ADSORPTION ISOTHERM STUDIES OF TETRACYCLINE ANTIBIOTICS FROM AQUEOUS SOLUTIONS BY MAIZE STALKS AS A CHEAP BIOSORBENT

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Abstract:
The maize stalks as a Cheap Biosorbent was used for removal of Tetracycline (TC) from aqueous solution in batch systems. The adsorption of TC occurred by studying the effects of contact time and temperature. Freundlich, Langmuir and Temkin isotherms were used to analyze the equilibrium data obtained at different adsorption conditions. It was observed that Langmuir isotherm provided better fit to the equilibrium data than other isotherms. The biosorption percentage decreased from 81.5 to 63.8% as temperature was increased from 25 to 55 ºC for the equilibrium time 90 min. These results indicated the exothermic nature of TC biosorption onto maize stalks. The prepared Maize Stalks were characterized by SEM, BET. The results showed that the TC adsorption capacity was positively correlated to the BET surface area. Maize stalks which is an agricultural waste material can be used for industrial water treatment to eliminate of antibiotics.

Keywords: Tetracycline, Maize Stalks, Adsorption, Isotherms, Temperature.

Introduction
Traditionally, the impact of chemical pollution has focused almost exclusively on the conventional priority pollutants(1, 2). However, the growing use of pharmaceuticals worldwide, classified as the so-called emerging pollutants, has become a new environmental problem, which has raised great concern among scientists in the last few years(3, 4). More than 3000 chemical products are used in human and veterinary medicine(5). The use of antibiotics and growth hormones in human and veterinary has a significant effect on the quality of surface and ground water(6, 7).
Currently, the production of antibiotics is far beyond all previous boundaries, and they enter the environment mainly through four routes: production process of antibiotics, sewage, land application of municipal biosolids and improper disposal of unused or expired drugs (8, 9).

Residues of these antibiotics discharged from agricultural runoff and municipal wastewater treatment plants are frequently detected in soil, surface water, groundwater, and even drinking water (10, 11). The widespread use of antibiotics has become a serious problem as it has a variety of potential adverse effects, including acute and chronic toxicity, impact on aquatic photosynthetic organisms, disruption of indigenous microbial populations, and dissemination into antibiotic-resistant genes among microorganisms (12-14).

Tetracyclines (TCs), including oxytetracycline (OTC), tetracycline (TC), and chlortetracycline (CTC), are a group of broadspectrum antibiotics applied to livestock as additives to combat diseases (15-17). In natural soils, the sorption and transport behaviors of these chemicals are similar despite their structural variances (18). Even low concentrations of pharmaceuticals released from the environmental matrix into water can pose serious environmental damages (19, 20). Thus, it is of great importance to develop some efficient and cost-effective treatment technologies to remove such compounds (21). The removal of pharmaceutical antibiotics by conventional water and wastewater treatment technologies is generally incomplete.

Treatment processes such as activated sludge, ozonation and biomembrane biological filtration, and reverse osmosis have been applied to remove pharmaceuticals from wastewater (22, 23). In this regard, adsorption is a simple and effective process, can be used as an efficient method in removal of pharmaceuticals from water and wastewater (24).

Also various adsorbents, including activated carbon, aluminum oxide, and chitosan, Lemna minor and canola have been reported to remove antibiotics by means of surface adsorption, Van der Waals forces, and p–p interactions between antibiotics and different adsorbents (25-28). However, such adsorbents are quite unaffordable for the treatment of a mass of sewage (29). Therefore, how to remove antibiotics from wastewater with low-cost adsorbent is an imperative subject faced by environmental researchers.

Maize is an economical crop in Iran, large areas are cultivated with it. The aim of the present study is to examine the ability of maize stalks as cheap bio-adsorbent for removal of TC antibiotics from aqueous solutions. The different factors affecting adsorption process were evaluated as time of contact time and temperature.
Materials and Methods:

Biomass preparation:

Maize stalks were collected and used as sorbent for the biosorption of TC antibiotics. The maize stalks sample was collected from agricultural land in Tabriz, Iran. Samples were washed several times using deionised water to remove extraneous and dust. They were then dried in an oven at 105 °C for 24 h. The dried biomass was chopped and filtered. The granules were sieved and the particles having sizes less than 100 mesh were used in the tests. The adsorbent was kept dry in a closed container until the time of use.

Specific surface areas were determined by the N₂ Brunauer-Emmett-Teller (BET) nitrogen adsorption method in a Micromeritics-Gemini 2360 surface area analyzer. The dry and degassed samples were then analyzed using a multipoint N₂ adsorption-desorption method at room temperature. The morphology of the material was analyzed with a scanning electron microscope, model JEOL 5900LV, at 25 kV.

