Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22984

133 (2018) 212–219
November

Removal of atenolol from aqueous solutions by multiwalled carbon nanotubes: isotherm study

Mohammad Mehdi Amin[a,b], Bahare Dehdashti[c,*], Lida Rafati[d], Hamid Reza Pourzamani[a,b], Mehdi Mokhtari[c], Maryam Khodadadi[e]

[a]*Environment Research Center, Research Institute for Primordial Prevention of Non-communicable Disease, Isfahan University of Medical Sciences, Isfahan, Iran, emails: amin@hlth.mui.ac.ir (M.M. Amin), pourzamani@hlth.mui.ac.ir (H.R. Pourzamani)*
[b]*Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran*
[c]*Environmental Science and Technology Research Center, Department of Environmental Health Engineering, School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran, Tel. +98 3538209100; Fax: +98 3538209119; emails: baharehdehdashty@yahoo.com (B. Dehdashti), mhimokhtari@gmail.com (M. Mokhtari)*
[d]*Deputy of Health, Hamadan University of Medical Sciences, Hamadan, Iran, email: l.rafati@yahoo.com*
[e]*Social Determinants of Health Research Center, Birjand University of Medical Sciences, Birjand, Iran, email: maryam.khodadadi@gmail.com*

Received 11 December 2017; Accepted 19 August 2018

ABSTRACT

Nowadays, ensuring the protection and health of the environment is an effective step toward sustainable development. One of the primary environmental concerns around the world is the removal of pharmaceutical contaminants from water and wastewater. Solving such problem and many other environmental issues, along with treading the path toward sustainable development, can be achieved with the use of nanotechnology. This study investigated the use of multiwalled carbon nanotubes (MWCNTs) in removing the beta-blocker atenolol from aqueous solutions. To achieve this goal, the efficiency of atenolol removal was evaluated in a four-level Taguchi experiment that involved the evaluation of pH value (2–11), contact time (5–90 min), adsorbent dose (0.5–2 g/L), and initial atenolol concentration (10–90 mg/L). Data analysis and interpretation were performed using Design Expert 6. The results indicated that the highest atenolol removal (94.8%) occurred at a pH of 7, a contact time of 20 min, an atenolol concentration of 10 mg/L, and a MWCNT dose of 0.5 g/L. The adsorption capacity of the MWCNTs used in this work was 16.76 mg/g. The data analysis based on the adsorption isotherm models of the Isotherm Fitting Tool showed good agreement with the results of a linear model. The findings confirmed that MWCNTs present great potential as effective adsorbents for the removal of atenolol from water and wastewater.

Keywords: Atenolol; Multiwalled carbon nanotube; Adsorption; Isotherm

1. Introduction

The use of medications today is considered an integral and very useful part of life. These pollutants and their effects on living organisms and the environment have been explored by researchers in recent years [1]. One such pollutant is the beta-blocker atenolol, which is an antagonist used to treat angina (chest pain) and control blood pressure and some forms of heart arrhythmias [2].

The widespread consumption of atenolol as a most-prescribed drug and its limited metabolic function in the human body make nondecomposability of its major part during excretion, resulting in a large presence of beta-blockers in wastewater and surface waters [3].

---

* Corresponding author.

Some of the toxic effects of beta-blockers on nontarget living organisms include effects on the endocrine glands and the consequent disturbance of testosterone levels in male organisms [4]. The presence of these pollutants in the environment has been exacerbated by advancements in the pharmaceutical industry, agricultural development, and inadequate wastewater treatment processes for the removal of beta-blockers [4]. Traditional and conventional systems for urban wastewater treatment, such as the activated sludge process, have been minimally effective because of insufficient technologies for pollutant removal [5]. This deficiency prompted practitioners to frequently adopt complementary treatment approaches, such as advanced oxidation [6], membrane filtration [7], reverse osmosis [8], and adsorption [9–22]. One of the most effective approaches for the removal of pollutants from water and wastewater is adsorption, which is a simple, inexpensive, and applicable method [23]. The most used adsorbents to remove pollutants from aqueous solution are activated carbons [24–26], clays [27,28], and carbon nanotubes (CNTs) [29,30].

As an adsorption material, CNTs have recently been among the most important contributions of nanotechnology to environmental protection efforts. These nanomaterials have high thermal resistance and high chemical stability; their high adsorption capacity has been one of the reasons for their use in environmental activities [31].

The application of CNTs in recent years has been among the most important parts of nanotechnology. They have an adsorption capacity higher than that of other compounds, such as porous graphitic carbon. CNTs also present high potential for reuse. Previous studies indicated that rehabilitation through nanomaterials is achieved in an economical manner with the use of methanol, ethanol, sodium hydroxide, and acetic acid. With respect to usage for the removal of atenolol, an effective factor in atenolol adsorption on an adsorbent, such as a CNT, is the presence of a hydroxyl functional group and a benzene ring in the chemical structure of the drug [19].

2. Materials and methods

2.1. Materials

In the experiment, atenolol ($C_{14}H_{22}N_2O_3$) with a purity ≥98% (Sigma Aldrich Co., USA) was used to prepare aqueous solutions (Fig. 1 shows the chemical structure of atenolol). To examine the adsorption process, multiwalled carbon nanotubes (MWCNTs; purity >95%, outer diameter <8 nm, inner diameter: 2–5 nm, length >10 μm, specific surface area >500 m^2/g, electric conductivity >100 S/cm) (Cheap Tubes Co., USA) were prepared. For pH adjustment, HCl ≥37% and NaOH ≥98% (Merck, Germany) were used. Deionized water was employed in the preparation of all the solutions.

