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STUDY OF MASS TRANSFER COEFFICIENT OF CEPHALEXIN ADSORPTION ONTO WALNUT SHELL-BASED ACTIVATED CARBON IN A FIXED-BED COLUMN

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Abstract. The adsorption of cephalexin (CFX) onto walnut shell-based activated carbon (AC) was investigated. The mass transfer coefficients were calculated by employing constant wave propagation theory. The effect of different conditions on the mass transfer coefficient was also studied. In addition, three models to predict the mass transfer coefficient were developed.

Keywords: adsorption, cephalexin, ctivated carbon, walnut shell, mass transfer coefficient, modeling.

1. Introduction

Effluent disposal is a major global problem. Growing industries, along with the population growth, create environmental problems and health hazards for the population. Therefore, it is necessary to remove pollutants before their discharged into the environment by using different methods, such as nanofiltration, reverse osmosis, ion exchange, *etc*. Although the Earth at 75 % consists of water, water for drinking, sanitation, agricultural and industrial processes is not easily available [1]. Antibiotics are the most extensively used pharmaceuticals by humans and animals. Among them, cephalexin is one of the most common antibiotics in the human and veterinary medicines to treat a variety of infections caused by bacteria, including ear infections, skin infections, and urinary tract infections. Thus, this compound is present as a main pollutant of wastewaters produced by different industries such as households, hospitals and pharmaceutical companies. Therefore, removal of pharmaceuticals from wastewater is necessary. Different techniques are used for the removal of pharmaceuticals from wastewater [2-4]. Over the last few decades, adsorption process has gained importance as an efficient method in purification, separation and recovery process. Adsorption of cephalexin onto different adsorbents has been studied by various researchers [5-8]. Nowadays, researches are focused towards the use of activated carbon due to large surface area and pore volume. Converting the waste materials into activated carbon [9-12] not only is a solution for the problem of waste disposal but also an adsorbent produced for various treatments. Walnut shell was selected as the precursor for the preparation of activated carbon in the present investigation. However, the adsorption capacity of the activated carbon for a specific adsorbate is highly dependent on the type of raw material and the processing techniques used. Activated carbon was prepared through chemical activation using $ZnCl_2$ and applied. Due to the importance of the volumetric transfer coefficient (K_{La}) in the performance and scale-up of the fixed-bed adsorption processes, this parameter should be well known. Also, to properly design and operate fixed-bed adsorption processes, the fixed-bed dynamics including the pollutant breakthrough curves should be fully recognized. Although, a variety of models are available to predict the fixed-bed dynamics, the non-linear wave propagation theory was used to determine the volumetric mass transfer coefficients of CFX on walnut shell AC in a fixed bed column. Because of some assumptions, infinite mass-transfer rate and local equilibrium, of the non-linear wave propagation theory, cannot always be applicable for fixed-bed operations. So, a constant pattern wave approach has been proposed to predict the breakthrough curves of fixed-bed adsorption processes using adsorption isotherm models. This research work focuses on the adsorption of CFX onto prepared walnut shell AC as an adsorbent in fixed bed column and the calculation of mass transfer coefficient by employing the constant wave propagation theory and the effect of flow rate, bed height and CFX initial concentration on these coefficients. Meanwhile, three models with EViews software were applied to predict the effect of flow rate on the mass transfer coefficient.

2. Experimental

2.1. Materials

Cephalexin ($C_{16}H_{17}N_3O_4S$) was purchased from LOGHMAN Pharmaceutical & Hygienic Co., Tehran, Iran) of purity 99.8 % and was used as adsorbate (Fig. 1). Zinc chloride ($ZnCl_2$) used in this study was supplied by Merck Company. The desired concentrations of the solutions were prepared by using distilled water. The experiments were performed using AC adsorbent. The adsorbent was prepared from walnut shell according to the procedure described in [13]. Table 1 summarizes the physical characteristics of the adsorbent studied.