The tetracycline hydrochloride (Molecular weight: 480.9, Molecular formula: C₂₂H₂₄N₂O₈·HCl) was purchased from Sigma-Aldrich, USA. The chemical structure of Tetracycline is presented in Fig 1. The distilled water was used to prepare the stock solution of tetracycline. Other chemical used in this study were prepared from Merck, Germany.

![Chemical structure of tetracycline hydrochloride](image_url)

**Fig. 1. The chemical structure of tetracycline hydrochloride.**

Batch sorption experiment

Using definite amount (0.5 g) of adsorbent in a 200 mL stopper conical flask containing 100 mL of TC solution, batch sorption studies were carried out at desired pH value, contact time, temperature. Different initial concentration of TC solutions were prepared by proper dilution from stock 1000 mg/L TC standard solutions.

The amount of biosorbent was then added to the TC solution in the conical flask and stirred for the desired contact time using a magnetic stirrer at 200 rpm. The time required for reaching equilibrium condition estimated by drawing samples
at regular interval of time till the equilibrium was reached. The content of the TC in the test flask was separated from biosorbent by filtration through a filter paper and initial and equilibrium concentration of TC in solution was determined by HPLC. In the HPLC analysis and a SPD-10A UV–Vis detector at maximum absorption wavelength of 365 nm which was determined using a Shimadzu UV-1700 spectrophotometer to scan from 200 to 800 nm. A 30:70 (v/v) acetonitrile and 0.01 M aqueous oxalic acid mixture was used as mobile phase at room temperature with a constant flow rate of 1.0 mL min⁻¹. The injection volume was 10 ml. The retention time of TC hydrochloride was 4 min. The samples were analyzed three times and the mean values were computed. The amount of TC adsorbed per unit mass of the biosorbent was evaluated by using following equations (30, 31):

\[ q_e = (C_0 - C_e) \times \frac{V}{W} \]

Where, \( C_0 \) is the initial TC concentration, and \( C_e \) is the antibiotic concentration at equilibrium and \( V \) is the volume of TC solution in milliliters, \( W \) is the mass of adsorbent in grams. The percent of TC removal was evaluated from the equation (32, 33):

\[ \% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \]

Results and discussion

The of morphology of biomass was investigated using SEM and the image is shown in Fig 2. The regular spherical shape of the biomass is preserved after the activation and the surface is quite smooth except for a few occasional cavities. Under high magnification (×100), Maize stalks is shown to exist as random arrays of thin sheets or layers, in which there are large amounts of interspaces with the size of several tens of mm, revealing a highly developed mesoporosity. The BET surface area of the biomass material was about 37.5 m²/g, with an average pore size of 1.33-2.47 μm.

Fig. 2. SEM micrographs of Maize stalks.
Effect of contact time and temperature:

Fig 3 shows the effect of contact time on the rate of TC uptake onto maize stalks. At the beginning of adsorption, the values of % removal increased quickly, and then after 45 min, the change turned slow. Thus, the adsorption of the TC on maize stalks was speedy. After about 90 min, the adsorbed quantity of the TC showed nearly no change. The two stage sorption mechanism with the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature(34, 35). This behavior gives away a slow approach to equilibrium.

The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium.

The effect of temperature of the adsorbate was also examined for solutions of 100 mg/L TC and 2.5 g/L adsorbent at pH=7. Fig 4 shows the biosorption of TC as a function of the temperature. The biosorption percentage decreased from 85.5 to 63.8% as temperature was increased from 25 to 55 °C for the equilibrium time 90 min. These results indicated the exothermic nature of TC biosorption onto maize stalks.

A decrease in TC biosorption with the rise in temperature may be due to either the damage of active binding sites in the biomass or increasing tendency to TC desorption from the interface to the solution by weakening of adsorptive forces between the active sites of the adsorbent species(36-38).

Adsorption isotherms

To describe the adsorption process of TC onto maize stalks, the three empirical models of Langmuir, Freundlich and Temkin isotherms were tested. The adsorption studies were conducted at fixed adsorbent dosage (2.5 g) by varying initial concentrations of TC (10-100mg/L). These isotherms relate metal uptake per unit weight of adsorbent qₑ to the equilibrium TC concentration in the bulk phase Cₑ.

