

Removal of atenolol from aqueous solutions by multiwalled carbon nanotubes modified with ozone: kinetic and equilibrium study

Bahare Dehdashti, Mohammad Mehdi Amin, Hamidreza Pourzamani, Lida Rafati and Mehdi Mokhtari

ABSTRACT

The aim of study is removal of atenolol from aqueous solutions by multiwalled carbon nanotubes modified with ozone. The design of the experiment was adopted across four levels with the L16 matrix arrangement. The factors influencing atenolol adsorption include changes in the pH value, contact time, the dose of the modified multiwall carbon nanotube, and the initial concentration of atenolol in the solution; these factors were evaluated along with the extent of their influence on removal efficiency. Data analyses were performed by the Design Expert 6 software. The results indicated that the pH, contact time, adsorbent dose, and the initial concentration were 7, 20 min, 0.15 g/L and 1 mg/L, respectively. In this state, the removal efficiency was calculated to be 75.79%. The maximum adsorption capacity was obtained as 5.05 mg/g under optimal conditions. The data were analyzed using adsorption models obtained from the isotherm fitting tool software. The results suggested that the data had a greater congruence with the Freundlich model (corrected Akaike information criterion = 2.58). Furthermore, the kinetics of the reactions followed pseudo second order kinetics ($R^2 = 0.95$). Based on this study, it can be concluded that modified multiwall carbon nanotubes enjoy high potential and efficiency as adsorbents for the removal of atenolol from aqueous solutions.

Key words | atenolol, modification, multiwall carbon nanotube, ozone

Bahare Dehdashti

Mehdi Mokhtari (corresponding author)
Environmental Science and Technology Research Center, Department of Environmental Health Engineering, School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran
E-mail: mhimokhtari@yahoo.com

Mohammad Mehdi Amin

Hamidreza Pourzamani
Environment Research Center, Research Institute for Primordial Prevention of Non-communicable Disease, Isfahan University of Medical Sciences, Isfahan, Iran and Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran

Lida Rafati

Research Center for Health, Safety and Environment (RCHSE), Alborz University of Medical Sciences, Karaj, Iran

INTRODUCTION

Drugs are among the essential and inseparable elements of modern human life. The presence of these contaminants in the environment is one of the primary concerns of the world today (Metcalf *et al.* 2003). The very high solubility of drugs in water causes their adsorption by target cells in human bodies, animals, and plants. Furthermore, high resistance to biodegradation has resulted in their non-biodegradable nature under normal conditions. They thus require special reactions under special conditions for degradation (Sayadi *et al.* 2010). The entrance of these contaminants into the food cycle and the drug resistance caused by them provide important reasons for the examination and monitoring of the environment, and bringing about various effects in terms of health and the environment

(Kümmerer 2004). Pharmaceutical compounds change into active compounds once again as they enter the environment, through the metabolic processes performed by microorganisms, especially bacteria (Carballa *et al.* 2004). Atenolol is a drug belonging to beta-blockers, which is used for controlling and treating hypertension, reducing the intensity of heart attacks, and controlling some forms of arrhythmia (Divya & Narayana 2014). Limited metabolism by the human body has led to a major part of atenolol being non-metabolized during excretion (Hu *et al.* 2015). Urban wastewater is, therefore, contaminated with drug contaminants, which change according to the time, site, and their type. In addition, given the presence of strict rules with high standards, studies conducted in European countries have

confirmed the fact that conventional water treatment has not been able to completely remove pharmaceutical contaminants (Zuccato *et al.* 2006; Schuster *et al.* 2008). Activated sludge processes, oxidation with ozone (Wilde *et al.* 2014), oxidation with light (Isarain-Chávez *et al.* 2011), the Fenton detector method (Hu & Cheng 2015), membrane filtration (Homem & Santos 2011), reverse osmosis (Urutiaga *et al.* 2013), adsorption (Sedaghat 2014; Rafati *et al.* 2016; Rafati *et al.* 2017) and activated carbon (Sotelo *et al.* 2012) have been used as conventional methods for drug removal. In spite of their advantages, conventional methods of drug removal have several disadvantages which include high degradation, the stability of wastewater toxicity, expensive facilities, high energy consumption, production of secondary products, and complex reaction paths (Zhao *et al.* 2008; Sotelo *et al.* 2012; Samadi *et al.* 2014; Wang *et al.* 2015). The creative use of nanoparticles for the treatment of industrial wastewaters is one of their potentially useful applications. The removal of contaminants and the recycling of treated water results in a significant reduction in cost, time, and workload in industries, and in turn have improved environmental protection (Savage & Diallo 2005). Carbon nanotubes have been one of the most important topics in nanotechnology in recent years. These nanotubes are a new member of the carbon family, which were discovered in 1993 (Iijima & Ichihashi 1993). These materials have unique physicochemical properties and have a greater adsorption capacity than other compounds such as graphite carbon (Rahmani *et al.* 2010). As they arrange themselves as graphite lamellae, weak intermolecular van der Waals forces are developed, causing the effective adsorption of compounds. Flat type with polar properties and superficial electric charge with π bands and free electron pairs, in particular, have conferred a greater adsorbability on the surface of carbon nanotubes (Augusto *et al.* 2010). The modification of these nanomaterials by sodium hypochlorite (NaOCl) solution to enhance the adsorption of benzene, toluene, ethyl benzene, and para-xylene (BTEX) was performed in 2010 (Su *et al.* 2010). Based on another study in 2008, out of HCl, H₂SO₄, HNO₃, and NaOCl solutions for enhancing the adsorption of benzene, toluene, and BTEX from aqueous solutions, NaOCl had the most effective role (Lu *et al.* 2008). The advantage of using ozone in the modification of these nanomaterials is related to its high performance, short duration of modification, and its exemption from any form of environmental contamination. Water salting can, however, be mentioned as one of its disadvantages (Pourzamani *et al.* 2015). The extended chemical formula of atenolol indicates that the hydroxyl functional group and the benzene

ring in its structure play a significant role in the adsorption process (DellaGreca *et al.* 2009). Note that the multiwall carbon nanotubes are reusable, and in order to reuse them, desorption experiments can be conducted using methanol, ethanol, sodium hydroxide, and acetic acid; the application of these adsorbents is, therefore, economically justifiable (Afkhami *et al.* 2010). This study was conducted with the aim of investigating the ability of treatment by ozone through the modification of the surface and the improvement of the adsorption capacity of multiwall carbon nanotubes as a new method in a batch system at the laboratory scale. This research has dealt with the examination of the potential uses of multiwall carbon nanotubes in removing the atenolol pharmaceutical contaminant from aqueous solutions and the determination of its importance and its optimal conditions (pH, dose of nanomaterials, initial concentrations of atenolol, and contact time).

MATERIALS AND METHODS

Materials

Atenolol (C₁₄H₂₂N₂O₃), which was used in this study, was purchased from the Sigma Aldrich Co. with a purity of $\geq 98\%$. Multiwall carbon nanotubes, made by Cheap Tubes Co., USA, were used as an adsorbent; their specifications are provided in Table 1. NaOCl, which was required for the modification of nanotubes with purity percentage of 70%; HCl, with a purity percentage $\geq 37\%$; and sodium hydroxide, with a purity percentage of $\geq 98\%$, were purchased from Merck Co., Germany. All of the solutions in this experiment were prepared by deionized water.

