Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21599

97 (2017) 285–294
November

Cyanide adsorption from aqueous solution using mesoporous zeolite modified by cetyltrimethylammonium bromide surfactant

Fatemeh Papari[a], Soleyman Sahebi[b], Esmaeil Kouhgardi[c], Rezvaneh Behresi[c], Seyedenayat Hashemi[d], Ghorban Asgari[e], Sahand Jorfi[f,g], Bahman Ramavandi[d,*]

[a]*Department of Chemical Engineering, Bushehr Branch, Islamic Azad University, Bushehr, Iran, email: fatemeh.papari@yahoo.com*
[b]*Research and Technology Center of Membrane Processes (RTCMP), School of Chemical, Petroleum and Gas Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran, Iran, email: soleysahebi@gmail.com*
[c]*Environmental Department, Bushehr Branch, Islamic Azad University, Bushehr, Iran, emails: kouhgardi@yahoo.com (E. Kouhgardi), rezvanehbehresi@gmail.com (R. Behresi)*
[d]*Department of Environmental Health Engineering, Faculty of Health and Nutrition, Bushehr University of Medical Sciences, Bushehr, Iran, Tel. +989363311903; Fax: +987733450134; emails: ramavandi_b@yahoo.com, b.ramavandi@bpums.ac.ir (B. Ramavandi), seyedenayat_hashemi@yahoo.com (S. Hashemi)*
[e]*Social Determinants of Health Research Center (SDHRC), Department of Environmental Health Engineering, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran, email: asgari@umsha.ac.ir*
[f]*Environmental Technologies Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran*
[g]*Department of Environmental Health Engineering, School of Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran, email: sahand369@yahoo.com*

Received 28 June 2017; Accepted 1 November 2017

ABSTRACT

The purpose of this study was the modification of zeolite with the cationic surfactant of cetyltrimethylammonium bromide for enhancing the adsorption of cyanide (CN^-) from aqueous solution. Hence, the batch tests were conducted under different conditions for CN^- removal by the surfactant-modified zeolite (SMZ). The effect of pH (3–10), SMZ dosage (0.25–5 g/L), CN^- concentration (50, 100, and 200 mg/L), and contact time (5–400 min) was evaluated. More than 95% of cyanide was removed at the conditions of pH of 10, the initial cyanide concentration of 100 mg/L, the SMZ dosage of 4 g/L, and the contact time of 250 min. The analysis of kinetics adsorption showed that cyanide ions adsorption onto the SMZ clearly followed the pseudo-second-order model. The isotherm adsorption data were mostly matched by Langmuir model with maximum adsorption capacity of 49.57 mg/g. The fresh and used SMZ was fully characterized by Brunauer–Emmett–Teller, Barrett–Joyner–Halenda, loss of ignition, X-ray powder diffraction, scanning electron microscope, Fourier transform infrared spectroscopy, and pH of zero point charge (pH_{zpc}). The surface study indicated that the adsorbent is mesoporous and crystalline. The adsorption–desorption study was done using three reagents of HNO_3, HCl, and NaOH. A metal plating wastewater was successfully treated using SMZ. Accordingly, the SMZ was found to be an effective adsorbent for the removal of different concentrations of cyanide from aqueous solution.

Keywords: Cyanide; Cetyltrimethylammonium bromide; Zeolite; Mesoporous; Metal plating wastewater; Desorption

---

* Corresponding author.

1. Introduction

Cyanide is the most commonly used chemical in the extraction of gold and silver ores. The high tendency of cyanide to bind with metals and to form metal complexes, especially gold, made it as an essential reactive for extraction processes [1]. Cyanide is very dangerous for humans and can put environment at stake. Initial symptoms of cyanide poisoning can arise from exposure to 20–40 ppm that result a rapid breathing and fast heart rate, vomiting, and toxicity of the neurological system. Moreover, high exposures to cyanide can lead to asphyxiation, coma, and even death [2]. Cyanide is released into the environment from both natural processes (such as biogenic or biomass burning) and human activities (such as metal plating, coal coking, chemical fertilizers, mining, etc.) [2,3]. The most dangerous form of cyanide is hydrogen cyanide and its salts like potassium and sodium cyanide. Upon inhalation or ingestion of potassium and sodium cyanide, these two compounds convert into hydrogen cyanide under the effect of stomach acid which may causes acute toxicity in the human body. It has been reported that the poisonous amount of hydrogen cyanide is 0.01 g/L and beyond 0.05 g/L of it can consequently lead to human death [4].

Considering toxicity of cyanide and its health effects on humans, different methods, including reverse osmosis [5], coagulation [6], oxidation [7], ozonation [8], and adsorption [9] have been investigated for its removal. Among all the above mentioned methods, adsorption is the most widely preferred in the wastewater treatment due to the high efficiency, economic viability, and the simplicity of the design and process [10]. Recently, different types of adsorbent have been studied for cyanide treatment such as the activated carbon [4,11], various agricultural products [3,12], resins [13], alumina [14], and clays and zeolites [15].

More recently, the ion-exchange zeolites have attracted much attention because of valuable properties such as high surface area, large pore volume, ion selectivity, thermal stability, and their low cost and worldwide occurrence [16]. The aluminosilicate framework of zeolites supplies a negative charge to the overall structure of them, the reason they are known as cation exchangers. To improve the adsorption efficiency of raw natural zeolites for negative ions removal, various reagents have been tested recently [17,18]. In this regard, Ning et al. [18] reported that impregnated zeolite with metal for the modification purpose has significantly enhanced cyanide adsorption ability. On the other hand, cationic surfactants are the approach to modify zeolites for the removal of several types of anionic contaminants all around the world [19–21]. Torabian et al. [22] investigated the removal of petroleum aromatic hydrocarbons by surfactant-modified zeolites (SMZs). They approved that the *N*-cetylpyridinium bromide-modified zeolite exhibited a higher selectivity for all the monoaromatic compounds at optimum experimental conditions.

Despite all the previous investigations, no data is available on the study of SMZs for cyanide removal from wastewater. Therefore, it is necessary to report the applicability of the surfactant for zeolite modification in the removal of CN^- from wastewater. In this study, cetyltrimethylammonium bromide (CTAB) surfactant has been used as modifier of the zeolite structure for the purpose of cyanide removal from wastewater. Thus, the main aims of this work were designed to optimize the effective parameters, characterize the adsorbent, and evaluate the isotherm and kinetic of cyanide adsorption onto SMZ.

2. Experimental

2.1. Chemicals

All the chemicals used in the present study including sodium cyanide, CTAB, nitric acid, and sodium hydroxide were supplied by Merck Company (Germany) with high purity. All the chemicals were of analytical grade and used directly without further purification. The stock solution was prepared by dissolving 1.8834 g of sodium cyanide in 1 L of doubly distilled water. The required concentrations of cyanide were provided by mixing sodium cyanide stock solution in double distilled water.

