Nickel Ions Adsorption by Prepared Zeolite-A: Examination of Process Parameters, Kinetics and Isotherms

Magdy A. Wassel[1*], Hassan A.Shehata[1], H. F. Youssef[2], Ahmed S. Elzaref[1], Alaa Fahmy[1]

1 Chemistry Department, Faculty of Science, Al-Azhar University, 11884 Cairo, Egypt
2 Inorganic Chemical Industries and Mineral Resources Division, National Research Center (NRC), Giza, Egypt

Abstract
Adsorption technique can be effectively employed for the elimination of nickel ions Ni(II) from wastewater by synthetic zeolite-A. Zeolite-A was prepared from very low cost local Egyptian clay (kaolin). This work study the removal efficiency of nickel ions at different initial concentrations ranging from 200 to 1000 mg.L-1, pH from 6.0 to 7.5, temperatures from 303 to 333 K and different contact time. In the elimination evaluation of the study, adsorption of Ni(II) onto zeolite-A match to not only adsorption isotherm models but also kinetic models has been investigated. The results showed that the kinetic data were well fitted to the pseudo first order and second order models, indicating that the adsorption behaviors were mainly described to both physical and chemical adsorption. The equilibrium data were best described by the Langmuir isotherm model. Zeolites-A was highly removal efficient of Ni(II) due to cubic structure including pores and channels enabling it for being effective in wastewater treatment.

Keywords: *Zeolite-A, Nickel, Adsorption process. Kinetic, Wastewater treatment.*

1. Introduction

Industrial factories results in the contamination of wastewater with several heavy metals such as (Ni, Zn, Pb and Co). The extensive use of nickel in industry means that considerable amounts of nickel ions can find the way into the drinking water source. Nickel is formed in several chemical activities, including mineral processing, electroplating, production of paints and batteries, manufacturing of sulfate and porcelain enameling [1,2].

Ion exchange process can be used for the removal of divalent metals from contaminated water. The competitive advantage of separation process can increase when low cost ion exchangers are used. A wide variety of heavy metals can be removed from the wastewater at significant quantities and kinetics are usually fast. The drawbacks are that the performance depends on adsorbent affinity towards the metal ions, while in many adsorbents activation is required to improve its adsorption capacity [3].

Adsorption of metal ions on the active centers due to the formation of outer and inner-surface complexes. Outer-surface complexes formed if at least one water molecule is interposed between negative and positive charge of the functional group and the metal ions. On the contrary, inner-surface complexes occur when water molecules are not interposed between the metal ions and the functional group of the adsorbent and the adsorbate forms a direct coordinate-covalent bond with surface functional groups on the variable charge surface [4].

Specific adsorption involves the formation of inner-surface complexes, while non-specific adsorption involves the formation of weaker complexes on outer-surface of adsorbent. Outer-surface complexes are formed via electrostatic interactions between metal positive charge and the negatively charged sites. Therefore, metal binding takes place through ion exchange at the planar centers of the ion exchanger [5].

Zeolites are hydrated alumina silicate minerals with crystalline microporous structure. Zeolite materials consists of three-dimensional frameworks of SiO_4 and AlO_4 that are bonded together by sharing oxygen atoms. The exchange of tetravalent silicon by trivalent aluminum in the mineral structure forms a net negative charge that is counterbalanced by the presence of cations (usually Ca^{+2}, Na^+ and K^+) which are presented in channels and pores [6].

These cations are exchangeable with other heavy metal ions. The zeolite framework structure encloses cavities occupied by large ions and water molecules which are able to move, allowing ion exchange. Zeolites can be classified by considering the topology of the framework. Zeolites having the same topology constitute a zeolite framework type. Currently there are 206 known framework types recognized by the Structure Commission of the International Zeolite Association [6].

An important feature is the effective width of the channels which determines the accessibility of the channels to incoming cations. Zeolite channels are formed by different combinations of linked tetrahedral rings. The channels that are wider at their narrowest parts can receive larger cations into their structure [7].

The initial concentration of metal ions affects the adsorption process. The adsorption depends on several condition, such as the type of metal and the liquid phase, the presence of competing cations, the availability of the functional groups on the adsorbent surface and the ability of these groups to bind metal ions. In most cases, the increase of the initial metal concentration results in an increase in the amount of metal adsorbed per unit mass of adsorbent until an equilibrium is reached [8,9].