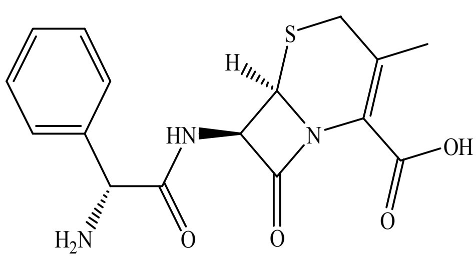

Fig. 1. CFX chemical structure

Table 1

Physical characteristics of the walnut shell AC

Surface area, $m^2 \cdot g^{-1}$	Total pore volume, $cm^3 \cdot g^{-1}$	Average pore diameter, nm
$1.452e^{+03}$	$7.151e^{-01}$	$1.970e^{+00}$

2.2. Experimental Procedure

Experiments were carried out in both batch and continuous tests. The adsorption isotherms of CFX onto walnut shell AC at 100, 125, 150, 175, and 200 mg/l CFX initial concentrations were experimentally determined. Series of column tests were performed to determine the breakthrough curves behavior at different flow rates (4.5, 6 and 7.5 ml/min), bed heights (1.5, 2.0 and 2.5 cm) and CFX initial concentrations (50, 100 and 150 mg/l) on walnut shell AC and investigating the volumetric mass transfer coefficient as well. The concentrations of the cephalexin in the outlet were verified at 263 nm employing a UV-vis spectrophotometer (UNICAM, 8700 series, USA).

3. Results and Discussion

3.1. Theory

To accurately evaluate the fix-bed adsorption column, the breakthrough curves should be determined either experimentally or by mathematical models. Lately, various mass-transfer models have been found for prediction of the fixed bed dynamics [14-19], of which the mathematical model based on non-linear wave propagation theory has been widely used [19]. In this present work, in order to obtain the k_La coefficient in a fixed-bed column, the following equation was used:

$$e_b \frac{\partial C}{\partial t} + U_0 e_b \frac{\partial C}{\partial z} + r \frac{\partial I}{\partial t} = 0 \tag{1}$$

The above equation was obtained from mass balance of CFX under unstable condition. The assumptions for Eq. (1) are included:

1. There is no chemical reaction in the column.
2. Bulk mass transfer is significant compared to diffusion.
3. Axial and radial dispersion is negligible.
4. Plug flow in the column is considered.
5. Temperature is identical throughout the column.

Initial and boundary condition for Eq. (1) is as follows:

$$\text{At } t = 0, \quad C = 0 \quad \text{for } z < L \tag{2}$$

$$\text{For } t > 0, \quad \text{at } z = 0, \quad C = C_F \tag{3}$$

In the wave propagation theory, feed entry causes wave self-sharpening and the curve calculates with the following equation:

$$C = 0 \text{ for } 0 \le t \le \frac{L}{u_0}[1 + \frac{r_b f(C_F)}{e_b C_F}]$$

and

$$C = C_F \text{ for } \frac{L}{u_0}[1 + \frac{r_b f(C_F)}{e_b C_F}] \le t \tag{4}$$

The concentration of the mobile phase can be expressed as the function of the adjusted time:

$$t = t - \frac{z}{U_c} \tag{5}$$

Eq. (5) substituted into Eq. (1):

$$(1 - \frac{U_0}{U_c})\frac{dC}{dt} + \frac{r_b}{e_b}\frac{dI}{dt} = 0 \tag{6}$$

Eq. (6) solved by integrating:

$$\int_0^C (1 - \frac{U_0}{U_c})dC + \int_0^I \frac{r_b}{e_b} dI = 0 \tag{7}$$

or

$$(1 - \frac{U_0}{U_c}) \cdot C + \frac{r_b}{e_b} \cdot I = 0 \tag{8}$$

With respect to both initial conditions ($C = C_F$ and $I = I_F$):

$$(1-\frac{U_0}{U_c})\cdot C_F+\frac{r_b}{e_b}\cdot I_F=0 \tag{9}$$

A combination of Eqs. ((8) and (9)) leads to:

$$\frac{C}{C_F}=\frac{I}{I_F} \tag{10}$$

The adsorption rate of the pollutant can be described by the linear driving force model in terms of the overall liquid-phase mass transfer coefficient:

$$r_b\frac{dI}{dt}=e_bK_La(C-C^*) \tag{11}$$

A combination of Eqs. (10) and (11) gives the following equation:

$$\frac{r_bI_F}{C_F}\frac{dC}{dt}=e_bK_La(C-C^*) \tag{12}$$

The relation between equilibrium concentration in the stationary and mobile phase is expressed as:

$$C^*=g(I)\ \text{or}\ I^*=I(C) \tag{13}$$

Integration of Eq. (12) at initial conditions ($t = t_{1/2}$ and $C = C_{1/2}$) leads to:

$$\int_{C_{F/2}}^{C_F}\frac{dC}{(C-g(\frac{I_FC}{C_F}))}=\int_{t_{1/2}}^{t}\frac{C_F}{r_bI_F}e_bK_Ladt \tag{14}$$

