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Application of Alumina-coated Carbon Nanotubes in Removal of Tetracycline from Aqueous Solution

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Authors' contributions

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

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ABSTRACT

The alumina-coated multi walled carbon nanotubes (Al_2O_3-coated MWCNTs) was used for removal of Tetracycline (TC) from aqueous solution in batch systems. The adsorption of TC occurred by studying the effects of adsorbent amount, TC concentration, contact time and temperature. The results suggested the adsorption capacity increased with increasing temperature. The equilibrium adsorption data were analyzed using three widely applied isotherms: Langmuir, Freundlich and Temkin. The results revealed that Langmuir isotherm fit the experimental results well. Kinetic analyses were conducted using pseudo-first and second-order models and the intraparticle diffusion model. The regression results showed that the adsorption kinetics were more accurately represented by pseudo-second-order model.

Keywords: Tetracycline; alumina-coated multi-wall carbon nanotube; adsorption; kinetics; isotherms.

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1. INTRODUCTION

In the last decades, the presence of emerging contaminants in different types of water appeared as a new environmental threat which needs to be faced by several governments around the word [1,2]. Pharmaceutical substances and personal care products are an emerging class of aquatic contaminants that have been increasingly detected in ground and surface water [3,4]. Generally, pharmaceuticals reach waterways through the discharge of wastewaters and effluents on environment, which often are not properly treated [5]. On the other hand, it was proved that when pharmaceuticals reach sewage wastewater treatment plants (SWTP), they are not completely removed [6,7]. The tetracycline (TC) group is one of the most commonly used antibiotics worldwide, which finds wide applications in human therapy and the livestock industry, and is difficult to be metabolized [8,9]. A large extent (up to 72%) of TC was excreted with unmetabolized form from human beings and animals [10,11]. Removing antibiotics is difficult and requires expensive process. Physical and physico-chemical techniques have proved their efficiency for this purpose [10]. Among the Physical techniques adsorption, flocculation, electro-flocculation, reverse osmosis, ultrafiltration, coagulation have been applied to remove recalcitrant pollutants [12,13]. Among the techniques, adsorption of TC to different sorbents is believed the easiest and cheapest one [14]. Inorganic (aluminum oxide [15], Fe–Mn binary oxide [16], zeolite beta [17], goethite [18], montmorillonite [19,20], cinnamon soil [21], kaolinite [22], illite [23] and swelling clay minerals [24], biological (algal ponds [25], nitrifying granules [26], bio-char [27], activated sludge system [28], synthetic (chitosan [29], and composite sorbents ($MnFe_2O_4$/ activated carbon magnetic composite [30], titania–silica composed materials [31] are widely used for the adsorptive removal of TCs. Nanotechnology has been successfully applied in the field of pollution abatement to remove of toxic contaminants, remediate of groundwater, etc [32,33]. The their high specific surface area, environmental benignity and capabilities as catalytic degradation of contaminants through changing reaction mechanism [34,35]. Due to their large specific surface area, small size, and hollow and layered structures, Carbon Nano Tube (CNT) have been proven to possess great potential as superior adsorbents for removing many kinds of organic and inorganic contaminants [36,37]. The uses of CNT as support of metallic oxides have still been reported. The advantages of this chemistry are that materials with higher sorption capacity, larger surface area and supported metallic oxides with better orientation degree with regard to net metallic oxides can be obtained [15,38]. This work aims to investigate the adsorption behavior of alumina supported on carbon nanotube for the treatment of TC aqueous solutions. For this purpose MWCNT/Al_2O_3 composites were synthesized and characterized. The effect of contact time, dosage of adsorbent and initial concentration of TC was studied.

2. MATERIALS AND METHODS

2.1 Chemicals

The tetracycline hydrochloride (Molecular weight: 480.9, Molecular formula: $C_{22}H_{24}N_2O_8\cdot HCl$) was purchased from Sigma-Aldrich, USA. The chemical structure of Tetracycline is presented in Fig. 1. The distilled water was used to prepare the stock solution of tetracycline. Other chemical used in this study were prepared from Merck, Germany.

