Removal of Ni(II) Ions From Aqueous Solutions by Nanoporous Material

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Abstract: The novel trends in green separation processes impose the need for application of natural, low-cast and high-efficiency selective adsorbents, such as natural zeolite, within the processes for the treatment of drinking water supplies. Lately, nano-porous inorganic sorbents represent an ongoing trend for elimination of heavy metals from water resources. In the frame of this work, the nanoporous material, clinoptilolite,was applied for removal of Ni(II) ions from water resource. The experimental results were obtained in a laboratory scale batch glass reactor with continuous stirring at 400 rpm. The effects of the mass of the nano-porous adsorbent and the initial pH of the solution were studied to optimize the conditions for maximal removal of Ni(II) ions. MATLAB/Curve Fitting Toolboxwas implemented to determine the adequate adsorption isotherm as well as to optimize the equilibrium state of the investigated system.

Keywords: natural zeolite - clynoptilolite, Ni(II) ions, adsorption, nano-porous sorbent, equilibrium study

Introduction

The rapid industrial development and urbanization have intensified environmental pollution and caused deterioration of eco-systems by accumulation of many pollutants, especially heavy metals. Most of the heavy metals are toxic and their ions are not biodegradable, hence they are significant environmental pollutants. Therefore, the removal of the heavy metal ions from water and wastewater is very important for environmental protection, and thus the public health.

The methods used for removal of heavy metals from water and wastewater include chemical precipitation, ion exchange, solvent extraction, electrolysis, membrane processes, adsorption (Fu and Wang 2011, Vindoh,Padmavathi and Sangeetha 2011, Bakalar, Bugel and Gajdosova 2009, Rahul 2013, Lokendra and Mukesh 2013).Among all the approaches proposed, adsorption is one of the most popular method and it is considered as an effective, efficient and economic method for wastewater purification and it is widely used in effluent treatment processes.Various materials such as natural and synthetic zeolites (Zoran et al., 2014, Anielak and Schmidt 2011, Shaheen, Derbalahand Moghanm 2012, Wang and Peng 2010), clay minerals (Ghormi, Lahsini,Laajeb and Addaou 2013), activated carbon (Kouakou, Ello, Yapo and Trokourey2013), biosorbents (Miretzky and Cirelli 2009), have been used as adsorbents for the removal of heavy metals from water and wastewater.

The zeolites are nanoporous minerals, characterized by specific structure of the frame and regulated pore geometry.The zeolites have high ion exchange capacity and selective adsorption capacity, thermal and mechanical stability(Passaglia and Sheppard 2001).There are natural and synthetic zeolites. The zeolite - clinoptilolite is natural zeolite. Natural zeolites are obtained by performing the excavation. Zeolites consist of SiO_4 and AlO_4 tetrahedrons, connected in skeletal structure. The aluminosilicate structure has negative charge that attracts the inside positive cations. The zeolites in their structure have large cavities where cations like K, Na, Ba or Ca, large molecules of organic compounds, cationic groups of ammonia, carbonate and nitrate ions, and ions of heavy metals can penetrate and can be adsorbed.

A great deal of interest in the research for the removal of heavy metals from aqueous solutions has been focused on the use of zeolites as adsorbents. High ion-exchange capacity, high specific surface area and their relatively low cost, make them attractive adsorbentsfor elimination of heavy metals from water systems.

Many research works have used natural zeolite as an appropriate adsorbent for heavy metals removal (Ghasemi, Gafar, Mousaviand Dehghan 2012, Sabry, Aly, and Farahat 2012, Salunkhe and Raut 2012). The aim of this article is to investigate the adsorption availability of natural zeolite - clinoptilolite to remove Ni(II) ions from aqueous solutions.

Materials and Methods

Adsorbent

The natural zeolite (clinoptilolite) used as adsorbent for Ni(II) ions removal from aqueous solutions, was taken from Kardzali, Bulgaria.

Reagents and Chemicals

Standard solution of nickel nitrate,$Ni(NO_3)_2$ (1 g/dm^3), hydrochloric acid, HCl (0.1 M), sodium hydroxide, NaOH (0.1 M), natural nano-porous zeolite. All the reagents and chemicals used in the experiment were analytical grade.

