Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2019.24657

169 (2019) 333–341
November

Mechanism, kinetics and thermodynamic of Penicillin G antibiotic removal by silica nanoparticles from simulated hospital wastewater

Fatemehsadat Masoudi[a], Mohammad Kamranifar[b], Fatemeh Safari[c], Ali Naghizadeh[b,*]

[a]*Department of Environmental Health Engineering, Faculty of Health, Birjand University of Medical Sciences (BUMS), Birjand, Iran, email: ftmmasoudi71@yahoo.com*
[b]*Medical Toxicology and Drug abuse Research Center (MTDRC), Birjand University of Medical Sciences (BUMS), Birjand, Iran, Tel. +985632395441; Fax: +985632381665; emails: al.naghizadeh@yahoo.com (A. Naghizadeh), mo.kamrani@yahoo.com (M. Kamranifar)*
[c]*BSN, Research committee, School of Nursing and Midwifery, Shahid Behehshti University of Medical Sciences (SBMU), Tehran, Iran, email: fatemesafari94@yahoo.com*

Received 2 February 2019; Accepted 5 July 2019

ABSTRACT

Today, the unusual use of antibiotics and the entry of these compounds into the environment have caused global concern. The antibiotics even in low concentrations in the range of ng/L and μg/L can cause effects in humans and animals due to their low degradability, high solubility and cumulative properties in water. This study was performed to removal of Penicillin G by silica nanoparticles in a batch system. The effects of different parameters including pH (3–11) adsorbent dosage (0.2–2 g/L), contact time (2–120 min), initial concentration (10–100 mg/L) and temperature (283–318 K) on the adsorption of Penicillin G by silica nanoparticles were investigated. The results of this study showed that the maximum adsorption of Penicillin G by silica nanoparticles has occurred in pH = 7. By increasing the adsorbent dose, adsorption capacity has decreased. Also, with increasing Penicillin G concentration, the adsorption capacity was increased. The maximum adsorption capacity of silica nanoparticles was 211.35 mg/g (optimum conditions of pH = 7, adsorbent dose of 0.2 g/L, contact time of 60 min, Penicillin G concentration of 100 mg/L and temperature of 218 K). The results showed that the adsorption of Penicillin G by silica nanoparticles was more consistent with Langmuir model (R^2 = 0.81). Also, the results of kinetic study showed that the adsorption process followed the pseudo-second-order kinetic. The result of temperature and thermodynamics parameter showed that the values of $\Delta S°$, $\Delta H°$ and $\Delta G°$ were positive, negative and negative respectively.

Keywords: Penicillin G; Silica; Isotherm; Kinetic; Thermodynamic

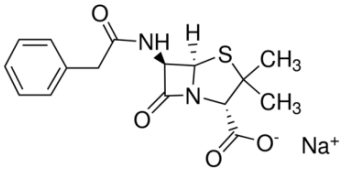
1. Introduction

Today, the unusual use of antibiotics and the entry of these compounds into the environment have caused global concern. Each year 100,000–200,000 tons antibiotics are used in the world [1,2]. One of the most important classifications of antibiotics is based on the existence of β-Lactam and non-β-Lactam. Penicillin G is classified as a β-Lactam antibiotic which is one of the most widespread and important antibiotics used in America and Europe. These antibiotic is sensitive to the temperature and acidic medium and is classified as a weak acid (pK_a = 2.75) [3–5]. Table 1 shows the physical and chemical properties and molecular structure of Penicillin G [6].

The presence of compounds and drug residues in the environment, especially water resources, is an important issue in the environment due to its stability and low degradability [7,8]. Among the sources that release antibiotics

* Corresponding author.

Table 1
Physical and chemical properties and molecular structure of Penicillin G

Properties	Values
Molecular formula	$C_{16}H_{18}N_2NaO_4S$
Molecular weight	356.4 g/mol
Other name	Benzylpenicillin
Structure	

into the environment, we can mention urban wastewater, industrial wastewater associated with the antibiotics industry such as pharmacy, animal waste and solid waste solids [9]. The wastewater of the pharmaceutical industry is also considered as one of the most important industries that import much of the drug, including antibiotics, into the environment [10]. Also, the antibiotics used by humans are only partly metabolized and 10%–90 % of them are excreted unchanged with urine and feces. Then, these remained antibiotics are discharged into the sewage systems. The wastewater treatment systems, disability to remove the high polar micro pollutants like the antibiotics cause these compounds to enter into the surface and underground water and then the water refineries. Finally, they entered into the drinking water distribution systems due to the non-removal of them in the water refineries [11,12]. Some studies have showed that most of the antibiotics are present in the environment including the surface water, underground water, soil, as well as sewage and drinking water [13]. The antibiotics in low concentrations in the ranges of ng/L and μg/L can cause effects in humans and animals due to their low degradability, high solubility and cumulative properties in water [14,15]. Antibiotics have various effects, such as drug resistance in humans, effects on non-target pathogens, altered algae in aquatic resources and interfere with photosynthesis of plants [16]. In addition, the widespread use of antibiotics has led to significant problems, including acute and chronic toxicity, effects on aquatic photosynthetic organisms, disruption of indigenous microbial populations and the release of antibiotic-resistant genes among microorganisms [17].

So far, different methods such as ozonation [18], fenton and photo-fenton [19], electrochemical method [20], nanofiltration [21], coagulation [22], ionic exchange [23] and adsorption process [24] to removal of antibiotics were used. Among these, adsorption is one of the most used methods in the removal of antibiotics. The adsorption process is very efficient, simple design and operation and relatively inexpensive. In addition, the adsorption process is widely used in the removal of organic pollutants. It should be noted that the efficiency of the adsorption process is strongly influenced by the type of adsorbent, adsorbate properties and the compositions of waste flow [25–27]. Among the adsorbents, silica nanoparticles (SiO_2) are made out of two elements silicon and oxygen and it is structurally similar to the water molecules and is one of the main soil constituents. Silica nanoparticles are very hard and stiff and hardly transformed [28]. Another important issue is when selecting nanoparticles for the removal of pollutants in the aquatic environment is their toxicity. Silica nanoparticles with very high percentage of silicon dioxide are a great candidate and have no known effects on health [29]. The silica nanoparticles have a large specific surface area and active surface which is very important in adsorption and ion exchange processes [30]. The performed studies showed that silica nanoparticles are an effective adsorbent for removing metal ions and natural pollutants [31]. The study of Luo et al. [32] to removal of humic acid by silica nanoparticles showed that materials obtained from the nature, considering their low cost, have a high adsorption potential [32]. In another studies, silica nanoparticles has presented reasonable result in the removal of nickel, cadmium and lead and the methyl red color [33,34]. Also, Li et al. [35] study on adsorption ciprofloxacin by C@silica core/shell nanoparticles showed that the maximum ciprofloxacin adsorption amount of the C@silica core/shell nanoparticles was 516.8 mg/g. In study of Aksu et al. [5] carried out to removal of Penicillin G by a bioadsorbent *Rhizopus arrhizus*, active mud and active carbon. They reported that the removal efficiency for each of these adsorbents were 78%, 61% and 57%, respectively [5].

