Oxytetracycline removal from aqueous solutions using activated carbon prepared from corn stalks

Danial Nayeri¹, Seyyed Alireza Mousavi²,³*, Azadeh Mehrabi¹

¹Social Research Committee, Kermanshah University of Medical Sciences, Kermanshah, Iran.
²Department of Environmental Health Engineering, Faculty of Health, and Research Center for Environmental Determinants of Health (RCEDH), Kermanshah University of Medical Sciences, Kermanshah, Iran.
³Social Development and Health Promotion Research Center, Kermanshah University of Medical Sciences, Kermanshah, Iran.

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ABSTRACT

In this study, oxytetracycline removal from aqueous solution by activated carbon prepared using corn stalks has been investigated. The adsorbent was characterized using Fourier transform infrared spectrophotometer (FTIR) and scanning electron microscope (SEM). The effects of main variables; adsorbent dose, contact time, pH, and initial oxytetracycline concentration on the efficiency of adsorption efficiency were investigated. Results confirmed the effects of main variables and the maximum removal of antibiotic (99.9 %) achieved at initial concentration of 10 mg/L, pH of 9, and contact time of 60 min, when adsorbent dose was 1.5 g. The results of isotherm and kinetic studies showed that the oxytetracycline adsorption onto activated carbon prepared from corn stalks follows Freundlich isotherm ($R^2 = 0.98$) and pseudo-second order kinetic model ($R^2 < 0.99$). The maximum adsorption capacity of oxytetracycline was 522.6 mg/g. In brief, the activated carbon that has been prepared from corn stalks as low cost, non-toxic and environment friendly adsorbent shows a good ability for removal of oxytetracycline form water and wastewater.

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1. Introduction

Pharmaceutical compounds can be evacuated in the environment through different sources such as hospital wastewater, pharmaceutical industries, domestic wastewater and veterinary clinics (Elmolla and Chaudhuri, 2010). Among them, antibiotics due to annual consumption of 100,000 to 200,000 tons worldwide are important and have high potential effect for environmental pollution, especially water and soil because of high stability and biological activity and acute effects on ecosystems (Ahmadi et al. 2017; Balarak et al. 2016; Jeong et al. 2010). One of the most common and widely used antibiotics for veterinary purposes is oxytetracycline (OTC) (Avisar et al. 2009). Antibiotics have potential to threat human health, therefore antibiotics removal is an important issue (Zhu et al. 2018). In order to remove antibiotics from the environment, various methods such as advanced oxidation (Lin et al. 2013), adsorption (Jiangguang Liu and Jia, 2013a) and electrocoagulation (Naryan et al. 2017) have been investigated. Among different methods, adsorption process is an efficient method due to high surface area, high capacity, and cost effectiveness, without sludge production, adsorbent recovery and process simplicity (Almasia et al. 2017; Mousavi et al. 2017). Due to various studies among adsorbents, activated carbon due to its high surface area, functional groups, high capacity has attracted a lot of attention. However, the limitations of commercial activated carbon are high cost (Zhai. 2014). For this reason, natural adsorbents at low prices and high potential for removal of pollutants that does not damage the environment have been used in many studies, including the use of Walnut shell (Almasi et al. 2016b), Nasturtium officinale (Almasia et al., 2017), N. Microphyllum (Mousavi et al. 2017), and Hazelnut (Balarak et al., 2016). Corn stalks as agricultural waste produce in large amounts annually in Iran and has no economic value; it seems to be the right source for producing activated carbon. Therefore, this study has been carried out to prepare and characterize an activated carbon from corn stalks (CSAC) to investigate the effect of independents variables on the efficiency removal of OTC, to study the isotherm and kinetics model.

2. Materials and methods

2.1. Materials

In this study, the synthetic wastewater was prepared from OTC powder (Merck Company, Germany). The OTC with molecular formula of $C_{22}H_{24}N_2O_8$, molecular weight of 460.434 g/mol, and molecular structural and $pK_a$ values according to Fig. 1 (Cheng et al. 2013b). Sulfuric acid and sodium hydroxide 1N (Merck Company, Germany) was employed to adjust pH at different values.

Fig. 1. Molecular structure and $pK_a$ values of OTC.

