Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21283

86 (2017) 131–138
August

Removal of 2,4,6-trichlorophenol from aqueous solutions by cetylpyridinium bromide (CPB)-modified zeolite in batch and continuous systems

Kazem Naddafi[a,b], Noushin Rastkari[b], Ramin Nabizadeh[a,b], Reza Saeedi[c], Maryam Gholami[a,d,*]

[a]*Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran, Tel. +98 917 1262204; Fax: +98 35 32838088; email: mgholami@alumnus.tums.ac.ir (M. Gholami), Tel. +98 21 88954914; email: knadafi@tums.ac.ir (K. Naddafi), Tel. +98 21 88954914; email: r_nabizadeh@tums.ac.ir (R. Nabizadeh)*
[b]*Center for Air Pollution Research (CAPR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran, Tel. +98 21 88978395; email: nr_rastkari@yahoo.com (N. Rastkari)*
[c]*Department of Health Sciences, School of Health, Safety and Environment, Shahid Beheshti University of Medical Sciences, Tehran, Iran, Tel. +98 21 88954914; Fax: +98 21 88950188; email: reza.saeedi@gmail.com*
[d]*Environmental Science and Technology Research Center, Department of Environmental Health Engineering, Shahid Sadoughi University of Medical Sciences, Yazd, Iran*

Received 13 February 2017; Accepted 3 August 2017

ABSTRACT

In this study, 2,4,6-trichlorophenol (TCP) was removed from aqueous solutions by clinoptilolite-rich tuff modified with cetylpyridinium bromide (CPB). CPB modification significantly increased the TCP adsorption capacity, so that the highest adsorption capacities of the natural zeolite and cetylpyridinium bromide-modified zeolite (CPB-MZ) at the same experimental conditions were determined to be 1.6 and 8.5 mg/g, respectively. Kinetic and isotherm of TCP adsorption were studied in a batch system in which kinetic experiments revealed that the TCP adsorption by the CPB-MZ reached to equilibrium in 45 min for all TCP concentrations. The kinetic of TCP adsorption onto the CPB-MZ was best described by the pseudo-second-order equation ($R^2 > 0.99$) while the isotherm data were best fitted with the Langmuir model ($R^2 > 0.99$). The continuous adsorption experiments were performed in a packed bed column. The maximum adsorption capacity (q_m) of TCP was 16.34 mg/g according to the Langmuir model. In this system, by increasing the influent TCP concentration from 100 to 200 mg/L, the adsorption capacity increased from 19.35 to 40.78 mg/g at complete exhaustion point.

Keywords: Adsorption; 2,4,6-Trichlorophenol; CPB-modified zeolite; Batch system; Continuous system

1. Introduction

Chlorophenols are a group of phenolic compounds that contain between one and five chlorine atoms. The phenolic compounds are persistent environmental pollutants that are mainly entered into the aqueous environment through wastewater of industries such as petrochemical, paint, solvent, pharmaceuticals, wood, pesticide, insecticide, leather, paper and pulp, etc. Chlorophenols also occur in drinking water as possible by-products of disinfection [1–5]. Among chlorophenols, 2,4,6-trichlorophenol (TCP) is of serious environmental concern due to its toxicity, widespread uses, persistence and unpleasant organoleptic properties [6–8]. TCP is readily absorbed by the skin and into the gastrointestinal tract, affecting the nervous system and causing respiratory problems such as cough, chronic bronchitis and pulmonary defects [9,10].

In order to control the adverse effects of organic compound such as TCP, a great deal of attention has been focused on its efficient removal from wastewater before discharged into the water bodies [11,12]. Different physical, chemical

---

* Corresponding author.

1944-3994/1944-3986

and biological methods such as activated carbon adsorption, chemical oxidation process, wet oxidation, ion-exchange resins, incineration, solvent extraction, irradiation and aerobic/anaerobic biological degradation have been examined for removing chlorophenols from wastewater [4,10,13]. Among these methods, adsorption and ion-exchange have been considered as promising techniques [5,14,15]. As activated carbon is relatively costly, attempts have been made to utilize lower cost and naturally abundant materials to remove toxic substances from wastewater [5,16]. Natural materials such as bagasse, biochar prepared from sugarcane bagasse, red mud, clay, zeolites and certain waste materials are classified as low-cost adsorbents [10,17].

Natural zeolites as crystalline microporous aluminosilicates consist of a framework of SiO_4 and AlO_4. There are permanent negative charges in the frameworks that are balanced by exchangeable cations such as Na^+, Ca^{2+}, K^+ and Mg^{2+} [18]. Zeolites are known as attractive adsorbents with excellent physicochemical characteristics such as high adsorption capacity, high specific surface area, cheap price, high mechanical resistance and efficient regeneration [19–21]. Because of negative charges in crystal structure, there is a repulsive force between natural zeolites and anionic or organic pollutants that prevents efficient adsorption. Modification of zeolites by cationic surfactants through reversing the surface charges can improve their adsorption properties for anionic and organic pollutants as well as conserves their cationic exchange properties [20,22–25]. Lei et al. [20] evaluated the removal of triclosan by cetylpyridinium bromide-modified zeolites (CPB-MZs) and showed that the modified zeolite can be an effective adsorbent for removal of triclosan. Torabian et al. [26] reported that CPB-MZ showed a higher adsorption capacity for petroleum aromatic hydrocarbons than that of hexadecyltrimethyl ammonium chloride (HDTMA)-modified zeolite.