Table 1 | Properties of carbon nanotubes

Properties	Unit	Amount
Outer diameter	nm	<8
Length	μm	>10
Purity	Wt%	>95
Electric conductivity	s/cm	>100
Special surface area	m ² /g	>500
Ash	Wt%	<1.5
Pore volume	cm ³ /g	Micropore = 0.0784 Mesopore = 0.3710

Preparation of the adsorbent

Firstly, solutions of 30% and 60% NaOCl were prepared in the form of 75 mL NaOCl + 250 mL H₂O and 150 mL NaOCl + 250 mL H₂O, respectively. In order to ensure that NaOCl would have no effect on the procedure of modification, distilled water was also used as another alternative. The nanotubes were brought into contact with the solutions of interest for 2 hours on a stirrer at 300 rpm. Next, after 5, 15, and 20 minutes, the solutions were exposed to ozone by an ozone generator device with an intensity of 80%. The ozone reactor consists of a kind of Pyrex with a height of 16 cm and inner diameter of 10 cm that is connected to an ozone generator (OWA-1000, Japan) and the amount of ozone capacity was 80%; also the concentration of ozone in the off-gas streams was destroyed in a 2% KI solution. After that, the nanotubes were washed with distilled water several times until the pH value reached a neutral level. They were then placed in an oven at 70 °C or on a heater at 70 °C in order to dry the nanotubes. Eventually, to prevent the effect of humidity, the nanotubes were kept in a desiccator.

Experimental conditions

In order to prepare the stock solution of 1,000 mg/L of atenolol, 100 mg of pure atenolol was weighed carefully, followed by dilution using deionized water. This substance can dissolve in water under 25 °C. The experiments were performed in 100 mL containers containing 50 mL of the sample. The examined parameters in this research were chosen according to conducted studies and similar works. The initial concentrations of the solutions required for each stage of the experiment were selected as 0.5, 1, 5, and 10 mg/L. Next, the pH value of the solutions was adjusted to 2, 4, 7, and 11 (the adjustment of the pH value was conducted using HCl (0.1 M) and NaOH (0.1 M) by a pH meter (Cyberscan pH1500, Thermo Fisher Scientific Inc., The Netherlands). A certain amount of the adsorbent was added to the solutions at each stage in proportion with the design of the experiment, which involved adding as much as 0.05, 0.1, 0.15, and 0.2 g/L. After this, the solutions were placed on a stirrer (Orbital Shaker, Model OS 625) and brought into contact with the adsorbent at 5, 20, 60, and 90 minutes at the rate of 250 rpm. Alongside the samples, a control sample was also taken into account into which no adsorbent was added in order to ensure that the reduction in the concentration of atenolol in the solution was only a result of

adsorption on the adsorbent and its concentration did not decrease in response to adsorption into the bottle's glass or through evaporation. Once they were passed through a filter (CA0/22) and the particles of the nanotube were separated, the samples were centrifuged for 10 minutes by a centrifuge at 10,000 rpm (Universal 320, Hettitech), and eventually, the amount of atenolol following the adsorption was read by a high pressure liquid chromatography (HPLC) device.

Chemical analysis

In order to measure the concentration of samples before and after the treatment, an HPLC device was used. The HPLC device used in this study was the Waters model with a UV-486 detector at a wavelength of 231 nm, stationary phase (column) (250 × 4.6 mm; 5 μm) C18-Waters-spbcri-sorb[®], an oven temperature of 25 °C, and the Melenium 32 software. The mobile phase of the HPLC device was a combination of 0.01 M potassium dihydrogen orthophosphate with a pH value = 3.5, and acetonitrile with a volumetric ratio of 60:40, an isocratic method with a flow rate of 1 mL/minute and a sample injection volume of 20 μL. The data obtained from plotting the calibration curve of atenolol within the concentration range of 0.1–10 mg/L in the water matrix suggested the linearity of the measurement method, with a correlation coefficient (R^2) as large as 0.99.

Data analysis and design of experiment

In this study, in order to optimize the process of atenolol adsorption by modified nanotubes, four factors influencing the adsorption process—the initial concentration, the adsorbent's dose, the pH value, and the contact time—were chosen as arrays. Each of these arrays had four levels (Table 2) determined using Design Expert 6 software (DOE 6), Stat-Ease, Inc., USA (Amin et al. 2014). The proposed design of the experiment method is the 'L16'

Table 2 | Controlling factors and their levels

Factors	Level 1	Level 2	Level 3	Level 4
Atenolol concentration (mg/L)	0.5	1	5	10
Adsorbent dose(mg/L)	50	100	150	200
Contact time (min)	5	20	60	90
pH	2	4	7	11

method, which has been mentioned in Table 4 along with the results of the experiments. Finally, the data were investigated by the DOE 6 software and the optimal removal conditions were determined.

The effect of the concentration of adsorbate and adsorption isotherm

An isotherm study was evaluated for atenolol adsorption by multiwalled carbon nanotubes (MWCNT) in optimal condition, with an initial adsorbate concentration of 0–10 mg/L, an adsorbent dose of 0.15 g/L, a contact time of 20 minutes, and a pH value of 7. The water solubility of atenolol was estimated as 300 mg/L at a pH value of 7. The isotherm fitting tool software ISOFIT was used to fit the isotherm parameters within the experimental data. ISOFIT is a software program that fits the isotherm parameters to the experimental data via the minimization of a weighted sum of squared error (WSSE) objective function.

ISOFIT supports a number of isotherms, including: Brunauer–Emmett–Teller (BET), Freundlich, Freundlich with linear partitioning (F-P), generalized Langmuir–Freundlich (GLF), Langmuir, Langmuir with linear partitioning (L-P), Linear, Polanyi with linear partitioning, and Toth.

The effect of contact time and adsorption kinetics

In order to investigate the adsorption kinetics of atenolol, 0.0075 g of the adsorbent was added to 50 mL of atenolol solution with a concentration of 1 mg/L, where the pH values of the solutions were adjusted to the optimal value of 7. Next, the contact between the adsorbent and the atenolol solution happened after periods of 2, 5, 7, 10, and 20 minutes on a stirrer (orbital shaker, Model OS 625). The intensity of the stirrer rate was adjusted to 250 rpm. After that, the solution was placed on a centrifuge at 10,000 rpm for 10 minutes. Finally, the secondary concentration of the drug was read by the HPLC device.

RESULTS AND DISCUSSION

The effect of different methods of modification of MWCNT

According to Table 3, a modification by a 30% NaOCl solution and a contact time of 15 minutes with an ozone dose of 80% has the maximum effectiveness on the elevation of the efficiency of MWCNT, achieving atenolol removal of

Table 3 | Modified conditions of carbon nanotubes with ozone

Solutions	Concentration of solutions	Time (min)	Contact time with solution (hour)	Ozone dose (%)	Removal (%)
NaOCl	60	5	2	80	55.88
NaOCl	60	15	2	80	48.87
NaOCl	60	20	2	80	48.12
NaOCl	30	5	2	80	49.87
NaOCl	30	15	2	80	58.39
NaOCl	30	20	2	80	58.14
Distilled water	–	5	2	80	53.13
Distilled water	–	15	2	80	55.13
Distilled water	–	20	2	80	44.86

58.39%, in comparison to the other states. A study conducted in 2010 suggested that out of different chemical solutions, NaOCl has the greatest effect on the modification of MWCNT for BTEX removal (Su *et al.* 2010). Furthermore, it is speculated that carbon nanotubes at a solution concentration of 30% have a better performance than a solution concentration of 60% according to Table 3, which is due to the balanced concentration of chlorine in 30% concentration solution that opens the mouth of the nanotubes, thereby increasing the removal efficiency. In the 60% concentration solution, however, the level of the present chlorine increases, causing oxidation of the nanotubes. Furthermore, a prolongation of the modification time also caused diminished efficiency due to further exposure to chlorine. Use of NaOCl solution as an oxidant led to removal of large amounts of metals as impurities on the surface of carbon nanotubes (Su *et al.* 2010). The modification of carbon nanotubes with ozone gas is a relatively new method that enjoys the advantages of high efficiency, low cost, and simple function (Pourzamani *et al.* 2014). Ozone gas causes the modification of the superficial characteristics of carbon nanotubes such as in the specific surface area, the volume of the pores, and the superficial functional groups (Li *et al.* 2008). Manchester and colleagues employed activated carbon modified with ozone for mercury removal and found that with the prolongation of modification time from 1 hour to 24 hours, the adsorption capacity declined from 60.4 to 3 µg/g (Manchester *et al.* 2008). Chiang and co-workers also modified activated carbon with ozone and concluded that the ozone results in elevation of specific surface area from 783 to 851 m²/g (Chiang *et al.* 2002).