Assuming that K_La is constant, Eq. (14) is simply determined by:

$$t=t_{1/2}+\frac{r_bI_F}{e_bK_LaC_F}\int_{C_{F/2}}^{C_F}\frac{dC}{(C-g(\frac{I_FC}{C_F}))} \tag{15}$$

With respect to $t - t_{1/2} = (t - Z/UC) - (t_{1/2} - Z/UC) = t - t_{1/2}$, breakthrough curve equation at $Z = L$ is expressed as:

$$t=t_{1/2}+\frac{r_bI_F}{e_bK_LaC_F}\int_{C_{F/2}}^{C_F}\frac{dC}{(C-g(\frac{I_FC}{C_F}))} \tag{16}$$

The Freundlich adsorption isotherm model is used to solve Eq. (16), which can be described as follows:

$$q_e=k_fC_e^{1/n}=k_fC_e^m \tag{17}$$

A combination of Eqs. (10) and (17) leads to:

$$q=\frac{q_fC}{C_f}=k_fC_f^m\frac{C}{C_f}=k_fC_f^{m-1}C \tag{18}$$

Substitution of Eq. (18) at right-hand side of Eq. (16) results in the following equation:

$$\int_{C_{f/2}}^{C_f}\frac{dC}{(C-g(\frac{I_fC}{C_f}))}=\int_{C_{f/2}}^{C_f}\frac{dC}{(C-(\frac{I}{k_f})^{1/m})}=$$

$$=\int_{C_{f/2}}^{C_f}\frac{dC}{(C-(\frac{k_fC_f^{m-1}C}{k_f})^{1/m})} \tag{19}$$

When the above equation is solved and substituted into Eq. (16) it results in the Eq. (20), which can be used to predict the breakthrough curve:

$$t=t_{1/2}+\frac{r_bk_fC_f^{m-1}}{e_bK_La}[\ln(2X)-\frac{1}{n-1}\ln(\frac{1-X^{m-1}}{1-2^{1-m}})] \tag{20}$$

where $X = C/C_F$ and also ρ_b and ε_b are determined by:

$$r_b=r_a(1-e_b) \tag{21}$$

$$e_b=1-\frac{W}{r_aV_b}=1-\frac{W}{pR_b^2H\,r_a} \tag{22}$$

3.2. Isotherms, Batch and Fixed-Bed Adsorption Studies

The q_e (mg·g^{-1}) was calculated by a mass balance relationship presented in Eq. (23).

$$q_e=\frac{(C_0-Ce)V}{W} \tag{23}$$

The adsorption isotherms of CFX with variations in the concentration of the solution at 303 K were measured and shown in Fig. 2. The experimental data were fitted with the Langmuir and Freundlich isotherm models. The Freundlich isotherm model was found to provide the best fit to the experimental data. The parameters of these models were approved by MATLAB software. The adsorption isotherm models, commonly found in the literature, and their parameters are listed in Table 2. The validity of these models was evaluated by Root Mean Square Error (RMSE), which is defined as:

$$RMSE=\sqrt{\frac{\sum_{n=1}^{n}(q_{e,\exp}-q_{e,cal})^2}{n}} \tag{24}$$

A fixed-bed column study was carried out in different conditions and the breakthrough curves were determined and show in Fig 3. Physical characteristic of fixed-bed adsorption column was calculated and are listed in Table 3.