Considering that there is not any study about Penicillin G adsorption from aqueous solutions by silica nanoparticles. In this research, silica nanoparticles was used as an adsorbent to removal of Penicillin G from aqueous solution and to evaluating the adsorption capacity of silica nanoparticles, different parameters such as pH, adsorbent dosage, initial concentration of penicillin G, contact time, isotherm kinetics and thermodynamic studies were studied.

2. Materials and methods

2.1. Materials and equipment

In this study, Penicillin G (purity 99%) purchased from Sigma Aldrich company (St. Louis, MO). Silica nanoparticles (purity 99.9% and surface area of 200 m^2/g) purchased from EVonik Company. In this study, characterization of Silica nanoparticles was investigated by scanning electron microscopy (SEM) (HITACHI, S4160, Japan) and X-ray diffraction (XRD) (GNA, Explorer, Italy). In order to determine the Penicillin G concentrations, a spectrophotometer UV-Visible (UV/VIS Spectrophotometer T80$^+$, PG Instrument) was used. The solution pH was set by pH meter HACH, HQ411d (USA) by using HCl and NaOH (1 and 0.1 N) before adding the adsorbent. To mix the solutions we used the shaker model (Multishaker, Model NB-101 MT, Korea) and to stabilize the temperature, the shaker incubator model SI-100R made in Korea was used.

2.2. Adsorption experiment

The stock solution of Penicillin G (500 mg/L) was prepared by dissolving a certain amount of Penicillin G in deionized water. Then, the effects of various parameters such as pH (3–11), adsorbent dosage (0.2–2 g/L), contact time (2–120 min), initial concentration (10–100 mg/L) and

temperature (283–318 K) on the removal of Penicillin G by silica nanoparticels were investigated.

2.2.1. Effect of pH

To determine the effect of pH on the removal of Penicillin G, the antibiotic solution of Penicillin G with concentration of 30 mg/L was used. The solution pH was set in values of 3, 5, 7, 9 and 11. Then, 0.5 g/L of silica nanoparticles was added into solutions. After that, the solutions were placed on a shaker with the mixing rate of 200 rpm for 60 min. After passing the mentioned time, the samples were filtered using the 0.45 micron filter. Finally, the concentration of Penicillin G was measured by the spectrophotometer at a wavelength of 290 nm [36].

2.2.2. Effect of adsorbent dosage

At this stage, according to the optimum pH obtained from the previous stage, solutions of Penicillin G at a concentration of 30 mg/L was made and then the effect of the adsorbent dose with 5 doses of silica nanoparticles (0.2, 0.5, 1, 1.5 and 2 g/L) on the removal of Penicillin G was studied. The contact time in this stage was 60 min.

2.2.3. Effect of initial concentration and contact time

After determining optimum pH and adsorbent dosage, the adsorption of Penicillin G by silica nanoparticles was determined for each of the initial concentrations 10–100 mg/L in contact time of 2–120 min.

The adsorption capacity of silica nanoparticles was determined by Eq. (1).

$$q_e = \frac{C_0 - C_e}{m} V \tag{1}$$

where q_e is the rate of antibiotic adsorbed from the solution per each gram of the adsorbent (mg/g), C_0 is the initial concentration of antibiotic (mg/L), C_e is the equilibrium concentration of antibiotic (m/L), V is the sample volume (L) and m is the amount of silica nanoparticles (g) [37].

2.3. Adsorption isotherms

For the study of adsorption isotherm, the compatibility of empirical adsorption equilibrium data with Langmuir, Freundlich, Brunauer–Emmett–Teller (BET), Temkin and Dubinin–Radushkevich (D–R) adsorption isotherm models were investigated according to the linear form of Eqs. (2)–(8), respectively.

Langmuir isotherm model equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{2}$$

where C_e is the equilibrium concentration of antibiotics in the solution (mg/L), q_e is the adsorption capacity of adsorbent in equilibrium state (mg/g), q_m is maximum Penicillin G adsorbed per gram of adsorbent, K_L is the equilibrium constant of Langmuir isotherm and shows the affinity of silica nanoparticles with antibiotic (L/mg) [38].

Another model used in this study is the Freundlich model. The equation of this model is shown below:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{3}$$

where q_e is the adsorption capacity of adsorbent (mg/g), C_e is the equilibrium concentration of antibiotic in the solution (mg/L), n and K_F are adsorption constants of Freundlich [38].

BET isotherm model is as follows:

$$\frac{C_e}{q_e\left(C_s - C_e\right)} = \frac{1}{q_s C_{\text{BET}}} + \frac{\left(C_{\text{BET}} - 1\right)}{q_s} \frac{C_e}{C_s} \tag{4}$$

where C_s is the saturation concentration of the solute in terms of g/L, K_b is the constant obtained from the line equation and represent the energy between adsorbate and adsorbent and has a direct relation with the adsorption energy. $Q_{\max}$ is the value of adsorbed material in the adsorbent mass unit (mg/g) [39].

The Temkin isotherm model is another model that can be presented as follows:

$$q_e = \frac{RT}{b_t} \ln A_T + \left(\frac{RT}{b_t}\right) \ln C_e \tag{5}$$

where B is the heat of sorption (J/mol), R is universal gas constant R = 8.31 J/K mol and T is the absolute temperature in terms of Kelvin. In this relation A_T in terms of L/mg is the linkage constant related to the maximum linkage energy, b_T in terms of J/mol is Temkin constant proportional to the surface of adsorption temperature [40].

