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Investigation of single-walled carbon nanotubes in removal of Penicillin G (Benzyl penicillin sodium) from aqueous environments

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ABSTRACT

The continuous entrance of antibiotics into the environment has caused various potential problems, including increased resistance in microorganisms. The current study was conducted to investigate the usage of single-walled carbon nanotubes for the removal of Penicillin G from aqueous environments. The efficiency of single-walled carbon nanotubes in the removal of Penicillin G was examined in terms of the effect of influential parameters in the adsorption process, including pH (3–9), adsorbent dose (0.05–0.9 g/L), initial concentration of penicillin G (20–150 mg/L), and contact time (10–180 min). Isotherm models and adsorption kinetics were also studied. The optimal conditions were examined and applied to a drinking water sample from Kerman City. The maximum removal efficiency rates of Penicillin G were 96.2% for the synthetic sample and 90.6% for the drinking water sample under the optimal conditions of pH = 3, adsorbent dose = 0.7 g/L, and contact time = 30 min. The adsorption of Penicillin G by the single-walled nanotubes followed the Langmuir isotherm (R^2 = 0.99). Kinetic studies indicated a greater correlation with pseudo-second-order kinetics with a correlation coefficient of R^2 = 0.99. The application of single-walled carbon nanotubes can be valuable as a very effective adsorbent with a relatively high efficiency of 90.6% in the removal of Penicillin G from aqueous environments.

Keywords: Removal; Penicillin G; Single-walled carbon nanotubes; Isotherm; Kinetics

1. Introduction

The consumption of antibiotic drugs increased by 36% between 2000 and 2010. The group of penicillins and cephalosporins accounted for 55% of the total consumption in 2010 [1]. Drug compounds have been observed in surface waters and the effluent of wastewater treatment facilities [2,3]. Due to their stability in the environment as well as high consumption and diversity, these compounds are among the most important water contaminants [4,5]. Many antibiotics are not well digested or adsorbed by organisms. Around 25–75% of them are excreted As a precursor through urine and stool in vitro [6]. The remnants of antibiotics in wastewater treatment facilities are not fully removed by biological treatments. These materials are discharged into receiving waters or soil, causing the resistance of microorganisms to increase [7–9]. As they find their way into surface and ground waters and eventually into water treatment plants, and since they are not completely removed in these plants, these materials enter drinking water distribution systems. Thus, the development of treatment technologies for the removal of this contaminant is essential [10–12].

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Penicillin G, with the chemical formula of $C_{16}H_{17}N_2NaO_4S$, is one of the antibiotics with a beta-lactam ring produced out of penicillium fungus. It is one of the first produced antibiotics to be highly effective against staphylococci and streptococci infections. The mechanism of action of this penicillin is to prevent the formation of peptidoglycan in the cellular wall, eventually causing the destruction of bacterial cells [13–15].

In comparison with other methods for the removal of contaminants from aqueous environments, the adsorption process is simpler, more practical, and less expensive in terms of operational costs [16]. Among adsorbents, active carbon is most efficient. However, due to high operational costs and its recovery, its use as an adsorbent is not economical. Single-walled carbon nanotubes are graphite sheets which have gained a great deal of attention as an alternative for the removal of contaminants because of their cylindrical shape and the number of layers in their structure categorized as single-walled and multi-walled [17]. High specific surface area, high permeability, suitable mechanical and thermal stability, reusability, large surface area, small size, hollowness, layered structure, high adsorption capacity, and simple modification are the advantages of single-walled carbon nanotubes [18,19].

Aksu in 2005 in Turkey used *Rhizopus Arhiusbio* adsorbent, active sludge, and active carbon to remove Penicillin G from aqueous environments [7]. Arsalan in 2004 in Turkey used photo-Fenton-like oxidation for the degradation of Procaine Penicillin G formulation effluent [20]. Sheikh Mohammadi and Sardar in 2013 in Iran utilized oak acorn peel modified with sulfuric acid for the removal of Penicillin G from aqueous environments [21]. Malakootian et al. in Iran investigated various methods, including the use of zeolite modified with surfactant, pumice modified with magnesium chloride, and *Azollafiliculoides* (Salvinia) plant, TiO_2-doped Fe^{3+},TiO_2-X photo catalystto remove pharmaceutical compounds from aqueous environments [3,5,22–25]. Ji et al. in 2010 in China used single-walled and multi-walled carbon nanotubes for the adsorption of tetracycline in aqueous solutions [26]. Kim et al. in 2014 in the Republic of Korea used single-walled and multi-walled carbon nanotubes for the adsorption of antibiotics and iopromide [27]. Li in 2014 in China used carbon nanotubes for the adsorption of the antibiotic ciprofloxacin [28]. Balarak et al. in 2016 in Iran used single-walled carbon nanotubes for the removal of amoxicillin [29].