Moreover, it directly leads to the development of carboxyl groups and other oxygen-containing groups such as hydroxyl, carbonyl, and ester at the end or inside the walls (Chiang *et al.* 2002). By oxidizing the carbon atoms on the surface of the nanotubes, ozone gas leads to opening of the tip of tubes (Manchester *et al.* 2008), the shortening of tubes (Liu *et al.* 1998), and development of pores across the nanotubes (Ziegler *et al.* 2005). The extent of each of these characteristics is contingent upon the nanotube properties, including the morphology of the tubes, such as micropores or the extent of graphite that exists in the nanotubes, along with the purity, the extent of attachment or bulking degree, and the diameter of tubes (Ziegler *et al.* 2005; Hemraj-Benny *et al.* 2008).

The results obtained for atenolol removal by the modified adsorbent

Atenolol removal efficiencies by the modified multiwalled carbon nanotubes (MMWCNT) and their adsorption capacities (q_e) under different initial concentrations of atenolol, different adsorbent doses, differing contact times, and varying pH values have been presented in Table 4. Furthermore, the effect of these factors and their interactions have been provided in Table 5.

The plots of atenolol adsorption by MMWCNT have been given in Figure 1(a)–1(d) in order to determine the optimal adsorption conditions.

The effect of changes in pH on adsorption of atenolol

Figure 1(a) shows the influence of different pH values on atenolol removal by the adsorbent. Furthermore, in this study, according to Table 4, at each stage, all the options (pH value, contact time, contaminant concentration, and adsorbent's dose) are variable, suggesting that a dramatic increase or decrease throughout the adsorption process represents the affectability of the process by all of the investigated parameters – just one variable has not been examined in isolation. According to Figure 1(a), within the pH range of 4–7, the removal efficiency has gradually increased, which can be due to the increase in the number of sites with a positive charge in the acidic solution and thus the electrostatic interaction between the adsorbent and the adsorbate (Zhou *et al.* 2001). Furthermore, according to other studies, functional groups affecting the adsorption process on modified carbon nanotubes increase in acidic environments (Lu *et al.* 2008). It is speculated that lower atenolol adsorption at pH values above 7 can be due to the low solubility of atenolol in alkaline environments, resulting in maximum adsorption

Table 4 | Design matrix and results of atenolol removal by MMWCNTs in different conditions

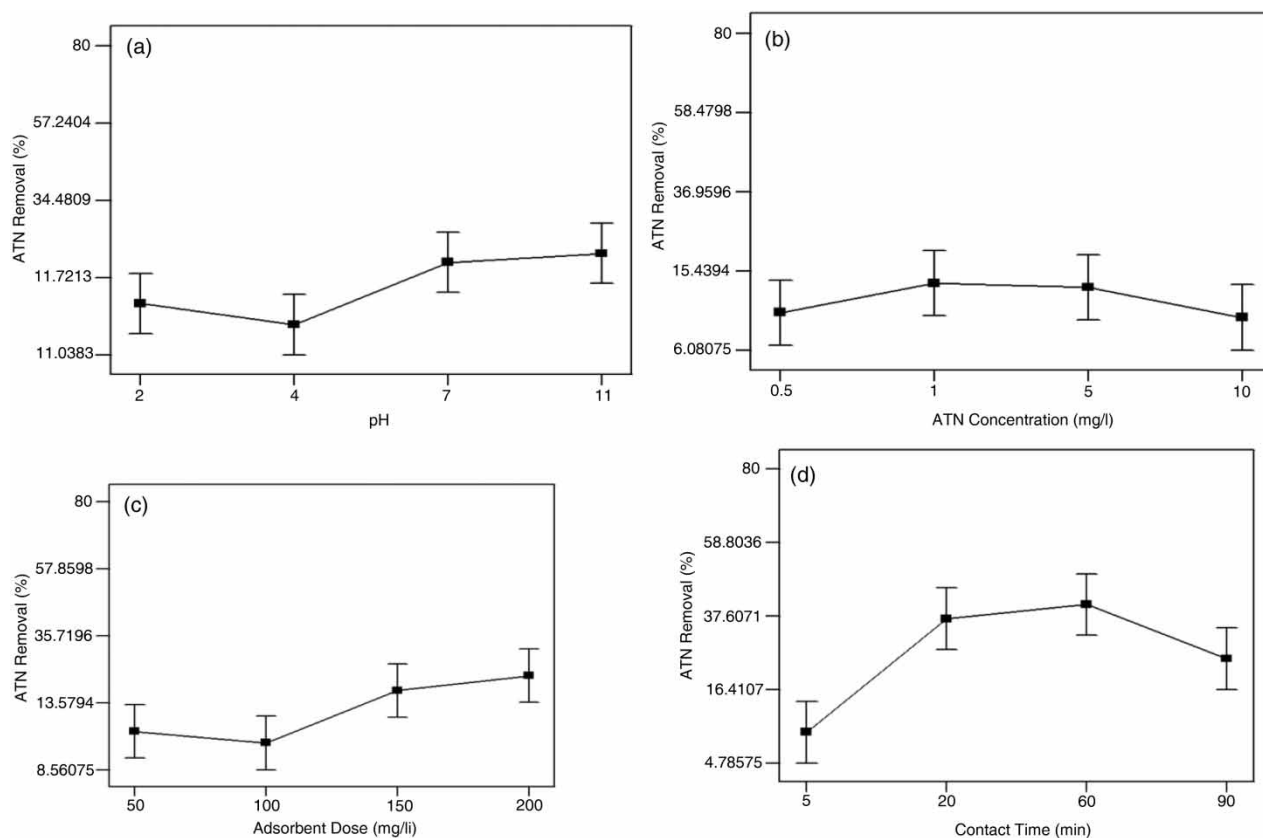
Run	Factors				Response		
	Atenolol concentration (mg/L)	Adsorbent dose (mg/L)	Time (min)	pH	Atenolol conc. at time <i>t</i> (mg/L)	Removal (%)	q_e (mg/g)
1	5	100	90	2	3.03	39.24	19.62
2	0.5	150	60	11	0.1	80	2.66
3	10	50	90	11	6.24	37.55	75.1
4	10	150	20	2	6.04	39.56	26.37
5	5	150	5	4	4.14	17.12	5.70
6	0.5	50	5	2	0.48	3.6	0.36
7	1	200	60	2	0.33	66.2	3.31
8	1	150	90	7	0.41	58.4	3.89
9	1	50	20	4	0.50	49.4	9.88
10	10	100	60	4	7.09	29.07	29.07
11	0.5	200	90	4	0.36	28	0.7
12	1	100	5	11	0.86	13.6	1.36
13	5	200	20	11	1.18	76.26	19.06
14	10	200	5	7	5.57	44.24	22.12
15	5	50	60	7	2.47	50.46	50.46
16	0.5	100	20	7	0.28	44	2.2

Table 5 | Effects of the factors and interactions for atenolol removal by MMWCNT

Factor/Interaction	Degrees of freedom	Sum of squares	Mean squares	F-value	P-value	% contribution
A: Adsorbent dose (mg/L)	3	2704.36	901.45	6.366×10^7	<0.0001	19.59
B: Atenolol concentration (mg/L)	3	534.43	178.14	6.366×10^7	<0.0001	3.87
C: Contact time (min)	3	6524.48	2174.83	6.366×10^7	<0.0001	47.26
D: pH	3	2371.52	790.51	6.366×10^7	<0.0001	17.18
AB interaction	3	1671.22	557.07	6.366×10^7	<0.0001	12.11
Lack of fit	0	0				0
Pure error	16	0	0			0
Residuals	16	0	0			0

(Ghobadi *et al.* 2014). Therefore, pH = 7 has been chosen as the optimal value. In 2010, the adsorption by non-modified carbon nanotubes and carbon nanotubes modified with NaOCl was studied; in this study, the effectiveness of carbon nanotubes modified with NaOCl was determined. The results also indicated that these nanotubes have a better performance in acidic to slightly above neutral pH (Su *et al.* 2010). The most effective pH value for removal of diclofenac drug by MWCNT

modified with nitric acid was also observed at a pH = 5 (in the acidic pH range). As no significant difference was observed between the pH = 5 and 7, the pH value of 7 was chosen as the optimal value (Hu *et al.* 2015). For atenolol removal by graphene oxide, a high efficiency was observed at a pH value of 2 (Vuković *et al.* 2010). In the removal of benzene by MWCNT modified with ozone, a suitable pH value for the reaction was considered to be 5 (Pourzamani *et al.* 2015).

