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Nonlinear Isotherms and Kinetics and Application Error Functions for Adsorption of Tetracycline on Lemna Minor

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

In this study, removal of Tetracycline (TC) antibiotics from artificially contaminated water has been investigated with the aim of detoxifying pharmaceutical wastewater before their safe disposal onto land or into river waters. The adsorption of TC occurred by studying the effects of adsorbent dose, TC concentration and contact time at fixed temperature= 25℃ and PH=7. The removal of TC effluent is a rapid process. At adsorbent dose 2 g/L and at room temperature, the adsorption equilibrium is reached after 60 min for low concentration and 90 min for high antibiotic concentration and kinetics follow a pseudo-second-order model. The adsorption isotherm is in good agreement with the Langmuir model. The adsorption of TC on the surface of LM biomass was done in monolayer and maximum adsorption capacity of TC was determined as 18.26 mg/g. Also in this study, have also been done five types of error functions. The results of error functions showed that the best fit was obtained for the Langmuir isotherm and pseudo-second-order model with R^2_{adj} =0.9975 and R^2_{adj} = 0.9912.

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1. INTRODUCTION

Antibiotics for many years have been used in both human and animals for treatment of microbial infections, and also as feed additives for the promotion of growth of livestock animals [1-3]. Pharmaceutical antibiotics have attracted increasing concern in recent years because they have been proved to be a class of potent pollutants [4,5]. Since most antibiotics including tetracycline are poorly metabolized and absorbed by the treated humans and animals, large fractions are excreted through urine and faeces as unmodified parent compound [6,7]. Except for the direct, acute toxic effect for creatures, one of the most serious risks of antibiotics in the water circulation is the potential, chronic antimicrobial resistance [8,9]. This suggests that antibiotics will gradually lose power over the diseases caused by the antibiotic-resistant bacteria [10,11].

Tetracycline (TC), as one of the most widely used antibiotics all over the world, is extensively used for human therapy and agricultural purposes [12,13]. However, TC is poorly absorbed and metabolized and has a long environmental half-life. Most TC is discharged into the environment through urine, faeces, municipal wastewater treatment plants and agricultural run-off [14,15]. Residues of TC even below the threshold levels have serious potential adverse effects on the target organisms, including acute chronic toxicity, endocrine disruption, and antibiotic-resistant genes [16]. Therefore, the occurrence of residual antibiotics in the environment has been a worldwide issue and warrants the development of inexpensive yet effective methods for antibiotics removal from contaminated water [17,18].

Techniques based on biological processes, chemical processes, physical processes, or a combination of these can be used to remove organic pollutants [19]. Processes that have been used to remove pollutants from wastewater include membrane process, ozonation, Fenton oxidation, chlorination, photocatalytic degradation using UV–vis radiation, adsorption and some new water treatment processes for sustainability have been reported [20-22].

Nowadays, biological process is still the core unit of the wastewater treatment plant, which is specifically designed for biological removal of soluble organics and nutrients. However, the conventional biological process is not tailored for treating antibiotics-bearing wastewater due to the specific antimicrobial property of antibiotics [23].

As well, the agricultural progress and increased waste has stimulated a renewed interest in utilizing these materials in adsorption applications for and wastewater water purification because this type of absorbent can meet the criteria required for a good adsorption process as they possess a high surface area, large pore volume, and strong physical and chemical interactions with pollutants [24-26]. Therefore, this kind of adsorbents has been used to remove antibiotics such as for penicillin, azithromycin, ciprofloxacin, tetracycline, Cephalexin from pharmaceutical wastewater [27-29].

Aquatic plants play a key role as biosorbents for the removal of pollutants from aqueous solutions [30]. Lemna minor (LM) known as duckweed, is a free-floating aquatic plant that is widely distributed in many countries. LM rapid growing and under optimum circumstances, it can be doubled in a week and adapt to a variety of conditions [31]. Previous studies have reported that LM has the potential for adsorption of contaminants such as heavy metal, fluoride, dyes and antibiotics such as penicillin from aqueous solutions [32].

The present study aims to investigate the adsorption of TC by modified LM as biosorbent. The effects of various parameters such as initial TC concentration, contact time, adsorbent dosage and temperature at fixed pH=7 were examined.