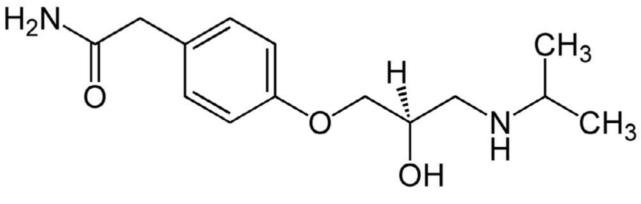

Fig. 1. Chemical structure of atenolol.

2.2. Characterization of the nanoparticles

The electron microscope imaging was recruited to investigate the surface shape and morphology of nanoparticles.

2.3. Batch adsorption study

Initially, 100 mg of atenolol was weighed to produce a stock solution (1,000 mg/L). The resultant substance is highly soluble in water at 25°C. On the basis of similar investigations, the factors evaluated in this study were initial atenolol concentration (10, 30, 70, and 90 mg/L), adsorbent dosage (0.5, 1, 1.5, and 2 g/L), contact time (5, 20, 60, and 90 min), and pH (2, 4, 7, and 11). The samples were stirred at 250 rpm and then passed through a filter (0.22 CA). Subsequently, they were centrifuged at 5,000 rpm for 15 min; a control sample was prepared to control the removal of pollutants by centrifugation. The final atenolol concentration was determined after adsorption using a Hach spectrophotometer instrument (DR 5000™, USA) set at a wavelength of 274 nm. This wavelength is the configuration employed in the scanning of drug samples in practice. The pH values were adjusted using 0.1 M HCl and 0.1 M NaOH.

2.4. Data analysis and design of experiment

As previously described, four parameters that influence atenolol adsorption (i.e., initial concentration, adsorbent dosage, contact time, and pH) were selected to optimize the adsorption process. Each of the parameters had four levels for selection, which were presented via the Taguchi approach using Design Expert 6 (Design Expert 6 Stat-Ease, Inc., USA) [31–35] (Table 1).

2.5. The effect of the concentration

Atenolol adsorption by the MWCNTs was evaluated in an isotherm study featuring optimal conditions, an initial atenolol concentration of 0–90 mg/L, an adsorbent dose of 0.5 g/L, a contact time of 20 min, and a pH of 7 at room temperature. The water solubility (S_w) of atenolol was estimated as 300 mg/L at pH 7. The Isotherm Fitting Tool (ISOFIT) was used to match the isotherm parameters to the experimental data. ISOFIT is a software program that implements the aforementioned matching procedure by minimizing the objective function of the weighted sum of squared error (WSEE). ISOFIT supports a number of isotherms, including

Table 1
Controlling factors and their levels

Factors	Level 1	Level 2	Level 3	Level 4
Atenolol concentration (mg/L)	10	30	70	90
Adsorbent dose (mg/L)	500	1,000	1,500	2,000
Contact time (min)	5	20	60	90
pH	2	4	7	11

Brunauer–Emmett–Teller (BET), Freundlich, Freundlich with Linear Partitioning (F-P), Generalized Langmuir–Freundlich (GLF), Langmuir, Langmuir with Linear Partitioning (L-P), Linear, Polanyi, and Toth isotherms.

3. Results

After the experiments were designed using the Taguchi approach, 16 test steps were performed (Table 2), the results of which have been mentioned. The percentage of efficiency and importance of each parameter are presented in Table 3. Charts regarding atenolol adsorption by the MWCNTs are shown in Figs. 2–5 to illustrate optimal adsorption conditions.

3.1. Isotherm studies

In this study, ISOFIT was used to analyze the adsorption of atenolol by the MWCNTs in batch conditions. Table 4 summarizes some of the diagnostic statistics computed by ISOFIT; these data are also reported in the output file. Notes: AICc: multimodel ranking, R_y^2: correlation between measured and simulated observations, R_N^2: correlation between residual and normality, M^2: Linssen measure of nonlinearity.

As shown in Table 5, the Linssen measure indicated significant WSSE nonlinearity near the optimal parameter values. Statistical measures, such as R_N^2 and the Durbin–Watson test (D), showed normally distributed weighted residuals with no serial autocorrelation. Fig. 5 presents a plot of the fitted isotherm, which was organized into visually indistinguishable groups, along the observed data points. q_e (the atenolol adsorption uptake of adsorbent) versus C_e (equilibrium adsorbate concentration) curve must be obtained for an adsorption isotherm graph.

3.2. Specifications of the adsorbent

Fig. 6 shows the MWCNTs used in this research using the scanning electron microscopy (SEM). The internal diameter

Table 2
Design matrix and results of atenolol removal by multiwalled carbon nanotubes in different conditions

