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A kinetic and thermodynamic study of Cd(II) removal by hexylamine-clinoptilolite nanoparticles composite

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ABSTRACT

Natural clinoptilolite tuff was pre-treated and changed to micro (MCP) and nano (NCP) particles by mechanical method. Modification of MCP and NCP particles and also their Cd-exchanged forms was done by alcoholic-aquatic Hexylamine (HA) solution. The raw and modified samples were characterized by XRD, FT-IR, SEM, TEM, BET and TG. Removal of Cd(II) by the modified and unmodified samples confirmed that NCP-HA sorbent is better sorbent with respect to MCP, NCP-HA, MCP-HA, NCP-Cd-HA and MCP-Cd-HA. The modified samples showed good selectivity for cadmium among various investigated multivalent cations. Obeying the adsorption isotherms from Langmuir equation indicates the monolayer sorption of Cd(II) onto the sorbent. Fitting the adsorption kinetic in the pseudo-second-order rate equation indicates that the chemical reaction rate limiting step for the process. The negative ΔH and ΔG indicate an exothermic and spontaneous process. The negative ΔS indicates that during the adsorption of cadmium cations from solution onto the sorbent shows that total entropy of the system was decreased.

Keywords: Clinoptilolite nano-particles; Cd(II) removal; Hexylamine; Adsorption isotherms; Semi- surfactant modified zeolite; Chemical sorption

1. Introduction

Heavy metals enter the aquatic environment mainly by direct discharges from industrial sources and hence they can be bioaccumulated in marine organisms and being conveyed through the food chain to humans [1]. Most heavy metals are toxic and carcinogenic even at very low concentrations and usually cause a serious threat to the environment and public health [1–6]. For example, as a non-essential and non-biodegradable ion, Cd(II) is a well known toxic metal ions which can accumulate in the blood and causes a variety of symptoms such as high blood pressure, kidney damage, and destruction of red blood cells [7]. Due to the low permissible limit for cadmium (10 μg/L) by the World Health Organization (WHO) [8], the removal of cadmium from wastewater is very important from an environmental point of view. So far, different methods and techniques including: filtration, ion exchange, reverse osmosis, solvent extraction etc. have been used/developed for Cd(II) removal and other heavy metals from aqueous solutions [9–17]. Most of them have disadvantages such as: needing to expensive equipment and monitoring systems, high reagent, energy and generation of toxic sludge or other waste products [18]. Among all, adsorption is a promising process, because it is a simple, economic and suitable operation method, and it is significant to exploit simple, novel and high efficient adsorbents for this approach [19–22]. Among the adsorbents, ion exchange usingnatural exchangers especially zeolites is being considered due to low cost, natural inherent, material availability and environmentally friendly advantages

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[23–26]. When zeolites modify with a bulky cationic surfactant, at higher concentrations of surfactant above its CMC value, a double layer of surfactant can form on the zeolite surface. In this case due to the occurring a charge reversal from negative to positive on the modified zeolite surface, the produced surfactant modified zeolite (SMZ) can efficiently adsorb anionic species [27–30]. It has reported that in SMZs, the entrance of pores of zeolite may be blocked by loaded surfactant molecules, causing a decrease in ion exchange capacity [31,32]. This cannot be count as a disadvantage for the resulted SMZs, because more of SMZs have anion exchange property and cannot exchange cationic species. In addition, SMZs can adsorb organic species via hydrophobic interactions with hydrocarbonic chains of the loaded surfactants.

In this work, modified clinoptilolite nanoparticles by hexylamine were used for the removal of Cd(II) from aqueous solutions. As mentioned above, SMZs have an anionic adsorption property and we expected that the resulted adsorbent in this work (NCP-HA) can adsorb anionic compounds similar to SMZs. Preliminary experiments confirmed that the resulted adsorbent can remove cationic species better than the anionic one. Also, modified sample showed better activity than the raw NCP for removal of some tested heavy metals. This confirms that in addition of ion-exchange capacity of the parent zeolite, the amine head groups of HA can complex such heavy metals and removed them further from aqueous solution. On the other hand, in the proposed sorbent a bi-layer of hexylamine was formed on the zeolite surface but with cation exchange property (in opposite of SMZs property) which of mechanism will illustrate in next sections. This sorbent was used for the removal of some heavy metal cations including: Cd(II), Co(II), Pb(II), Ni(II), Mn(II), Zn(II), Al(III), Hg(II) and Cu(II) and the best efficiency of the proposed sorbent was observed in the removal of Cd(II).

2. Experimental

2.1. Materials and solutions

An Iranian natural Clinoptilolite tuffs (belong to the Semnan region in the north-east of Iran), were obtained from Afrandtooska Co. (Isfahan, Iran). Analytical grade Hexylamine ($C_6H_{15}N$) and other analytical grade chemicals were obtained from Merck Company. All solutions were prepared in distilled water. The standard solutions of Cd(II) ions were prepared by dissolving reagent grade $Cd(NO_3)_2{\cdot}4H_2O$ with water to the desired concentrations. In batch experiments, the optimum pH of the solution was adjusted to 5.0 by addition of 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCl solution or much diluter solutions for much precise pH adjustment.

2.2. Pre-treatment and modification of clinoptilolite

The micronized clinoptilolite particles (MCP) were obtained by crushing natural Clinoptilolite (CP) clogs in an agate mortar and sieving in analytical sieves, for separating the particles with mesh –350/+400. The obtained powder was converted to clinoptilolite nanoparticles (NCP) by mechanical ball-mill method. A dry milling process at the milling duration of 6 h, speed of 600 rpm and balls-to-powder ratio of 4 was used for preparation of NCP.

To remove any water soluble and also the magnetic impurities, the NCP powder was suspended in water and heated at 70°C on a magnetic stirrer for 8 h. The suspension was centrifuged (>13,000 rpm for 15 min) and the solid material was re-suspended in water and the previous step was repeated again for better removal of the mentioned impurities. Finally, the solid material was separated by centrifugation and air dried.

To prepare the modified samples some experiments were done as follows: 2.5 g of MCP or NCP powder was added to 50 mL of 0.1 mol L^{-1} hexylamine (prepared in water/ethanol, 90/10 v/v), agitated at room temperature for 24 h. Finally, the suspensions were centrifuged (>13,000 rpm for 15 min) and the resulted solid modifiers were re-suspended in water for removing and adsorbed species and finally the suspension was centrifuged. This was done in duplicates for complete removing of adsorbed materials. Finally, the modified sample was dried at room temperature. Resulted modified materials were assigned as: NCP-HA and MCP-HA. When these modifiers were suspended in Cd(II) solutions for adsorbing Cd(II) cations,they were assigned as: NCP-HA-Cd and MCP-HA-Cd, respectively.