2. MATERIALS AND METHODS

2.1 Preparation of Biomass

LM was collected from Sari, Iran. Before use, biomass was washed several times using sterile distilled water and dried under sunlight for 24 h. To prepare the modified biomass, LM was immersed in 0.1 M HCl for 5 h. Finally, modified LM was washed with distilled water several times and dried. After drying, all the adsorbents were straitened to obtain a particle size of 2 mm to use for adsorption studies.

2.2 Chemicals

All the chemicals used were of analytical grade reagent. The tetracycline hydrochloride (Molecular weight: 480.9, Molecular formula: $C_{22}H_{24}N_2O_8 \cdot HCl$) 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 chemicals used in this study were prepared from Merck, Germany.

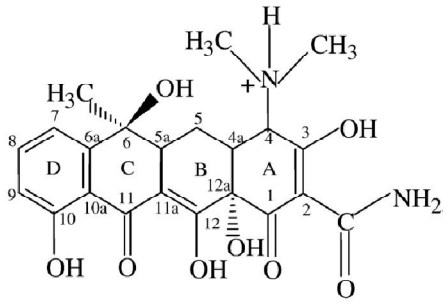

Fig. 1. The chemical structure of tetracycline hydrochloride

2.3 Adsorption Experiment

Batch adsorption experiments were performed using 200 ml glass bottles with the addition of 2 g LM biomass and 100 mL of TC solution with initial concentrations 10 to 200 mg/L. The glass bottles were sealed and placed within a temperature control box to maintain water temperature. The pH of the samples was adjusted by adding 0.1 M HCl or 0.1 M NaOH. At the end of the equilibrium period, the suspensions were separated for later analysis of the TC concentration. The supernatants were filtered through Whatman 42 filter paper. All the experiments and analysis have been carried out in duplicate. The adsorbed phase concentration (q, mg/g) was calculated using the following equation [33,34]:

$$q_e = \frac{(C_0 - C_e)V}{M}$$

Where C_0 and Ce (mg/L) are the liquid-phase concentrations of TC at initial and equilibrium, respectively, V (L) the volume of the solution and M (g) is the mass of adsorbent used.

Final concentration of TC in solution was determined by HPLC. In the HPLC analysis and an SPD-10A UV–Vis detector at the 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.

3. RESULTS AND DISCUSSION

3.1 Effect of Adsorption Contact Time and Initial TC Concentration

For different TC concentrations (10-200 mg/L), the change of adsorption on LM biomass with time is seen in Figure 2. As shown in Fig. 2, the time for reaching the adsorption equilibrium is not identical for each initial TC concentration. For instance, the time for reaching the equilibrium 60 min for 10 mg/L TC concentration, while the time for reaching the equilibrium is 90 min for 200 mg/L TC concentration. Moreover, the adsorption at first occurs very fast, and it becomes slower in later times. This case can be explained that the active central on LM biomass are more available for adsorption at the initial times, and it becomes vice versa in later times [35]. Additionally, the adsorption efficiency is lower at higher concentration, due to the electrostatic repulsion between the protein molecules in solution and the TC molecules on LM surface [36,37].

3.2 Effect of Adsorbent Dosage

The adsorption percent at various doses of LM biomass from 0.5 to 4 g/L is shown in Fig 3. The optimum adsorbent dosage was found to be 2.5 g/L. It was found that the removal of TC by any of the adsorbents increases with an increase in the adsorbent dosage initially and, thereafter, becomes constant after some value of dose. This value is taken as the optimum dosage. The increase in adsorption with the adsorbent dosage can be attributed to the availability of the greater surface area and a larger number of adsorption sites [38]. At doses higher from optimum dosage, the adsorbent surface becomes saturated with TC and the residual TC concentration in the solution is large. With an increase in dose, the TC removal increases due to increased TC uptake by the increased amount of adsorbent [39].