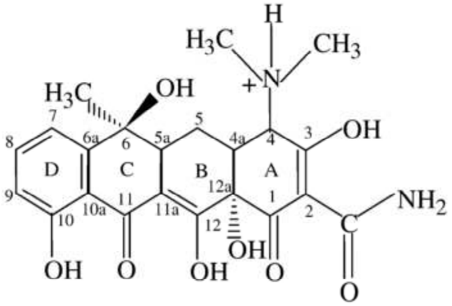

Fig. 1. The chemical structure of tetracycline hydrochloride

2.2 Adsorbent Preparation

The multi-wall carbon nanotubes (MWCNTs) used in this study were of more than 98% purity and provided from Research Institute of Petroleum Industry (RIPI), Tehran, Iran). Further purification of the MWCNTs was accomplished by stirring them in concentrated nitric acid at 70℃ for 12 h, followed by filtering and washing with distilled water, and then drying at 110℃ for 6 h. Then, the MWCNTs were oxidized by refluxing with 50% nitric acid at 120℃ for 12 h under stirring conditions. The product was then filtered and rinsed with doubly distilled water and dried overnight in the oven. The preparation of

Al_2O_3/MWCNT composites was accomplished as follows: All glassware was cleaned by aqua regia freshly prepared prior to use. Typically, some amounts of MWCNTs were dispersed into deionized water and magnetically agitated 6 h at which acceptable level of dispersion was observed. A specific amount of aluminum nitrate was properly dissolved in deionized water. Carefully, the aluminum nitrate solution was drop wise added into dispersed MWCNTs. Between consecutive drops, there should be an appropriate time for the aluminum to reach, appropriately disperse and engage to the MWCNTs' surface. After that, the suspension was dried at 110℃. The obtained material was heated up to 400℃ for 90 min, where the pyrolysis process resulted in alumina formation supported onto the MWCNTs' surface [39,40].

The surface area of the samples were determined by using Micromeritics ASAP 2020 volumetric adsorption analyzer. The BET surface area was measured from the adsorption isotherm using Brunauer–Emmett–Teller equation. The surface morphology of the MWCNTs and Al_2O_3-coated MWCNTs were examined using a environmental scanning electron microscopy (ESEM) instrument (Philips XL30 ESEM-TMP) and also a X-ray diffraction spectrometer (Philips-X'Pert Pro MPD) with the conditions: generator voltage of 40 kV, tube current of 40 mA, scan step size of 0.02°, and the scan range of 5–90°.

2.3 Adsorption Experiment

Adsorption experiments were conducted by varying contact time, adsorbent dose, temperature, initial TC concentration at pH fixed 7 under the aspects of thermodynamic study, adsorption isotherms and adsorption kinetics. The experiments were carried out in 200 mL Erlenmeyer flasks and the total volume of the reaction mixture was kept at 100 mL. The pH of solution was maintained at a desired value byadding 0.1 M NaOH or HCl. The flasks were shaken for the requiredtime period in a water bath shaker. The kinetic studies was carried out by agitating 200 mL flasks containing 1 g/L of adsorbent and 100 mL TC solutions of different concentrations i.e. from 10 to 100 mg/L, in water bath shaker. The mixture was agitated at 180 rpm at 25℃. The contact time was varied from 5 to 120 min. The initial and equilibrium concentration of TC in solution was determined by HPLC. In the HPLC analysis and a SPD-10A UV–Vis detector at maximum absorption wavelength of 365 nm which was detemined using a Shimadzu UV-1700 spectrophotometer to scan from 200 to 800 nm. A 30:70 (v/v) acetonitrile and 0.01 M aqueous oxalic acid mixture was used as mobile phase at room temperature with a constant flow rate of 1.0 mL min^{-1}. The injection volume was 10 ml. The retention time of TC hydrochloride was 4 min. All of adsorption experiments in this study were performed in triplicate and the results were given as average.

The adsorption capacity of the Al_2O_3-coated MWCNTs at the equilibrium state was calculated as follows [41,42]:

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

where q_e (mg/g) is the TC adsorption capacity, V (L) is the volume of solution, M (g) is the weight of adsorbent, C_0 and C_e (mg/L) denote the initial and equilibrium concentrations of TC, respectively. All experiments were conducted in duplicates and the average values were adopted for the analysis.

3. RESULTS AND DISCUSSION

The MWCNT surface presents polar groups, such as hydroxyl or carboxyl groups which are able to interact, by hydrogen bonding with the Al_2O_3 surface. The presence of these groups onto MWCNT surface is consequence of acid treatment employed during synthesis process to dissolve the catalysts [40,43]. The Al_2O_3 wrapping layer surrounds the MWCNT surface, in which the oxide layer stays fixed. However, some agglomerate Al_2O_3 particles were also observed in the material, as can be seen in Fig. 2. Also specific surface area of the adsorbent used in this study was 441.2 m^2/g.