2.2. Preparation and characterization of activated carbon

First, corn stalks were washed with tap water several times to remove dust and impurities. Second, the stalks have been cut into smaller pieces (2 to 5 cm), and then were rinsed with distilled water. At
chemical activation step, phosphoric acid (85 %) (Merck Co., Germany) was used for chemical activation of stalks with a mass ratio of 1 to 10 for 24 h. After this step, the acidified corn stalks have been rinsed and were placed at oven (Memmert 141, Germany) in 150 °C for 4 hours. Finally, in order to complete the activation process by thermal process, the corn stalks were placed in a pottery vessel that covered by pottery mud with an opening, and then the vessel was placed in an electric furnace (Nabertherm 527, Germany) in 500 °C for total activation time of 2 hours. In the final stage, the prepared carbon was washed with distilled water and its neutralization was done with using of 0.1 N NaOH (Merck Co., Germany). The prepared activated carbon stored in desiccators for future experimental works after has been powdered and passed through sieve (mesh 50). The morphological features of adsorbent surfaces are characterized by Scanning Electron Microscope (SEM) (Philips X130, Philips, Netherlands) (Dehghani et al. 2015), and the infrared spectroscopy FTIR, (WQF-520 resoltuio, China) was employed for identifying the material agent groups (Madivoli. 2016).

2.3. Experimental procedure

To prepare a stoke solution, 1 g of OTC has been mixed with 1 L of distilled water. All experiments were carried out in containers with a volume of 100 ml using shaker (IKA KS 501, Germany) at 150 rpm. After each stage of the experiments, the achieved samples were placed in the centrifuge (GUNT CE 148, Germany) at 6000 rpm for 10 min to eliminate the inhibitory factors in determining the OTC concentration. The concentration of dye has been determined by a spectrophotometer (JENWAY 6305, England) at a wavelength of 348 nm. The removal efficiency (R), and absorption capacity (q) of the samples are calculated by equations 1 and 2, respectively.

\[
R(%) = \frac{C_0 - C_e}{C_0} \times 100
\]  
\[
q_e = \frac{C_0 - C_e}{M} \times \frac{V}{c_0}
\]  

where, \(C_0\) is initial concentration of solution (mg/L), \(C_e\) is equilibrium concentration (mg/L), \(V\) is volume of the solution (mL) and \(M\) is absorbent weight (g).

2.4. Adsorption isotherms

Adsorption isotherm is a main tool for evaluating the adsorbate distribution over solid/liquid boundaries, as well as for the estimation of adsorbent adsorption capacity (Beltrame et al. 2018). To describe the equilibrium relations, there are several important isotherms models including Langmuir, Freundlich and Temkin models (Mousavi et al. 2017). The assumptions of Langmuir model are uniform adsorption, similar energy for attracting to all sites. The Langmuir model linear equation can be expressed into equation 3.

\[
c_e = \frac{1}{q_e} \left( \frac{K_L}{K_L - q_m} \right) + \frac{c_0}{q_m}
\]  

where, \(c_e\) is antibiotic equilibrium in solution (mg/L), \(q_e\) is the maximum adsorption capacity (mg/g) and \(K_L\) is Langmuir constant calculated by \(C_e\) vs. \(C_0/q_0\) (mg/g). Freundlich isotherm is widely used to describe surface adsorption with an asymmetric energy distribution whose equation is as equation 4 (Bao and Zhang. 2012).

\[
Q = K_r \left( c_e \right)^{1/n}
\]  

where, \(K_r\) and \(n\) are the Freundlich isotherm constants. Freundlich isotherm is an experimental equation and reliable for interpreting experimental data. The Freundlich equation can be classified as equation below.

\[
\ln q_e = \ln K_f + \left( \frac{1}{n} \right) \ln C_e
\]  

If \(\ln q_e\) vs. \(C_e\) is plotted, should obtain a straight line with: slope=1/n and intercept=\(\ln K_f\).