The D–R isotherm model is as follows:

$$\ln q_e = \ln q_m - K_{\text{ad}} \varepsilon^2 \tag{6}$$

$$\varepsilon = RT \ln\left(1 + \left(\frac{1}{C_e}\right)\right) \tag{7}$$

where ε is the Polanyi potential, T is the solution temperature and R is the universal gas constant, q_e is the valve of dissolved material solution the adsorbent mass unit and q_m is the adsorption capacity of the single layer. β (mol²/kj²) is a constant related to the average adsorption energy. The average adsorption free energy E in terms of kJ/mol is calculated as follows [41].

$$E = \frac{1}{\sqrt{-2B}} \tag{8}$$

2.4. Adsorption kinetics

To the study of adsorption kinetics, the pseudo-first-order and pseudo-second-order models were investigated Eqs. 9 and 10.

$$\frac{dq_t}{dt} = K_1\left(q_e - q_t\right) \tag{9}$$

$$\frac{dq_t}{dt} = K_2\left(q_e - q_t\right)^2 \tag{10}$$

where q_t is the value of antibiotic adsorbed on the adsorbent surface in time t (mg/g), q_e is the value of antibiotic adsorbed in equilibrium state (mg/g), t is the time (min), K_1 is the constant of pseudo-first-order equation (1/min) and K_2 is the constant of pseudo-second-order equation (g/mg min) [42,43].

2.5. Adsorption thermodynamics

To determine the temperature effect and thermodynamic of adsorption process on the removal of Penicillin G by silica nanoparticles, experiment was done at 283, 298, 308 and 318 K. The adsorption thermodynamics are obtained by the following Eqs. (11)–(13):

$$\Delta G^\circ = -RT\ln k_c \tag{11}$$

where ΔG° is indicative of Gibbs free energy in terms of kJ/mol, R is the universal gas constant (8.314 J/mol k) and T represents the absolute temperature based on Kelvin.

The enthalpy parameters (ΔH°) and the entropy (ΔS°) in the adsorption process were calculated by the following equations:

$$\ln k_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{12}$$

$$k_c = \frac{q_e}{C_e} \tag{13}$$

where k_c (L/g) is the ratio of antibiotic value adsorbed on silica nanoparticles (mg/g) to the value remained in the solution (mg/L). The resultant line slope represents the value of ΔH° in terms of kJ/mol and the ordinate indicates the parameter ΔS° in terms of (J/mol k) [44].

3. Results and discussion

3.1. Characterization of Silica nanoparticles

The adsorbent surface morphology was identified by a SEM. As shown in the below figure, the size of the nanoparticles is below 100 nm (Fig. 1). The silica nanoparticles showed a spherical shape with individual distribution in homogeneous shape [45]. The SEM images showed that the maximum and minimum nanoparticles size was approximately between 53 and 31 nm, respectively. Also, in order to determine the crystalline structure of nanoparticles as well as operational groups existed in their structures used was XRD analyzes (Fig. 2). Considering the study of XRD pattern, the sharp peak ($2q$ = 22) in the X-ray pattern of the silica nanoparticles shows the nature of the nanoparticles and silica nanoparticles crystalline phase are glass (amorphous) [46].

3.2. Effect of pH

To determine the optimum pH, the effect of Penicillin G solution pH in the range of 3–11 was investigated.

Fig. 1. SEM image of silica nanoparticles.

Considering Fig. 3, the optimum pH for removal of Penicillin G by silica nanoparticles is 7 with adsorption capacity of 28.4 mg/g. As a result, the maximum adsorption capacity has occurred in neutral conditions.

In the adsorption process OH^- and H^+ are the two ions responsible for and determinant of the surface charge. With regard to pKa, the charge of Penicillin G is positive in pH_S below 2.7 and negative in pH_S above 2.7 [47]. Also, in $pH_S \leq 3$ the silica surface has positive charge but in pH_S higher than 3, due to the separation of silica adsorbent from H^+ and OH^-, the surface charge increases and in fact, it obtains desorption property. In other words the surface charge of silica in pH_S above 3 is negative due to Si–O– production [31,48]. Therefore, Penicillin G anions do not interact electrostatically with the negative surfaces of silica nanoparticles. They are probably adsorbed by physical or chemical forces. Reducing the adsorption capacity of Penicillin G on silica nanoparticles at higher pH may be attributed to changes in charge and surface characteristics. Accordingly, the adsorption mechanism at different pHs is difficult due to the large number of variables involved in the Penicillin G adsorption and the complexity of chemistry in the adsorption and water [5]. In this connection, similar results were found by Aksu et al. [5] by using bioadsorbent *Rhizopus arrhizus*, activated sludge and activated carbon in the removal of Penicillin G [5].

3.3. Effect of adsorbent dosage

In this stage, to determine the optimum adsorbent dosage different values of adsorbent (0.2, 0.5, 1, 1.5 and 2 g/L) in the optimum pH and contact time of 60 min were used. The results in Fig. 4 show the effect of different adsorbent doses on Penicillin G removal by silica nanoparticles. Considering the figure, the maximum adsorption capacity of silica nanoparticles is 0.2 g/L with the adsorption capacity rate of 43 mg/g. Also, the results showed that increasing the adsorbent dose value decreases the adsorption capacity of silica nanoparticles.

The results from Fig. 4 showed that in the process of Penicillin G removal by silica nanoparticles, increasing the adsorbent dosage decreases the adsorption capacity of the adsorbent. By increasing the adsorbent dosage, the capacity

