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Investigating the efficiency of single-walled and multi-walled carbon nanotubes in removal of penicillin G from aqueous solutions

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Abstract
Background: Drugs, especially antibiotics, are one of the serious problems of modern life and the main pollution sources of the environment, especially in the last decade, which are harmful to human health and environment. The aim of this study was to investigate the removal of penicillin G from aqueous solutions using single-walled and multi-walled carbon nanotubes.
Methods: In this study, the effect of different parameters including pH (3, 5, 7, 9, and 11), initial concentration of pollutant (50, 100, 150, and 200 mg/l), absorbent dose (0.25, 0.5, 0.75, and 1 g/L), mixing speed (0, 100, 200, and 300 rpm), and temperature (10, 15, 25, 35, 45°C) were investigated. The Langmuir, Freundlich, Temkin, BET, Dubinin-Radushkevich isotherms and adsorption kinetics of the first- and second-order equations were determined.
Results: The results showed that the efficiency of single-walled and multi-walled carbon nanotubes in the removal of penicillin G was 68.25% and 56.37%, respectively, and adsorption capacity of the nanotubes was 141 mg/g and 119 mg/g at initial concentration of 50 mg/l and pH=5 with adsorption dose of 0.8 g/L for 105 minutes at 300 rpm and temperature of 10°C from aqueous solutions. Also, it was revealed that the adsorption process had the highest correlation with the Langmuir model and second-order kinetics, and the maximum adsorption capacity based on Langmuir model was 373.80 mg/g.
Conclusion: According to the results, it was found that single-walled and multi-walled carbon nanotubes can be used as effective absorbents in the removal of penicillin G from aqueous solutions.
Keywords: Single-walled carbon, Multi-walled carbon, Adsorption, Penicillin G, Antibiotics
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Introduction

Drugs are considered as highly important compounds and an integral part of modern life, which are used for treatment of human and animal diseases. Today, the presence of drugs in the environment is one of the important and considerable issues in the world. Recently, some of developed countries such as the United States, England, Germany, and Italy have started to examine the negative effects of these pollutants on the environment. Drugs essentially have very strong biological activity, which affects the living organisms (1). In addition, they are highly resistant to biological degradation and are not degraded under normal conditions but require specific reactions under special conditions. Finally, drug compounds enter water resources, and affect the environment (1). Among different drug compounds, antibiotics are the most important group of drugs because these compounds are extensively used for the treatment of various diseases (2). The studies have shown that annually 100-200 tons of antibiotics are consumed in the world (3,4). These substances enter the environment through various ways such as pharmaceutical industry wastewater, hospital sewage and fecal and urine of humans and animals (5). Penicillin is the common group of antibiotics that is applied to treat the infections of ear, nose, throat, urinary tract, and skin due to gram-positive bacteria. The mechanism of this antibiotic is degradation the wall cell of bacterial preventing the formation of peptidoglycan (6). In recent years, the bacterial resistance has increased and researchers believe that the increased resistance is due to the excessive consumption of antibiotics (7). The problem is the bacterial resistance against antibiotics despite their low concentrations (7). Moreover, the antibiotic-resistant genes can enter drinking water sources, thereby, causing antibiotic-resistant diseases (8). Recent studies have shown that antibiotics can be found in surface waters and sewage treatment plants (3,4,9). The results show that these drugs cannot be completely removed during biological purification and enter receiving waters, therefore, the removal of antibiotics from wastewater before discharge to receiving water systems is highly important (10). Different methods are used for the removal of antibiotics from aquatic solutions (water and sewage) such as adsorption (11), biological processes (12,13), and oxidations processes (14-17). Biological methods have low removal efficiency for antibiotics but oxidation processes result in degradation of antibiotics although they make borderline materials dangerous. Adsorption is an effective method for the removal of pollutants from water and wastewater even at very low concentrations (below 1 mg/L). The adsorption is a simple and feasible method with low operating cost in comparison with other methods for the separation of pollutants from aqueous solutions (18). Therefore, many researchers have focused on the optimization of adsorption process and finding new absorbents with high adsorption capacity and low cost (18). Despite the widespread use of activated carbon in the adsorption process, the production and recovering problems have encouraged researchers to find new recoverable adsorbents with high adsorption capacity (11). In this regard, nanotechnology has received considerable attention. The carbon nanotubes are graphite sheets that are wrapped as cylindrical tubes and divided into single-walled (SWCNTs) and multi-walled (MWCNTs) groups based on the number of layers in their structure (19-21). The unique properties of carbon nanotubes include high specific surface and permeability, good mechanical and thermal resistance, electrical stability, and reusability. Also, the carbon nanotubes have shown excellent adsorption properties for various organic compounds and mineral ions (21-23).

