and unchanged metabolites and enter water sources and the environment and causes harmful effects [3,4]. Antibiotics, due to their wide application in the field of animal husbandry, veterinary medicine, and aquaculture, and due to the unchanged structure of these compounds in the body of living organisms, therefore, enter water and soil sources directly [5,6]. Although we use antibiotics a lot, they are mentioned as environmental pollutants due to their harmful effects, such as bacterial resistance and adverse effects on the wastewater treatment process [7]. Tetracycline's are one of the most commonly used antibiotics in the world, the indiscriminate

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and widespread use of these antibiotics in large quantities has caused them to be found in water sources from a few micrograms to higher doses, thus causing health risks. Humans and the environment [8].

Every day, by finding different methods, it is possible to minimize the amount of these antibiotics in the pharmaceutical effluents of water and soil sources [9]. In recent years, due to the new properties they create [10], nanocomposite materials have been widely used in various fields, such as the identification of poisons, electrochemical sensors, sensors to identify nitrogen dioxide, batteries and their properties, and polymer ceramic computers that are used in medicine and dentistry. In general, it can be said that these nanocomposites are widely used in agriculture, environmental medicine and others [11]. Several methods have been introduced to remove antibiotics by chemical doping into structures such as g-C_3N_4 and zeolite [12–15].

Among the various combinations of different elements, iron is very important because of its special properties and its special compatibility with the environment and humans, and because of its high abundance in the earth's crust [16,17], and aluminum because of its soil properties and many uses in various industries [18]. It has been taken into consideration and also zeolite is a porous compound of aluminum silica and due to its abundance in nature, it has wide applications in the water and wastewater treatment industry, the effect of waste gases, the catalyst of detergents and medicine [19–21]. Therefore, considering the unique properties of zeolite, according to the mentioned properties and the advantages that these elements have due to their abundance and availability, in this research, zeolite was modified with iron and aluminum at a high temperature (1,000°C) and a very resistant was synthesized. Then, it was characterized using different techniques such as X-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) and various parameters such as time, catalyst amount and pH were studied. The best conditions for removing the largest amount of tetracycline were reported in this research.

2. Experimental

2.1. Materials and methods

$FeCl_3·6H_2O$ and $Al(NO_3)_2·4H_2O$ were supplied by Merck (Germany), zeolite (96096, potassium, 3Å type) was purchased from Sigma-Aldrich (USA), HCl, NaOH, were obtained from System Co., (Malaysia).

2.2. Instruments

Zeolite/Fe/Al, particle size and phase purity of the samples were investigated by X-ray diffraction (Philips PW 1840, k = 1.54056 Å). Typically, the peaks of the adsorbent diffraction pattern in the 2θ range between 10° and 80° were scan with a velocity of 1.5°min^{-1}. For measure nanoparticles size, a transmission electron microscopy (Philips CM200-FEG, USA) and a SEM electron microscope image (Philips XL30 scanning microscope, Philips, The Netherlands) were used. A Cary 100 UV-Vis Spectrometer (Varian, USA) was used to study UV-Vis absorption spectra at 23°C–25°C temperature. FTIR spectra are examined by an FTIR spectrophotometer (Thermo (Avatar) model) in the range of 400–4,000 cm^{-1} was used and KBr was used to make plate.

2.3. Synthesis of zeolite/Fe/Al

2 g of zeolite with $FeCl_3$ (1 g) and aluminum (1 g) with 50 mL of distilled water on a stirrer for 5 h and then put it in an electric furnace at a temperature of 700°C for another 5 h and after this time, take out the sample and cool it in a desiccator. Then, the sample is washed 2–3 times with distilled water and then placed in an 80°C oven for 1 h to dry completely. Sample is then collected and is characterized using various characterization techniques.