2.2. Adsorbent preparation

The external surface of zeolite modified by CTAB followed the method proposed by Shayesteh et al. [23]. Briefly, the amount of 0.03 M of surfactant powder was poured to 1,000 mL of double distilled water for the preparation of 1% CTAB. After that, the amount of 30 g of zeolite was added to the surfactant solution and then mixed at 120 rpm for 48 h to obtain modified zeolite. After the requisite contact time, the sample was rinsed by distilled water to remove the excess traces of the surfactant and dried in an oven at 70°C for 8 h. The SMZ was maintained in glass bottles for use in adsorption tests.

2.3. Experimental design

The batch adsorption tests were conducted in 250 mL Erlenmeyer flasks inside a shaker-incubator (Parsazma model, Iran). Known quantities of cyanide for each sample (100 mL) were added to the Erlenmeyer flasks. The initial pH of working solutions was regulated by using 0.1 M HCl or NaOH, the fixed amount of modified zeolite was added to the flasks and the suspensions were shaken at 120 rpm. After a defined contact time, the suspensions were passed through Whatman filter paper and then the residual cyanide ions in the resultant filtrates were analyzed. The main parameters for evaluation the optimum conditions were: solution pH (3, 4, 6, 7, 9, and 10), initial cyanide concentration (50, 100, and 200 mg/L), SMZ dose (0.25, 0.5, 1, 2, 3, 4, and 5 g/L), and contact time (5, 10, 30, 60, 100, 140, 180, 200, 250, 300, 350, and 400 min for kinetic tests and 350 min for equilibrium tests). To assure the reproducibility of the results, duplicate tests were done and the mean of the findings were reported herein. A blank test (the sample without SMZ) was also provided for interference control. The cyanide adsorption efficiency (CAE) and the amount of cyanide adsorbed per unit mass of adsorbent, q_e (mg/g) were determined through the following equations:

$$\text{CAE} = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{V\left(C_0 - C_e\right)}{M} \tag{2}$$

where C_0 (mg/L), C_t (mg/L), and C_e (mg/L) are the initial, final, and equilibrium concentrations of CN^- ions, respectively. M (g) and V (L) are the mass of SMZ and the volume of the aqueous solution, respectively.

The kinetics of cyanide adsorption on the modified zeolite with CTAB was estimated by adsorption experiments carried out in Erlenmeyer flasks containing 100 mL of 50, 100, and 200 mg/L cyanide solutions and 4 g/L of SMZ at pH 10 and mixing rate of 120 rpm. The test was done at different time intervals (5–400 min). At the end of each test, the suspension was analyzed. Two famous kinetics models, pseudo-first-order and pseudo-second-order, were used to analyze the adsorption data (Table 1).

To assess the adsorption equilibrium, 4 g/L SMZ was added to 100 mL of various cyanide concentrations (50–250 mg/L) at the fixed pH solution of 10, mixing rate of 120 rpm, and solution temperature of 24°C. After that, the equilibrium adsorption of cyanide on modified zeolite was modeled using the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models (Table 1).

A desorption study was carried out with 4 g/L SMZ and 100 mL solution containing 100 mg/L of CN^- ions at conditions of initial pH 10, mixing rate of 120 rpm, solution temperature of 24°C, and contact time of 250 min. Upon completion of the tests, the used SMZ was separated using the filter paper and rinsed with double distilled water to remove extra ions deposited on the surface of SMZ. Then, 4 g/L SMZ was mixed with 10 mL of HCl, HNO_3, and NaOH solution with different concentrations (0.05, 1, and 1.5 mol/L) for 2 h. After that, the solution was filtered and the concentration of cyanide ions was analyzed. Four cycles of adsorption–desorption were done. Each cycle study was repeated two times and the desorption percentage was determined according to the following equation:

$$\text{Cyanide desorption}\left(\%\right) = \frac{\text{Amount of cyanide desorbed}}{\text{Amount of cyanide adsorbed}} \times 100 \tag{3}$$

2.4. Measurements

The surface measurements including the specific surface area of Brunauer–Emmett–Teller (BET) and pore volume of the zeolite, and both fresh and used SMZ was performed by the N_2 adsorption/desorption method at −196°C using a Micromeritics model TriStar II-3020 instrument. The adsorbents samples were degassed for 24 h at 250°C to remove any adsorbed contaminants or moisture that might have been existed on the surface. The manufacturer's software provided the BET surface area of SMZ using the BET equation within $P/P_0 = 0$–1:

$$\frac{1}{V[(P_0/P)-1]} = \frac{C-1}{V_m C}\left(\frac{P}{P_0}\right) + \frac{1}{V_m C} \tag{4}$$

where C is the constant of BET, P and P_0 are the equilibrium and saturation pressure of adsorbates at the adsorption temperature, V is the amount of gas adsorbed, and V_m is the amount of monolayer adsorbed gas.

A scanning electron microscope (SEM; Hitachi S4160 type) was applied to analyze the surface of the fresh and CN-loaded SMZ. The surface of SMZ was scanned after covering the surface with a thin layer of gold and then investigated with the SEM. A Fourier transform infrared (FTIR) spectrometer (NICOLET 5700-FTIR) in the range of 400–4,000 cm^{-1} was applied to determine the functional groups in the adsorbents surface. The X-ray fluorescence (XRF; PW2404 X-ray spectrometer) technique was applied to determine the mineral content of zeolite and SMZ. The mineralogical phases and crystallinity of zeolite and SMZ were analyzed by X-ray diffraction (XRD, Pert MPD.α') method. The concentration of cyanide was analyzed by a spectrophotometer (Shimadzu-1601 UV–VIS) at 530 nm. The concentration Cr^{6+} and Ni^{2+} was measured according to the method presented in the Standard Methods for the Examination of Water and Wastewater [26]. The solution temperature was determined using a mercury thermometer. The measurement of pH at zero point charge (pH_{zpc}) for SMZ was done according to our previous study [27,28]. The working

Table 1
Isotherm and kinetic models used in this work [24,25]

Models	Name	Equation	Plot
Isotherm	Langmuir	$q_e = \frac{q_{\max} k_L C_e}{1 + k_L C_e}$	$\frac{1}{q_e}\text{vs.}\frac{1}{C_e}$
	Freundlich	$q_e = k_F C_e^{1/n}$	$\log q_e$ vs. $\log C_e$
	D–R	$\ln q_e = \ln q_m - K_{\text{D-R}}\varepsilon^2$	$\ln q_e$ vs. ε^2
Kinetic	Pseudo-first-order	$q_t = q_e[1 - \exp(-k_1 t)]$	$\log(q_e - q_t)$ vs. t
	Pseudo-second-order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	$\frac{t}{q_t}\text{vs.}t$

$q_{\max}$ = maximum adsorption capacity (mg/g), k_L = Langmuir constant (L/mg), k_F = Freundlich constant, n = Freundlich constant (mg/g(L/mg)$^{1/n}$), $K_{\text{D-R}}$ = D–R constant (mol^2/kJ^2), ε = Polanyi potential (J/mol), k_1 = rate constant of pseudo-first-order model (1/min), k_2 = rate constant of pseudo-second-order model (mg/g min), q_t = adsorbed amount at any time (mg/g), and q_e = adsorbed amount at equilibrium (mg/g).

solutions pH was analyzed using a pH-meter (Sense Ion 378, Hack).