Run	Factors			Response			
	Atenolol concentration (mg/L)	Adsorbent dose (mg/L)	Time (min)	pH	C_t	R (%)	q_e (mg/g)
1	70	1,000	90	2	33.8 ± 0.2	51.62	36.14
2	10	1,500	60	11	7.36 ± 2.4	26.31	1.75
3	90	500	90	11	39.82 ± 2.4	55.75	100.35
4	90	1,500	20	2	39.73 ± 2.3	55.84	33.50
5	70	1,500	5	4	26.22 ± 0.3	62.53	29.18
6	10	500	5	2	0.95 ± 0	90.49	18.1
7	30	2,000	60	2	7.89 ± 2.2	73.68	11.05
8	30	1,500	90	7	5.52 ± 3.5	81.57	16.31
9	30	500	20	4	16.49 ± 0.2	45.02	27.01
10	90	1,000	60	4	27.98 ± 3.3	68.90	62.01
11	10	2,000	90	4	5.70 ± 4.8	42.98	2.14
12	30	1,000	5	11	14.21 ± 1.9	52.63	15.78
13	70	2,000	20	11	16.57 ± 0.6	76.31	26.71
14	90	2,000	5	7	19.82 ± 7.9	77.97	35.08
15	70	500	60	7	34.21 ± 0.2	51.12	71.57
16	10	1,000	20	7	6.75 ± 0.1	32.45	3.24

Table 3
Effects of the factors and interactions for atenolol removal by multiwalled carbon nanotubes

Factor/interaction	Degree of freedom	Sum of squares	Mean squares	F-Value	p-Value	Contribution (%)
A: Adsorbent dose (mg/L)	3	1,189.83	396.61	1.92	0.1674	8.55
B: Atenolol concentration (mg/L)	3	1,117.70	372.57	1.80	0.1875	8.04
C: Contact time (min)	3	1,914.19	638.06	3.09	0.0571	13.76
D: pH	3	1,335.43	445.14	2.15	0.1336	9.60
AB interaction	3	5,043.08	1,681.03	8.13	0.0016	36.26
Lack of fit	0	0				
Pure error	16	3,308.95	206.8			0
Residuals	16	3,308.95	206.8			23.79

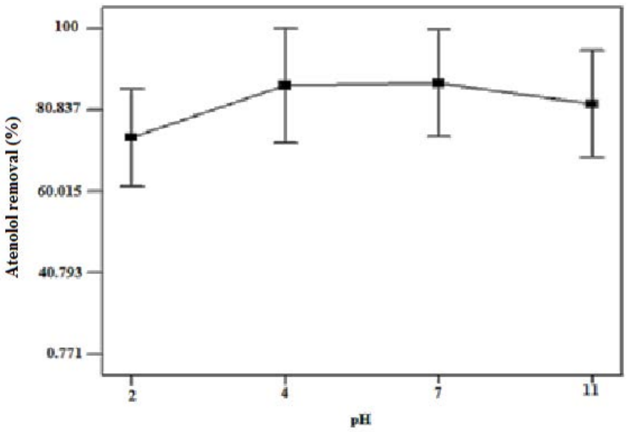

Fig. 2. pH effect on atenolol removal by MWCNT.

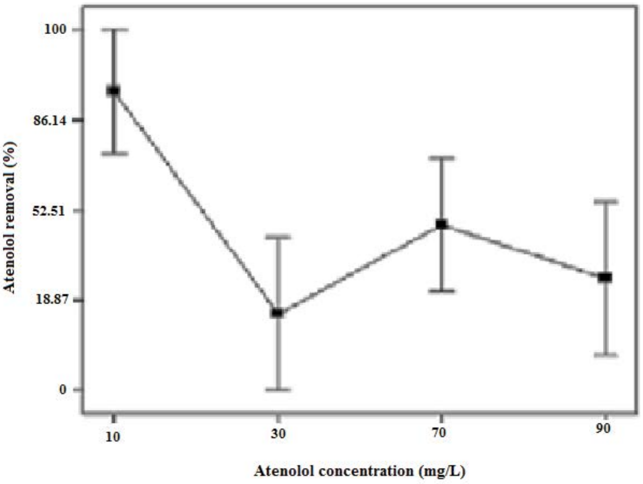

Fig. 3. Effect of initial concentration on atenolol removal by MWCNT.

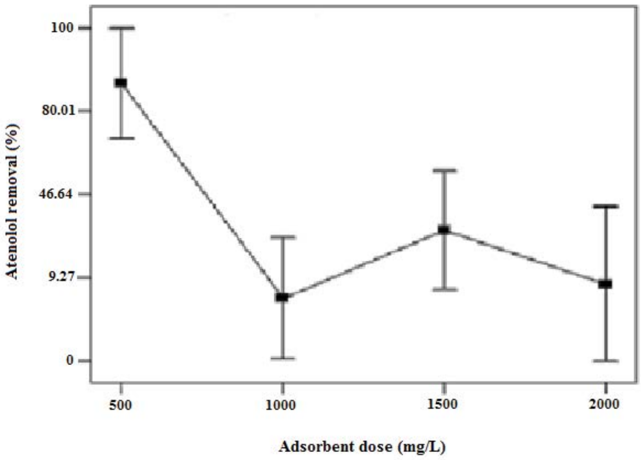

Fig. 4. Adsorbent dose effect on atenolol removal by MWCNT.

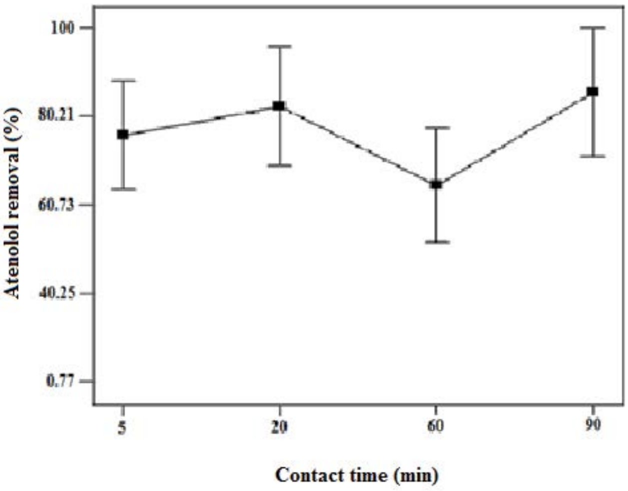

Fig. 5. Contact time effect on atenolol removal by MWCNT.

of raw nanotubes (ID = inner diameter) was 2–5 nm, whereas their external diameter (OD = outer diameter) was less than 8 nm. Its length was determined to be over 10 μm [19].

