Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.771285

51 (2013) 7172–7180
November

Taylor & Francis
Taylor & Francis Group

Removal of Nickel (II) from aqueous solutions with polypyrrole modified clinoptilolite: kinetic and isotherm studies

Ali Olad*, Shirin Ahmadi, Azam Rashidzadeh

Polymer Composite Research Laboratory, Faculty of Chemistry, Department of Applied Chemistry, University of Tabriz, Tabriz, Iran
Tel. +98 411 3393164; Fax: +98 411 3340191; email: a_oladgz@tabrizu.ac.ir

Received 27 September 2012; Accepted 23 January 2013

ABSTRACT

In this work, natural and modified clinoptilolite as low-cost adsorbents have been used for removal of Ni(II) from aqueous solutions in batch experiments. Modification of clinoptilolite zeolite was done with polymerization of polypyrrole in and outside of zeolite surface. The prepared polypyrrole/clinoptilolite nanocomposite was characterized using FTIR and scanning electronic microscopy techniques. The effect of various factors like solution pH, contact time, and concentration of Ni(II) solution on the removal efficiency was investigated. The optimum conditions for high removal efficiency included adjustment of solution pH value to 4, using nanocomposite for a time period of about 24 h. The adsorption isotherms and kinetic study result showed that the adsorption data were well described by the Freundlich isotherm model and pseudo-second-order reaction kinetics. It was concluded that in the case of nanocomposite, the chelating and ion exchange interactions are the governing adsorption mechanisms. The results of adsorption–desorption cycle experiments indicated that polypyrrole/clinoptilolite nanocomposite can be used as a novel, economic, and efficient adsorbent for Ni(II) ions removal.

Keywords: Clinoptilolite; Polypyrrole; Nanocomposite; Removal; Nickel

1. Introduction

The presence of heavy metals in the wastewater and therefore release of them in the environment has been of great concern because of their high toxicity, non-biodegradable nature, and their tendency to accumulate in organisms, which cause numerous diseases and disorders [1]. Nickel is one of the toxic heavy metals which is found in the wastewaters with high concentration. The acceptable limit of nickel in drinking water is 0.01 $\text{mg}\,\text{l}^{-1}$ and the industrial discharge limit in wastewater is 2 $\text{mg}\,\text{l}^{-1}$ [2]. Therefore, wastewaters containing nickel are required to be treated prior to discharge into the environments. Removal of heavy metal ions can be accomplished by a variety of techniques [3]. Among these methods, adsorption is currently considered to be very simple and cost-effective method [4]. Various materials are generally used as adsorbents among which zeolites have been widely used to adsorb high amount of heavy metals [5]. Besides that, zeolites have a net negative structural charge which makes them suitable for ion exchange process and selective for certain cations. This property makes zeolites of interest for use in the treatment of

---

*Corresponding author.

nuclear, municipal, and industrial wastewaters. Panneerselvam and coworkers [6] studied removal of Ni(II) from aqueous solutions with modified synthetic ZSM-5 zeolites. It was concluded that phosphoric acid modified ZSM-5 zeolite can be a better adsorbent than the parent zeolite. Clinoptilolite (CL) as one of the natural zeolites, due to its large surface area, high cation exchange capacity (CEC), physicochemical stability, and low cost is one of the important class of materials being considered for adsorption of different species [7]. The structure of zeolite, involving pores, channels, and cages of different shapes and dimensions of the nanometer order of magnitude, as well as high ion exchange capacities, is expected to be an efficient material for removal of heavy metals through two mechanisms of ion exchange and adsorption [8]. In the ion exchange process, substitution of ions present in zeolite crystalline lattice by metal ions from the solution takes place. Rajic and coworkers [9] have used natural CL as adsorbent for removal of Ni(II) ions from aqueous solutions. Also, CL from Caimanes deposit (Moa-Cuba) has been used for the nickel removal from aqueous solution by Rodrıguez–Iznaga and coworkers [10].

But because of low-removal capacity of clinoptilolite, it was suggested to modify it with organic materials like conducting polymers, in order to increase pollutants uptake [11,12]. By exchanging the inorganic cations with organic cations, it is possible to convert a naturally hydrophilic property of zeolite into a hydrophobic and organophilic property [13]. In this regard, the zeolite has been ion exchanged with aniline hydrochloride in aqueous suspension and then oxidized to encapsulate polyaniline in the crystalline channel system of zeolite to form a hybrid nanocomposite [14,15]. The modified clinoptilolite zeolite with polyaniline was used for the removal of Cr(VI) from aqueous solutions by Olad et al. [16].

Conducting polypyrrole (PPY) and its nanocomposites were also investigated for use in removal of heavy metals as an efficient adsorbent [17,18]. Functional amine groups of PPY form strong chemical bonds with metal ions and result in formation of stable complexes [19]. Bein et al. reported the synthesis of various conducting polymers into zeolite pores and investigated their properties [15,20]. The polymerization of pyrrole molecules into the channels of zeolite was also reported [21]. The metallic ions introduced by the ion exchange are used as oxidizing agents for the polymerization reaction [22].

The main aim of present work is to use polypyrrole/clinoptilolite (PPY/CL) nanocomposite prepared in our previous work [23], as an efficient material for removal of Ni(II) from aqueous solutions. The effect of various parameters on the removal efficiency was investigated and optimized. Also, the Ni(II) ion sorption isotherms of natural clinoptilolite and PPY/CL nanocomposite as well as kinetic studies were studied.