The activity of the functional groups on the surface of ion exchanger is strongly affected by pH of solution. The point of zero charge pH is the pH of the solution at which the overall charge on the surface of the adsorbent is zero. At pH lower than point of zero charge pH, the functional groups are protonated and the positively charged surfaces dominate. In this case, the attraction of negatively charged ions is possible to occur. In highly acidic medium, several active sites become protonated and act as positively charged species, resulting in reduced attraction between the metals and the minerals. Deprotonation of functional groups occurs at increasing pH and these behave as negatively charged formed to attracting heavy metals. However, at alkaline environment, the solubility of metals decreases allowing precipitation, which may complicate the sorption process [10,11].

Precipitation occurring at alkaline environment masks the true extent of metal sorption on minerals; this is why it is important when the mineral behavior is examined at high pH values to determine the soluble metal concentration prior to the addition of the mineral [12].

Temperature is related to the kinetic energy of the metal ions in the aqueous phase. By increasing in temperature subsequently results in an increase in the diffusion rate of the adsorbate. In addition, temperature alternations will affect the equilibrium adsorption capacity of the adsorbent for a particular metal ions (adsorbate). Generally, at elevated temperatures the metal uptake is higher due to higher affinity of the mineral for the metal and/or an increase in the active sites of the surface of adsorbent. At higher temperature the energy of the system facilitates the attachment of metals on the mineral surface [13,14].

In this study, Zeolite -A is synthesized from Egyptian kaolin by microwave hydrothermal technique and used as adsorbent for the removal of Ni(II) ions from aqueous solutions. The effects of operating conditions, such as initial concentration of nickel ions, pH value of solutions and temperature on the adsorption efficiency are investigated. The equilibrium adsorption data are fitted with Langmuir model. The kinetic models were studied using the pseudo first-order and pseudo-second-order, results showed that the pseudo-second order equation model provided the best correlation with the experimental data.

2. Experimental

2.1 Ion exchanger and Materials

Zeolite-A prepared by microwave hydrothermal technique from Egyptian kaolin has a cubic structure with LTA-type ($Na_{12}Al_{12}Si_{12}O_{48}$) formula and an aperture of 4x4 A°. The starting materials for zeolite-A synthesis are sodium hydroxide pellets (NaOH) of analyzed A.C.S. reagent with the composition of 98.6 % NaOH + 0.4 % Chloride (Baker, SG403INT, Sanford, ME, USA); refined Egyptian kaolin is supplied by Middle East Mining Investments Company (MEMCO) for more details see [15-17].

All chemicals used were of analytical reagent grade and obtained from commercial suppliers without further purification. Nickel chloride salt ($NiCl_2.6H_2O$) was supplied by Sigma Aldrich as analytical-grade was used for preparing a synthetic solution containing 200- 1000 mg/L. These solutions were prepared by dissolving a calculated quantity of the nickel ions in De-ionized water (ultrahigh purity water, resistivity > 18 MΩ/cm, Millipore). Acetic acid and ammonium hydroxide solution were used to adjust the initial pH values in the range from 6.0 to 7.5. For testing the cation exchange property for zeolite, 25 ml of synthetic solutions containing different initial concentrations of Ni(II) were added to 0.25g of zeolite-A.

The experiments were set for wide range of temperature ranging from 303 to 333K during batch testing till reach to equilibrium state. After different time, the metal ion concentrations left in the liquid phase was determined by using atomic absorption spectroscopy (AAS vario® 6, Analytic Jena, Egypt).

The amount of Ni(II) ions adsorbed on the surface of zeolite-A (q_t) mg. g^{-1}, per unit weight at time (t), was calculated from the mass balance equation as shown in Eq. (1)

$$q_t = \frac{C_0 - C_t}{M} V \qquad (1)$$

Where C_o: the initial concentration of Ni(II) (mg . L^{-1}), C_t: the concentration at time t, V: the volume of solution (L) and M: the mass (g) of zeolite-A.

3. Results and Discussion

3.1 Effect of Initial concentration on the adsorption process

The adsorption of Ni(II) ions onto zeolite-A as a function of it is concentrations was studied at constant temperature (303 K) by varying the metal ion concentration from 200 to 1000 mg/L while keeping all other parameters constant.

