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A batch study of Ni(II) sorption on natural Slovak zeolite

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Abstract. The adsorption mechanism of nickel on natural Slovak zeolite, a regional low-cost material, was studied in a batch system. The effect of various initial concentrations of metal ions in the adsorption process was tested. The highest adsorption efficiency (almost 70%) was reached at a concentration of 50 mg/L. The lowest efficiency was determined at a concentration of 350 mg/L (approx. 19%). Sorption data have been interpreted in terms of Langmuir and Freundlich isotherms. The Freundlich model with regression coefficient 0.83 better fitted for the batch experiments. The change of pH in equilibrium showed to ion-exchange reaction. The conductivity increases in all cases. Due to relatively low efficiency in higher concentration of aquatic solutions, further research and modification of zeolite is needed.

1. Introduction

The aquatic ecosystem is frequently contaminated by heavy metals from diverse sources like industrial wastewater, urban runoff, agricultural processes and others. Nickel belongs to toxic heavy metals and is non-biodegradable in environment. The industries such as connector, electroplating, metal finishing, nickel-cadmium batteries, lead frame, plastics manufacturing, fertilizers, pigments, mining and metallurgical processes are the source of nickel in wastewaters. Higher concentration of nickel causes severe health problems like pulmonary fibrosis, renal edema, damage to lungs, kidneys, gastrointestinal distress, e.g., abdominal discomfort, nausea, vomiting, diarrhoea and skin dermatitis. It is also a carcinogenic and in teratogenic to live beings in its metallic form [1]-[4][4].

There are many processes dedicated to water treatment, such as biological methods, electrocoagulation and electrodialysis, coagulation and flotation, membrane separation. Adsorption onto zeolites has advantages such as a simple process, easy maintenance, large adsorption capacities, appropriate selectivity and relatively low cost. Zeolites belong to aluminosilicates, they have a framework silicate with a three-dimensional cage structure. They represent a proper material for removing heavy metal ions from wastewater because their structure provides negative charges, which can balance by adsorption of exchangeable cations [4]-[7].

Zeolites were investigated to have high selectivity for heavy metal ions, like Pb(II), Cd(II), Zn(II), and Cu(II) [6],[8],[9].

The aim of this study was to examine the effectiveness of natural zeolite as a sorbent for nickel removal. In the experiments, the influence of pH, conductivity and various concentration of nickel in aqueous solutions on adsorption behaviour of zeolite was studied. To evaluate sorption process onto Slovak zeolite, the data from batch experiments were evaluated using Langmuir and Freundlich isotherms [2],[5].



2. Material and methods

2.1. Preparation of material

In the experiments, the natural zeolite (particle size 0.2-1.0 mm) from the Nizny Hrabovec (Zeocem, Inc.; Bystre, Slovakia), was used.

The chemical composition of studied sorbent was determined by X-ray fluorescence (XRF) spectrometry Philips-Magix Pro (Philips Electronics Co. Netherlands). XRF analyser determines the chemistry of a sample by measuring the fluorescent (or secondary) X-ray radiation emitted from a sample when it is excited by a primary X-ray source [10],[11].

Adequate amounts of $\text{Ni}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$ were dissolved in de-ionized water to obtain the stock solutions of concentration 1000 mg/L of Ni. Concentrations of solutions (50, 100, 200, 350 and 500 mg/L) used in the batch studies were prepared by dilution of stock solution with de-ionized water.

2.2. Batch experiments

5 g of zeolite and 100 mL of single-component solution was added into 100 mL bottle vial. The vials were shaken at a regular rate in a magnetic shaker at 200 rpm. After 24 h reaction time, sorbent was removed by filtration through a laboratory filter paper. Residual concentration of nickel in filtrate was determined by ICP-MS Spectrometer PQ-ExCell (VG-Thermo Elemental, Winsford, Cheshire, UK).

In the filtrates, pH (Hach sensION+ PH1, USA) and conductivity (Sension+ EC5, Hach, USA) were measured. All experiments were performed at laboratory temperature ($23 \pm 0,2^\circ\text{C}$).

The removal efficiency (E) was calculated by following formula as

$$E = \frac{(C_i - C_e)}{C_i} \cdot 100 \% \quad (1)$$

where C_i is the initial concentration (mg/L) and C_e is the equilibrium concentration (mg/L) [3][12],[13].

2.3. Sorption models

Adsorption isotherm is a function that associates the amount of adsorbate on the adsorbent. Several models can represent placement of metal ions between the liquid and the solid phase. Ones of most using are Langmuir and Freundlich.

The Langmuir model assumes monolayer adsorption onto a surface containing a limited quantity of adsorption sites of uniform strategies with no transmigration of adsorbate in the surface [12]. This model is represented by

$$Q_e = Q_{max} \cdot \frac{K_L \cdot C_e}{1 + K_L C_e} \quad (2)$$

where Q_{max} (mg/g) is the Langmuir constant corresponding to the uptake capacity, and K_L (L/mg) is the adsorption energy as well as the equilibrium constant of the adsorption-desorption process. The constants in the Langmuir model, Q_{max} and K_L , were evaluated using the slope ($1/Q_{max}$) and the intercept ($1/K_L Q_{max}$), respectively, of the plot of C_e/Q_e vs. C_e [14].

The Freundlich isotherm is recognised as an empirical model and represents a direct relationship between concentration and adsorption. The formula of this this model is:

$$Q_e = K_F \cdot C_e^{1/n} \quad (3)$$

where Q_e (mg/g) represents the amount sorbed per amount of adsorbent at the equilibrium, C_e (mg/L) represents the equilibrium concentration, and K_F is Freundlich constant corresponding to adsorption capacity and n value the degree of nonlinearity between solution concentration and adsorption. If $1/n$ approaches 1, isotherm equation becomes linear [15].