The aim of the current study was to investigate single-walled carbon nanotubes (SWNTs) for their potential to adsorb Penicillin G from aqueous environments.

2. Materials and methods

This experimental study was conducted in 2016 at the Environmental Health Engineering Research Center of Kerman University of Medical Sciences. All experiments and samplings were performed according to the Standard Methods for the Examination of Water and Wastewater, 20th ed. [30]. Data analysis was conducted by descriptive statistics. The stock solution of Penicillin G was prepared daily with the concentration of 1000 mg/L, and the required concentrations were subsequently prepared. The experiments were performed under different conditions, including various doses of SWCNTs (0.05, 0.3, 0.5, 0.7, and 0.9 g/L), different concentrations of Penicillin G (20, 50, 100, and 150 mg/L), different pH values (3, 5, 7, and 9), and various contact times (10, 20, 30, 60, 90, 120, 150, and 180 min) at the mixing rate of 180 rpm and temperature of 25°C. The optimal conditions were obtained for the synthetic sample, and all experiments were conducted under optimal conditions on a water sample from the distribution system of Kerman City, once its quality was determined. The physical and chemical properties of the drinking water sample of the distribution system of Kerman City are provided in Table 1. Penicillin G was not observed in the urban drinking water system. To measure the efficiency of single-walled carbon nanotubes on removing Penicillin G from urban water samples, 50 mg/L of Penicillin G was added to the drinking water sample under experimental conditions. Eventually, the removal efficiency was calculated. The experiments were replicated three times, and the results were reported as mean values. A centrifuge device (Hettich D-78532) and cellulose acetate filters with pore diameters of 0.2 micron were used to separate single-walled carbon nanotubes from aqueous environments. To determine the concentration of the remaining Penicillin G at the end of the experiment, a spectrometer device (Shimadzu, UV/VIS, 1800) was used. The concentration of unadsorbed Penicillin G in the solution was determined using the hydroxylamine method, which is based on the reaction between Penicillin G and hydroxylamine in the presence of ferric ions to give hydroxamic acid, which forms an orange–yellow colored complex with ferric ions. The absorbance of the color was read at λ_{max}: 515 nm with the spectrometer [7,31,32].

To calculate the adsorption capacity q_{eq} (mg/g) per mass unit of the adsorbent, Eq. (1) was used:

$$q_e = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where q_e is the amount of adsorbed Penicillin G per unit weight of adsorbent (mg/g), C_0 and C_e are the initial and equilibrium concentrations of liquid phase (mg/L), V is the volume of the solution (L), and m is the mass of the adsorbent.

2.1. Adsorption kinetics

The kinetics of absorption reveal important information about the absorption mechanism, absorption rate, and time control in the adsorption process. Kinetic models are used

Table 1
Physical and chemical properties of water from Kerman City distribution system

Parameter	Value
pH	7.6
Cl remaining (mg/L)	0.6
Electrical conductivity (µm/cm)	881
Total hardness $CaCO_3$ (mg/L)	244.5
Total alkalinity $CaCO_3$ (mg/L)	242
Total solids (TS) (mg/L)	440
Temperature (°C)	22

to examine the rate of the adsorption process and potential rate controlling step. To examine the adsorption kinetics of Penicillin G on single-walled carbon nanotubes,pseudo-first and second-order kinetic equations were used for data analysis, as shown in Eqs. (2) and (3), respectively.

$$\log (q_e - q_t) = \log (q_e) - k_1 t/2.303 \quad (2)$$

where q_e and q_t are the amount of Penicillin G adsorbed on the sorbent (mg g^{-1}) at equilibrium and at time t, respectively, and k_1 is the rate constant of the first-order adsorption (min^{-1}). The values k_1 for Penicillin G adsorption on SWCNT were determined from the plot of log $(q_e - q_t)$ against t.

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{1}{q_{eq}} t \quad (3)$$

The value k_2 is the rate constant of the second-order adsorption (g mg^{-1} min^{-1}). The straight-line plots of t/q_t versus t were tested to obtain rate parameters.