The results are shown in (Fig. 1) revealed the adsorption of nickel on zeolite-A found that the adsorption capacity increased with increasing metal concentration, while after a certain concentration (1000 mg/L) a plateau was reached. Uptake of nickel ions is explained by different mechanisms of ion-exchange processes as well as to the adsorption process. During the ion-exchange process, metal ions had not only to move through the pores of the zeolite-A, but also through channels of the crystal lattice, and replace exchangeable cations (mainly sodium) [16].
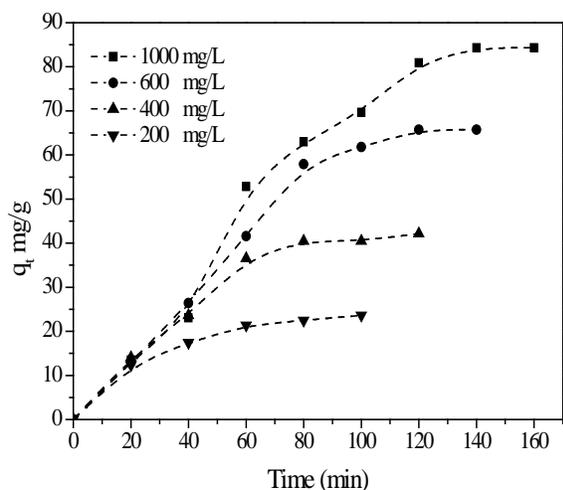

Fig. 1 Effect of initial concentration on the adsorption of Ni(II) onto zeolite-A at pH= 7.5

From the results obtained, the increase of the Ni(II) concentration increased the amount adsorbed due to presence a lot of active sites on the surface of zeolite-A. The adsorption capacity increased due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration. All Ni(II) ions were adsorbed very quickly on the surface of zeolite-A. However, further increase of the initial concentration of Ni(II) leads to the fast saturation of zeolite-A [18].

3.2 Effect of Temperatures on the adsorption process

Temperature has an important effect on the process of adsorption of nickel ions yield, Different sets of batch experiments were performed over different temperatures at 303, 313, 323 and 333 K at initial concentrations 1000 mg/L and a pH (7.5) and adsorption was found to be temperature dependent.

The results are evident in the (Fig. 2), where we notice that the temperature increase improved the adsorption process. In fact, the adsorption percentage of nickel ions onto zeolite-A reached 98.78%, at the temperature of 333 K. The adsorption of nickel ions is therefore endothermic process [19].
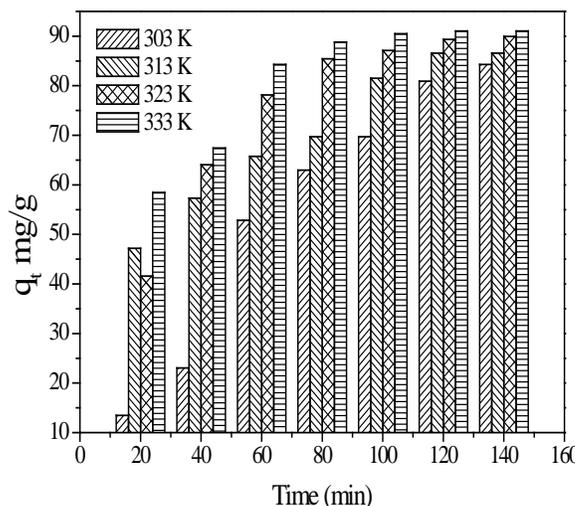

Fig.2 Comparison between the amount of Ni(II) ions adsorbed onto zeolite-A at different temperatures and pH = 7.5

The rate of adsorption in the first minutes increase but after some time, the rate increases due to increase the temperature but in the end, near equilibrium, the rate of adsorption becomes nearly equal [20].

As seen in (Fig. 2) that the adsorbed amount of nickel ions increases with increasing temperature. At higher temperatures zeolite-A pore sizes could increase enhancing high interaction with particle of zeolite-A (adsorbent) and therefore high removal of the Ni(II) ions from aqueous phase [21]. Moreover, the nickel ions adsorbed by zeolite-A is directly proportional to temperature. Increase of metal ion removal with increasing of temperature might be due to the providing of additional kinetic energy and high mobility of ions for diffusion of the nickel ions into the pores of the zeolite-A [22].