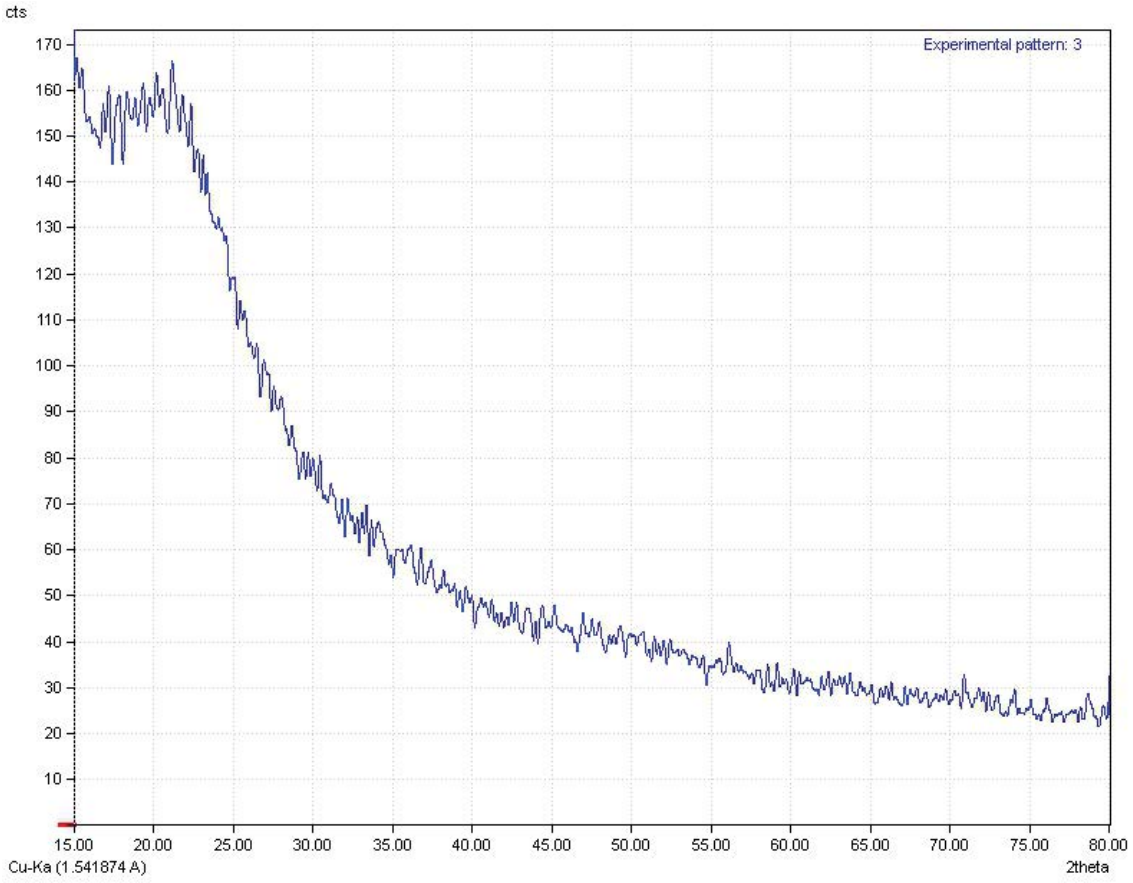


Fig. 2. XRD spectrum of silica nanoparticles.

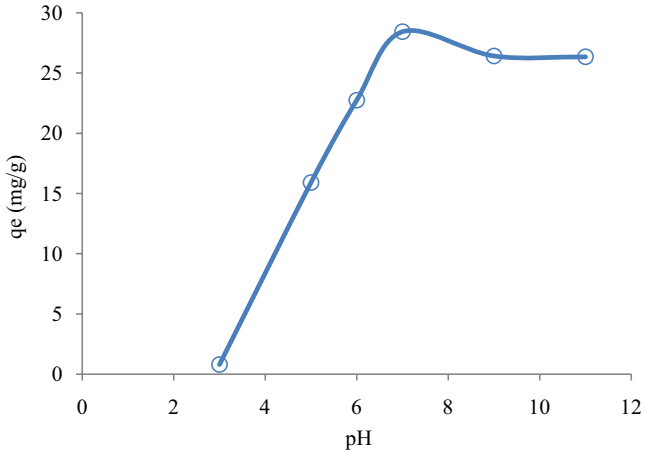


Fig. 3. Effect of pH on the adsorption of Penicillin G by silica nanoparticles (Penicillin G concentration: 30 mg/L, adsorbent dosage: 0.5 g/L, contact time: 60 min).

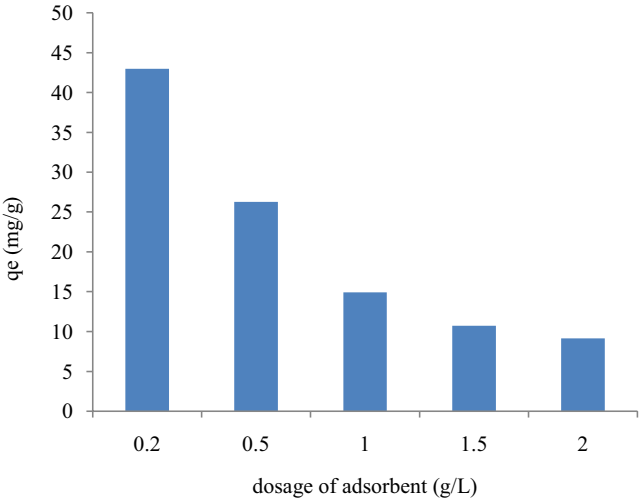


Fig. 4. Effect of adsorbent dosage on the adsorption of Penicillin G by silica nanoparticles (pH: 7, Penicillin G concentration: 30 mg/L, contact time: 60 min).

of the total active sites in the adsorbent surface has not been used entirely. Therefore, the adsorption capacity decreases [49]. In other words, by increasing the amount of adsorbent, some of the adsorbent active sites remain non-saturated, which leads to a lack of utilization of total adsorbent capacity and hence the adsorption of Penicillin per unit mass decreases [50]. The results of this study are completely consistent with the research performed on that removal of amoxicillin by carbon nanotubes. In this study the adsorption capacity was reduced by the adsorbent dose, which could

be due to the lack of saturation of active sites by increasing adsorbent dosage [51].

3.4. Effect of initial concentration and contact time

Fig. 5 shows the results from the effect of different concentrations of Penicillin G solutions and different contact times on removal of Penicillin G by Silica nanoparticles. The adsorption process was performed in contact time of 10–120 min. The results showed that adsorption of Penicillin G by silica nanoparticles has been done rapidly up to the contact time of 60 min and after that up to the contact time of 120 min the variance trend has been almost unchanged. Also, the result showed that by increasing the antibiotic concentration from 10 to 100 mg/L, the adsorption capacity has been increased. The adsorption capacity in contact time of 60 min for concentration of 10, 30, 50, 70 and 100 mg/L were 37.58, 69.96, 109.76, 191.17 and 270.73 mg/g respectively.