Temkin isotherm assumes that the absorption temperature of all molecules is linearly reduced. In other words, the Temkin isotherm Fig. 2. SEM of activated carbon prepared from CSAC:equation implies the effects of indirect interaction between adsorbent molecules on the basis that the strength temperature and then the vessel was placed in an electric furnace (Nabertherm 527, Germany) in 500 °C for total activation time of 2 hours. In the final stage, the prepared carbon was washed with distilled water and its neutralization was done with using of 0.1 N NaOH (Merck Co., Germany). The prepared activated carbon stored in desiccators for future experimental works after has been powdered and passed through sieve (mesh 50). The morphological features of adsorbent surfaces are characterized by Scanning Electron Microscope (SEM) (Philips X130, Philips, Netherlands) (Dehghani et al. 2015), and the infrared spectroscopy FTIR, (WQF-520 resoltuio, China) was employed for identifying the material agent groups (Madivoli. 2016).

\[
q_e = B \ln A + B \ln C_e
\]  

where, \(B = RT/b,\) and \(b\) is the Temkin constant related to the heat of adsorption (J/mol); \(A\) is the Temkin isotherm constant (L/g), \(R\) is the universal gas constant (8.314 J/mol K) and \(T\) is the absolute temperature (K).

2.5. Adsorption kinetics

An adsorption kinetic model can provide appropriate information to design of system for pollutants removal by activated carbon. In purpose to express the kinetics of OTC adsorption onto the CSAC, the pseudo-first-order, pseudo-second-order based on the adsorption rate law and Weber and Morris based on intra particle diffusion kinetic models were applied (Mousavi et al. 2017; Zhu et al. 2018).

Pseudo first-order kinetic model is expressed as equation 8.

\[
\log (q_e - q) = \log q_e - \frac{k_1}{2.303} t
\]  

where, \(q_e\) is the amount of antibiotics absorbed at any time (mg/g), \(q\) is the amount of antibiotics absorbed in equilibrium state (mg/g) and \(k_1\) is adsorption rate constant (1/min). Also Pseudo second-order kinetic model (Ho. 1995) is expressed absorption behavior in a wide range and can be written as equation 9.

\[
\frac{dt}{dt} = k_2 (q_e - q)^2
\]  

where, \(k_2\) is the apperceived second-order adsorption rate constant of the kinetic state (g/(mg min)).

The intra-particle diffusion model using the Weber and Morris (1963) theory is expressed as equation 10.

\[
q_t = k_i \times t^{1/2}
\]  

where, \(q\) is the amount of solvable sorbent at time \(t\) (mg/g) and \(k_i\) is the rate constant for intra-particle diffusion (mg min\(^{-1/2}\)).

3. Results and discussion

3.1. Adsorbent specifications

Scanning electron microscope (SEM) as a usefull tool to describe the surface morphology and physical properties of the adsorbent has been used in previous research works (Balarak et al. 2016). Fig. 2 shows SEM micrograph of activated carbon that show porous surface. FTIR spectroscopy is described functional groups of materials and chemical structure (Madivoli, 2016; Khodadadi and Dorri. 2015). According to characteristics that has been reported by FT-IR spectroscopy (Fig. 3) peak points of 1330, 1700, 1221, 800, 1600, 950, 1470, 798 and 600 are represent the functional groups of C-H, C-CI, C-OH, C\(_2\)H\(_2\), OH, N-H, Si-O-Si, C-O-C, C=O, and C=N, respectively. Aforementioned functional group are shown in previous researches (Ahmadi et al. 2017; Ghadimi et al. 2013; Jia et al. 2013).

3.2. Effect of independent variables

3.2.1. Effects of initial OTC concentration

The effect of the initial OTC concentration on the OTC removal efficiency is shown in Fig. 4. The initial concentration varied from 10 to 400 mg/L, when other parameters; adsorption dose, contact time, pH were constant. According to results by increasing the initial concentration of OTC the removal efficiency of antibiotic decreased. Based on Fig. 4, when concentration increased from 10 to 400 mg/L, the removal efficiency of OTC reduced from 99.90 % to 49.21 %, which confirmed unsuitable effect of high initial concentrationon the adsorption process. Results of this part of present investigation were in agreement with achievements of previous studies; Ahile et al. (2018) represented the OTC removal efficiency from aqueous solution using melon husk decreased by increasing the initial OTC concentration (Ahile and Utange. 2018). Balarak et al. (2017) studied removal of amoxicillin antibiotic using an adsorbent prepared from Azolla Filiculoides. They found that with increasing the concentration of amoxicillin from 10 to 200 mg/l, the antibiotics removal efficiency reduces from 96.26 % to 70.38 % (Balarak et al. 2017).