Continuous packed bed column is the most common option for full-scale application of adsorption process due to a number of process engineering advantages including high yield operations, high removal efficiency, no need to adsorbent separation and relatively low capital and operating costs [27]. Column experiments give important parameters for design and scale-up of continuous packed bed sorption processes that cannot be obtained from batch experiments [28].

Based on the literature, CPB-MZs may have a higher adsorption capacity for some organic compounds than that of HDTMA-modified zeolites, it is reasonable to presume that CPB-MZ may be more effective than that of HDTMA-modified zeolite on TCP removal. In addition, to the best of our knowledge, no study has been devoted to address CPB-MZ for removal of TCP. The objective of this work was to determine the adsorption properties of the CPB-MZ for TCP removal from aqueous environments. In addition to kinetic and equilibrium studies in a batch system, performance of the packed bed sorption process was studied in a continuous system.

2. Materials and methods

2.1. Materials

The zeolitic tuff was obtained from a quarry in Semnan, Iran. CPB ($C_{21}H_{38}BrN.H_2O$) and NaCl supplied by Merck Co. (Germany) and used for modification of the zeolite. The deionized water and analytical grade TCP with purity greater than 97% (Merck) were applied to prepare experimental solutions.

2.2. Preparation of adsorbent

After obtaining zeolite tuff, it was crushed and sieved to select particles with a size range of 250–300 μm. Using deionized water, the zeolite was washed with deionized water to remove any dissolved salts and then was put in an oven at 200°C for 24 h. To produce sodium-modified zeolite (NaZ), the zeolite with concentration of 100 g/L was subsequently contacted with 1 M NaCl solution at laboratory temperature (20°C ± 2°C) for 24 h under slow shaking. According to the literature, the critical micelle concentration (CMC) of CPB was 1.8 mmol/L. In order to determine the effect of CPB concentration on the TCP adsorption, the NaZ was contacted with 0.5 (<CMC), 2 (≈CMC) and 25 mmol/L (>CMC) CPB solutions in a manner similar to the NaZ production and then the zeolites were washed with deionized water and finally the produced CPB-MZs were dried in an oven at 50°C. The corresponding modified zeolites were addressed as CPB-MZ#1, CPB-MZ#2 and CPB-MZ#3, respectively. Adsorption capacity of natural and modified zeolites on TCP adsorption was examined in pH of 5.0, contact time of 60 min, adsorbent dosage of 10 g/L and TCP initial concentration of 100 mg/L.

2.3. Characteristics of zeolite

X-ray fluorescence (XRF) analysis was used to obtain the chemical composition of the natural zeolite. The particle properties of the zeolite before and after adsorption were examined by the scanning electron microscope (SEM). The crystal structure of natural zeolite and CPB-MZ were characterized using X-ray diffraction (XRD) analysis.

2.4. Batch adsorption experiments

To conduct the batch experiments, the adsorbent was added to a solution with 50 mL volume, and then the mixture of solution and adsorbent was agitated in 250 rpm on a rotary shaker at laboratory temperature (20°C ± 2°C). The TCP removal efficiency and adsorption capacity were calculated by Eqs. (1) and (2), respectively [1,5,29]:

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

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

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 (%) stands for the removal efficiency.

Kinetic of the adsorption process was examined in adsorbent dosage of 500 mg, pH value of 5, initial TCP concentrations of 25, 50, 100, 150 and 200 mg/L and contact times of 5, 10, 15, 30, 45, 60, 90, 120, 180 and 240 min. Isotherm experiments were conducted in contact time of 24 h, and the other conditions of the isotherm experiments were the same as those of the kinetic tests. The effect of pH on TCP equilibrium adsorption was determined in initial TCP concentrations of 25–200 mg/L and adsorbent dosage of 500 mg by varying initial pH of solutions in the range of 3–11. The pH of experimental solutions was adjusted to desired values by 0.1 M NaOH and/or 0.1 M HCl and was measured using a pH meter (Metrohm Herisau-E520).

2.5. Continuous adsorption experiments

Apart from the batch experiments, the performance of the adsorption process was also evaluated in a continuous downflow packed bed column. TCP solutions of known concentrations (100 and 200 mg/L) at initial pH value of 5.0 through a packed bed column in a downflow mode. Bed depth, bed volume and inner diameter of the column were 6.5 cm, 6.2 mL and 1.1 cm, respectively. Weight of the loaded CPB-MZ into the column was 6.0 g. The column was being operated at constant flow rate and empty bed contact time of 4 mL/min and 1.5 min, respectively. In each run of the 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 experiment, the mixture was filtered to separate the CPB-MZ and the supernatant was taken for analysis of effluent TCP concentration. According to the instructions of Standard Methods, a UV–Vis spectrophotometer (Lambda 25; PerkinElmer Inc.) at the wavelength of 500 nm was applied to determine the concentration of TCP [30].