The results showed that by increasing the contact time to 60 min the Penicillin G adsorption by silica nanoparticles increased and then the adsorption rate was approximately constant. It can be due to the decrease in Penicillin G concentration and also to decrease active sites in the adsorbent surface and reduces the transfer of penicillin molecules to surface of silica nanoparticles [5,52]. The long range diffusion effect of Penicillin G diffusing slowly into the intra-particle pores of the silica nanoparticles can be another reason for reduction of adsorption capacity [53]. Also, the results showed that by increasing the concentration of Penicillin G, the adsorption capacity was increased. Increasing penicillin G concentration will increase the diffusion of Penicillin G molecules from the silica nanoparticles surface into the micropores [54]. Also another reason for increasing of adsorption capacity is due to the increased likelihood of contact between the silica nanoparticles and Penicillin G [55]. Bajpai et al. [54] in their study by using sawdust as an adsorbent for removing antibiotic ciprofloxacin found that the greatest amount of ciprofloxacin is adsorbed during the first 5 min and after that the process is slow and at last in 40 to 60 min equilibrium is obtained.

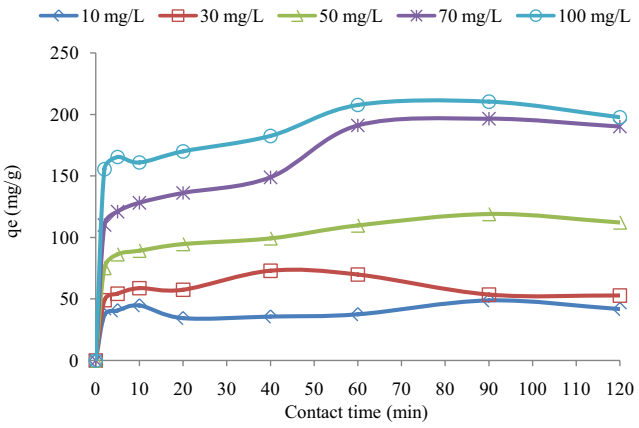


Fig. 5. Effect of contact time and Penicillin G concentration on the adsorption of Penicillin G by silica nanoparticles (pH: 7, Adsorbent dosage: 0.2 g/L).

Increasing the initial concentration of antibiotic from 10 to 20 mg/L increased the adsorption capacity from 3.74 to 11.32 mg/g.

3.5. Adsorption isotherms

The result of adsorption isotherms are shown in Table 2. Considering the result of the table and also regression coefficient of different isotherms, the adsorption process is more consistent with Langmuir isotherms ($R^2 = 0.81$). In Langmuir isotherm, adsorption occurs in special and homogeneous sites within the adsorbent [5]. One of the important parameters that approves Langmuir isotherm and should be determined in adsorption equations for appropriateness or inappropriateness of adsorption is dimensionless coefficient R_L obtained from Langmuir curve. If R_L is more than 1, it is indicative of the adsorption inappropriateness. If R_L equals to 1, it is indicative of linear adsorption and if R_L equals to zero, it is indicative of irreversible adsorption. If R_L is between 0 and 1, it is indicative of an appropriate adsorption [56,57]. In adsorption of Penicillin G by silica nanoparticles R_L was equal to 0.04 which approves the accuracy of Langmuir isotherm.

3.6. Adsorption kinetic

The result of kinetics study of Penicillin G adsorption process by silica nanoparticles are shown in Table 3 and Figs. 6 and 7. The adsorption kinetic is used to determine

Table 2
Results of isotherms calculations for Penicillin G adsorption by silica nanoparticles

Isotherms	Constants	Values
Langmuir	q_{max} (mg/g)	138.65
	K_L (L/mg)	0.23
	R_L	0.04
	R^2	0.81
Freundlich	k_f(mg/g)	28.55
	$1/n$	0.45
	n	2.22
	R^2	0.79
BET	$1/A.X_m$	0.00
	$(A–1)/(A.X_m)$	0.02
	A	1.00
	X_m	50.94
	R^2	0.32
Temkin	A_T, L/mg	0.97
	b_T	57.06
	B	43.42
	R^2	0.63
Dubinin–Radushkevich	β, mol²/kJ²	0.00
	E, kJ/mole	0.70
	q_m, mg/g	133.45
	R^2	0.59

Table 3
Results of kinetic calculations for Penicillin G adsorption by silica nanoparticles

	Pseudo-first-order			Pseudo-second-order			
C_0 (mg/L)	K_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	K_2 (g/mg min)	$q_{e,cal}$ (mg/g)	R^2	$q_{e,exp}$ (mg/g)
10.20	0.003	6.85	0.01	0.006	43.92	0.98	49.9
31.82	0.009	11.23	0.04	0.003	53.66	0.98	74.0
54.73	0.008	38.56	0.15	0.003	116.77	1.00	120.1
68.56	0.009	89.17	0.22	0.001	200.83	0.99	197.6
98.85	0.015	49.58	0.13	0.002	206.02	1.00	211.4

Table 4
Thermodynamics parameters for Penicillin G adsorption by silica nanoparticles

		Thermodynamic parameters		
T (K)	q_e (mg/g)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
283	211.35	–3.03	–1.68	4.78
298	207.75	–3.11		
308	204.15	–3.14		
318	181.65	–2.74		

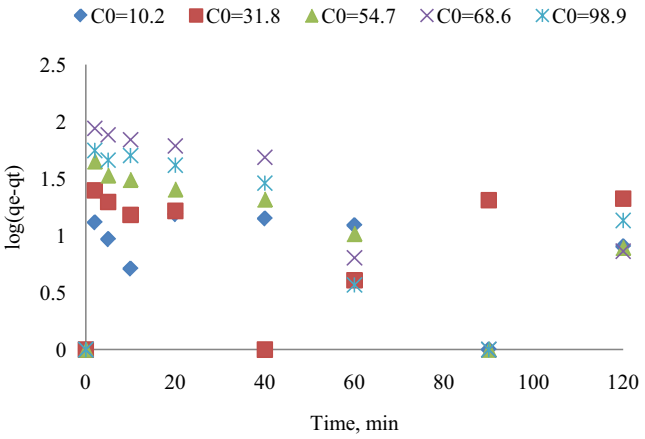


Fig. 6. Pseudo-first-order kinetic model for adsorption of the Penicillin G by silica nanoparticles.