Other modifiers were prepared after preparation of Cd(II)-exchanged clinoptilolite. In these modifiers, first NCP or MCP were ion exchanged in Cd(II) solutions and their ion exchange sites were occupied by Cd(II) cations. The resulted Cd(II)-NCP or Cd(II)-MCP were then modified by HA. The process is illustrated below 0.3 g of NCP or MCP powder was added to 50 mL 2000 mg L^{-1} Cd^{2+} solution and the resulted suspensions were shaken at room temperature for 24 h. Resulted ion-exchanged materials (Cd(II)-NCP or Cd(II)-MCP) were centrifuged (>13,000 rpm for 15 min) and re-suspended in water and shaken for 20 min to separate any adsorbed species. Finally the suspensions were centrifuged (>13,000 rpm for 15 min) and resulted solid materials were dried at room temperature. The obtained samples were assigned as: NCP-Cd and MCP-Cd. Modification of these samples with hexylamine was performed by the above mentioned method used for the modification of the raw NCP and MCP. The resulting materials were assigned as: NCP-Cd-HA and MCP-Cd-HA. When these modifiers were suspended in Cd(II) solutions for adsorbing Cd(II) cations, they were assigned as: NCP-Cd-HA-Cd and MCP-Cd-HA-Cd, respectively. Difference between NCP-Cd-HA-Cd and NCP-HA (and also between MCP-Cd-HA-Cd and MCP-HA) is illustrated in section 3.2.1.

To study the effect of pH of HA solution on the modification of NCP, 0.3 g of NCP powder was dispersed in 10 mL 0.1 mol L^{-1} HA solutions with different pHs covering the range from 2 to 12.5 and the resulted suspension were shaken at 150 rpm for 24 h. Finally, the suspensions were centrifuged at >13,000 rpm for 15 min.

The effect of several interfering cations (Zn(II), Mn(II), Pb(II), Co(II), Al(III), Ni(II) and Cu(II)) was tested in the ability of NCP-HA towards Cd(II). For this goal, suspensions of 1.3 g L^{-1} of the adsorbent containing 1000 mg L^{-1} Cd(II) and different concentrations of the other competitor cations varied as: 0.0, 50, 100, 250, 500 and 1000 mg L^{-1} were shaken at 5 h and 298 K. Finally, the suspensions were centrifuged at >13000 rpm and the supernatant was used for the determination of Cd(II) content. The removed Cd(II) was determined by the procedure will illustrate in section 2.4.

2.3. Instruments and characterization methods

Following instruments were used to prepare, characterize and analysis of the samples: Planetary ball-mill (SP4 FaraPajohesh, Iran); an adsorption-desorption technique using Belsorp max instrument (BEL Japan Ins.), Flame Atomic Absorption Spectrometer (AAnalyst 300 PerkinElmer, USA, whit air-acetylene flame and λ = 228.8 nm); a Bruker XRD diffractometer (D8 Advance, with Ni-filtered copper radiation; Kα = 1.5406Å); a Fourier transformation infrared spectra (Nicolet single beam FT-IR; Impact 400D); a Philips XL30 scanning electron microscope (SEM) and Phillips CM10 transmission electron microscope (TEM).

2.4. Removal of Cd^{2+} in batch experiment

For a typical experiment run, 0.1 g of each prepared adsorbent was added to separate 15 mL of Cd(II) solution of a desired concentration in a 100 mL closed polyethylene bottle and the suspension was shaken (250 rpm) for 24 h. At the end of process, the suspension was centrifuged (rpm> 13,000, for 15 min) and the supernatant was used for the determination of its Cd(II) content using an atomic absorption spectrophotometer. The amount of adsorbed metal ions wascalculated by the following equations:

$$q_e = \frac{(C_i - C_e) \times V}{M} \tag{1}$$

$$\text{Removal\%} = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

In these equations, q_e is the amount of Cd(II) adsorbed by adsorbents (mg/g); C_i and C_e are respectively the initial and equilibrium concentration of Cd(II) (mg/L); *M* is mass of the adsorbent in mg and *V* is solution volume (mL). All experiments were performed in triplicate and averaged. All conditions applied to study the effect of experimental variables on the Cd(II) removal by the proposed NCP-HA adsorbent are mentioned in the captions of the corresponding figures.

3. Results and discussion

3.1. Characterization studies

3.1.1. XRD results

The X-ray diffraction (XRD) pattern of the prepared nano particles is shown in Fig. 1A which also reported in our previous work [27]. The characteristic lines located at 2θ values of 9.8°, 11.19°, 13.06°, 17.36°, 19.1°, 26.4°, 30.5° and 32°can be indexed to the clinoptilolite crystalline structure according to JCPDS file No. 39-1383 and also in the literature [33,34]. The following Scherer's equation was used for estimation of average particles size of the powder:

$$D = 0.9\ \lambda/(B \cdot \cos\theta) \tag{3}$$

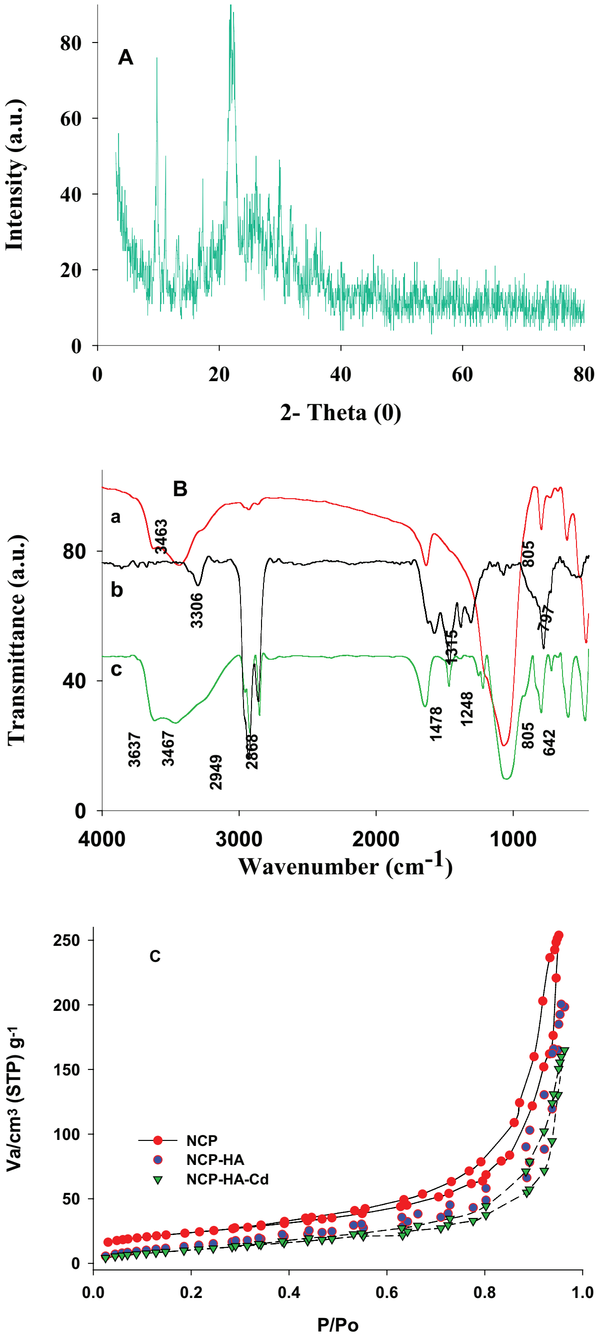

Fig. 1. A) X-ray diffraction pattern of clinoptilolite (Kα Cu = 1.5406 Å, in the 2θ range of 5–60°) [27]; B) FT-IR spectra of NCP (a), hexylamine (b), and NCP-HA (c); C) Typical N_2 adsorption-desorption plots of the raw NCP and its modified samples.