4. Discussion

4.1. Effect of pH

According to Fig. 2, the maximum removal efficiency occurred within a pH range of 4–7. With increasing pH and a decrease in this value to below 4, removal efficiency exhibited a descending trend. Given the absence of significant differences in removal efficiency at different pH values, 7 was chosen as the optimal pH. Solution pH is one of the most important factors that affect the adsorption process because it indicates the statuses of adsorbent surface charges and drugs. It also affects adsorbents and adsorbate interactions. The increase in atenolol removal efficiency at a pH of 4–7 can be interpreted according to the pH_{ZPC} of the MWCNTs, which was equal to 8, as determined in the present research and by Lu et al. [31]. Nanotubes exhibit a positive pH charge lower than the pH_{ZPC} and a negative charge higher than the pH_{ZPC}.

Decreased adsorption efficiency occurs at pH values higher than 8 through the electron repulsion of negative charges. Additionally, increased pH values due to the competition of OH^- ions with atenolol for activated sites can reduce atenolol removal. In acidic conditions, the carboxyl and hydroxyl groups on an adsorbent surface are protonated, thereby producing a positively charged surface. This phenomenon increases adsorption through the electrostatic interaction between an adsorbent and an adsorbate [36]. In evaluating the efficiency of MWCNTs in removing Janus Green B dye, they considered 7 as the optimal pH for the removal process [36]. A previous study reported that a pH of 6 enabled the highest efficiency in amoxicillin removal by commercial activated carbon and activated carbon modified with ammonium hydroxide [37]. Tetracycline removal by MWCNTs was achieved at a maximum pH range of 4.5–7; the minimum efficiency was observed at pH values smaller than 4.5 and greater than 7 [38].

Table 4
Summary of selected diagnostics for atenolol adsorbed by MWCNT

Isotherms	AICc	R_y^2	R_N^2	M^2	linearity assessment	Constants	Parameter values
Langmuir	25.82	0.950	0.935	9.43×10^{-1}	Nonlinear	Q_0 (mg/g)	8.52
						B	0.0023
BET	25.07	0.953	0.943	1.107	Nonlinear	Q_0 (mg/g)	1.5×10^3
						B	0.001
Linear	22.61	0.966	0.890	1.20×10^{-9}	Linear	K_d	1.7
F–P	43.22	0.966	0.954	5.81	Nonlinear	k_f	6×10^{-7}
						$1/n_f$	0.12
						K_d	1.4
L–P	43.24	0.966	0.952	1.179	Nonlinear	Q_0 (mg/g)	1.6
						B	3.3×10^{-10}
Freundlich	24.29	0.958	0.964	1.709	Nonlinear	k_f	0.0232
						$1/n_f$	1.022
Toth	44.76	0.956	0.934	3.03×10^{-1}	Nonlinear	Q_0 (mg/g)	1.6
						B	2.2×10^{-5}
						n_T	0.214
GLF	44.81	0.954	0.926	2.50×10^3	Nonlinear	Q_0 (mg/g)	1.23×10^3
						B	2.6×10^{-3}
Polanyi	33.43	0.000	0.946	1.83×10^{-15}	Linear	Q_0 (mg/g)	76.4
						A	0.0006
						B	0.15

Table 5
Selected ISOFIT post regression output (linear isotherm)

Parameter or statistic		ISOFT result
Overall quality of fit	WSSE	2.36×10^2
	RMSE	6.87
	R_y	0.983
Parameter statistics	k_d	8.82×10^{-1}
Parameter standard error	k_d	5.98×10^{-2}
Test of assumptions	M^2	1.20×10^{-9}
Linssen (M^2)	Threshold	1.16×10^{-2}
	Assessment	Linear
Normality (R_N^2)	R_N^2	0.890
	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	1.29
	p-Value	0.55
	Assessment	No correlation

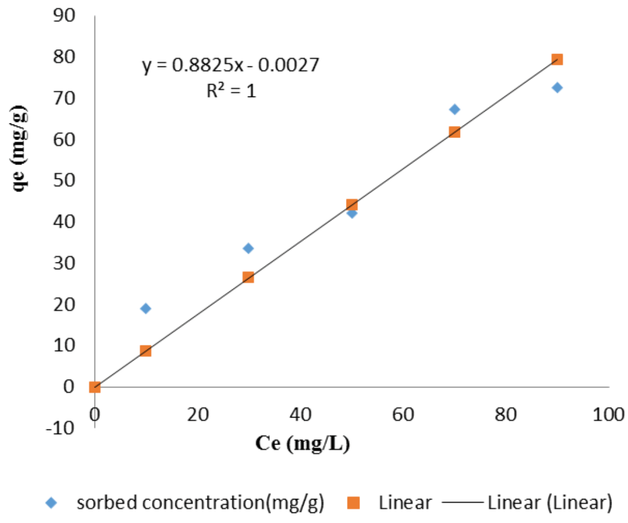

Fig. 6. Plots of the linear isotherm.