3.3 Effect of pH

Adsorption of nickel ions from the wastewater by zeolite-A is mainly influenced by the pH of the solution. pH can influence the surface charge of the zeolite-A, the degree of ionization also the species of adsorbate [23].

The variations in adsorption capacity of zeolite-A with increasing pH is shown in (Fig. 3), it could be referred that the adsorption capacity increased as solution pH increased from pH 6.0 to 7.5.
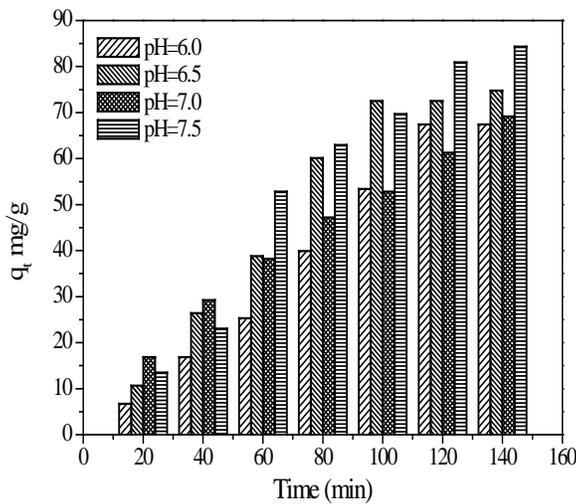
As shown in Figs. 3 and 4 the amount of nickel ions adsorbed till adsorption equilibrium occur and the adsorption percentage versus initial solution pH. The obtained data indicate that metal ions adsorption is strongly pH-dependent and increases with the pH increase until it reaches a maximum at around pH value (7.5). Initially, as the pH of solution was increased from 6.0 to 7.5, the removal percentage of Ni (II) increased from 88.23 to 98.78%.
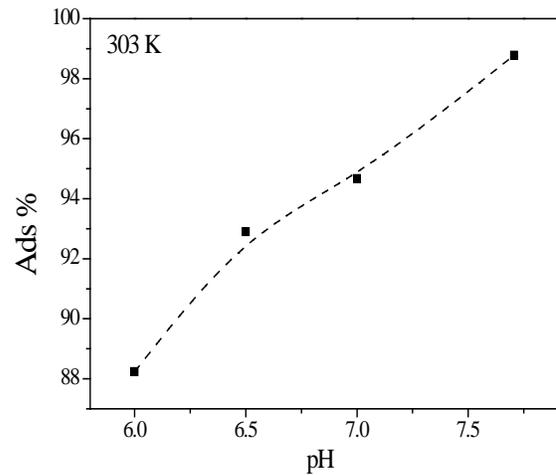

Fig.4 Average percentage of adsorbed nickel ions by zeolite-A at different pH values.

Due to low pH the concentration of protons (H^+) was high and metal binding sites became positively charged repelling the Ni (II) cations. With an increase in pH, the negative charge density on the adsorbent increases due to deprotonating of the metal binding sites, thus increasing metal adsorption [24].

On the other hand, the point of zero charge pH (PZCpH) for zeolite-A was 5.5. This indicates that at pH lower than 5.5, the surface of zeolite is positively charged and metal adsorption is decreased, due to electrostatic repulsion between nickel ions and cationic active centers. Conversely, for pH > 5.5, the number of anionic active centers on surface of zeolite-A increases, and increase the amount of nickel ions removed [25,26].

Fig.3 Variation of Adsorption capacity for Ni(II) ions with time onto zeolite-A at different pH value. (Dose= 0.25g, C_0: 0.008 M, equilibrium time: 140 min and temperature: 303 K).

3.4 Kinetic Models

Studying kinetics of adsorption were applied to determine the reaction rate constant and find out the solute uptake rates which clearly can be used to control the residence time of adsorbate uptake at solid-solution interface.

3.4.1 Pseudo First Order Model

A pseudo-first order equation for the adsorption of liquid/solid interface declares that the rate of change occurred in adsorbate uptake with the passage of time is directly proportional to the difference in the saturation concentration and the rate of solid uptake with time. The Lagergren equation is the most commonly used to determine the rate equation in liquid phase adsorption.

The general mathematical expression is [27-29].

