

57 (2016) 5789–5799 March



www.deswater.com

doi: 10.1080/19443994.2015.1005693

Adsorption of 2,4,6-trichlorophenol from aqueous solutions by a surfactant-modified zeolitic tuff: batch and continuous studies

Kazem Naddafi^a, Noushin Rastkari^{a,b}, Ramin Nabizadeh^a, Reza Saeedi^c, Maryam Gholami^{a,d,*}, Maryam Sarkhosh^a

^aDepartment of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran, Tel. +98 21 88954914; email: knadafi@tums.ac.ir (K. Naddafi), Tel. +98 21 88978395; email: n_rastkari@yahoo.com (N. Rastkari), Tel. +98 21 88954914; email: r_nabizadeh@tums.ac.ir (R. Nabizadeh), Tel. +98 917 1262204; Fax: +98 352 6824880;

emails: mgholami@alumnus.tums.ac.ir (M. Gholami), marya.sarkhosh@yahoo.com (M. Sarkhosh)

^bCenter for Air Pollution Research (CAPR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran

^cFaculty of Health, Safety and Environment, Department of Public Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran, Tel. +98 21 88954914; Fax: +98 21 88950188; email: reza.saeedi@gmail.com

^dDepartment of Environmental Health Engineering, Abarkouh Paramedical College, Shahid Sadoughi University of Medical Sciences, Yazd, Iran

Received 12 August 2014; Accepted 1 January 2015

ABSTRACT

In the present study, a clinoptilolite-rich tuff was modified with hexadecyl trimethyl ammonium chloride and was used for the removal of 2,4,6-trichlorophenol (TCP) from aqueous solutions. Kinetic and isotherm of TCP adsorption were studied in a batch system, and the continuous adsorption experiments were performed as a function of initial TCP concentration in a packed bed column. Kinetic experiments indicated that the TCP adsorption by the surfactant-modified zeolite (SMZ) was rapid and reached to equilibrium in 30 min for all TCP concentrations. The pseudo-second-order rate equation best described the kinetic of TCP adsorption onto the SMZ ($R^2 > 0.99$). Isotherm experiments were conducted in an initial TCP concentration range of 25–200 mg/L, and the isotherm data were found to be in the best fitness with the Langmuir model ($R^2 > 0.99$). According to the Langmuir model, the maximum adsorption capacity (q_m) of TCP was obtained to be 12.9 mg/g. In the packed bed column, by increasing the influent TCP concentration from 100 to 200 mg/L, the adsorption capacity at complete exhaustion point drastically increased from 14.7 to 35.5 mg/L. The breakthrough curves were predicted with the suitable fitness by both the Thomas and Yoon–Nelson models ($R^2 > 0.93$).

Keywords: Adsorption; 2,4,6-trichlorophenol; Clinoptilolite; Batch system; Packed bed column

^{*}Corresponding author.

^{1944-3994/1944-3986 © 2015} Balaban Desalination Publications. All rights reserved.

1. Introduction

2,4,6-Trichlorophenol (TCP, $C_6H_3Cl_3O$) is one of the important organic pollutants being continuously discharged into the aqueous environment. The compound is mainly used as board range pesticide and wood and glue preservative. TCP is also produced during water disinfection as a result of chlorination of phenolic compounds. Based on the toxicological studies, International Agency for Research on Cancer has classified TCP as a possibly carcinogenic to humans in Group 2B. In addition to the adverse health effect, TCP can cause unpleasant taste and odor in drinking water. The taste and odor thresholds of TCP in water are 2 and 300 μ g/L, respectively [1,2].

Several methods have been developed for the removal of phenolic compounds from water and wastewater, such as biodegradation, photochemical oxidation, catalytic wet oxidation, and adsorption process. Among these techniques, the adsorption process, especially using inexpensive natural adsorbents, is considered to be the most applicable method for removing TCP from water and wastewater. In recent years, a great attention has been paid to low-cost natural adsorbents to treat wastewater-containing organic pollutants [1,3–6]. Abu-Lail et al. [3] evaluated the performance of a commercial zeolite for the removal of methyl tertiary butyl ether (MTBE) from water and showed the zeolite was capable to remove MTBE in batch and column systems. Kuleyin [4] observed that the phenol and 4-chlorophenol were efficiently removed by surfactant-modified natural zeolites with maximum adsorption capacities of 1.3 and 12.7 mg/g, respectively. Yousef et al. [7] used zeolitic tuff for the adsorption of phenol, the kinetic and isotherm data were described by the pseudo-second-order and Freundlich models, respectively, and the mechanism of adsorption was found to be physical. The previous studies indicated that the modification of natural adsorbents is a useful measure to improve their removal efficiency and capacity [4,8].

