Cyanide uptake from wastewater by modified natrolite zeolite–iron oxyhydroxide system: Application of isotherm and kinetic models

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A B S T R A C T

A method for the removal of cyanides from wastewater is described. The method involves the adsorption of cyanides by a modified natural zeolite (natrolite) using batch technique. A new iron oxyhydroxide–natrolite system was used in this study. A combination of XRD, XRF and FTIR spectroscopies, as well as TG/DSC thermal analyses was used for characterization of zeolitic materials. Effects of parameters such as pH, amount of adsorbent and contact time on the cyanide removing yield are studied. It was observed that the yield increases by increasing dosage of adsorbent and contact time at a fixed pH 7.5. A yield of 82% was achieved at optimum conditions for removing cyanide from industrial wastewaters. The experimental data obtained for optimum conditions were selected for modeling the adsorption behavior of the materials using six isotherm equations (Freundlich, Langmuir, Langmuir–Freundlich, Dubinin–Radushkevich, Redlich–Peterson and Toth). The obtained modeling results indicated that, although the three-parameter models, taking into account the surface heterogeneity, provided the closest approach to the measurement data, the parameters estimates could be highly biased. The kinetic studies proved that the second-order kinetic was the applicable model.

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1. Introduction

Cyanide waste streams are produced by several industries including ore extraction, photographic processing, manufacturing of synthetic organic and inorganic compounds and metal finishing. The most significant source of hazardous cyanide waste is the metal finishing industry. For example, it is used at nearly 90% of the gold mines worldwide and is potentially toxic [1]. The effluent waste waters from these processes contain different forms of cyanides. In the case of free cyanide, a concentration of $0.02\,mg\,L^{-1}$ has been reported to be lethal for certain species of sea animals, whereas a concentration of $0.2\,mg\,L^{-1}$ is allowable for drinking water supplies [1,2]. The cyanide toxic effect is due to its reaction with the trivalent iron in the cytochrome oxidase to inhibit electron transport and thus preventing the cells from consuming oxygen, leading to a rapid impairment of the vital functions.

Unit processes typically used for the treatment of cyanide wastes are different oxidation method [3–5] and adsorption techniques. Adsorption is a widely used technology for the removal of cyanide [6]. There are several reports on the treatment cyanide compounds by adsorption on plain and metal-impregnated activated carbons

[7–12]. Huff et al. examined the feasibility of removing cyanide from refinery wastewater with powdered activated carbon [7]. The mining operations mostly use adsorbents for recovery and removal of cyanide from effluents [7,8]. Granular/powdered carbon is the most widely used adsorbent, as it has a good capacity for the adsorption of cyanide compounds [9]. However, high cost of activated carbon and 10–15% loss during conventional regeneration has been the disadvantages in the utilization of activated carbon in the developing countries [13]. Say et al. have been used a column packed with cyanide-imprinted polymeric microbeads for cyanide removing [14]. Monser and Adhoum have investigated fixed bed activated carbon columns modified with tetrabutyl-ammonium iodide [15] and silver and/or nickel impregnated carbon columns [10] for removing cyanide from wastewater. Cyanide can be removed using chemical, catalytic, electrolytic, photocatalysts, biological, ultrasonic, and photolytic methods [1,16–20].

The work presented in this paper concentrated on developing a simple method for treating cyanides in wastewater by modified natural zeolite with $Fe(NO_3)_3$–KOH system. Modified zeolite was used as a new sorbent, and the effects of some operating parameters on removing yield were investigated. The cyanide removing from aqueous solution on the original zeolite and modified zeolites were studied. The adsorption data for modified zeolite were studied with different isotherm equations. Also, the modified zeolite has been used for removing cyanides from several industrial wastewaters.

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2. Experimental

2.1. Reagents and materials

All reagents were prepared from analytical reagent grade chemicals unless specified otherwise and purchased from Merck Company. All aqueous solutions were prepared with double-distilled water (DDW). A suitable volume of acid (nitric acid) or base (sodium hydroxide) solution was added to adjust pH that was measured with pH meter. Natural Iranian natrolite zeolite from the Hormak area (Zahedan city, Sistan & Baluchestan province, Iran) was used in this work.

2.2. Instrumentation

XRD data were obtained using a Phillips XPERT diffractometer and was performed with computer via the Apdw Phillips software's. Cu Kα emission was used with a Ni filter. The diffractions were monitored in the 2θ range of 2–70° (θ: Bragg angle). XRF experiments were recorded on Phillips PW-1480 spectrometers was performed with computer via the X40 Phillips software's.

Modified zeolite (0.15 g) was thoroughly mixed with KBr powder (IR-grade, Wako) to be 1.0 wt.% and pressed into a disk of 20 mm in diameter. The Fourier-transformed infrared (FTIR) spectra were measured in transmission mode using Valor III (JASCO) equipped with a MCT detector. The energy resolution was set to 1 cm^{-1}.