**Figure 1** | Effect of (a) pH, (b) initial adsorbate concentration, (c) adsorbent dose and (d) contact time on atenolol (ATN) removal by MMWCNT.

The effect of changes in the initial adsorbate concentration on atenolol removal

Figure 1(b) represents the trend of changes in the removal of atenolol in terms of the initial concentration of the contaminant. With the increase in the initial concentration of atenolol from 0.5 to 1 mg/L, the process followed an ascending trend with a mild slope. After that, it remained constant until the concentration of atenolol reached 5 mg/L, and then it declined. As they have limited adsorption sites, adsorbents become saturated more quickly with an increase in the initial concentration of the contaminant, thereby decreasing the removal efficiency. Furthermore, another reason for this can be attributed to the selective adsorption of the adsorbent by a certain type of contaminant (Zhou *et al.* 2001). For this reason, in such cases, there are specific sites for the adsorption of the contaminant on the adsorbent, where only these specific sites are involved in the adsorption process; other processes involved in adsorption including inter-particle diffusion or bulk diffusion are not influential. In addition, according to the design of experiment as the Taguchi method, it should be considered that the trend of removal is influenced not only by the initial concentration of the atenolol: it is believed that other factors including the diversity in the pH value or the contact time and the variable adsorbent doses also have influential impacts. In the investigation of atenolol removal in comparison to paracetamol by Iraqi cherry seeds (Ismael *et al.* 2014), it was found that the optimal value of atenolol in the adsorption process was 0.05 g; an increase in this value resulted in diminished adsorption efficiency, which is congruent with this study. These authors also found that the adsorption of atenolol on Iraqi cherry seeds enjoys a greater efficiency in comparison to paracetamol. This is because in similar adsorption situations, the high molecular weight of atenolol results in diminished polarity and its ionization in the solution. Consequently, the atenolol molecule is vertically adsorbed on the surface of the adsorbent, occupying small and selected sites of the adsorbent (Ismael *et al.* 2014). The high removal of the diclofenac drug from aqueous solutions by MWCNT modified with nitric acid also occurred at lower concentrations of the contaminant, i.e., 5 mg/L. After this, an ascending trend was observed until 12.5 mg/L, then it remained constant until 50 mg/L, and accordingly, the value of 50 mg/L was chosen as the optimal concentration (Hu *et al.* 2015). While using carbon nanotubes modified with cation surfactant for dye removal, the elevation of the dye concentration also resulted in diminished efficiency (Zhou *et al.* 2001). In this study, 5 mg/L has been chosen as the optimal initial concentration.

The effect of changes in dose (MMWCNT) on atenolol adsorption

Figure 1(c) reveals the effect of the adsorbent's dose on the trend of atenolol adsorption on MMWCNT. With an increase in the adsorbent's dose, due to an increase in the number of active sites, the increased contact area and in turn the developed electrostatic interaction result in an ascending trend in the adsorption performance. According to other studies, the removal of nitrate improves with the increase in the dose of functionalized carbon nanotube sheets due to an increase in the number of active available and at surface sites (Tofighy & Mohammadi 2012). Furthermore, the elevation of the dose of magnetic multi-walled carbon nanotube nanocomposites by 0.3–0.9 g/L increased the removal efficiency of cation dyes in aqueous solutions. At doses above 0.9 g/L in MWCNT, however, the removal of different dyes was negligible (Tofighy & Mohammadi 2012). In the investigation of the effect of MMWCNT in benzene removal from aqueous solutions, the optimal dose of the adsorbent was found to be 2 g/L, and there appeared to be a direct relationship between the elevation of the adsorbent's dose and the increased removal efficiency. This increase has been attributed to an increase in the number of active adsorption sites and the probability of collision of adsorbate particles with the adsorbent (Pourzamani *et al.* 2015). In this study, no significant difference was observed between 150 and 200 mg/L, so 150 mg/L was chosen as the optimal value.

The effect of changes in the contact time on atenolol removal

Figure 1(d) illustrates the effect of the changes in time on the atenolol adsorption performance. With a prolongation of contact time from 5 to 60 minutes, an ascending trend was observed in the adsorption process. After that, a descending trend occurred until 90 minutes had passed. The maximum removal of Eriochrome Black T was obtained on the magnetic multiwalled carbon nanotube nanocomposites within an optimal time of 78 minutes. Furthermore, the greatest removal of alkylbenzene sulfonate from aqueous solutions occurred at initial times of 45 minutes by functionalized MWCNT (COOH); after this point, the rate dropped. The reason behind this phenomenon was mentioned to be the rapid filling of adsorption active sites by the adsorbate at the initial times (Gong *et al.* 2009; Heibati *et al.* 2016). Moreover,

Table 6 | Summary of selected diagnostics for atenolol adsorbed by MMWCNT

Isotherms	AICc	R_y^2	R_N^2	M^2	Linearity assessment
Langmuir	10.94	0.997	0.748	5.84	Non-linear
BET	10.76	0.997	0.743	6.067	Non-linear
Linear	12.36	0.997	0.873	4.66×10^{-9}	Linear
F-P	20.30	1	0.920	26.51	Non-linear
L-P	10.94	0.997	0.748	5.84	Non-linear
Freundlich	2.58	0.999	0.853	9.45×10^{-3}	Uncertain
Toth	26.72	0.999	0.721	2.99	Non-linear
GLF	27.41	0.998	0.629	4.94×10^3	Non-linear
Polanyi-partition	29.01	0.997	0.996	1.94×10^2	Non-linear

AICc: multi-model ranking, R_y^2 : correlation between measured and simulated observation, R_N^2 : correlation between residual and normality, M^2 : Linssen measure of non-linearity.

in the study by on atenolol removal by a cherry seed, the best adsorption time that was achieved was 1 hour; after this, with the prolongation of the contact time, a descending trend was observed in the adsorption process, possibly due to the presence of negative charge space within 1 hour after the reaction (Ismael et al. 2014). In addition to the reasons mentioned for diminished performance of adsorption between 60 and 90 minutes, the effect of the other variable factors such as the initial concentration of atenolol or the adsorbent's dose, and the pH throughout the process can also be mentioned.

Furthermore, as shown in Table 5, significant statistical relationships have been obtained between the parameters by comparing the mean squares versus the experimental error. The study of these factors and the extent of their effects indicated that all of the five factors have a significant difference from zero at a confidence level of 95% (as probability > F is smaller than 0.05), and they have an influential role in the adsorption process. However, contact time has the greatest impact (47.26%) in atenolol removal by MMWCNT. On the other hand, the initial concentration of atenolol, with an effect of 3.87%, has the least impact. The order of the major factors and the important interactions between them in terms of the extent of effect of each factor in removal of atenolol by MMWCNT is as follows: initial concentration of atenolol < interaction between the initial concentration of atenolol and adsorbent's dose < pH value < adsorbent's dose < contact time.

Furthermore, the removal of atenolol by MMWCNT follows the following equation:

$$\begin{aligned} \text{Atenolol removal (\%)} &= 42.29 \\ &- (11.38 \times \text{adsorbent dose}) + (4.7 \times \text{atenolol concentration}) \\ &- (13.12 \times \text{contact time}) - (14.79 \times \text{pH}). \end{aligned}$$

Adsorption isotherm studies

In this study, ISOFIT was applied to the process involving the adsorption of atenolol by MMWCNT in the batch condition. Water solubility of atenolol was estimated as 300 mg/L at a pH value of 7. Table 6 summarizes some of the diagnostic statistics computed by ISOFIT, which are reported in the output file.