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{2}$$

Where q_t and q_e: the amounts of metal ions adsorbed at time t and at equilibrium (mg.g^{-1}), respectively, and K_1: the rate constant of pseudo-first-order adsorption process (min^{-1}). Integrating the equation at boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, it becomes
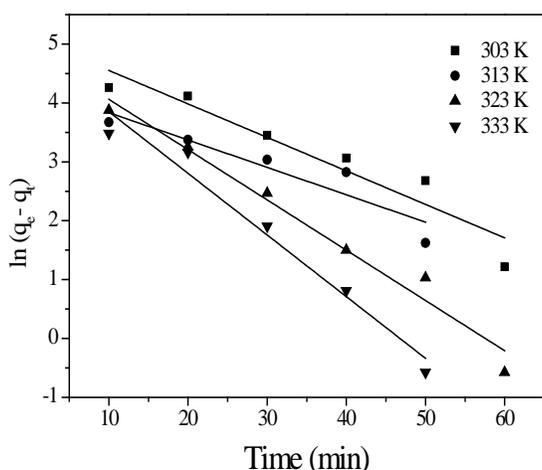
$$ln(q_e - q_t) = lnq_e - K_1t \tag{3}$$

Fig.5 Pseudo-first-order kinetic plot for the adsorption of nickel Ni(II) ions onto zeolite-A at pH= 7.5

From (Fig. 5) The value of K_1, q_e and correlation coefficient R^2 could be calculated from the slope and intercept of the linear plot of $ln(qe - qt)$ versus t, respectively. The results are summarized in Table 1. The correlation coefficients for the pseudo-first-order equation obtained at all the studied pH (7.5) were determined. This equation is generally fit with this adsorption process.

3.4.2 Pseudo Second Order Model

Ho and McKay were developed the equation of second order by based on the amount of nickel ions (adsorbate) which was adsorbed onto zeolite-A (adsorbent). The equations 4 and 5 form in terms of solid phase concentration is [27,28,30,31].

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{4}$$

For boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the linear pseudo-second-order equation given by Eq. (5)

$$\frac{t}{q_t} = \left(\frac{1}{K_2q_e^2}\right) + \left(\frac{1}{q_e}\right)t \tag{5}$$

Where K_2: the rate constant of pseudo-second-order (g mg^{-1} min^{-1}), q_e : the amount adsorbed at equilibrium, and q_t : the amount of metal ions adsorbed at time t.
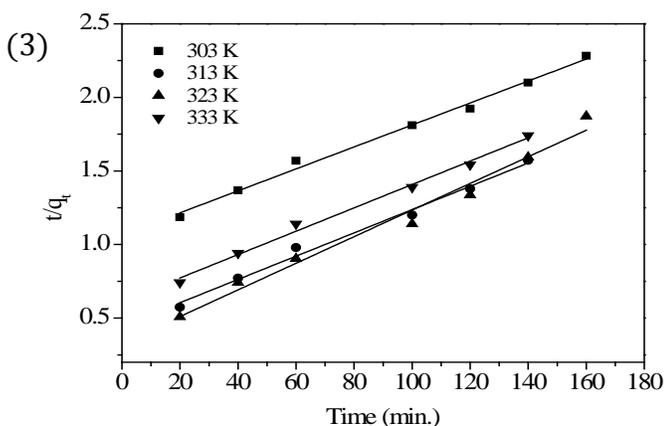

Fig. 6 Pseudo-second-order kinetic plot for the adsorption of nickel Ni(II) ions onto zeolite-A at pH= 7.5

The rate constant can be evaluated from the slope of the straight line of the plot of t/q_t vs. t. The rate constant can be evaluated from the slope of the straight line of the plot of t/q_t vs. t as shown in (Fig. 6).

The linearization proved that the pseudo-second kinetic order well describes the adsorption mechanism for Ni^{+2} ions and have best correlation factor ($R^2 \approx 0.99$). The kinetic parameters and the correlation coefficients calculated from the linear form for nickel ions Ni(II) removed from aqueous solution at pH (7.5) are presented in Table 1.

Table 1: Kinetic parameters of nickel ion adsorbed onto zeolite-A.