Thermogravimetric-differential thermal analysis (TG-DTA) was performed using STA 1500$^+$ Rheometric Scientific (England). The flow rate of air was 120 ml min^{-1} and the ramping rate of sample was 2 °C min^{-1}.

2.3. Surface modification

The Na-form of the zeolitic material was prepared prior to modification. For this purpose the zeolitic material was agitated for 48 h in a 1 mol L^{-1} NaCl solution at 25 °C, washed using distilled water until free of chloride ions (AgNO$_3$ test) and dried at 105 °C to constant weight.

The natrolite–Fe system was synthesised by following the method of pure goethite preparation, as described by Schwertmann and Cornell [21]. The modified zeolite system was prepared by mixing 20.0 g of natural zeolite, 100 ml of freshly prepared 1 M Fe(NO$_3$)$_3$ solution, and 180 ml of 5 mol L^{-1} KOH solution in a 2 L polyethylene flask. The addition of KOH solution was rapid with stirring. The suspension was diluted to 2 L with twice distilled water and was held in a closed polyethylene flask at 70 °C for 60 h. After the appropriate period the reaction vessel was removed from the oven, and the precipitate was centrifuged, washed with DDW and finally dried.

2.4. Characterizations of zeolitic materiel

The raw as well as the Na- and surface-modified forms of the zeolitic material were characterized. The natrolite zeolite crystals were separated by hand. The X-ray diffraction pattern of the natural zeolite is completely matched with that of the natrolite zeolite. The composition of natural zeolite is Na$_2$[Al$_2$Si$_3$O$_{10}$]·2H$_2$O. The SiO$_2$/Al$_2$O$_3$ ratio of the material is 1.77 corresponding to a natrolite zeolite [22]. The mineral content of the zeolitic material from quarry face, based on the XRF technique, was natrolite 99.63% (w/w). The FTIR spectra of the zeolites are shown in Fig. 1. From Fig. 1a, the Na-form zeolite contains bands due to Si–O–Si and Si–O–Al vibrations (1200–950 cm^{-1}), the presence of zeolitic water (3619, 3440 and 1640 cm^{-1}) and pseudo-lattice vibrations (800–500 cm^{-1}). For modified zeolites, the region corresponding to high wave numbers show a broad band centered at 3300 cm^{-1} (Fig. 1b and c). This band is generally attributed to the (O–H) vibration of water and oxyhy-
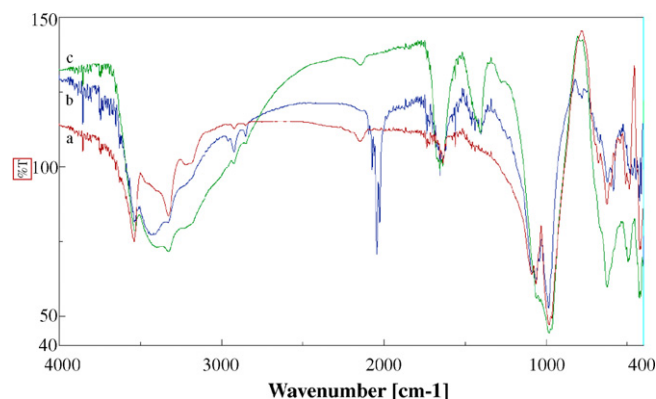

Fig. 1. FTIR spectra of the zeolite samples: (a) natural natrolite zeolite, (b) modified natrolite zeolite–iron oxyhydroxide system after removing cyanide and (c) modified natrolite zeolite–iron oxyhydroxide system before removing cyanide.

droxides (Fe$_s$–OH). Also, the spectra weak bands were observed in the range of 1460–1420 cm^{-1}. These bands can be assigned to the O–H in-plane deformation mode of hydroxyl group (Fig. 1b and c) [23]. The spectra further show peaks originated from C≡N stretching vibrations of cyanides in the range of 2000–2100 cm^{-1} (Fig. 1b).

In TG-DTA data of unmodified zeolite was observed only a gradual weight decreasing between 300 and 400 °C due to the desorption of surface water. TG-DTA data were measured for modified natrolite zeolite samples (see Fig. 2). Abrupt weight decrease was observed between 180 and 220 °C due to the desorption of surface water and then an gradual weight decrease between 400 and 500 °C was associated with exothermic peak due to the desorption of lattice water.

Also, the XRD pattern of modified zeolite adsorbent for removing cyanide showed that no obvious crystalline peak was detected, indicating that both modified reagent and cyanide composite exist mainly in amorphous form.

The pH measurement as a function of solution pH was studied with the following method. 10 mg of the zeolite in different forms were mixed for 24 h with 10 ml of deionized water in 15-ml centrifuge tubes placed in the rotary evaporator. The pH range of deionized water (with pH 6.5) for the Na-form zeolite was 7.1.