4.2. *Effect of initial concentration*

The effects of initial atenolol concentration on adsorption efficiency are illustrated in Fig. 3. Maximum removal occurred at low concentrations, and efficiency decreased with increasing concentration. As a result, 10 mg/L was regarded as the optimal initial atenolol concentration. Limited adsorption sites on an adsorbent cause the rapid saturation of these sites because of the increase in initial concentrations of atenolol. This increase, in turn, diminishes removal efficiency. Consequently, other processes involved in adsorption, such as particle penetration or mass influx, will be ineffective. The selective adsorption of a type of pollutant on an adsorbent leads to limited adsorption. In one study, Iraqi cherry seeds were used as adsorbents to compare atenolol and paracetamol removal [39]. The results showed that the optimum weight of atenolol in the adsorption process was 0.05 g; this increase resulted in decreased adsorption efficiency – a finding that is consistent with the results of the current work. The researchers also found that atenolol was more effectively adsorbed on the Iraqi cherry seeds than paracetamol because the higher molecular weight of the former under the same adsorption conditions reduced polarity and ionization in the solution. Consequently, the atenolol molecules were adsorbed vertically on the adsorbent surface, occupying small and selective adsorbent sites [40].

4.3. Effect of adsorbent dose

Fig. 4 illustrates the effects of adsorbent dosage on atenolol adsorption. The adsorbent dosage at low concentrations played a significant role in removal efficiency. Because a downward trend occurred with increasing adsorbent dosage, 500 mg/L was chosen as the optimal dosage. The results of this experiment (Table 3) indicated that the adsorbent–adsorbate interaction played a significant role compared with the other factors [41]. Such significance is attributed to the high reactivity between the adsorbent and adsorbate in low doses relative to high doses; such reactivity resulted in the rapid saturation of activated adsorption sites [41]. Although the adsorbent dosage and the initial pollutant concentration exerted strong effects on removal efficiency, the relevant curves followed, in principle, an upward trend between the increase in adsorbent dosage and the increase in removal efficiency. This experiment showed that on the basis of the stated reasons, the best efficiency was achieved at low adsorbent dosages and pollutant concentrations. This outcome is economically acceptable. Furthermore, a decreasing trend occurred with increasing adsorbent dosage. According to previous studies, the collision between adsorbent particles probably increases with rising adsorbent dosage and contact time. This phenomenon then results in increased adhesion and decreased efficiency [40]. However, nitrate removal efficiency is improved by the increase in the dose of functionalized CNTs given the increased number of active sites and surfaces available [41].

4.4. Effect of contact time

The effects of contact time on atenolol removal efficiency showed that maximum adsorption occurred at contact times of 20 and 90 min (Fig. 5). Correspondingly, the selected optimal contact time was 20 min given the absence of significant differences. This decision was also driven by the fact that MWCNTs are highly efficient in atenolol removal at early stages, thereby enabling the rapid occupation of active sites in the adsorption process. A contact time of 20 min was thus regarded as optimal in terms of time and energy savings. Equilibrium time is influenced by several factors, such as adsorbent properties, adsorbate properties, and the interactions between these materials. In previous research, the highest removal efficiency of benzene from aqueous solutions using modified MWCNTs occurred at a contact time of 20 min [31]. In this study, a direct correlation was found between removal efficiency and contact time; in this research, a nearly direct relationship was observed. In another study, the optimal contact time for dye removal using CNTs was 75 min [35]. In atenolol removal by cherry seeds, the optimal contact time was 1 h; increasing contact time resulted in reduced adsorption because of the presence of a negatively charged space after an hour of reaction, which provided conditions for adsorption on the cherry seeds [39].

The effects of the factors shown in Table 3 and their interactions showed that initial concentration, adsorbent dosage, contact time, and pH effectively facilitated atenolol removal but that contact times and their interactions were more effective than the rest of the factors, as indicated by the significance level of less than 0.05. The significance levels of initial atenolol concentration, pH, and dosage were greater than 0.05. The strongest effect was related to interaction (36.26%), and the weakest effect was associated with initial atenolol concentration (8.04%). The severity of the effect of any of the factors on atenolol removal via the MWCNTs followed the order interaction between initial atenolol concentration and MWCNT dosage > contact time > pH > adsorbent dosage > initial atenolol concentration.

The removal of atenolol by MWCNT was calculated by Eq. (1) as follows:

$$\text{Atenolol removal percent (\%)} = 59.45 - (8.28 \times \text{Adsorbent dose (mg/L)}) - (5.16 \times \text{atenolol concentration (mg/L)}) - (13.42 \times \text{Contact time (min)}) + (0.62 \times \text{pH}) \quad (1)$$

The corrected Akaike Information Criterion (AICc) values indicated that the linear isotherm expression exhibited the best fit with the sorption data, as determined on the basis of its lowest value in the multimodel ranking (Table 4).