Adsorption experiment

Batch adsorption experiments were performed to obtain equilibrium data. Standard solution of $Ni(NO_3)_2$ with concentration of 1 g/l was used to prepare solution with different initial Ni(II) concentration (350-650μg/l). The effect of the amount of zeolite and the influence of pH were investigated. 0.25, 0.5 and 1 g/l of the applied zeolite were placed at three different bakers, then 2l of the Ni(II) solution with the desired concentration were added in each beaker. The mixture of natural zeolite and Ni(II) solution with 450 µg/lconcentration and pH = 6.0, were stirred using magnetic stirrer at 400rpm, at constant room temperature for 5h, sufficient time to reach equilibrium.The influence of pH was conducted with adsorbent amount of 0.3 g/l at 2 l of the solution with 450μg/l concentration of nickel ions and at the same stirring conditions as mentioned before. The initial pH of 4, 6 and 8 were adjusted by adding either 0.1 M HCl or 0.1 M NaOH solutions.

The samples were taken at particular time, filtered and the remaining concentrations of Ni(II) ions in the filtrate were determined using atomic absorption spectrophotometer,AAS Perkin Elmer model AA700.

Experimental data were processed by the three most commonly used isotherms: Langmuir, Langmuir-Freundlich and Redlich - Peterson isotherm, by using MATLAB/Curve Fitting Toolbox.

Results and Discussion

Material characterization

The clinoptilolite used for experimental analysis is in the form of granules and the particle size range of the natural zeolites used in this study was 0.8 to 2.5 mm.

The results of chemical composition of clinoptilolite determined by classical silicate chemical analysis are presented in Table 1.

Table 1. Chemical composition of clinoptilolite

Oxides	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	TiO_2	LOI
wt.%	72.0	12.0	3.7	1.9	1.2	0.5	3.8	0.04	4.86

The monolayer capacity and specific surface of clinoptilolite are evaluated from data of equilibrium adsorption of water vapor at 298K, using linear form of Langmuir equation. The values of the parameters of the Langmuir equation, monolayer capacity, n_m^a and constant b, and the specific surface, a_s are 4,2 · 10^{-3}mol/g, 0,56, and 268 m²/g, respectively (Katerina, Blagica, Biljana and Vesna2014). The high value of specific surface of clinoptilolite enables it to be used as adsorbent for heavy metals removal from industrial wastewaters (Milicevic et al., 2013).

ADSORPTION STUDIES

The adsorbed amount of metal ion q [μg/g], was calculated using the following equation expressed as:

$$q = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 is initial concentration of the Ni(II) ions [μg/l], C_t is concentration of Ni(II) ions [μg/l] at particular time of adsorption, V is volume of the solution [l] and m is mass of the adsorbent [g].
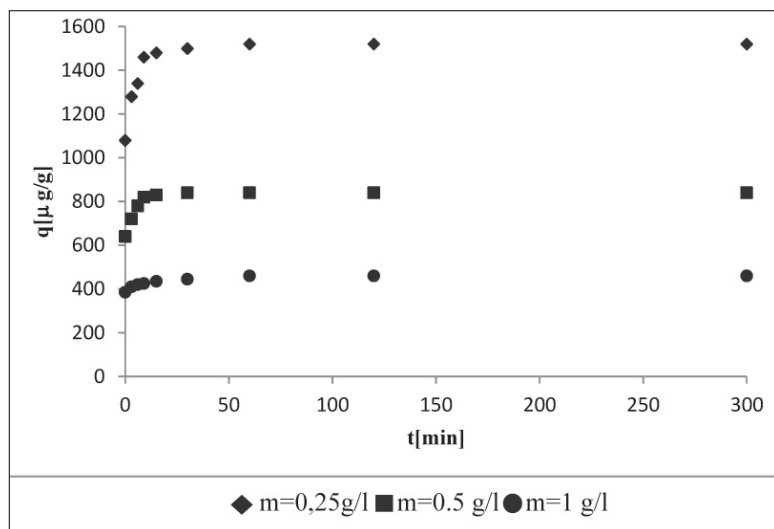
The percentage of removal of Ni(II) ions was determined using the Equation 2:

$$\%R = \frac{C_0 - C_e}{C_0} \cdot 100 \tag{2}$$

where C_e is equilibrium concentration of Ni(II) ions [μg/l].