The method loss on ignition (LOI) at 1,050°C was used to obtain water content (w/w) of SMZ and zeolite. The LOI method was also used to estimate the organic matter content of the SMZ or zeolite.

3. Results and discussion

3.1. Physical and chemical characteristics of adsorbent

Chemical and physical properties of the SMZ and the structural information which play an important role in cyanide adsorption are presented in this section. Table 2 shows the characteristics of the natural zeolite as well as SMZ before and after cyanide adsorption. The specific area of the zeolite after modification reduced from 114.02 to 10.75 m^2/g. Also, the pore volume size of SMZ increased from 0.0498 to 0.0547 m^3/g. These two findings reveal the main channels blocking of the zeolite by the cationic surfactant. In this case, zeolite surface covers with the massive molecules of CTAB. The average pore diameter of SMZ before and after adsorption was 206.50 and 151.67 Å which affirmed that the adsorbent is mesoporous type. Also, Fig. 1 depicts the N_2 adsorption–desorption isotherm of zeolite, fresh SMZ, and cyanide-loaded SMZ samples. Both isotherms of all samples are classified as a type IV adsorption–desorption isotherm with a hysteresis loop type H3 according to the IUPAC, indicating the existence of slit-like pores and mesopores [29,30]. The XRF measurement (Table 3) showed that the major components in the natural zeolite and SMZ are SiO_2 and Al_2O_3. According to the XRF analysis, the identical ratio of SiO_2/Al_2O_3 (=6.9) for both zeolite and SMZ, indicating that the structure of aluminum atoms was not destroyed by the surfactant modification and still has the ability to generate the anion exchange sites [31,32]. The percentage of volatile components (in the term of LOI) in natural zeolite and SMZ was 12.83% and 18.62%, respectively. The increasing of LOI level in SMZ may be attributed to the existing water in the SMZ structure and also degradation of the organic matter in the surfactant compound.

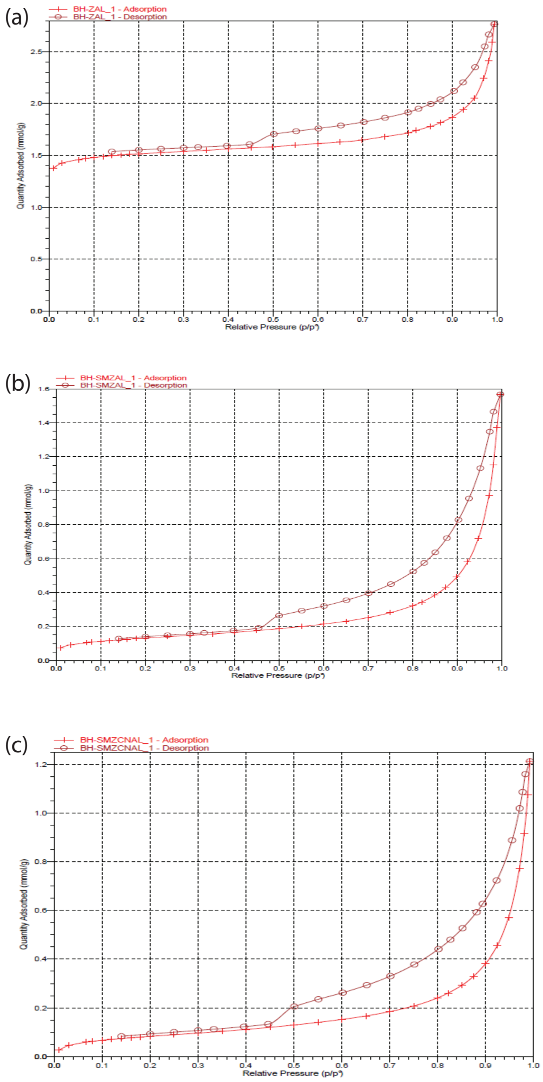

Fig. 1. N_2 adsorption–desorption isotherm (BET) of (a) zeolite, (b) fresh SMZ, and (c) cyanide-loaded SMZ.

Table 2
Main characteristics of the adsorbents used in this study

Characteristic		Z	Fresh SMZ	CN-loaded SMZ
Surface area	Single point surface area at $p/p° = 0.19979$, m^2/g	118.33	10.33	6.48
	BET surface area, m^2/g	114.01	10.74	7.07
	Langmuir surface area, m^2/g	150.77	14.97	10.15
	t-Plot micropore area, m^2/g	96.887	1.116	–
	t-Plot external surface area, m^2/g	17.130	9.63	8.002
	BJH adsorption cumulative surface area of pores, m^2/g	13.83	10.60	8.44
Pore volume	Single point adsorption total pore volume of pores, cm^3/g	0.0778	0.033	0.0268
	t-Plot micropore volume, cm^3/g	0.04503	0.00036	–0.00062
	BJH adsorption cumulative volume of pores, cm^3/g	0.0498	0.0547	0.0422
Pore size	BJH adsorption average pore diameter, Å	27.31	206.50	151.67
	Type of adsorbent	Mesopore	Mesopore	Mesopore

Table 3
Chemical analysis of the zeolite and SMZ

Composition (*W* %)	Zeolite	SMZ[b]
P_2O_5	0.023	0.028
CaO	1.3	0.635
MgO	0.507	0.727
Fe_2O_3	1.026	0.869
Na_2O	3.727	3.563
K_2O	3.618	2.24
Al_2O_3	9.85	9.23
SiO_2	68.61	64.16
LOI[a]	12.83	18.62

[a]Loss of ignition.
[b]Surfactant-modified zeolite.

The structure and texture of zeolite, fresh SMZ, and cyanide-loaded SMZ were measured and determined using the SEM test. As shown in Fig. 2(a), the adsorbent used has layers in which some cavities are created by these layers. There are white beads on the surface of Fig. 2(b), which is probably due to the presence of surfactant. These seed-colored beads are larger in Fig. 2(c), which can be indicative of a cyanide reaction with adsorbent surface.

The XRD pattern for zeolite, fresh SMZ, and cyanide-loaded SMZ is demonstrated in Fig. 3. The diffractograms disclosed that the zeolite structure (both the zeolite and SMZ) was crystalline. Very minor changes in crystalline phase of zeolite occurred after modification and cyanide adsorption. Additionally, clinoptilolite and SiO_2 were the main compounds resulting from XRD analysis.

The results of the FTIR spectrum analysis of zeolite and SMZ before and after cyanide adsorption are depicted in Figs. 4(a)–(c). As shown in the figures, the peaks of FTIR spectra of the SMZ are somewhat different from those of the zeolite alone. Additionally, the functional groups for both the zeolite and SMZ are: OH, CH, NH, Si=OR, and N=O. Some changes in the FTIR peaks are observed for the SMZ which might be an indication of successful modification of zeolite by the surfactant. From comparison of Figs. 4(a) and (b), the FTIR peaks shifted from 3,457.9 to 3,434.07 cm^{-1} and from 1,654.46 to 1,643.07 cm^{-1} for O–H and C=O functional groups, respectively [33]. Also, some peaks at 2,853.82 and 2,923.68 cm^{-1} in the FTIR analysis of fresh SMZ appeared which can be due to the adsorption of the cationic surfactant to the zeolite. The changes in the peaks positions of the SMZ after cyanide adsorption revealed that cyanide is reacted with the SMZ surface.

