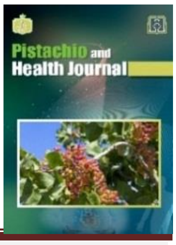

Evaluation of Activated Carbon Prepared from Pistachio Shell as an Adsorbent for the Removal of Tetracycline Antibiotics from Aqueous Solution: Kinetic and Isotherm Study

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Abstract

Introduction: In recent decades, antibiotics have received much attention as emerging contaminants in aqueous environments. Tetracycline is one of the most widely used antibiotics all over the world and has been detected in aqueous environments at high concentrations. Antibiotic residues in aqueous environments may have toxic and adverse effects on the biological balance of aquatic ecosystems, leading to antibiotic resistance in microorganisms. Therefore, the treatment and removal of these pollutants from aqueous environments are essential.

Materials and Methods: In this study, tetracycline antibiotic was removed using activated carbon prepared from hard pistachio shell as adsorbent in this treatment process, and the effect of various variables such as initial antibiotic concentration, solution pH, adsorbent level, and reaction time were investigated. The analysis of adsorption kinetics, isotherms, and the structural properties of the adsorbent was performed using scanning electron microscopy (SEM) and isoelectric point of zero charge (pHpzc).

Results: The results showed that maximum efficiency of antibiotic removal under optimum conditions at the initial concentration of 20 mg/L, pH of 5, adsorbent level of 0.35 mg/L, and reaction time of 45 minutes was equal to 99.8%. The adsorption process of tetracycline antibiotics follows second-order kinetic model (R^2= 0.9973) and Langmuir isotherm (R^2= 0.995).

Conclusion: This study showed that the adsorption process using activated carbon prepared from hard pistachio shell has high efficiency in terms of the removal of tetracycline antibiotics and can be used as an adsorbent to replace expensive adsorbents.

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1. Introduction

Antibiotics are large pharmaceutical groups that are frequently-used for improve and prevention of disease, veterinary, and other infectious diseases. The presence of antibiotics and their metabolites in aqueous environments and their harmful effects on the environment in the last decade has attracted the attention of many researchers [1]. Antibiotics enter aqueous environments through various routes such as hospital and veterinary wastewater, direct discharge from municipal treatment plants, excreta from human and animal bodies, direct disposal of pharmaceutical wastewater, etc. [2]. The important thing about antibiotices are that less than 10% of antibiotices are metabolized in the human body and the remaining more than 90% of antibiotices are excreted from the human and animal body. The presence of antibiotics as pollutants, in the aqueous ecosystems and various environments including water, air, and soil leads to antibiotic-resistant bacteria that possibly threaten environmental health and human and social health. In terms of production and consumption of the antibiotics in the world, tetracyclines are ranked second. They are effective against many microorganisms but are used indiscriminately and frequently [3]. In recent years, various concentrations of tetracycline have been reported in surface and groundwater. Some studies have reported the concentration of tetracycline in surface water to be in the range of ng to mg/L (3). Accordingly, an efficient system is essential to remove tetracycline antibiotics from aqueous environments. Various techniques have been useful to purification and remove antibiotics from aqueous media such as water, leachates of landfill, and polluted water, amongst physical methods for treatment such as and filtration [4], adsorption [5], biological methods [6], chemical process such as flocculation, sedimentation [7], ozonation [8, 9], and photocatalytic decomposition [10]. Each of these purification techniques has advantages and disadvantages.

Biological treatment of antibiotics is not recommended because it causes bacterial resistance in microorganisms used in the purification. Chemical techniques are limited due to their need for chemicals and storage space, and the production of sludge, which necessitates the managed and disposal facilities of sludge. Besides, oxidation methods, notwithstanding their extraordinary efficiency in removal and treatment, require energy consumption, so they are limited due to economic constraints [11, 12].

In contrast, adsorption as one of the physicochemical methods most widely used technique in water and wastewater treatment due to the easy design; no sludge production, easy management, high efficiency, environmental compatibility, etc. have been considered by many researchers [13, 14].

Therefore, this study uses activated carbon prepared from hard pistachio shells to remove tetracycline antibiotics. It also explores the effect of various variables such as initial antibiotic concentration, solution pH, adsorbent level, and time of reaction, kinetics, and isotherms adsorption study.