EFFECT OF AMOUNT OF ADSORBENT

The effect of the dosage of the natural zeolite on the removal of Ni(II) is given in Figure 1 and Figure 2. The Figure 1 shows that the amount of Ni(II) adsorbed per unit mass, q, decreases with increase of the adsorbent amount. It was found that, when adsorbent dose increases the total surface area decreases, this increase in diffusion path length, could be explained as a result of aggregation of zeolite particles.

However, the percentage of removal of Ni(II) increases by increasing the adsorbent amount. The removal percentages are 80, 89 and 96 % for adsorbent dosage of 0.25, 0.5 and 1 g/l, respectively, as it is shown at Figure 2. This is to be expected because, for a fixed initial concentration of the solution, increasing adsorbent amount provides greater surface area or adsorption sites.
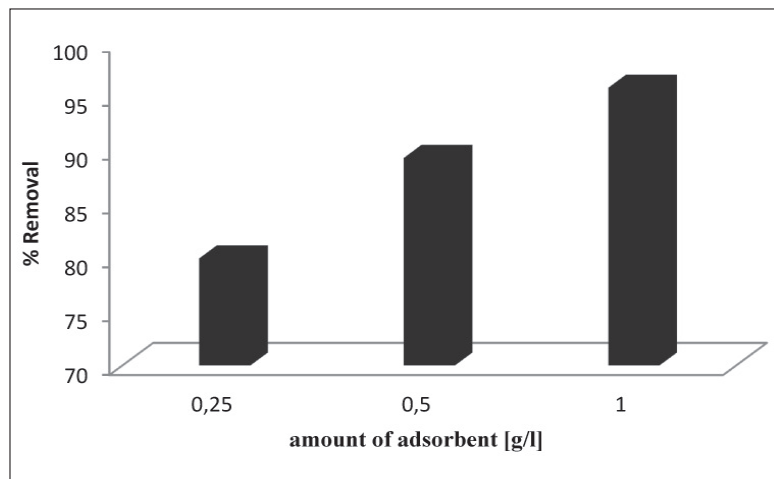

Figure 1. Experimental equilibrium data of the system Ni(II) - natural zeolite

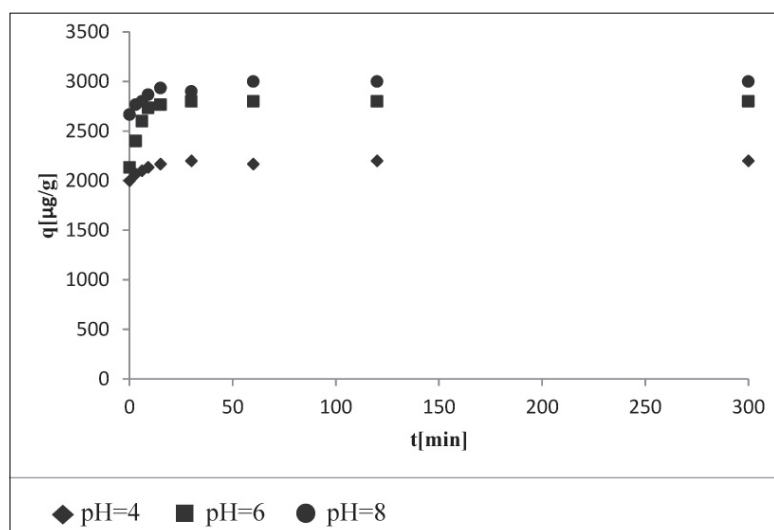**Figure 2.** Function of NI(II) removal from amount of adsorbent