In this equation, D is the crystallite size contribution to the peak width (integral or full width at half maximum) in radians, λ is wavelength of X-ray, B is full width at half maximum and θ is the diffraction angle [35,36]. The average particle size of the prepared powder was estimated in the range between 15 to 72 nm.

The chemical composition of the used clinoptilolite has determined by X-ray florescent (XRF) and the results were reported in our previous work [37]. The chemical composition is: SiO_2: 67.1 ± 0.20, Al_2O_3: 11.7 ± 0.05, Fe_2O_3: 1.51 ± 0.01, CaO: 2.64 ± 0.03, MgO: V, Na_2O: 1.84 ± 0.02, K_2O: 1.93 ± 0.03, L.O.I (Loss on ignition: 12.3 ± 0.07.

3.1.2. FT-IR study

The FTIR spectra of the raw NCP, hexylamine and the prepared NCP-HA are shown in the inset of Fig. 1. In the FTIR spectrum of clinoptilolite, based on the fact that zeolites are significantly hydrated by the discrete water absorption, two bands are present in IR spectrum at 3500 and 1640 cm^{-1}. These bands which centered at 3456 and 1656 cm^{-1} refer to water molecules associated with Na and Ca in the channels and cages of the zeolite structure. As shown, the observed bands at 805, 628 and 480 cm^{-1} are in agreement with IR spectral data reported for the stretching and bending vibration modes of O–Al–O and O–Si–O groups in the zeolite structure [38,39]. The FTIR spectrum of hexylamine shows characteristic peaks at 2949, 2868, 1588, 1315 and 797 cm^{-1} belong to the C-H, C-C and C-N vibration modes. The IR spectrum of NCP-HA shows characteristic peaks at 2868, 1647 and 1247 cm^{-1} (related to C–H, N–H and N–C stretching in hexylamine, respectively), that are absent in the raw NCP spectrum, confirming loading of hexylamine onto the zeolite surface. Although, there are slight shifts in peaks' positions, but spectra of NCP and NCP-HA samples are nearly the same because the main peaks of zeolite are important peaks.

3.1.3. Surface texture study

Surface texture properties of the raw NCP and its modified sample before and after Cd(II) removal were studied by BET technique and the corresponding N_2 adsorption/desorption plots are shown in Fig. 1C. The raw NCP sample had the BET surface area (S_{BET}) of 55.6 $m^2 g^{-1}$, pore volume (V_p) of 0.243 $cm^3 g^{-1}$ and particle diameter (d_p) of 27.9 nm. These values were changed to 52.3 $m^2 g^{-1}$, 0.237 $cm^3 g^{-1}$ and 35.6 nm for the modified NCP-HA sample, respectively. Relatively decrease in surface area is due to loading HA double layer on surface of NCP (see section 3.2.1). Although, HA loading may close some surface pores of NCP and it maybe decrease the surface area, but the formation of porous HA- double layer increased the surface area. In conclusion, surface area is relatively increased. Loading of HA molecules increased also the crystallite size of the modified sample. Loading of Cd(II) cations during the removal process changed S_{BET}, V_p and d_p of the modified sample to 49.5 $m^2 g^{-1}$, 0.203 $cm^3 g^{-1}$ and 36.5 nm for the NCP-HA-Cd sample, respectively.

3.1.4. SEM, TEM studies

The surface morphology of the used NCP (a) and NCP-HA (b) was studied by scanning electron microscope and the SEM pictures are presented in Fig. 2. The crystallites of the raw zeolite have a very well defined spherical grain like crystals. The size of NCP and NCP-HA particles were estimated by Transmission electron microscope (TEM) and the corresponding images are presented in Figs. 2c and d.

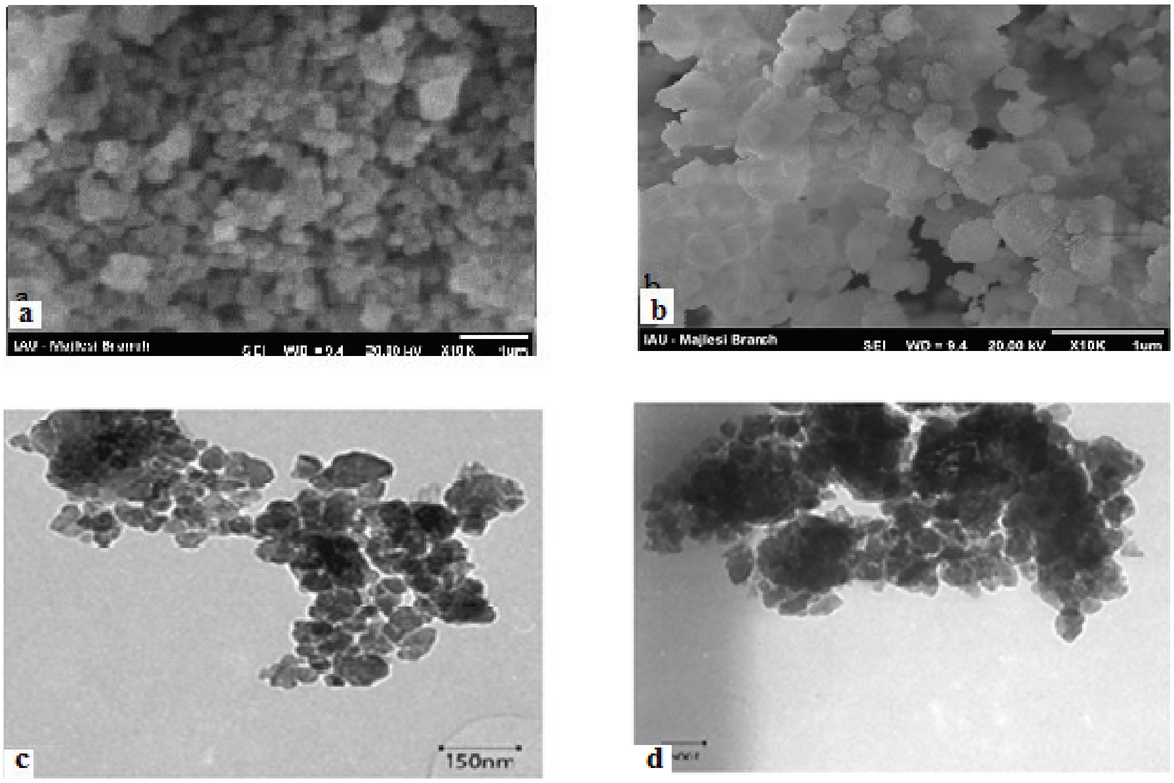

Fig. 2. SEM and TEM images of NCP (a) and NCP-HA (b), SEM and TEM images of NCP (c) and NCP-HA (d) samples.

The average crystallite sizes of the NCP and NCP-HA samples are less than 100 nm.