2. Materials and methods

2.1-Preparation of absorbent

To produce activated carbon, first, hard pistachio shells were collected. After crushing, the shells were washed numerous times with distilled water to eliminate surface contaminants and then dried for one hour at 110±5°C. In the next step, the shells were mixed using 95% phosphoric acid with a mass/volume ratio of 1:10 (1 g of hard pistachio shell/10 mL of phosphoric acid). The resulting combination was placed inside a metal container and then the electric temperature of the oven was adjusted so that the temperature slowly reached 900°C within 3 hours. Then, the mixture was kept at 900°C for one hour, after which time the oven was returned to its original temperature within 3 hours. The produced carbon is washed with distilled water to reach a pH of about 6.5 to 7.5. The final product was again kept for one hour at 110±°C to dry, then meshed with a standard sieve, and finally used as an adsorbent to remove the tetracycline antibiotics.

2.2- Absorption process

To perform the tests, 100-mL glass containers were used. The absorption process was examined by mixing different antibiotic concentrations (10-50 mg/L), adsorbent (0.1-0.5 g/L^{-1}), pH (4–11), and process times (10-90 min).

The solutions were mixed by a shaker at a suitable speed and laboratory temperature (20±3°C). To set the pH of the samples, hydrochloric acid and sodium hydroxide were used. The set of pH the samples was measured by a pH meter (Model HQ440d HACH). After completion of the reaction, the samples were taken out of the reactor and after filtration and were measured using a UV/Vis spectrophotometer (Shimadzu-1700 Model) at the 360 nm. In each step, by keeping the entire variables constant and changing only one variable, the optimal value for the variable in question was determined. To ensure the reproducibility of the collected data, each test was performed three times and average values were reported. Finally, the data were analyzed. Percentage of tetracycline removal (%) and adsorption capacity (mg/g) were calculated using Equations 1 and 2 [15, 16].

$$\% R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

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

Where

R: Removal efficiency (%)

q_e: Adsorbent capacity in equilibrium time (mg/g^{-1})

C_0: Initial contaminant concentration (mg/L)

C_e: The contaminant concentration after the adsorption process (mg/L)

V: Volume (L)

M: Adsorbent mass (g)

2.3- Kinetics and adsorption isotherms

Kinetic equations are used to describe the transport behavior of adsorbed molecules per unit time or to study variables affecting the reaction speed [17]. The linear model of the first-order kinetics is presented in Eq. (3).

The adsorption isotherm defines the interaction between the adsorbent and the adsorbed. In this study, two Freundlich and Langmuir isotherms were studied. The Langmuir model is credible for the monolayer adsorption on the surface of an adsorbent. The linear equation this model is expressed as Eq. (5).

An essential characteristic of the mention isotherm presented by the R_L constant is obtained from Eq. (6) [18, 19]:

The Freundlich isotherm is introduced based on monolayer adsorption. In other words, the Freundlich equation expresses adsorption at a heterogeneous level in terms of adsorption energy and as shown by Eq. (7).

$$\log(q_e - q_t) = \log(q_e) - k_1 t/2.303 \quad (3)$$

Where

q_t: Shows the adsorbent capacity at t time (mg g^{-1})

q_e: Is the adsorbent capacity in equilibrium time (mg/g^{-1})

K_1: Is the equilibrium constant of the first-order kinetic model (min^{-1})

The sound-kinetics model equation is as follow [17]

$$(4)\quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where:

q_t: Adsorbent capacity in t time (mg/g^{-1})

q_e: Adsorbent capacity in equilibrium time (mg/g^{-1})

K_2: Is the equilibrium constant of the sound-kinetics model equation

t: Reaction time (min)

$$(5)\quad \frac{Ce}{qe} = \frac{1}{bqm} + \frac{Ce}{qm}$$

Where:

q_e: Adsorbent capacity in equilibrium time (mg/g)

q_m: Maximum adsorption capacity (mg/g)

C_e: concentration of pollutant after the adsorption process (mg/L)

b: constant of isotherm.

$$(6)\quad R_L = \frac{1}{1+bC_0}$$

$$(7)\quad Lnq_e = Ln\ K_f + 1/n\ LnC_e$$

Where:

C_e: concentration of pollutant after the adsorption process (mg/L)

q_e: Adsorbent capacity in equilibrium time (mg/g)

K_f and n: Freundlich constants

2.4- Determination of isoelectric point of zero charge (pHpzc)

To determine the pH of the activated carbon isoelectric point of zero charge (pHpzc) prepared from the hard pistachio shells, 100 ml of 0.01 M potassium nitrate was added separately in 6 containers. The pH was then seted with hydrochloric acid and sodium in the range of 2-12. Afterward, 0.4 mg of adsorbent was added to each of the containers (100 mL in total) and stirred for 48 hours with a magnetic stirrer. Finally, the final pH was measured using a pH meter. The initial pH curve was plotted against the final pH. The intersection point of the two curves was introduced as the pH of the pHpzc [17].