2. Experimental

2.1. Reagents and material

Pyrrole (Merck) was purified under vacuum distillation prior to polymerization. Ferric chloride ($FeCl_3$), nickel (II) chloride ($NiCl_2$), ammonium persolfate (APS), hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), methanol, dimethylglyoxime (DMG), and acetone were all purchased from Merck (Germany) and used as received without any further purification. Clinoptilolite (CL) obtained from Meianah mine in East Azerbaijan, Iran. The mineralogical composition of Meianah clinoptilolite obtained from X-ray diffraction of pure clinoptilolite powder has been shown in Table 1. As shown in Table 1, this type of zeolite characterization as clinoptilolite is further supported by the Si/Al ratio, which is equal to 5.4.

The cation exchange capacity of CL which is the capacity to adsorb exchangeable cations was determined by atomic absorption spectrometry. The amount of equilibrium concentrations of exchangeable cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) in the supernatant after saturation of the clinoptilolite samples with NH_4^+ ions was measured. According to the results, the ion exchange capacity of the pure clinoptilolite was about 1.975 meq/g.

2.2. Preparation of PPY/CL nanocomposite

In order to prepare acidic clinoptilolite, the natural zeolite rocks were first hammered to break down them into smaller particles. Then the smaller particles were grinded and magnetically stirred for 48 h in HCl (0.1 M) solution. The slurry was then filtered and washed with excess deionized water until neutral, followed by drying at 150˚C for a period of 2 h. By acidifying the clinoptilolite zeolite, the adhesion of polymer to the zeolite can be increased. PPY/CL nanocomposite preparation was carried out by the polymerization of pyrrole monomer in the presence of the clinoptilolite nanoparticles. Detailed synthesis procedure and also information about Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) spectra, and also surface morphology of prepared nanocomposite can be found in our previous work [23].

Table 1
Chemical composition of Meianah clinoptilolite

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	MnO	TiO_2	L.O.I
(%)	65	12.03	1.5	2.3	0.72	1.8	3	0.01	0.1	0.03	13.51

2.3. Heavy metals removal experiments

Adsorption experiments were done using UV-vis spectrophotometer, Shimadzu (Japan) for determination of Ni(II) in a batch equilibrium technique. The Ni (II) solutions were prepared from $NiCl_2$ in different concentrations that ranged from 10 to 400 ppm by diluting of stock solutions (1,000 ppm). The sample dilution method was used for spectrophotometric determination of higher concentrations. The adsorption of Ni(II) solutions was performed by stirring various amount of nanocomposite powder in 100 ml of Ni (II) solutions with different concentrations. In order to determine the concentration of Ni(II) by spectrophotometry, its complex with DMG was prepared. Ni(II) forms a red complex with organic compound DMG. The complexation of Ni(II) with DMG occurs quantitatively in a solution in which the pH is buffered in the range of 5–9 by use of ammonia solution as illustrated in Fig. 1 [24]. Then after different contact times, the determination of Ni(II) concentration was done spectrophotometrically by measuring absorbance at $\lambda_{\max}$ of 450 nm. The calibration curve for Ni(II) solution was established as a function of Ni(II) concentration. The adsorption capacity was calculated by the following formula:

$$Q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

where Q_e = adsorption capacity or amount of Ni(II) adsorbed by adsorbent ($mg\,g^{-1}$), C_i = initial Ni(II) concentration ($mg\,l^{-1}$), C_e = equilibrium or residual Ni(II) concentration ($mg\,l^{-1}$), V = the volume of the solution (l), and m = mass of adsorbent (g). The removal efficiency of Ni(II) was calculated according to the (Eq. (2))

$$R = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

The influence of initial pH, exposure time, and initial metal ion concentration on metal removal efficiency was investigated. For adsorption isotherms, samples with concentrations ranging from 10 to 400 ppm were agitated till the equilibrium was achieved.

Desorption studies were performed by contacting used adsorbents with HCl (0.1 M) then the desorbed amount of Ni was obtained spectrophotometrically. Desorption ration was calculated using Eq. (3):

$$\text{Desorption ratio} = \frac{C}{C_0} \times 100 \tag{3}$$

where C is the amount of Ni desorbed to the elution medium, C_0 is the amount of Ni adsorbed on the adsorbent. To determine the reusability of the nanocomposite, consecutive adsorption–desorption cycle was repeated five times with the same sample recovered by NaOH (0.1 M) solution.

2.3.1. Effect of pH

In order to investigate the effect of the solution pH on the Ni(II) removal efficiency, solutions with different pH values of 3–6 were prepared by adding 0.1 M

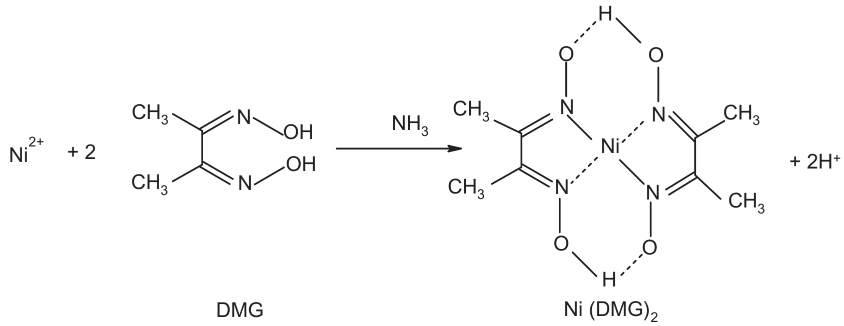

Fig. 1. Chemical structure diagram of bis-(dimethylglyoximato) nickel(II) complex.