3. Results and discussion

3.1. Characteristics of zeolite

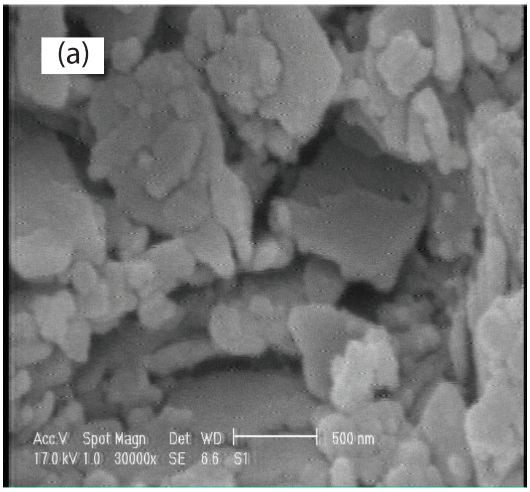
Table 1 shows the chemical composition of the natural zeolite sample applied in this study. Based on the XRF analysis, the major constituents of zeolite were silica and alumina. The ion-exchange capacity of zeolite depends on silica to alumina (Si/Al) ratio [31]. The Si/Al ratio was found to be 6.93 representing a high potential of ion-exchange capacity. In addition, the XRF analysis indicated the presence of metal oxides. In aqueous solutions, the metal oxides form functional groups on the zeolite surface. In fact, these functional groups play an important role in the adsorption of pollutants from aqueous solutions [32]. Fig. 1 shows the SEM images of the natural zeolite (a) and CPB-MZ (b). As shown in the figures, there is a morphological difference between natural zeolite and CPB-MZ. According to Fig. 1(b) after modifying the zeolite, the surfaces of the zeolite crystals were covered with an organic layer and the edges of the zeolite crystals were disappearing. XRD analyses of natural zeolite (Fig. 2(a)) and CPB-MZ (Fig. 2(b)) were carried out to confirm their crystal structure. The results of XRD patterns confirmed the existence of clinoptilolite, quartz and cristobalite in natural zeolite and CPB-MZ. Also, the difference in peak at 2θ of CPB-MZ with natural zeolite, conformed the adsorption of CPB onto zeolite. The effect of CPB concentration on the adsorption of TCP is shown in Fig. 3. According to Fig. 3, CPB-MZ#3 was the most effective adsorbent; therefore, this adsorbent was selected as the best adsorbent for investigating the other parameters and was addressed as CPB-MZ in this study.

Table 1
Chemical composition of the raw natural clinoptilolite-rich tuff used in this study

Compound	Mass (%)	Compound	Mass (%)
SiO_2	69.321	TiO_2	0.191
Al_2O_3	10.475	SO_3	0.045
CaO	1.289	Sr	0.028
K_2O	4.028	P_2O_3	0.020
Na_2O	2.244	Zr	0.017
Fe_2O_3	0.662	Loss on ignition	11.270
MgO	0.410		

3.2. Effect of pH

Fig. 4 shows the effect of pH on TCP adsorption by the CPB-MZ. As can be seen from this plot, TCP adsorption capacity was found to decline by increasing pH. In this study,



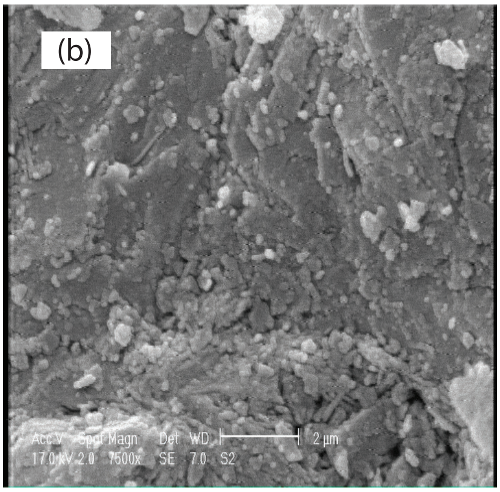


Fig. 1. SEM images of the zeolitic materials: natural zeolite (a) and CPB-MZ (b).