3.1.5. Thermal analysis results

Thermal behavior of MCP, NCP, MCP-HA and NCP-HA was studied using common thermogravimetric method using platinum crucibles in oven. The mass loss of samples, due to removing the adsorbed water and HA molecules at their boiling points [29,30], was followed during the heating process at 100°C steps in the range of 25 to 700°C. The final mass losses of 10.0 ± 0.2, 12.6 ± 0.1, 18.3 ± 0.1 and 20.4 ± 0.3 were respectively obtained for MCP, NCP, MCP-HA and NCP-HA samples (*n* = 2). The raw and modified NCP samples were undergone much mass losses with respect to the micronized one because NCP, due to its higher effective surface area, can sorb more HA molecules than MCP. Based on the results, about 0.295 ± 0.011 and 0.278 ± 0.009 mmol HA molecules were respectively adsorbed per gram of the modified NCP and MCP. The cation exchange capacity (CEC) and ECEC the used clinoptilolite have determined as 1.370 meq g^{-1} and 0.146 meq g^{-1} in our previous work [29], respectively. The ECEC value of clinoptilolite which was reported in the range of 0.105–0.140 meq g^{-1} [40,41]. The loaded HA onto the NCP particles is about twice greater than the ECEC of the used clinoptilolite, confirming formation of a double layer of HA chains onto the NCP surface.

3.2. Removal experiments

3.2.1. Effect of modification of the zeolite

Potential of the raw NCP and the modified NCP-HA samples prepared in the pH range of 2–12.5 was tested for the removal of some transition metal cations including: Zn(II), Hg(II), Ni(II), Mn(II), Cu(II), Co(II), Pb(II), Cd(II) and Al(III) from aqueous solution which of results are summarized in Table 1. The following trend was obtained in the removing of the tested cations by the modified NCP.

Pb(II) > Cu(II) > Zn(II) > Cd(II) > Hg(II) > Ni(II) > Co(II) > Al(III) > Mn(II)

The obtained trend by the raw NCP can be illustrated by the difference between the bare and hydrated ionic radius of the cations presented in Table 1 by the following trend:

Al(III) (4.8,0.54) > Zn(II) (4.3,0.74) > Cd(II) (4.26,0.97) > Co(II) (4.23,0.79) > Mn(II) (?,0.80) > Cu(II) (4.19,0.73) > Ni(II) (4.04,0.69) > Pb(II) (4.01,1.19) > Hg(II) (4.8,0.54)

The numbers in the parenthesis are respectively the hydrated and bare radius for the mentioned cations in Å [42–45]. The observed selectivity trend has good agreement with literature [43]. It seems that cations with smaller hydrated radius and smaller charge density can loss some water molecules in hydrated sphere easier and enter in the NCP pores. Also, completer fitting of the cations in the NCP cavity causes to greater cation exchange efficiency. Based on the values, the best removal efficiency by the raw NCP was obtained for Pb(II). As the results show, there are significant differences between the removal efficiencies of the raw and modified NCP especially for removal of Cd(II). Hence we prompted that to modelize these observations. By changing the HA concentration, which of results will discuss at follows, the efficiency of the modified NCPs towards Cd(II) removal was changed. These observations confirm that in the modified samples, other phenomenon is responsible for the removal of the cations in addition of ion exchange process. We believed that this phenomenon is a complexation process and the following model, which is schematically shown in Fig. 3, was suggested for the process. Hexylamine can hydrolyze in aquatic media based on the following process, and yields $R\text{-}NH_3^+$ cations.

$R\text{-}NH_2 + H_2O \rightarrow R\text{-}NH_3^+ + OH^-$ ($R = C_6H_{13}$) $pk_b = 3.44$

In this condition, cationic $R\text{-}NH_3^+$ can exchange with cations present on the surface of NCP via an ion exchange process. On the other hand, a monolayer of HA can form onto the NCP (or MCP) during the ion exchange process. At higher concentrations of HA the second layer of HA can adsorb onto the first layer due to the hydrophobic forces between the alkyl chains of HA molecules. On the other hand, the modified samples act as surfactant modified zeolites (SMZ) [27–30] but with cationic adsorption property. In the second layer of the adsorbed HA, neutral $R\text{-}NH_2$ can complex with cationic species in the solution in addition of common ion exchange process. Because of significant difference in the removal efficiencies of the raw and modified NCP samples for Cd(II) removal with respect to other cations studied, Cd(II) was subjected as pollutant in the next experiments and the effects of key operating parameters were optimized. The soft cations such as Pb(II) and Cd(II) give good interactions with the soft nitrogen atoms in HA present on the adsorbent and hence better selectivity could be expected towards these cations. As mentioned above, Cd(II) was selected for the next steps.

3.2.2. Effect of particle size of the zeolite

The effect of particle size of the zeolite on the removal extent of Cd(II) was studied by using the raw and modified samples of both micro and nanoparticles. The results in Table 1 confirm that the raw and modified nano-particles have better efficiencies with respect to micronized one, because decreasing in the particle size caused larger external surface areas available for interaction and also shorter diffusion path lengths which reduces mass transfer resistance during the ion exchange process. As a consequence, more ion exchange sites are available for Cd^{2+} ions. In addition, more hexylamine cations were loaded which causes to higher removal efficiency of NCP-HA than MCP-HA. As shown, both NCP-HA and MCP-HA have more efficiencies than the corresponding raw samples because of simultaneous roles of ion-exchange and complexation processes for removing of Cd(II) cations.

3.2.3. Effect of pH of HA solution and HA concentration on the modification process

Effect of pH of HA solution on the removal of Cd(II) is shown in Fig. 4. As shown, the best removal efficiency was observed at pH 12.5 based on the above mentioned discussion. Similar results were also observed for other cations at pH 12.5 (Table 1). Hence the modified NCP at pH 12.5 was used for next studies. Regarding pK_b value of 3.44 for hydrolysis of HA the ratio of $^+NH_3\text{-}R/NH_2\text{-}R$ is about 31 at pH 12.5. Hence in this pH, there are sufficient $^+NH_3\text{-}R$ cations for occupying the surface ion exchange sites of NCP. In

Table 1
Removal efficiency of different adsorbents for removal of Cd(II), isotherms results and kinetics results

Removal results and ionic radios of the investigated cations

Cations	Cations-removal extent (mmol g^{-1}) by:			Ionic radios (Å)	
	NCP	HA-NCP	Enhanced removal by HA-NCP (%)	Bare	Hydrated
Cd(II)	0.235	0.394	67.70	0.97	4.26
Zn(II)	0.288	0.339	17.80	0.74	4.30
Hg(II)	0.228	0.239	4.80	1.01	–
Pb(II)	0.478	0.500	4.80	1.19	4.01
Ni(II)	0.198	0.204	3.00	0.69	4.04
Cu(II)	0.399	0.404	1.25	0.73	4.19
Al(III)	0.101	0.102	0.99	0.54	4.80
Co(II)	0.178	0.181	1.68	0.72	4.23
Mn(II)	0.018	0.020	1.10	0.80	–