3. Results and discussion

3.1. XRF analysis

A series of XRF analyses were carried out at the Department of Civil Engineering at University of Alicante – Polytechnic School, for the chemical characterization of zeolite. The obtained XRF analysis together with declared parameters from manufacturer is shown in table 1.

Table 1. XRF Analysis of raw zeolite.

Chemical component	Declared content (mass %)	XRF analysis (mass %)
SiO ₂	62.25-68.28	60.62
Al ₂ O ₃	12.22-12.62	10.81
CaO	2.67-2.98	3.50
K ₂ O	-	3.05
Fe ₂ O ₃	1.31-1.66	1.39
MgO	-	0.58
Na ₂ O	-	0.41
BaO	-	0.20
WO ₃	-	0.16
TiO ₂	-	0.15

This analysis determined that the content of silica and alumina is the main components of natural zeolite. Calcium and potassium ions can be exchanged with metal or non-metal ions [11],[16]. Ratio of Si/Al in the natural zeolite is 4.95 which is little lower like in [17].

3.2. Sorption efficiency

The sorption efficiency, change of pH and conductivity are presented in table 2. The maximum amount Ni(II) removal (69,51%) was achieved at concentrations of 50 mg/L. The sorption efficiency decreased with higher concentration (at 500 mg/L was only 20.3%). The results indicated that nickel uptake rate was relatively high at the beginning of the process due to abundance possible adsorption sites. However, the number of active sites decreases towards to the formation of the adsorption equilibrium [5].

The pH of the solution is one of the most important parameters in the sorption process of heavy metals by zeolites, for its effect on the charge state of metals and adsorbent surface [5].

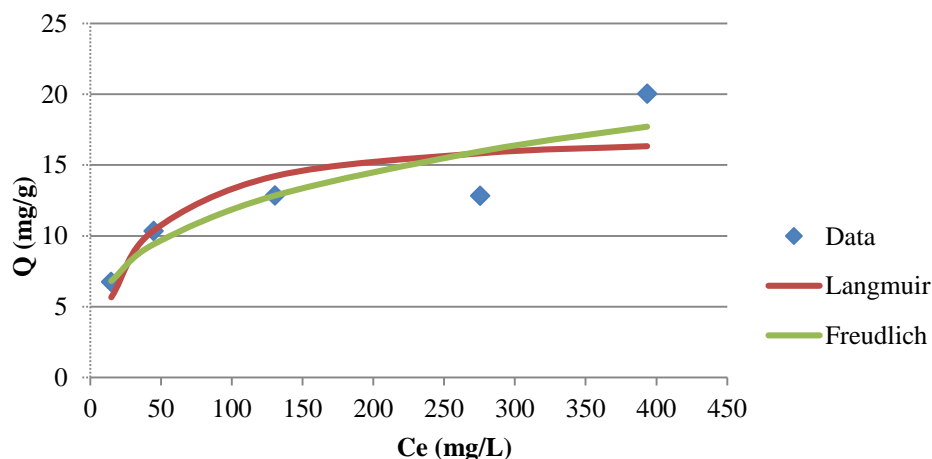
It was observed that pH of solutions 50 and 100 mg/L increased and 200, 350, and 500 mg/L decreased during experiments. The values of conductivity of all solutions increased during 24 h of reaction time.

Table 2. The pH, conductivity and efficiency of Ni(II) sorption.

Concentration (mg/L)	Initial parameters		Final parameters		
	pH	γ ($\mu\text{S}/\text{cm}$)	pH	γ ($\mu\text{S}/\text{cm}$)	E (%)
50	6.1	200	6.6	251	69.51
100	5.9	427	6.5	489	53.62
200	6.4	765	6.2	862	33.01
350	6.6	1312	6.3	1393	18.89
500	6,7	1815	6.4	1841	20.30

3.3. Isotherm models

To find the most appropriate model, data were fitted to Langmuir and Freundlich isotherms (figure 1). Both isotherm models indicated that during adsorption process monolayer ion-exchange was formed [7].

**Figure 1.** Langmuir and Freundlich isotherm models for the Ni(II) adsorption.

The isotherm coefficients are presented in table 3. The coefficient of determination (R^2) values derived from the Langmuir fitting was 0.728 for nickel and 0.830 was obtained from the Freundlich model. The statistical correlation using the Freundlich isotherm was better than the Langmuir isotherm. Freundlich isotherm is realized on heterogeneous surfaces. This model defines surface heterogeneity and exponential distribution active sites and energy [18].

Table 3. Isotherm parameters for adsorption of Ni(II).

	Langmuir constants			Freundlich constants		
	Q_{\max} (mg/g)	K_L (L/mg)	R^2	K_F (mg/g(L/mg) ^{1/n})	1/n	R^2
Ni(II)	17.6236	0.03196	0.728	3.1170	0.2907	0.830

4. Conclusion

In this paper, the sorption of Ni(II) on a natural Slovak zeolite was investigated. The chemical composition of tested sorbent was characterized by XRF spectroscopy. The maximum removal efficiency (almost 70%) was achieved in solution with concentration of nickel 50 mg/L. Change of the pH can be caused ion-exchange process. Results from experiment fit to the Freundlich isotherm, which

means that the sorption happens on heterogeneous surface. It can be concluded that zeolite is promising for the removal of metal ions from aqueous solution but had relatively lower efficiency in higher concentration. To improve the efficiency of sorption, next study will be aimed to modification of zeolite.

5. References

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