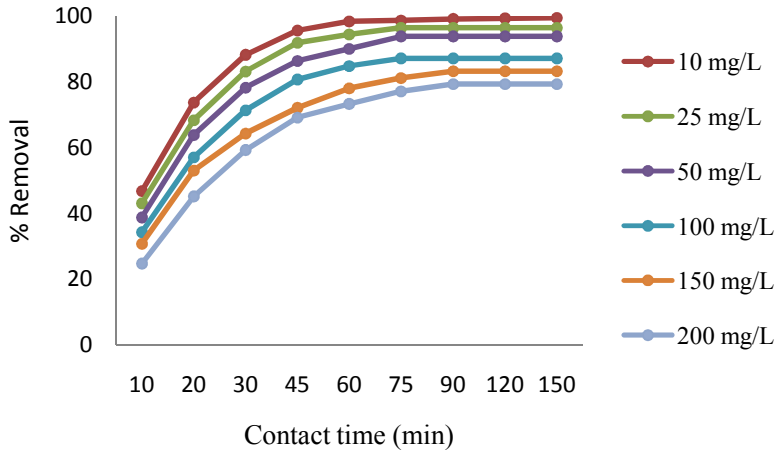

Fig. 2. Effect of contact time and concentration on TC removal (Dose = 2.5 g/L, pH = 7 and Temp= 30℃)

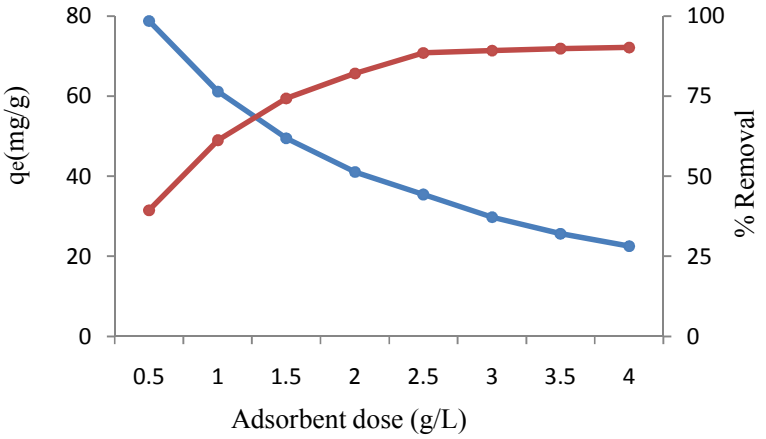

Fig. 3. The effect of adsorbent dose on TC removal efficiency (contact time= 60 min, C_0=100 mg/L, pH=7 and Temp= 30℃)

3.3 Adsorption Isotherms Study

The adsorption isotherm can describe the distribution of TC between the solid phase and the solution at a certain temperature when the equilibrium was reached. The Langmuir and Freundlich models were applied to fit the equilibrium data.

3.4 Langmuir Isotherm

The Langmuir theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. Once an adsorbate molecule occupies a site, no further adsorption can take place at that site. The sorbent has a finite capacity for the adsorbate. The Langmuir equation is applicable to homogeneous sorption where the sorption of each molecule has equal sorption activation energy [40].

$$q_e = \frac{K_L C_e}{1 + a_L C_e}$$

Where K_L is Langmuir isotherm constant (L/g), a_L is Langmuir isotherm constant (L/mmol).

3.5 Freundlich Isotherm

The Freundlich equation is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity

factor 1/n. Hence, the empirical equation can be written [41,42]:

$$q_e = K_F C_e^{1/n}$$

Where q_e is solid phase sorbate concentration in equilibrium (mmol/g), Ce is liquid phase sorbate concentration in equilibrium (mmol/L), K_F is Freundlich constant (L/mg$^{1/n-1}$g) and 1/n is the heterogeneity factor. When n = 1, the Freundlich equation reduces to Henry's Law.

3.6 Error Functions

In order to evaluate the validity of the adsorption mathematical models with experimental results, a number of error functions are available in the literature. The use of only one R^2 for isotherm and kinetic data analysis is not sufficient, because the experimental results may have high R^2 value. It is, therefore, necessary to diagnose the result of a regression for residue analysis. In this study, five types of statistical functions among the most widely used in such studies [43-47]:

Standard deviation (SD)

$$SD = \sqrt{\left(\frac{1}{N-P}\right)\sum_{i=1}^{N}\left(q_{i,observed} - q_{i,calc}\right)^2}$$

The coefficient of determination (R^2)

$$R^2 = \left[\frac{\sum_{i=1}^{N}\left(q_{i,observed} - \bar{q}_{observed}\right)^2 - \sum_{i=1}^{N}\left(q_{i,observed} - q_{i,calc}\right)^2}{\sum_{i=1}^{N}\left(q_{i,observed} - \bar{q}_{observed}\right)^2}\right]$$