3. Results

3.1- The surface structure of the absorbent

3.1.1- Isoelectric point of zero charge (pHpzc)

In fact, pH_{pzc} plays an important role in explaining how adsorbent behaves in aqueous solutions to remove contaminants. The pHpzc, is the point at which the number of positive and negative charges are equal, that is, the charge on the absorbent surface is zero. Figure 1 shows the pH of an pHpzc to 6.4:

3.1.2- Scanning electron microscope image

Figure 1 shows the scanning electron microscopy image of the adsorbent (activated carbon prepared from hard pistachio shells):

3.2- The impact of the variables on the process

3.2.1- The effect of the initial concentration of tetracycline antibiotic

To assess the effect of the initial concentration of antibiotic onto activated carbon prepared from hard pistachio shells, tetracycline antibiotic at concentrations of 10 to 50 mg/L were tested as displayed in Figure 2:

The maximum removal efficiency at concentrations of 10, 20, 35, and 50 mg/L were 68.6%, 63.8%, 43.4%, and 30.2%, respectively. Since at concentrations of 10 mg/L and 20 mg/L, the removal efficiency is less than 5%, so the concentration of 20 mg/L was taken as the optimal concentration. Therefore, the concentration of tetracycline antibiotic was considered to be constant and equal to 20 mg/L.

3.2.2- The impact of the solution pH

To assess the effect of pH, different pH levels of 4, 5, 7, 9, and 11 were examined as displayed in Figure 3.

As displayed in Figure 3, the maximum removal efficiency values at pH of 4, 5, 7, 9, and 11 are equal to 100%, 99.8%, 61.5%, 31.9% and 21.6%, respectively. Since at pHs 4 and 5, the highest removal efficiencies are 100% and 99.8%, respectively, pH 5 was considered as the optimal pH. Therefore, the pH of the samples was taken to be constant and equal to 5.

Figure 1- The potential at the pHpzc of activated carbon prepared from hard pistachio shells