the control mechanism of the surface adsorption processes like adsorption on the surface, chemical reactions and or influence mechanisms. Indeed, kinetic equations are used to explain the transfer behavior of the adsorbate molecules in time unit and or to investigate the variables effective in the reaction rate [58]. The results from Table 3 show that the regression coefficient for Penicillin G in pseudo-second-order kinetic is higher than the regression coefficient of pseudo-first-order kinetic and as a result, the behavior of Penicillin G adsorption by silica nanoparticles has followed the pseudo-second-order kinetic so that the regression coefficient values in all concentrations of Penicillin G in pseudo-second-order equation are higher. Aksu et al. [5] in their study about Penicillin G adsorption on the bioadsorbent *Rhizopus arrhizus* reported that the adsorption process

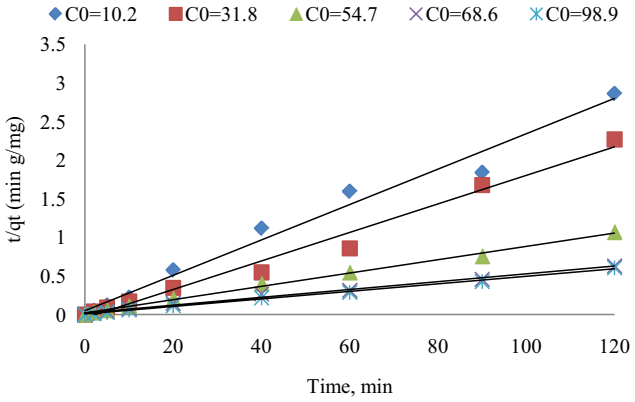


Fig. 7. Pseudo-second-order kinetic model for adsorption of the Penicillin G by silica nanoparticles.

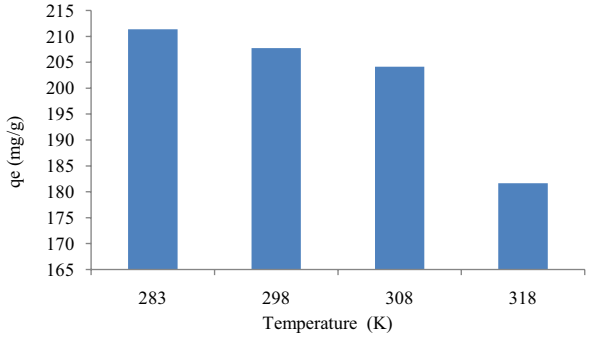


Fig. 8. Effect of temperature on adsorption of Penicillin G by silica nanoparticles (pH: 7, Penicillin G concentration: 100 mg/L, adsorbent dosage: 0.2 g/L, contact time: 60 min).

followed the second-order kinetic [5]. Also, in Table 3 it is found that calculation adsorption capacity ($q_{e,cal}$) resulted from the pseudo-second-order kinetic model is nearer to the empirical capacity resulted from the empirical experiments compared to the pseudo-first-order kinetic model ($q_{e,cal}$) and, as a result, the dominant mechanism in Penicillin G adsorption process on silica nanoparticles is a chemical adsorption [59].

3.7. Effect of temperature and thermodynamic study

In fig. 8, the effect of temperature on adsorption of Penicillin G by silica nanoparticles was showed. In thermodynamic

studies of the adsorption process, considering Table 4, the values of ΔH and ΔS were –2.18 kJ/mol and 3.14 J/mol, respectively. The negative value obtained for ΔH indicates that the Penicillin G adsorption process by silica nanoparticles is exothermic and increasing the temperature decreases the adsorption rate. The positive value of ΔS indicates that with increasing the temperature in the common gas and liquid phase during the adsorption process, the entropy increases. The negative value of ΔG indicates that the removal of Penicillin G by silica nanoparticles is spontaneous. Homem et al. [60] in their study on removal of amoxicillin on nut-shell ash reported that the values of ΔH and ΔS were negative and positive, respectively and also the value of ΔG was negative [60].

3.8. Comparison of silica nanoparticles with other adsorbent

The results of Table 5 show the comparison between maximum adsorption capacities of silica nanoparticles used in this study with other adsorbents.

4. Conclusion

Penicillin G adsorption by silica nanoparticles was occurred in pH = 7. By increasing the adsorbent dose, the value of adsorption capacity was decreased. Also, with increasing Penicillin G concentration the adsorption capacity decreased and in contact time of 60 min the adsorption process achieved the equilibrium state. The equilibrium data obtained are more consistent with Langmuir isotherm model. Also, Penicillin G adsorption kinetic by silica nanoparticles from the pseudo-second-order kinetic model was better than the pseudo-first-order kinetic model. The results from the thermodynamic studies and the effect of temperature on the adsorption process showed that the reaction was exothermic and spontaneous.

Acknowledgment

This study was carried out in the form of a research project coded 4576 approved by Birjand University of Medical Sciences (BUMS), Iran. We are grateful to the never-ending support of this university for financial support of this research.