In a study conducted by Ncibi and Sillanpaa, the removal of antibiotic drugs from aqueous solutions was investigated using single-, double-, and multi-walled carbon nanotubes and the results showed that the highest adsorption capacity for oxytetracycline and ciprofloxacin was 554 and 724 mg/g, respectively (24). In another study conducted by Kim et al, the adsorption of antibiotics on single-walled and multi-walled carbon nanotubes was investigated and it was reported that the adsorption generally followed the order SWCNT > MWCNT. The relatively low adsorption on MWCNT was probably due to its lower specific surface area than other carbon materials (25). The other study conducted by Peng et al, on the adsorption of ofloxacin using carbon nanotubes showed that cationic and anionic ofloxacin had much higher solubility than zwitterionic ofloxacin and with increase of methanol fraction, both OFL solubility and sorption decreased (26).

The aim of this study was to evaluate the efficiency of single-walled and multi-walled carbon nanotubes in the removal of penicillin G from aqueous solutions.

Materials and Methods

In the present study, penicillin G, single-walled and multi-walled nanotubes (manufactured by Noyan TebPadideh, Western Tehran), HCL and NaOH 0.1 N (manufactured by Merck Germany) specifications related to penicillin G were used (Table 1).

In order to study the shape, average diameter, surface details, determine functional groups on the absorbent surface and analyze the structure of carbon nanotubes, scanning electron microscope (SEM) (SIGMA VP-500 manufactured by ZEISS, Germany), X-ray diffraction (XRD) (Pert x, Pro model, manufactured by PANalytical Corporation) and Fourier-transform infrared spectroscopy (FT-IR) by AVATAR 370 were used. The adsorption test was carried out in a continuous adsorption system using penicillin G as an absorbed material and carbon nanotubes as adsorbents. The stock solution was prepared by dissolving 1 g penicillin G in deionized water, and then, the required concentrations were made by diluting the stock solution. The parameters studied in the removal process include pH (3, 5, 7, 9, and 11), initial concentration (50, 100, 150, and 200 mg/L), adsorbent dose (0.25, 0.5, 0.75, and 1 g/L), mixing speed (0, 100, 200, and 300 rpm), and temperature (10, 15, 25, 35, and 45°C). For measurement, first, the calibration curve was drawn with different concentrations of penicillin G, where R^2 was 0.99, then, the residual concentration of penicillin G was measured using a spectrophotometer at wavelength of 283 nm (wavelength of maximum adsorption) (27). To ensure the accuracy of results, each step of the experiment was repeated twice and the average results were reported. The adsorption isotherms were evaluated using Langmuir, Freundlich, Temkin, BET and Dubinin-Radushkevich models, and the adsorption kinetics was investigated using the first-order and second-order equations. The results of adsorption and its isotherms were analyzed using

Table 1. Physical and chemical properties of penicillin G

Penicillin G	Shape	Brand	Molecular Weight (g/mol)	Formula
	Crystal and white powder	BenPen	356. 37	$C_{16}H_{18}N_2O_4S$

Langmuir and Freundlich models. The linear equations of these two models are shown in equations (1) and (2), respectively.

$C_e/q_e = 1/bq_m + C_e/q_m$ (1)

$Lnq_0 = LnK_f + 1/n\ LnC_0$ (2)

In these equations, C_e and q_e are the equilibrium concentration in the soluble (mg/L) and solid (mg/L) phase, respectively, *qm* is maximum adsorption capacity (mg/g), and *k*, *n*, and *b* are model constants.

In the Temkin adsorption isotherm model, the positive or negative values of b_T indicate the exothermic or endothermic adsorption process.

$q_e = (RT/b_T)Ln(A_T C_e)$ (3)

In the equation (3), A_T, b_T, *R*, and *T* are bond constants, which indicate the maximum bond energy ($L.g^{-1}$), Temkin constant (J/mol), gas constant, and absolute temperature, respectively.

$q_e = (q_{max}\ K_b C_e)/(C_s - C_e)[1+(K_b - 1)(C_e/C_s)]$ (4)

In the equation (4), C_S, K_b, and q_{max} are saturation concentration of the soluble phase (mg/L), model constant, and absorbed content per adsorbent unit, respectively.

The Dobinin-Radushkevich model is often used to determine the nature and characteristics of the adsorption process and free energy.

$qe = \exp(-k2)\ E=R.T.\ln(1+1/ce) \quad E= 1/\sqrt{2B}$ (5)

In the equation (5), *E*, *B*, *R*, and *T* are Polanyi adsorption potential ($KJ^2.mol^{-2}$), free energy of adsorption ($mol^2.kj^{-2}$), gas constant ($J.mol^{-1}.k^{-}$), and temperature (k), respectively (25).

Chemical kinetics indicates the speed of chemical reactions. In this study, penicillin G adsorption rate constant with single-walled and multi-walled carbon nanotubes was checked using pseudo-first-order and pseudo-second-order kinetics models, and the most appropriate model was determined. The pseudo-first-order and pseudo-second-order kinetic models are represented in equations (6) and (7), respectively.

$Ln(q_e - q_t) = Lnq_e - K_1 t$ 6

$t/q_t = 1/k_2 q_e^2 + t/q_e$ 7

In equations (6) and (7), q_e, q_t, k_1, and k_2 are the equilibrium concentration of adsorption phase (mg/g), antibiotic concentration at time of *T* (mg/g), rate constants of pseudo-first-order and pseudo-second-order equations, respectively (28).