In Table 6 the corrected Akaike information criterion (AICc) values indicate that the Freundlich isotherm expression provides the best fit for the sorption data based on its lowest value of multi-model ranking. The Freundlich

Table 7 | Selected ISOFIT post regression output (Freundlich isotherm)

Parameter or statistic	ISOFIT result
Overall quality of fit	
WSSE	4.16×10^{-1}
RMSE	0.322
R_y	1
Parameter statistic	
kf	5.93
Parameter standard error	
kf	10.22
Test of assumptions Linssen (M^2)	
M^2	9.45×10^{-3}
Threshold	-
Assessment	Uncertain
Normality (R_N^2)	
R_N^2	0.853
Critical value	0.71
Assessment	Normal residuals
Runs test	
Number of runs	4
P-value	0.9
Assessment	No correlation
Durbin-Watson test (D)	
D	2.87
P-value	0.78
Assessment	No correlation

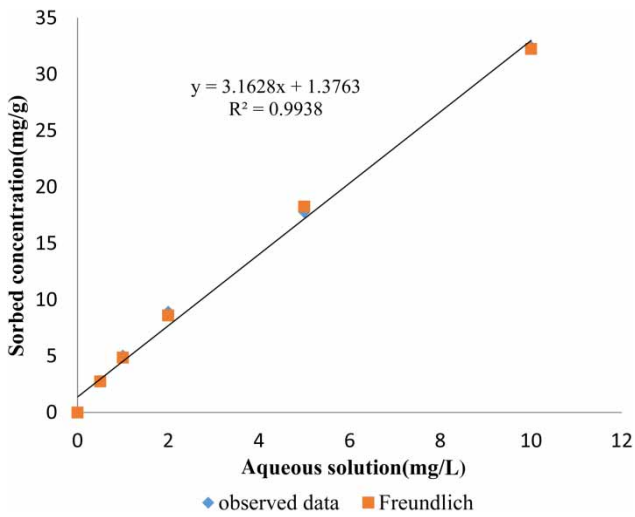


Figure 2 | Plot of fitted isotherm and observed data: Freundlich.

constant b was calculated to be less than unity for the majority of the adsorbate and the adsorbent combinations, indicating that the adsorption of the selected contaminants onto the MMWCNT samples is favorable. Uncertain regression techniques overcome many of the deficiencies associated with the trial-and-error and the linearization approaches to isotherm fitting. The performance of uncertain regression techniques, however, can be impeded by the presence of local minima or excessive parameter correlation.

Table 7 contains the selected ISOFIT output for the Freundlich isotherm. In Table 7, the Linssen measure indicates significant WSSE non-linearity near the optimal parameter values. The statistical measures such as R_N^2 and the Durbin–Watson Test (D) show normally distributed weighted residuals with no serial autocorrelation. The ISOFIT software provides two ‘standard’ measures for evaluating the isotherm fit, namely the root mean squared error (RMSE, Equation (1)) and the correlation between the measured and the fitted observations (R_y , Equation (2)).

$$\text{RMSE} = \sqrt{\frac{\text{WSSE}}{(m-p)}} \quad (1)$$

$$R_y = \frac{\sum_{i=1}^m (w_i S_{i,\text{obs}} - S_{\text{obs}}^{\text{avg}})(w_i S_i - S^{\text{avg}})}{\sqrt{\sum_{i=1}^m (w_i S_{i,\text{obs}} - S_{\text{obs}}^{\text{avg}})^2 \sum_{i=1}^m (w_i S_i - S^{\text{avg}})^2}} \quad (2)$$

where WSSE is the weighted sum of squared error; m is the total number of experimental observations; p is the number of isotherm parameters; w_i is the weight given to the observation i ; $S_{i,\text{obs}}$ is the i_{th} experimentally measured sorbed concentration; S_i is the i_{th} simulated sorbed concentration computed via an isotherm expression; $S_{\text{obs}}^{\text{avg}}$ and S^{avg} are the averages of the weighted measured and weighted isotherm simulated adsorbed concentrations, respectively.

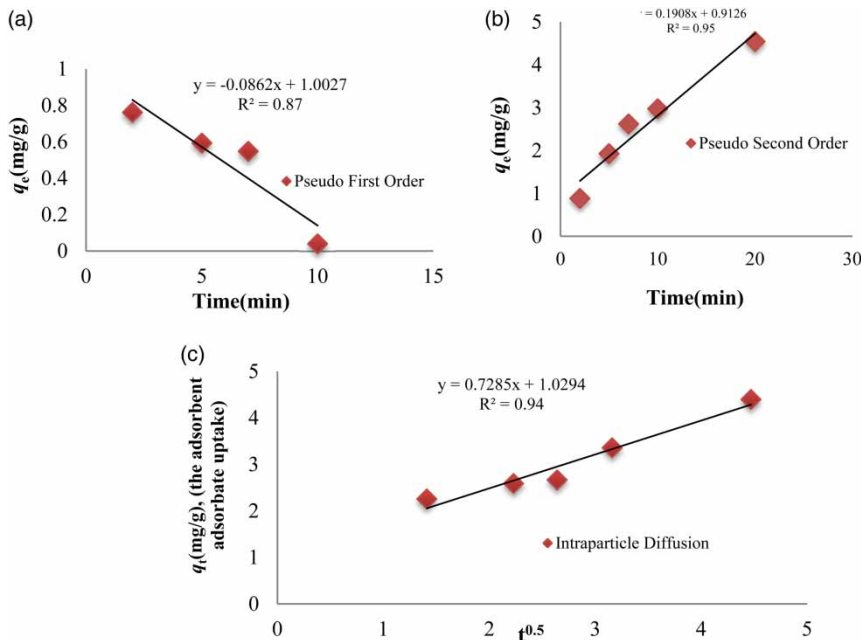


Figure 3 | Plot of pseudo first order, pseudo second order and intraparticle diffusion kinetics and observed data.

Table 8 | Kinetic parameters for atenolol adsorbed by MMWCNT

Kinetic Models	Parameters	Value
Pseudo first order	k_1 (rate constant)	0.0862
	q_{e1}	2.72
	R^2	0.87
Pseudo second order	k_2 (rate constant)	0.039
	q_{e2}	5.24
	R^2	0.95
Intraparticle diffusion	K_{dif} (rate constant)	0.58
	C_i (y intercept)	1.34
	R^2	0.94

In another study, the removal of atenolol by a magnetic composite clay polymer was congruent with the Freundlich model (Xiong *et al.* 2011). On the other hand, in another investigation for the removal of amoxicillin by MWCNT, the adsorption isotherm followed the Langmuir model (Samadi *et al.* 2014). Moreover, in the adsorption of cadmium by single-walled carbon nanotubes functionalized with L-cysteine, the Langmuir isotherm model was selected (Zazouli *et al.* 2013; Arya & Philip 2016). In the Freundlich model, the areas on the surface of the adsorbent's body are not homogeneous and have different adsorption abilities, and the model can be applied for describing heterogeneous systems (Gulnaz *et al.* 2011). Figure 2 reveals the Freundlich isotherm diagram of this study.

