ORIGINAL RESEARCH PAPER

Modification of natural zeolite for effective removal of Cd(II) from wastewater

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ABSTRACT

In the current research work the Iranian natural zeolite (clinoptililite) was modified with Cobalt Hexacyanoferrate nanopatricles. The natural and Cobalt Hexacyanoferrat modifed zeolites were characterized by FTIR and SEM techniques and were empolyed as an adsorbent for removal Cd(II) ions from aqueous sloution. The adsorption expriments were performed in bach mode. The Cd(II) sorption capacity of Cobalt Hexacyanoferrat modified zeolite was 51 mg g^{-1}. The effect of influceing factors such as time, temperature and initial concentration were investigated. A fast sorption was observed in the initial contact time and equilibrium was achieved in less than 100 min. The equilibrium adsorption data for Cd (II) were better fitted to the Longmuir adsorption isotherm model. The increase in temperature has a slight positive effect on the uptake of Cd(II) ions. The results indicated that the Cobalt Hexacyanoferrate nanopatricles modified natural zeolite has effective potential for the adsorption of Cd(II) from the wastewater.

Keywords: *Adsorptiom; Clinoptilolite; Cobal Hexacyanoferrate; Nanoparticle; Zeolite*

INTRODUCTION

Cd(II) is one of the most toxic heavy metal ions even at very low concentrations for human beings and it can pollute drinking water resources [1]. Cd(II) can penetrate into the human body through the food chain and thus can cause anemia, hypertension, muscular cramp, osteoporosis, cancer and eventually leads to death [2]. The wide occurrence of Cd(II) contamination in environment mainly originates from a range of anthropogenic sources, including fertilizers industry, battery industry (Cd-Ni battery), paint industry, mining and smelting processes [3].Thus the removal of the Cd(II) ions from the wastes is necessary before the their entering into the environmental. Conventional methods for removal of Cd(II) ions from wastewater include reduction, precipitation, ion exchange, filtration, electrochemical treatment, membrane technology, and evaporation. The mentioned methods are ineffective or extremely expensive when a large volumes of solution at relatively low concentrations is considered for remediation [4]. Adsorption process is one of the most favor technique applied in industries for removal of the Cd(II) and a lot of studies on this process have performed [5]. In order to finding cheaper adsorbent materials for removal of Cd(II) ions from aqueous solution instead of conventional sorbent material (such as activated

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carbon) compressive studies have performed [6-10]. Therefore, usage of several inexpensive sorbent materials, such as chitin, anaerobic sludge, apple residue, sawdust, rice polish, clay, zeolite, fly ash, chitosan, waste tea, seaweeds, and polyaniline coated on sawdust [11-23] have been reported. In this work the modification of natural zeolite with Cobalt Hexacyanoferrate (CoHCF) nanoparticles for effective removal of Cd(II) would be reported.

EXPERIMENTAL
Materials and Characterization
The materials including of $CoCl_2.6H_2O$, $K_3Fe(CN)_6$, and $Cd(NO_3)_2$ were from Merck Co., and used without further purification. The solutions were prepared by distilled water. The Iranian natural zeolite was supplied from mining Companies. The natural and modified zeolite were characterization by X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) techniques.

Zeolite modifying
The modification of the natural zeolite was performed according to following order: 5 g of the zeolite was powdered and dried at 150 °C, and added to a 100 ml solution of 0.1M $Co(NO_3)_2$ under continuous string condition at 25 °C for 2 hours. After filtering, the zeolite was washed and mixed with a 100 ml of 0.1M $K_4Fe(CN)_6$ solution to deposition of the CoHCF in the surface and channels of zeolite. Then the treated zeolite was

washed and dried at 60 °C for 2 hours.

Cd(II) sorption
The Cd(II) sorption studies were performed in batch mode according to following: 0.1 g of the natural or modified zeolites was added to 20 ml of Cd(II) solutions under gentle stirring for a period of time. Then the samples were filtered and the remained Cd(II) ions in the solution were determined by ICP techniques. The Cd(II) removal capacity was defined as:

$$q_e=(C_i-C_e)\frac{V}{W} \qquad (1)$$

where v(L) is the volume of Cd(II) solution, C_i (mg/L) is initial Cd(II) concentration, C_e(mg/L) is final Cd(II) concentration, and w (g) is the mass of the solid phase.

The percentage of adsorption was calculated as follows:

$$Adsorption\ (\%) = \frac{C_i - C_e}{C_i} \times 100 \qquad (2)$$

The effect of contact time, initial concentration, and temperature parameters were studied to evaluate the modified zeolite characteristics and the adsorption thermodynamic parameters.