2.5. General procedure

For the individual experiments 0.2–2 g of modified zeolitic materials were shaken for 48 h with 10–50 ml of the individual solutions of cyanide in polypropylene-centrifuge tubes at ambient temperature. The concentration of the cyanide in the resultant solu-
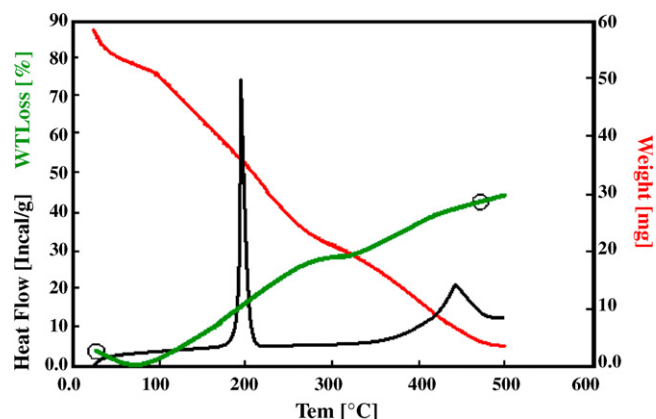

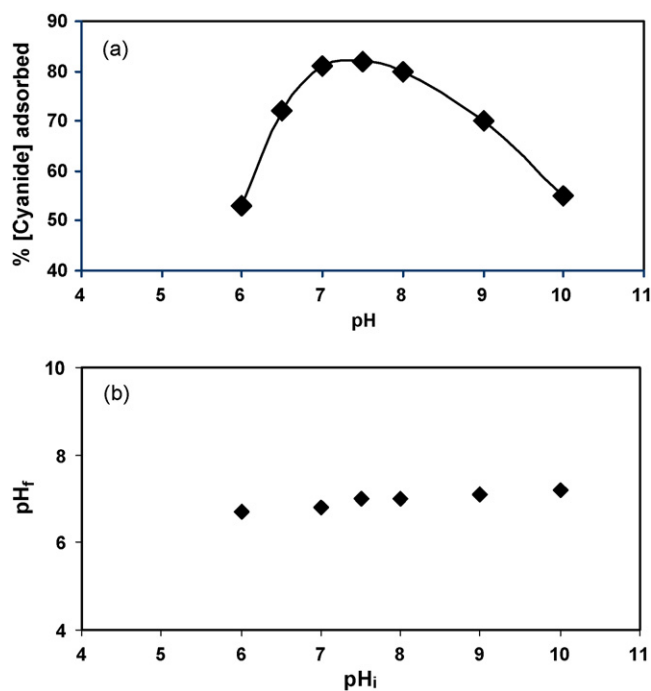**Fig. 2.** TG-DTA data measured for modified natrolite zeolite.

Fig. 3. (a) Influence of the initial solution pH on adsorption of cyanide using modified zeolite and (b) the variation of final pH versus initial pH.

tion was determined using our previous published work [24]. The amount of cyanide adsorbed on the zeolite surface was determined by difference of initial concentration and the concentration of cyanide in the centrifuge and filtrate solution. The parallel tests on blank samples have been used for comparison. The pH of the solutions was checked before beginning and at the end of the sorption experiments. Duplicate samples were prepared for all experimental conditions.

3. Results and discussion

Key parameters that influence the performance of the proposed method such as pH effect, amount of modified zeolite and contact time were studied in order to establish the optimum working configurations.

3.1. Effect of initial solution pH on cyanide uptake

Most cyanide used in industrial processes is added in the form of sodium cyanide (NaCN) or hydrogen cyanide (HCN). Sodium cyanide hydrolyzes to form hydrocyanic acid and sodium hydroxide:

$$NaCN + H_2O \rightarrow HCN + NaOH \tag{1}$$

Hydrogen cyanide is a weak acid with a dissociation constant of 4.8×10^{-10} ($pK_a = 9.32$) at $25\,°C$. It evaporates easily from these solutions as a very toxic gas. At pH values higher than 11, cyanide is completely dissociated into its ions and at a pH of 9.32, 50% of the hydrocyanic acid is in the form of free cyanide (CN^-) [25]. So, with decreasing of pH to acidic media, the percentage of HCN increases. At pH values lower than 7 most of the cyanide is present as hydrogen cyanide acid gas, dissolved in the solution. The effect of initial pH on the rate of cyanide removal has been illustrated in Fig. 3a and b. The dependence of removal percentage for CN^- upon pH of the aqueous solution is shown in Fig. 3a. The adsorptions of cyanide increased with an increase in pH from 6.0 to 8 and then decreased until 10.0. A pH 7.5 was chosen as the optimum pH. In this pH, HCN and CN^-

are the predominate species. Fig. 3b shows the variation of final pH versus initial pH. As shown in Fig. 3b the final pH for all initial solution is around 7.0. The experimental results were shown that the pure zeolite is not suitable without modification for the sorption of cyanide. The differences in chemical behavior; in adsorption of CN^- ions, in counterbalanced ions release are owed to the different surface species, which are located on the two substrates. The new material, due to the presence of the Fe oxides located in the zeolite channels or on its external sites, is characterized by the presence of additional active sites (–Fe–OH), which are influenced by the solution pH and are potential adsorption sites [26]. Owing to the presence of non-crystalline Fe formations located in cationic positions in the zeolite channels, of Fe binuclear and in general iron complexes in extra-framework positions, as well as of amorphous iron oxides FeO_x located at the surface of the zeolite crystal, higher adsorption capacity than untreated natrolite [27].