Results

The properties of adsorbents were investigated using specific analysis techniques, as following.

FT-IR analysis

To determine the functional groups on the adsorbent surface after the adsorption process of pollutant, FT-IR spectrum was used and the results are shown in Figure 1. In the FT-IR spectrometry of single-walled carbon nanotubes after penicillin G adsorption, the peaks in range of 3432.59 cm^{-1} are related to vibrating modes of O-H, the peaks in range of 1052.19 cm^{-1} are related to tensile C-O groups in the composition, and the peaks in range of 2900, 1600, and 2300 cm^{-1} are respectively related to tensile bonds C-H, C=O, and S-H. The adsorption peaks below 100 cm^{-1} are related to tensile peaks of C-S groups. And in FT-IR spectroscopy of the multi-walled carbon nanotubes after penicillin G adsorption, the peaks in the range of 3435.5 cm^{-1} are related to vibrating modes of O-H, the peaks in range of 1037.3 cm^{-1} are related to tensile C-O groups in the composition, and the peaks in range of 2919.6, 1637.3 and 2300 cm^{-1} are respectively related to tensile bonds C-H, C=O, and S-H. The adsorption peaks below 1000 cm^{-1} are related to tensile bonds of the C-S groups, and all of these variations in the FT-IR spectrum approve the functional groups of penicillin G adsorbed on the structure of single-walled and multi-walled nanotubes. These variations in the FT-IR spectrum show that penicillin G is located on the surface of single-walled and multi-walled carbon nanotubes.

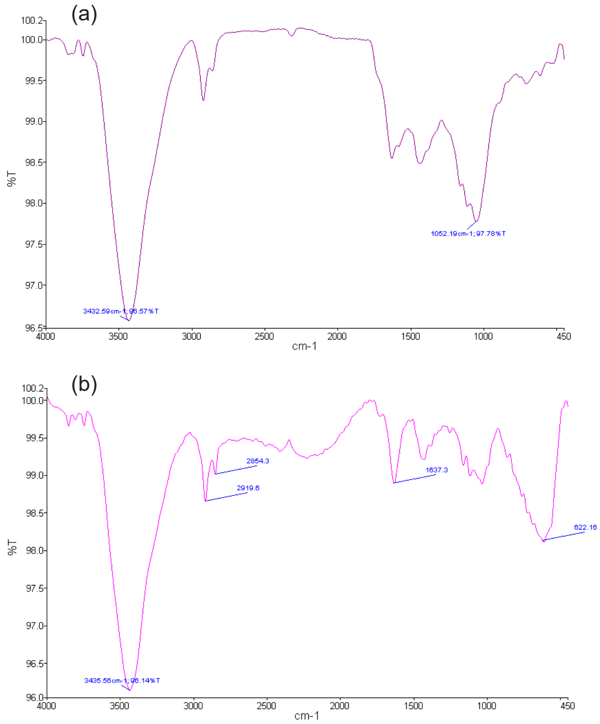

Figure 1. FT-IR analysis of single-walled carbon nanotubes (a) and multi-walled carbon nanotubes (b) after the adsorption process.

XRD analysis

The XRD spectrum of single-walled carbon nanotubes before adsorption of penicillin G (a), and multi-walled carbon nanotubes before adsorption of penicillin G (b), single-walled carbon nanotubes after adsorption of penicillin G (c), and multi-walled carbon nanotubes after adsorption of penicillin G (d) is presented in Figure 2a-d. The crystal structure of single-walled and multi-walled carbon nanotubes before and after adsorption of the pollutant is presented in Figure 2a-d. XRD patterns show