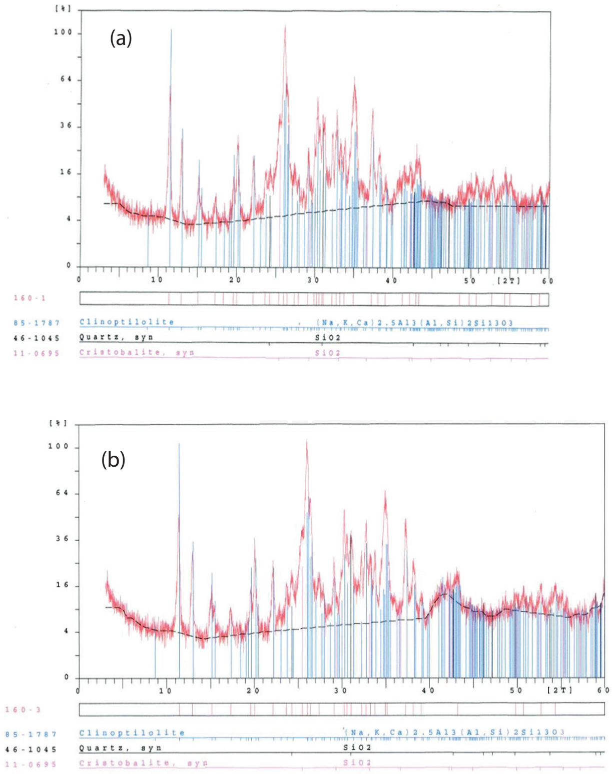


Fig. 2. XRD patterns of the zeolitic materials: natural zeolite (a) and CPB-MZ (b).

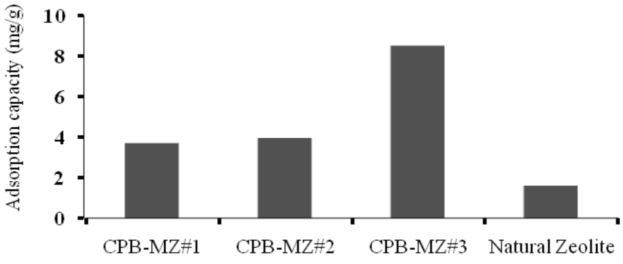


Fig. 3. The effect of CPB concentration on the adsorption of TCP by the zeolite.

the highest TCP adsorption capacity was achieved at pH 3 to be as high as 13.1 mg/g. This result could be due to the chemical characteristics of the CPB-MZ and acidic point of zero charge pH (pH_{pzc}) to be around 6.2. At solution pH lower than the pH_{pzc}, the total surface charge would be on average positive that would be more attractive for adsorption of undissociated TCP due to the electrostatic attraction. Similar trends were reported in the adsorption of TCP on coconut shell-based activated carbon and activated clay as well as adsorption of 4-chlorophenol and 2,4-dichlorophenol on anaerobic granular sludge [1,5,11,33].

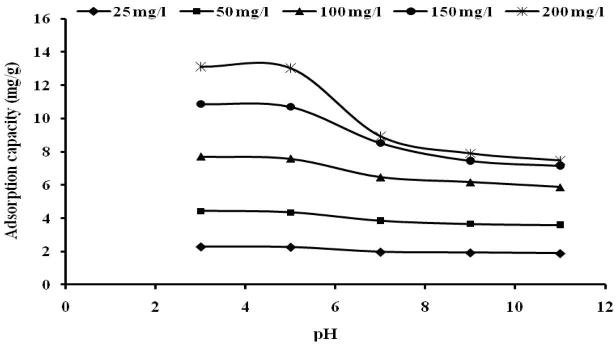


Fig. 4. Effect of solution pH on TCP adsorption on CPB-MZ.

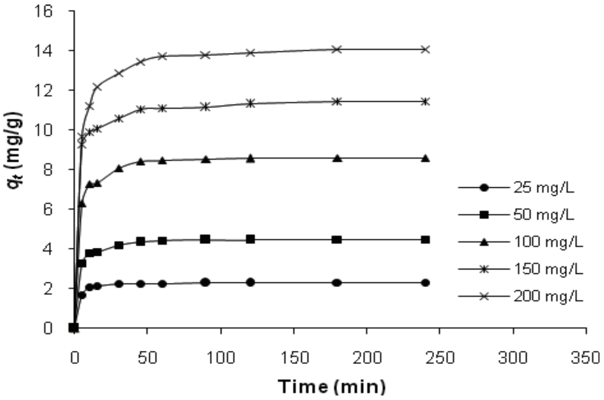


Fig. 5. Kinetic profiles for adsorption of TCP on CPB-MZ.

3.3. Kinetic study

Fig. 5 shows kinetic profiles of TCP adsorption onto the CPB-MZ. The adsorption process was rapid and the time necessary to reach the equilibrium was about 45 min. This result is consistent with previous study on adsorption of phenol and 4-chlorophenol by Romanian-modified zeolite as well as the removal of TCP by surfactant-modified bentonite [5,24].