3.2. Adsorption mechanism

The mechanism by which anions are adsorbed onto modified zeolite has been a matter of considerable debate. Theories include ion exchange, surface adsorption, chemisorption, complexation, and adsorption–complexation. Opinions differ as to how complexation between modified zeolite and anions occurs. Evidence has also been found that chemisorption, a strong type of adsorption in which ions are not exchanged but electrons may be exchanged, can be involved in modified zeolite–anion binding. Different mechanisms, such as electrostatic forces, ion exchange, and chemical complexation, must be taken into account when examining the effect of pH on CN^- sorption. One of the commonly proposed mechanisms is electrostatic attraction/repulsion between sorbent and sorbate.
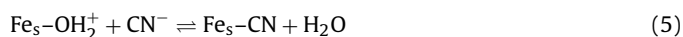
The prevalent forms of cyanide at pH 7.5 are HCN and CN^-. In other hand, in aqueous solution iron compounds forms in oxyhydroxides that can undergo protonation (Eq. (2)) or deprotonation (Eq. (3)), yielding a positive or negative charge:
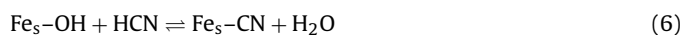
$$Fe_s–OH + H^+ \rightleftharpoons Fe_s–OH_2^+ \tag{2}$$

$$Fe_s–OH \rightleftharpoons H^+ + Fe_s–O^- \tag{3}$$
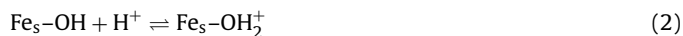
Hence, anions such as CN^- can be adsorbed in the first case, through non-specific coulombic interaction according to the scheme:

$$Fe_s–OH_2^+ + CN^- \rightleftharpoons Fe_s–OH_2^+ \cdots CN^- \tag{4}$$

Or they can undergo direct exchange:

$$Fe_s–OH_2^+ + CN^- \rightleftharpoons Fe_s–CN + H_2O \tag{5}$$

or

$$Fe_s–OH + HCN \rightleftharpoons Fe_s–CN + H_2O \tag{6}$$

3.3. Effect of adsorbent dose on cyanide adsorption and contact time

The effects of variation of the modified zeolite amount on the removal of cyanide by the modified zeolite are shown in Fig. 4. Amount of the modified zeolite was varied from 0.1 to 0.7 g and equilibrated for 48 h at a fixed initial cyanide concentration of 50 ppm. It is apparent that the equilibrium concentration in solution phase decreases with increasing the modified zeolite amount for a given initial cyanide concentration, since the fraction of anion removed from the aqueous phase increases as the sorbent amount is increased in the batch vessel with a fixed initial anion concentration, as shown in the curves in Fig. 4. This result was anticipated because for a fixed initial solute concentration, an increasing amount of adsorbent provides a greater surface area (or adsorption sites).
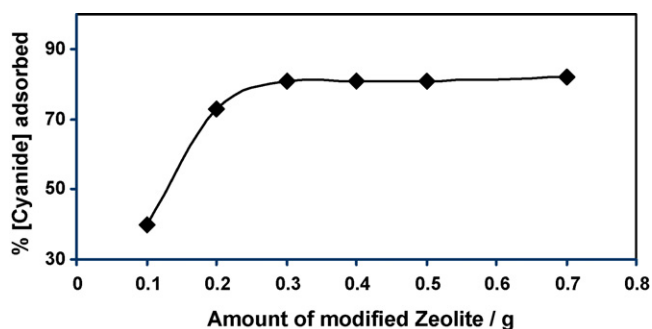
Fig. 4. The effect of amount of modified zeolite on adsorption of cyanide, pH 7.5 and 50 ml cyanides 0.2 mM.
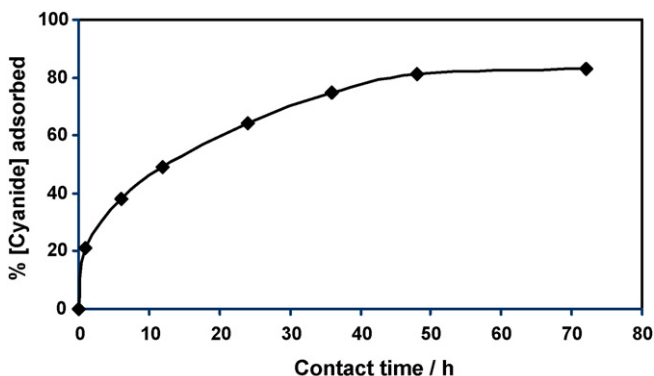

Fig. 5. Influence of the contact time adsorption of cyanide using modified natural natrolite zeolite, pH 7.5 and 50 ml cyanides 0.2 mM and 0.7 g modified zeolite.