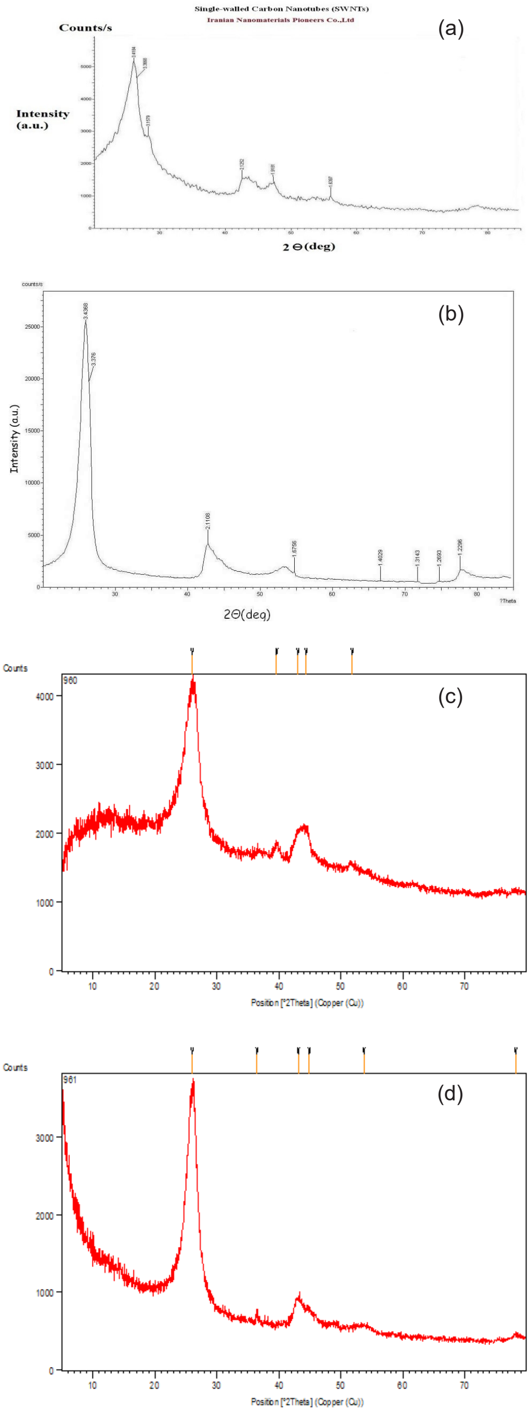

Figure 2. XRD images of single-walled carbon nanotubes (a) and multi-walled carbon nanotubes (b) before the adsorption process, single-walled carbon nanotubes (c), and multi-walled carbon nanotubes (d) after the adsorption process.

certain peaks for SWCNT before penicillin G adsorption at angles 2, 16, 18, 24, 43, 48, and 56 **θ**, which is in accordance with the JCPDS database. XRD patterns show certain peaks for SWCNT after penicillin G adsorption at angles 2, 26.021, 43.1, and 44.4 **θ**, and for MWCNT at angles 2, 25.98, and 43.12 **θ**, which made few changes in the adsorption structure compared to the peaks before the adsorption process, which is in accordance with the JCPDS database. The shape and size of carbon nanotubes were determined by SEM.

SEM images

Figure 3 shows SEM images of (a) single-walled carbon nanotubes powder before adsorption process and (b) single-walled carbon nanotubes after adsorption process (c) SEM images of multi-walled carbon nanotubes powder before adsorption process and (d) multi-walled carbon nanotubes after adsorption process. SEM is widely used to determine the morphology, shape, and size of particles in micro- and nano-scale. These images indicate the nanotube string structures. SEM images of these nanoparticles can be seen and size of single-walled carbon nanotube before adsorption was in range of 1-3 nm, and diameter of these nanotubes after penicillin G adsorption increased to 42.95-89.32 nm, and diameter of multi-walled carbon nanotubes is in the range of 20-30 nm, and diameter of the multi-walled nanotubes after penicillin G adsorption increased to 31.26-63.94 nm. As shown in Figure 3a and Figure 3d, the diameter of the nanotubes increased after adsorption process; the adsorption images also indicate that after the adsorption process, most of the sites and pores of the studied adsorbents were filled with penicillin G in the spherical and string forms in line with the surface of the nanotubes.

Effect of pH on removal efficiency of penicillin G using single-walled and multi-walled carbon nanotubes

Figure 4 shows the effect of pH on the removal of penicillin G by single-walled carbon nanotubes (a) and multi-walled carbon nanotubes (b). Based on the results of the experiments on single-walled and multi-walled carbon nanotubes as adsorbents, the increase of pH from 3 to 9 has a positive effect on the removal of penicillin G, and

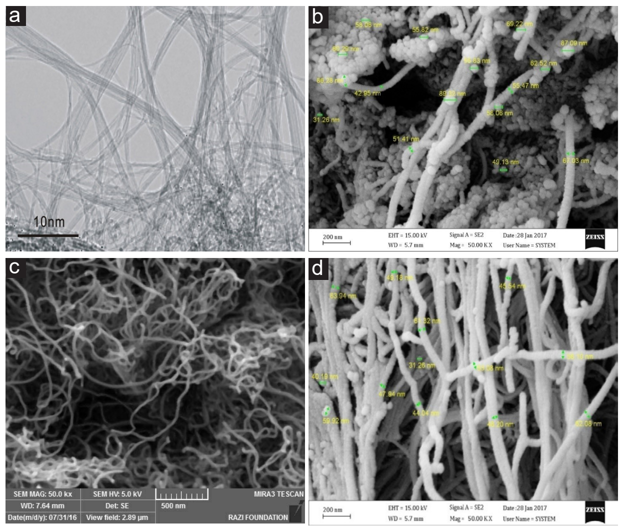

Figure 3. SEM images of single-walled carbon nanotubes powder before adsorption process (a), single-walled carbon nanotubes after adsorption process (b), multi-walled carbon nanotubes powder before adsorption process (c), and multi-walled carbon nanotubes after adsorption process (d).