HNO_3 and 0.1 M NaOH solutions. The influence of solution pH value on Ni(II) removal was investigated under the following conditions: solution concentrations of 10 $mg\,l^{-1}$, exposure time of 24 h, and adsorbent amount 0.2 g. Then the concentration of Ni(II) was measured spectrophotometrically.

2.3.2. Effect of exposure time

After determination of optimum initial pH values, a series of experiments has been carried out to determine the equilibration period or exposure time for the heavy metal solution adsorbent at an initial metal concentration of 10 $mg\,l^{-1}$ and 0.2 g of adsorbent.

3. Results and discussion

3.1. Removal studies

3.1.1. Effect of pH

It is well known that pH of the aqueous solution is an important controlling parameter in the metal removal process since it can influence both the character of clinoptilolite and formation of polymer. The effect of pH on the adsorption of Ni(II) ions onto both adsorbents is shown in Fig. 2. As is shown, at pH values below 4.0, hydrogen ions compete with the Ni(II) ions for the exchange sites in clinoptilolite and in higher pH values, Ni(II) ions may form complexes with inorganic ligands such as OH^-. Therefore, solution pH of 4 was selected as the optimum pH value since the removal efficiency is high in this pH.

3.1.2. Effect of contact time and kinetics of adsorption

A series of experiments has been carried out to optimize the contact time. The Ni(II) removal efficiency after different contact times was calculated using Eq. (2) and plotted against exposure time in Fig. 3. Results showed that after 7 h (420 min) of exposure, over 87.5% of Ni(II) in the solution has been removed by nanocomposite powder and by increasing the contact time to 24 h (1,440 min), removal efficiency increases to 98.5% and it can be concluded that further increase of contact time does not have significant effect on removal efficiency. Therefore 24 h was chosen as optimum contact time.

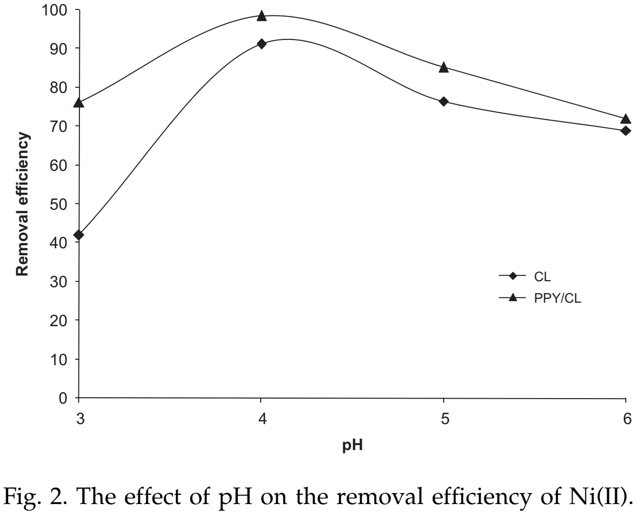

Fig. 2. The effect of pH on the removal efficiency of Ni(II).

In this work, pseudo-first-order equation [25], pseudo-second-order equation [26], and intraparticle diffusion model [27] have been used to describe the adsorption of an Ni(II) from aqueous solutions, which is shown as below.

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t \tag{4}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e}t \tag{5}$$

$$Q_t = k_i t^{1/2} + C \tag{6}$$

where Q_e is the adsorbed metal ion concentration at equilibrium, k_1 is the rate constant of the pseudo-first-order sorption (min^{-1}), and k_2 is the rate constant of the pseudo-second-order kinetics ($g\,mg^{-1}\,min^{-1}$), k_i ($mg\,g^{-1}\,min^{-1/2}$) is the intraparticle diffusion rate constant, and C ($mg\,g^{-1}$) is the constant which is related to the thickness of boundary layer.

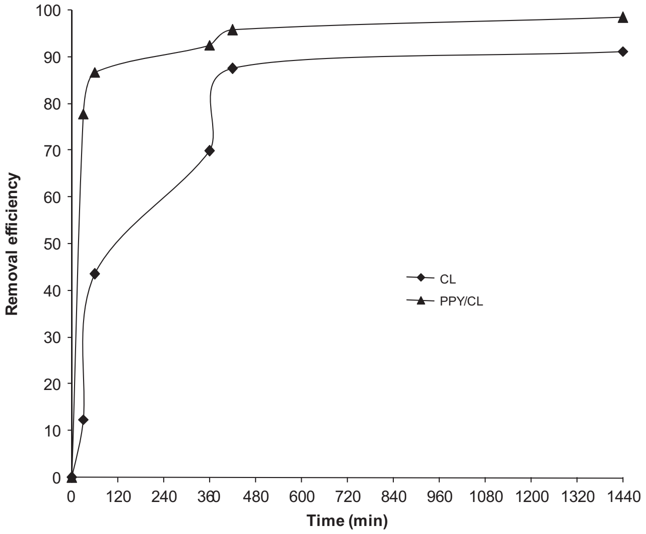

Fig. 3. The effect of contact time on the removal efficiency of Ni(II).