The pH_{zpc} value for the SMZ was obtained around 6.5 (Fig. 5). This means that the SMZ surface was positively charged at pHs below this amount and negatively charged at pHs above this amount [34].

3.2. Influence of pH on CN^- adsorption

The pH of the solution is one of the most important parameters in the adsorption tests which influence the surface charge of the adsorbent, the degree of ionization, and speciation of the pollutant. Fig. 6 shows the effect of the solution

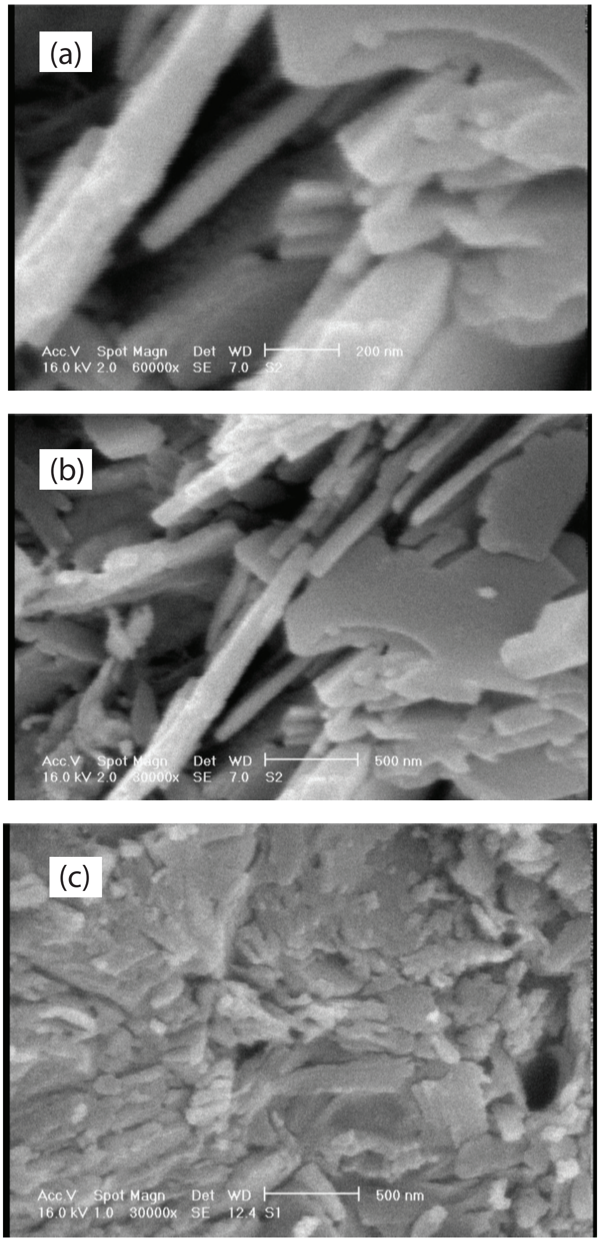

Fig. 2. SEM images of (a) zeolite, (b) fresh SMZ, and (c) cyanide-loaded SMZ.

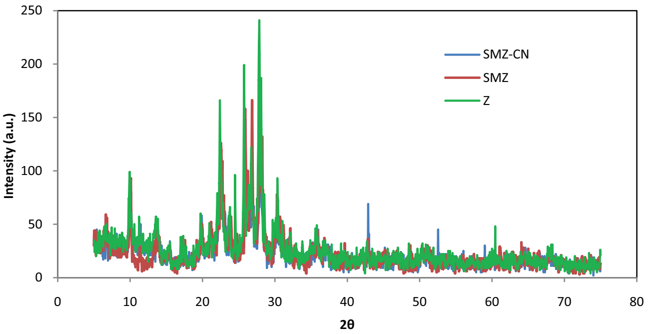

Fig. 3. XRD pattern of (a) zeolite, (b) fresh SMZ, and (c) cyanide-loaded SMZ.

pH on cyanide adsorption. As depicted in this figure, with increase of pH value from 3 to 10 the removal efficiency of cyanide increased. Increasing the cyanide removal by increasing the pH value and attaining the maximum removal efficiency of cyanide (97.6%) at pH of 10 could be explained by pK_a of HCN and pH_{zpc} of the SMZ. The amount of pK_a for HCN is about 9 [3] and pH_{zpc} was obtained 6.5 for the studied adsorbent. This means that HCN is totally dissociated to CN^- at pH value greater than 9 and the surface of the adsorbent (SMZ) is negatively charged at pH values above 6.5 (pH_{zpc}). Moreover, CN^- is a nucleophilic ion so when it contacts with negative charge adsorbent it tends to bond with anionic functional groups on the adsorbent surface and this is the reason that the adsorption efficiency increases. Furthermore, some cyanide removal may be happened by the surface sedimentations, chemical reaction between cyanide, and the surface sites, as well as complexing of CN^- with the functional groups. Most of the researchers also reported the pH values of 9–11 as optimal pH values for cyanide adsorption [13,35]. Here, we also proposed the pH of 10 as optimal value.

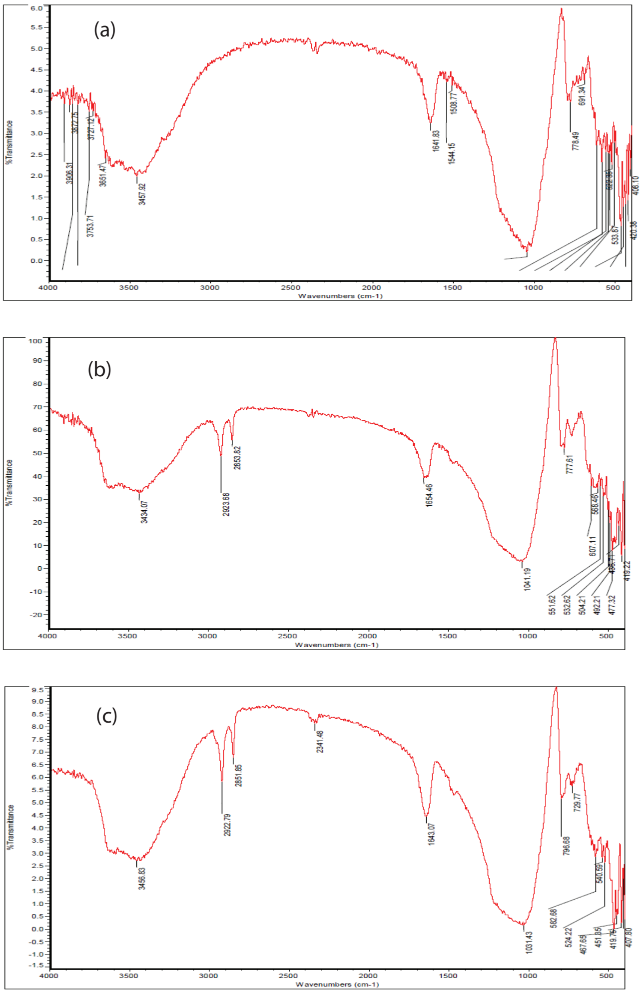

Fig. 4. FTIR spectra of (a) zeolite, (b) fresh SMZ, and (c) cyanide-loaded SMZ.