Figure 3. Experimental equilibrium data for the system Ni(II) - natural zeolite
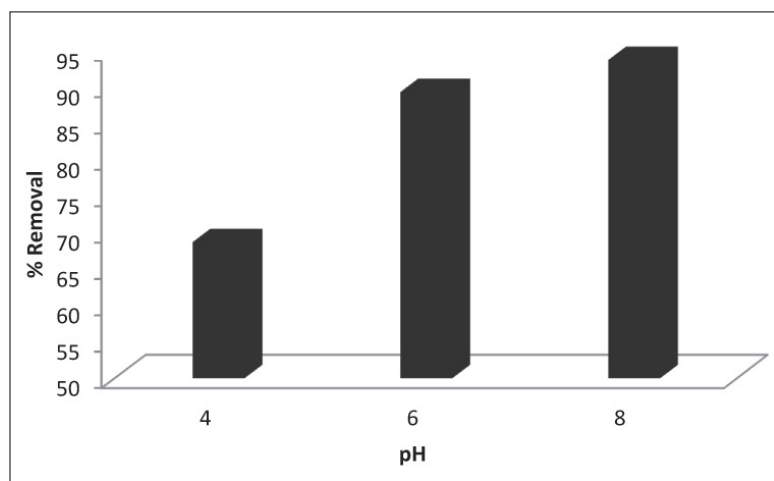

Figure 4. Function of NI(II) removal from pH of the solution

EFFECT OF pH

The pH of the solution is an important variable which controls the adsorption of the metal ions at the solid-water interface. The influence of pH on the adsorption of Ni(II) ions onto natural zeolite was examined at pH 4, 6 and 8. The general trend in the amount adsorbed (*q*) as well as the percentage of removal with increase in pH is positive. Figure 3 represents the trend in the amount of Ni(II) ions adsorbed in respect of time at different pH of the solution.It is observed that adsorption increases with increase in pH value of Ni(II) solution.

The percentage of removal of Ni(II) ions, also increases by increasing the pH of the solution, Figure 4. The removal percentages are 69, 89 and 94% for pH 4, 6 and 8, respectively. Similar studies were in agreement with this findings (Ismail, Zhang and Adnan, 2012).

Generally, the acidification of the aqueous phase leads to an increase of proton occupying the active sites in the adsorbent structure (Singh, Verma, Sambi and Sharma 2008). At low pH, the number of H^{+} ions exceeds several times than metal ions and the Ni(II) ions can hardly compete with H^{+} ions for the binding sites on the zeolite. When an increase of pH, the concentration of H^{+} ions decreases and there are more active sites of clinoptilolite available for metal ions. Hence, pH 6 was chosen as the optimum pH value for this adsorption process.

ADSORPTION ISOTHERMS

Adsorption isotherms are important for adsorption processes research. Figure 5 shows the plot of adsorbed amount of Ni(II) ions at equilibrium versus equilibrium concentrations.
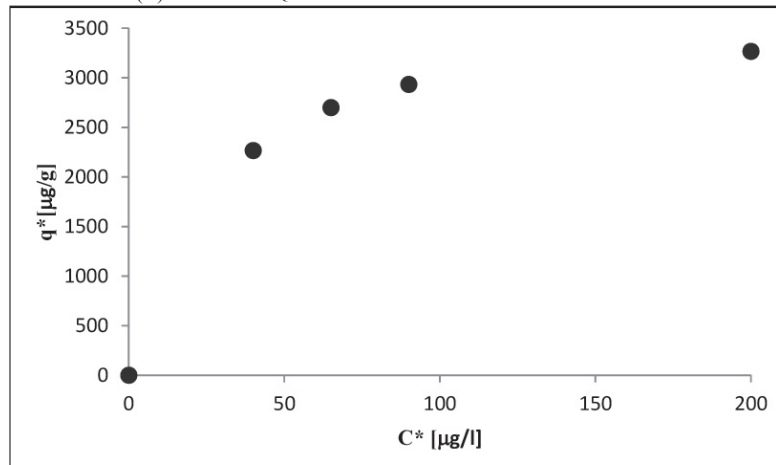
Figure 5. Experimental adsorption isotherm for the system Ni(II) ions - natural zeolite