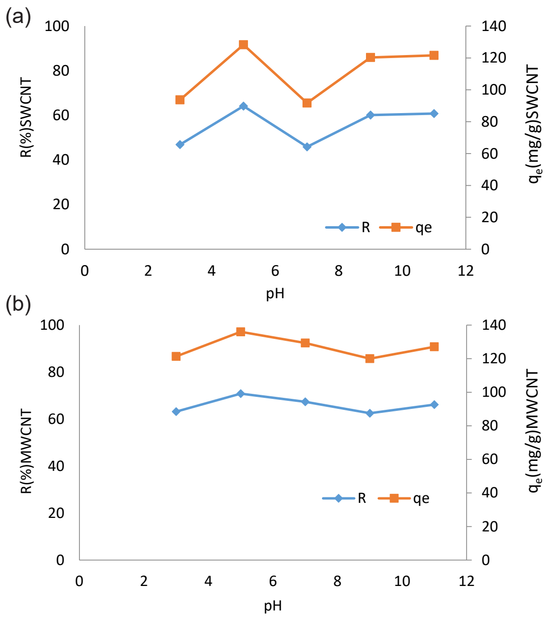

Figure 4. Effect of pH on the removal of penicillin G using single-walled carbon nanotubes (a) and multi-walled carbon nanotubes (b).

by increasing pH to above 9, the efficiency of the removal process of penicillin G was kept constant. SWCNTS and MWCNTs had the highest removal efficiency at pH=5 (64.13% and 70.83%, respectively). According to the results, pH 5 was chosen as the optimum pH.

Effect of adsorbent dose on the removal efficiency of penicillin G using single-walled and multi-walled carbon nanotubes

Effect of adsorbent dose on the removal of penicillin G using single-walled carbon nanotubes powder (a) and multi-walled carbon nanotubes powder is shown in Figure 5. According to the figure, an increase in the carbon nanotubes dosage has a significant effect on the removal of penicillin G by the carbon nanotubes. Although by increasing carbon nanotubes from 0.25 g/L to 1 g/L, the efficiency augmented, but 0.8 g/L of carbon nanotube had the highest removal efficiency (nearly 80%), so the optimum dosage was chosen 0.8 g/L and used in the following steps.

Effect of contact time and concentration on the removal efficiency of penicillin G using single-walled and multi-walled carbon nanotubes

Figure 6 indicates the effect of initial concentration and contact time on the removal of penicillin G using single-walled carbon nanotubes powder (a) and multi-walled carbon nanotubes powder (b). By increasing the contact time, the removal efficiency also increased. The optimum contact time was 105 minutes for SWCNT and MWCNT, the quantity of which is shown in Figure 6a and b. As the initial concentration of penicillin increased, the removal efficiency was reduced but the adsorption capacity was increased, which can be due to the filling active adsorption

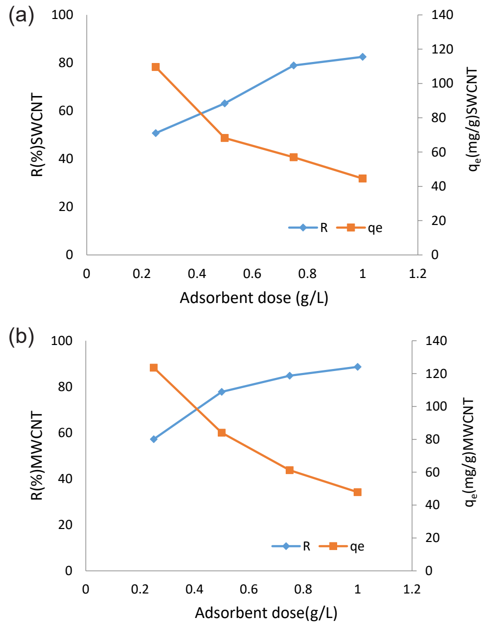

Figure 5. Effect of adsorbent dose on the removal of penicillin G using single-walled carbon nanotubes powder (a) and multi-walled carbon nanotubes powder (b).

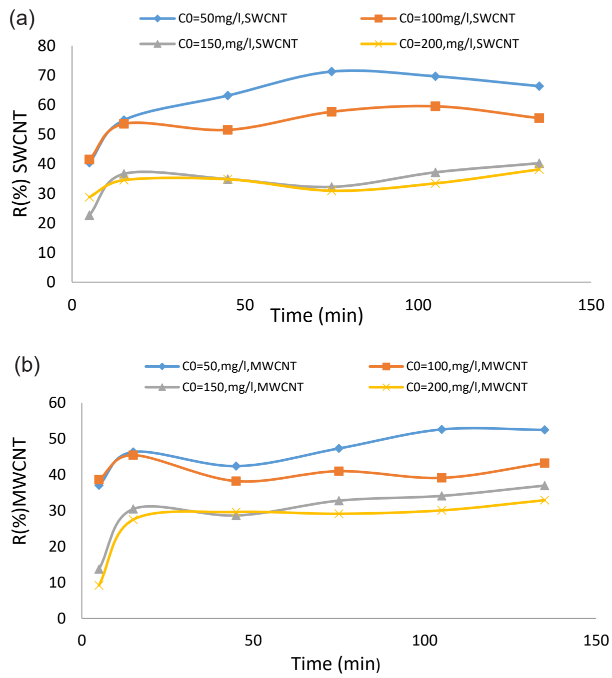

Figure 6. Effect of initial concentration and contact time on the removal of penicillin G using single-walled carbon nanotubes powder (a) and multi-walled carbon nanotubes powder (b).

sites of nanotubes, and as the concentration of penicillin G increased, adsorption process was carried out gradually from surface of the nanotubes. According to the figure, the highest adsorption at initial concentration 50 mg/L and contact time 70 and 105 minutes for single-walled and multi-walled carbon nanotubes was respectively achieved, and in this condition, the removal efficiency was 71% and 53% for single-walled and multi-walled carbon nanotubes, respectively.