In full-scale application of adsorption process, continuous-flow packed bed columns are preferable; because the reactors employ the concentration difference as a driving force for adsorption of pollutants resulted in more efficient utilization of adsorbent capacity. In the operation of the packed bed columns, the plot of effluent concentration (or effluent concentration to influent concentration ratio, C/C_0) vs. operation time (or throughput volume) is called breakthrough curve. Breakthrough and complete exhaustion points of a breakthrough curve are typically assumed, where C/C_0 ratios are equal to 0.05 and 1.0, respectively. The experimental data obtained

from the laboratory-scale packed bed column along with the batch mode are helpful for full-scale applications [9–11]. The objective of the present study was to evaluate the performance of a zeolitic tuff for TCP removal from aqueous solutions. The zeolitic tuff was modified using hexadecyl trimethyl ammonium chloride (HDTMA-Cl), and then the effectiveness of the surfactant-modified zeolite (SMZ) for TCP removal was studied in both batch and continuous systems.

2. Materials and methods

2.1. Materials and chemicals

The zeolitic tuff was obtained from a quarry in Semnan, Iran. HDTMA-Cl ($C_{19}H_{42}$ ClN) and NaCl supplied by Merck (Germany) were used for modification of the zeolite. The experimental solutions were synthetically prepared using deionized water and analytical grade TCP with a purity greater than 97% (Merck supplied). The pH of the experimental solutions was adjusted to 5.0 (the optimum pH determined in the preliminary experiments) by 0.1 M NaOH and/or 0.1 M HCl.

2.2. Preparation of adsorbent

The zeolitic tuff was crushed and sieved to select the particles with desired size (250-300 µm) for future use. The zeolite particles were washed with deionized water to remove any dissolved salts and then heated to 200°C for 24 h. The zeolite particles were subsequently loaded with sodium ions (Na⁺) in a 1 M NaCl solution (zeolite concentration of 100 g/L) at room temperature for 24 h under slow shaking to produce sodium-modified zeolite (NaZ). The NaZ was subsequently contacted with 0.025 M HDTMA-Cl solution in a manner similar to the NaZ production. Later, the zeolite was washed with deionized water to remove chloride ions. Finally, the produced SMZ was dried in an oven at 50°C. The effect of sodium and surfactant modifications on TCP adsorption by the zeolite was studied in pH of 5.0, contact time of 60 min, zeolite dosage of 10 g/L, and TCP initial concentration of 100 mg/L.

2.3. Characteristics of zeolitic tuff

Chemical composition of the natural zeolitic tuff was obtained by X-ray fluorescence (XRF) analysis. The crystal structure and morphology of the natural zeolite and SMZ particles were determined using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques, respectively.

2.4. Batch adsorption experiments

In all of the batch experiments, the volume of solution was 50 mL, initial pH of solution was adjusted to 5.0 (before addition of adsorbent), and the mixture of solution and adsorbent was agitated in 250 rpm on a rotary shaker with laboratory temperature $(20 \pm 2 °C)$. Adsorption kinetic experiments were carried out in five initial TCP concentrations (25, 50, 100, 150, and 200 mg/L) and an equal adsorbent mass of 500 mg. In the kinetic experiments, the aqueous samples were taken from experiment vessels at preset time intervals (5, 10, 15, 30, 45, 60, 90, 120, 180, and 240 min) for analysis. Isotherm experiments were conducted in contact time of 24 h. The other conditions of the isotherm experiments were the same as those of the kinetic tests.

2.5. Continuous adsorption experiments

Continuous experiments were conducted by passing the TCP solutions of known concentrations (100 and 200 mg/L at initial pH value of 5.0) through a packed bed column in a down-flow mode. Inner diameter, bed depth, and bed volume of the column were 1.1 cm, 6.5 cm, and 6.2 mL, respectively. Weight of the loaded SMZ into the column was 6.0 g. The column was operated at a constant flow rate and the empty bed contact time to be 4 mL/min and 1.5 min, respectively. In each run of the column experiment, operation of the column was continued until the effluent to influent TCP concentration ratio (C/C_0) reached to 1.0.