RESULTS AND DISCUSSION
Characterization
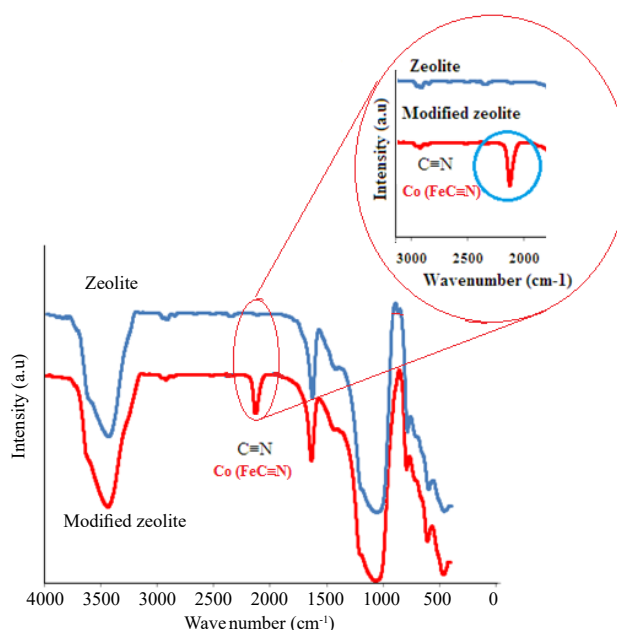The FT-IR spectra of the natural zeolite and CoHCF-zeolite are shown Fig. 1. The indicated

Fig. 1: FTIR spectra of bare and CoHCF loaded zeolites.

J. Water Environ. Nanotechnol., 3(2): 150-156 Spring 2018

151

common peaks in the two spectra at 1060, 794 and 609 cm^{-1} are characteristic index of clinoptilolite [24]. The observed band at 1060 cm^{-1} was assigned to the asymmetric internal tetrahedral bending. The second strongest band at 465 cm^{-1} was corresponded to the internal bending. The band at 609 cm^{-1} was attributed to the presence of double rings in the framework structure. Other bands at 1208 cm^{-1}, 790 cm^{-1} and 711 cm^{-1} were assigned to the asymmetric stretching modes of internal tetrahedra, symmetric stretching of external tetrahedra and symmetric stretching of internal tetrahedra, respectively. The 670 cm^{-1} band arises from symmetric tetrahedral stretching [25]. A sharp peak which appeared at 2090 cm^{-1}, in modified zeolite is a characteristic of the cyanide group (C≡N) and confirms the successful anchoring of CoHCF particles on the zeolite [26].

Fig. 2 (a, b) shows the SEM images of the natural and modified zeolites in different magnifications. The SEM images indicate that the morphology of the samples are nearly the same and modification
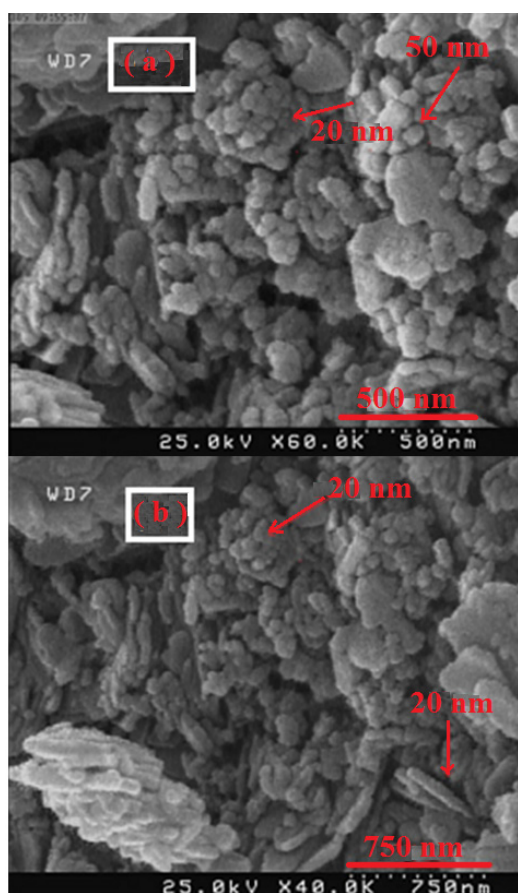
didn't changed the appearance of zeolite considerably. The large clusters formed from the sub-grain irregular particles with the average size of about 50 nm can be seen in images. Close examination of the modified zeolite image indicates that the fine nanostructures are interconnected to each other giving a porous and rod-like (diameter about 15 nm) appearance to the morphology.