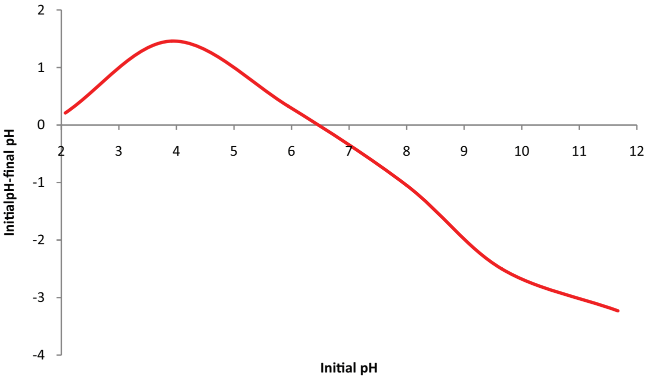

Fig. 5. 'Initial pH-final pH' vs. initial pH for determination of pH_{zpc} of fresh SMZ.

3.3. Influence of the adsorbent dosage on adsorption

The adsorption process is a surface phenomenon and thus the surface area available for adsorbate removal can highly affect the adsorption efficiency. Hence, the effect of the adsorbent dose on cyanide adsorption was investigated. Fig. 7 demonstrates the effect of the zeolite and SMZ dosage on cyanide removal from aqueous solution. As shown in Fig. 7, the adsorption efficiency for both the zeolite and SMZ increased by increasing the dosage from 0.25 to 4 g/L and after that remained almost constant by increasing the adsorbent dosage. Increase in cyanide adsorption by increasing the adsorbent dosage may be due to increase of the number of active sites and available surface area of the adsorbent. The adsorption efficiency remained unchanged at the adsorbent

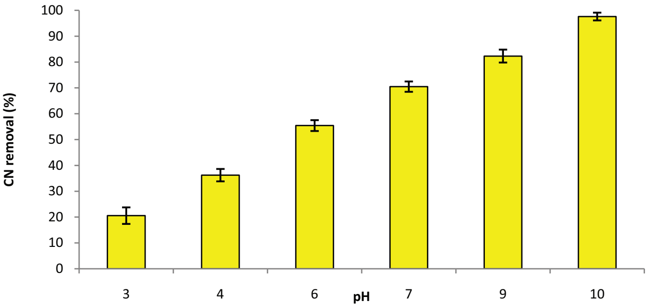

Fig. 6. Influence of the initial pH on CN^- removal (SMZ dose: 4 g/L, CN^-: 100 mg/L).

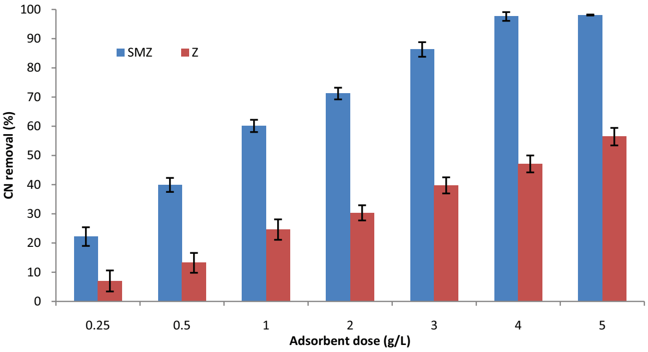

Fig. 7. Influence of zeolite and SMZ on CN^- removal (pH: 10, SMZ dose: 4 g/L, CN^-: 100 mg/L).

dosages above 4 g/L which may be attributed by the overlapping and aggregating of the adsorbent. Zheng et al. [13] also reported that increase in the adsorbent dosage resulted in an increase in the adsorption efficiency up to a certain value and thereafter remained constant which supports our findings. Thus, the proper adsorbent dosage was determined as 4 g/L.

3.4. Influence of contact time and initial cyanide concentration

Overall, the contact time in the batch systems is a key factor to enhance the removal efficiency. However, the conditions can be varied depending on the adsorbent type and the initial solution specifications. It seems that the adsorbate concentration in the solution has always been more than that of the solid phase based on Donnan phenomenon, hence, will never reach the equilibrium point [13]. In this regard, the adsorption–desorption of the ions occurs continuously. This situation is very obvious especially in the short contact times. In the long contact times, particularly for the adsorbents containing the components with low adsorption rate, the contact time would be an effective factor which enhances the adsorption efficiency of these components [13]. The adsorption capacity increases with an increment in time and remains constant in a certain time. At this time, the amount of adsorbed pollutant with the amount of desorbed pollutant remains in the state of dynamic equilibrium [36]. The effect of various initial concentrations of cyanide (50, 100, and 200 mg/L) on the adsorption efficiency as a function of the contact time is illustrated in Fig. 8. As shown in Fig. 8, for the first 60 min of the contact time, the percentage of cyanide removal was measured as 95%, 84.7%, and 72.6% for initial cyanide concentrations of 50, 100, and 200 mg/L, respectively. In overall, cyanide adsorption for all the initial concentrations was obtained more than 57% at fifth minute of the contact time. This result indicated that the studied adsorbent has a high tendency to adsorb cyanide ion from aqueous solution. Also, at the contact time of 250 min the percentage of cyanide removal was obtained 99.65%, 95.7%, and 88.5% for cyanide initial concentrations of 50, 100, and 200 mg/L, respectively. The decrease of CN^- removal as a function of its concentration can be described by the restriction of available and constant free sites for adsorption. According to Fig. 8, the optimum contact time was achieved about 250 min. Other researchers reported 24 h for the equilibrium time, after which the adsorption remained constant [2,13].

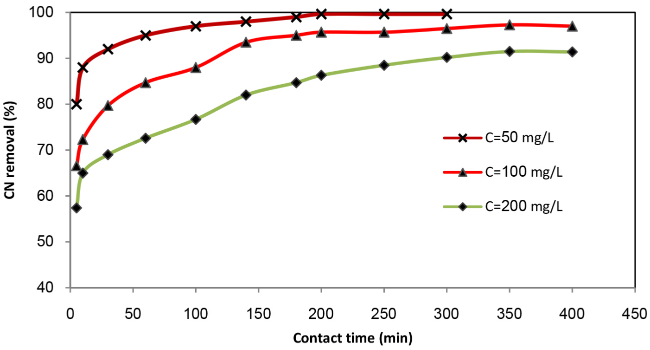

Fig. 8. Influence of contact time and initial CN^- concentration (pH: 10, SMZ dose: 4 g/L).