2.6. Analytical methods

After each test, the mixture was centrifuged in 5,000 rpm to separate the SMZ, and the supernatant was taken for analysis of effluent TCP level. The concentration of TCP was determined using a UV–vis spectrophotometer (Lambda 25; PerkinElmer Inc.) at the wavelength of 500 nm according to the instructions of standard methods [12].

2.7. Calculations

The TCP removal efficiency and adsorption capacity are calculated by Eqs. (1) and (2) [13]:

$$q = \frac{(C_0 - C)V}{m} \tag{1}$$

$$E = \frac{(C_0 - C)}{C_0} \times 100$$
 (2)

where q (mg/g) is the adsorption capacity, C_0 (mg/L) and C (mg/L) are the initial and final concentrations, respectively, V (L) is the solution volume, m (g) is the adsorbent mass, and E (%) is the removal efficiency.

The kinetic data of TCP adsorption were analyzed using the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models. The pseudo-first-order and pseudo-second-order rate equations are presented below, respectively, as Eqs. (3) and (4) [5,13]:

$$\ln\left(\frac{q_e - q_t}{q_e}\right) = -k_1 t \tag{3}$$

$$\frac{1}{q_t} = \frac{1}{k_2 \ q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacities at equilibrium and at time *t*, respectively, *t* (min) is the contact time, k_1 (1/min) is the pseudofirst-order rate constant, and k_2 (g/mg min) is the pseudo-second-order rate constant of adsorption.

The Elovich equation is applied to gaseous as well as aqueous adsorption systems. This model is given by Eq. (5) [5]:

$$q_t = \beta \, \ln(\alpha) + \beta \, \ln(t) \tag{5}$$

where α (mg/g min) and β (g/mg) are the rate constants of the Elovich model.

The intraparticle diffusion model was used to determine the rate-limiting step of the adsorption process. This model is expressed as follows [14]:

$$q_t = k_{\rm id} t^{0.5} + a \tag{6}$$

where k_{id} (mg/g min^{0.5}) is the rate constant of intraparticle diffusion and *a* (mg/g) reflects the boundary-layer thickness. If the plot of q_t vs. $t^{0.5}$ produces a straight line and passes through the origin, then the rate-limiting step is suggested to be the only intraparticle diffusion. Otherwise, one of the other sorption steps controls the overall rate of the adsorption process.

In order to analyze the TCP adsorption isotherm, the Freundlich, Langmuir, Freundlich–Langmuir and Temkin isotherm models were used as they are given, respectively, in Eqs. (7)–(10) [5,13,15]:

$$\log (q_e) = \log (K_F) + \frac{1}{n} \log (C_e)$$
(7)

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{8}$$

$$\log\left(\frac{1}{q_e} - \frac{1}{q_m}\right) = \log\left(\frac{1}{bq_m}\right) + \frac{1}{n}\log\left(\frac{1}{C_e}\right) \tag{9}$$

$$q_e = \frac{RT}{b_T} \ln (A_T) + \frac{RT}{b_T} \ln (C_e)$$
(10)

where C_e (mg/L) is the equilibrium concentration; K_F and n are the Freundlich constants that are indicators of the adsorption capacity and intensity, respectively; q_m (mg/g) is the maximum adsorption capacity; b(L/mg) is the Langmuir constant related to the adsorption energy; R (8.314 J/mol K) is the universal gas constant; T (K) is the absolute temperature; b_T (J/mol) is the Temkin constant related to heat adsorption; and A_T (L/g) is the Temkin binding constant.

In the continuous adsorption system, the total mass of TCP adsorbed by the SMZ was determined by calculating the enclosed area between the break-through curve and a horizontal line drawn at the point of $C/C_0 = 1.0$. The Thomas and Yoon–Nelson models were used to represent the dynamics of the packed bed column. These models predict the effluent concentration of adsorbate as a function of the operation time. The Thomas and Yoon–Nelson models are written, respectively, as below [16,17]:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{\rm Th}q_0m}{Q} - K_{\rm Th}C_0t_s \tag{11}$$

$$\ln\left(\frac{C}{C_0 - C}\right) = k_{\rm YN} t_s - k_{\rm YN} \tau \tag{12}$$

where k_{Th} (mL/mg min) is the Thomas rate constant, *Q* (L/min) is the flow rate, q_0 (mg/g) is the adsorption capacity at complete exhaustion point, t_s (min) is the operation time, k_{YN} (1/min) is the Yoon–Nelson rate constant, and τ (min) is the time to 50% adsorbate breakthrough (*C*/*C*₀ = 0.5).