References

[1] J.L. Martinez, Environmental pollution by antibiotics and by antibiotic resistance determinants, Environ. Pollut., 157 (2009) 2893–2902.
[2] M. Hoseini, Gh.H. Safari, H. Kamani, J. Jaafari, A.H. Mahvi, Survey on removal of tetracycline antibiotic from aqueous solutions by nano-sonochemical process and evaluation of the influencing parameters, Iran. J. Health Environ., 8 (2015) 141–152.
[3] J.W. Peterson, L.J. Petrasky, M.D. Seymour, R.S. Burkhart, A.B. Schuiling, Adsorption and breakdown of penicillin antibiotic in the presence of titanium oxide nanoparticles in water, Chemosphere, 87 (2012) 911–917.
[4] P.Y. Bi, H.R. Dong, Q.Z. Guo, Separation and purification of Penicillin G from fermentation broth by solvent sublation, Sep. Purif. Technol., 65 (2009) 228–231.
[5] Z. Aksu, Ö. Tunç, Application of biosorption for penicillin G removal: comparison with activated carbon, Process Biochem., 40 (2005) 831–847.
[6] C.O. Ania, J.G. Pelayo, T.J. Bandosz, Reactive adsorption of penicillin on activated carbons, Adsorption, 17 (2011) 421–429.
[7] C. Gagnon, A. Lajeunesse, P. Cejka, F. Gagné, R. Hausler, Degradation of selected acidic and neutral pharmaceutical products in a primary-treated wastewater by disinfection processes, Ozone Sci. Eng., 30 (2008) 387–392.
[8] A. Dirany, I. Sirés, N. Oturan, M.A. Oturan, Electrochemical abatement of the antibiotic sulfamethoxazole from water, Chemosphere, 81 (2010) 594–602.
[9] T.M. LaPara, T.R. Burch, P.J. McNamara, D.T. Tan, M. Yan, J.J. Eichmiller, Tertiary-treated municipal wastewater is a significant point source of antibiotic resistance genes into Duluth-Superior Harbor, Environ. Sci. Technol., 45 (2011) 9543–9549.
[10] E.S. Elmolla, M. Chaudhuri, Degradation of the antibiotics amoxicillin, ampicillin and cloxacillin in aqueous solution by the photo-Fenton process, J. Hazard. Mater., 172 (2009) 1476–1481.
[11] W.-h. Xu, G. Zhang, S.-c. Zou, X.-d. Li, Y.-c. Liu, Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high-performance liquid chromatography-electrospray ionization tandem mass spectrometry, Environ. Pollut., 145 (2007) 672–679.
[12] S. Mompelat, B. Le Bot, O. Thomas, Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water, Environ. Int., 35 (2009) 803–814.
[13] E.S. Elmolla, M. Chaudhuri, The feasibility of using combined TiO_2 photocatalysis-SBR process for antibiotic wastewater treatment, Desalination, 272 (2011) 218–224.
[14] J. Jeong, W. Song, W.J. Cooper, J. Jung, J. Greaves, Degradation of tetracycline antibiotics: mechanisms and kinetic studies for advanced oxidation/reduction processes, Chemosphere, 78 (2010) 533–540.
[15] R. Mostafaloo, A.R. Yari, M.J. Mohammadi, Y.O. Khaniabadi, M. Asadi-Ghalhari, Optimization of the electrocoagulation process on the effectiveness of removal of Cefixime antibiotic from aqueous solutions, Desal. Wat. Treat, 144 (2019) 138–144.
[16] R. Wei, F. Ge, S. Huang, M. Chen, R. Wang, Occurrence of veterinary antibiotics in animal wastewater and surface water around farms in Jiangsu Province, China, Chemosphere, 82 (2011) 1408–1414.
[17] Y. Gao, Y. Li, L. Zhang, H. Huang, J. Hu, S.M. Shah, X. Su, Adsorption and removal of tetracycline antibiotics from aqueous solution by graphene oxide, J. Colloid Interface Sci., 368 (2012) 540–546.
[18] S. Carabineiro, T. Thavorn-Amornsri, M. Pereira, J. Figueiredo, Adsorption of ciprofloxacin on surface-modified carbon materials, Water Res., 45 (2011) 4583–4591.
[19] A.Y.-C. Lin, C.-F. Lin, J.-M. Chiou, P.A. Hong, O_3 and O_3/H_2O_2 treatment of sulfonamide and macrolide antibiotics in wastewater, J. Hazard. Mater., 171 (2009) 452–458.
[20] O. Rozas, D. Contreras, M.A. Mondaca, M. Pérez-Moya, H.D. Mansilla, Experimental design of Fenton and photo-Fenton reactions for the treatment of ampicillin solutions, J. Hazard. Mater., 177 (2010) 1025–1030.
[21] I. Koyuncu, O.A. Arikan, M.R. Wiesner, C. Rice, Removal of hormones and antibiotics by nanofiltration membranes, J. Membr. Sci., 309 (2008) 94–101.
[22] K.-J. Choi, S.-G. Kim, S.-H. Kim, Removal of antibiotics by coagulation and granular activated carbon filtration, J. Hazard. Mater., 151 (2008) 38–43.
[23] K.-J. Choi, H.-J. Son, S.-H. Kim, Ionic treatment for removal of sulfonamide and tetracycline classes of antibiotic, Sci. Total Environ., 387 (2007) 247–256.
[24] R. Crisafully, M.A.L. Milhome, R.M. Cavalcante, E.R. Silveira, D. De Keukeleire, R.F. Nascimento, Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin, Bioresour. Technol., 99 (2008) 4515–4519.
[25] M.B. Ahmed, J.L. Zhou, H.H. Ngo, W. Guo, Adsorptive removal of antibiotics from water and wastewater: progress and challenges, Sci. Total Environ., 532 (2015) 112–126.
[26] Z. Bozorgpanah Kharat, M. Mohammadi Galangash, A. Ghavidast, M. Shirzad-Siboni, Removal of reactive black 5 dye from aqueous solutions by Fe_3O_4@SiO_2-APTES nanoparticles, Caspian J. Environ. Sci., 16 (2018) 287–301.