The Cd(II) removal by different sorbents (sorbent dosage: 6.7 g L^{-1}, C_{Cd}: 1000 mg L^{-1})

Sorbent	Removed Cd(II), mmol g^{-1}	Sorbent	Removed Cd(II), mmol g^{-1}
MCP	0.233	NCP	0.242
MCP-HA	0.355	NCP-HA	0.406
MCP-Cd-HA	0.276	NCP-Cd-HA	0.294

The Langmuir and Freundlich results

T (°C)	Langmuir isotherm			Freundlich isotherm		
	$q_{\max}$	b	R^2	n	k	R^2
25	0.540	1.841	0.9905	2.338	0.172	0.8914
30	0.533	0.553	0.9959	2.058	0.125	0.8767
40	0.436	0.566	0.9996	2.099	0.078	0.8739
50	0.368	0.547	0.9966	2.107	0.029	0.8973
60	0.328	0.343	0.9970	2.055	0.018	0.9289

Dubinin–Radushkviech isotherm parameters of Cd(II)

Temperature (K)	β (mol^2 kJ^{-2})	q_m (mmol g^{-1})	R^2	E (kJ mol^{-1})
298	0.245×10^{-8}	0.528	0.949	14.434
303	0.336×10^{-8}	0.481	0.971	12.194
313	0.302×10^{-8}	0.389	0.839	12.856
323	0.373×10^{-8}	0.354	0.942	11.583
333	0.473×10^{-8}	0.277	0.967	10.282

Kinetic properties for Cd(II) removal. (sorbent dosage: 6.7 g L^{-1}, C_{Cd}(II): 1000 mg L^{-1})

Equation	Regression equation	k	R^2
Pseudo first-order	$\log(q_e - q_t) = -0.644-(0.0011 \times t(\text{min}))$	$k_1 = 2.607 \times 10^{-3}$	0.833
Pseudo second-order	$t/q(\text{min}\cdot g^{-1}\ \text{mmol}^{-1}) = 64.938 + 1.4842 \times t(\text{min}))$	$k_2 = 0.0339$	0.998

addition, there are sufficient NH_2-Rmolecules to complete bi-layer of HA molecules onto the NCP surface (see section 3.2.1). Hence, there are sufficient complexation agents on the modified NCP to complex Cd(II) cations for the prepared adsorbent at pH 12.5.

As mentioned above, the removal extent of Cd(II) cations from aqueous solution was a HA-concentration dependent process which of results are shown in the inset of Fig. 4. As shown with increasing in the HA concentration from 0.1 to 0.15 mol L^{-1}, the removed Cd(II) cations was increased and thereafter not considerable change was observed. Hence, 0.15 mol L^{-1} HA was used for the modification of NCP for next experiments. Based on the above discussion, at higher dosages a completer double layer formed onto the NCP sample and due to the available more coordination sites, more Cd(II) can be removed from solution. At the dos-

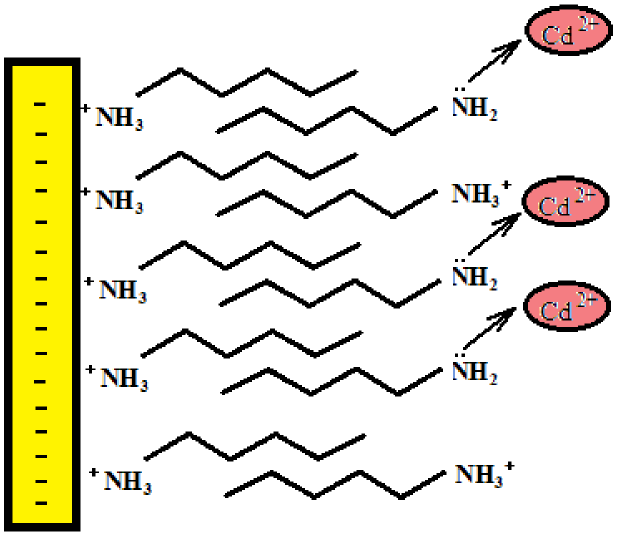

Fig. 3. A model of modification of zeolite surface by hexylamine species for removal of Cd(II).

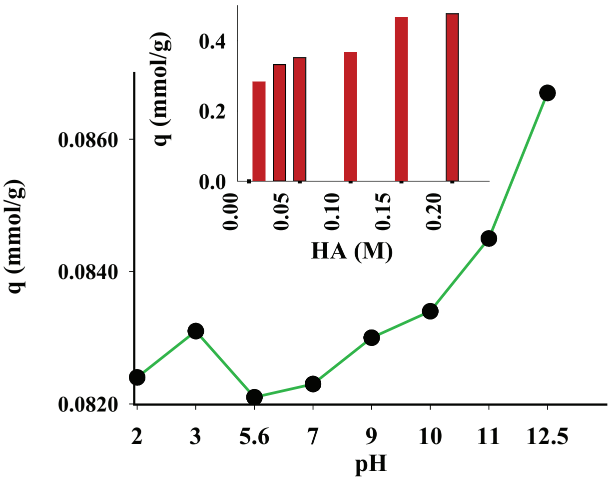

Fig. 4. Effect of pH of HA solutions for preparation of the NCP-HA sorbent for the removal of Cd(II); Inset: effect of hexylamine dose on Cd(II) removal by the NCP-HA adsorbents prepared at pH 12.5 (conditions: $C_{Cd(II)}$: 1000 mg L^{-1}, sorbent dosage: 6.7 g L^{-1}, agitation time: 24 h, pH of Cd(II) solution: 6, T: 298 K).

age of HA above 0.15 mol L^{-1}, its adsorbed molecules may blockages the zeolite pores by excess sorbed hexylamine molecules which reduces the removal extent of cadmium via ion exchange process. Also, in this condition it would be expected that the hydrophilisity of the HA-NCP surface decreases due to high loading of HA. In this case, smaller Cd(II) cations can reach to the surface of the sorbent.

3.2.4. Effect of contact time of Cd(II) solution

Fig. 5A shows the effect of contact time of Cd solution with NCP particles. As shown the removal extent was increased from 30 min to 300 min and thereafter no considerable increase was observed. At the initial times, the removal efficiency of Cd(II) cations was increased rapidly due to the abundant availability of active binding sites on the sorbent, and with gradual occupancy of these sites, the sorption became less efficient in the later stages [41]. Hence a contact time of 300 min was used for next studies.