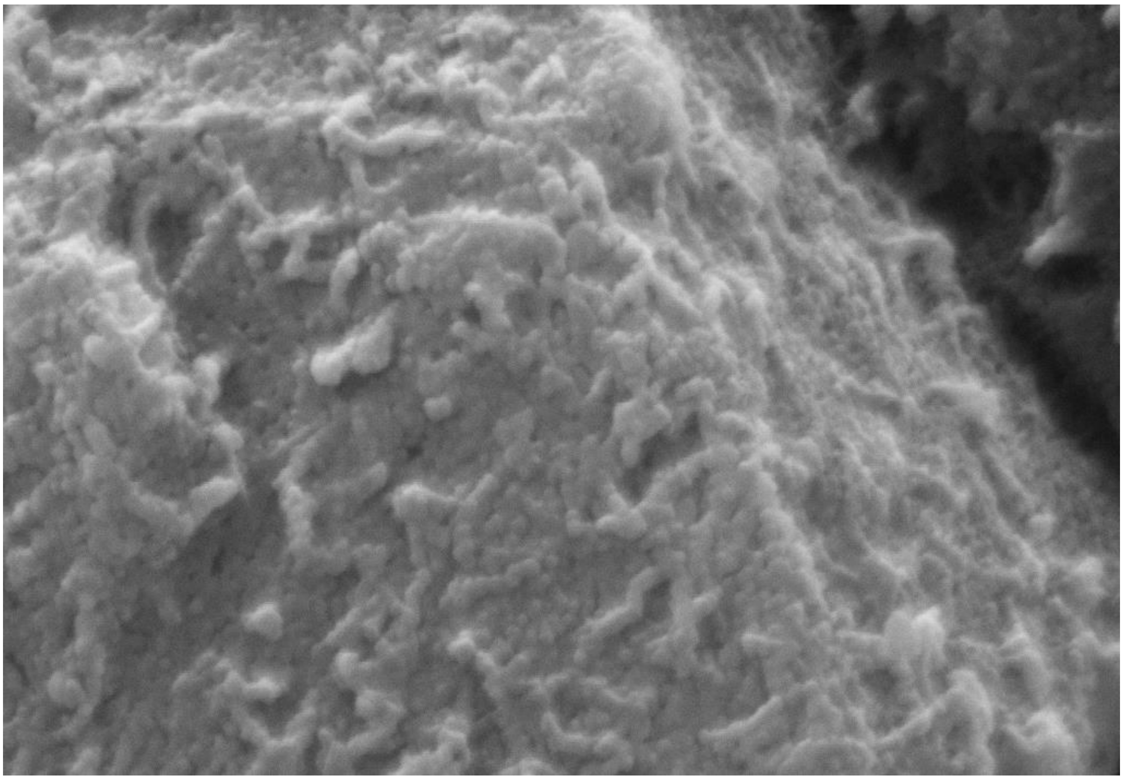

Figure 1- Electron microscope image of activated carbon

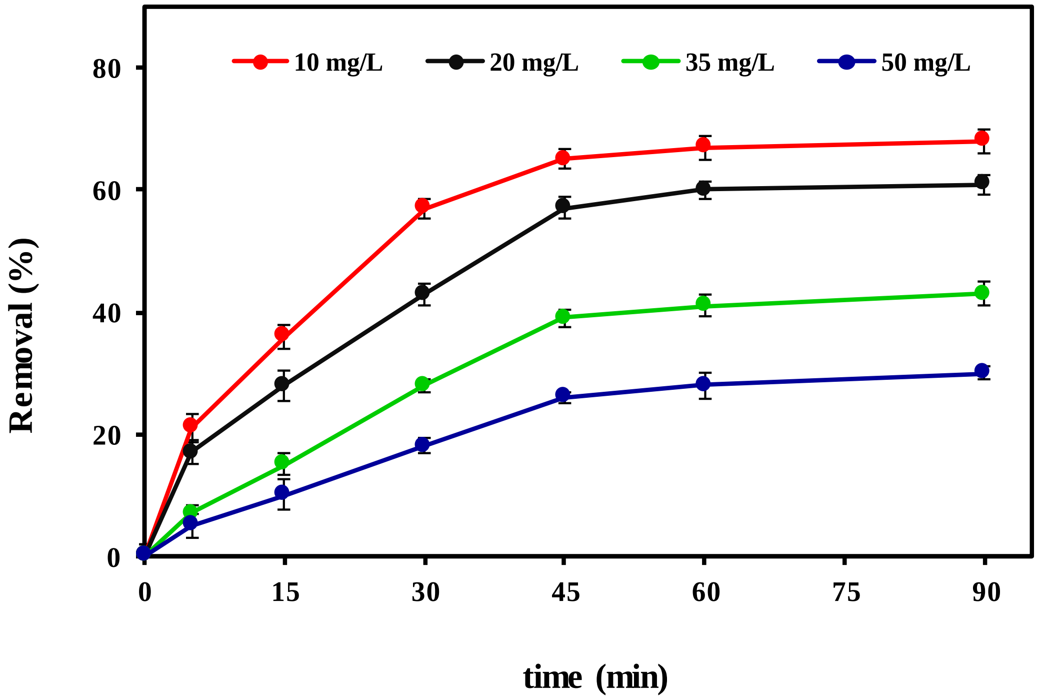

Figure 2- The effect of the initial concentration of tetracycline antibiotic (pH=7 and adsorbent value 0.35 g/L)