3.2.2. Effects of contact time

As shown in Fig. 5, with an increase in contact time from 20 min to 60 min, the OTC removal efficiency rises from 44.30 % to 99.90 %, but after that, by increasing of time the OTC removal efficiency decreases, which means the time of equilibrium in adsorption is 60 min. At the beginning of the process, adsorbent active sites are high but over time because of their fullness, the efficiency of deletion is also reduced (Abdulmajeed, 2017; Ahile and Utange, 2018). Ammar and Abbas (2016) applied activated carbon for removal of Fluoroquinolones antibiotic, and they found with increasing of contact time, the Fluoroquinolones removal efficiency also increased, and the duration of 90 min was chosen as the time of equilibrium (Ammar S. Abbas. 2016).

3.2.3. Effects of adsorption dose

One of the main parameters in the adsorption process is activated carbon dosage because the adsorption dose controls the capacity of a sorbent to adsorb a certain concentration of an adsorbate under specific performance conditions (Barka et al. 2011). The effect of adsorbent dose on the OTC removal efficiency is shown in Fig. 6. Results confirmed that with an increase in the adsorbent dose from 0.15 to 1.5 g, the OTC removal efficiency rises from 30.67 % to 99.90 % and the maximum OTC removal achieved in adsorbent dose of 1.5 g. In a study by Liu et al. (2013) a powdered activated carbon has been used for antibiotics removal, it was observed by increasing the adsorbent dose from 10 mg/l to 20 mg/l the removal efficiency of process increased from 76.71% to 95% (Liu and Jia. 2013b). In another study.
by Mohseni-Bandpi et al. (2016), cephalexin antibiotic was removed using natural zeolite and FeO nanoparticles. It was observed that the cephalexin antibiotic removal increased with an increase of adsorbent to 6 g/L, but the efficiency of process was constant at higher dosage (Mohseni-Bandpi et al. 2016).

The adsorption isotherm indicates that how a molecule behaves between solution phase and solid phase to achieve equilibrium in the adsorption process. Studying the isothermal data and fitting them to different isotherm models is an important step to find an appropriate model (Almasi et al. 2016a; Sun et al. 2012). The equilibrium data for the OTC removal onto the CSAC were modeled using the Langmuir, Freundlich and Temkin adsorption isotherms. The values of the isotherm model parameters are illustrated in Table 1 in comparison with results of previous studies. As can be seen from Table 1, Langmuir and Freundlich isotherms have better correlation due to higher valve of R2, but there is more in tune with Langmuir isotherm. It can be seen from Table 1 that the values of the Freundlich exponent n is less than 1. It is demonstrated the adsorption process to be undesirable due to surface heterogeneity (Santhi et al. 2016). On the other hand, because in Langmuir isotherm, the dimensionless parameter 0 ≤ RL <1, isotherm is desirable (Geçgel et al. 2016).

Table 1. The results of isotherms modeling for the OTC adsorption.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>qm, mg/g</td>
<td>K, L/mg</td>
<td>R²</td>
<td>k, mg/L</td>
</tr>
<tr>
<td>Cotton linter fibers</td>
<td>869.57</td>
<td>0.11</td>
<td>0.99</td>
<td>293.92</td>
</tr>
<tr>
<td>Sediment</td>
<td>54.66</td>
<td>0.026</td>
<td>0.99</td>
<td>1.5054</td>
</tr>
<tr>
<td>CSAC</td>
<td>522.6</td>
<td>0.01</td>
<td>0.96</td>
<td>1.036</td>
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3.3. Equilibrium adsorption isotherms

The adsorption isotherm indicates that how a molecule behaves between solution phase and solid phase to achieve equilibrium in the adsorption process. Studying the isothermal data and fitting them to different isotherm models is an important step to find an appropriate model (Almasi et al. 2016a; Sun et al. 2012). The equilibrium data for the OTC removal onto the CSAC were modeled using the Langmuir, Freundlich and Temkin adsorption isotherms. The values of the isotherm model parameters are illustrated in Table 1 in comparison with results of previous studies. As can be seen from Table 1, Langmuir and Freundlich isotherms have better correlation due to higher valve of R2, but there is more in tune with Langmuir isotherm. It can be seen from Table 1 that the values of the Freundlich exponent n is less than 1. It is demonstrated the adsorption process to be undesirable due to surface heterogeneity (Santhi et al. 2016). On the other hand, because in Langmuir isotherm, the dimensionless parameter 0 ≤ RL <1, isotherm is desirable (Geçgel et al. 2016).