Time Effect

By measuring sorption capacity of CoHCF-Zeolite at different interval contact times the sorption kinetics parameters were determined (Fig. 3a). The time-sorption behavior of Cd(II) ions, was measured by varying the equilibrium time (15-480 min). A fast sorption was observed in the initial contact time and equilibrium was achieved in less than 100 min. Due to the large concentration gradient between the solution and adsorbent surface, at initial contact step, the uptake capacity increased fast and achieved 90 % of the equilibrium value [27] Then, the adsorption slowed down, because more sorption sites were occupied [27].

The kinetic parameters were extracted from fitting of obtained experimental data with kinetic models. Thus, the pseudo-first-order and pseudo-

Fig. 2: SEM images of (a) bare zeolite, (b) modified zeolites.
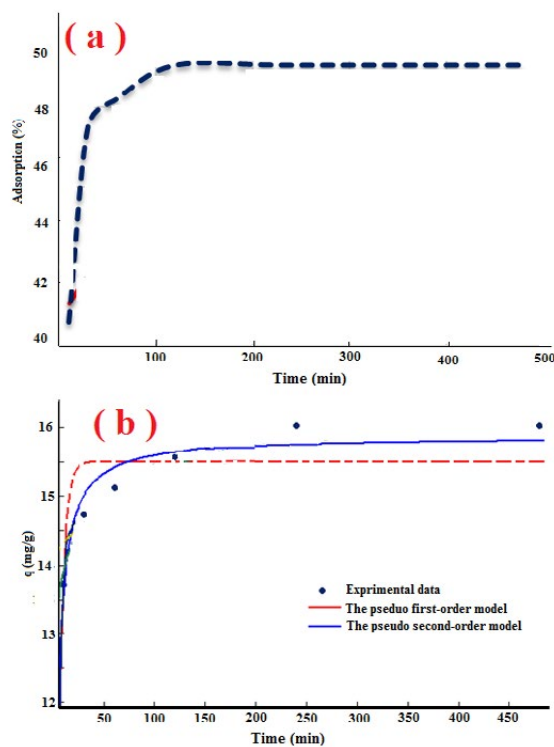

Fig. 3: (a) Effect of contact time on Cd(II) adsorptions and (b) Kinetic models plots of Cd(II) adsorptions on modified zeolite

second-order models were the equations used to fit the experimental data (Fig. 3b).

The pseudo-first-order rate expression based on the solid capacity is the earliest known equation describing the adsorption rate of an adsorbate from a liquid phase and it is represented as [27]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{3}$$

where q_e and q_t are the amount of ions adsorbed (mg/g) on the adsorbent at the equilibrium and at time t, respectively, and K_1 (1/min) is the rate of constant adsorption.

The (q_e) and (K_1) parameters can be individually calculated from the slope and intercept of the plot of $\text{Ln}(q_e-q_t)$ versus time

A pseudo second-order rate model is also used to describe the kinetics of the sorption of Cd(II) ions onto the adsorbent materials. The pseudo-second-order rate model is expressed as [28]:

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

where k_2 is the rate constant of pseudo-second-order equation (g/mg min).

If the initial sorption rate h (mg h/L) is:

$$h = k_2 q_e^2 \tag{5}$$

then Eqs. (4) and (5) become:

$$\frac{t}{q} = \frac{1}{h} + \frac{1}{q_e} t \tag{6}$$

The kinetic plots of t/q_t versus t for ions sorption are used for parameters extraction, and the correlation coefficient (R^2) suggests correlation between the parameters and experimental data (Table 1). The results clarified the matching of the experimental data to the pseudo-second-order rate model.

Effect of temperature and initial concentration

The Cd(II) sorption at different initial concentrations of 50, 250, 500, 750, 1000, 1500 and 2000 mg L^{-1} and different temperatures of 298, 313 and 333 °K in contact time of 100 were studied to realize the relation between the adsorption capacity vs. concentration and temperature (Fig. 4). As can be seen, in concentration range of 50 to 500 mg L^{-1} the removal increased by the increasing the

Table 1. Kinetic parameters for Cd(II) sorption by modified zeolite

Kinetic models		
The pseudo first-order model	$k_1(\text{min}^{-1})$	0.2139
	$q_e(\text{mg/g})$	15.5
	R^2	0.675
The pseudo second-order model	k_2' (g/mg min)	0.03667
	q_e (mg/g)	15.86
	h (mg/g min)	9.224
	R^2	0.914

Fig. 4: Effect of initial Cd(II) ion concentrations on the amount of sorption.