Adjusted R-squared $\left(R^2_{ajd}\right)$

$$R^2_{adj} = 1 - \left(1 - R^2\right)\left(\frac{N-1}{N-P-1}\right)$$

Reduced Chi-squared (χ^2_{red})

$$\chi^2_{red} = \sum_{i=1}^{N}\frac{\left(q_{i,observed} - q_{i,calc}\right)^2}{N-P}$$

Residual Sum of Squares (RSS)

$$RSS = \sum_{i=1}^{N}\left(q_{i,observed} - q_{i,calc}\right)^2$$

Where N: number of performed experiments, P: number of parameters of the fitted model, R^2: coefficient of determination.

The results of isotherm modelling data for are summarized in Tables 2 and Fig. 4. By comparing the results of the values of the error functions (Table 1), it is found that the Langmuir model is the most suitable model to satisfactorily describe the studied sorption phenomenon. The value of Freundlich exponent n is greater than 1, indicating a favourable adsorption of TC at experimental conditions.

According to the results, the TC adsorption on the LM biomass follows Langmuir isotherm and it is assumed in this isotherm that monomolecular layer is formed when biosorption takes place without any interaction between the adsorbed.

3.7 Adsorption Kinetics Study

To determine the kinetic order and the time required to reach adsorption equilibrium, the adsorption kinetic study of TC on LM biomass is carried out at room temperature. The amount of adsorbed TC onto LM biomass is calculated according to Equation [48,49]:

$$q_t = \frac{(C_0 - C_t)V}{M}$$

Moreover, to acquire the order of the TC adsorption kinetic, five kinetic models (pseudo-first-order, pseudo-second–order, Avrami, general order and Elovich models) were used.

The pseudo first-order model was described by Lagergren. The expression of the pseudo-first-order model is as follows [38]:

$$\frac{dq_t}{dt} = K_1(q_e - q_t)$$

Integrating equation above with the boundary conditions, t=0 to t and from 0 to q_t leads to non-linear form [50]:

$$q_t = q_e(1 - \exp(-k_1 t))$$

Where k_1: pseudo-first-order adsorption rate constant (min^{-1}).

The Pseudo-second-order kinetic model is described by Ho and Mckay. The expression of the pseudo-second-order model is as follows [51]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

The integration of equation above leads to the non-linear form (48):

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$

The advantage of using the non-linear form lies directly on the fact that we don't need to know the equilibrium capacity q_e from experience since it can be determined from the model. This makes it possible to determine K_2 and the initial rate of adsorption following equation [49]:

$$h_O = k_2(q_e)^2$$

Where K_2: pseudo-second-order adsorption rate constant (g/mg.min), h_0: initial sorption rate for pseudo-second-order adsorption (mg/g.min).

The General order kinetic models based on the number of sites available on the surface of the adsorbent for adsorption. The general order kinetic model equation is given following equation [47]:

$$q_t = q_e - \frac{q_e}{\left[k_N (q_e)^{n-1}.t.(n-1)+1\right]^{1/1-n}} \qquad \text{with } n \neq 1$$

Where: k_N: kinetic adsorption rate constant (min^{-1}. $(g.mg^{-1})^{n-1}$), n: order of adsorption.

The Elovich model is generally applied to chemisorption kinetics. The equation has been used to cover a wide range of slow adsorption rates. The same equation is often valid for systems in which the adsorbing surface is heterogeneous. The Elovich equation is given in following equation [52, 53]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$$

Integrating equation above with the boundary conditions; t=0 to t and from 0 to q_t gives following equation [54,55]:

$$q_t = \frac{1}{\beta}\ln(\alpha.\beta) + \frac{1}{\beta}\ln(t)$$

Where: α: initial adsorption rate (mg/g.min), β: adsorption constant related to the surface coverage (g/mg).

The Avrami equation is used to verify specific changes of kinetic parameters as functions of the temperature, initial concentration and adsorption time. Avrami model is expressed mathematically by following equation [56,57]:

$$q_t = q_e\left(1 - \exp\left(-(k_{AV}.t)^{n_{AV}}\right)\right)$$

Where k_{AV}: Avrami kinetic constant (min^{-1}), n_{AV}: fractional adsorption order.