3.2.5. Effect of pH of Cd(II)solution

Presence of hydrogen ion in solution is an important parameter that influences the adsorption behavior of metal ions because it affects the solubility of the metallic ions in the solution, competes with cationic species to occupy the active sites in the used adsorbent, and affects the degree of ionization of the adsorbate during the reaction [42]. The effect of the initial pH on the sorption of Cd(II) ions onto the NCP-HA was evaluated within the pH range of 2–12 (Fig. 5B). At strong acidic pHs, protons can significantly compete with Cd(II) cations to occupy the active sites of the sorbent resulting to smaller Cd(II) removed cations. Hence, by increasing the pH this competition was decreased and the removal extent of Cd(II) was increased until pH 8.8. Based on the inset of Fig. 5B, pH_{PZC} of the sorbent is about 8.4. The surface of the sorbent is positively charged before this pH which can led to reach lesser Cd(II) cations near the sorbent because of the repulsive forces between the positive charges of Cd(II) and the surface of the sorbent. Based on the solubility product constant for $Cd(OH)_2$ (pK_{sp} = 14.14) and the used Cd(II) concentration (1000 mg L^{-1}), cadmium cations can precipitate at pH 9.5. Hence, at higher pHs, precipitation of Cd(II) as hydroxide can cause to removing more Cd(II) cations from the solution [43,44]. To have a net removal extent of Cd(II) via ion exchange and complexation processes (or eliminate the Cd(II) removal by precipitation process), removal extent of the blank solutions without NCP-HA at each pH was determined and subtracted from total removal extent in the presence of the sorbent. The obtained results are shown in the inset (b) of Fig. 5B which shows that at pH 8.8 the removal extent of Cd(II) via ion exchange and complexation processes was decreased. At higher pHs due to precipitation of Cd(II) its concentration in solution was decreased which have a negative role on the Cd(II) removal by the sorbent during ion exchange and complexation processes.

3.2.6. Effect of initial concentration of Cd(II) solution

As Fig. 5C shows, the amount of sorbed Cd(II) ions was increased with the increasing in initial Cd(II) concentration from 10 to 1000 mg L^{-1} and thereafter decreased, because of saturation of active sites. Also, higher initial sorbate concentration (until 1000 mg L^{-1}) may provide higher driving force to overcome all mass transfer resistances of the metal ions from water to the solid phase resulting in higher probability of collision between Cd(II) ions and active sites present in the NCP-HA adsorbent [45]. Our results are consistent with the previous reports on the effects of initial sorbate concentration [46,47]. Beyond 1000 mg L^{-1} of Cd(II) saturation of the active sites of the sorbent and also increasing in the mass transfer resistances led to reach a constant removal extent for Cd(II) cations. In addition, at high concentrations about 5000 mg L^{-1} of Cd(II), ionic strength of solution tends

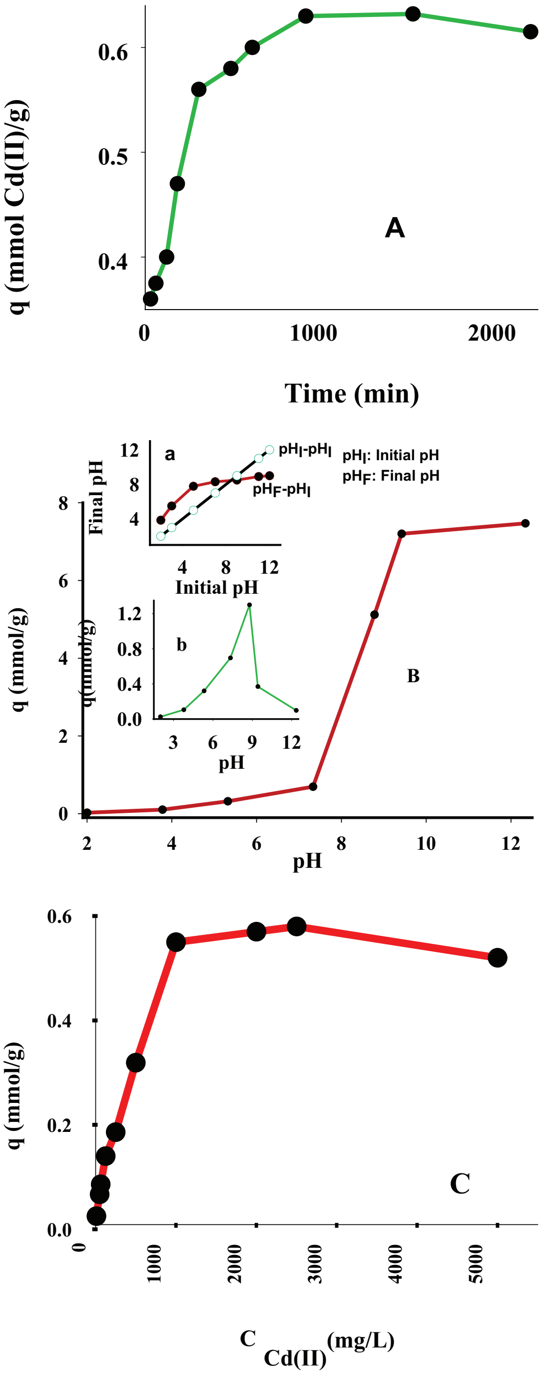

Fig. 5. (A) Effect of agitation time on Cd(II) removal by NCP-HA (conditions: agitation time: 30–2160 min, $C_{Cd(II)}$: 1000 mg L^{-1}, sorbent dosage: 6.7 g L^{-1} T: 298 K); (B) Effect of pH of Cd(II) solution on Cd(II) removal by NCP-HA (conditions: initial pH: 2–12.5, $C_{Cd(II)}$: 1000 mg L^{-1}, sorbent dosage: 1.3 g L^{-1}, agitation time: 5 h, T: 298 K), all compared with Cd(II) solution at initial natural pH 6.5. Insets: a) Typical plots for the determination of pH_{PZC} of NCP-HA (conditions: C_{NaCl}: 0.01 mol L^{-1}, sorbent dosage: 1.3 g L^{-1}, initial pH: 2–12, T: 298 K, agitation time: 24 h); (b) Effect of pH of Cd(II) solutions on Cd(II) removal, the results obtained in curve (B) compared with the corresponding blank Cd(II) solution with the same pH; C) Effect of initial concentration on Cd(II) removal by NCP-HA (conditions: $C_{Cd(II)}$: 10–5000 mg L^{-1}, sorbent dosage: 6.7 g L^{-1}, agitation time: 5 h, T: 298 K).

to increase and hence activity of Cd(II) cations decreases. This causes to relatively decrease in the Cd(II) removal at such high concentrations.

3.2.7. Isotherm models

Some isotherm models including Langmuir, Freundlich and Dubinin-Radushkevish (D-R) were used to describe the experimental data. The linearized form of D-R isotherm model can be written as [48]:

$$\ln(q_e) = \ln(q_{max}) - K_D[\mathrm{RT}\ln(1 + [1/C_e])]^2 \quad (4)$$

where C_e (mol L^{-1}) is the equilibrium concentration of Cd(II) in solution. The q_e and q_{max} (mol g^{-1}) terms are respectively the equilibrium and maximum adsorption capacity of the sorbent (mol g^{-1}). While R (8.314 J mol^{-1} K^{-1}) and T (K) have their common meanings, K_D (mol^2 kJ^{-2}) is the D-R isotherm constant relates to the free energy of adsorption. The D–R isotherm can also be written in the following form [49]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (5)$$

where β *is* a constant relates to the sorption energy (mol^2 kJ^{-2}); and ε is the Polanyi potential = $RT\ln(1 + 1/C_e)$.