Linear constant b was calculated to be less than unity for the majority of the adsorbent and the adsorbent combinations, indicating that the adsorption of the selected contaminant onto the MWCNT samples was favorable. Uncertain regression techniques overcome many of the deficiencies associated with trial-and-error approaches and the linearization approaches to isotherm fitting. The effectiveness of uncertain regression techniques, however, can be impeded by the presence of local minima or excessive parameter correlations. Table 5 presents the selected ISOFIT output for the linear isotherm. ISOFIT provides two "standard" measures for evaluating isotherm fit, namely root mean square (RMSE, Eq. (2)) and the correlation between the measured and the fitted observations (R_y, Eq. (3)).

$$\text{RMSE} = \sqrt{\frac{\text{WSSE}}{(m-p)}} \quad (2)$$

$$R_y = \frac{\sum_{i=1}^{m}\left(w_i S_{i,\text{obs}} - S_{\text{obs}}^{\text{avg}}\right)\left(w_i S_i - S^{\text{avg}}\right)}{\sqrt{\sum_{i=1}^{m}\left(w_i S_{i,\text{obs}} - S_{\text{obs}}^{\text{avg}}\right)^2 \sum_{i=1}^{m}\left(w_i S_{i,\text{obs}} - S^{\text{avg}}\right)^2}} \quad (3)$$

In these measures, WSSE is the weighted sum of squared error, m denotes the total number of experimental observations, p represents the number of isotherm parameters, w_i is the weight assigned to observation i, $S_{i,\text{obs}}$ is the ith experimentally measured sorbed concentration, S_i denotes the ith simulated sorbed concentration computed via an isotherm

Table 6
Comparison of our study with some recently reported adsorbents

Adsorbate	Adsorbent	q_e (mg/g)	pH	T (°C)	Reference
Atenolol	Cherry seeds	1.33	10	25	[39]
	Fe_3O_4-coated polymer clay composite	15.6	11	25	[44]
	Graphene oxide	116	10	25	[45]
	Multiwalled carbon nanotubes	100.35	11	25	This study

expression, and S^{avg}_{obs} and S^{avg} are the averages of the weighted measure and weighted isotherm-simulated adsorbed concentrations, respectively.

Fig. 6 shows plots of the linear isotherm, which described the equilibrium adsorption data better than did the other isotherm alternative.

4.5. SEM analysis of the MWCNT

SEM determined the morphology of the nanoparticles, their surface properties, and the degree of purity of the samples. As shown in Fig. 7 [42,43], the adsorbent sample exhibited a regular structure and uniform distribution. Significant purity and homogeneity in the adsorbent sample were remarkable points in the SEM image; these properties were also determined on the basis of the mentioned characteristics of CNTs.

5. Conclusion

The findings indicated that contact time and the interaction between the adsorbent and the adsorbate had the greatest effects on removal efficiency. The most efficient pH for the adsorption process was 4–7, but a neutral value was selected as the optimal pH because of its cost-effectiveness. On the basis of the results, population growth and industrial development play significant roles in increasing the amount of pollutants in the environment. Such pollutants should be managed using easy, fast, high-efficiency, and affordable strategies. Previous studies showed that CNTs have a high capacity to remove various pollutants and that even their modified forms can be used as novel removal materials (Table 6). The environment-friendly nature and reusability of these nanomaterials have rendered them valuable tools for water and wastewater treatment.

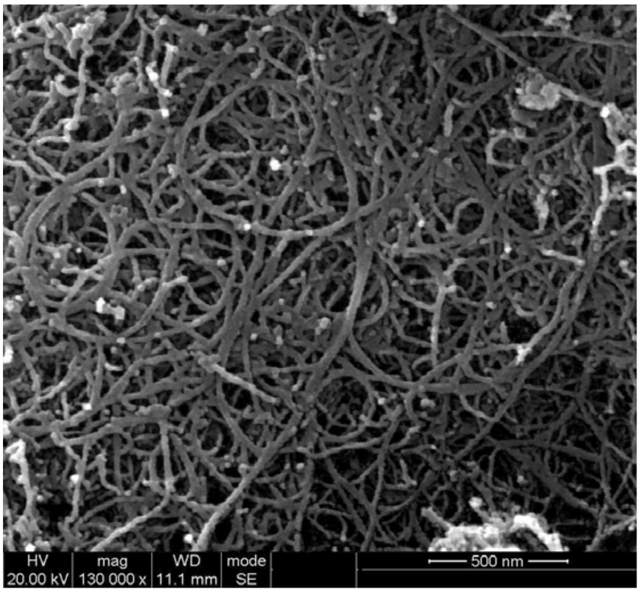

Fig. 7. SEM image of multiwalled carbon nanotubes.

Acknowledgment

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

References

[1] M. Sayadi, R. Trivedy, R. Pathak, Pollution of pharmaceutical in environment, Indo. Am. J. Pharm. Res., 26 (2010) 89–94.

[2] K. Divya, B. Narayana, New visible spectrophotometric methods for the determination of atenolol in pure and dosage forms via complex formation, Indo. Am. J. Pharm. Res., 4 (2014) 194–203.

[3] Y. Hu, N.M. Fitzgerald, G. Lv, X. Xing, W.T. Jiang, Z. Li, Adsorption of atenolol on kaolinite, Adv. Mater. Sci. Eng., 2015 (2015) 1–8.

[4] J. Maszkowsk, S. Stolte, J. Kumirska, P. Łukaszewicz, K. Mioduszewska, A. Puckowski, M. Caban,M. Wagil, P. Stepnowski, A. Białk-Bielińska, Beta-blockers in the environment: Part I. Mobility and hydrolysis study, Sci. Total Environ., 493 (2014) 1112–1121.

[11] A. Deegan, B. Shaik, K. Nolan, K. Urell, M. Oelgemöller, J. Tobin, A. Morrissey, Treatment options for wastewater effluents from pharmaceutical companies, Int. J. Environ. Sci. Technol., 8 (2011) 649–666.