Figs. 3a and 3b shows the XRD patterns of MWCNTs and Al_2O_3-coated MWCNTs. It was observed that the two peaks corresponding to the structure of MWCNTs (Fig. 3a) also exist in the XRD pattern of the Al_2O_3-coated MWCNTs (Fig. 3b). The broad peak of MWCNTs in XRD was seen narrow in the XRD of the composite because MWCNT in the composite was coated with alumina. The observed XRD of the synthesized Al_2O_3-coated MWCNTs was in convenience with that reported for the synthesis of alumina carbon nanotube composite using thermal pressure method.

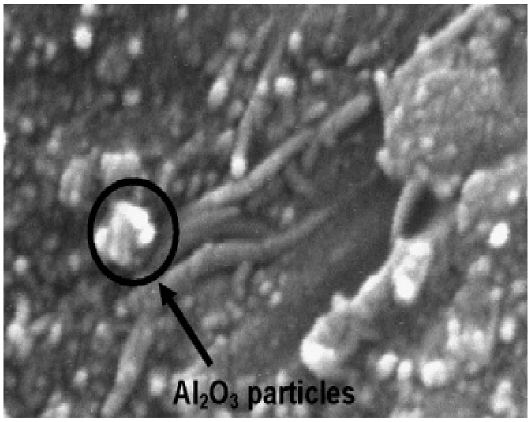

Fig. 2. SEM photograph of Al_2O_3-coated MWCNTs

3.1 Effect of Adsorption Contact Time and Initial TC Concentration

Effect of contact time for the removal of TC by the Al_2O_3-coated MWCNTs at Co=10 to 100 mg/L for the adsorbent dose of 1 g/L showed rapid adsorption of TC in the first 30 min and, thereafter, the adsorption rate decreased gradually and the adsorption reached equilibrium in about 60 min as shown in Fig. 4. Initially, a large number of vacant surface sites are available for adsorption. The adsorption rate is very fast thus rapidly increases the amount of adsorbates accumulated on the Al_2O_3-coated MWCNTs surface mainly within the first 30 min of adsorption. As a result, the remaining vacant surface sites are difficult to be occupied due to formation of repulsive forces between the TC molecules on the solid surface and in the bulk phase [44,45]. Also Fig. 4 describes the effect of TC initial concentrations on the removal percentage by Al_2O_3-coated MWCNTs. The TC removal percentage via Al_2O_3-coated MWCNTs was found to decrease with increase in initial concentrations. This may be due to the vacant sites are filled up and no further adsorption occurs due to saturation of vacant sites of adsorbent [46,47].

3.2 Effect of Adsorbent Dosage

The adsorption percent at various doses of Al_2O_3-coated MWCNTs from 0.01 to 2 g/L is shown in Fig. 5. Increasing the adsorbent dose to 1 g/L increase the adsorption percent of TC, which is due to the increasing in adsorption sites of adsorbent material resulting from increasing of surface area of adsorbent [48]. However, further increase of adsorbent dosage does not afford exhaustive adsorption of TC. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [49].

3.3 Adsorption Isotherms Study

Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at different temperature. Freundlich, Langmuir and Temkin isotherms are the earliest and simplest known relationships describing the adsorption equation.

3.4 Langmuir Isotherm

The Langmuir isotherm is derived on the assumption of mono-layer adsorption on a homogenous surface. It is expressed by [50,51]:

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

where C_e is the equilibrium concentration (mg/L), q_e is the amount of TC adsorbed (mg/g), q_m is q_e for complete monolayer adsorption capacity (mg/g), and K_L is the equilibrium adsorption constant (L/mg).

The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L [52]:

$$R_L = \frac{1}{1+K_L C_O}$$

where K_L is the Langmuir constant and C_0 is the lowest initial TC concentration (mg/L).

The Freundlich isotherm is suitable for non-ideal adsorption on heterogeneous surfaces. The heterogeneity is caused by the presence of different functional groups on the surface, and several adsorbent–adsorbate interactions. The Freundlich isotherm is expressed by the following empirical equation [53,54]:

$$\text{Log } q_e = \frac{1}{n} \log Ce + \log K_F$$

Where q_e is the equilibrium TC concentration on the adsorbent (mg g^{-1}); C_e, the equilibrium TC concentration in solution (mg L^{-1}); and K_F is the Freundlich constant.