3. Results and discussion

3.1. Characteristics of zeolitic tuff

The chemical composition of the clinoptilolite-rich tuff used in this study as compared to that of the same material from other places is given in Table 1. The XRF analysis indicated that the main compounds of the zeolite were silica (SiO₂) and alumina (Al₂O₃), and the mass ratio of silica to alumina was 6.93. According to Table 1, the chemical composition of the

clinoptilolite-rich tuff used in this study was approximately similar to that of clinoptilolite zeolite from other places such as Turkey [4], Greece [18], China [19], and New Mexico [20]. The XRF analysis also indicated the presence of metal oxides. In aqueous solutions, the metal oxides form functional groups that were formed on the surface of the zeolite. These functional groups play an important role in the adsorption of pollutants from aqueous solutions [21].

Fig. 1 shows the XRD patterns of the natural zeolite and SMZ. The major X-ray peaks of the natural zeolite and SMZ differed only in their relative intensity but not in their positions which imply that the crystalline nature of the zeolite remained unchanged during the surfactant modification. The results also confirmed the existence of clinoptilolite, quartz, and cristobalite in the natural zeolite and SMZ. The SEM images of the natural zeolite and SMZ are presented in Fig. 2. As seen in Fig. 2, the morphological difference between the natural zeolite and SMZ was apparent. After surfactant modification, the surfaces of the zeolite crystals were covered with an organic layer, but the edges of the zeolite crystals did not completely disappear. The effect of sodium and surfactant modifications on TCP adsorption by the zeolite is shown in Fig. 3. According to Fig. 3, surfactant modification significantly increased the TCP removal efficiency by the zeolite; therefore, the main TCP adsorption experiments were continued using the SMZ.

3.2. Batch system study

3.2.1. Kinetic study

The kinetic profiles of TCP adsorption by the SMZ are shown in Fig. 4. As can be seen in the figure, the adsorption process was so rapid that a considerable fraction of the equilibrium adsorption (over 90%) was attained in 30 min, and the maximum required time to reach the equilibrium was about 45 min in all of the examined initial concentrations of TCP. Therefore, the contact time required for the removal of TCP by SMZ was short. This rapid kinetic will decrease the reactor volume in full-scale applications and affect the feasibility and effectiveness of the process. Similar to this study, Apreutesei et al. [22] reported that the rate of phenol and 4-chlorophenol removal by a Romanian surfactant-modified zeolite was very high during the first 30 min, and that the equilibrium was reached in about 4 h.

Determination of the kinetic model and parameters of an adsorption process is useful to predict its rate and efficiency [13]. Table 2 represents the fitness of the kinetic data with the pseudo-first-order, Table 1

Chemical composition of the raw natural clinoptilolite-rich tuff used in this study as compared to that of the same material from other places

	Concentration (mass percent)						
Compound	Iran (this study)	Turkey [4]	Greece [18]	China [19]	New Mexico [20]		
SiO ₂	69.321	65.0	77.08	71.53	66.61		
Al_2O_3	10.475	13.7	13.08	13.65	12.91		
CaO	1.289	3.1	3.63	1.89	3.18		
K ₂ O	4.028	1.0	4.00	4.14	2.44		
Na ₂ O	2.244	5.6	0.32	1.86	0.39		
Fe ₂ O ₃	0.662	-	0.97	2.82	1.7		
MgO	0.410	1.0	0.76	1.61	1.54		
TiO ₂	0.191	0.3	0.11	0.28	0.25		
SO ₃	0.045	-	-	-	-		
Sr	0.028	-	-	-	-		
P_2O_3	0.020	-	-	-	-		
Zr	0.017	-	-	-	-		
Loss on ignition	11.270	-	-	5.6	10.72		



Fig. 1. XRD patterns of the zeolitic materials: (a) natural zeolite and (b) SMZ.



Fig. 2. SEM images of the zeolitic materials: (a) natural zeolite and (b) SMZ.