2.4. Tetracycline batch adsorption

A tetracycline removal experiments using heterogeneous method by zeolite/Fe/Al nanocomposite and repeating the test results in three times on average and under optimal conditions is reported. Many parameters such as water (pH 2–11), tetracycline (TC) concentration (10–60 mg/L), time (30–100 min), mL/mg of zeolite modified/Al/Fe. were explored in the removal process. To carry out the absorption experiments, first prepare a solution of 100 mg/L of TC and prepare the following solutions by diluting tetracycline. The effect of pH to remove tetracycline in removable was evaluated from 2 to 10 with an interval of 1. Adjust the pH value of water using HCl and NaOH (0.1 M), and added zeolite/Fe/Al nanocomposite separately into a 10 mL solution with a pH adjusted with a concentration of 10 ppm of TC and 25°C for 20 min at a shaker in 200 rpm. After the reaction is complete, measure the amount of remaining tetracycline using a spectrophotometer at a wavelength of 357 nm and calculate the amount of removal using Eq. (1).

$$\%\text{Removal} = \frac{\left(C_i - C_f\right)}{C_i \times 100} \quad (1)$$

3. Results and discussion

3.1. Characterized of zeolite/Fe/Al

After the modification of nano zeolite using iron and aluminum, the diameter of the particles on the surface was first studied using the TEM. The observations show that particles with a diameter of 50 nm are synthesized (Fig. 1). The subsequent analyzes include SEM, energy-dispersive X-ray spectroscopy (EDX), mapping, lain scan (Fig. 2), which also shows the morphology of the surface, it is shown that the spherical particles and the elements with certain percentages of iron, aluminum, and silicon have been shown. The amount of aluminum has increased dramatically due to the presence of Al_2O_3 on the surface (Fig. 2A and B). Another analysis related to the mapping and distribution of elements shows the percentage and indicated by red and blue colors that each color corresponds to a specific element such as silica and aluminum (Fig. 2C). And by using line scan analysis, iron and aluminum can be seen up to a certain level of the catalyst, which shows the availability of metals on the catalyst surface. And by using line scan analysis, iron, and aluminum can be seen on the catalyst surface, which shows the availability of metals on the catalyst surface to remove pollution (Fig. 3). The subsequent analysis of the XRD shown in Fig. 4 shows a good comparison between zeolite and modified zeolite. The simplest result that can be deduced from it is that the particles placed in zeolite caused the creation of new peaks that can be seen in the region of 10° and 15°. In Fig. 5, which is related to AFM, zeolite holes are seen and particles are placed inside some holes and other particles are placed on the surface of zeolite. To compare zeolite and modified zeolite, the FTIR spectra was used, which is shown in Fig. 6. The peak at 1,450; 638; 677; 769; 1,036 and 1,645 cm^{-1} indicates the bond related to nano zeolite and also the peak at 343 cm^{-1}. It is related to stretching vibrations in the OH ions of terminal Si groups and the peak in the area of 769 and 1,036 cm^{-1} is related to Si–O and Al–O Fig. 6A [22,23]. Fig. 6B, which is related to nano zeolite modified with iron and aluminum, is similar to Fig. 6A, with the difference that the peak in the area of 604 and 790 cm^{-1} is related to iron and aluminum, which this peak shows due to the presence of O–Fe and O–Al.

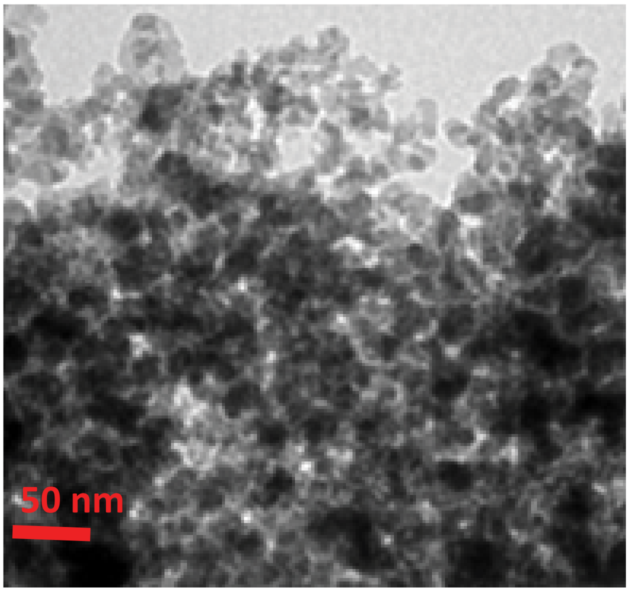

Fig. 1. Transmission electron microscopy images of zeolite/Al/Fe.