3.4. Effect of contact time on cyanide adsorption

The experiment of adsorption as a function of contact time was conducted at known initial CN^- concentration, dose of 0.7 g modified zeolite in 40 ml (see Fig. 5). The removal was 50% and 82% after 12 and 48 h, respectively. A selection of optimal parameters for the proposed method was shown in Table 1.

4. Isotherm and kinetic studies

4.1. Isotherm data analysis

The study data obtained for the CN^- sorption from aqueous solutions were fitted using six mathematical expressions (Freundlich (F), Langmuir (L), Langmuir–Freundlich (L–F), Dubinin–Radushkevich (D–R), Redlich–Peterson (R–P) and Toth (T)) are given in Figs. 6–11 and details in Table 2. The cyanide sorption data set of $pH_{init} = 7.5$ was selected for the mathematical modeling because of the smooth form of the obtained experimental data covering the range from the near origin of the plot $q = x/m$ versus c to the q_{max}. In this study all the model parameters were evaluated by non-linear regression. The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data. Not only the correlation

Table 1
Optimum conditions for removing cyanide using proposed modified zeolite.

Parameter	Study range	Optimum
pH	6–10	7.5
Amount of modified zeolite (g)	0.1–0.7	0.25
Contact time (h)	0–80	12 (for 50%) and 48 (for 82%)

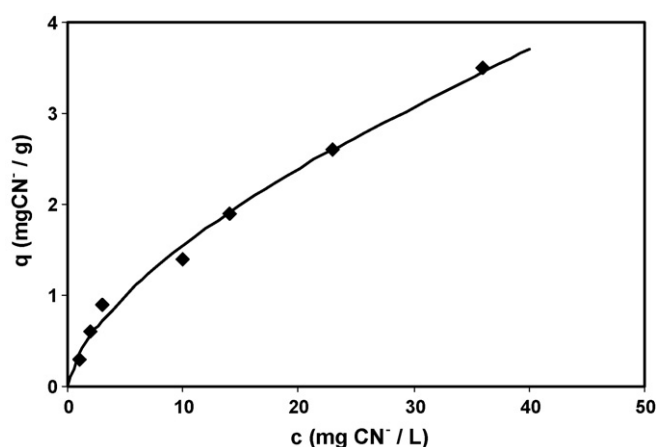**Fig. 6.** Modeling of the cyanide sorption behavior of modified zeolite from solutions of $pH_{init} = 7.5$ using two-parameters isotherm Freundlich equation ($q = x/m$).

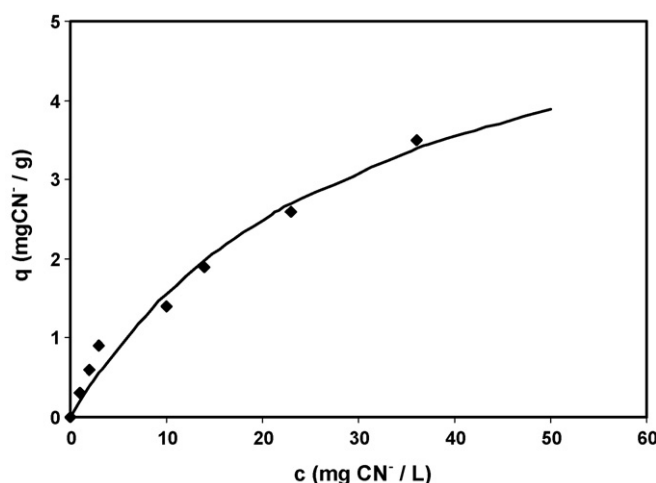**Fig. 7.** Modeling of the cyanide sorption behavior of modified zeolite from solutions of $pH_{init} = 7.5$ using two-parameters isotherm Langmuir equation ($q = x/m$).

coefficient (R^2) but also the residual root mean square error (R) and the chi-square test were used to measure the goodness-of-fit. R [28] can be represented as follows:

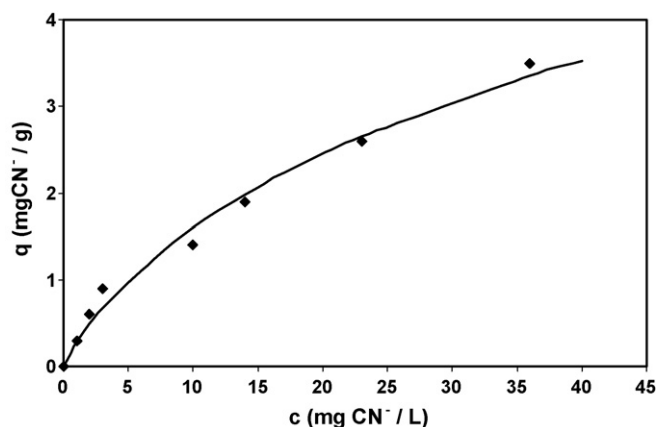$$R = \sqrt{\frac{\sum_{i=1}^{m}(Q_i - q_i)^2}{m - 2}} \qquad (7)$$

Fig. 8. Modeling of the cyanide sorption behavior of modified zeolite from solutions of $pH_{init} = 7.5$ using three-parameter isotherm Langmuir–Freundlich equation ($q = x/m$).