Kinetic studies of the reaction

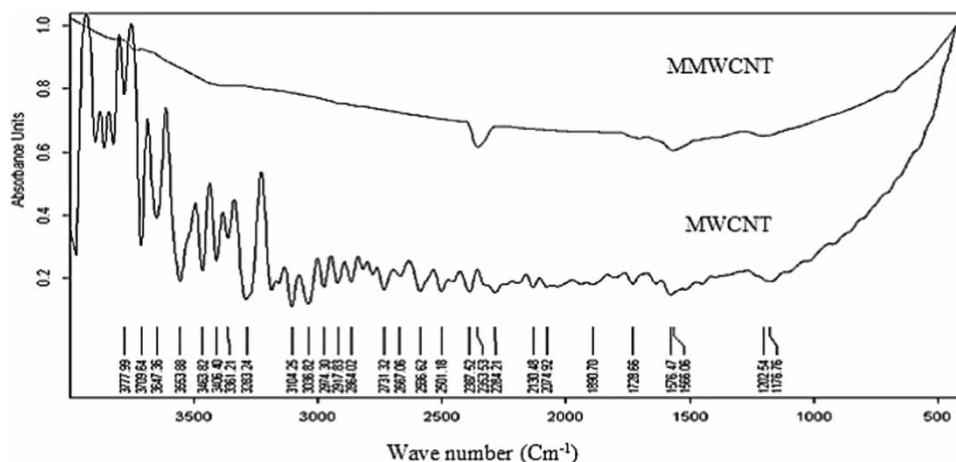
Adsorption kinetics state important information about the adsorption mechanism, the adsorption rate of the adsorbate, and the control of time in the adsorption process. In the

pseudo first order kinetic model, it is assumed that the rate of changes in the withdrawal of the adsorbate in relation to time is directly related to the changes in the initial concentration, and the amount of withdrawal of the adsorbent over time. On the other hand, in the pseudo second order model, two parallel or serial reactions affect the adsorption of the adsorbate on the adsorbent; the first model is rapid and reaches equilibrium quickly, while the second model has a slower rate and continues for a longer time. Second order reactions, therefore, progress at a rate in proportion with the second power of the reactant (Samadi *et al.* 2014). Intraparticle diffusion is another kind of kinetic model to identify the diffusion mechanism. In this model there are no baffles for transferring mass from solution to surface area (Behnamfard & Salarirad 2009). In this study, the kinetics of atenolol adsorption by carbon nanotubes modified with ozone followed pseudo second order kinetics with $R^2 = 0.95$, according to Figure 3(a)–3(c) and kinetic parameters are shown in Table 8. In the investigation of the removal of amoxicillin antibiotic by MWCNT, the reaction kinetics also followed second order kinetics (Samadi *et al.* 2014). Furthermore, in the study of dye removal by carbon nanotubes modified with cation surfactants, a second order reaction kinetics was chosen as with this study (Zhou *et al.* 2001).

Specifications of the adsorbent

FTIR analysis of the MMWCNT

In order to determine the functional groups and investigate the chemical bonds of the modified carbon nanotubes, Fourier transform infrared (FTIR) analysis was used, with Figure 4 representing the raw and modified states.

**Figure 4** | FTIR spectra of MWCNT and MMWCNT.

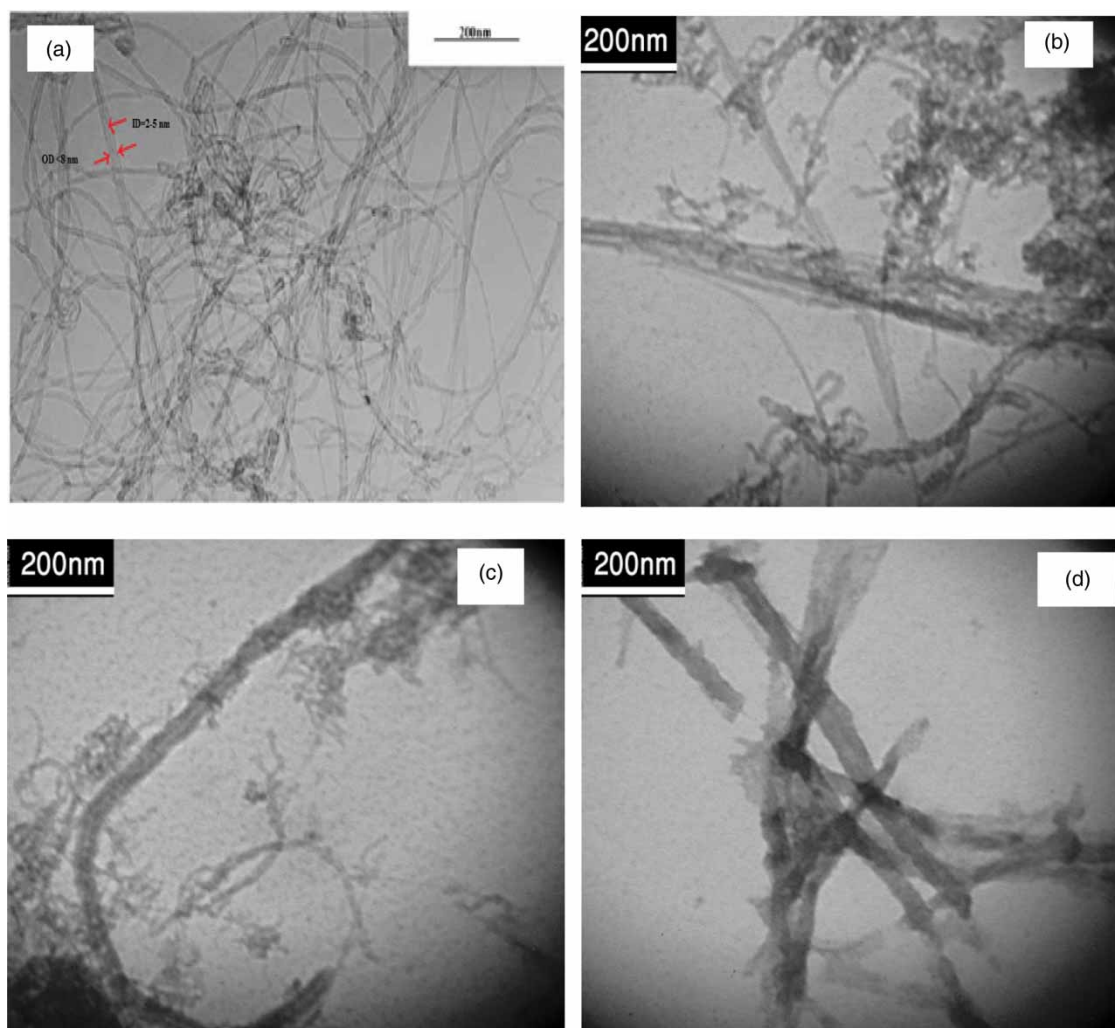


Figure 5 | Transmission electron microscope images of MWCNT (a) and MMWCNT (b)–(d).

There are various functional groups such as hydroxyl, carboxyl, and carbonyl, given the fabrication process and the purification stages on this group of nanomaterials.

According to Figure 4, infrared spectra indicated the existence of active adsorption bands. Based on these studies, in the following instances of oxidation of MWCNT, various

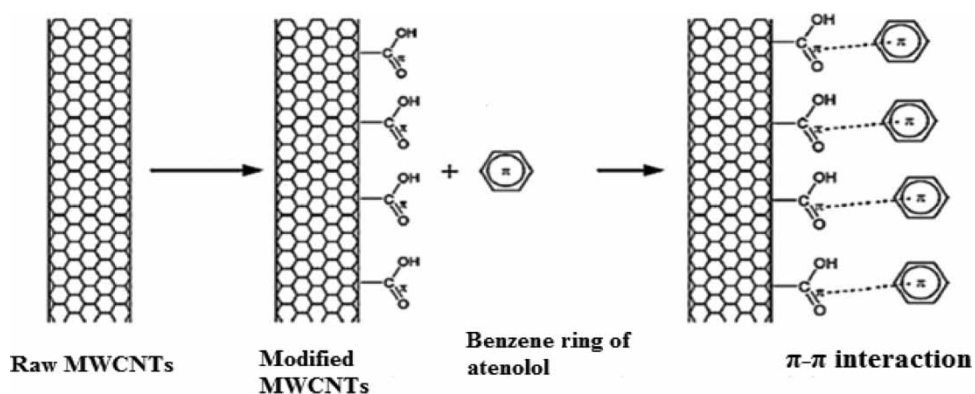


Figure 6 | Schematic of the mechanism for adsorption of atenolol on MMWCNT.

functional groups are produced on the internal and external surface of the MWCNT, causing increased superficial polarity and changes in the superficial charges (Lu *et al.* 2008). In a modification by nitric acid and sulfuric acid (Xu *et al.* 2008) and by NaOCl (Pourzamani *et al.* 2015), it was found that within the range of 1,000–2,000, 1,500–2,500, and 2,500–3,500 cm^{-1} , the carboxylic, carbonyl, and hydroxyl functional groups, respectively, have been mainly developed. Functional groups can alter the status of the surfaces of the carbon nanotube and its potentials. In some cases, these groups cause the carbon nanotube to become more hydrophilic, making it more suitable for adsorption of relatively low molecular weights and polar compounds. Occasionally, the functional groups may provide an increased resistance to diffusion, and bring about a lesser availability and continuity on the surface of carbon nanotubes for organic chemicals (Pan & Xing 2008).