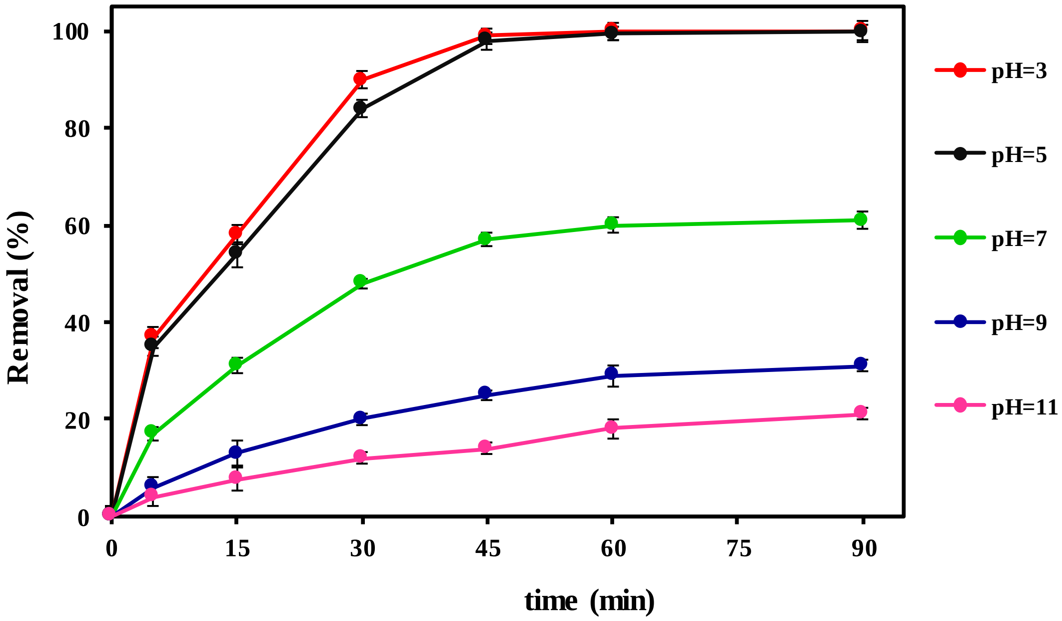

Figure 3- Effect of pH level: (20 mg/L initial tetracycline antibiotic plus 0.135 L adsorbent)

3.2.3- The impact of the adsorbent concentration

In this study, the adsorbent (activated carbon prepared from hard pistachio shell) was used at concentrations of 0.1 to 0.5 g/L. The effect of the adsorbent concentrations on the removal efficiency of tetracycline is shown in Figure 4. As shown in the figure above, the maximum removal efficiency rates of tetracycline at concentrations of 0.1, 0.2, 0.35, and 0.5 mg/L of activated carbon prepared from hard pistachio shells were equal to 48.1%,74%, 99.8%, and 100%, respectively. Given that the adsorbent values of 0.35 and 0.5 mg/L, the removal efficiencies are very close to each other, so the solution at the concentration of 0.135 mg/L was considered as the optimal adsorbent concentrations.

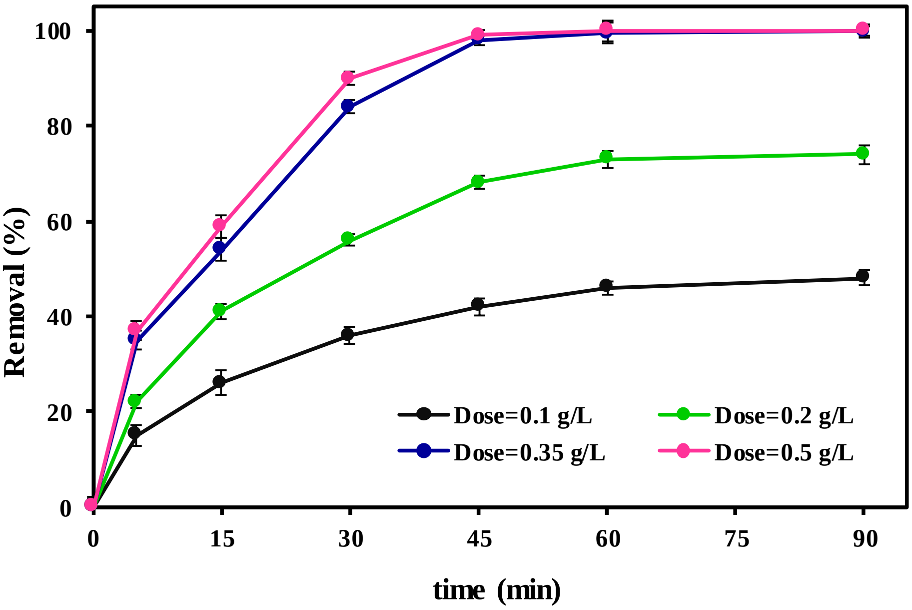

Figure 4- Effect of adsorbent concentrations (20 mg/L tetracycline antibiotic and pH of 5)

3.2.4- Adsorption kinetics

First and second-order kinetics models were investigated under optimal conditions. The first and second- order kinetics models are shown in Figure 5. The parameters and coefficients related to the first and second- order kinetic models are summarized in Table 1.

The Freundlich and Langmuir isotherm analyses were performed under optimal conditions and the related curves are shown in Figure 6. The parameters and coefficients related to the Freundlich and Langmuir isotherms are summarized in Table 2.