Fig. 3. Effect of sodium and surfactant modifications on TCP adsorption by the zeolite.

pseudo-second-order, Elovich, and intraparticle diffusion models. The kinetic of TCP adsorption onto the SMZ was described by the pseudo-second-order rate equation with the best fitness ($R^2 > 0.99$). In the TCP concentration range of 25–200 mg/L, the pseudo-second-order rate constant was obtained to be in the



Fig. 4. Kinetic profiles of TCP adsorption by the SMZ.

range of 0.034–0.329 g/mg.min. As given in Table 2, since the plot of q_t vs. $t^{0.5}$ was not linear, it was concluded that the kinetic of TCP adsorption was not limited by the intraparticle diffusion step.

3.2.2. Isotherm study

The isotherm study produces necessary data for design, operation, and cost-efficiency assessment of the adsorption systems. The isotherm models predict the q_e as a function of C_{er} , help to understand the adsorption mechanisms and produce efficient parameters for comparing different adsorbents for the same adsorbate [23]. The isotherm data of TCP adsorption by the SMZ and their prediction using the Freundlich, Langmuir, Freundlich-Langmuir and Temkin isotherm models are displayed in Fig. 5. The isotherm parameters of these models are also given in Table 3. As indicated in Fig. 5 and Table 3, the isotherm data of TCP adsorption by the SMZ were better described by the Langmuir model rather than the other isotherm models ($R^2 > 0.99$). The data also showed good fitness with the other isotherm models, especially the Freundlich-Langmuir model ($R^2 > 0.98$). The parameter *n* in the Freundlich model is a function of adsorption intensity and would be more than 1.0 for a favorable adsorption process [24]. In this study, the value of parameter n was obtained to be 1.9, indicating the favorable conditions for the TCP adsorption onto the SMZ. Based on the Langmuir isotherm model, the predicted maximum monolayer adsorption capacity (q_m) of TCP by the SMZ was found to be 12.9 mg/g. This value is promising as compared to those obtained by similar adsorption systems. Díaz Nava et al. [25] investigated the phenol removal efficiency of a Mexican SMZ and found that the parameter q_m derived from the Langmuir model was 0.59 mg/g. Sprynskyy [5]

Table 2

Kinetic parameters of the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models for TCP adsorption by the SMZ

	Parameter	Initial concentration (mg/L)					
Kinetic model		25	50	100	150	200	
Pseudo-first-order	q_e	0.47	1.21	1.85	3.59	4.96	
	\dot{k}_1	0.041	0.012	0.033	0.061	0.054	
	R^2	0.789	0.462	0.878	0.872	0.965	
Pseudo-second-order	q_e	2.17	4.30	7.32	10.78	12.36	
	k_2	0.329	0.050	0.061	0.034	0.046	
	R^2	1.000	0.998	1.000	1.000	1.000	
Elovich	α	36,570	58	2,436	466	2,069	
	β	0.142	0.473	0.575	0.971	0.993	
	R^2	0.689	0.776	0.843	0.852	0.780	
Intraparticle diffusion	k_{id}	0.033	5.540	0.142	0.244	0.239	
	а	1.769	2.800	5.540	7.725	9.468	
	R^2	0.461	0.561	0.627	0.652	0.547	



Fig. 5. Isotherm data of TCP adsorption by the SMZ and their prediction using the isotherm models: (a) Freundlich model, (b) Langmuir model, (c) Freundlich–Langmuir model, and (d) Temkin model.

Table 3

Parameters of the Freundlich, Langmuir, Freundlich–Langmuir, and Temkin isotherm models for TCP adsorption by the SMZ

Isotherm model	Parameter	Value
Freundlich	п	1.95
	K _f	1.25
	R^{2}	0.967
Langmuir	q_m	13.24
C C	b	0.053
	R^2	0.995
Freundlich–Langmuir	q_m	13.93
C C	b	0.054
	п	1.06
	R^2	0.989
Temkin	A_T	0.548
	b_T	854
	R^2	0.982

reported that the parameter q_m for phenol adsorption by an Ukrainian SMZ was found to be 11.7 mg/g. Apreutesei et al. [22] evaluated the efficiency of a Romanian SMZ for 4-chlorophenol removal and found that the parameter q_m was 4.1 mg/g.