The linear plot of log ($Q_e - Q_t$) against time t and the straight line of t/Q_1 vs. t demonstrates the applicability of the pseudo-first-order and pseudo-second-order kinetic models for adsorption of Ni(II) on adsorbents (Figs. 4 and 5, respectively). The plots of intraparticle diffusion of Ni(II) onto the CL and PPY/CL nanocomposite are illustrated in Fig. 6. The calculated kinetic constants values and the corresponding linear regression correlation constants were given in Table 2. According to the Table 2, kinetic data of Ni (II) sorption on both adsorbents can be more appropriately defined by the pseudo-first-order sorption rate since the correlation coefficient (R^2) values are higher for the pseudo-first-order compared to the pseudo-second-order sorption rate.

The intraparticle diffusion rate constant k_i was calculated from the slope of the second linear section (Fig. 6, Table 2). As the plot is often multilinear for many adsorption systems, it is common to segment it into two or more straight lines and to assume that different adsorption mechanisms control the step represented by each straight line [28]. Referring to PPY/CL adsorbent, two distinct regions are observed (Fig. 6). The first section of plots indicates that boundary layer diffusion probably limited Ni(II) adsorption. The second section shows the occurrence of intraparticle diffusion as the adsorption-limiting step. As shown in Fig. 6, the intraparticle diffusion model presents a nonlinear distribution ($R^2 = 0.76$–0.81) and therefore cannot be considered as a determining step. The deviation of the lines from the origin indicates that the pore diffusion is not the only rate-controlling step. Values of the C give an idea about the thickness of boundary layer, i.e. the larger the intercept is the greater the boundary layer effect. Larger intercept C suggests that surface diffusion has a larger role as the rate-limiting step [29].

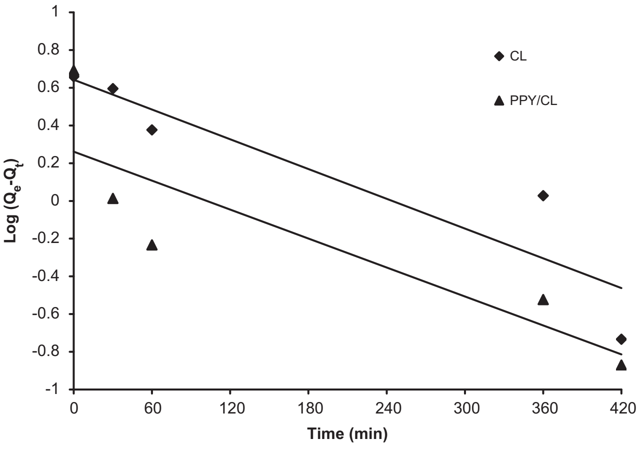

Fig. 4. Pseudo-first-order reaction kinetics for the adsorption of Ni(II).

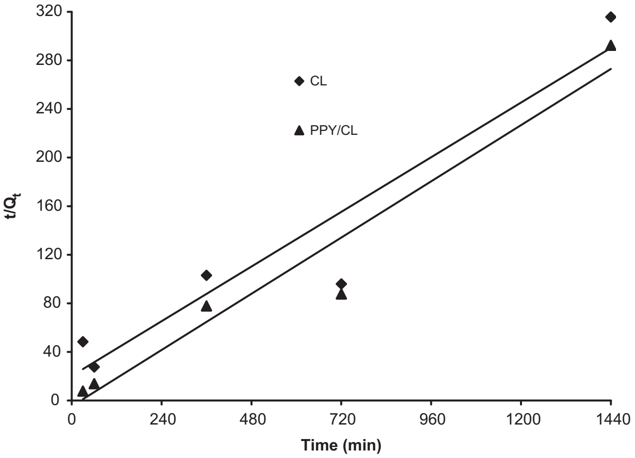

Fig. 5. Pseudo-second-order reaction kinetics for the adsorption of Ni(II).

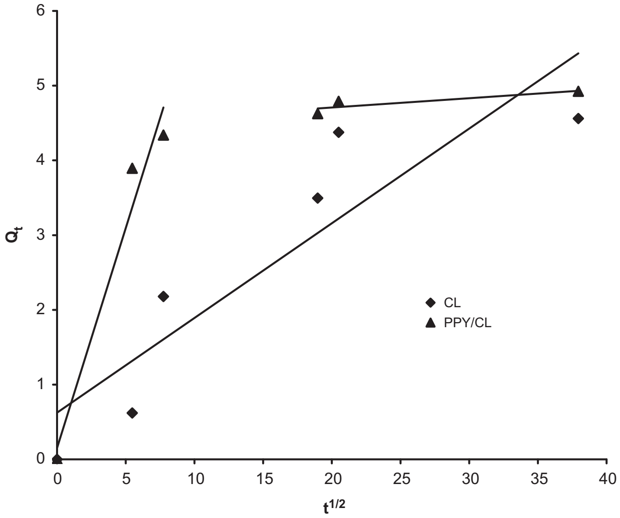

Fig. 6. Intraparticle diffusion model for the adsorption of Ni(II).