Ni(II)		Pseudo-first order			Pseudo-second order		
	T (K)	K_1 [min^{-1}]	q_e [mg/g]	R^2	q_e [mg/g]	$K_2 \times 10^{-5}$ [g/mg. min]	R^2
pH= 7.5	303	28.04	83.02	0.95	134.05	5.22	0.99
	313	19.32	62.41	0.98	126.42	1.40	0.99
	323	9.96	124.35	0.92	110.5	2.48	0.98
	333	8.24	229.54	0.95	125.94	1.02	0.99

As seen in Table 1 the experimental data were fitted better by the pseudo-second order model and the pseudo-first order model with high value of correlation coefficient (R^2). The high values of R^2 implied the good applicability of the pseudo first-order and second-order kinetic equations for the nickel ions adsorption on zeolite-A. These results suggested that both physical and chemical adsorption might be involved in the adsorption process.

3.5 Adsorption Isotherms Models

The adsorption isotherms express the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface. Several isotherm models have been used to fit to the experimental data and evaluate the isotherm performance for nickel adsorption, these isotherm models included the Langmuir model [32] and Freundlich model [33]

The adsorption plots and the fitting model parameters with R^2 for the different models were separately shown in (Figs 7 and 8) and Table 2. In terms of R^2 values, the applicability of the above two models for present experimental data approximately followed the order: Langmuir model > Freundlich model. It was shown that the Langmuir equation had the best fit to the experimental data. The maximum adsorption capacity calculated by this function was 65.66 mg g^{-1}, which was quite close to the value experimentally determined (67.45 mg g^{-1}).

The conformity of adsorption data to the Langmuir isotherm ($R^2 \approx 0.99$) could be interpreted as a homogenous

adsorption process, leading to monolayer binding. Based on the effect of equilibrium parameter R_L values were in the range of $0 < R_L < 1$, which further indicated that zeolite-A was favorable for the nickel ions elimination from aqueous solution (see Table 2).
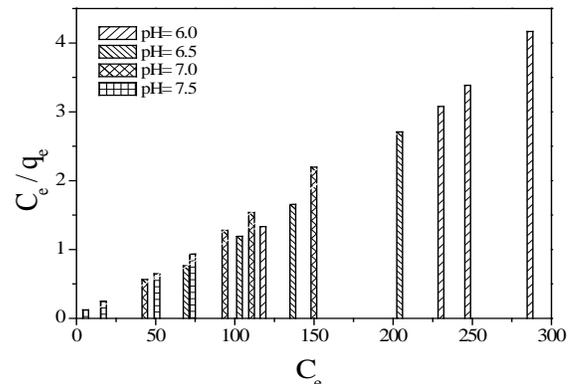

Fig.7 Langmuir plot for nickel ions adsorption onto zeolite-A at 303, 313, 323 and 333 K
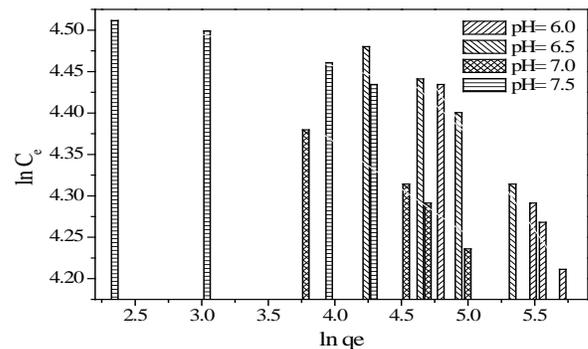

Fig.8 Freundlich plot for nickel ions adsorption onto zeolite-A at 303, 313, 323 and 333 K.

Table 2: Adsorption isotherm models, the corresponding linear forms and parameters obtained from adsorption of nickel ions at pH 7.5.

Isotherm models	Linear form	Parameters	values
Langmuir	$$\frac{C_e}{q_e} = \frac{1}{q^* \, k_L} + \frac{C_e}{q^*}$$	q^* (mg/g)	65.66
		k_L (L/mg)	0.103
		$R_L \times 10^{-4}$	201.36
		R^2	0.99647
Freundlich	$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$$	k_f	100.66
		n	25.72
		R^2	0.92103

Where C_e: the equilibrium concentration of the remaining metal ions in the solution (mg/L), q_e: the amount of metal ions adsorbed per mass unit of adsorbent at equilibrium (mg/g), q^*: the amount of metal ions adsorbed per mass unit of zeolite-A at complete monolayer coverage (mg/g), K_L: the Langmuir constant relating to the strength of adsorption or adsorption energy (L/mg), R_L: equilibrium parameter, K_f: the Freundlich constants related to removal capacity (mg/g) and *1/n* : "heterogeneity factor" the constant to indicate of the intensity of the adsorption process.