2.2. Adsorption isotherms

To investigate the isotherm of the adsorption process, the Freundlich and Langmuir isotherms were employed, as indicated in Eqs. (4) and (5), respectively.

$$\log\left(q_{eq}\right) = \log\left(K_f\right) + \frac{1}{n}\log\left(C_{eq}\right) \quad (4)$$

where k_f and $1/n$ are the Freundlich constant, representing adsorption capacity and intensity, respectively. The Freundlich isotherm supposition is non-uniformity of the active sites of energies, which means that different functional groups are absorbed on the surface with different energies.

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q_{max} b} + \frac{C_{eq}}{Q_{max}} \quad (5)$$

where b is Langmuir constant (l mg^{-1}), Q_{max} is the maximum sorbate uptake per unit mass of sorbent (mg g^{-1}), q_{eq} is the adsorbed amount on unit mass of the adsorbent (mg g^{-1}), and C_{eq} is the equilibrium concentration of the sorption solution. The Langmuir and Freundlich isotherm constants were determined from the plots of C_e/q_e against C_e and log q_e versus log C_e, respectively.

The main characteristic of the Langmuir constant is a dimensionless constant called the equilibrium parameter (R_L), as defined by Eq. (6).

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

where C_0 is the initial Penicillin G concentration (mg L^{-1}) and b is the Langmuir adsorption equilibrium constant (L mg^{-1}). The amount of R_L, a dimensionless factor given by Eq. (6), It indicates that $0 < R_L < 1$ means favorable, $R_L > 1$ means unfavorable, $R_L = 1$ means linear, $R_L = 0$ means irreversible.

Penicillin G, with the molecular weight of 356.37 g/mol, was purchased from Sigma Aldrich Co., USA. HCl and NaOH along with the other required chemicals were supplied by Merck Co., Germany. Single-walled carbon nanotubes were purchased from the Research Institute of Petroleum Industry and used as adsorbent for removing Penicillin G in this study. The nanotubes had the following characteristics: external diameter: 10–30 nm, internal diameter: 0.8–1.1 nm, length: 10 µm, specific surface area: 700 m^2/g, purity:<90%, and catalyst residue: >5%.

2.3. FTIR

FTIR is used as qualitative technique for evaluation of functional group [33].

The FTIR analysis performed shows since the attraction happened in the band of 3400 cm^{-1} and represents O-H stretching in alcoholic or phenolic groups [34]. The study conducted by Kim et al. in 2005 in Brazil confirms these results [34]. Due to that there is no adsorption in other bands, it indicates that Single walled carbon nanotubes are subjected to pH changes that carboxylic groups (–COOH) and hydroxylic groups (–OH) groups on the surface of single walled carbon nanotubes [35].

2.4. SEM

SEM image of the SWCNTs used in our experiment are shown in Fig. 2.

3. Results and discussion

3.1. Effect of initial pH

The effects of pH on the removal efficiency of Penicillin G by SWCNTs are shown in Fig. 3.

Increases in pH from 3 to 9 caused the extent of removal to be diminished, with the maximum removal percentage being 96.2% at pH = 3. The removal efficiency was greater in acidic pHs (pH = 3) than in alkaline pHs due to the protonation of the active sites and the increased charge density present on the adsorbent's surface. Penicillin G anions were adsorbed by the positive charges produced on the adsorbent through electrostatic forces. At high pHs, the electrostatic repulsion resulting from the negative ions of Penicillin G, the π–π electron donor–acceptor interactions, carboxyl negative ions (C=O), and hydroxide (OH$^-$) on the adsorbent's surface led to diminished efficiency. In their

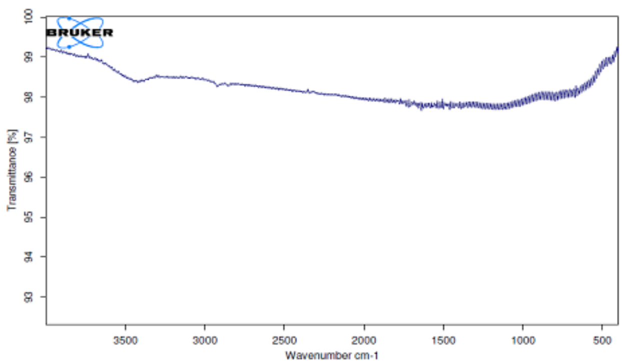

Fig. 1. FTIR analyses from single-walled carbon nanotubes.