The free energy of sorption can be calculated by the following equation:

$$E = (-2\beta)^{-1/2} \quad (6)$$

The reaction mechanism can be distinguished from the magnitude of *E*, so in ion exchange and chemical reactions *E* locates in the range of 8–16 kJ mol^{-1} while in physical sorption mechanism $E < 8.0$ kJ mol^{-1} [50]. The D–R plots of ln q_e versus ε^2 at different temperatures are given in Fig. 6A. The D–R parameters are presented in Table 1. The values of the mean free energy, *E*, of sorption in all cases are located in the range of 8–16 kJ mol^{-1}, confirm that chemical reactions are responsible for the removing of Cd(II) by the proposed sorbent.

The adsorption isotherms could also be explained by the Langmuir and Freundlich models. The Langmuir and Freundlich equations are respectively shown by Eqs. (7) and (8):

$$C_e/q_e = [1/(q_{max} \times b)] + C_e/q_{max} \quad (7)$$

$$\log q_e = \log K_F + (1/n)\log C_e \quad (8)$$

In theses equations, q_e and q_m are the equilibrium and maximum adsorption capacity of the adsorbent (mg g^{-1}), respectively; C_e, the equilibrium ions concentration in solution (mg L^{-1}); K_L and K_f are respectively the Langmuir and Freundlich adsorption constants (L mg^{-1}) and *n* is the heterogeneity factor [51]. The corresponding adsorption isotherms are shown in Fig. 6B. The adsorption isotherms data are summarized in Table 1. The results confirm that the removal process can be well fitted by Langmuir isotherm. This confirms that a monolayer adsorption was done for Cd(II) adsorbed on the NCP-HA surface. The monolayer is

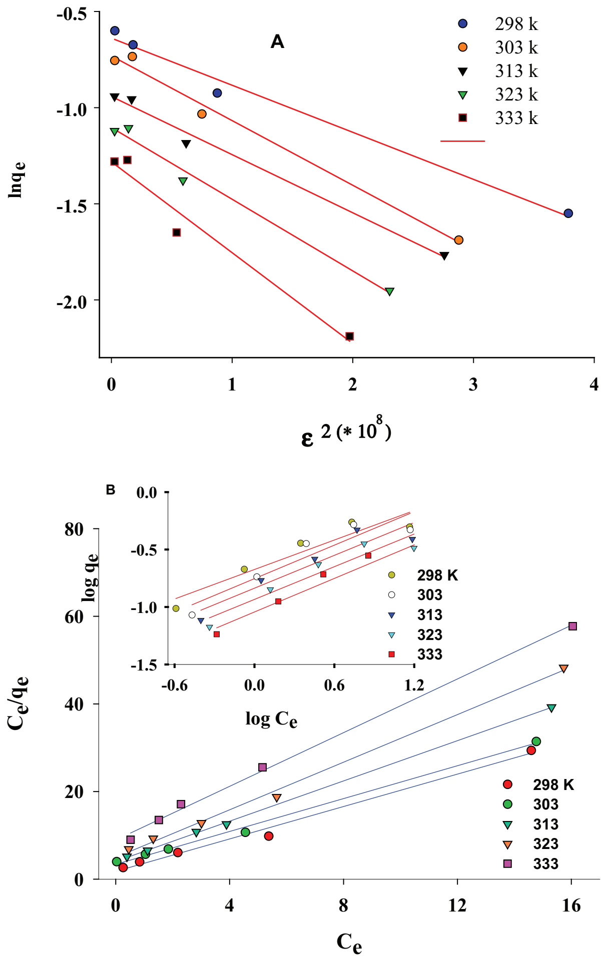

Fig. 6.Dubinin-Radushkevish (A), Langmuir (B) and Freundlich (inset B) isotherms for Cd(II) removal by NSMZ-DTZ, (conditions: sorbent dosage: 1.3 g L^{-1}, agitation time: 5 h).

Table 2
Thermodynamics and regeneration results

Thermodynamic parameters for Cd(II) ion removal					
C_i (mg L^{-1})	T (°K)	lnK_d	ΔG (kJ mol^{-1})	Δ*H* (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
100	298	5.944	–14.440	–26.840	–41.610
	303	5.534	–14.232		
	313	5.278	–13.816		
	323	4.991	–13.400		
	333	4.724	–12.984		
250	298	5.538	–13.569	–26.739	–44.195
	303	5.168	–13.348		
	313	5.026	–12.906		
	323	4.677	–12.464		
	333	4.306	–12.022		
500	298	5.104	–12.525	–23.519	–36.894
	303	4.874	–12.340		
	313	4.527	–11.971		
	323	4.358	–11.602		
	333	4.067	–11.233		
1000	298	4.623	–11.629	–22.857	–37.678
	303	4.541	–11.440		
	313	3.379	–11.064		
	323	3.977	–10.689		
	333	3.668	–10.310		
2000	298	3.527	–8.891	–16.398	–25.527
	303	3.459	–8.663		
	313	3.327	–8.408		
	323	3.030	–8.153		
	333	2.850	–7.897		

due to chemisorptions of Cd(II) cations via ion exchange and complexation between Cd(II) and NH_2 on NCP-HA sorbent.

3.2.8. Kinetic models

Kinetics of adsorption data was analyzed using different kinetic models, such as pseudo-first order and pseudo-second order [21,51] which expressed in the following equations:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \tag{9}$$

$$t/q_t = 1/(k_2 \times q_e^2) + (1/q_e)t \tag{10}$$

where q_e and q_t are amounts of cadmium adsorbed (mg g^{-1}) at equilibrium and at time (t) (min), respectively, k_1 and k_2 are respectively the rate constants of pseudo-first adsorption (min^{-1}) and pseudo-second adsorption processes (g mg^{-1} min^{-1}), which can be obtained from the slope of log ($q_e - q_t$) vs t and t/q vs t plots, respectively [30]. Based on Fig. 7A and the corresponding kinetics data in Table 1, the plot of t/q *vs* t will gives a straight line if the experimental data conform to this kinetic model.

3.2.9. Thermodynamic parameters

Thermodynamic parameters such as standard Gibbs free energy (ΔG), enthalpy (ΔH), and entropy changes (ΔS) for the sorption process can be determined using the following equations [51,52]:

$$\ln K_d = \Delta S/R - \Delta H/RT \tag{11}$$

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

K_d (mL g^{-1}) is distribution coefficient which can be obtained by the following equation (V is the volume of the solution (mL) and m is the grams of the adsorbent):

$$K_d = q_e/C_e = [C_i - C_e/C_e]\ (V/m) \tag{13}$$

Corresponding curves are shown in Fig. 7B and the resulted thermodynamic data are summarized in Table 2. The negative ΔH_{ads} values indicate the exothermic

