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ZAŠTITA MATERIJALA I ŽIVOTNE SREDINE

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ČASOPIS: ZAŠTITA MATERIJALA I ŽIVOTNE SREDINE

Glavni urednik: Dr Darko Vuksanović,
Univerzitet Crne Gore,
Metalurško-tehnološki fakultet

Za izdavača:
Prof. dr Darko Vuksanović

Izdavač:
Crnogorsko društvo za koroziju, zaštitu materijala i zaštitu životne sredine

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SEPARATION OF Co(II) IONS FROM WATER RESOURCES BY NATURAL ZEOLITE (CLINOPTILOLITE)

Shaban Jakupi[1],Kiril Lisichkov[2]*, Mirjana Golomeova[1],
Katerina Atkovska[2], Mirko Marinkovski[2],
Stefan Kuvendziev[2], Hamdije Memedi[3]

[1] *Faculty of Natural and Technical sciences, University "Goce Delchev", Stip, Republic of Macedonia*

[2] *Faculty of Technology and Metallurgy, University "Ss. Cyril and Methodius", Skopje, Republic of Macedonia*

[3] *Faculty of Natural Sciences and Mathematics, State University of Tetovo, Tetovo, Republic of Macedonia*

[1] *klisickov@yahoo.com; phone: +389 71 391 433; fax: +389 2 3065 389*

Abstract

The contemporary trends in green separation processes impose the need for application of natural, low-cost and high-efficiency selective adsorbents 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. Natural zeolite (clinoptilolite) was used as a potential raw material for the purpose of removal of Co(II) ions from model solutions. The experimental results were obtained in a laboratory scale batch glass reactor with continuous stirring at 400 rpm. The effects of operational parameters such as the initial concentration of Co(II) ions in the aqueous solution, the mass of the nano-porous adsorbent and the pH were studied to optimize the conditions for maximum removal of Co(II) ions. The process equilibrium was investigated at the following operating conditions: initial adsorbate concentration of Co(II) ions from 350 – 650 μg/dm^3, mass of nano-porous sorbent from 0.1 – 0.5 g, initial pH value from 4 – 8 and adsorption time from 1 – 300 min. The equilibrium study generated the maximal adsorption capacity of the system natural zeolite – Co(II) ions with different initial concentrations. MATLAB/Simulink process software was implemented to determine the adequate adsorption isotherm as well as to optimize the steady state of the investigated system. These results were used for further analysis of the kinetics of the studied process.

Key words: *natural zeolite - clinoptilolite, Co(II) ions, adsorption, equilibrium study*

Introduction

The global industrial development requires environmental technologies aimed to reduce environmental impact and increase efficiency. Hence, the problem of modeling environmental processes becomes a big challenge. Today, process simulators are big engines which can be used in each phase of the development of the project, and together with including of the engineer intuition we can get the right solution for one process. During process development, process simulation software is used to perform material and energy balances, estimate the size of equipment, calculate demand for utilities as a function of time, asses the environmental impact, etc.

The methods used for removal of pollutants, especially heavy metals, from water and wastewater include chemical precipitation, ion exchange, solvent extraction, electrolysis, membrane processes, adsorption (1 - 5). Adsorption as one of the most popular and effective method, is widely used in effluent treatment processes. Various materials can been used as adsorbents for the removal of heavy metals from aqueous solutions. A great deal of interest in the research for the removal of heavy metals from water resources has been focused on the use of zeolites (nanoporous materials) as adsorbents (6 - 9). High ion-exchange capacity, high specific surface area and their relatively low cost, make them attractive adsorbents for elimination of heavy metals from water systems.

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 (10). 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.

Many research works have used natural zeolite as an appropriate adsorbent for heavy metals removal (11 - 14). The aim of this article is to investigate the adsorption availability of natural zeolite - clinoptilolite to remove Co(II) ions from aqueous solutions.

Materials and methods

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

Standard solution of cobalt nitrate, $Co(NO_3)_2$ (1 g/dm^3), hydrochloric acid, HCl (0.1 M), sodium hydroxide, NaOH (0.1 M), used in the experiment were analytical grade.

X-Ray Difractometer 6100 from Shimadzu was used to investigate the mineralogical structure of natural zeolite samples.