The kinetic parameters are useful to predict adsorption rate and render important information for designing and modeling the process [1]. In order to investigate the adsorption kinetic rate equation, the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models were fitted to the experimental data. These kinetic models are, respectively, expressed as follows [1,21]:

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

$$t / q_t = 1/(k_2 q_e^2) + 1/q_e t \tag{4}$$

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

$$q_t = k_{id} t^{1/2} + a \tag{6}$$

where q_t (mg/g) and q_e (mg/g) are the amounts of TCP adsorbed at time t and at equilibrium, respectively, k_1 (min^{-1}) is the pseudo-first-order rate constant, k_2 (g/mg min) is the pseudo-second-order rate constant, α (mg/g min) and β (g/mg) are the rate constants of the Elovich model and k_{id} (mg/g.min$^{1/2}$) is the intraparticle diffusion rate constant and *a* (mg/g) is the constant of the intraparticle diffusion model. The kinetic parameters of TCP adsorption by the CPB-MZ are given in Table 2. According to Table 2, the pseudo-second-order rate equation best described the kinetic of TCP adsorption by the CPB-MZ ($R^2 > 0.99$). A good agreement was also observed between the experimental and the predicted q_e values. This model is more likely to predict the behavior over the whole range of adsorption systems [1]. Kuleyin [23] evaluated adsorption of phenol and 4-chlorophenol by Turkish surfactant-modified zeolite and reported good correlation coefficients for the pseudo-second-order model. Elena Apreutesei et al. [24] reported that pseudo-second-order model could adequately describe kinetic of 4-chlorophenol adsorption by HDTMA-modified zeolite as well as this results were obtained by the adsorption of TCP on biochar prepared from sugarcane bagasse [10]. Fig. 6 shows kinetic data of TCP adsorption by the CPB-MZ in accordance with the intraparticle diffusion model. Based on the intraparticle diffusion model, if the plot of q_t against $t^{1/2}$ passes through the origin and produces a straight line, then the sorption process is suggested to be controlled by the intraparticle diffusion. The kinetic data produced multilinear plot suggesting two or more steps which affect the sorption process [34].

3.4. Isotherm study

The isotherm data of TCP adsorption onto the CPB-MZ are shown in Fig. 7. Adsorption isotherm models are generally used to estimate adsorption capacity for any desirable effluent concentration as well as to investigate adsorption mechanisms. In this study, the Langmuir, Freundlich and Temkin isotherm models were used to analyze the experimental data. The linearized form of the isotherm models are, respectively, expressed as follows [23,29]:

$$C_e/q_e = 1/(K_L q_m) + C_e/q_e \tag{7}$$

$$\log(q_e) = \log(K_F) + 1/n \log(C_e) \tag{8}$$

$$q_e = RT/b_T \ln(A_T) + RT/b_T \ln(C_e) \tag{9}$$

where C_e (mg/L) is the equilibrium concentration of TCP; q_m (mg/g) is the maximum TCP adsorption capacity, K_L (L/mg) is the Langmuir adsorption equilibrium constant related to the adsorption energy, K_F and *n* are the Freundlich constants related to the adsorption capacity and intensity, respectively, *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 of adsorption and A_T (L/g) is the Temkin binding constant.

Table 3 provides isotherm parameters of the Langmuir, Freundlich and Temkin models for TCP adsorption by the CPB-MZ. The Langmuir isotherm model best fitted the experimental data with a very high correlation coefficient ($R^2 = 0.9991$). Similar trend was obtained by the adsorption of TCP on biochar prepared from sugarcane bagasse [10]. Based on the Langmuir model, the predicted maximum monolayer TCP adsorption capacity by the CPB-MZ was found to be 16.34 mg/g. The value of the Freundlich parameter 1/*n* should be between 0.1 and 1.0 for a favorable adsorption process [18].

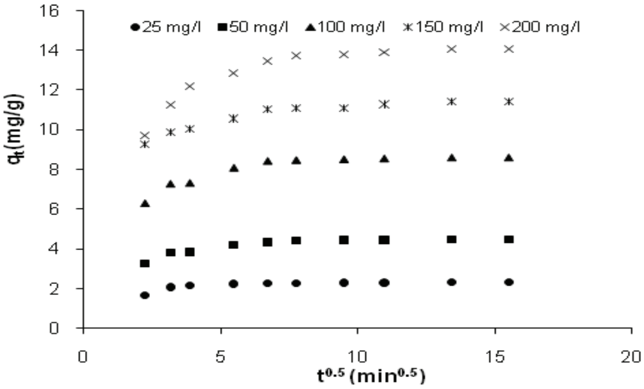


Fig. 6. Intraparticle diffusion model for adsorption of TCP on CPB-MZ.