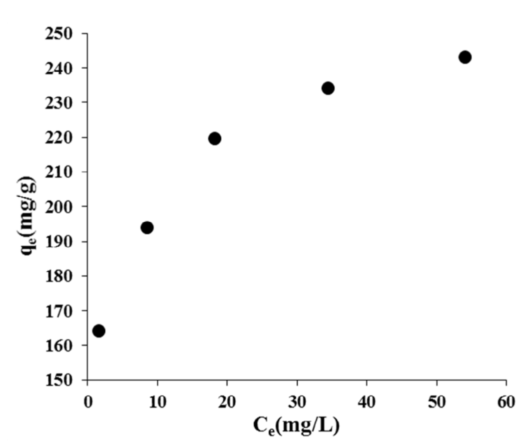

Fig. 2. Equilibrium adsorption isotherm of CFX on walnut shell AC

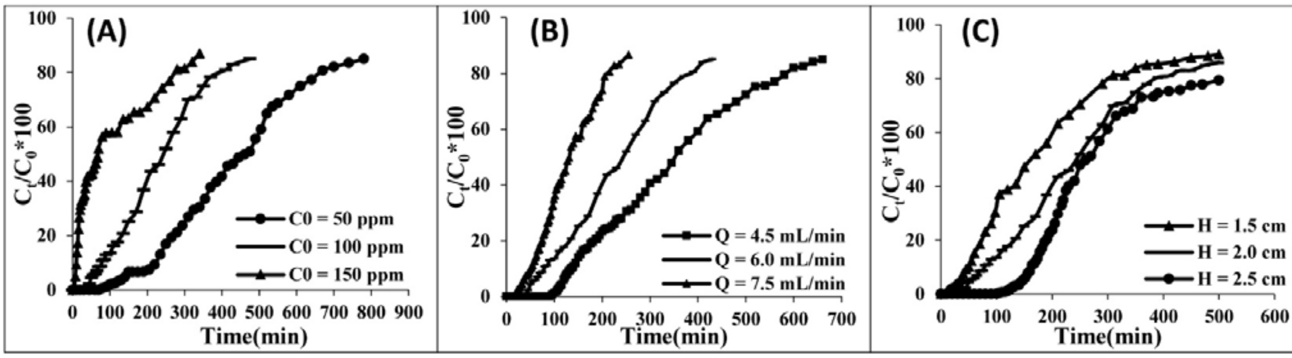

Fig. 3. Effect of different CFX initial concentration (a), feed flow rate (b) and bed height (c) on the breakthrough curves

Table 2

The parameters of Freundlich and Langmuir isotherm models

Isotherm model	Expression	Parameters	R^2	AR^2	RMSE
Langmuir model	$q_e = \frac{q_m b C_e}{1+bC_e}$	$q_m(mg/g) = 233.1$ $b(L/mg) = 1.355$	0.8328	0.8312	15.17
Freundlich model	$q_e = K_F C_e^{1/n}$	$K_F(\frac{(mg/g)}{(1/mg)^{-1/n}}) = 155.2$ $n = 8.772$	0.9913	0.9884	3.459

Table 3

Physical characteristic of fixed-bed adsorption column

H, cm	*m*,g	e_b	r_b, g/cm^3
1.5	0.75	0.3946	1.21
2.0	1.0	0.3946	1.21
2.5	1.25	0.3946	1.21

Table 4

Effect of different CFX initial concentration, feed flow rate and bed height on the volumetric mass transfer coefficient K_La

C_0, mg/l	*Q*, ml/min	*H*, cm	K_La, min^{-1}	R^2	AR^2	RSS
50	6	2	0.0467	0.843	0.812	1.412
100	6	2	0.0513	0.949	0.953	0.231
150	6	2	0.0553	0.871	0.864	1.116
100	4.5	2	0.0258	0.981	0.988	0.056
100	6	2	0.0511	0.949	0.944	0.138
100	7.5	2	0.0752	0.948	0.957	0.231
100	6	1.5	0.0383	0.989	0.993	0.035
100	6	2	0.0467	0.949	0.967	0.119
100	6	2	0.0513	0.910	0.917	0.452

3.3. Mass Transfer Coefficients

The transfer coefficient from the constant-pattern wave approach (Eq. (16)) was calculated using the Freundlich isotherm model (Eq. (17)) employing the experimental breakthrough curves as explained previously. To properly design the fix-bed adsorption process, it is frequently necessary to be able to calculate the volumetric mass transfer coefficient (K_La). A better prediction of the k_La value would help the optimization of the installations in terms of both cost and effectiveness. Various mass-transfer models are proposed for the prediction of the fixed bed dynamics [15-18], of which the mathematical model based on non-linear wave propagation theory was widely used as expressed in Eqs. (11) to (20) [19]. The results calculated from K_La (min^{-1}) are listed in Table 4. As it can be seen from Table 4, increasing in the CFX initial concentration from 50 to 150 mg/l at both constant flow rate and bed height leads to rising the K_La from 0.0467 to 0.0553, which can be due to higher driving force in the high initial concentrations. Also, at constant both initial concentration and bed height, an enhancement in the flow rate from 4.5 to 7.5 ml/min resulted in the increasing at K_La from 0.0258 to 0.0752 min^{-1} (Table 4). The reason for this behavior probably is the rise of driving force because of entrance of new feed. Finally, with increasing in the bed height from 1.5 to 2.5 cm at both constant initial concentration and flow rate, K_La increases from 0.0383 to 0.0441. This trend can be due to increasing at surface area caused by enhancement at adsorbent particles.