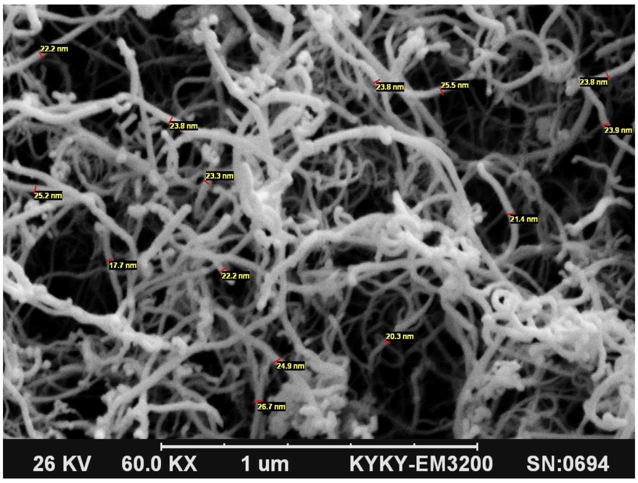

Fig. 2. SEM of single-walled carbon nanotubes.

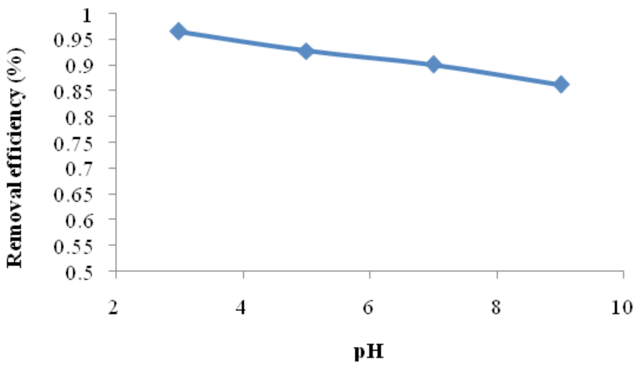

Fig. 3. Removal efficiency of Penicillin G within 180 min with SWCNTs dose of 0.7 g/L at pHs of 3, 5, 7, and 9 and initial Penicillin G concentration of 50 mg/L.

2016 study in Iran, Sheikh Mohammadi and Sardar investigated the removal of Penicillin G by modified oak acorn peel and reported the optimal pH as being acidic, which is in agreement with the results of this study [7,21,36].

3.2. Effects of contact time

The effects of contact time on the removal efficiency of Penicillin G are demonstrated in Fig. 4.

Increases in contact time up to 30 min led to increased Penicillin G removal levels, and the adsorption reached equilibrium following 30 min. Prolongation of the contact time had no effect on removal efficiency. Thus, the contact time of 30 min was chosen as the optimal time.

3.3. Effect of the adsorbent's dose

The results obtained from determining the effects of adsorbent dose on the Penicillin G removal efficiency are shown in Fig.5.

Increases in the adsorbent dose from 0.05 to 0.9 g/L caused the removal efficiency to increase from 23% to 96.6%, while the adsorption capacity diminished per mass unit

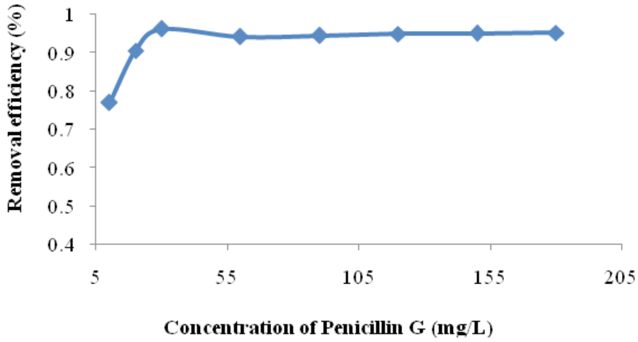

Fig. 4. Changes in Penicillin G concentration versus time with the dose of 0.7 g/L of the SWCNTs and pH = 3 along with an initial Penicillin G concentration of 50 mg/L.