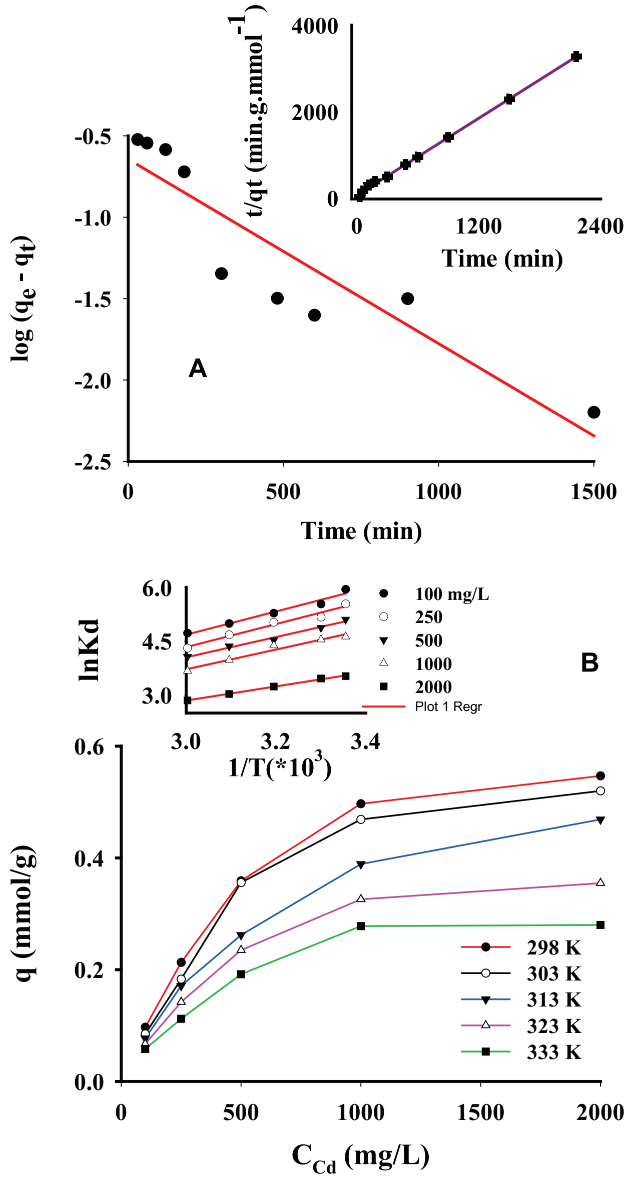

Fig. 7. A) Linearized first-order rate equation plots for Cd(II) removal by NCP-HA; Inset: linearized second-order rate equation plots for Cd(II) removal by NCP-HA (conditions: $C_{Cd(II)}$: 1000 mg L^{-1}, sorbent dosage: 6.7 g L^{-1}, T: 298 K); B) Effect of temperature on Cd(II) removal by NCP-HA (conditions: 100 mg L^{-1}, sorbent dosage: 1.3 g L^{-1}, agitation time: 5 h); Inset: Plot of lnK_d vs. 1/T (K) for calculation of thermodynamic parameters (conditions: $C_{Cd(II)}$: 2000, 1000 and 100 mg L^{-1}, T: 298, 313 and 333 K, sorbent dosage: 1.3 g L^{-1}, agitation time: 5 h).

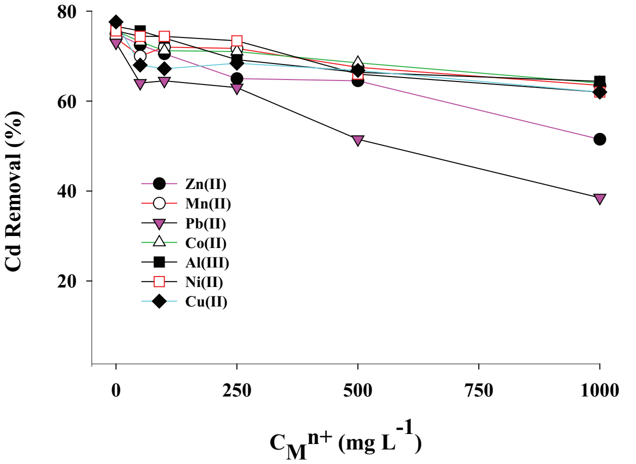

Fig. 8. Effect of different concentration of other cations in removal of Cd(II)($C_{Cd(II)}$: 1000 mg L^{-1}, C(Zn(II), Mn(II), Pb(II), Co(II), Al(III), Ni(II) and Cu(II)) 50–1000 mg L^{-1}, sorbent: 1.3 g L^{-1}, agitation time: 5 h, T: 298 K).

nature of the adsorption process for the present system. In a net ion exchange process in the raw NCP, Cd(II) cations present in solution can replace with a divalent ions (Ca^{2+}) or two mono valent ions (K^+ or Na^+) in the NCP ion exchange sites. In general, if more cations enter to the solution during the ion exchange process theΔS should increase. In contrast, if number of Cd(II) cations entered to the zeolite and cations exited from the zeolite to be equal, change in ΔS of the system should be negligible. Negative ΔS in the presence of the modified sorbent indicates that adsorption of Cd(II) ions occurs with low amount ion replacement and complex formation is dominant process with respect to ion exchange. By complexation of Cd(II) onto sorbent, entropy of the system tend to decrease.

3.2.10. Adsorption of Cd^{2+} in binary-ion systems

As shown in Fig. 8 presence and also increasing in the concentration of the interfering cations led to decreasing in the removed Cd(II) cations because of their competition with Cd(II) to occupy the active sites of the sorbent. Higher concentrations of Pb(II) and Zn(II) showed the higher interfering effects. Among the tested cations Mn(II) had lower interfering effect in the Cd(II) removal. In general, soft metal cations such as Pb(II) and Zn(II) much interfere in Cd(II) removal due to stronger interaction with soft nitrogen atoms of ligand, while harder cations such as Mn(II) have little affinity for the ligand and hence show lower interference on the Cd(II) removal.

3.2.11. Reusing experiments

For testing the ability of the proposed adsorbent for Cd(II) removal during successive runs, the used adsorbents were suspended in 0.1 mol L^{-1} HNO_3 or KNO_3 solution in separate bottles and shaken for 1 h. The recovered adsorbents (after washing and drying) were used again for Cd(II) removal at the optimized conditions. The results showed that the reused catalyst in HNO_3 solution retained 97% of its initial activity after the first reusing run that decreased to 89% after 4th successive runs, while for the reused adsorbent in KNO_3 solution the values are 92% and 86%, respectively. On the other hand, both protons and potassium cations can desorb the Cd(II) cations adsorbed in previous removal runs from surface of the adsorbent and provide new surface for the next runs. The results confirm reasonable stability and hence applicability of the adsorbent in successive removal runs.

4. Conclusions

Based on the results, we concluded that the modified clinoptilolite nano-particles with hexylamine forms a semi-surfactant modified zeolite with cationic adsorption property. The modified NCP-HA showed the best removal efficiency for removing Cd(II) cations from aqueous solution with respect to other used cations. NCP-HA acted as both ion-exchanger and complexation agents during removal process while NCP acted only as an ion-exchanger agent. The adsorption process obeyed from Langmuir isotherm, confirming monolayer adsorption of Cd(II) adsorbed on the NCP-HA surface. The monolayer sorption relates to chemisorptions of Cd(II) cations via ion exchange and complexation between Cd(II) and NH_2 on NCP-HA sorbent. The second-order rate kinetics equation model can effectively described the sorption data. Thermodynamic studies indicate the sorption is an exothermic and spontaneous process.

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