3.1.3. Effect of initial concentration of Ni(II)

To investigate the effect of initial concentration of Ni(II) on the removal efficiency of Ni(II) by both adsorbents, 0.2 g of adsorbents powder was allowed to contact for for 24 h with different initial concentrations of Ni(II) (10–400 ppm). As shown in Fig. 7, the removal efficiency decreased by increasing the initial concentration of Ni(II) solution which may be due to the saturation of adsorption sites on the adsorbent surface. However, with increasing initial concentration

Table 2
Parameters of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models for the adsorption of Ni(II)

Adsorbent	Q_e (exp)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
		R^2	Q_e (cal)	k_1	R^2	Q_e (cal)	k_2	R^2	C	K_i
CL	4.56	0.85	4.38	0.0046	0.90	5.35	0.0017	0.81	0.62	0.1267
PPY/CL	4.925	0.75	1.82	0.0046	0.95	5.20	0.0077	0.7624	4.46	0.0124

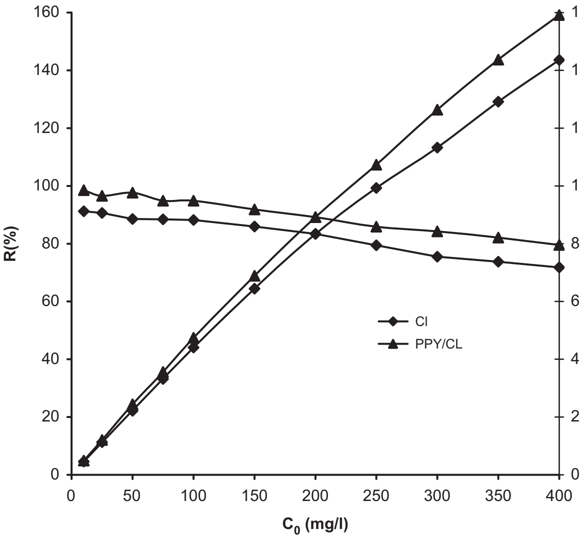

Fig. 7. The effect of initial concentration of Ni(II) on the removal efficiency and adsorption capacity.

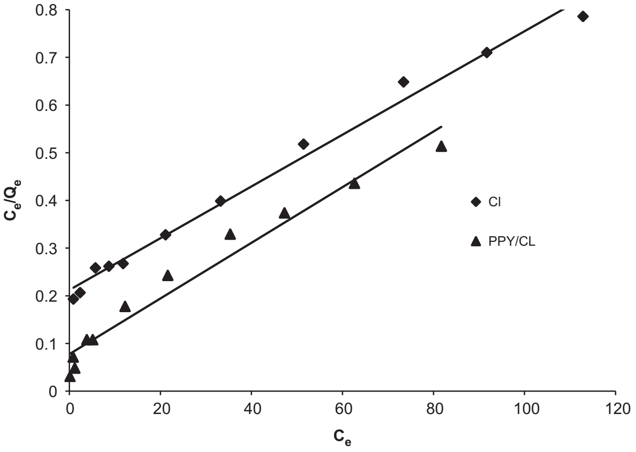

Fig. 8. Linearized form of Langmuir isotherm for the adsorption of Ni(II).

of Ni(II), adsorption capacity increases due to the high driving force for mass at a high initial concentration of Ni(II). In other words, the residual concentration of Ni(II) ions will be higher for higher initial concentrations of Ni(II) ions.

3.1.4. Application of Langmuir and Freundlich models to the equilibrium data

The adsorption isotherms of Ni(II) were simulated by the mathematical equations of Langmuir and Freundlich. The linear form of Langmuir model is represented by the following equation:

$$\frac{C_e}{Q_e} = \left(\frac{1}{Q_{\max}}\right) C_e + \frac{1}{Q_{\max} b} \tag{7}$$

where C_e ($\mathrm{mg\,l^{-1}}$) is the equilibrium concentration, Q_e ($\mathrm{mg g^{-1}}$) is the amount adsorbed at equilibrium, $Q_{\max}$ ($\mathrm{mg\,g^{-1}}$) is the sorption capacity, and b ($\mathrm{l\,mg^{-1}}$) is the Langmuir constant. $Q_{\max}$ and b can be calculated from the slope and intercept of the plot of C_e/Q_e vs. C_e [30]. The linear form of Freundlich equation is expressed as:

$$\log Q_e = \frac{1}{n} \log C_e + \log K_f \tag{8}$$

where K_f ($\mathrm{mg\,g^{-1}}$) and n are the Freundlich constants related to adsorption capacity and adsorption intensity of adsorbents, respectively [31]. The Freundlich constant K_f and n can be calculated from the intercept and slope of plot between log Q_e and log C_e. The

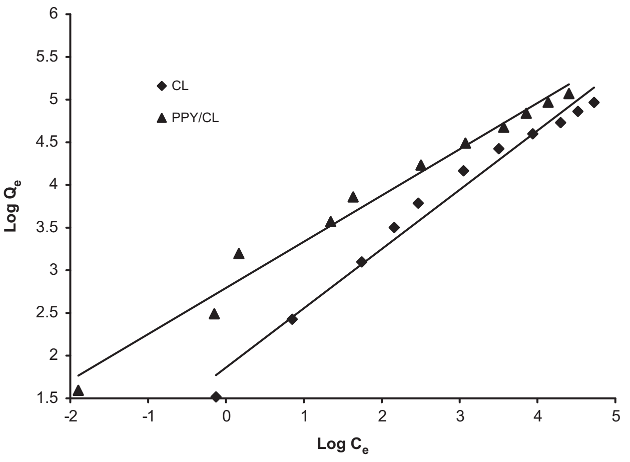

Fig. 9. Linearized form of Freundlich isotherm for the adsorption of Ni(II).