3.3. Continuous system study

In design and operation of a packed bed column, the required time for the appearance of breakthrough as well as the shape of the breakthrough curve is a very important characteristic [16,17,26]. The results of TCP adsorption by the SMZ in the packed bed column as the breakthrough curves are presented in Fig. 6. Table 4 presents the operation parameters of the packed bed column during the experimental runs. As given in Table 4, doubling the influent TCP concentration (from 100 to 200 mg/L) caused a considerable increase in the total TCP uptake capacity from 14.7 to 35.5 mg/g. Similar trends have also been observed in the adsorption of TCP by oil palm shell-based activated carbon, removal of chromium ions using modified corn stalk, and removal of cobalt ions using granular-activated carbon [16,26,27]. This observation could be attributed to the increased driving force



Fig. 6. Breakthrough curves of TCP adsorption by the SMZ in the packed bed column and their prediction using the breakthrough curve models: (a) $C_0 = 100 \text{ mg/L}$ and Thomas model, (b) $C_0 = 200 \text{ mg/L}$ and Thomas model, (c) $C_0 = 100 \text{ mg/L}$ and Yoon–Nelson model, and (d) $C_0 = 200 \text{ mg/L}$ and Yoon–Nelson model.

Table 4

	Breakthroug $(C/C_0 = 0.05)$	Breakthrough point $(C/C_0 = 0.05)$		Exhaustion point $(C/C_0 = 0.95)$		Complete exhaustion point $(C/C_0 = 1.00)$	
$C_0 (mg/L)$	t_s (min)	<i>q</i> (mg/g)	t_s (min)	<i>q</i> (mg/g)	t_s (min)	q (mg/g)	
100	32	2.1	532	15.4	732	15.6	
200	58	7.5	480	34.9	580	35.0	

Breakthrough curve characteristics of the packed bed column used for TCP adsorption by the SMZ in the continuous mode

against mass-transfer resistance in higher inlet TCP concentration; therefore, by increasing the inlet TCP concentration, it would be easier to overcome mass-transfer resistance and hence, adsorption capacity would increase [26,28].

The breakthrough curves of packed bed columns can be explained through the mathematical models. The breakthrough curve models describe and analyze the result of packed bed column studies for the purpose of industrial applications [29]. Fig. 6 displays the fitness of the Thomas and Yoon-Nelson models to the breakthrough curves of the packed bed column. The Thomas and Yoon-Nelson parameters for TCP adsorption by the SMZ in the packed bed column are presented in Table 5. The breakthrough curves were found in relatively good fitness with both the Thomas and Yoon–Nelson models ($R^2 > 0.93$), and the predicted breakthrough curves by these models were complied with each other. Similarly, Huang et al. [30] observed that the removal of phenol by a diethylenetriamine-modified hypercrosslinked styrene-divinylbenzene was described by both the Thomas and Yoon–Nelson models.

According to the Thomas model, the values of parameter q_0 (adsorption capacity at complete exhaustion point) for inlet TCP concentrations of 100 and 200 mg/L

Table 5

Parameters of the Thomas and Yoon–Nelson models for breakthrough curve analysis of TCP adsorption by the SMZ

		Initial concentration (mg/L)		
Breakthrough models	Parameters	100	200	
Thomas	$k_{\rm Th}$	0.131	0.077	
	q_0	16.44	33.48	
	R^2	0.968	0.930	
Yoon–Nelson	$k_{\rm YN}$	0.013	0.015	
	τ	247	251	
	R^2	0.968	0.930	

were determined to be 16.4 and 33.5 mg/g that were consistent with the experimental values. The kinetic constant $k_{\rm Th}$ decreased from 0.131 to 0.077 mL/mg min as the TCP concentration increased. Based on the Yoon–Nelson model, the values of the parameter τ indicating the time to 50% breakthrough were calculated to be 247 and 251 min for influent TCP concentrations of 100 and 200 mg/L, respectively, which were almost close to the actual values. According to the results, both the Thomas and Yoon–Nelson models could be used to predict the breakthrough curves of the TCP adsorption by the SMZ.

4. Conclusions

In this research, the capability of the SMZ for TCP removal from aqueous solutions was investigated. The kinetic of the TCP adsorption onto the SMZ was found to be in the best fitness with the pseudosecond-order rate model. The kinetic of TCP adsorption was not limited by the intraparticle diffusion step. The Langmuir isotherm model best described the TCP adsorption process. Based on the Langmuir model, the maximum adsorption capacity (q_m) of TCP by the SMZ was determined to be 12.9 mg/g. In the packed bed column, the increase in influent TCP concentration caused a significant increase in the total TCP uptake capacity. The breakthrough curves were well predicted by both the Thomas and Yoon-Nelson models. In the Thomas model, the values of parameter q_0 (adsorption capacity at complete exhaustion point) for inlet TCP concentrations of 100 and 200 mg/L were found to be 16.4 and 33.5 mg/g, respectively. This study identified the SMZ as an effective and promising adsorbent for the removal of TCP from water and wastewater.