3.5. Isotherms study

The adsorption isotherm offers very useful and important information for the process design and optimization. The isotherm constants can reveal the adsorbent surface characteristics, the attraction between the adsorbent and the pollutant, and also the adsorption capacity [37]. The equilibrium data were analyzed using Freundlich, Langmuir, and D–R adsorption isotherms for the purpose of cyanide adsorption analysis on the modified zeolite (Figs. 9(a)–(c)). The linear regression used to predict the best fit of data with the adsorption models. Fig. 9 clearly presents the applicability of Langmuir isotherm model for cyanide adsorption on the SMZ. The maximum amount of cyanide adsorption (q_{max}) on the SMZ was obtained 49.57 mg/g which was much more than cyanide adsorption by the other adsorbents [7,38]. The main

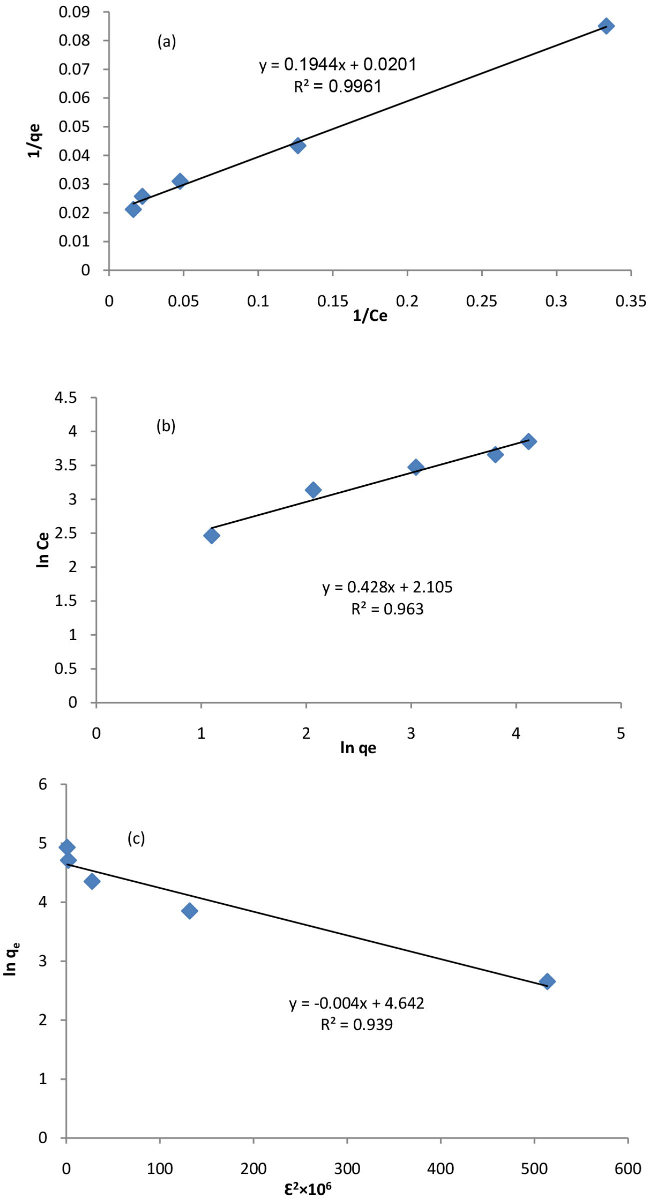

Fig. 9. Adsorption isotherms of CN^- ions onto SMZ (a) Langmuir, (b) Freundlich, and (c) D–R.

characteristic of Langmuir model is defined by a dimensionless constant called R_L (Table 4). The value of this parameter was between 0 and 1 for all concentrations of cyanide, which clearly shows the desirable adsorption of cyanide by this adsorbent. As shown in Table 4, the E parameter (the adsorption energy of cyanide by SMZ) in the D–R isotherm was obtained 11.18 kJ/mol. The value of E falls within the range of 8–16 kJ/mol [22,39] which confirm that the adsorption of cyanide onto the SMZ takes place by chemisorption mechanism.

3.6. Kinetics study

The adsorption kinetic is useful in understanding the dynamics of the adsorption reaction and is expressed by a certain degree. Also, they are necessary for modeling and designing novel adsorption materials and processes. All experimental data for the adsorption of cyanide onto the SMZ were analyzed by pseudo-first-order and pseudo-second-order models. Table 5 represents the kinetic information achieved from models illustrated in Fig. 10. According to Fig. 10, the experimental data obtained from cyanide adsorption on the SMZ are best fitted to the pseudo-second-order model with higher R^2 value than pseudo-first-order model. This finding confirms that the adsorption of cyanide on the SMZ is depended on the both adsorbent and the adsorbate concentration in the studied condition [40]. As shown in Table 5, the value of k_2 was reduced by increase in cyanide concentration. This finding can be described by increasing the rate of the mass transfer by increase in the gradient of the cyanide concentration. Most researchers have also reported pseudo-second-order as the best fitted model for the pollutant removal processes [41,42].

Table 4
Results of isotherm modeling for adsorption of CN^- onto SMZ

Isotherm model	Parameter	Value
Langmuir	q_{max} (mg/g)	49.57
	k_L (L/mg)	0.103
	R^2	0.9961
	$R_L = 1/1 + k_L C_i$	0.16–1
Freundlich	k_F	8.21
	n (mg/g(L/mg)$^{1/n}$)	2.33
	R^2	0.963
Dubinin–Radushkevich	$K_{D\text{–}R}$ (mol²/kJ²)	0.004
	q_m (mg/g)	103.8
	$E = 1/(2K_{D\text{–}R})^{0.5}$ (kJ/mol)	11.18
	R^2	0.9398

3.7. Desorption and reusability

In order to make the adsorption process more economical through repeated use of the adsorbent, desorption potential of SMZ was studied. Three reagents including one alkaline and two acid solutions were used as desorbing agents for the recovery of CN^- from used SMZ (Fig. 11). Various concentrations of NaOH, HNO_3, and HCl were applied in

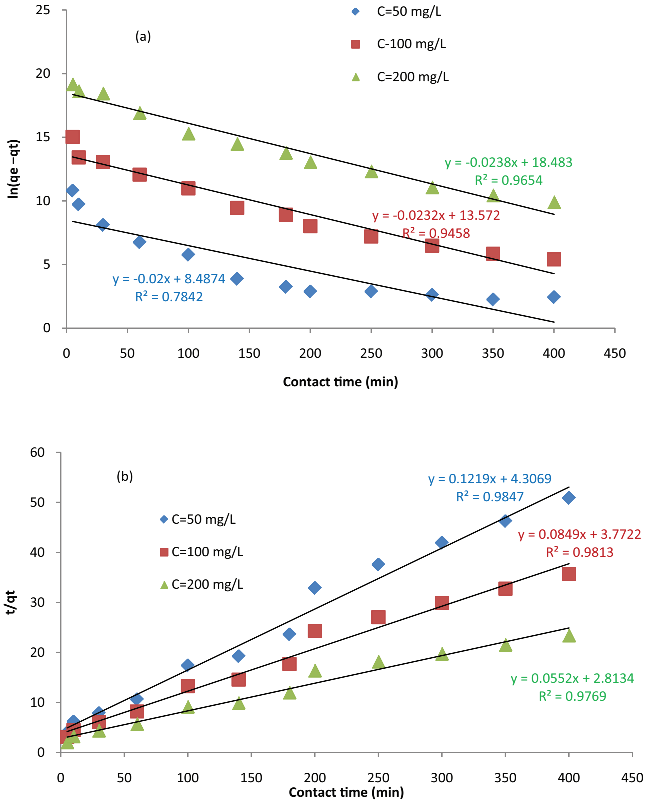

Fig. 10. Kinetic model of (a) pseudo-first-order and (b) pseudo-second-order.