3.2. Effect of adsorbent

To study the best conditions for the amount of zeolite/Al/Fe, different amounts of catalyst from 5.0–50.0 mg/mL were added to tetracycline with a concentration of 10 ppm under conditions of pH 5.5 and with a shaker of 200 rpm and using a spectrophotometer at a wavelength of 257 nm. The amount of tetracycline remaining in 15 min was

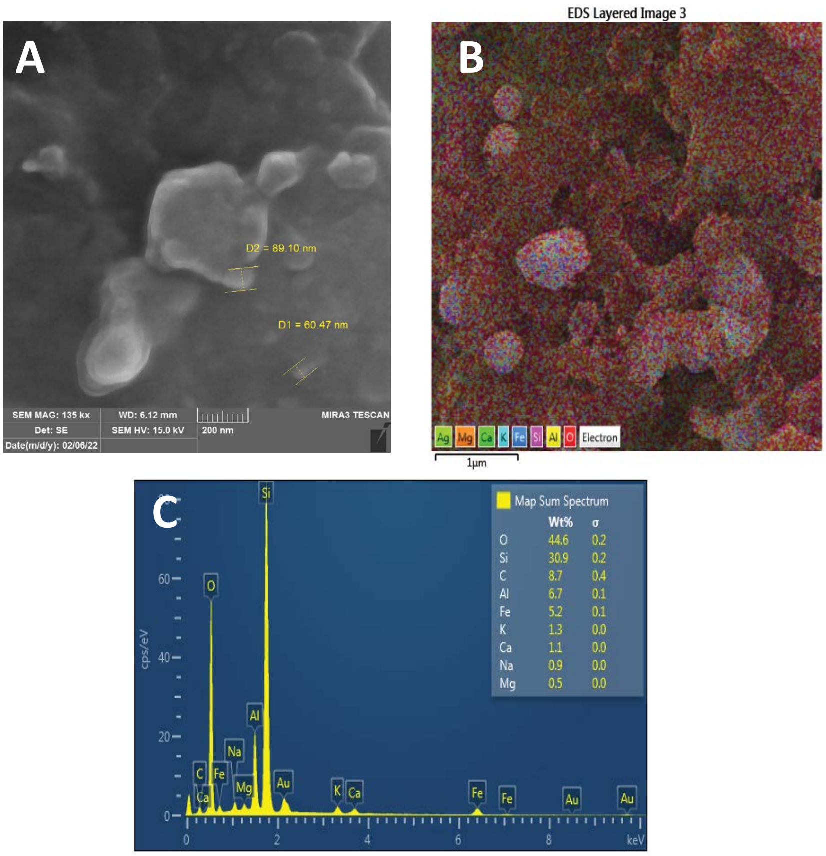

Fig. 2. (A) Scanning electron microscopy images of zeolite/Al/Fe, (B) mapping images of zeolite/Al/Fe, and (C) EDX images of zeolite/Al/Fe.