Effect of mixing speed on the removal efficiency of penicillin G using single-walled and multi-walled carbon nanotubes

Figure 7 represents the effect of stirring on the removal of penicillin G using single-walled carbon nanotubes (a) and multi-walled carbon nanotubes (b). According to the figure, mixing speed had a direct effect on the removal efficiency. By increasing the mixing speed of the nanotubes and aqueous phase of penicillin G and the contact surface between the two phases, the removal efficiency also increased. As the mixing speed increased, the removal of penicillin G was increased, and the optimum speed of 300 rpm was considered for the above mentioned adsorbents.

Adsorption isotherms

In the adsorption process of pollutants on different adsorbents, determination of adsorption isotherm is one of the most important characteristics that should be considered. In fact, the isotherm parameters provide important information for design and modeling of the adsorption process. The adsorption isotherms are often used to explain the adsorption of materials on the adsorbent. In this study, Langmuir, Freundlich, BET, Temkin and Dubinin-Radushkevich isotherms were examined for SWCNT and MWCNT nanotubes after the adsorption of penicillin G, and the coefficients and constants of each one are shown in Table 2 and 3. As shown in these tables, the studied adsorption process followed the Langmuir isotherm model.

Adsorption kinetics

Table 4 shows kinetic parameters for the adsorption of penicillin G onto single-walled and multi-walled carbon nanotubes. Chemical kinetics indicates the chemical reaction rate. In this study, penicillin G adsorption rate constant with single-walled and multi-walled carbon nanotubes was compatible with pseudo-first-order and pseudo-second-order kinetic models, and the most suitable model was determined.

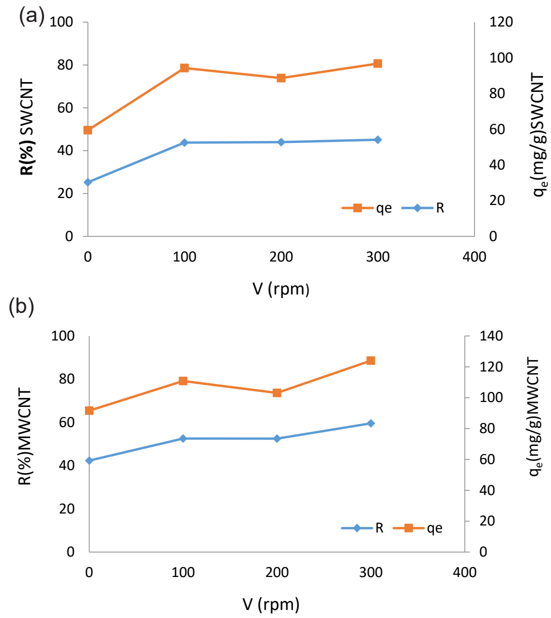

Figure 7. Effect of mixing rate on the removal of penicillin G using single-walled carbon nanotubes (a) and multi-walled carbon nanotubes (b).

Table 4 shows the kinetic parameters and their correlation coefficients. As shown in this table, penicillin G adsorption by SWCNT and MWCNT was better matched with pseudo-second-order model.

Adsorption thermodynamic

The efficiency of temperature and thermodynamics of pollutant adsorption by the adsorbents considered in this study is shown in Table 5. After calculating the constant of equilibrium of thermodynamic for various temperatures and the free energy released during the adsorption process of penicillin G, the diagram of LnKd versus 1/T was plotted. As presented in this table, values of (ΔH) and (ΔS) were positive and the values of (ΔG) were negative. Negative variation of Gibbs free energy (Δg) represents possibility of the adsorption process. Positive value of (ΔH) indicates that the adsorption process is naturally endothermic and the capacity of adsorption increases with

Table 2. Isotherm parameters for various common adsorption isotherms for the adsorption of penicillin G on single-walled carbon nanotubes

		q_{max}, mg/g	q_{max}, mg/g	R_L	R^2
Langmuir constants	L1	337.80	0.041	0.50	0.97
	L2	368.25662	0.0418653		
Freundlich constants		k_f, mg/g	n	1/n	R^2
		56.21	2.74	0.36	0.90
BET constants	X_m	A	(A-1)/(A.Xm)	$1/A.X_m$	R^2
	133	1.0	0.0075	0.0003	0.790
Temkin constants		B	b_T	A_T, L/mg	R^2
		77.93	31.79	0.46	0.90
Dubinin- Radushkevich constants		q_m, mg/g	E, kJ/mole	B, $mole^2/kJ^2$	R^2
		290.08682	0.1318402	2.877E-05	0.94