Table 5
Kinetic parameter details of CN^- adsorption onto SMZ

Kinetic model	Pseudo-first-order			Pseudo-second-order		
Concentration	50	100	200	50	100	200
R^2	0.7842	0.9458	0.9654	0.9847	0.9813	0.9769
Constant	$k_1 = 0.065$ min^{-1}	$k_1 = 0.035$ min^{-1}	$k_1 = 0.16$ min^{-1}	$k_2 = 0.003$ mg/g min	$k_2 = 0.002$ mg/g min	$k_2 = 0.001$ mg/g min
Calculated q_e, (q_{cal}) (mg/g)	106,430.2	783.87	4.85	8.20	11.78	18.12
Experimental q_e, (q_{exp}) (mg/g)	10.1	13.2	23.1	10.1	13.2	23.1

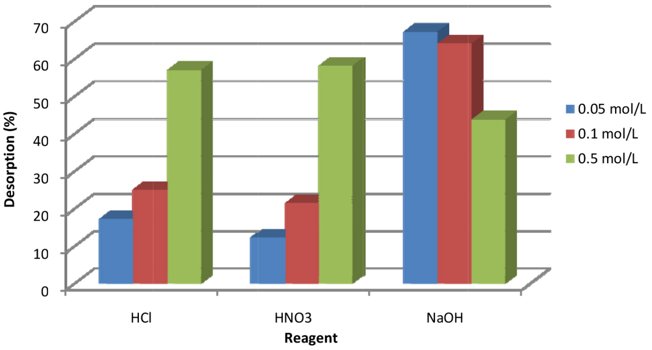

Fig. 11. Desorption of cyanide from cyanide-loaded SMZ using varying reagent with different concentrations.

the batch desorption studies. It was revealed that maximum desorption was 67.2% for cyanide with 0.05 M NaOH. As cyanide ion is hazardous in nature, the cyanide-loaded SMZ creates disposal problem. This problem may be solving to some extent by using elution techniques. The elution of the cyanide allows recovery of the cyanide in the concentrated solution and the regenerated SMZ. The regenerated adsorbent could be recycled and finally the adsorbents must be incinerated. Adsorption–desorption performance of SMZ slightly decreases as the number of cycle increases. More than 55% cyanide removal is possible using four cycles. Thus, the cyanide desorption is not very effective [13], so it will need further study for regeneration of SMZ.

3.8. Real wastewater treatment by SMZ

To test the field applicability of the SMZ, a metal plating wastewater was treated. The bulk of real wastewater with an initial cyanide concentration of 25.22 mg/L was sampled from a metal plating plant around Shiraz city, Iran. The sample wastewater was treated under the optimal conditions (adsorbent dose of 4 g/L and contact time of 250 min). To more confirm SMZ applicability, the origin pH of the wastewater was not set to the desired level. After treatment with SMZ, cyanide removal was 73.5%. The Cr^{6+} and Ni^{2+} concentrations were decreased by 21.8% and 19.9%. From the above decrease in concentration, SMZ is shown to be excellent promising adsorbent for eliminating cyanide from cyanide-laden wastewater.

4. Conclusions

In this study, the potential of the SMZ was evaluated for the cyanide removal from aqueous solution. The characteristics of the SMZ were studied by FTIR, BET, Barrett–Joyner–Halenda (BJH), XRD, SEM, and XRF method. The surface study showed that the adsorbent was mesoporous and crystalline with the surface area of 10.74 m^2/g. Also, the effect of the different variations was studied. The optimal conditions for adsorption of cyanide onto the SMZ were identified at pH 10, adsorbent dose of 4 g/L, and the contact time of 250 min. The equilibrium data were best fitted with Langmuir model isotherm with the maximum adsorption capacity of 49.57 mg/g. The best fitting adsorption kinetic model was pseudo-second-order model. The field applicability of the SMZ was successfully tested by treating the metal plating wastewater. The results confirm that the SMZ is an effective method for cyanide removal and a hopeful technique for treatment of cyanide-containing wastewater.

Acknowledgment

The authors would like to thank the Bushehr University of Medical Sciences for providing technical support to conduct this work.

References

[1] A.W. Rate, R.E. Hamon, L.F. Bettenay, R.J. Gilkes, Adjustment of weak partial extraction data assuming metal ion adsorption: examples using bulk cyanide leach, Geochem. Explor. Environ. Anal., 10 (2010) 199–206.

[2] R.R. Dash, C. Balomajumder, A. Kumar, Removal of cyanide from water and wastewater using granular activated carbon, Chem. Eng. J., 146 (2009) 408–413.

[3] G. Moussavi, R. Khosravi, Removal of cyanide from wastewater by adsorption onto pistachio hull wastes: parametric experiments, kinetics and equilibrium analysis, J. Hazard. Mater., 183 (2010) 724–730.

[4] M. Fooladvand, B. Ramavandi, Adsorption potential of NH_4Br-soaked activated carbon for cyanide removal from wastewater, Ind. J. Chem. Technol., 22 (2015) 183–193.

[5] I.A. Talalaj, Removal of organic and inorganic compounds from landfill leachate using reverse osmosis, Int. J. Environ. Sci. Technol., 12 (2015) 2791–2800.

[6] J. Shen, H. Zhao, Y. Xie, H. Cao, Y. Zhang, Coagulation behaviors and in-situ flocs characteristics of composite coagulants in cyanide-containing wastewater: role of cationic polyelectrolyte, Sci. China Chem., 56 (2013) 1765–1774.

[7] E. Yazıcı, H. Deveci, I. Alp, Treatment of cyanide effluents by oxidation and adsorption in batch and column studies, J. Hazard. Mater., 166 (2009) 1362–1366.

[8] S. Hanela, J. Durán, S. Jacobo, Removal of iron–cyanide complexes from wastewaters by combined UV–ozone and modified zeolite treatment, J. Environ. Chem. Eng., 3 (2015) 1794–1801.

[9] H. Uppal, S.S. Tripathy, S. Chawla, B. Sharma, M. Dalai, S. Singh, S. Singh, N. Singh, Study of cyanide removal from contaminated water using zinc peroxide nanomaterial, J. Environ. Sci., 55 (2017) 76–85.

[10] Y. Yu, C. Wang, X. Guo, J.P. Chen, Modification of carbon derived from *Sargassum* sp. by lanthanum for enhanced adsorption of fluoride, J. Colloid Interface Sci., 441 (2015) 113–120.

[11] A. Behnamfard, M.S. Rad, Adsorption kinetic modeling of cyanide by activated carbon from solution by using of kinetic models and adaptive neuro-fuzzy inference system, Asian J. Chem., 22 (2010) 271–282.

[12] H. El-Aila, K. El-Sousy, K. Hartany, Kinetics, equilibrium and isotherm of the adsorption of cyanide by MDFSD, Arabian J. Chem., 9 (2011) S198–S203.