J. Water Environ. Nanotechnol., 3(2): 150-156 Spring 2018

153

concentration, but the sorption became constant at higher concentration. Factors including a) mass transfer at the aqueous and the solid interfaces and b) probability of collision between ions and the adsorbent active sites would be changed with varying concentration and led to increasing of the adsorption capacity at higher concentration. The higher ions concentration eliminates the mass transfer limitation at solid and aqueous interfaces and increase probability of collision between ions and the adsorbent particles [27]. In summary all active sites of the adsorbent are vacant and the ion concentration gradient is relatively high, in initial contact time causing high sorption. With increasing ion concentration, the saturation of the active sites leads to a decrease in the available position for interaction with metal ions (plateau represents). The results shows that the adsorption capacities of natural zeolite was improved to 90 mg/g for Cd(II) ions which it was more greater than adsorption capacity of unmodified zeolite.

Fig. 4. Shows the temperature effect on Cd(II) sorption value of modified zeolite. The results indicated that the increase in temperature has a slight positive effect on the uptake of Cd(II) ions. Decreasing of solution viscosity and increasing of diffusion coefficient of ions in boundary layer of the adsorbent can be results of temperature increasing.

Isotherms equations

The Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin isotherm models are the sorption isotherm models have been applied to describe experimental data of sorption isotherms. The nonlinear form of Langmuir isotherm can be expressed as:

$$q_e = \frac{q_{max}bC_e}{1+bC_e} \qquad (7)$$

Where q_e (mg/g) is the amount adsorbed per unit mass of adsorbent at equilibrium concentration; C_e (mg/L) is the equilibrium concentration of the adsorbate; q_{max} (mg/g) is the maximum adsorption capacity; b is the adsorption equilibrium constant, characteristic of the affinity between the adsorbent and adsorbate.

Another studied isotherm model, was the Freundlich isotherm. This isotherm is more general than the Langmuir isotherm since it does not assume a homogenous surface or constant sorption potential and the Freundlich isotherm model can

be expressed as [28]:

$$q_e = K_F C_e^{1/n} \;\; or \;\; logq_e = log\,K_F + 1/n\,LogC_e \qquad (8)$$

where K_F (mg/g) is the Freundlich constant related to the sorption capacity of the sorbent, and 1/n is the Freundlich constant related to the energy heterogeneity of the system and the size of the adsorbed molecule.

In the Temkin isotherm, the interactions between the adsorbed species aren't ignored and the enthalpy of all the adsorbed ions in solution is accomplished [29]. The Temkin isotherm can be expressed as:

$$q_e = BLnA_T C_e \qquad (9)$$

Where B (J/mol) and A_T (L/g) are the constants related to the sorption heat and Temkin isotherm equilibrium binding respectively. The Temkin isotherm is not valid in the extremely high and low concentrations. The linear decrease of the molecules adsorption heat rather than logarithmic coverage is main consideration of this model [28].

The final studied model was the Dubinin-Radushkevich (D-R) isotherm. This model is similar to Langmuir isotherm, however it does not assume a homogeneous surface or constant sorption potential [28]. The D–R isotherm can be expressed as:

$$Lnq_e = Lnq_m - \beta\,\varepsilon^2 \qquad (10)$$

where, q_m is the maximum of sorped ion by adsorbent (mmol/kg), β is a constant related to the sorption energy (mol²/kJ²); and ε is the Polanyi potential (RT ln (1 + 1/Ce)), where R and T are the gas constant (kJ/mol.K), the absolute temperature respectively. The ε is equal to:

$$\varepsilon = RT\,ln(1+ 1/C_e) \qquad (11)$$

where C_e is the adsorbate equilibrium concentration (mg/lit).

Figs. 5 (a- d) shows the adsorption isotherms of Cd(II) ions on the CoHCF-Zeolite. Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich constants, and regression values are listed in Table 2. The regression values and correlation coefficients (R^2) presented in Table 2 indicated that the adsorption data for Cd(II) removal best fitted the Langmuir adsorption isotherm.