TEM image

Figure 5 presents the transmission electron microscopy (TEM) images of raw and modified carbon nanotubes. The morphology of MWCNT samples, including the internal and the external diameter, was determined by TEM. The internal diameter (ID) of raw nanotubes was 2–5 nm, whereas their external diameter (OD) was less than 8 nm. Their length was determined to be over 10 μm (Dehdashti *et al.* 2017). According to Figure 5, an increase in the diameter of modified nanotubes, which was due to covalent bonds with NaOCl and the formation of functional groups, was detectable (Zhao *et al.* 2015). Following this increase of diameter, the number of pores, intermediate channels, and external grooves, and in turn the increase in active sites were expected to contribute to the adsorption process (Zhang *et al.* 2011). Figure 6 shows schematic of the mechanism for adsorption of atenolol on MMWCNT.

CONCLUSION

Following the investigation of the effectiveness of the different methods for the modification of MWCNT, the combined employment of the NaOCl solution with a concentration of 30%, a contact time of 15 minutes, and an ozone dose of 80% was chosen as the most suitable method with a high efficiency for removing atenolol; this process had an efficiency of 58.39%. Furthermore, the results indicated that with the prolongation of contact time and an increase in the adsorbent's dose, the removal efficiency increased.

Moreover, as the initial concentration of atenolol increased, an ascending trend with a low slope was observed in the removal efficiency. The most effective pH value in the adsorption process was detected to be within the neutral range. Therefore, the application of these nanomaterials as a novel, effective, efficient, and economical adsorbent is recommended for water and wastewater treatment.

ACKNOWLEDGEMENTS

The authors of this paper feel obliged to appreciate the support and cooperation of the environmental health engineering group and environmental research center of the health faculty of Isfahan University of Medical Sciences together with Shahid Sadoughi University of Medical Sciences.

REFERENCES

- Afkhami, A., Saber-Tehrani, M. & Bagheri, H. 2010 Modified maghemite nanoparticles as an efficient adsorbent for removing some cationic dyes from aqueous solution. *Desalination* **263** (1), 240–248.
- Amin, M. M., Bina, B., Majd, A. M. S. & Pourzamani, H. 2014 Benzene removal by nano magnetic particles under continuous condition from aqueous solutions. *Frontiers of Environmental Science & Engineering* **8** (3), 345–356.
- Arya, V. & Philip, L. 2016 Adsorption of pharmaceuticals in water using Fe_3O_4 coated polymer clay composite. *Microporous Mesoporous Materials* **232**, 273–280.
- Augusto, F., Carasek, E., Silva, R. G., Rivellino, S. R., Batista, A. D. & Martendal, E. 2010 New sorbents for extraction and microextraction techniques. *Journal of Chromatography A* **1217** (16), 2533–2542.
- Behnamfard, A. & Salarirad, M. M. 2009 Equilibrium and kinetic studies on free cyanide adsorption from aqueous solution by activated carbon. *Journal of Hazardous Materials* **170**, 127–133.
- Carballa, M., Omil, F., Lema, J. M., Llopart, M., García-Jares, C., Rodríguez, I., Gómez, M. & Ternes, T. 2004 Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. *Water Research* **38** (12), 2918–2926.
- Chiang, H. L., Chiang, P. C. & Huang, C. P. 2002 Ozonation of activated carbon and its effects on the adsorption of VOCs exemplified by methylethylketone and benzene. *Chemosphere* **47** (3), 267–275.
- Dehdashti, B., Amin, M. M., Pourzamani, H., Ehrampoush, M. H. & Mokhtari, M. 2017 Atenolol adsorption by multi-wall carbon nanotubes from aqueous solutions. *Journal of Mazandaran University of Medical Sciences* **26** (144), 152–170.

- DellaGreca, M., Iesce, M. R., Pistillo, P., Previtera, L. & Temussi, F. 2009 Unusual products of the aqueous chlorination of atenolol. *Chemosphere* **74** (5), 730–734.
- Divya, K. & Narayana, B. 2014 New visible spectrophotometric methods for the determination of atenolol in pure and dosage forms via complex formation. *Indo American Journal of Pharmaceutical Sciences* **4** (1), 194–203.
- Ghobadi, J., Arami, M., Bahrami, H. & Mahmoodi, N. M. 2014 Modification of carbon nanotubes with cationic surfactant and its application for removal of direct dyes. *Desalination Water Treatment* **52** (22–24), 4356–4368.
- Gong, J. L., Wang, B., Zeng, G. M., Yang, C. P., Niu, C. G., Niu, Q. Y., Niu, Q. Y., Zhou, W. J. & Liang, Y. 2009 Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. *Journal of Hazardous Materials* **164** (2), 1517–1522.
- Gulnaz, O., Sahmurova, A. & Kama, S. 2011 Removal of Reactive Red 198 from aqueous solution by *Potamogeton crispus*. *Chemical Engineering Journal* **174** (2–3), 579–585.
- Heibati, B., Ghoochani, M., Albadarin, A. B., Mesdaghinia, A. R., Makhlof, A. S. H., Asif, M., Maity, A., Tyagi, I., Agarwal, S. & Gupta, V. K. 2016 Removal of linear alkyl benzene sulfonate from aqueous solutions by functionalized multi-walled carbon nanotubes. *Journal of Molecular Liquids* **213**, 339–344.
- Hemraj-Benny, T., Bandosz, T. J. & Wong, S. S. 2008 Effect of ozonolysis on the pore structure, surface chemistry, and bundling of single-walled carbon nanotubes. *Journal of Colloid and Interface Science* **317** (2), 375–382.
- Homem, V. & Santos, L. 2011 Degradation and removal methods of antibiotics from aqueous matrices—a review. *Journal of Environmental Management* **92** (10), 2304–2347.
- Hu, X. & Cheng, Z. 2015 Removal of diclofenac from aqueous solution with multi-walled carbon nanotubes modified by nitric acid. *Chinese Journal of Chemical Engineering* **23** (9), 551–556.
- Hu, Y., Fitzgerald, N. M., Lv, G., Xing, X., Jiang, W. T. & Li, Z. 2015 Adsorption of atenolol on kaolinite. *Advances in Cryogenic Engineering* **2015**, 1–8.
- Iijima, S. & Ichihashi, T. 1993 Single-shell carbon nanotubes of 1-nm diameter. *Nature* **363**, 603–605.
- Isarain-Chávez, E., Rodríguez, R. M., Cabot, P. L., Centellas, F., Arias, C., Garrido, J. A. & Brillas, E. 2011 Degradation of pharmaceutical beta-blockers by electrochemical advanced oxidation processes using a flow plant with a solar compound parabolic collector. *Water Research* **45** (14), 4119–4130.
- Ismael, H. A., Kh dum, L. H. & Lafta, A. J. 2014 Use of Iraqi cherry seeds in the removal of paracetamol and atenolol medicines from their aqueous solutions. *International Journal of Science and Research* **3** (12), 2290–2295.
- Kümmerer, K. 2004 Pharmaceuticals in the environment—scope of the book and introduction. In: *Pharmaceuticals in the Environment*. Springer-Verlag, Berlin, pp. 3–11.
- Kyzas, G. Z., Koltsakidou, A., Nanaki, S. G., Bikiaris, D. N. & Lambropoulou, D. A. 2015 Removal of beta-blockers from aqueous media by adsorption onto graphene oxide. *Science of the Total Environment* **537**, 411–420.
- Li, M., Boggs, M., Beebe, T. P. & Huang, C. 2008 Oxidation of single-walled carbon nanotubes in dilute aqueous solutions by ozone as affected by ultrasound. *Carbon* **46** (3), 466–475.
- Liu, J., Rinzler, A. G., Dai, H., Hafner, J. H., Bradley, R. K., Boul, P. J., Lu, A., Iverson, T., Shelimov, K., Huffman, C. B., Rodriguez-Macias, F., Shon, Y. S., Lee, T. R., Colbert, D. T. & Smalley, R. E. 1998 Fullerene pipes. *Science* **280** (5367), 1253–1256.
- Lu, C., Su, F. & Hu, S. 2008 Surface modification of carbon nanotubes for enhancing BTEX adsorption from aqueous solutions. *Applied Surface Science* **254** (21), 7035–7041.
- Manchester, S., Wang, X., Kulaots, I., Gao, Y. & Hurt, R. H. 2008 High capacity mercury adsorption on freshly ozone-treated carbon surfaces. *Carbon* **46** (3), 518–524.
- Metcalfe, C. D., Koenig, B. G., Bennie, D. T., Servos, M., Ternes, T. A. & Hirsch, R. 2005 Occurrence of neutral and acidic drugs in the effluents of Canadian sewage treatment plants. *Environmental Toxicology and Chemistry* **22** (12), 2872–2880.
- Pan, B. & Xing, B. 2008 Adsorption mechanisms of organic chemicals on carbon nanotubes. *Environmental Science & Technology* **42** (24), 9005–9013.
- Pourzamani, H., Fadaei, S. & Amin, M. M. 2014 Release control of nanomagnetic particles in water and wastewater treatment. *Anuário do Instituto de Geociências* **37** (2), 223–231.
- Pourzamani, H., Hajizadeh, Y. & Fadaei, S. 2015 Efficiency enhancement of multi-walled carbon nanotubes by ozone for benzene removal from aqueous solution. *International Journal of Environmental Health Engineering* **4** (1), 29.
- Rafati, L., Ehrampoush, M. H., Rafati, A. A., Mokhtari, M. & Mahvi, A. H. 2016 Modeling of adsorption kinetic and equilibrium isotherms of naproxen onto functionalized nano-clay composite adsorbent. *Journal of Molecular Liquids* **224**, 832–841.
- Rafati, L., Ehrampoush, M. H., Rafati, A. A., Mokhtari, M. & Mahvi, A. H. 2017 Removal of ibuprofen from aqueous solution by functionalized strong nano-clay composite adsorbent: kinetic and equilibrium isotherm studies. *International Journal of Environmental Science and Technology* **15**, 513–524.
- Rahmani, A., Mousavi, H. Z. & Fazli, M. 2010 Effect of nanostructure alumina on adsorption of heavy metals. *Desalination* **253** (1), 94–100.
- Samadi, M. T., Shokoohi, R., Araghchian, M. & Tarlani Azar, M. 2014 Amoxicillin removal from aquatic solutions using multi-walled carbon nanotubes. *Journal of Mazandaran University of Medical Sciences* **24** (117), 103–115.
- Savage, N. & Diallo, M. S. 2005 Nanomaterials and water purification: opportunities and challenges. *Journal of Nanoparticle Research* **7** (4–5), 331–342.
- Sayadi, M., Trivedy, R. & Patha, R. 2010 Pollution of pharmaceutical in environment. *Industrial Safety and Pollution Control* **26** (1), 89–94.
- Schuster, A., Hädrich, C. & Kümmerer, K. 2008 Flows of active pharmaceutical ingredients originating from health care practices on a local, regional, and nationwide level in Germany – is hospital effluent treatment an effective approach for risk reduction? *Water, Air, & Soil Pollution* **8** (5–6), 457–471.