Table 2
Kinetic parameters of the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models for TCP adsorption by the CPB-MZ

Kinetic model	Parameter	Initial concentration (mg/L)				
		25	50	100	150	200
Pseudo-first-order	q_e	0.4284	1.292	2.4495	2.7657	4.3706
	k_1	0.0323	0.0421	0.0391	0.0284	0.0321
	R^2	0.7041	0.8679	0.8598	0.7782	0.8397
Pseudo-second-order	q_e	2.326	4.5125	8.969	11.521	14.205
	k_2	0.321	0.103	0.056	0.041	0.027
	R^2	1.000	0.9999	0.9999	0.9999	0.9998
Elovich	α	995,499.6	36,170.5	27,282.5	4,214,325	3,987.8
	β	0.1246	0.2924	0.5725	0.563	1.0666
	R^2	0.7002	0.8584	0.8615	0.949	0.8845
Intraparticle diffusion	k_{id}	0.0895	0.2198	0.4334	0.4733	0.8395
	a	1.9599	3.606	6.895	9.562	10.776
	R^2	0.48	0.6421	0.6482	0.7881	0.6775

The obtained value of 0.541 for 1/*n* indicated favorable conditions for the TCP adsorption onto the CPB-MZ. The maximum adsorption capacity (q_m) of the CPB-MZ for TCP is promising as compared with the parameter of other adsorbent for phenolic compounds. Table 4 provides maximum monolayer adsorption capacity of the CPB-MZ in comparison with those of other adsorbent reported in references. According to Table 4, the maximum adsorption capacity of the CPB-MZ in this study was promising and therefore the CPB-MZ can be considered as a suitable adsorbent for the removal of chlorophenols.

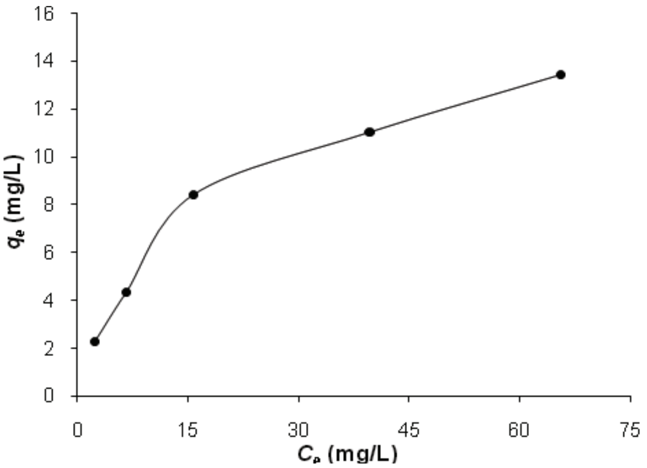


Fig. 7. Isotherm data of TCP adsorption by the CPB-MZ.

Table 3
Parameters of the Freundlich, Langmuir, Freundlich–Langmuir and Temkin isotherm models for TCP adsorption by the CPB-MZ

Isotherm model	Parameter	Value
Freundlich	1/*n*	0.541
	K_F	1.055
	R^2	0.9661
Langmuir	q_m	16.34
	b	0.074
	R^2	0.9991
Temkin	A_T	0.081
	b_T	3.5541
	R^2	0.9913

3.5. Continuous system study

The time of breakthrough appearance and the shape of the breakthrough curve are very important characteristics of an adsorption column for determining the operation and dynamic response [36]. Fig. 8 presents results of TCP adsorption by the CPB-MZ using the fixed-bed column in the form of breakthrough curves. Table 5 presents breakthrough curve characteristics of the packed bed column used for TCP adsorption by the CPB-MZ in the continuous mode with the continuous experiments. The break point time was found to decrease with increasing inlet TCP concentration as the

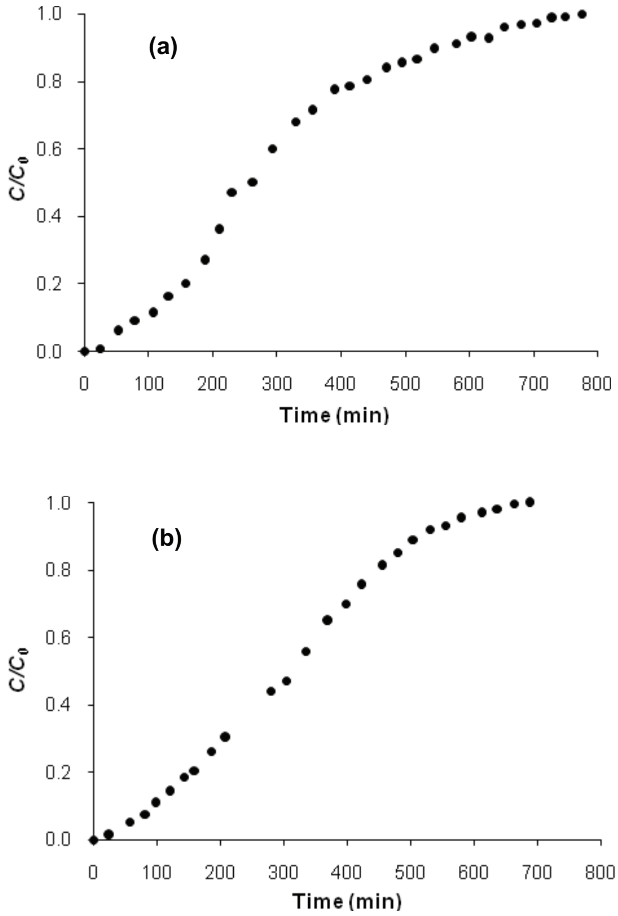


Fig. 8. Breakthrough curves of TCP adsorption by the CPB-MZ in the packed bed column: (a) C_0 = 100 mg/L and (b) C_0 = 200 mg/L.