Table 5

The parameters of mass transfer coefficient models

Model	Expression	Constants			R^2	AR^2	RSS
		C_1	C_2	C_3			
Model (1)	$K_La = C_1 + C_2Q^{C_3}$	-0.066	0.026	0.840	1	–	$1.06\cdot10^{-25}$
Model (2)	$K_La = C_1\exp(Q^{C2})$	-1.044	0.015	–	0.9996	0.9993	$4.04\cdot10^{-7}$
Model (3)	$K_La = C_1 + C_2\exp(Q^{C_3})$	-1.095	1.051	0.014	0.9996	–	$3.92\cdot10^{-7}$

3.4. Modeling of Mass Transfer Coefficient

According to Table 3, it is observed that the K_La has been varied in special form with respect to volumetric feed flow rate. In this section, three models to achieve to relation for the prediction of K_La based on feed flow rate variations are developed. The equations are investigated for K_La as the following equations [20]:

$$\text{Model (1): } K_La = C_1 + C_2Q^n \quad (25)$$

$$\text{Model (2): } K_La = C_1\exp(Q^n) \quad (26)$$

$$\text{Model (3): } K_La = C_1 + C_2\exp(Q^n) \quad (27)$$

Eqs. (25)–(27) are analyzed and the amount of R^2, adjusted R^2 (AR^2), the residual sum of squares (RSS), and other statistical functions were determined with respect to O.L.S method by EViews software and are listed in Table 5. The results in Table 5 show that the model (1) is the best model for the prediction of K_La at different feed flow rates ($R^2 = 1$). This proves the validity of this model and reveals that it can be applied to predict the K_La in other volumetric feed rates successfully.

4. Conclusions

By studying of cephalexin adsorption onto walnut shell activated carbon the following results were achieved in this study. The prepared adsorbent showed highly efficient removal for cephalexin (CFX) from aqueous solution. The experimental data were fitted with the Freundlich and Langmuir isotherm models. The Freundlich isotherm model was found to provide the best fit to the experimental data. The effect of different bed height, feed flow rate and CFX initial concentration on the volumetric mass transfer coefficient, K_La, were also studied. The results showed that the K_La increased with enhancement at the bed height, feed flow rate and CFX initial concentration. By considering several mathematical functions, an appropriate model was developed to predict the volumetric feed effect on the K_La. One of the models was the best model with the level of significance of $R^2 = 1$, though, all the models could be well fitted to the experimental data.

Nomenclature

a, cm^{-1}	mass-transfer area per unit volume of the bed
C, mg/l	concentration in the mobile phase
H, cm	bed height
K_L, cm/min	liquid-side mass transfer coefficient
K_La, min^{-1}	volumetric mass transfer coefficient
n	experimental data
Q, ml/min	flow rate
I, mg/l	concentration in the stationary phase
q, mg/g	adsorption capacity
R, cm	radius
t, min	time
U	constant velocity
V, l	volume of the solution
W, g	dry weight of the adsorbent
X	dimensionless effluent concentration
Z, cm	column length

Greek letters

ε	bed void fraction
ρ, kg/m^3	bed density

Subscripts

0	at initial condition
1/2	half-time for X=1/2
a	apparent
b	bed
cal	calculated value
e	at equilibrium state
exp	experimental value
c	constant
*	mobile-phase in equilibrium with the stationary-phase

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ВИВЧЕННЯ КОЕФІЦІЄНТА МАСОПЕРЕДАЧІ АДСОРБЦІЇ ЦЕФАЛЕКСИНУ НА АКТИВОВАНОМУ ВУГІЛЛІ НА ОСНОВІ ГОРІХОВОЇ ШКАРАЛУПИ В КОЛОНЦІ ЗІ СТАЦІОНАРНИМ ШАРОМ

Анотація. *Досліджено адсорбцію цефалексину на активованому вугіллі на основі шкаралупи волоського горіха. З використанням теорії поширення хвиль розраховано коефіцієнти масопередачі. Встановлено вплив різних чинників на коефіцієнт переносу. Розроблено три моделі для прогнозування коефіцієнта масопередачі.*

Ключові слова: *адсорбція, цефалексин, активоване вугілля, шкаралупа волоського горіха, коефіцієнт масопередачі, моделювання.*