Table 3
Parameters of Langmuir and Freundlich equations for the adsorption of Ni(II) (C_0 10 mg/L, pH 4, contact time 24 h, and adsorbent dosage 0.2 g/L)

Adsorbent	Q_e (exp)	Langmuir equation parameters			Freundlich equation parameters		
		R^2	Q_{max} (mg/g)	b	R^2	n	k_f
CL	143.57	0.9894	185.18	0.025	0.9799	1.44	6.42
PPY/CL	159.12	0.9635	172.41	0.075	0.9806	1.84	16.34

obtained experimental data were fitted with the linearized form of Langmuir and Freundlich models, which are shown in Figs. 8 and 9, respectively. The constants, parameters, and correlation coefficients were calculated and presented in Table 3. As it can be seen from the results, in the case of nanocomposite, the Langmuir model did not fit the experimental data due to lower R^2 value which suggested that heterogeneous and multilayer mode of adsorption was suitable. But in the case of pure clinoptilolite, the Langmuir model matched reasonably well the experimental sorption data since the correlation coefficient value was higher than that of nanocomposite. This good fit to the experimental data suggested that the mode of adsorption of Ni(II) on clinoptilolite adsorbent was homogeneous. As we know the polymerization of PPY inside and outside of clinoptilolite channels forms a multilayer adsorbent which suggests that some heterogeneity in the surface or pores of PPY/CL adsorbent as a result of addition of PPY will play an important role in the adsorption of Ni(II). Moreover, the clinoptilolite adsorbent presented lower K_f (6.42 mg g^{-1}) for Ni(II) ions than the PPY/CL adsorbent (16.34 mg g^{-1}). The K_f value is related to the variation of surface area of the adsorbent [32]. Higher surface area of PPY/CL nanocomposite will generally result in higher adsorption capacity [33]. The value of n, which is higher than 1, indicated that Ni(II) ions are favorably adsorbed by nanocomposite under the experimental conditions.

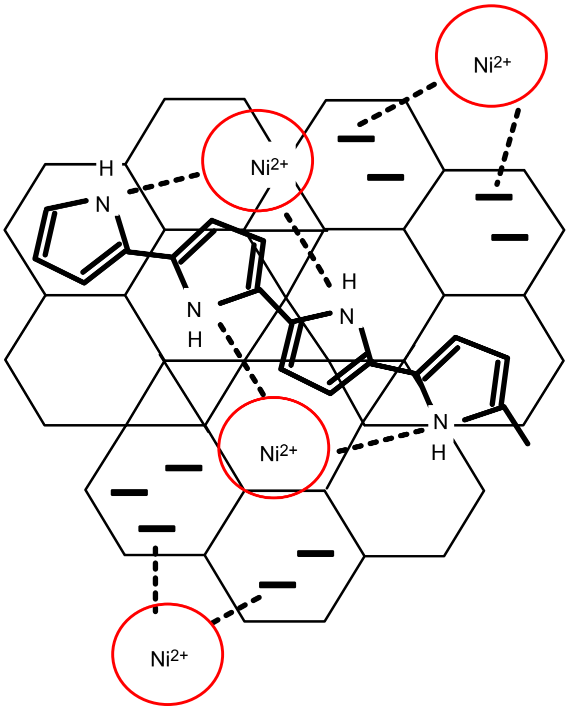

Fig. 10. Schematic illustration of adsorption of Ni(II) ions onto the prepared nanocomposite.

3.2. Mechanism of adsorption

As it was seen from previous sections, the prepared PPY/CL nanocomposite had high removal efficiency to remove Ni(II) from aqueous solutions. This can be related to the adsorbent which composed of PPY and CL which can be serving as adsorbent for Ni(II) individually. As schematically shown in Fig. 10, polymerized polypyrrole inside and outside of clinoptilolite channels, forms coordinate bond via its nitrogen atoms with positive charge of Ni(II) ions. Moreover, clinoptilolite zeolite due to its large surface area, valuable ion exchange capability, and also net negative structural charge is suitable for ion exchange process and formation of electrostatic attraction between Ni(II) and zeolite. Therefore, it can be concluded that the type of interaction between nanocomposite and Ni(II) ions can be described by chelation and ion exchange. As shown in previous section about adsorption isotherms, PPY/CL nanocomposite has higher adsorption capacity, indicating strong electrostatic force of attraction between Ni(II) ions and sorbent binding sites as a result of addition of PPY to CL [33].

3.3. Comparison of adsorption capacity with other similar systems

The maximum adsorption capacities of Ni(II) ions for the adsorbent used in this work were compared

Table 4
Adsorption capacities of different adsorbents for removal of Ni (II)

Adsorbents	Adsorption capacity (mg g^{-1})	Sources
Natural clinoptilolite	3.8–7	[9,34]
Biomass	15.75	[35]
Chitosan hydrogel	50.8	[36]
This work	159.12	-
Chitosan–Poly acrylic acid	435	[37]

with other adsorbents (Table 4). As can be observed, the adsorption capacity of PPY/CL nanocomposite for Ni(II) ions is higher than that of other potential adsorbents such as cliniotilolite [9,34], biomass [35], chitosan hydrogel [36], but it is lower than that of chitosan–polyacrylic acid [37]. According to the results obtained, PPY/CL nanocomposite could be employed as an alternative adsorbent for the removal of Ni(II) .

3.4. Desorption and reusability studies

For practical applications, desorption experiments were performed to regenerate Ni(II) ions loaded nanocomposites. As mentioned, the PPY/CL nanocomposite had high adsorption efficiency for Ni(II) and could adsorb about 98% of the Ni(II) ions. Therefore, the adsorption and desorption processes were repeated to examine the reusability potential of nanocomposite for economical purposes. Fig. 11 shows the adsorption and desorption percentages of Ni(II) ions in five cycles. As shown in Fig. 11, the removal efficiency and desorption ratio decreased per cycle as a result of occupation of some adsorption sites by Ni(II) ions. Moreover, incomplete desorption could be attributed to the formation of very strong complexes between the functional groups of the adsorbent and Ni(II) ions. Nevertheless, the removal efficiency in the fifth cycle showed a little decrease from 98.5 to 91.5%, meaning its high reusability.