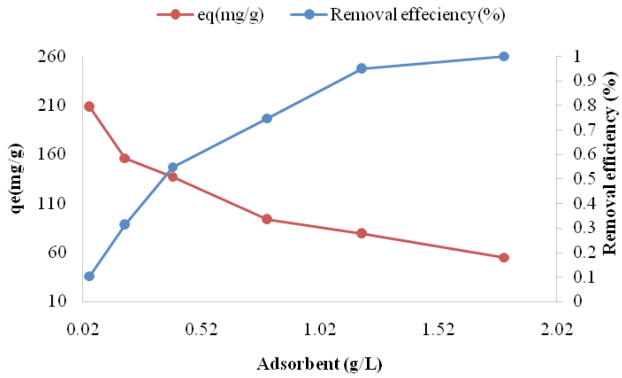

Fig. 5. Changes in Penicillin G removal efficiency and adsorption capacity with the concentration of 50 mg/L per dose of SWCNTs (0.05, 0.1, 0.3, 0.5, 0.7, and 0.9 g/L) within the contact time of 30 min and pH = 3.

of the adsorbent. As the extent of adsorption showed no increase with the adsorbent dose of 0.8 g/L, the amount 0.7 g/L was chosen as the optimal dose of adsorbent. Increasing the dose of carbon nanotubes resulted in an elevated number of active sites of adsorbent, thereby increasing the removal efficiency of Penicillin G. With increases in the adsorbent dose, Penicillin G removal efficiency increased, but the level of Penicillin G removed per mass unit of adsorbent dropped, as the active points present on the adsorbent's surface were not saturated. Moreover, the capacity of all active sites available on the surface of the adsorbent was not utilized completely. The results of the current study are in line with those of a 2016 study by Balarak et al. in Iran on the adsorption of Penicillin G using modified canola. In the current study, removal efficiency increased with increases in adsorbent dose, but adsorption capacity decreased due to the saturation of adsorption sites. The optimal dose adsorbent in the current study was 0.7 g/L [36].

3.4. Effects of the initial Penicillin G

The effects of the initial Penicillin G concentration on its removal efficiency by SWCNTs are shown in Fig. 6.

With increases in the initial concentration of Penicillin G, removal efficiency declined, such that for concentrations

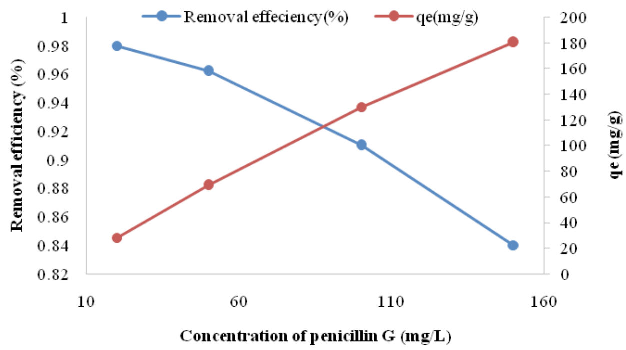

Fig. 6. Removal efficiency of Penicillin G at concentrations of 20, 50, 100, and 150 mg/L, contact time of 30 min, and SWCNTs dose of 0.7 g/L at pH = 3.

of 20 and 150 mg/L, removal efficiency was 98.4% and 84%, respectively. The decrease in the removal efficiency with the increase in Penicillin G concentration is due to the constancy of active sites of adsorption on the adsorbent's surface. Increasing the Penicillin G concentration resulted in increased adsorption capacity due to the increased probability of collision and contact between the adsorbent and the adsorbate. Malakootian et al. in 2015 in Iran investigated the removal of antibiotics from wastewater using Azola (Salvinia) and observed that removal efficiency dropped with increases in the concentration of the antibiotic [5]. Similarly, Zazuoli et al. in Iran researched the usage of Azola to remove 2,4-chlorophenol from aqueous environments. They observed that increases in the initial concentration of the adsorbate caused the removal efficiency to decrease, confirming the results obtained in the current study [37].

3.5. Effect of temperature

Results obtained in the study of different temperature effects on the efficiency of single-walled carbon nanotubes are shown in Fig. 7.

Since the increase in removal efficiency is low at temperatures above 25°C, the temperature of 25°C was determined to be optimum.

3.6. The removal efficiency of Penicillin G from drinking water

The results obtained from investigating the physical and chemical properties of water are provided in Table 1.