Acknowledgments

The authors wish to thank the laboratory staff of Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Iran, for their collaboration in this research.

List of symbols

- A rate constant of the Elovich model (mg/g min)
- B rate constant of the Elovich model (g/mg)
- T time to 50% adsorbate breakthrough (min)
- A constant of the boundary-layer thickness (mg/g)
- A_T Temkin binding constant (L/g)
- B Langmuir isotherm constant (L/mg)
- b_T Temkin constant related to heat of sorption (J/mol)
- C final or effluent concentration (mg/L)
- C_0 initial or influent concentration (mg/L)
- C_e equilibrium concentration (mg/L)
- E removal efficiency (%)
- k_1 pseudo-first-order rate constant (1/min)
- k_2 pseudo-second-order rate constant (g/mg min)
- K_f Freundlich isotherm constant
- k_{id} rate constant of intraparticle diffusion (mg/g.min^{0.5})
- $k_{\rm Th}$ Thomas rate constant (mL/mg min)
- $k_{\rm YN}$ Yoon–Nelson rate constant (1/min)
- *m* adsorbent mass (g)
- *n* Freundlich isotherm constant
- Q flow rate (L/min)
- q adsorption capacity (mg/g)
- q_0 adsorption capacity at complete exhaustion point (mg/g)
- q_e equilibrium adsorption capacity (mg/g)
- q_m maximum adsorption capacity (mg/g)
- q_t adsorption capacity at any contact time (mg/g)
- R universal gas constant (8.314 J/mol K)
- T temperature (K)
- T contact time (min)
- t_s operation time (min)
- V solution volume (L)

References

- I. Tan, A. Ahmad, B. Hameed, Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2, 4, 6-trichlorophenol on oil palm empty fruit bunchbased activated carbon, J. Hazard. Mater. 164 (2009) 473–482.
- [2] WHO, Guidelines for Drinking Water Quality, fourth ed., World Health Organization, Geneva, 2011.
- [3] L. Abu-Lail, J.A. Bergendahl, R.W. Thompson, Adsorption of methyl tertiary butyl ether on granular zeolites: Batch and column studies, J. Hazard. Mater. 178 (2010) 363–369.
- [4] A. Kuleyin, Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite, J. Hazard. Mater. 144 (2007) 307–315.
- [5] M. Sprynskyy, T. Ligor, M. Lebedynets, B. Buszewski, Kinetic and equilibrium studies of phenol adsorption by natural and modified forms of the clinoptilolite, J. Hazard. Mater. 169 (2009) 847–854.
- [6] R.I. Yousef, B. El-Eswed, The effect of pH on the adsorption of phenol and chlorophenols onto natural zeolite, Colloids Surf., A 334 (2009) 92–99.
- [7] R.I. Yousef, B. El-Eswed, A.a.H. Al-Muhtaseb, Adsorption characteristics of natural zeolites as solid adsor-

bents for phenol removal from aqueous solutions: Kinetics, mechanism, and thermodynamics studies, Chem. Eng. J. 171 (2011) 1143–1149.