Fig. 4. Effect of initial OTC concentration on the removal of OTC.

Fig. 5. Effect of contact time on the removal of OTC.

Fig. 6. Effect of adsorption dose on the removal of OTC.

Fig. 7. Effect pH on the removal of OTC.

3.2.4. Effects of pH

In order to study the effect of initial pH of solutions on the adsorption process, experiments were performed on a wide range of initial pH (3 to 11) at the best value of other parameters; adsorbent dose of 1.5 g, contact time of 60 min, and OTC concentration of 10 mg/L (Fig. 7). It is seen that with increasing pH from 3 to 9, the OTC removal efficiency increased from 96.96% to 99.90%, but decreased to 44.33 at pH of 11 (Fig. 7). According to the results, the pH of 9 was selected as the equilibrium pH. In a study that was carried out by Hojjatyar (2017) to remove tetracycline antibiotic using zeolite adsorbent, it was observed that antibiotic adsorption capacity increased by increasing pH from 2 to 5, but then adsorption capacity decreased at higher pH (Hojjatyar. 2017). Ghadim et al. (2013) studied tetracycline removal by graphene oxide. They found that tetracycline removal efficiency increased with increasing pH from 4 to 7, and at higher value of pH the percentage removal of antibiotic was less than other value of pH (Ezzatpour Ghadim and Kimiaigard. 2013). Roca Jalil et al. (2017) represented the effect of pH changes from 3 to 12 on the ciprofloxacin removal using clay as an adsorbent. Results shown that with pH increasing from 3 to 6, ciprofloxacin adsorption capacity raised and more value of pH had negative effect on the capacity of adsorption (Roca Jalil et al. 2017).

3.4. Adsorption kinetics

The adsorption kinetics is one of the important data in order to understand the mechanisms of adsorption and to evaluate the performance of adsorption (Sun et al. 2012). The adsorption kinetics for the OTC removal by CSAC using pseudo first-order and pseudo second-order kinetic models based on the rate law, and intra-particle diffusion using Weber and Morris are used in this study. Results that have been listed in Table 2 are compared with results of kinetic studies in previous research works. The results showed that the pseudo second-order reaction model fit the reduction of oxytetracycline antibiotic, also showed good linear relationship with a correlation coefficient (R²) larger than 0.9.

Table 1. The results of isotherms modeling for the OTC adsorption.

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Table 2. The results of kinetics models for the OTC adsorption.

<table>
<thead>
<tr>
<th>Adsorbent</th>
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<th>Pseudo-second-order</th>
<th>Intra-particle diffusion</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>q, mg/g</td>
<td>K1, 1/min</td>
<td>R2</td>
</tr>
<tr>
<td>Cotton linter fibers</td>
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<td>0.97</td>
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<tr>
<td>Sediment</td>
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<td>0.99</td>
</tr>
<tr>
<td>CSAC</td>
<td>14.19</td>
<td>0.037</td>
<td>0.909</td>
</tr>
</tbody>
</table>

4. Conclusions

The effects of adsorbent dose, contact time, pH, and initial OTC concentration on the OTC removal from aqueous solution using CSAC have been investigated. The results confirmed that suggested activated carbon has ability to remove antibiotic because of porous surface and functional groups. Furthermore, aforementioned variables have important effects on the process; high concentration of OTC negatively affected the removal efficiency, contact time at high level cause desorption, the adsorbent at the higher dose increased the OTC removal, and pH from 3 to 9 was efficient for adsorption of OTC by CSAC. The results of isotherm and kinetic studies showed that Langmuir isotherm and pseudo-second order kinetic are suitable models to describe the experimental data.

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