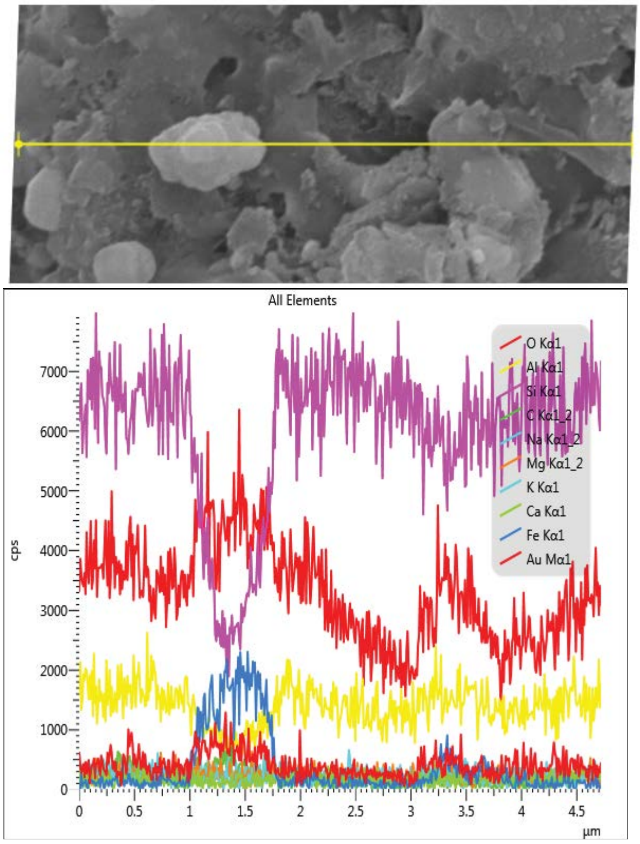

Fig. 3. EDX line scan analysis for zeolite/Al/Fe.

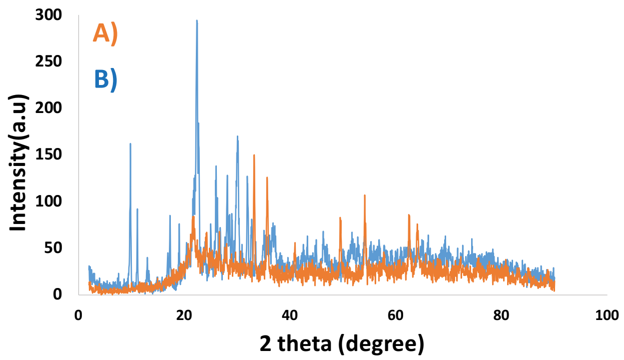

Fig. 4. X-ray diffraction patterns of (A) zeolite and (B) zeolite/Al/Fe.

calculated. Fig. 7 shows that at 30 mg/mL, the percentage of removal has its highest value, further this value, the rate of removal does not change much, and less than 30 mg/mL, because the surface of the adsorbent is saturated, the percentage of removal is lower. Therefore, it can be concluded that 0.2 mg/mL is the best condition with a percentage of 99%.

3.3. Effect of pH on the removal efficiency

To evaluate the optimal pH conditions, 30 mg/mL of zeolite/Al/Fe was mixed with 10 ppm tetracycline at room

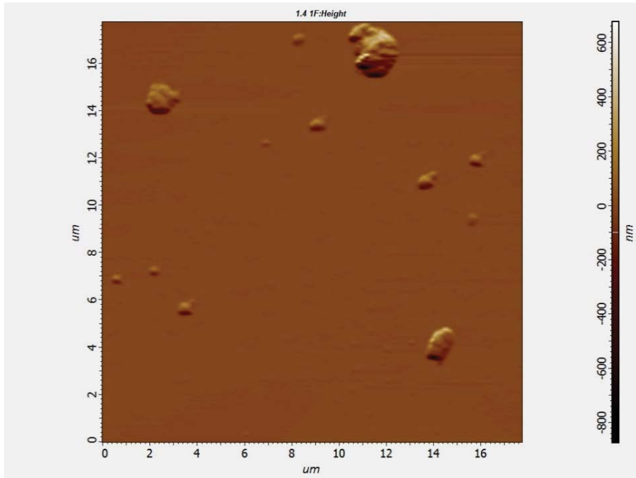

Fig. 5. Atomic force microscopy of zeolite/Al/Fe.

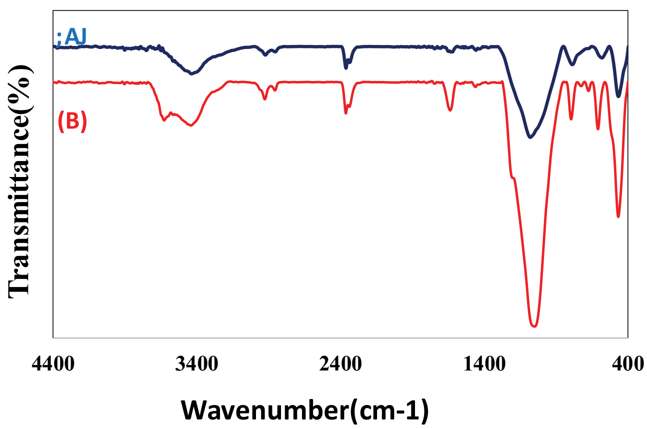

Fig. 6. Fourier-transform infrared spectrum of the (A) zeolite and (B) zeolite/Al/Fe.