Experimental data were processed by the three most commonly used isotherms: Langmuir equation (Equation. 3), Langmuir-Freundlich (Equation 4) and Redlich - Peterson (Equation 5), by using MATLAB/Curve Fitting Toolbox. The correct choice of the equilibrium isotherm is an important segment for determining the maximal capacity of the adsorbent for the investigated adsorbate, and for modeling the kinetics and dynamics of adsorption.

$$q^* = \frac{q_m \cdot K_L \cdot C^*}{1 + K_L \cdot C^*} \tag{3}$$

$$q^* = \frac{q_m \cdot K_C \cdot C^{*1/n}}{1 + K_C \cdot C^{*1/n}} \tag{4}$$

$$q^* = \frac{K_{RP} \cdot C^*}{1 + A \cdot C^{*\beta}} \tag{5}$$

where, q_m[µg/g], K_C [l/µg]$^{1/n}$, K_L [l/µg] and n are parameters of Langmuir and Langmuir - Freundlich'sisotherms, K_{RP}[l//µg], A [l/µg]^b and$b$ are parameters of Redlich - Peterson's isotherm.
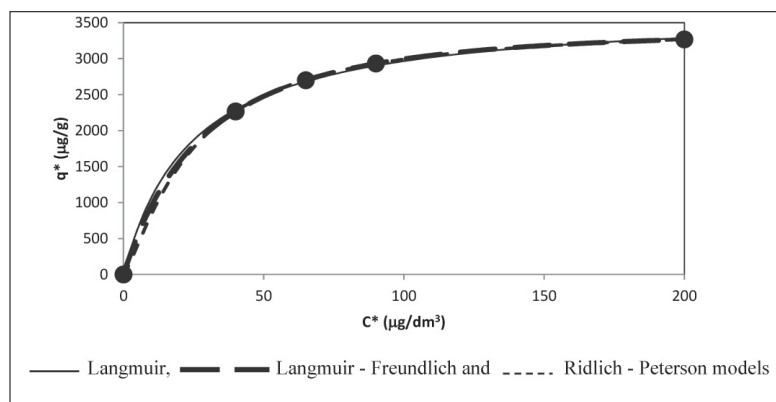
Figure 6. Modeling of the experimental data for the system Ni(II) ions - natural zeolite using

The modeling of the experimental data for the investigated system applying Langmuir, Langmuir - Freundlich and Ridlich - Petrson models are given in Figure 6.

Table 2 contains the data of model parameters of the applied adsorption isotherms for Ni(II) ions adsorption on natural zeolite.

Table 2. Model parameters of the applied adsorption isotherms

	Langmuir	Langmuir-Freundlich	Ridlich-Petrson
q_m[μg/g]	3687.03	3513.1	
K_L[l/μg]	0.04109		
K_C[l/μg]$^{1/n}$		0.01688	
n		0.7862	
A[l/g]			0.02106
K_{RP}[l/μg]$^{1/n}$			120.3
b			1.078
R^2	0.9995	0.9999	0.9999

Satisfactory values of the maximal adsorption capacities of natural zeolite for Ni(II) removal were obtained by Langmuir and Langmuir - Freundlich isothermsand are 3687 and 3513 μg/g, respectively.

The high values of coefficients of correlation reveal that experimental results correspond well to the three used adsorption isotherm models.

Conclusion

In this study, the adsorption of Ni(II) ions on natural zeolite - clinoptilolite, was investigated. Chemical analysis showed that SiO_2 is major component in the clinoptilolite. This nanoporous material has high specific surface area of 268 m^2/g. Batch experiments were conducted and showed that the adsorption of Ni(II) on natural zeolite is dependent of the adsorbent dosage and pH dependent.The Langmuir, Langmuir - Freundlich and Redlich - Peterson isotherms were applied to study equilibrium data and all models indicate good correspondence to the experimental results.

It can be concluded that natural zeolite - clinoptilolite, considered in this work appears to be promising adsorbent with acceptable adsorption capacity for removal of nickel ions from aqueous solutions.

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