- [8] R. Cortés-Martínez, M. Solache-Ríos, V. Martínez-Miranda, Sorption behavior of 4-Chlorophenol from aqueous solutions by a surfactant-modified Mexican zeolitic rock in batch and fixed bed systems, Water Air Soil Pollut. 183 (2007) 85–94.
- [9] Metcalf & Eddy Inc, Wastewater Engineering: Treatment and Reuse, McGraw-Hill, New York, NY, 2003.
- [10] K. Naddafi, R. Nabizadeh, R. Saeedi, A.H. Mahvi, F. Vaezi, K. Yaghmaeian, A. Ghasri, S. Nazmara, Biosorption of lead (II) and cadmium (II) by protonated *Sargassum glaucescens* biomass in a continuous packed bed column, J. Hazard. Mater. 147 (2007) 785–791.
- [11] J. Warchoł, P. Misaelides, R. Petrus, D. Zamboulis, Preparation and application of organo-modified zeolitic material in the removal of chromates and iodides, J. Hazard. Mater. 137 (2006) 1410–1416.
- [12] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, DC, 2005.
- [13] B. Hameed, I. Tan, A. Ahmad, Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon, Chem. Eng. J. 144 (2008) 235–244.
- [14] L. Ren, J. Zhang, Y. Li, C. Zhang, Preparation and evaluation of cattail fiber-based activated carbon for 2,4-dichlorophenol and 2,4,6-trichlorophenol removal, Chem. Eng. J. 168 (2011) 553–561.
- [15] M. Abtahi, A. Mesdaghinia, R. Saeedi, S. Nazmara, Biosorption of As (III) and As (V) from aqueous solutions by brown macroalga *Colpomenia sinuosa* biomass: Kinetic and equilibrium studies, Desalin. Water Treat. 51 (2013) 3224–3232.
- [16] S. Chen, Q. Yue, B. Gao, Q. Li, X. Xu, K. Fu, Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: A fixed-bed column study, Bioresour. Technol. 113 (2012) 114–120.
- [17] J. Salman, V. Njoku, B. Hameed, Batch and fixed-bed adsorption of 2,4-dichlorophenoxyacetic acid onto oil palm frond activated carbon, Chem. Eng. J. 174 (2011) 33–40.
- [18] E. Katsou, S. Malamis, M. Tzanoudaki, K.J. Haralambous, M. Loizidou, Regeneration of natural zeolite polluted by lead and zinc in wastewater treatment systems, J. Hazard. Mater. 189 (2011) 773–786.
- [19] H. Huang, X. Xiao, B. Yan, L. Yang, Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent, J. Hazard. Mater. 175 (2010) 247–252.
- [20] L.M. Camacho, R.R. Parra, S. Deng, Arsenic removal from groundwater by MnO₂-modified natural clinoptilolite zeolite: Effects of pH and initial feed concentration, J. Hazard. Mater. 189 (2011) 286–293.
- [21] G. Asgari, A. Sidmohammadi, A. Ebrahimi, Z. Gholami, E. Hoseinzadeh, Study on phenol removing by using modified zeolite (clinoptilolite) with FeCl₃ from aqueous solutions, J. Health System Res. 6 (2010) 848–852. (in Persian).
- [22] R.E. Apreutesei, C. Catrinescu, C. Teodosiu, Studies regarding phenol and 4-chlorophenol sorption by surfactant modified zeolites, Environ. Eng. Manage. J. 8 (2009) 651–656.

- [23] K. Naddafi, R. Saeedi, Biosorption of copper (II) from aqueous solutions by brown macroalga *Cystoseira myrica* biomass, Environ. Eng. Manage. 26 (2009) 1009–1015.
- [24] Z. Zhang, L. Moghaddam, I.M. O'Hara, W.O. Doherty, Congo Red adsorption by ball-milled sugarcane bagasse, Chem. Eng. J. 178 (2011) 122–128.
- [25] C. Díaz-Nava, M. Olguín, M. Solache-Ríos, M. Alarcón-Herrera, A. Aguilar-Elguezabal, Phenol sorption on surfactant-modified Mexican zeolitic-rich tuff in batch and continuous systems, J. Hazard. Mater. 167 (2009) 1063–1069.
- [26] A.H. Sulaymon, B.A. Abid, J.A. Al-Najar, Removal of lead copper chromium and cobalt ions onto granular activated carbon in batch and fixed-bed adsorbers, Chem. Eng. J. 155 (2009) 647–653.

- [27] I. Tan, A. Ahmad, B. Hameed, Fixed-bed adsorption performance of oil palm shell-based activated carbon for removal of 2,4,6-trichlorophenol, Bioresour. Technol. 100 (2009) 1494–1496.
- [28] S. Baral, N. Das, T. Ramulu, S. Sahoo, S. Das, G.R. Chaudhury, Removal of Cr(VI) by thermally activated weed *Salvinia cucullata* in a fixed-bed column, J. Hazard. Mater. 161 (2009) 1427–1435.
- [29] V. Vinodhini, N. Das, Packed bed column studies on Cr(VI) removal from tannery wastewater by neem sawdust, Desalination 264 (2010) 9–14.
- [30] J. Huang, X. Jin, J. Mao, B. Yuan, R. Deng, S. Deng, Synthesis, characterization and adsorption properties of diethylenetriamine-modified hypercrosslinked resins for efficient removal of salicylic acid from aqueous solution, J. Hazard. Mater. 217 (2012) 406–415.