Table 4
Maximum monolayer adsorption capacity of the CPB-MZ used in this study as compared with other adsorbent reported in references

Adsorbent	Adsorbate	Maximum monolayer adsorption capacity (mg/g)	References
Rice straw-based carbon	3-Chlorophenol	14.20	[2]
HDTMA-modified zeolite	4-Chlorophenol	12.71	[23]
Coir pith carbon	2,4-Dichlorophenol	19.12	[33]
Anaerobic granular sludge	4-Chlorophenol	6.32	[33]
HDTMA-modified zeolite	2,4,6-Trichlorophenol	12.9	[35]
CPB-MZ	2,4,6-Trichlorophenol	16.34	This study

Table 5
Breakthrough curve characteristics of the packed bed column used for TCP adsorption by the CPB-MZ in the continuous mode

C_0 (mg/L)	Breakthrough point (C/C_0 = 0.05)		Exhaustion point (C/C_0 = 0.95)		Complete exhaustion point (C/C_0 = 1.00)	
	t_s (min)	q (mg/g)	t_s (min)	q (mg/g)	t_s (min)	q (mg/g)
100	53	3.37	655	19.25	775	19.35
200	58	7.45	580	40.5	688	40.78

binding sites became more quickly saturated in the column. According to Table 5, increasing inlet TCP concentration from 100 to 200 mg/L caused to an increase in the total TCP uptake from 19.35 to 40.78 mg/g at complete exhaustion point and a decline in the exhaust time from 775 to 688 min. The increase of adsorption capacity could be due to providing higher driving force for mass transfer process in higher TCP concentration [37].

Similar trends have also been reported in the adsorption of TCP using oil palm shell-based activated carbon, adsorption of hexavalent chromium ions by modified corn stalk, and adsorption of cobalt ions using granular-activated carbon in fixed-bed columns [35].

4. Conclusions

The locally derived zeolite was modified by CPB and then was used for TCP adsorption from aqueous environments. The optimum condition of pH for TCP adsorption by the CPB-MZ was determined to be 3.0. The pseudo-second-order model best fitted with the kinetic data. The adsorption process was rapid and reached to equilibrium only in 45 min. The isotherm data were described by the Langmuir isotherm model and the parameter q_m was found to be as high as 16.34 mg/g. In the continuous packed bed column, by increasing inlet TCP concentration from 100 to 200 mg/L, the total adsorption capacity rose from 19.35 to 40.78 mg/g. This study identified the CPB-MZ as an effective and promising adsorbent for the removal of TCP from aqueous solutions in batch and continuous systems.

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.