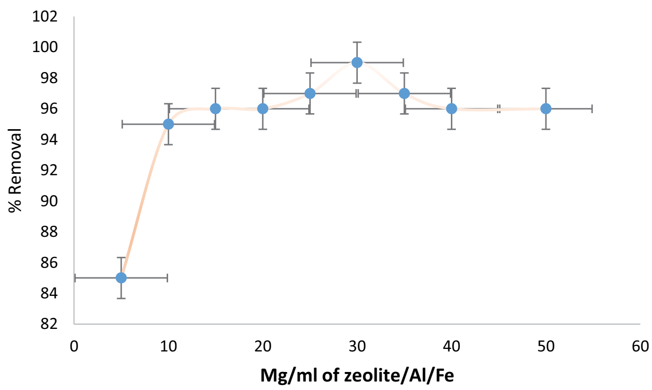

Fig. 7. Effect of the amount of zeolite/Al/Fe.

temperature and 200 rpm for 15 min and studied at different pHs from 2.0 to 9.0 NaOH and HCl were used to adjust the pH to acidic or alkaline environments. Considering that the pH_{zpc} for the adsorbent is 4.0, therefore a lower pHs have a positive charge and a higher pHs have a negative charge. When the pH of the TC solution is less than 3.3, the tetracycline has a positive charge, resulting in a repulsive force between the tetracycline and the zeolite/Al/Fe surface. Also, when the pH of the tetracycline solution is more than 7.7, the tetracycline molecule has a negative charge, which has a negative charge between the adsorbent and TC. When the pH is in the range of 4.0 to 7.0, the tetracycline molecule has a negative and positive charge therefore the surface charge is positive and negative at pH 5.5, so, the amount of electrostatic interaction attraction is the highest in the pH region of 5.5 (Fig. 8).

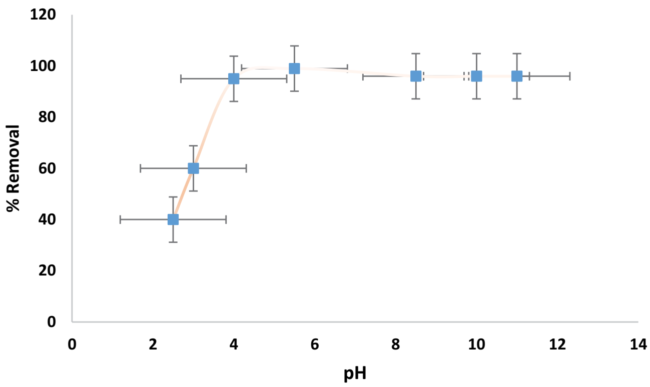

Fig. 8. Effect of initial pH on the removable of tetracycline.

3.4. Investigation of the effect of reaction time on removal efficiency

The reaction time to remove tetracycline from the water environment is a critical parameter because the shorter the time, the higher the water purification efficiency. So, the results of the effect of time (30–100 min) on the removable of TC with a concentration of 10 ppm, at the optimal pH (pH = 5.5) and the amount of 30.0 mg/mL of zeolite/Al/Fe are shown in Fig. 9. The highest removable efficiencies of tetracycline are in 90 min, therefore, the 90 min is optimal for the removable tetracycline in solution. the effect of temperature on the adsorption of tetracycline by zeolite/Al/Fe, the temperature analysis showed that removal of tetracycline by zeolite/Al/Fe at pH = 5.5 and with 30 mg/mL of zeolite/Al/Fe and a concentration of 10 ppm of TC in 90 min in 25°C. In 25°C, it removes about 99% of tetracycline from the environment, so with increasing temperature, there is not much change in the removal and only the absorption time decreases.