[13] W. Zheng, Y. Wang, L. Yang, X. Li, L. Zhou, Y. Li, Novel adsorbent of polymeric complex derived from chaleting resin with Cu(II) and its removal properties for cyanide in aqueous solution, Colloids Surf., A, 455 (2014) 136–146.

[14] R. Mohamed, M.M. Mohamed, Copper (II) phthalocyanines immobilized on alumina and encapsulated inside zeolite-X and their applications in photocatalytic degradation of cyanide: a comparative study, Appl. Catal., A, 340 (2008) 16–24.

[15] H. Faghihian, M. Kamali, Synthesis of Na-Pc zeolite from perlite and study of its ability to remove cyanide from liquid wastes, Int. J. Environ. Pollut., 19 (2003) 557–566.

[16] N. Li, T. Li, H. Liu, Y. Yue, X. Bao, A novel approach to synthesize in-situ crystallized zeolite/kaolin composites with high zeolite content, Appl. Clay Sci., 144 (2017) 150–156.

[17] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, Chem. Eng. J., 156 (2010) 11–24.

[18] P. Ning, J. Qiu, X. Wang, W. Liu, W. Chen, Metal loaded zeolite adsorbents for hydrogen cyanide removal, J. Environ. Sci., 25 (2013) 808–814.

[19] J. Liu, X. Cheng, Y. Zhang, X. Wang, Q. Zou, L. Fu, Zeolite modification for adsorptive removal of nitrite from aqueous solutions, Microporous Mesoporous Mater., 252 (2017) 179–187.

[20] G. Asgari, B. Ramavandi, L. Rasuli, M. Ahmadi, Cr (VI) adsorption from aqueous solution using a surfactant-modified Iranian zeolite: characterization, optimization, and kinetic approach, Desal. Wat. Treat., 51 (2013) 6009–6020.

[21] Z. Wang, S. Lu, D. Wu, F. Chen, Control of internal phosphorus loading in eutrophic lakes using lanthanum-modified zeolite, Chem. Eng. J., 327 (2017) 505–513.

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

[23] H. Shayesteh, A. Rahbar-Kelishami, R. Norouzbeigi, Evaluation of natural and cationic surfactant modified pumice for congo red removal in batch mode: kinetic, equilibrium, and thermodynamic studies, J. Mol. Liq., 221 (2016) 1–11.

[24] B. Ramavandi, A. Rahbar, S. Sahebi, Effective removal of Hg^{2+} from aqueous solutions and seawater by *Malva sylvestris*, Desal. Wat. Treat., 57 (2016) 23814–23826.

[25] Z. Khademi, B. Ramavandi, M.T. Ghaneian, The behaviors and characteristics of a mesoporous activated carbon prepared from *Tamarix hispida* for Zn(II) adsorption from wastewater, J. Environ. Chem. Eng., 3 (2015) 2057–2067.

[26] Water Environment Federation, American Public Health Association, Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), Washington, D.C., USA, 2005.

[27] G. Asgari, A.S. Mohammadi, S.B. Mortazavi, B. Ramavandi, Investigation on the pyrolysis of cow bone as a catalyst for ozone aqueous decomposition: kinetic approach, J. Anal. Appl. Pyrolysis, 99 (2013) 149–154.

[28] B. Ramavandi, Treatment of water turbidity and bacteria by using a coagulant extracted from *Plantago ovata*, Water Res. Ind., 6 (2014) 36–50.

[29] Y. Gao, H. Gan, G. Zhang, Y. Guo, Visible light assisted Fenton-like degradation of rhodamine B and 4-nitrophenol solutions with a stable poly-hydroxyl-iron/sepiolite catalyst, Chem. Eng. J., 217 (2013) 221–230.

[30] Y. Ma, X. Wu, G. Zhang, Core-shell Ag@Pt nanoparticles supported on sepiolite nanofibers for the catalytic reduction of nitrophenols in water: enhanced catalytic performance and DFT study, Appl. Catal., B, 205 (2017) 262–270.

[31] R. Leyva-Ramos, A. Jacobo-Azuara, P. Diaz-Flores, R. Guerrero-Coronado, J. Mendoza-Barron, M. Berber-Mendoza, Adsorption of chromium(VI) from an aqueous solution on a surfactant-modified zeolite, Colloids Surf., A, 330 (2008) 35–41.

[32] P. Chutia, S. Kato, T. Kojima, S. Satokawa, Adsorption of As(V) on surfactant-modified natural zeolites, J. Hazard. Mater., 162 (2009) 204–211.

[33] Y. Ma, G. Zhang, Sepiolite nanofiber-supported platinum nanoparticle catalysts toward the catalytic oxidation of formaldehyde at ambient temperature: efficient and stable performance and mechanism, Chem. Eng. J., 288 (2016) 70–78.

[34] R. Foroutan, F.S. Khoo, B. Ramavandi, S. Abbasi, Heavy metals removal from synthetic and shipyard wastewater using Phoenix dactylifera activated carbon, Desal. Wat. Treat., 82 (2017) 146–156.

[35] M. Kitis, E. Karakaya, N.O. Yigit, G. Civelekoglu, A. Akcil, Heterogeneous catalytic degradation of cyanide using copper-impregnated pumice and hydrogen peroxide, Water Res., 39 (2005) 1652–1662.

[36] S.-H. Do, Y.-H. Jo, H.-D. Park, S.-H. Kong, Synthesis of iron composites on nano-pore substrates: identification and its application to removal of cyanide, Chemosphere, 89 (2012) 1450–1456.

[37] A. Rezaee, B. Ramavandi, F. Ganati, Equilibrium and spectroscopic studies on biosorption of mercury by algae biomass, Pak. J. Biol. Sci., 9 (2006) 777–782.

[38] C. Chen, C. Kao, S. Chen, Application of *Klebsiella oxytoca* immobilized cells on the treatment of cyanide wastewater, Chemosphere, 71 (2008) 133–139.

[39] F. Saberzadeh Sarvestani, H. Esmaeili, B. Ramavandi, Modification of *Sargassum angustifolium* by molybdate during a facile cultivation for high-rate phosphate removal from wastewater: structural characterization and adsorptive behavior, 3 Biotech, 6 (2016) 251.

[40] M. Shams, I. Nabipour, S. Dobaradaran, B. Ramavandi, M. Qasemi, M. Afsharnia, An environmental friendly and cheap adsorbent (municipal solid waste compost ash) with high efficiency in removal of phosphorus from aqueous solution, Fresenius Environ. Bull., 22 (2013) 722–726.

[41] K. Padmavathy, G. Madhu, P. Haseena, A study on effects of pH, adsorbent dosage, time, initial concentration and adsorption isotherm study for the removal of hexavalent chromium (Cr (VI)) from wastewater by magnetite nanoparticles, Procedia Technol., 24 (2016) 585–594.

[42] M. Karimi, A. Nematollahzadeh, A. Shojaei, Amino functionalized hierarchically produced porous polyacrylamide microspheres for the removal of chromium(VI) from aqueous solution, J. Porous Mater., 24 (2017) 1705–1715.