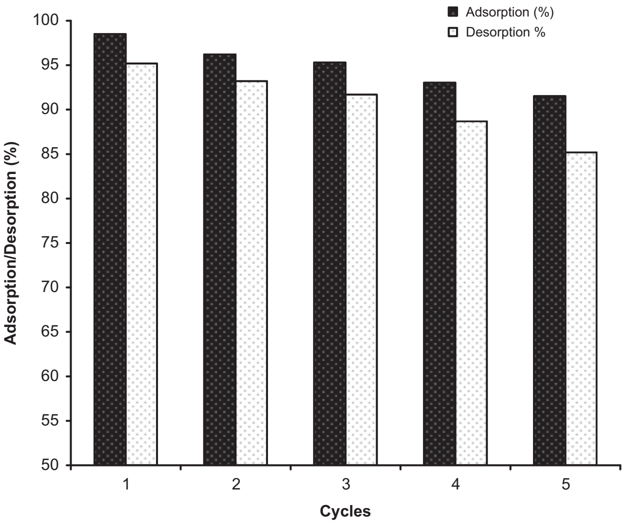

Fig. 11. Adsorption and desorption percentages of Ni (II) ions from PPY/CL nanocomposite in five cycles.

4. Conclusion

Clinoptilolite as a natural zeolite was treated by polypyrrole. Polymerization of pyrrole in the presence of clinoptilolite nanoparticles caused the encapsulation of zeolite surface by polypyrrole chains and also the incorporation of polypyrrole chains in clinoptilolite channels. Removal of Ni(II) by pure clinoptilolite and PPY/CL nanocomposite powders showed the improved removal efficiency of Ni(II) using PPY/CL nanocomposite as adsorbent compared with pristine clinoptilolite. The batch sorption kinetics was tested for pseudo-first-order, pseudo-second-order reaction, and intraparticle diffusion models. The pseudo-second-order kinetic reaction model was found to be the best for the correlation of data for Ni(II) removal from aqueous solution. Also, it was seen that Freundlich isotherm has a better correspondence with the experimental findings rather than with Langmuir. Finally, the adsorption mechanism of nanocomposite is defined by both chelating and ion exchange. In conclusion, the PPY/CL nanocomposite prepared in this work is distinguished by higher adsorption capability, reusability, and stability making it an economical and successful adsorbent to remove toxic Ni (II) ions from solutions.

Acknowledgment

The financial support for this research by the University of Tabriz is gratefully acknowledged.

References

[1] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: A review. J. Hazard. Mater. B 97 (2003) 219–243.
[2] Y.C. Sharma, G. Prasad, D.C. Rupainwar, Removal of Ni(II) from aqueous solutions by sorption, Int. J. Env. Stud. 37 (1991) 183–191.
[3] F. Fenglian, W. Qi, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407–418.
[4] M.A. Hashim, S. Mukhopadhyay, J.N. Sahu, B. Sengupta, Remediation technologies for heavy metal contaminated groundwater, J. Environ. Manage. 92 (2011) 2355–2388.
[5] A. Krobba, D. Nibou, S. Amokrane, H. Mekatel, Adsorption of copper (II) onto molecular sieves NaY, Desalin. Water Treat. 37 (2012) 31–37.

[6] P. Panneerselvam, V. Sathya Selva Bala, N. Thinakaran, P. Baskaralingam, M. Palanichamy, S. Sivanesan, Removal of nickel(II) from aqueous solutions by adsorption with modified ZSM-5 zeolites. Eur. J. Chem. 6 (2009) 729–736.

[7] M.E. Argun, Use of clinoptilolite for the removal of nickel ions from water: Kinetics and thermodynamics, J. Hazard. Mater. 150 (2008) 587–595.

[8] M.K. Doula, A. Dimirkou, Use of an iron-overexchanged clinoptilolite for the removal of Cu^{2+} ions from heavily contaminated drinking water samples, J. Hazard. Mater. 151 (2008) 738–745.

[9] N. Rajic, D. Stojakov, M. Jovanovi, N.Z. Logar, M. Mazaj, V. Kaucic, Removal of nickel(II) ions from aqueous solutions using the natural clinoptilolite and preparation of nano-NiO on the exhausted clinoptilolite, Appl. Surf. Sci. 257 (2010) 1524–1532.

[10] I. Rodrıguez–Iznaga, A. Gomez, G. Rodrıguez–Fuentes, A. Benıtez-Aguilar, J. Serrano-Ballan, Natural clinoptilolite as an exchanger of Ni^{2+} and NH_4^+ ions under hydrothermal conditions and high ammonia concentration, Micropor. Mesopor. Mat. 53 (2002) 71–80.

[11] B. Armagan, O. Ozdemir, M. Turan, M.S. Celik, The removal of reactive azo dyes by natural and modified zeolites, J. Chem. Technol. Biotechnol. 78 (2003) 725–732.

[12] M. Arora, N.K. Eddy, K.A. Mumford, Y. Baba, J.M. Perera, G. W. Stevens, Surface modification of natural zeolite by chitosan and its use for nitrate removal in cold regions, Cold. Reg. Sci. Technol. 62 (2010) 92–97.