The fitting parameters of the kinetics models were summarized in Table 2. As can observe from the table 2, the modelling kinetic data could conform to Avarmi kinetic model and pseudo–second order.

The results revels that of the five kinetics model, the best fit was obtained for the pseudo-second-order and Avarmi kinetic model with a high value of R²adj wish is equal to 0.9912 and 0.9948 respectively. The adsorption capacity at equilibrium is very close to experimental value. Based on the correlation coefficient (R^2) (Table 2), the adsorption of TC is more best fit by the pseudo–second-order model (Fig. 5).

Table 1. Parameters of the Langmuir, Freundlich isotherms for the TC onto LM

Langmuir		Freundlich	
K_L	0.0972	K_F	1.793
q_m	26.42	n	4.281
RSS	0.0321	RSS	0.0592
χ^2_{red}	0.0072	χ^2_{red}	0.0156
SD	0.0825	SD	0.0125
R²	0.9982	R²	0.937
R^2_{ajd}	0.9975	R^2_{ajd}	0.928

Table 2. Kinetic parameters for adsorption of TC onto LM biomass

Pseudo-first order		Pseudo-second order		Avrami	
k_1	0.0547	k_2	0.0821	q_e(cal)	18.74
q_e(cal)	19.66	q_e(cal)	28.3	k_{AV}	0.071
RSS	0.0019	h_0	0.0118	n_{AV}	0.0823
χ^2_{red}	0.00189	RSS	0.0039	RSS	0.0028
SD	0.0217	χ^2_{red}	0.00041	χ^2_{red}	0.00042
R^2	0.928	SD	0.0195	SD	0.0193
R^2_{adj}	0.914	R^2	0.994	R^2	0.9972
		R^2_{adj}	0.9912	R^2_{adj}	0.981

Elovich		General order	
α	0.418	q_e(cal)	9.284
β	11.25	k_N	0.0782
RSS	0.00146	n	1.086
χ^2_{red}	.007810	RSS	0.00125
SD	0.0235	χ^2_{red}	0.00018
R^2	0.918	SD	0.0017
R^2_{adj}	0.9137	R^2	0.948
		R^2_{adj}	0.9427

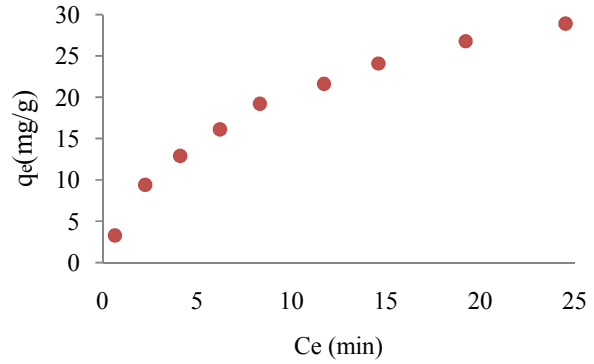

Fig. 4. Langmuir isotherm plots for TC adsorption onto LM

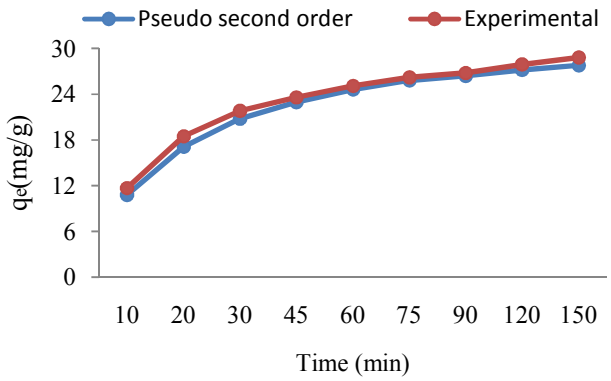

Fig. 5. Pseudo-second-order kinetics and experimental data plots to adsorb TC by LM

4. CONCLUSION

In this study ,LM biomass used as an effective adsorbent for the removal of TC antibiotics in aqueous solution. For this purpose, we have studied different parameters such as initial concentration of TC, contact time and adsorbent dose. The adsorption capacity of LM increased when the initial concentration of TC increased from 10 to 200 mg/L. Langmuir isotherm and pseudo-second-order model fitted well with the adsorption data. These findings suggest that LM is a promising low-cost absorbent for the treatment of wastewater containing TC antibiotics.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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