4. Conclusions

The results presented in this study show that zeolite-A were successfully prepared and employed for nickel ions adsorption from aqueous solution with high removal efficiency (from 88.23 to 98.78%). The effects of various conditions (initial concentration, temperature and pH value) for Ni(II) ions adsorption were investigated systematically. The adsorption capacity for Ni(II) ions removal was found to be significantly increased with the increase in pH value. The Langmuir adsorption model agrees well with the experimental data, with maximum monolayer adsorption capacity of 65.66 mg g^{-1}. A kinetic study was performed that suggests that the adsorption of Ni(II) ions onto zeolite-A can be fitted to both pseudo first order and pseudo second order model, respectively. Moreover, the adsorption of Ni(II) ions onto zeolite-A give further validated of prepared zeolite for the excellent adsorption ability of another heavy metal ions. The experimental results indicate that zeolite-A was a good adsorbent and can be further applied to the treatment of wastewater contaminated with heavy metal ions.

References

[1] N. Akhtar, J. Iqbal, M. Iqbal, "Removal and recovery of nickel (II) from aqueous solution by loofa sponge-immobilized biomass of Chlorella sorokiniana: characterization studies", J. Hazard. Mater., B 108, 2004, 85–94.

[2] U. Farooq, J.A. Kozinski, M.A. Khan, M. Athar, "Biosorption of heavy metal ions using wheat based biosorbents – a review of the recent literature", Bioresour. Technol., 101, 2010, 5043–5053.

[3] D. W. O'Connell, C. Birkinshaw, T. F. O'Dwyer, "Heavy metal adsorbents prepared from the modification of cellulose: a review", Bioresour. Technol., 99, 2008, 6709–6724.

[4] Y. F. Zhou, R. J. Haynes, "Sorption of heavy metals by inorganic and organic components of solid wastes: significance to use of wastes as low-cost adsorbents and immobilizing agents", Crit. Rev. Environ. Sci. Technol., 40, 2010, 909–977.

[5] O. Abollino, A. Giacomino, M. Malandrino, E. Mentasti, 'Interaction of metal ions with montmorillonite and vermiculite", Appl. Clay Sci., 38, 2008, 227–236.

[6] S. Malamis, E. Katsou, "A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: Examination of process parameters, kinetics and isotherms", Journal of Hazardous Materials, 252– 253, 2013, 428– 461.

[7] S. Kulprathipanja, "Zeolites in Industrial Separation and Catalysis", Wiley-VCH Verlag GmbH & Co KGaA: Weinheim, 2010.

[8] S. C. oruh, O. N. Ergun, "Ni^{2+} removal from aqueous solutions using conditioned clinoptilolites: kinetic and isotherm studies", Environ. Prog. Sustain. Energy, 28, 2009, 162–172.

[9] B. Erdem, A. Ozcan, O. Gok, A. S. Ozcan, "Immobilization of 2,2-dipyridyl onto bentonite and its adsorption behavior of copper(II) ions", J. Hazard. Mater., 163, 2009, 418–426.

[10] U. Farooq, J.A. Kozinski, M.A. Khan, M. Athar, "Biosorption of heavy metal ions using wheat based biosorbents – a review of the recent literature", Bioresour. Technol., 101, 2010, 5043–5053.

[11] M. A. Acheampong, R. J. W. Meulepas, P. N. L. Lens, "Removal of heavy metals and cyanide from gold mine wastewater", J. Chem. Technol. Biotechnol., 85, 2010, 590–613.

[12] K. Vijayaraghavan, Y.-S. Yun, "Bacterial biosorbents and biosorption", Biotechnol. Adv., 26, 2008, 266–291.

[13] L. Nouri, I. Ghodbane, O. Hamdaoui, M. Chiha, "Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran", J. Hazard. Mater., 149, 2007, 115–125.

[14] N. Goyal, S. C. Jain, U. C. Banerjee, "Comparative studies on the microbial adsorption of heavy metals", Adv. Environ. Res., 7, 2003, 311–319.