The removal efficiency of Penicillin G from the drinking water sample was 90.6% under the following optimal experimental conditions: pH = 3, adsorbent dose = 0.7 g/L, initial Penicillin G concentration of 50 mg/L, mixing rate of 180 rpm, temperature of 25°C, and contact time of 30 min. Penicillin G removal efficiency from water of the urban distribution system under optimal conditions was 90.6%, which was lower than that of the synthetic sample. This difference could be explained by the presence of anions and other impurities, including total solids, hardness, alkalinity, and the residual chlorine in the urban distribution system. With the adsorption on SWCNTs and by occupying the active adsorption sites, the Penicillin G removal efficiency decreased in comparison with the synthetic sample.

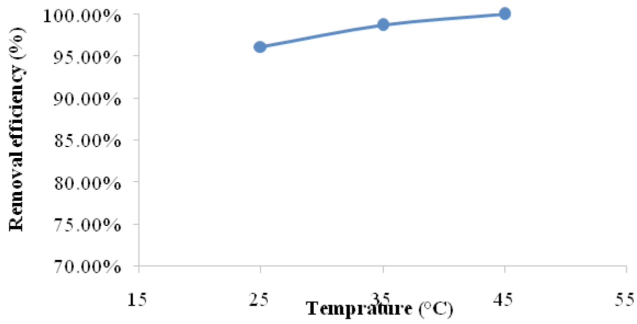

Fig. 7. Removal efficiency of Penicillin G at concentration of 50 mg/L, contact time of 30 min, SWCNTs dose of 0.7 g/L, pH = 3, and different temperatures (25°C, 35°C, 45°C).

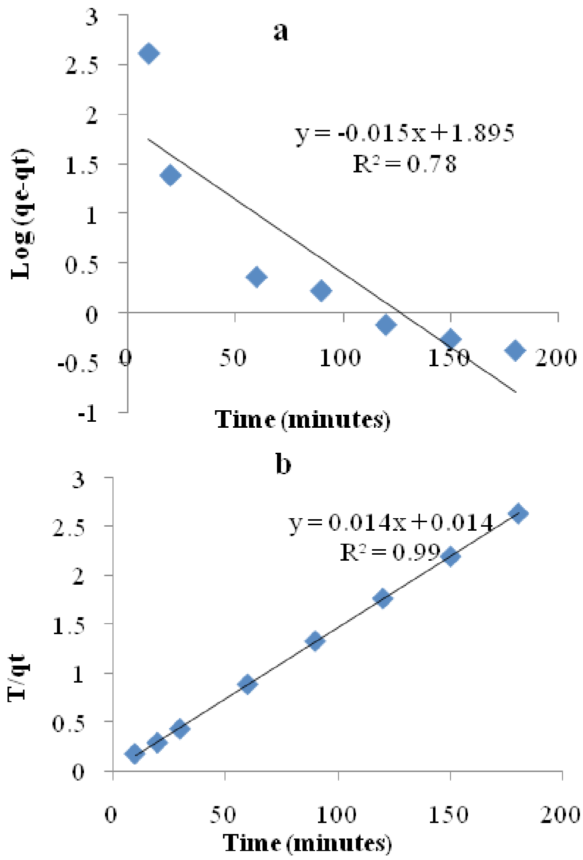

Fig. 8. Pseudo-first-order (a) and pseudo-second-order (b) kinetics with the adsorbent dose of 0.7 g/L of SWCNTs, pH = 3, initial Penicillin G concentration of 50 mg/L.

3.7. Adsorption kinetics

The results obtained from the investigation of adsorption kinetics of Penicillin G on SWCNTs are shown in Fig. 8.

The results obtained from the investigation of the kinetic parameters of the Penicillin G removal process by SWCNTs are provided in Table 2.

Considering the comparison of correlation coefficients between adsorption kinetics in Table 2 and the pseudo-second-order Pearson correlation coefficient (R^2 = 0.99), it can

Table 2
Parameters calculated for pseudo-first and second-order adsorption kinetics

Pseudo-second-order kinetics			Pseudo-first-order kinetics			$q_{e,exp}$ (mg/g)	Initial concentration of Penicillin G mg/L))
R^2	K_2(g/mg*min)	$q_{e,cal}$ (mg/g)	R^2	k_1(min^{-1})	$q_{e\,cal}$ (mg/g)		
0.99	0.014	71.42	0.78	0.034	6.65	68.71	50