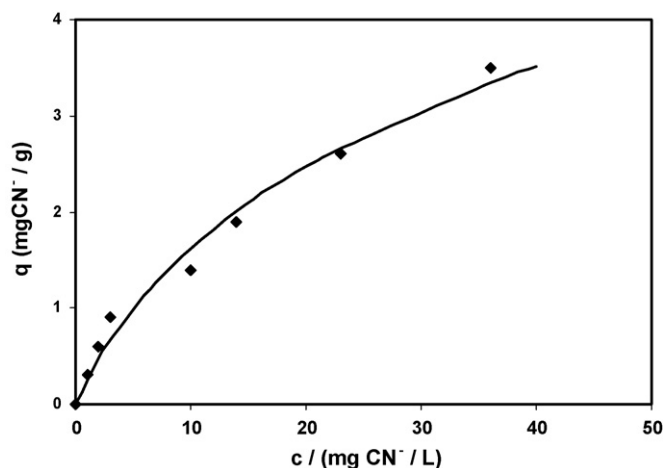**Fig. 9.** Modeling of the cyanide sorption behavior of modified zeolite from solutions of pH_{init} = 7.5 using three-parameters isotherm Dubinin–Radushkevich equation ($q = x/m$).

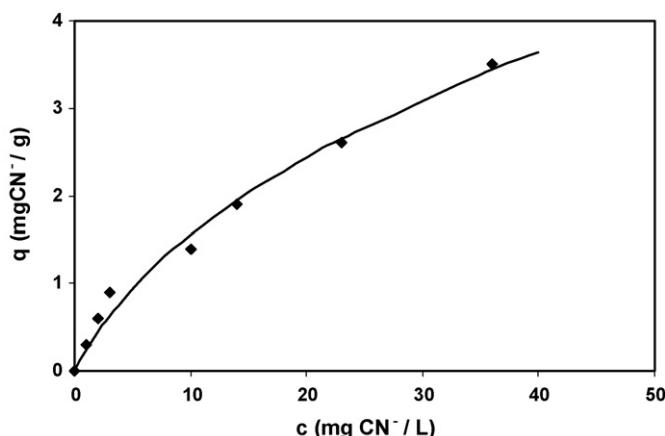**Fig. 10.** Modeling of the cyanide sorption behavior of modified zeolite from solutions of pH_{init} = 7.5 using three-parameters isotherm Redlich–Peterson equation ($q = x/m$).

where Q_i is the observation from the batch experiment, q_i is the estimate from the isotherm for corresponding Q_i and m is the number of observations in the experimental isotherm. The smaller R value indicates the better curve fitting.

The calculated isotherm parameters and the corresponding residual root mean square error for each model are given in Table 2. The comparison of the obtained values indicated that the application of different models resulted in deferent value of estimated constants as well as calculation errors. The estimate surface het-
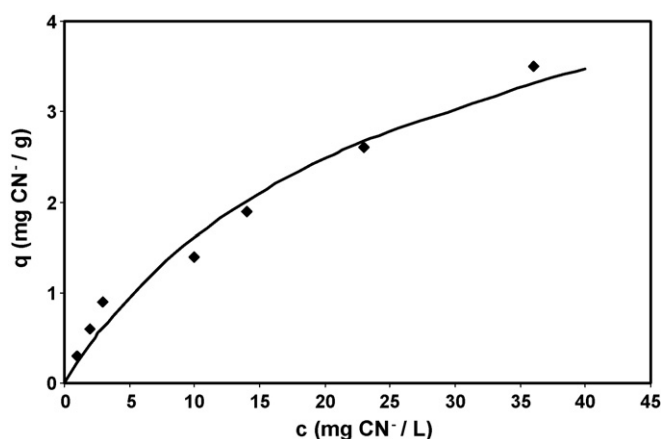

Fig. 11. Modeling of the cyanide sorption behavior of modified zeolite from solutions of pH_{init} = 7.5 using three-parameters isotherm Toth equations ($q = x/m$).

erogeneity factor (n) is lower than 0.25 for D–R model, lower than 1 for the rest three-parameter models (L–F, R–P and T) and more than 1 for the F, since the sorption mechanism could be explained by the presence of less available active sites compared to the Freundlich isotherm [29]. The absolute average deviation obtained for modified zeolite is 0.07, which indicates that the experimental data fitted well to Freundlich model. The n value (1.58) is higher than 1.0, indicating that CN^- is favorably adsorbed by modifier.