[5] K.D. Brown, J. Kulis, B. Thomson, T.H. Chapman, D.B. Mawhinney, Occurrence of antibiotics in hospital, residential, and dairy effluent, municipal wastewater, and the Rio Grande in New Mexico, Sci. Total Environ., 366 (2006) 772–783.

[6] S. Veloutsou, E. Bizani, K. Fytianos, Photo-Fenton decomposition of β-blockers atenolol and metoprolol; study and optimization of system parameters and identification of intermediates, Chemosphere, 107 (2014) 180–186.

[7] V. Homem, L. Santos, Degradation and removal methods of antibiotics from aqueous matrices – a review, J. Environ. Manage., 92 (2011) 2304–2347.

[8] A. Urtiaga, G. Pérez, R. Ibáñez, I. Ortiz, Removal of pharmaceuticals from a WWTP secondary effluent by ultrafiltration/reverse osmosis followed by electrochemical oxidation of the RO concentrate, Desalination, 331 (2013) 26–34.

[9] J. Sotelo, A. Rodríguez, S. Álvarez, J. García, Modeling and elimination of atenolol on granular activated carbon in fixed bed column, Int. J. Environ. Res., 6 (2012) 961–968.

[10] A. Seyed Mohammadi, G. Asgari, A. Dargahi, S.A. Mobarakian, Equilibrium and synthetic equations for index removal of methylene blue using activated carbon from oak fruit bark, J. Mazandaran Univ. Med. Sci., 24 (2015) 172–187.

[11] A. Deegan, B. Shaik, K. Nolan, K. Urell, M. Oelgemöller, J. Tobin, et al., Treatment options for wastewater effluents from pharmaceutical companies, Int. J. Environ. Sci. Technol., 8 (2011) 649–666.

[12] M. Kamranifar, M. Khodadadi, V. Samiei, B. Dehdashti, M. Noori Sepehr, L. Rafati, N. Nasseh, Comparison the removal of reactive red 195 dye using powder and ash of barberry stem as a low cost adsorbent from aqueous solutions: Isotherm and kinetic study, J. Mol. Liq., 255 (2018) 572–577.

[13] L. Rafati, M.H. Ehrampoush, A.A. Rafati, M. Mokhtari, A.H. Mahvi, Removal of ibuprofen from aqueous solution by functionalized strong nano-clay composite adsorbent: kinetic and equilibrium isotherm studies, Int. J. Environ. Sci. Technol., 15 (2018) 513–524.

[14] L. Rafati, M.H. Ehrampoush, A.A. Rafati, M. Mokhtari, A.H. Mahvi, Modeling of adsorption kinetic and equilibrium isotherms of naproxen onto functionalized nano-clay composite adsorbent, J. Mol. Liq., 224 (2016) 832–841.

[15] M.H. Ehrampoush, M. Miri, S.M. Momtaz, M.T. Ghaneian, L. Rafati, H. Karimi, S. Rahimi, Selecting the optimal process for the removal of reactive red 198 dye from textile wastewater using analytical hierarchy process (AHP), Desal. Wat. Treat., 57 (2016) 27237–27242.

[16] M. Khodadadi, A.H. Mahvi, M.T. Ghaneian, M.H. Ehrampoush, H. Dorri, L. Rafati, The role of desalination in removal of the chemical, physical and biological parameters of drinking water (a case study of Birjand City, Iran), Desal. Wat. Treat., 57 (2016) 25331–25336.

[17] L. Rafati, R. Nabizadeh, A.H. Mahvi, M.H. Dehghani, Removal of phosphate from aqueous solutions by iron nano-particle resin Lewatit (FO36), Korean J. Chem. Eng., 29 (2012) 473–477.

[18] L. Rafati, A.H. Mahvi, A.R. Asgari, S.S. Hosseini, Removal of chromium (VI) from aqueous solutions using Lewatit FO36 nano ion exchange resin, Int. J. Environ. Sci. Technol., 7 (2010) 147–156.

[19] B. Dehdashti, M.M. Amin, H. Pourzamani, M.H. Ehrampoush, M. Mokhtari, Atenolol absorption by multi-wall carbon nanotubes from aqueous solutions, J. Mazandaran Univ. Med. Sci., 26 (2017) 152–170.

[20] A. Almasi, M. Mohammadi, Z. Atafar, A. Azizi, F. Amirian, A. Dargahi, Study the efficiency of processed walnut bark powder for methylene blue color removal from aqueous solution, De Pharma Chem., 8 (2016) 253–257.

[21] A. Mohseni Bandpei, S.M. Mohseni, A. Sheikhmohammadi, M. Sardar, M. Sarkhosh, M. Almasian, M. Avazpour, Z. Mosallanejad, Z. Atafar, S. Nazari, S. Rezaei, Optimization of arsenite removal by adsorption onto organically modified montmorillonite clay: experimental & theoretical approaches, Korean J. Chem. Eng., 34 (2017) 376–383.

[22] A. Sheikhmohammadi, Z. Dahaghin, S.M. Mohseni, M. Sarkhosh, H. Azarpira, Z. Atafar, M. Abtahi, S. Rezaei, M. Sardar, H. Masoudi, M. Faraji, S. Nazari, R.H.l. Pouya, M. Almasian, The synthesis and application of the SiO_2@Fe_3O_4@MBT nanocomposite as a new magnetic sorbent for the adsorption of arsenate from aqueous solutions: modeling, optimization, and adsorption studies, J. Mol. Liq., 255 (2018) 313–323.