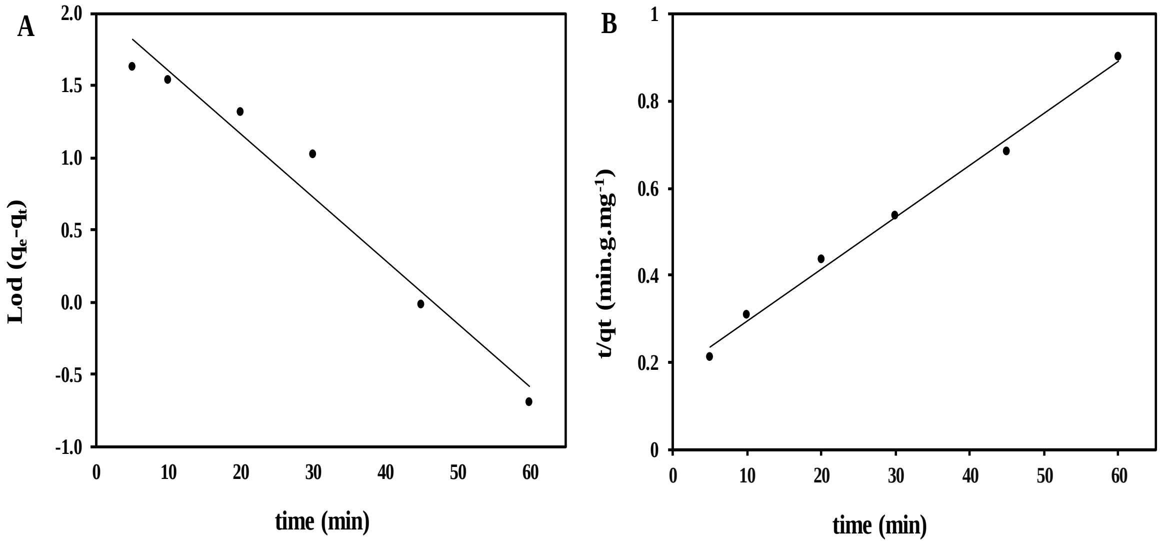

Figure 5- A) First- order kinetics model, B) Second- order kinetics model

Table 1- The parameters of first and second- order kinetics models

kinetics models	**q_e (mg/g)**	**K_1 (min^{-1})**	**R^2**
First- order	109.7	0.1008	0.9616
Second- order	83.3	0.00082	0.9935

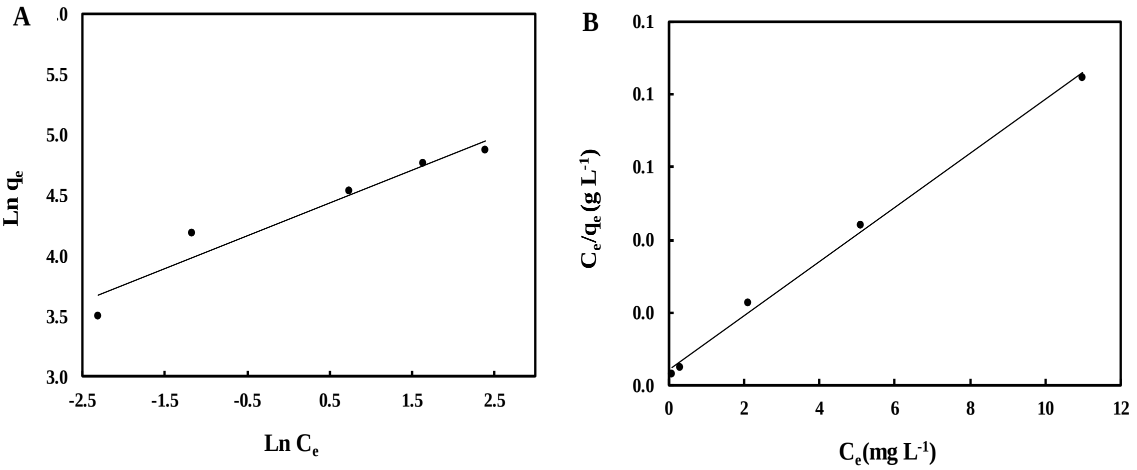

Figure 6- A) Freundlich isotherm, B) Langmuir isotherm

Table 2- The parameters and correlation coefficients of Freundlich and Langmuir isotherms.