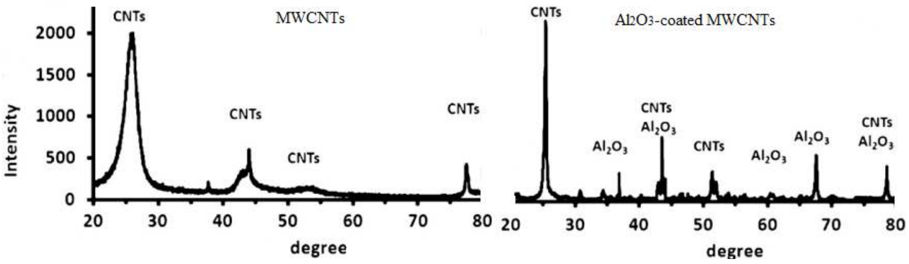

Fig. 3. X-ray diffraction of uncoated MWCNTs and Al_2O_3-coated MWCNTs

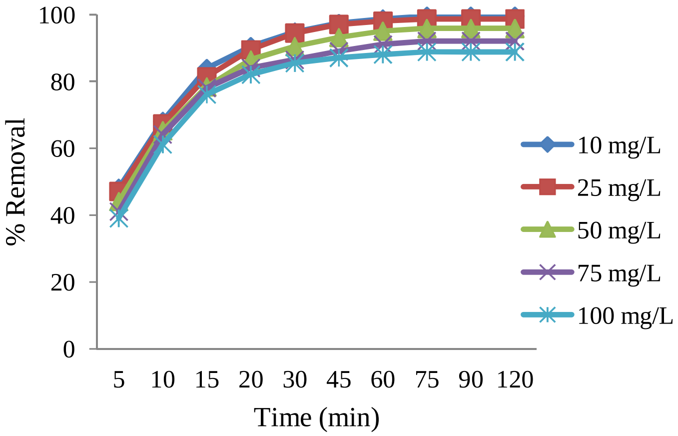

Fig. 4. Effect of contact time and initial TC concentration (pH =7, Adsorbent dosage 0.1 g/L and temperature = 25±3ºC)

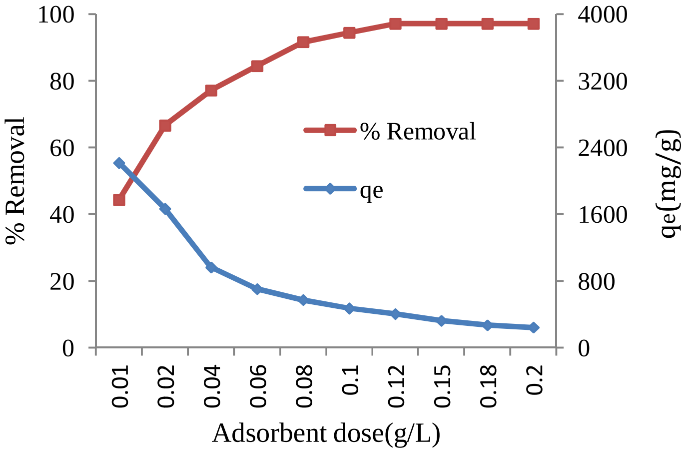

Fig. 5. Effect of adsorbent dosage on TC adsorption onto Al_2O_3-coated MWCNTs (C_0 = 100 mg/L, time = 60 min, pH = 7, temperature = 25±3ºC)

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent–adsorbate interactions. The adsorption is characterized by a uniform distribution of binding energies. The Temkin isotherm has been generally applied in the following form [55,56]:

$$q_e = \frac{RT}{b} \ln (AC_e)$$

And it can be linearized as [57]:

$$q_e = B \ln A + B \ln C_e$$

where B = RT/b, b is the Temkin constant related to heat of sorption (J/mol), A is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/(mol K)) and T is the absolute temperature (K).