[27] M. Mohammadi Galangash, M. Mohaghegh Montazeri, A. Ghavidast, M. Shirzad-Siboni, Synthesis of carboxyl-functionalized magnetic nanoparticles for adsorption of malachite green from water: kinetics and thermodynamics studies, J. Chin. Chem. Soc.-TAIP, 65 (2018) 940–950.
[28] J. Zhai, X. Tao, Y. Pu, X.-F. Zeng, J.-F. Chen, Core/shell structured ZnO/SiO_2 nanoparticles: preparation, characterization and photocatalytic property, Appl. Surf. Sci., 257 (2010) 393–397.
[29] S. Syed, M. Alhazzaa, M. Asif, Treatment of oily water using hydrophobic nano-silica, Chem. Eng. J., 167 (2011) 99–103.
[30] P.K. Jal, S. Patel, B.K. Mishra, Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions, Talanta, 62 (2004) 1005–1028.
[31] J. Lu, Y. Li, X. Yan, B. Shi, D. Wang, H. Tang, Sorption of atrazine onto humic acids (HAs) coated nanoparticles, Colloids Surf., A, 347 (2009) 90–96.
[32] D. Luo, Q.-W. Yu, H.-R. Yin, Y.-Q. Feng, Humic acid-bonded silica as a novel sorbent for solid-phase extraction of benzo [a] pyrene in edible oils, Anal. Chim. Acta, 588 (2007) 261–267.
[33] A. Heidari, H. Younesi, Z. Mehraban, Removal of Ni(II), Cd(II), and Pb(II) from a ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica, Chem. Eng. J., 153 (2009) 70–79.
[34] Y. Badr, M.A. El-Wahed, M. Mahmoud, Photocatalytic degradation of methyl red dye by silica nanoparticles, J. Hazard. Mater., 154 (2008) 245–253.
[35] Y. Li, C. Zeng, C. Wang, L. Zhang, Preparation of C@ silica core/shell nanoparticles from ZIF-8 for efficient ciprofloxacin adsorption, Chem. Eng. J., 343 (2018) 645–653.
[36] H. Pouretedal, N. Sadegh, Effective removal of amoxicillin, cephalexin, tetracycline and penicillin G from aqueous solutions using activated carbon nanoparticles prepared from vine wood, J. Water Process Eng., 1 (2014) 64–73.
[37] L. Rafati, M. Ehrampoush, A. Rafati, M. Mokhtari, A. Mahvi, Removal of ibuprofen from aqueous solution by functionalized strong nano-clay composite adsorbent: kinetic and equilibrium isotherm studies, Int. J. Environ. Sci. Technol., 15 (2018) 513–524.
[38] S. Agarwal, I. Tyagi, V.K. Gupta, M.H. Dehghani, J. Jaafari, D. Balarak, M. Asif, Rapid removal of noxious nickel(II) using novel γ-alumina nanoparticles and multiwalled carbon nanotubes: kinetic and isotherm studies, J. Mol. Liq., 224 (2016) 618–623.
[39] S. Yusan, Preparation and characterization of magnetic graphene oxide nanocomposite (GO-Fe_3O_4) for removal of strontium and cesium from aqueous solutions, Compos. Mater. Res., 6 (2018) 1–16.
[40] M. Özacar, İ.A. Şengil, Adsorption of metal complex dyes from aqueous solutions by pine sawdust, Bioresour. Technol., 96 (2005) 791–795.
[41] A. Şeker, T. Shahwan, A.E. Eroğlu, S. Yılmaz, Z. Demirel, M.C. Dalay, Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II), cadmium(II) and nickel(II) ions on *Spirulina platensis*, J. Hazard. Mater., 154 (2008) 973–980.
[42] A. Bashammakh, The retention profile of phosphate ions in aqueous media onto ion pairing immobilized polyurethane foam: kinetics, sorption and chromatographic separation, J. Mol. Liq., 220 (2016) 426–431.
[43] A. Bhattacharya, T. Naiya, S. Mandal, S. Das, Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents, Chem. Eng. J., 137 (2008) 529–541.
[44] H.K. Boparai, M. Joseph, D.M. O'Carroll, Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles, J. Hazard. Mater., 186 (2011) 458–465.
[45] M.E. Mahmoud, A.A. Yakout, H. Abdel-Aal, M.M. Osman, Enhanced biosorptive removal of cadmium from aqueous solutions by silicon dioxide nano-powder, heat inactivated and immobilized *Aspergillus ustus*, Desalination, 279 (2011) 291–297.
[46] G. Nallathambi, T. Ramachandran, V. Rajendran, R. Palanivelu, Effect of silica nanoparticles and BTCA on physical properties of cotton fabrics, Mat. Res., 14 (2011) 552–559.
[47] M.M. Hossain, J. Dean, Extraction of penicillin G from aqueous solutions: analysis of reaction equilibrium and mass transfer, Sep. Purif. Technol., 62 (2008) 437–443.
[48] T. Moriguchi, K. Yano, M. Tahara, K. Yaguchi, Metal-modified silica adsorbents for removal of humic substances in water, J. Colloid Interface Sci., 283 (2005) 300–310.
[49] L. Zhang, X. Song, X. Liu, L. Yang, F. Pan, J. Lv, Studies on the removal of tetracycline by multi-walled carbon nanotubes, Chem. Eng. J., 178 (2011) 26–33.
[50] K.V. Kumar, K. Porkodi, Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum notatum*, J. Hazard. Mater., 146 (2007) 214–226.
[51] D. Balarak, Y. Mahdavi, A. Maleki, H. Daraei, S. Sadeghi, Studies on the removal of amoxicillin by single walled carbon nanotubes, Br. J. Pharmacol. Res., 10 (2016) 1.
[52] W. Adriano, V. Veredas, C. Santana, L.B. Gonçalves, Adsorption of amoxicillin on chitosan beads: kinetics, equilibrium and validation of finite bath models, Biochem. Eng. J., 27 (2005) 132–137.
[53] S. Wu, X. Zhao, Y. Li, C. Zhao, Q. Du, J. Sun, Y. Wang, X. Peng, Y. Xia, Z. Wang, Adsorption of ciprofloxacin onto biocomposite fibers of graphene oxide/calcium alginate, Chem. Eng. J., 230 (2013) 389–395.
[54] S.K. Bajpai, M. Bajpai, N. Rai, Sorptive removal of ciprofloxacin hydrochloride from simulated wastewater using sawdust: kinetic study and effect of pH, Water SA, 38 (2012) 673–682.
[55] W. Yang, Y. Lu, F. Zheng, X. Xue, N. Li, D. Liu, Adsorption behavior and mechanisms of norfloxacin onto porous resins and carbon nanotube, Chem. Eng. J., 179 (2012) 112–118.
[56] J. Su, H.-f. Lin, Q.-P. Wang, Z.-M. Xie, Z.-l. Chen, Adsorption of phenol from aqueous solutions by organomontmorillonite, Desalination, 269 (2011) 163–169.
[57] Y. Ho, J. Porter, G. McKay, Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, Water Air Soil Pollut., 141 (2002) 1–33.
[58] D. Kavitha, C. Namasivayam, Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, Bioresour. Technol., 98 (2007) 14–21.
[59] S. Budyanto, S. Soedjono, W. Irawaty, N. Indraswati, Studies of adsorption equilibria and kinetics of amoxicillin from simulated wastewater using activated carbon and natural bentonite, J. Environ. Prot. Sci., 2 (2008) 72–80.
[60] V. Homem, A. Alves, L. Santos, Amoxicillin removal from aqueous matrices by sorption with almond shell ashes, Int. J. Environ. Anal. Chem., 90 (2010) 1063–1084.
[61] M.J. Ahmed, Adsorption of quinolone, tetracycline, and penicillin antibiotics from aqueous solution using activated carbons, Environ. Toxicol. Pharmacol., 50 (2017) 1–10.
[62] D. Balarak, F.K. Mostafapour, A. Joghataei, Experimental and kinetic studies on penicillin G adsorption by *Lemna minor*, J. Pharm. Res. Int., 9 (2016) 1–10.