[13] M. Rozic, D. Ivanec Sipusic, L. Sekovanic, S. Miljanic, L.C. Urkovic, J. Hrenovic, Sorption phenomena of modification of clinoptilolite tuffs by surfactant cations, J. Colloid Interf. Sci. 331 (2009) 295–301.

[14] A. Maity, N. Ballav, M. Biswas, Conducting composites of poly(N-vinylcarbazole), polypyrrole, and polyaniline with 13X-zeolite, J. Appl. Polym. Sci. 101 (2006) 913–921.

[15] T. Bein, P. Enzel, Encapsulation of polyaniline in zeolite y and mordenite, Synth. Met. 29 (1989) 163–168.

[16] A. Olad, M. Khatamian, B. Naseri, Removal of toxic hexavalent chromium by polyaniline modified clinoptilolite nanoparticles, J. Iran. Chem. Soc. 8 (2011) S141–S151.

[17] A. Olad, M. Amini, A. Rashidzadeh, Electrodeposition of homogeneous and adherent polypyrrole/Na^+-Cloisite nanocomposite on iron electrodes, Fiber Polym. 13 (2012) 475–480.

[18] M. Omraei, H. Esfandian, R. Katal, M. Ghorbani, Study of the removal of Zn(II) from aqueous solution using polypyrrole nanocomposite, Desalination 271 (2011) 248–256.

[19] M. Bhaumik, A. Maity, V.V. Srinivasu, M.S. Onyango, Enhanced removal of Cr(VI) from aqueous solution using polypyrrole/Fe_3O_4 magnetic nanocomposite, J. Hazard. Mater. 190 (2011) 381–390.

[20] P. Enzel, T. Bein, Polythiophenes and oligothiophenes in zeolite hosts; conjugated nanometer size filaments, Synth. Met. 55–57 (1993) 1238–1245.

[21] T. Bein, P. Enzel, Encapsulation of polypyrrole chains in zeolite channel, Angew. Chem. Int. Ed. 28 (1989) 1692–1694.

[22] R. Roque, J. de Onate, E. Reguera, E. Navarro, Pyrrole oligomerization within H-Fe-FAU zeolite, J. Mater. Sci. 28 (1993) 2321–2323.

[23] A. Rashidzadeh, A. Olad, Sh. Ahmadi, Preparation and characterization of polypyrrole/clinoptilolite nanocomposite with enhanced electrical conductivity by surface polymerization method. doi:10.1002/pen.23346 (Article first published online: 28 SEP 2012).

[24] A.A. Dakhel, Y. Ali-Mohamed Ahmed, F.Z. Henari, Structural and optical studies of evaporated bis-(dimethylglyoximato) nickel(II) thin films, Opt. Mater. 28 (2006) 925–929.

[25] Y.S. Ho, C.C. Chiang, Sorption studies of acid dye by mixed sorbents, Adsorption 7 (2001) 139–147.

[26] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process. Biochem. 34 (1999) 451–465.

[27] S.R. Taffarel, J. Rubio, On the removal of Mn^{2+} ions by adsorption onto natural and activated Chilean zeolites, Miner. Eng. 22 (2009) 336–343.

[28] H.K. Boparai, M. Joseph, D.M. OCarroll, Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles, J. Hazard. Mater. 186 (2011) 458–465.

[29] D.A. Fungaro, M. Yamaura, T.E.M. Carvalho, Adsorption of anionic dyes from aqueous solution on zeolite from fly ash-iron oxide magnetic nanocomposite, J. At. Mol. Sci. 2 (2011) 305–316.

[30] N.A. Oztas, A. Karabakana, O. Topala, Removal of Fe (III) ion from aqueous solution by adsorption on raw and treated clinoptilolite samples, Micropor. Mesopor. Mat. 111 (2008) 200–205.

[31] E. Rosales, M. Pazos, M.A. Sanroman, T. Tavares, Application of zeolite-Arthrobacter viscosus system for the removal of heavy metal and dye: Chromium and Azure B, Desalination 284 (2012) 150–156.

[32] D.A. Fungaroa, L.C. Groschea, A.S. Pinheirob, J.C. Izidoroa, S.I. Borrely, Adsorption of methylene blue from aqueous solution on zeolitic material and the improvement as toxicity removal to living organisms, Orbital Elec. J. Chem., Campo Grande, 2(3) (2010) 235–247.

[33] R. Ansari, Z. Mosayebzadeh, Application of polyaniline as an efficient and novel adsorbent for azo dyes removal from textile wastewaters, Chem. Pap. 65(1) (2011) 1–8.

[34] S. Coruh, O.N. Ergun, Ni^{2+} removal from aqueous solutions using conditioned clinoptilolites: Kinetic and isotherm studies, Environ. Prog. Sustain. Energy 28 (2009) 162–172.

[35] P.K. Pandey, Sh. Choubey, Y. Verma, M. Pandey, S.S. Kalyan Kamal, K. Chandrashekhar, Biosorptive removal of Ni(II) from wastewater and industrial effluent, Int. J. Environ. Res. Public Health 4 (2007) 332–339.

[36] I. Kavianinia, P.G. Plieger, N.G. Kandile, D.R.K. Harding, New hydrogels based on symmetrical aromatic anhydrides: Synthesis, characterization and metal ion adsorption evaluation, Carbohyd. Polym. 87 (2012) 881–893.

[37] J.-W. Wang, Y.-M. Kuo, Preparation and adsorption properties of chitosan–poly(acrylic acid) nanoparticles for the removal of nickel ions, J. Appl. Polym. Sci. 107 (2008) 2333–2342.