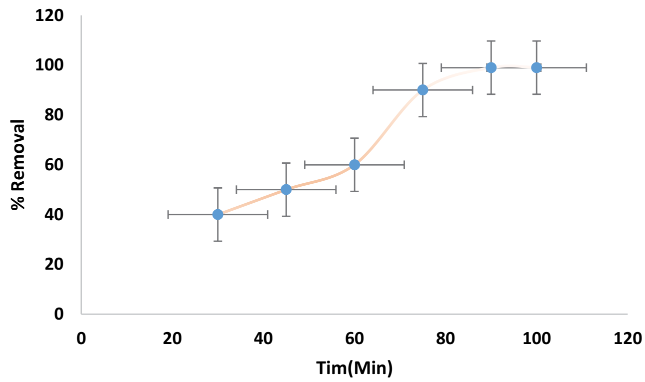

Fig. 9. Effect of time on the removable of tetracycline.

3.5. Effect of TC concentrations on removable efficiency

Fig. 10 shows the effect of the initial concentrations of TC in removal by zeolite/Al/Fe. to perform this experiment, the time parameters, zeolite/Al/Fe and pH were set to their optimal values (i.e., 30 mg/mL of zeolite/Al/Fe and a time of 90 min and pH = 5.5). by increasing the initial concentration of tetracycline, the percentage of tetracycline removed decreases, so that it can be said that the removal of TC under the influence of the initial concentration.

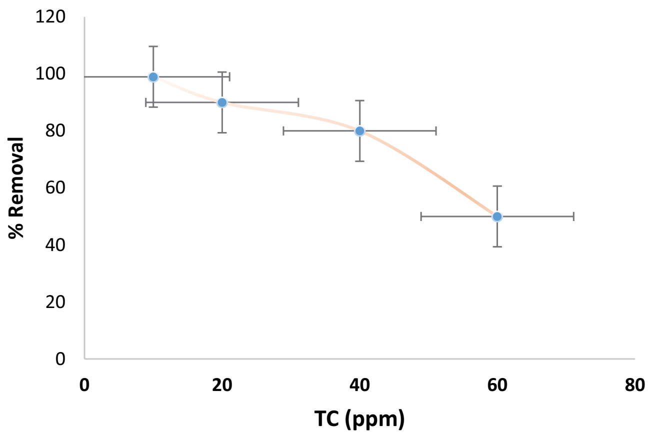

Fig. 10. Effect of tetracycline concentrations.

3.6. Mechanisms

In the removal of tetracycline from aqueous environments, physical factors such as particle penetration, electrostatic interactions, particle diameter, and chemical factors such as hydrogen bonding, aromatic rings, π–π interactions, are effective. The zeolite/Al/Fe have a nano diameter, therefore, it has a high specific surface, which causes interaction between the particles and TC [24]. The electrostatic interaction that is associated with the decrease and increase of the surface charge so it is effective on the removal of tetracycline, and the factors that change the surface charge have an effect on each, one of these factors is the pH of the environment. The pH_{zpc} for the adsorbent is 5, therefore a lower pHs have a positive charge and a higher pHs have a negative charge. When the pH of the TC solution is less than 3.3, the tetracycline has a positive charge, resulting in a repulsive force between the tetracycline and the zeolite/Al/Fe surface. Also, when the pH of the tetracycline solution is more than 7.7, the tetracycline molecule has a negative charge, which has a negative charge between the adsorbent and tetracycline. When the pH is in the range of 3–7, the tetracycline molecule has a negative and positive charge and considering that the surface charge is positive and negative at pH 5.5 (Fig. 11), therefore, the amount of electrostatic interaction is the highest in the pH region of 5.5. Another factor, tetracycline has OH, C=O and NH_2 groups, which