154

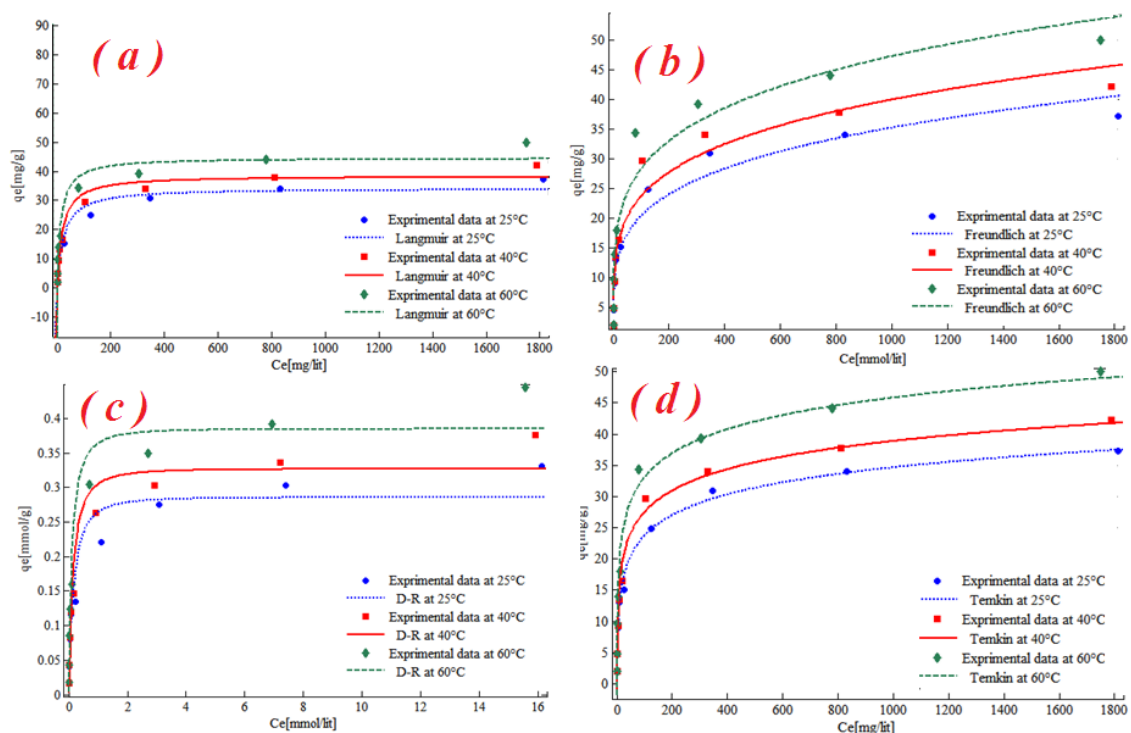*J. Water Environ. Nanotechnol., 3(2): 150-156 Spring 2018*

Fig. 5: the sorption isotherms of (a-d) Cd(II), at different temperatures on modified zeolite.

Table 2. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) constants and correlation coefficients of isotherm models at different temperature

Isotherms		298 K	313 K	333 K
Langmuir	q_m (mg/g)	34.12	38.42	44.75
	K_L (L/mg)	0.04413	0.05381	0.07515
	R^2	0.9881	0.9902	0.9869
Freundlich	K_F (mg/g)	6.872	8.383	10.21
	n	0.2366	0.226	0.2219
	R^2	0.9506	0.9511	0.9449
D–R	q_{max} (mmol/g)	0.286	0.3271	0.3849
	B_{DR} (mol^2/J^2)	2.62E-08	2.13E-08	1.50E-08
	E_a (KJ/mol)	4.367	4.839	5.779
	R^2	0.9293	0.9447	0.9592
Temkin	b_T (J/mol)	525.4	532	502.1
	K_T (L/mg)	1.549	2.814	4.057
	R^2	0.9748	0.9815	0.9889

However, the Freundlich isotherms are important because they do not assume a homogeneous surface [27]. The Freundlich constant, K_F, which is related to the adsorption capacity, increased with temperature, indicating that the adsorption process is endothermic [27].

CONCLUSION

Natural clinoptilolite was modified by Cobalt Hexacyanoferrate nanoparticles and the characterized using, FTIR and SEM techniques. The

SEM image of the modified zeoilite confirms the presence of particles with the average size of about 50 nm on zeolite structure. The modified zeolite used as adsorbent material for the adsorption of cadmium ions from aqueous solutions. The anchoring CoHCF nanoparticles into zeolite structure improved the sorption capacity for Cd(II) ions and the maximum adsorption capacity of 51 mg/g was achieved which it was nearly two time greater than adsorption capacity of non-modified zeolite. The adsorption isotherm was

in good agreement with Langmuir model. The influence of parameters such as shaking time, initial concentration and temperature were tested to evaluate the zeolite material characteristics.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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156

J. Water Environ. Nanotechnol., 3(2): 150-156 Spring 2018