Langmuir Model

The Langmuir isotherm models is used to describe the relationship between the amount of adsorbed material and its equilibrium concentration in solutions. The Langmuir isotherm is valid for monolayer adsorption on a surface containing finite number of identical sites. The model assumes a uniform adsorption on the surface and transmigration in the plane of the surface. The Langmuir isotherm is expressed as follows(39, 40):

\[
\frac{Cₑ}{qₑ} = \frac{1}{qₘK_L} + \frac{Cₑ}{qₘ}
\]
where, $q_e$ is the adsorption capacity at equilibrium in mg/g, $C_e$ is the concentration at equilibrium (mg/L) and $K_L$ is the Langmuir equilibrium constant in (mL/mg). The linear plots of $C_e/q_e$ vs $C_e$ examines the that adsorption follows the Langmuir adsorption model (not shown). The values of $Q_m$ and $K_L$ can be calculated (Table 1) from the slope and intercept of the plot, respectively. The correlation coefficients are 0.998, 0.996, 0.994 and 0.999 for temperatures 25, 35, 45, 55 °C respectively. These results reveal that the Langmuir-type sorption isotherm is suitable for equilibrium studies, suggesting the formation of monolayer coverage of the adsorbate on the surface of adsorbent. The amount of TC adsorbed per unit mass of the adsorbent decreased with the temperatures as expected and the sorption capacities were 36.5, 35.2, 33.9 and 31.7 mg/g for temperatures 25, 35, 45, 55 °C respectively.

The essential characteristics of the Langmuir isotherm can be explained by the equilibrium separation factor $R_L$ defined as follows (41):

$$R_L=\frac{1}{1+K_L C_0}$$

Depending on the value of $R_L$, the shape of the isotherm and whether the adsorption is favorable or not can be determined. The calculated $R_L$ values were represented in Table 1. It was observed that at these experimental conditions, sorption of the different TC by maize stalks was found to be a favorable process as the values of $R_L$ are 0.879, 0.647, 0.448 and 0.229 for temperatures 25, 35, 45, 55 °C respectively.

**Freundlich Model**

The Freundlich isotherm assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of the adsorbent. The Freundlich model is based on the following expression (42, 43):

$$q_e=\ln K_F C_e^{\frac{1}{n}}$$

Where, $K_F$ is the Freundlich constant and $1/n$ is a constant indicating the reaction intensity. The two Freundlich parameters $K_F$ and $1/n$ can be determined graphically by plotting the experimental data and then using the Freundlich equation in the following form (44):

$$\log q_e=\frac{1}{n} \log C_e + \log K_F$$
The values of $K_F$ and $n$ and $R^2$ are presented in Table 1. It can be seen from the table 1 that the adsorption of the TC on maize stalks follows the Freundlich model. The $n$ values are 3.84, 3.06, 2.41 and 1.85 for temperatures 25, 35, 45, 55 °C respectively, (greater than 1), indicating that the adsorption is favorable.

**Temkin Isotherm**

This isotherm was developed by Temkin and Pyzhev, and it is based on the assumption that the heat of adsorption decreases linearly with the increase of coverage of adsorbent. Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic. This model can be shown by the equation (45):

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$$

Where, $K_T$ (L/g) is Temkin adsorption potential and $b$ (kJ/mol) is heat of sorption (Table 1).

The linear plots of $\ln C_e$ vs $q_e$ examines the that adsorption follows the Temkin adsorption model (not shown). From the slope and intercept of the straight line $b$ and $K_T$ can be evaluated, respectively. By comparing the correlation coefficients ($R^2$) obtained from the three isotherms (Table 1), it can be concluded that Langmuir model can be applied successfully for TC adsorption onto maize stalks biomass more than Freundlich and temkin model.

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**Fig. 3.** Effect of Contact time on TC Removal (Dose = 2.5 g/L, TC concentration = 100 mg/L, pH = 7 and Temp= 30 °C).

**Fig. 4.** Effect of temperatures on TC Removal (Dose = 2.5 g/L, TC concentration = 100 mg/L, pH = 7, Contact time 90 min).
Conclusion:

The biosorption of Tetracycline on maize stalks was investigated. The removal percentage of methylene blue can reach to 85.5% when the biomass dose was 2.5 g/L, indicating that the prepared biomass is a good candidate for water treatment to remove some TC antibiotics. The maximum surface area of 37.5 m$^2$/g and average pore size of 1.33-2.47 µm were obtained under the following optimal conditions. The amount of TC adsorbed per unit mass of the adsorbent decreased with the temperatures as expected and the sorption capacities were 36.5, 35.2, 33.9 and 31.7 mg/g for temperatures 25, 35, 45, 55 ºC respectively.

References


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