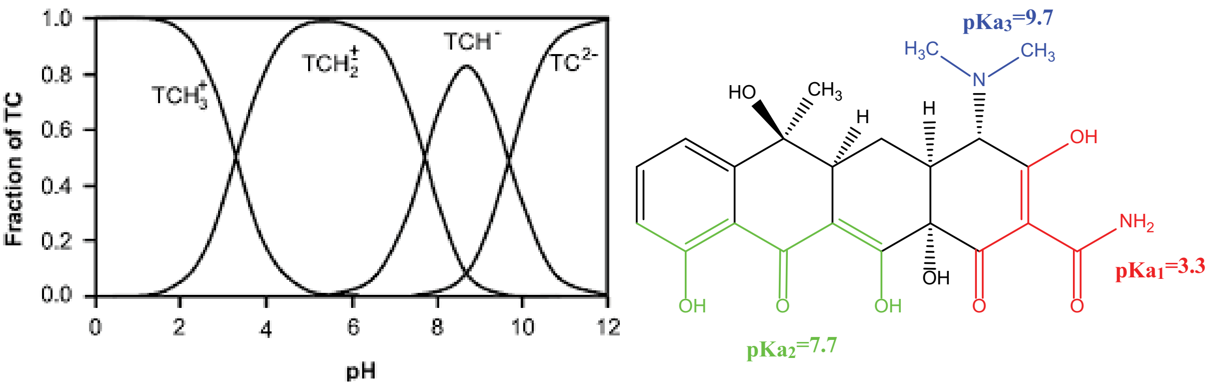

Fig. 11. Different states of tetracycline and its pKa at different pH values.

Table 1
Comparing removal of tetracyclines

S. No.	Catalyst	Pollutant conc. (mg/L)	Time (min)	Removal efficiency (%)	References
1	P-S-g-C_3N_4	10	60	85	[9]
4	ZnO-coated hybrid biochar	10	120	95	[12]
5	Pumice stone	10	120	98	[25]
6	$MnFe_2O_4$	10	120	95	[26]
7	Magnetic biochar	10	100	96	[27]

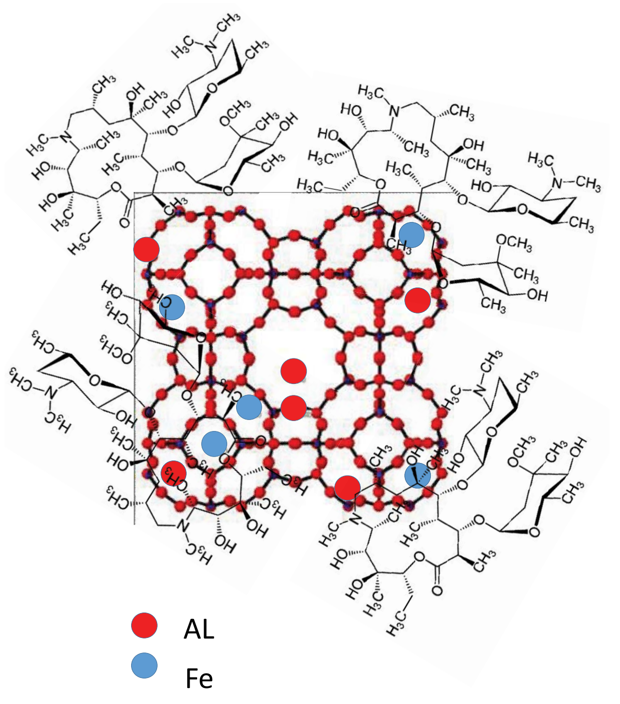

Fig. 12. Illustration of interaction between zeolite/Al/Fe and tetracycline.

are adsorbed by zeolite/Al/Fe due to the presence of metals such as iron, Al. These electron donor–acceptor interactions including the π–π conjugation and σ–π hyperconjugation between the OH and N groups and metal surfaces in zeolite/Al/Fe nanocomposite may also promote the adsorption of the selected tetracycline on this composite (Fig. 12). By comparing this research with the previous research reported in Table 1, it can be seen that acceptable results were obtained in terms of removal and reaction time [9,12,25–27].

4. Conclusion

After zeolite was modified with iron and aluminum, it was characterized using different techniques (SEM, mapping, EDX, TEM, and FTIR), and the diameter of particles and their elements were determined using SEM and AFM. Then, zeolite/Al/Fe was used as a nanocomposite to remove tetracycline, and parameters such as time, temperature, pH, and tetracycline concentration were evaluated. The best conditions for removing tetracycline with a concentration of 10 ppm at room temperature, the time required to remove 99% of tetracycline is 10 min, and the required pH for a solution is 5.5. Now, this method can be used as a useful and practical method in the water and sewage industry to remove tetracycline due to the availability of initial materials, simplicity in synthesizing the catalyst, resistance to heat due to synthesized at 1,000°C, and recycling.

Acknowledgements

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