Table 3. Isotherm parameters for various common adsorption isotherms for the adsorption of penicillin G on multi-walled carbon nanotubes

		q_{max}, mg/g	q_{max}, mg/g	R_L	R^2
Langmuir constants	L1	550.54	0.009	0.50	0.97
	L2	713.06901	0.0064013		
Freundlich constants		kf, mg/g	n	1/n	R^2
		10.47	1.41	0.71	0.97
BET constants	X_m	A	(A-1)/(A.Xm)	1/A.Xm	R^2
	-37	1.0	-0.0271	0.0218	0.433
Temkin constants		B	bT	AT, L/mg	R^2
		132.14	18.75	0.08	0.93
		10.47	1.41	0.71	0.97

Table 4. Kinetic parameters for the adsorption of penicillin G on single-walled and multi-walled carbon nanotubes

Concentration (mg/L)	Pseudo-first-order Kinetic Model			Pseudo-second-order Kinetic Model		
	MWCNT	SWCNT		MWCNT	SWCNT	
50	0.0066	0.0482	K_1	0.0052	0.0015	K_2
	12.0697	64.5216	q_e	108.1081	156.25	q_e
	0.156	0.991	R^2	0.994	0.988	R^2

increase of temperature. Positive value of (ΔS) indicates the tendency of absorbent to absorb the liquid and make some structural changes in the adsorbate and adsorbent. Positive value of (ΔS) suggests the adsorbate tendency to be adsorbed in the solution and some structural changes in. Positive entropy value of (ΔS) indicates that the freedom degree of the solid-liquid transition state was increased during adsorption.

Discussion

The pH of solution is an important parameter that influences the adsorption of pollutant using adsorbent. The results of the experiments on single-walled and multi-walled carbon nanotube adsorbents showed that with an increase in pH from 3 to 5, the uptake of penicillin G also increased, but by increasing pH above 5, the rate of penicillin G adsorption decreased abruptly. Penicillin G have a pka=2.75 with a weak moocarboxylic acid (29). Therefore, penicillin G is an acidic compound that could be dissociated at pH>pka (30). At higher pH>pka, penicillin G ionization and OH^- ions increase, resulting in the electrostatic repulsion between the OH^- and negative charge on the adsorbents (SWCNT and MWCNT) surface (30,31).

According to above description, at lower pH, the removal efficiency of penicillin G was notably higher. In similar studies (29,30), pH 5 was selected as the optimum pH. By increasing the contact time from 5 to 105 minutes, the removal efficiency was increased, so, the removal efficiency was constant. Therefore, the optimum contact time for SWCNT and MWCNT was 105 minutes. Also, by increasing the initial concentration of penicillin G, the removal efficiency was reduced but the adsorption capacity was increased It can be concluded that in the early stages of the reaction, the effect of contact time and initial concentration on the adsorption of antibiotics penicillin G using single-wall and multi nanotubes was slowly developed, so that the equilibrium time was observed at 105 minutes. Secondly, the highest antibiotic adsorption was seen at lower concentrations. In the adsorption process, since the removal of pollutant is done through adsorption on the surface of adsorbent, therefore, specified ion exchange sites can be seen on the adsorbent surface that bind to pollutants. This is done when the amount of pollutant remains constant around the adsorbent. As the concentration of pollutant increases in the solution, the thrust force will be generated by the concentration gradient that will lead pollutants into the adsorbent internal pores, and due to the gradual filling of the sites, by increasing the concentration of penicillin G, the desorption process occurs on the surface of nanotube. According to the study by Gao et al, an increase in ionic concentration of the solution led to a decrease in the adsorption of tetracycline by graphene oxide (32). The adsorption rate at initial concentration of tetracycline (166.67 mg/L) and NaCl (100 Mmol/L) was above 50%. This decrease was not considerable in the tetracycline adsorption at low concentrations. Another study by Ji et al showed that the increased ionic concentration of the solution on tetracycline adsorption onto multi-walled carbon nanotubes decreased the reaction efficiency (33).

Table 5. Thermodynamic parameters for the adsorption of penicillin G onto single-walled and multi-walled carbon nanotubes