It was obvious that the curves obtained applying all models could satisfactorily reproduce the experimental data. The fits obtained using Freundlich isotherms showed the lowest deviation from the experiment. It was also evident that the three-parameter models gave a better fit than the two-parameter ones (Table 2). The Freundlich isotherm allowed the best approximation of the experimental data giving a lower R value than the other models. In addition Table 3 shows that the other three-parameter isotherms (L–F, R–P, D–R and T) also fitted the data well.

4.2. Kinetic studies

Batch experiments were conducted to explore the rate of cyanide ions adsorption by modified zeolite at pH 7.5. The kinetic adsorption data can be processed to understand the dynamics of the adsorption reaction in terms of the order of the rate constant. The kinetic of CN^- adsorption modified zeolite is required for selecting optimum operating conditions for the full-scale batch process. Moreover, it is helpful for the prediction of adsorption rate, gives important information for designing and modeling the processes. Thus, the process of cyanide removal from aqueous phase by modified zeolite may be represented by pseudo first-order, pseudo second-order

Table 2

Isotherm parameters obtained by fitting of the experimental data for the sorption of cyanide by modified natural zeolite. R gives the average deviation of the calculated from the experimental values.

Calculation method	Estimated parameters				
	Equation	K	q_{max}	n	R
Freundlich	$q = k \times c^{1/n}$	0.361	–	1.58	0.07
Langmuir	$q = \frac{k \times c \times q_{max}}{1 + k \times c}$	0.033	6.21	–	0.16
Langmuir–Freundlich	$q = \frac{(k \times c)^n \times q_{max}}{1 + (k \times c)^n}$	0.019	8.00	0.83	0.12
Dubinin–Radushkevich	$\log q = -n(\log^2(k \times c)) + \log q_{max}$	0.001	7.35	0.16	0.14
Redlich–Peterson	$q = \frac{k \times c \times q_{max}}{1 + (k \times c)^n}$	0.84	3.5	0.66	0.11
Toth	$q = \frac{k \times c \times q_{max}}{(1 + (k \times c)^n)^{1/n}}$	0.039	6.2	0.89	0.16

($q = x/m$, c = concentration, q_{max} = sorption capacity, R = residual root mean square error, n and K = constant).

Table 3
Efficiency of proposed method for removing CN⁻ from three industrial wastewaters.

Sample	Initial [CN⁻] (ppm)	[CN⁻] (ppm) (after treatment)
Cupper electroplating wastewater	10.3	2.24
Gold electroplating wastewater 1	24.3	6.62
Gold electroplating wastewater 2	47.8	13.1

Experimental conditions, pH 7.5, amount of modified zeolite = 0.25 g and contact time = 32 h.

and Elovich kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2, values close to 1). The relatively higher value is the more applicable model to the kinetics of CN⁻ adsorption.

4.2.1. Pseudo first-order kinetic model

The kinetic data were treated with the Lagergren first-order model [30] which is the earliest known one describing the adsorption rate based on the adsorption capacity. It is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{8}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg g⁻¹), and k_1 is the rate constant of pseudo first-order adsorption (min⁻¹). Eq. (8) was integrated with the boundary conditions of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ and rearranged to the following linear equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k1}{2.303}t \tag{9}$$

If the pseudo first-order kinetics is applicable, a plot of $\log(q_e - q_t)$ versus t should provide a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively (Fig. 12a). The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. It was observed from Fig. 10a that the Lagergren model does not fit the experimental data. On the other hand, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots even when the correlation coefficient R^2 are relatively high. This shows that the adsorption of cyanide ions onto modified zeolite is not appropriate to describe the entire process and not a first-order reaction.

4.2.2. Pseudo second-order kinetic model

Adsorption kinetic was explained by the pseudo second-order model given by Ho et al. [31] as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

where k_2 (g mg⁻¹ min⁻¹) is the second-order rate constant of adsorption. Integrating Eq. (10) for the boundary conditions $q = 0$ to $q = q_t$ at $t = 0$ to $t = t$ is linearized to obtain the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \tag{11}$$

The second-order rate constants were used to calculate the initial sorption rate (h), given by the following Eq. (12):