- Sedaghat, S. 2014 Synthesis and modification of carboxylated multi wall nanotubes with atenolol. *Soft Nanoscience Letters* **4** (3), 75–81.
- Sotelo, J., Rodríguez, A., Álvarez, S. & García, J. 2012 Modeling and elimination of atenolol on granular activated carbon in fixed bed column. *International Journal of Environmental Research and Public Health* **6** (4), 961–968.
- Su, F., Lu, C. & Hu, S. 2010 Adsorption of benzene, toluene, ethylbenzene and *p*-xylene by NaOCl-oxidized carbon nanotubes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **353** (1), 83–91.
- Tofiqhy, M. A. & Mohammadi, T. 2012 Nitrate removal from water using functionalized carbon nanotube sheets. *Chemical Engineering Research and Design* **90** (11), 1815–1822.
- Urtiaga, A., Pérez, G., Ibáñez, R. & Ortiz, I. 2013 Removal of pharmaceuticals from a WWTP secondary effluent by ultrafiltration/reverse osmosis followed by electrochemical oxidation of the RO concentrate. *Desalination* **331**, 26–34.
- Vuković, G. D., Marinković, A. D., Čolić, M., Ristić, M. Đ., Aleksić, R., Perić-Grujić, A. A. & Uskoković, P. S. 2010 Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes. *Chemical Engineering Journal* **157** (1), 238–248.
- Wang, H., Yu, Y. F., Chen, Q. W. & Cheng, K. 2015 Carboxyl-functionalized nanoparticles with magnetic core and mesopore carbon shell as adsorbents for the removal of heavy metal ions from aqueous solution. *Dalton Transactions* **40** (3), 559–563.
- Wilde, M. L., Montipó, S. & Martins, A. F. 2014 Degradation of β -blockers in hospital wastewater by means of ozonation and Fe^{2+} /ozonation. *Water Research* **48**, 280–295.
- Xiong, L., Chen, C., Chen, Q. & Ni, J. 2011 Adsorption of Pb(II) and Cd(II) from aqueous solutions using titanate nanotubes prepared via hydrothermal method. *Journal of Hazardous Materials* **189** (3), 741–748.
- Xu, D., Tan, X., Chen, C. & Wang, X. 2008 Removal of Pb(II) from aqueous solution by oxidized MWCNT. *Journal of Hazardous Materials* **154** (1), 407–416.
- Zazouli, M. A., Yousefi, Z., Taghavi, M., Akbari-adergani, B., Cherati, J. Y. & Sari, I. 2013 Cadmium removal from aqueous solutions using L-cysteine functionalized single-walled carbon nanotubes. *Journal of Medical Science* **23** (98), 37–47.
- Zhang, L., Song, X., Liu, X., Yang, L., Pan, F. & Lv, J. 2011 Studies on the removal of tetracycline by multi-walled carbon nanotubes. *Chemical Engineering Journal* **178**, 26–33.
- Zhao, X., Shi, Y., Cai, Y. & Mou, S. 2008 Cetyltrimethylammonium bromide-coated magnetic nanoparticles for the preconcentration of phenolic compounds from environmental water samples. *Environmental Science & Technology* **42** (4), 1201–1206.
- Zhao, X. H., Jiao, F. P., Yu, J. G., Xi, Y., Jiang, X. Y. & Chen, X. Q. 2015 Removal of Cu(II) from aqueous solutions by tartaric acid modified multi-walled carbon nanotubes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **476**, 35–41.
- Zhou, W., Ooi, Y., Russo, R., Papanek, P., Luzzi, D., Fischer, J., Bronikowski, M. J., Willis, P. A. & Smalley, R. E. 2001 Structural characterization and diameter-dependent oxidative stability of single wall carbon nanotubes synthesized by the catalytic decomposition of CO. *Chemical Physics Letters* **350** (1), 6–14.
- Ziegler, K. J., Gu, Z., Peng, H., Flor, E. L., Hauge, R. H. & Smalley, R. E. 2005 Controlled oxidative cutting of single-walled carbon nanotubes. *Journal of the American Chemical Society* **127** (5), 1541–1547.
- Zuccato, E., Castiglioni, S., Fanelli, R., Reitano, G., Bagnati, R., Chiabrando, C., Pomati, F., Rossetti, C. & Calamari, D. 2006 Pharmaceuticals in the environment in Italy: causes, occurrence, effects and control. *Environmental Science and Pollution Research* **13** (1), 15–21.

First received 2 September 2017; accepted in revised form 22 February 2018. Available online 15 March 2018