The equilibrium isotherms was studied by varying the initial concentration of TC at temperure 273, 298 and 323 K under the conditions of pH 7.0, contact time of 60 min and adsorbent dose 0.1 g/L. The fitting results, i.e. isotherm parameters and the coefficient of determination, R^2, were shown in Table 1. The value of R_L for adsorption of TC indicated that the adsorption behavior of Al_2O_3-coated MWCNTs was favorable for the TC (R_L<1). According to a linear regression method, the Freundlich and Temkin isotherms were poorly suitability to the adsorption of Al_2O_3-coated MWCNTs in comparison to Langmuir isotherm. The validity of the Langmuir model suggested the TC uptake was due to monolayer coverage of solute particles onto the surface of the activated carbon and adsorption of each molecule has equal activation energy. All three models suggest that increasing temperature increased adsorption capacity, revealing that the adsorption is endothermic. The same behavior was observed by Balarak et al. [7].

3.5 Adsorption Kinetics

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic equations were used to test the experimental data. The pseudo-first-order kinetic model has commonly been applied in the following form [58]:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$

Where q_t is the adsorption capacity at time t (mg/g) and k_1 (min^{-1}) is the rate constant of the pseudo- first order adsorption, was applied to the present study of TC adsorption. The rate constant, k_1 and correlation coefficients of the TC under different concentrations were calculated from the linear plots of ln(q_e −q_t) versus t (Fig. 6a) and listed in Table 2. The correlation coefficients for the pseudo-first-order kinetic model are low. Moreover, a large difference of equilibrium adsorption capacity (q_e) between the experiment and calculation was observed, indicating a poor pseudo-first-order fit to the experimental data.

The pseudo-second-order kinetic model is expressed as [59]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{qe}$$

where $h = kq_e^2$ (mg g^{-1} min^{-1}) can be regarded as the initial adsorption rate as t→0 and k is the rate constant of pseudo-second- order adsorption (g mg^{-1} min^{-1}). The plot t/q_t versus t (Fig. 6b) should give a straight line if pseudo-second-order kinetics is applicable and q_e , k and h can be determined from the slope and intercept of the plot, respectively. At all studied initial TC concentrations, the straight lines with extremely high correlation coefficients (> 0.997) were obtained. In addition, the calculated q_e values also agree with the experimental data in the case of pseudo- second-order kinetics. These suggest that the adsorption data are well represented by pseudo-second-order kinetics and this supports the assumption that the rate-limiting step of TC onto Al_2O_3-coated MWCNTs may be chemical sorption or chemisorption. From Table 2, the values of the rate constant k decrease with increasing initial TC concentration for the Al_2O_3-coated MWCNTs. The reason for this behavior can be attributed to the lower competition for the sorption surface sites at lower concentration. At higher concentrations, the competition for the surface active sites will be high and consequently lower sorption rates are obtained. Similar phenomena have been observed in the adsorption of amoxicillin on Single Walled Carbon Nanotubes [60,61].

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber's intraparticle diffusion. The kinetic results were analyzed by the intraparticle model to elucidate the diffusion mechanism, which model is expressed as [62,63]:

$$q_t = k\, t^{1/2} + C$$

Where C is the intercept and k is the intraparticle diffusion rate constant, ($mg/gmin^{1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ as shown in Fig. 6c. The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate controlling step. The calculated intraparticle diffusion coefficient k values are listed in Table 2. The If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each concentration did not pass through the origin. This indicates that the intraparticle diffusion was not only a rate controlling step.