Temp	ΔG	ΔS	ΔH
10	-149.65	0.105	1.05
15	-187.065		
25	-274.34		
35	-331.73		

The effect of ionic concentration on the adsorption on single-walled carbon nanotubes was more than the multi-walled ones, however, it was unclear in the graphite due to the lack of surface required (34). Chang et al used palygorskite to absorb tetracycline. They reported that the equilibrium time to absorb tetracycline on palygorskite was about 2 hours (35). In the other study on the removal of tetracycline from synthetic solutions using raw LECA by Noori Sepehr et al, it was shown that the highest removal efficiency occurred at 180 minutes (36). In this study, the penicillin G adsorption on single-walled and multi-walled carbon nanotubes was tested as a function of adsorbents in dosages of 0.25-1 g/L and at constant conditions (initial concentration= 50 mg/L, pH=11, and contact time= 60 minutes). The effect of adsorbent dosage on the removal of penicillin G on single-walled carbon nanotubes powder (a) and multi-walled carbon nanotubes powder has been shown in Figure 5. According to this figure, removal efficiency increased with increase of adsorbent dose. Physically, it can be described by the aggregation of exchangeable binding sites of the adsorbents used for HA molecules. In a study by Ncibi and Sillanpaa (24) on the removal of antibiotics from aqueous solutions using single-, double- and multi-walled carbon nanotubes and the study by Peng et al (37) on the adsorption of ofloxacin and norfloxacin on carbon nanotubes, similar results were obtained. In this study, since the adsorption capacity was not changed much with an increase in the adsorbent dose, and the lowest amount of adsorbent with the highest removal efficiency was chosen as the optimal dose, 0.25 g/L of absorbent was used in the next steps. In this study, stirring the solution had a direct effect on the removal efficiency. Since the mixing speed of the nanotubes and aqueous phase of penicillin G increased the contact surface between two phases, therefore, the removal efficiency was also increased. By increasing the stirring speed, the removal efficiency of penicillin G was increased and the speed of 300 rpm was considered as the optimum speed for these absorbents. However, by increasing temperature, the removal efficiency of penicillin G by nanotubes was reduced. The Langmuir and Freundlich isotherm models are widely used to study the adsorption process. The Langmuir model is based on the single-layer adsorption in few equal sites. In this model, it is assumed that the adsorption occurs in sites with the same energy on the absorbent surface, while in the Freundlich isotherm, the soluble matter is absorbed on uneven surfaces in several layers. In the present study, five isotherm models including Langmuir, Freundlich, BET, Temkin, and Dubinin-Radushkevich were studied, and it was revealed that the highest removal efficiency belonged to Langmuir, Dubinin-Radushkevich, Temkin Freundlich, and BET models, respectively. According to Table 2, the maximum penicillin G adsorption (G q_{max}) by single-walled nanotubes was calculated as 373 mg/g. The results of this study indicated better compatibility with Langmuir isotherm model, which represented the adsorption of a penicillin G layer on single-walled carbon nanotubes and homogeneous absorbent surface. For the multi-walled nanotubes, the isotherm models were also investigated, and it was revealed that the highest removal efficiency belonged to Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, and BET models. According to Table 3, the highest penicillin G adsorption (G q_{max}) by multi-walled nanotubes was 550.50 mg/g. The results of this study showed better compatibility with Langmuir isotherm model. In the study of Zhang et al, the tetracycline adsorption by multi-walled carbon nanotubes had better compatibility with Langmuir isotherm (28). The adsorption kinetics describes important information about the adsorption mechanism, uptake rate of carbon nanotubes and contact time of adsorption process (38). In a pseudo-first-order kinetic model, it is assumed that the rate of changes in removal of penicillin G per time is directly proportional to the variations in saturation concentration and removal of adsorbent per time (39). The pseudo-second-order model assumes that two reactions (parallel or serial) are effective in adsorption of penicillin G on the carbon nanotubes; the first one is fast and rapidly reaches equilibrium, while the second one is slow and continues for longer period of time (40). In this study, the laboratory data showed that the penicillin G adsorption follows the second-order equation. The second-order reactions proceed at a speed proportional to the second exponent of the primary material (40). This result shows that the penicillin G adsorption mechanism on carbon nanotubes can be a physical adsorption. In the research by Samadi et al, use of multi-walled carbon nanotubes in the removal of amoxicillin from aqueous solution was investigated and the results showed that the adsorption equilibrium data were compatible with Langmuir isotherm (R2=0.9108) and adsorption kinetics had better compatibility with the second-order kinetic equation (41). In a research by Naghizadeh et al, the efficiency of single-walled and multi-walled carbon nanotubes in the removal of arsenic from aqueous solutions was compared and the results showed that the adsorption capacity of single-walled and multi-walled carbon nanotubes is 148 and 95 mg/g, respectively. In this study, the laboratory data were analyzed using Freundlich and Langmuir isotherm models, and the equilibrium data showed that the Langmuir isotherm model is the best compatible model to describe the behavior of arsenic adsorption on carbon nanotubes (42). In the present study, the adsorption capacity of single-walled and multi-walled carbon nanotubes was 141 and 119 mg/g, respectively, and the results showed that single-walled and multi-walled carbon nanotubes can be used as effective absorbents in the removal of penicillin G from aqueous solutions.

Conclusion

The results showed that the removal efficiency of penicillin G by single-walled and multi-walled nanotubes in the optimal conditions (initial concentration=50 mg/L, pH=5, adsorption dose= 0.8 g/L, contact time= 105 minutes, mixing speed= 300 rpm and temperature= 10°C) was 68.25% and 56.37%, respectively. Adsorption capacity of the single-walled and multi-walled carbon nanotubes was 141 mg/g and 119 mg/g, respectively. According to the results, it was found that single-walled and multi-walled carbon nanotubes can be used as an effective adsorbent in the removal of penicillin G from aqueous solutions.

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Ethical issues

The author hereby certify that all data collected during the research are as expressed in the manuscript, and no data from the study has been or will be published elsewhere separately.

Competing interests

The authors have declared that they have no conflicts of interest.

Authors' contribution

All authors contributed in data collection, analysis, and interpretation. All authors reviewed, refined, and approved the manuscript.

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