References

[1] 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.
[2] B.H. Hameed, I.A.W. Tan, A.L. Ahmad, Preparation of oil palm empty fruit bunch-based activated carbon for removal of 2,4,6-trichlorophenol: optimization using response surface methodology, J. Hazard. Mater., 164 (2009) 1316–1324.
[3] P.S. Majumder, S.K. Gupta, Removal of chlorophenols in sequential anaerobic–aerobic reactors, Bioresour. Technol., 98 (2007) 118–129.
[4] D. Krishnaiah, S.M. Anisuzzaman, A. Bono, R. Sarbatly, Adsorption of 2,4,6-trichlorophenol (TCP) onto activated carbon, J. King Saud Univ. Sci., 25 (2013) 251–255.
[5] T.S. Anirudhan, M. Ramachandran, Removal of 2,4,6-trichlorophenol from water and petroleum refinery industry effluents by surfactant-modified bentonite, J. Water Process Eng., 1 (2014) 46–53.
[6] Á. Kovács, A. Kende, M. Mörtl, G. Volk, T. Rikker, K. Torkos, Determination of phenols and chlorophenols as trimethylsilyl derivatives using gas chromatography-mass spectrometry, J. Chromatogr., A, 1194 (2008) 139–142.
[7] J.M. Li, X.G. Meng, C.W. Hu, J. Du, Adsorption of phenol, *p*-chlorophenol and *p*-nitrophenol onto functional chitosan, Bioresour. Technol., 100 (2009) 1168–1173.
[8] A.O. Olaniran, E.O. Igbinosa, Chlorophenols and other related derivatives of environmental concern: properties, distribution and microbial degradation processes, Chemosphere, 83 (2011) 1297–1306.
[9] C.G. Joseph, G.L. Puma, A. Bono, Y.H. Taufiq-Yap, D. Krishnaiah, Operating parameters and synergistic effects of combining ultrasound and ultraviolet irradiation in the degradation of 2,4,6-trichlorophenol, Desalination, 276 (2011) 303–309.
[10] S. Mubarik, A. Saeed, M.M. Athar, M. Iqbal, Characterization and mechanism of the adsorptive removal of 2,4,6-trichlorophenol by biochar prepared from sugarcane bagasse, J. Ind. Eng. Chem., 33 (2016) 115–121.
[11] B. Hameed, Equilibrium and kinetics studies of 2,4,6-trichlorophenol adsorption onto activated clay, Colloids Surf., A, 307 (2007) 45–52.
[12] E. Saputra, M.A. Budihardjo, S. Bahri, J.A. Pinem, Cobalt-exchanged natural zeolite catalysts for catalytic oxidation of phenolic contaminants in aqueous solutions, J. Water Process Eng., 12 (2016) 47–51.
[13] M.Y. Pamukoglu, F. Kargi, Biodegradation kinetics of 2,4,6-trichlorophenol by *Rhodococcus rhodochrous* in batch culture, Enzyme Microb. Technol., 43 (2008) 43–47.
[14] M. Baeza-Alvarado, M. Olguín, Surfactant-modified clinoptilolite-rich tuff to remove barium (Ba^{2+}) and fulvic acid from mono-and bi-component aqueous media, Microporous Mesoporous Mater., 139 (2011) 81–86.
[15] N. Chaouati, A. Soualah, M. Chater, Adsorption of phenol from aqueous solution onto zeolites Y modified by silylation, C.R. Chim., 16 (2013) 222–228.
[16] H.M. Baker, R. Ghanem, Evaluation of treated natural zeolite for the removal of o-chlorophenol from aqueous solution, Desalination, 249 (2009) 1265–1272.
[17] S.H. Lin, R.S. Juang, Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review, J. Environ. Manage., 90 (2009) 1336–1349.
[18] J. Lin, Y. Zhan, Z. Zhu, Adsorption characteristics of copper (II) ions from aqueous solution onto humic acid-immobilized surfactant-modified zeolite, Colloids Surf., A, 384 (2011) 9–16.
[19] M. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: a review, Adv. Colloid Interface Sci., 143 (2008) 48–67.
[20] C. Lei, Y.-y. Hu, M.-z. He, Adsorption characteristics of triclosan from aqueous solution onto cetylpyridinium bromide (CPB) modified zeolites, Chem. Eng. J., 219 (2013) 361–370.
[21] H. Zaghouane-Boudiaf, M. Boutahala, S. Sahnoun, C. Tiar, F. Gomri, Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing the 2,4,5-trichlorophenol, Appl. Clay Sci., 90 (2014) 81–87.
[22] Y. Dong, D. Wu, X. Chen, Y. Lin, Adsorption of bisphenol A from water by surfactant-modified zeolite, J. Colloid Interface Sci., 348 (2010) 585–590.

[23] A. Kuleyin, Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite, J. Hazard. Mater., 144 (2007) 307–315.

[24] R. Elena Apreutesei, C. Teodosiu, C. Catrinescu, Studies regarding phenol and 4-chlorophenol sorption by surfactant modified zeolites, Environ. Eng. Manage. J., 8 (2009) 651–656.

[25] Q. Tao, M. Hu, X. Ma, M. Xiang, T.C. Zhang, C. Li, J. Yao, Y. Liang, Simultaneous removal of ammonium and nitrate by HDTMA-modified zeolite, Water Sci. Technol., 72 (2015) 1931–1939.

[26] A. Torabian, H. Kazemian, L. Seifi, G. Nabi Bidhendi, A.A. Azimi, S.K. Ghadiri, Removal of petroleum aromatic hydrocarbons by surfactant-modified natural zeolite: the effect of surfactant, Clean,38 (2010) 77–83.

[27] Z. Aksu, F. Gönen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, Process Biochem., 39 (2004) 599–613.

[28] C. Díaz-Nava, M.T. Olguín, M. Solache-Ríos, M.T. 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.

[29] T.M. Aversa, C.M.F. da Silva, P.C.S. da Rocha, E.F. Lucas, Influence of exchange group of modified glycidyl methacrylate polymer on phenol removal: a study by batch and continuous flow processes, J. Environ. Manage., 182 (2016) 301–307.

[30] APHA, AWWA, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, D.C., USA, 2005.

[31] M. Macedo-Miranda, M. Olguín, Arsenic sorption by modified clinoptilolite–heulandite rich tuffs, J. Inclusion Phenom. Macrocyclic Chem., 59 (2007) 131–142.

[32] G. Asgari, A. Sidmohammadi, A. Ebrahimi, Z. Gholami, E. Hoseinzadeh, Study on phenol removing by using modified zeolite (clinoptilolite) with $FeCl_3$ from aqueous solutions, J. Health Syst. Res., 6 (2010) 848–852.

[33] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon, J. Hazard. Mater., 164 (2009) 473–482.

[34] 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.

[35] K. Naddafi, N. Rastkari, R. Nabizadeh, R. Saeedi, M. Gholami, M. Sarkhosh, Adsorption of 2,4,6-trichlorophenol from aqueous solutions by a surfactant-modified zeolitic tuff: batch and continuous studies, Desal. Water Treat., 57 (2016) 5789–5799.

[36] 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.

[37] 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.