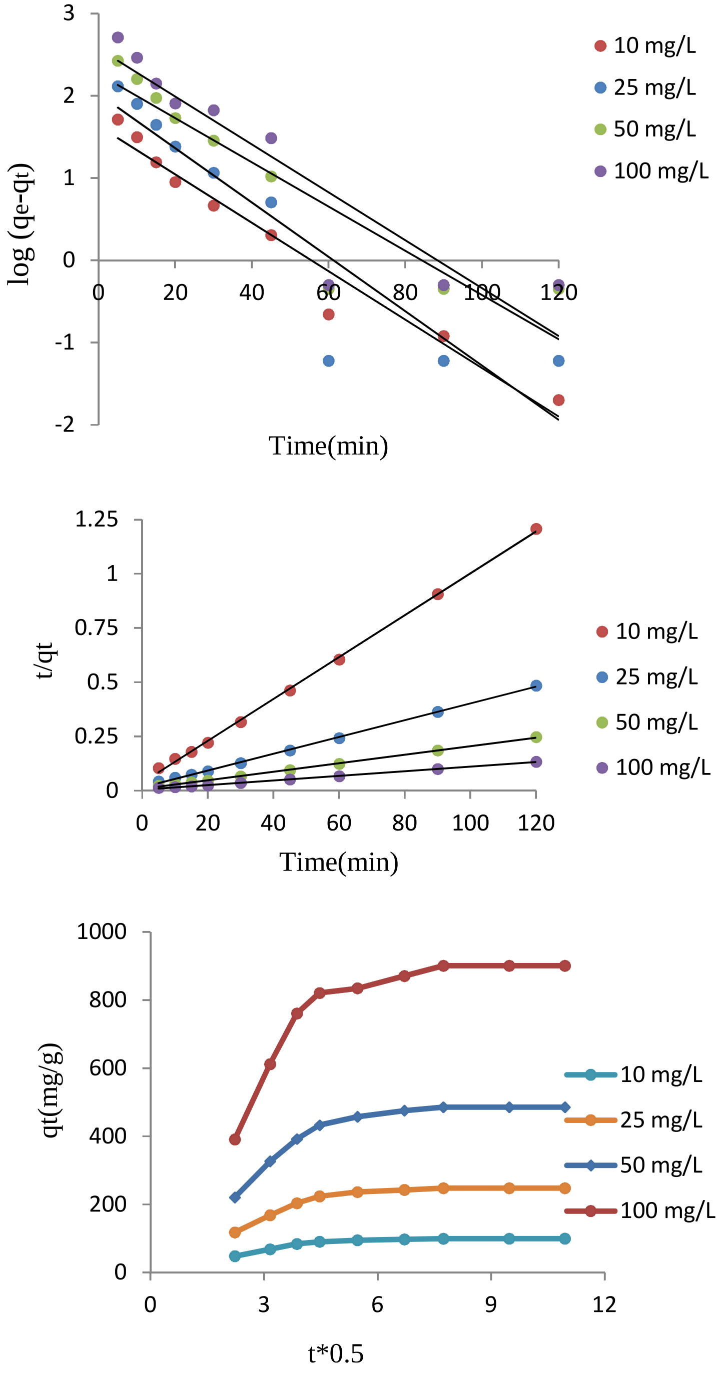

Fig. 6. Biosorption kinetics (a): pseudo first-order (b): pseudo-second-order (C): intraparticle diffusion

Table 1. The adsorption isotherms constants for the removal TC

	Langmuir model					Freundlich model			Temkin model		
Temp (K)	**$q_{e\ exp}$**	**q_m**	**K_L**	**R_L**	**R^2**	**n**	**K_F**	**R^2**	**B**	**A**	**R^2**
273	851.2	833.4	0.012	0. 45	0.998	2.81	59.36	0.842	47.69	12.84	0.799
298	874.3	855.6	0.031	0.59	0.997	3.17	72.11	0.858	53.46	9.424	0.808
323	895.7	876.8	0.056	0.74	0.999	3.64	84.48	0.817	61.87	7.436	0.824

Table 2. Kinetic parameters for TC adsorption onto Al_2O_3-coated MWCNTs

	Pseudo second-order model				Pseudo first-order model			Intraparticle diffusion		
C_o	**q_e,exp (mg/g)**	**k_2**	**R^2**	**$q_{e\ cal}$**	**K_1**	**R^2**	**$q_{e\ cal}$**	**K**	**C**	**R^2**
10	99.4	0.0041	0.997	94.46	0.094	0.841	56.24	0.061	0.805	0.736
25	247.75	0.0059	0.998	249.8	0.042	0.823	214.7	0.122	1.245	0.759
50	485.5	0.0074	0.998	474.2	0.035	0.796	402.8	0.179	1.517	0.784
100	901.2	0.0088	0.997	889.5	0.019	0.803	745.2	0.252	1.985	0.802

4. CONCLUSION

The batch removal of TC from aqueous solution by using Al_2O_3-coated MWCNTs was studied. The effect of temperure, initial concentration of TC, Al_2O_3-coated MWCNTs content and contact time on the removal of TC was also investigated. The Langmuir adsorption isotherms are found to provide the best fit to the experimental data with a maximum adsorption capacity of 855.6 mg/g at room temperure. The adsorption kinetics can be determined by pseudo-second-order kinetics. The results of the present investigation indicate that the Al_2O_3-coated MWCNTs has potential for use in removing TC antibiotic from aqueous solutions.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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