$$h = k_2 q_e^2 \tag{12}$$

The plot of t/q_t versus t should show a linear relationship if the second-order kinetics is applicable. Values of k_2 and q_e were calculated from the intercept and slope of the plots of t/q_t versus t (Fig. 12b). The linear plots of t/q_t versus t show good agreement
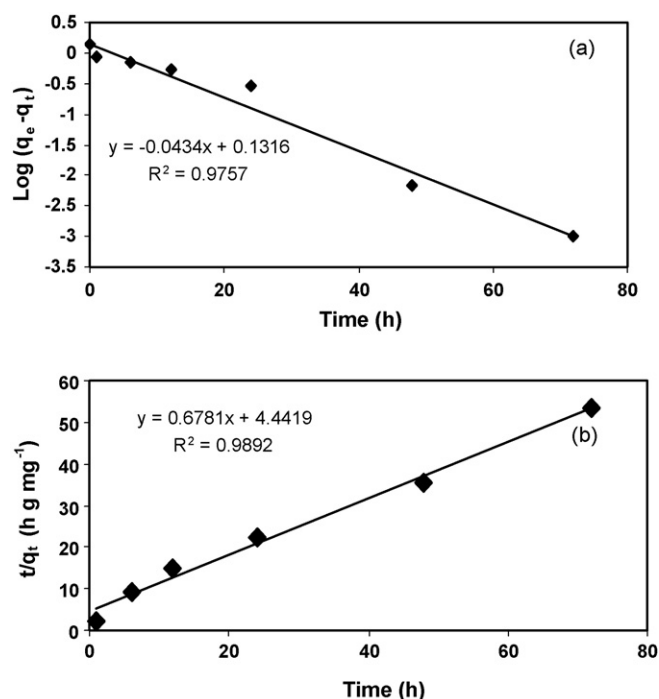

Fig. 12. Plot of the (a) pseudo first-order and (b) pseudo second-order models for the adsorption of CN⁻ 0.2 mM onto modified zeolite.

between experimental and calculated q_e values at different initial CN⁻ and adsorbent concentrations with correlation coefficients $R^2 = 0.989$, which indicated that the pseudo second-order kinetic model provided good correlation for the adsorption of CN⁻ onto modified zeolite for all studied initial CN⁻ and adsorbent concentrations in contrast to the pseudo first-order model. Moreover, values for the rate of initial adsorption, h, have no specific role, while the pseudo second-order rate constant (k_2) decreases with increase the initial CN⁻ concentration for all studied doses of modified zeolite.

4.2.3. Elovich kinetic model

Elovich kinetic equation is another rate equation based on the adsorption capacity, which is generally expressed as [32–34]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{13}$$

where α is the initial adsorption rate (mg g⁻¹ min⁻¹) and β is the desorption constant (g mg⁻¹) during any one experiment. It is simplified by assuming $\alpha\beta t \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$. Eq. (13) becomes form as followed:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{14}$$

If CN⁻ adsorption by modified zeolite fits the Elovich model, a plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \times \ln(\alpha\beta)$ (Fig. 13). Thus, the constants can be obtained from the slope and the intercept of the straight line. Correlation coefficients obtained by Elovich model were higher than that obtained from pseudo first-order model and comparable to that obtained from pseudo second-order model.
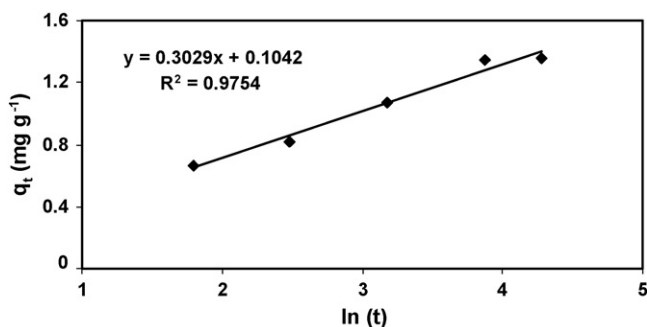
Fig. 13. Elovich model plot for the adsorption of CN⁻ (0.2 mM) onto modified zeolite.

5. Effect of real wastewater on the adsorption process

The studies of the effects of real wastewater on the capability of the modified zeolite to remove CN⁻ ions from solution were investigated. The above work was achieved using three real electroplating wastewater and the results are reported in Table 3. Salt concentration is directly proportional to the ionic strength of aqueous solutions. Ionic strength is also one of the important factors that influence the equilibrium uptake. However, the percentage of CN⁻ removal from aqueous solution prepared by dissolving of the CN⁻ into distilled water and wastewater was higher than 82% for modified zeolite, respectively, which indicates that the removal percentage of CN⁻ adsorption were not affecting by the changing of the type of cyanide ion solution. These results indicate that the modified zeolite is applicable material for the removal of CN⁻ ions from different types of aqueous solutions including wastewater.

6. Conclusions

A natrolite–Fe system synthesised and characterized with different spectroscopy methods. This study investigates the adsorption of cyanide toxic ions on this adsorbent. The adsorption process is pH dependent and the optimum pH was 7.5. The kinetic studies proved that the second-order kinetic was the applicable model. Furthermore, the isotherm equilibrium studies confirmed that the Freundlich form and generalized models are the highest fitted models for the adsorption process of CN⁻ by modified zeolite. The inorgano-modified zeolites are inexpensive and easy to prepare materials that can find, regardless of their relatively low uptake capacity compared to other natural and synthetic sorbents, very important environmental applications (e.g., for engineered protective barriers). The proposed sorbents are efficient, environment friendly and can reduce the huge amount of toxic cyanide ions from effluent discharges by the industries around the big cities.

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