Langmuir isotherms models	**q_m (mg/g)**	**b**	**R^2**
	135.13	1.85	0.9958
Freundlich isotherms models	K_f	n	R^2
	73.65	3.66	0.9339

4. Discussion

4.1- Assessment of the adsorbent properties

According to the results, the pH_{pzc} value was 6.4. Accordingly, at pHs higher than 6.4, the charge potential is negative and at pH less than 6.4, the charge potential is positive. Besides, at a pH of 6.4, the adsorbent is uncharged. The SEM images of activated carbon adsorbent prepared from hard pistachio shells (Figure 1) revealed that the structure of activated carbon is composed of a network of nested and porous apertures that are uniformly dispersed on the adsorbent. The porous structure of the adsorbent increases the adsorption capacity, thus enhancing the efficiency of the adsorbent in the adsorption process.

4.2- The impact of the initial antibiotic concentration

The initial tetracycline concentrations were set in a range of 10 to 50 mg/L in this study. As shown in Figure 2, the initial concentration of tetracycline adversely effects on the adsorption process for the removal of tetracycline. Thus, an addition of concentration of antibiotics from 10 mg/L to 50 mg/L decreased the removal from 68.6% to 30.2%. The reason for the downward trend in the removal by increasing concentration is because, with a constant concentration of adsorbent, the active absorption sites are constant. However, with increasing concentration of the adsorbent (contaminant), the number of contaminant molecules in the reaction medium increases, lowering the removal [15, 16]. Zhao et al. (2014) observed that with increasing tetracycline concentration, the removal decreases when using goethite adsorbent [20].

4.3- The impact of the solution pH

One of the factors affecting the treatment processes such as adsorption is pH. The pH of the solution affects the chemistry of the aqueous medium and adsorbent surface bonds. The impact of the pH variations in the range of 4 to 11 on removal was measured. The results showed that the removal process by activated carbon prepared from hard pistachio shells at acidic pHs in the range of 4 to 5 had the highest efficiency. However, with increasing pH, the removal decreased so that the removal was at its minimum level at pH equal to 11. Given this molecule has three pk_a of 3.1, 7.7, and 9.7, tetracycline forms at pH less than 3.3 due to the protonation of amine groups in the cationic form with two positive charges. At pH between 3.1 and 7.7, one end of the molecule has a positive charge and the other end has a negative charge. Besides, at a pH level between 7.7 to 9.7, it has a positive charge and two negative charges. Finally, at a pH higher than 9.7, tetracycline appears in a completely anionic form with two negative charges due to the loss of protons from the carboxylic-group in the structure. Therefore, the removal increases due to the presence of positive and negative ions in the absorbent and tetracycline. Moreover, the presence of a H-bond between hydrogen, oxygen, and nitrogen atoms in the tetracycline molecule leads to the adsorption of this antibiotic in the range of acidic pHs. At pHs above 7.7, tetracycline has a negative charge and the adsorbent also has a negative charge, leading to electrostatic repulsion and decreasing the removal efficiency [15]. Zhao et al. (2014) showed that at a pH of 8.5 the removal was optimal for tetracycline with the optimal pH goethite. Besides, at pHs higher or less than 8.5 the removal decreases. The authors attributed the decreased efficiency to the electrostatic repulsion between the adsorbent and the tetracycline molecule.

4.4- The impact of the adsorbent concentration

The effect on the removal of tetracycline antibiotics was evaluated at adsorbent concentrations of 0.1 to 0.5 g/L. The results showed that a constant concentration of antibiotics, an increase in the adsorbent concentration enhances the removal. The reason is that at a constant antibiotic concentration, an increase in the adsorbent concentration, there is a greater of sites onto adsorbent compared to the absorbed molecules (the pollutant), thus improving the removal efficiency. However, at lower adsorbent concentrations, the ratio of active sites to molecules of the adsorbed material decreases, and this lowers the adsorption capacity [21, 22]. However, increasing the adsorbent concentration beyond the optimal level, the adsorption capacity decreases making the total capacity of the active sites in the adsorbent surface not fully used, and thus decreasing the adsorption capacity. In this study, the adsorbent concentration of 0.3 g/L was considered as the optimal concentration. At this concentration, the removal efficiency increases but not significantly. Therefore, removal remains constant.