[15] H. S. Ibrahim, T. S. Jamil, E. Z. Hegazy, "Application of zeolite prepared from Egyptian kaolin for the removal of heavy metals: II. Isotherm models", J Hazard Mater., 182 , 2010, 842–847.

[16] T. S. Jamil, H. S. Ibrahim, I. H. Abd El-Maksoud, S. T. El-Wakee, "Application of zeolite prepared from Egyptian kaolin for removal of heavy metals: I. Optimum conditions", Desalination, 258, 2010, 34–40.

[17] H. F. Youssef, D. M. Ibrahim, S. Komarneni, 'Microwave-assisted versus conventional synthesis of zeolite A from metakaolinite" Microporous Mesoporous Mater., 115, 2008, 527.

[18] K. Banerjee, S. T., R. Ramesh, P. V. Gandimathi, Nidheesh and K.S. B. Iranica, "A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions", Iranica Journal of Energy and Environment, 3, No. 2, 2012, 143-156.

[19] C. Kutahyah, M. Eral, J. Nucl. Mater., 39, 2010, 251–256.

[20] A. H. Ismail, Z. A. Abd-aljaleel, A. S. Jaffer", Removal of Ni (II) and Cd (II) Ions from Aqueous Solutions by Adsorption on to Synthetic Zeolite", Eng. Tech. Journal, 31, No. A, 2013, 8.

[2 1] E. Muzenda, J. Kabuba, F. Ntuli, M. Mollagee, A. F. Mulaba-Bafubiandi; "Cu (II) Removal from Synthetic Waste Water by Ion Exchange Process" Proceedings of the World Congress on Engineering and Computer Science WCECS San Francisco, USA 2011 Vol. II

[22] M. Deravanesiyan, M. Beheshti, A. Malekpour; "The removal of Cr (III) and Co (II) ions from aqueous solution by two mechanisms using a new sorbent (alumina nanoparticles immobilized zeolite) - Equilibrium, kinetic and thermodynamic studies", Journal of Molecular Liquids, 209, 2015, 246–257.

[23] S. N. A. Abas, M. H. S. Ismail, M. L. Kamal and S. Izhar, "Adsorption Process of Heavy Metals by Low-Cost Adsorbent: A Review", World Applied Sciences Journal, 28, No. 11, 2013, 1518-1530.

[24] S. Mehdizadeh, S. Sadjadi, S. J. Ahmadi, M. Outokesh, Journal of Environmental Health Science & Engineering, 12, 2014, 7.

[25] H. Katsuki, S. Komarneni, "Synthesis of Na-A and/or Na-X zeolite/porous 688 carbon composites from carbonized rice husk", J. Solid State Chem., 182, No. 7, 2009, 1749–1753.

[26] C. Santasnachok , W. Kurniawan, H. Hinode,"The use of synthesized zeolites from power plant rice husk ash obtained from Thailand as adsorbent for cadmium contamination removal from zinc mining", Journal of Environmental Chemical Engineering, 3, 2015, 2115–2126.

[27] M. Visa, "Synthesis and characterization of new zeolite materials obtained from fly ash for heavy metals removal in advanced wastewater treatment", Powder Technology, 294, 2016, 338–347.

[28] O. Abdelwahab, N. K. Amin, E-S. Z. El-Ashtoukhy; "Removal of zinc ions from aqueous solution using a cation exchange resin", chemical engineering research and design, 91, 2013, 165–173

[29] S. Lagergren, "About the theory of so-called adsorption of soluble substances", Kungliga Svenska Vetenskapsakademiens, Handlingar, 24, No. 4, 1898, 1–39.

[30] G. McKay, "The kinetics of sorption of di valent metal ions onto sphagnum moss flat", Water Res., 34, 2000, 735–742.

[31] S. Ho, G. McKay, "Pseudo-second order model for sorption processes", J. Process. Biochem., 34, 1999, 51–465.

[32] X. Liu, L. Zhang, "Removal of phosphate anions using the modified chitosan beads: Adsorption kinetic, isotherm and mechanism studies", Powder Technology, 277, 2015, 112–119

[33] X. Song, Y. Pan, Q.Wu, Z. Cheng,W. Ma, "Phosphate removal from aqueous solutions by adsorption using ferric sludge", Desalination, 280, 2011, 384–390.