[23] T. Madrakian, A. Afkhami, M. Ahmadi, H. Bagheri, Removal of some cationic dyes from aqueous solutions using magnetic-modified multi-walled carbon nanotubes, J. Hazard. Mater., 196 (2011) 109–114.

[24] E. Ayranci, O. Duman, In-situ UV-visible spectroscopic study on the adsorption of some dyes onto activated carbon cloth, Sep. Sci. Technol., 44 (2009) 3735–3752.

[25] O. Duman, Structural effects on the interactions of benzene and naphthalene sulfonates with activated carbon cloth during adsorption from aqueous solutions, Chem. Eng. J., 156 (2010) 70–76.

[26] O. Duman, E. Ayranci, Adsorptive removal of cationic surfactants from aqueous solutions onto high-area activated carbon cloth monitored by in situ UV spectroscopy, J. Hazard. Mater., 174 (2010) 359–367.

[27] O. Duman, S. Tunç, T.G. Polat, Determination of adsorptive properties of expanded vermiculite for the removal of C. I. Basic Red 9 from aqueous solution: kinetic, isotherm and thermodynamic studies, Appl. Clay Sci., 109–110 (2015) 22–32.

[28] O. Duman, S. Tunç, T.G. Polat, Adsorptive removal of triarylmethane dye (Basic Red 9) from aqueous solution by sepiolite as effective and low-cost adsorbent, Microporous Mesoporous Mater., 210 (2015) 176–184.

[29] O. Duman, S. Tunç, B.K. Bozoğlan, T.G. Polat, Removal of triphenylmethane and reactive azo dyes from aqueous solution by magnetic carbon nanotube-κ-carrageenan-Fe_3O_4 nanocomposite, J. Alloy. Compd., 687 (2016) 370–383.

[30] O. Duman, S. Tunç, T.G. Polat, B.K. Bozoğlan, Synthesis of magnetic oxidized multiwalled carbon nanotube-κ-carrageenan-Fe_3O_4 nanocomposite adsorbent and its application in cationic Methylene Blue dye adsorption, Carbohydr. Polym., 147 (2016) 79–88.

[31] C. Lu, F. Su, S. Hu, Surface modification of carbon nanotubes for enhancing BTEX adsorption from aqueous solutions, Appl. Surf. Sci., 254 (2008) 7035–7041.

[32] H. Pourzamani, Y. Hajizadeh, S. Fadaei, Efficiency enhancement of multi-walled carbon nanotubes by ozone for benzene removal from aqueous solution, Int. J. Environ. Health Eng., 4 (2015) 29, doi: 10.4103/2277-9183.163972.

[33] M.M. Amin, B. Bina, A.M.S. Majd, H. Pourzamani, Benzene removal by nano magnetic particles under continuous condition from aqueous solutions, Front. Environ. Sci. Eng., 8 (2014) 345–356.

[34] B. Bina, M. Amin, A. Rashidi, H. Pourzamani, Benzene and toluene removal by carbon nanotubes from aqueous solution, Arch. Environ. Prot., 38 (2012) 3–25.

[35] H. Pourzamani, S. Fadaei, M.M. Amin, Release control of nanomagnetic particles in water and wastewater treatment, Anu. Inst. Geociênc., 37 (2014) 223–231.

[36] S. Sobhanardakani, R. Zandipak, Evaluation of carbon nanotubes efficiency for removal of Janus Green dye from Ganjnameh River water sample, J. Health Dev., 3 (2015) 282–292.

[37] G. Moussavi, A. Alahabadi, K. Yaghmaeian, M. Eskandari, Preparation, characterization and adsorption potential of the NH_4Cl-induced activated carbon for the removal of amoxicillin antibiotic from water, Chem. Eng. J., 217 (2013) 119–128.

[38] L. Zhang, X. Song, X. Liu, L. Yang, F. Pan, J. Lv, Studies on the removal of tetracycline by multi-walled carbon nanotubes, Chem. Eng. J., 178 (2011) 26–33.

[39] H.A. Ismael, L.H. Khdum, A.J. Lafta, Use of Iraqi cherry seeds in the removal of paracetamol and atenolol medicines from their aqueous solutions, Int. J. Sci. Res., 3 (2014) 2290–2295.

[40] J.C. Hsu, C.H. Liao, Y.L. Wei, Nitrate removal by synthetic nanoscale zero-valent iron in aqueous recirculated reactor, Sustainable Environ. Res., 6 (2011) 353–359.

[41] M.A. Tofighy, T. Mohammadi, Nitrate removal from water using functionalized carbon nanotube sheets, Chem. Eng. Res. Des., 90 (2012) 1815–1822.

[42] B. Pan, B. Xing, Adsorption mechanisms of organic chemicals on carbon nanotubes, Environ. Sci. Technol., 42 (2008) 9005–9013.

[43] B. Dehdashti, M.M. Amin, H.R. Pourzamani, L. Rafati, M. Mokhtari, Removal of atenolol from aqueous solutions by multiwalled carbon nanotubes modified with ozone: kinetic and equilibrium study, Water Sci. Technol., 2017 (2018) 636–649.

[44] V. Arya, L. Philip, Adsorption of pharmaceuticals in water using Fe_3O_4 coated polymer clay composite, Microporous Mesoporous Mater., 232 (2016) 273–280.

[45] G.Z. Kyzas, A. Koltsakidou, S.G. Nanaki, D.N. Bikiaris, D.A. Lambropoulou, Removal of beta-blockers from aqueous media by adsorption onto graphene oxide, Sci. Total Environ., 537 (2015) 411–420.