4.5- The impact of the reaction time

The present study addressed the effect of the reaction time in the range of 10 to 90 minutes on the removal efficiency of tetracycline antibiotics. The results showed that the adsorption process increased as the reaction time increased. Besides, at different antibiotic concentrations, the adsorption process equilibrated at different times. The adsorption process equilibrated a concentration of 20 mg/L and a reaction time of 45 minutes. Then, the process became relatively constant. Besides, as the reaction time increased, the probability of tetracycline molecules colliding with the adsorbent increases, thus increasing the removal efficiency. Liu et al. (2012) found an equilibrium time of 8 hours in the removal of tetracycline by montmorillonite. They also found that as the reaction time increased the removal efficiency reduced to the lowest level at the equilibrium time of 120 minutes [23].

4.6- Investigation of adsorption kinetics models

This study addressed two first and second- order kinetics models. The correlation coefficients (R^2) for the first and second order kinetics models were 0.9616 and 0.9935, respectively. The results show that the removal process of tetracycline antibiotics follows the second-order kinetic model. Besides, the equilibrium adsorption capacity (q_e) was equal to 83.3 mg/g, implying that the greater the equilibrium adsorption capacity, the more desirable the process. Other studies have shown that the first-order kinetic process occurs for reversible reactions and equilibrium between solid and liquid phases. However, in the second-order kinetic model, chemical adsorption undergoes an upward trend.

4.7- Adsorption isotherms

The correlation coefficients (R^2) for the Freundlich and Langmuir isotherms were 0.9339 and 0.9958, respectively. Therefore, the removal of the tetracycline antibiotics via the adsorption process by activated carbon prepared from the hard shell is more likely to follows the Langmuir isotherm. The Langmuir isotherm represents the adsorption of a monolayer on the outer surface of the adsorbent, while the Freundlich isotherm applies to both physical and chemical adsorption. The Freundlich isotherm constants are n and K_f, where the coefficient n indicates the adsorption intensity and the K_f coefficient indicates an adsorption capacity. A value of n between 1 and 10 indicates an effective adsorption process. If the value of n is close to 1, the surface heterogeneity becomes less important, and if it is close to 10, it becomes more important. The value of n in the present study was 3.66, which was greater than 1, indicating the optimal absorption of the contaminant by the adsorbent. When K_f increases in the Freundlich isotherm, the adsorbent has a higher capacity to absorb the contaminant. Besides, a higher K_f indicates an increase in the adsorption capacity of the adsorbent to capture the contaminant molecules from the solution. In this study, the K_f value was equal to 73.65 mg/g. In the Langmuir isotherm, q_m denotes the maximum absorption capacity and b is a coefficient that depends on the absorption energy and as it increases, the absorption bond force increases. The coefficient b is used in the Langmuir model to calculate the R_L parameter. The isotherm is irreversible when $R_L=0$, the isotherm is desirable when $0<R_L<1$, and the isotherm is undesirable when $R_L<1$ (24). The q_m value in the present study was 135.13 mg/g. Besides, the R_L value was equal to 0.026, which is in the range of 0 to 1, indicating that the isotherm is desirable. Goa et al. (2012) also concluded that the adsorption process of tetracycline using graphene oxide also follows the Langmuir isotherm with R^2 equal to 0.992 and the coefficient $_n$ in the Freundlich isotherm was 2.346 [25].

So far, various adsorbents have been used to remove tetracycline, including nanoparticles, chitosan, sawdust, and zeolites. Although nanoparticles have considerable efficiency in removing tetracycline antibiotics, they are not economically viable to synthesize. Chitosan and sawdust have also been used as adsorbents in the removal of tetracycline antibiotics. However, they are more effective in high levels of adsorbents and low concentrations of antibiotics. Furthermore, the reaction time for removal is very long, which restricts the use of these adsorbents. The results showed that the activated carbon was obtained from hard pistachio shells with a high removal efficiency of 99.8% in high antibiotic concentrations and minimum adsorbent rates (0.35 mg/L) in a short time (45 minutes).

5. Conclusion

This study explored the use of activated carbon prepared from hard pistachio shells to remove tetracycline antibiotics from water solutions. Considering that hard pistachio shells are very abundant and available in Iran without any particular applications, they can be used as raw materials to prepare activated carbon. This study addressed the effect of various parameters on the adsorption process including the initial antibiotic concentration, solution pH, adsorbent concentration, and reaction time. The results suggested that activated carbon prepared from hard pistachio shells has a significant efficiency in the removal of tetracycline antibiotics and also has a relatively high specific surface area and low preparation cost. Accordingly, activated carbon produced from hard pistachio shell can be used as an effective and environmentally-friendly and safe adsorbent for the treatment.

Conflict of interest

The authors of present research declare that there is no conflict of interest.

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