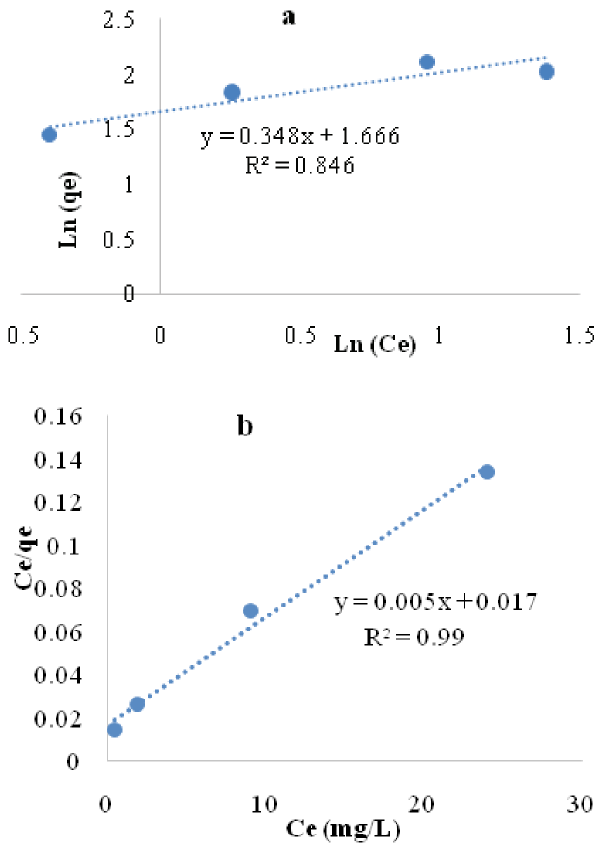

Fig. 9. Results of investigation of Freundlich adsorption isotherm model (a) and of Langmuir adsorption isotherm (b) at carbon nanotubes concentration of 0.7 g/L and initial Penicillin G concentrations of 20–150 mg/L (pH = 3).

be concluded that the adsorption kinetics follow pseudo-second-order kinetics. This model is more likely to predict the behavior over the whole range of adsorption, and it is in agreement with chemisorption being the rate-limiting step. In the research conducted by Aksu and Tunc in 2005 in Turkey, it was also found that Penicillin G adsorption on Rhizopus bio-adsorbent in aqueous solutions followed pseudo-second-order kinetics. Furthermore, the adsorption of amoxicillin on single-walled nanotubes in a 2016 study conducted by Balarak et al. in Iran also followed pseudo-second-order kinetics [7,29].

3.8. Adsorption isotherms

The results obtained from the investigation of Freundlich and Langmuir isotherms of Penicillin G adsorption on SWCNTs are revealed in Fig. 9.

Table 3
Parameters calculated for Freundlich and Langmuir isotherms

Freundlich isotherm (a)			Langmuir isotherm (b)			
R^2	$1/n$	K_f (mg/g)	R^2	R_L	b (l/mg)	Q_{max} (mg/g)
0.846	0.34	46	0.99	0.016	0.29	200

Table 4
Results of regeneration of single-walled carbon nanotubes conducted with microwave irradiation

Equilibrium absorption capacity (mg/g)	Penicillin G. removal efficiency	Adsorbents
66.7 mg/g	93.4%	Single-walled carbon nanotubes (one cycle of regeneration)
62.35 mg/g	87.3%	Single-walled carbon nanotubes (two cycles of regeneration)

The results obtained from examining the isotherm parameters of the Penicillin G adsorption process by SWCNTs are presented in Table 3.

The Penicillin G adsorption isotherm on SWCNTs follows the Langmuir isotherm (R^2 = 0.99). This suggests that the adsorbent's surface is a homogenous surface with a uniform distribution of adsorbed heat and the adsorption of a layer of Penicillin G on the SWCNTs on the adsorbent's surface (38). In a 2016 study by Balarak et al. in Iran, the results also indicated that the adsorption of amoxicillin follows the Langmuir isotherm (29).

The value of R_L obtained in this research was 0.03; considering the fact that R_L lies within 0–1, this result suggests optimal adsorption.

The low decrease in adsorption capacity may be due to the deposition of decomposition residue of single-walled carbon nanotubes in pores, which blocked the single-walled carbon nanotubes' porosity and reduced the absorption capacity [39].

4. Conclusion

The removal of antibiotics from aquatic environments is an important consideration for public and environmental health. The data obtained in this study shows that single-walled carbon nanotubes have the favorable capacity to remove Penicillin G from aqueous solutions, especially in acidic and ordinary conditions. Single-walled carbon nanotubes can be used as a suitable adsorbent with a relatively high efficiency in the removal of Penicillin G from aqueous solutions.

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