Batch adsorption experiments were performed to obtain equilibrium data. Standard solution of $Co(NO_3)_2$ with concentration of 1 g/dm^3 was used to prepare solution with different initial Co(II) concentration (350-650µg/dm^3). The effect of the amount of zeolite (0.1, 0.15 and 0.25 g/dm^3) and the influence of pH (4, 6 and 8) were investigated. The initial pH of 4, 6 and 8 were adjusted by adding either 0.1 M HCl or 0.1 M NaOH solutions. The mixture of natural zeolite and Co(II) solution were stirred using magnetic stirrer at 400rpm, at constant room temperature for 5h, sufficient time to reach equilibrium. The samples were taken at particular time, filtered and the remaining concentrations of Co(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 Ridlich - Peterson isotherm, by using MATLAB/Simulink process software.

Results and discussion

Material characterization

The natural zeolite - clinoptilolite used for experimental analysis is in the form of granules and the particle size range was 0.8 - 1.0 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 results of XRD, Figure 1, determine that the sample of natural zeolite contains the major percentage of clinoptilolite .

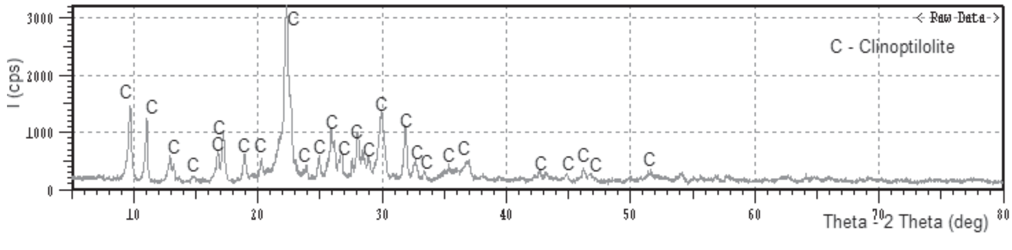

Figure 1. *X–Ray diffraction of natural zeolite*

Adsorption studies

The influence of the initial metal ion concentration, mass of adsorbent and initial pH value of the solution, on the process equilibrium, was investigated.

Effect of initial metal ion concentration

The reduction of the concentration of the Co(II) ions over time at various initial metal concentrations (350, 450, 550 and 650 μg/dm^3) was studied for the system Co(II) - natural zeolite, Figure 2. The experiments were conducted at room temperature at pH of the solution 6, with constant amount of the adsorbent 0.15 g/dm^3, volume of the solution 2 dm^3, at 400 rpm of magnetic stirring.

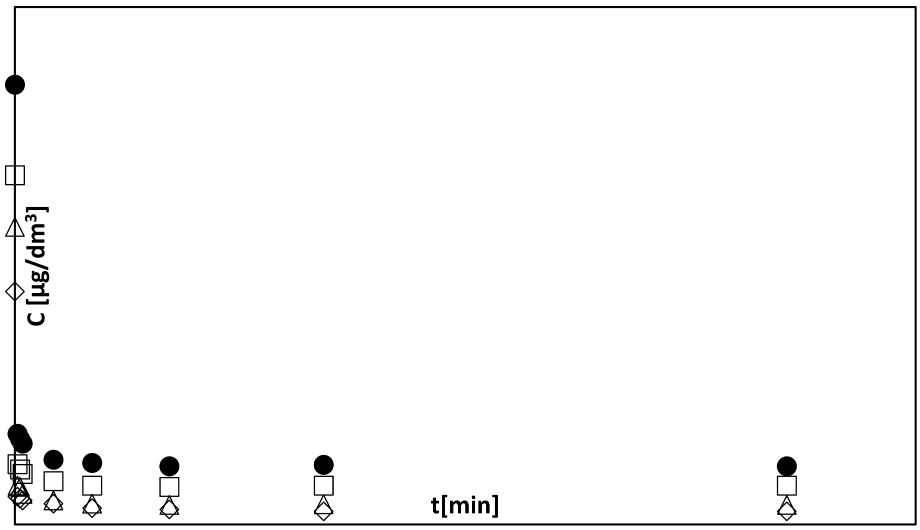

Figure 2. *Adsorbate concentration versus adsorption time for the system Co(II) ions – natural zeolite*

◇ C_0=350 μg/ dm^3 △ C_0=450 μg/dm^3 □ C_0=550 μg/dm^3 ● C_0=650μg/dm^3

The effect of the initial concentration on the percentage of removal is shown in Figure 3. It can be seen from the figure that the removal percentage decreases with the increase in initial Co(II) ions concentration. At lowest initial metal ion concentration of 350 μg/dm^3 the percentage of removal is 97% after which it decreases gradually to 93, 89 and 75% as initial concentration of Co(II) increases at 450, 550 and 650 μg/dm^3, respectively. This happens because at lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption, whereas at higher concentrations, more ions are left un-adsorbed in the solution due to the saturation of the adsorption sites.

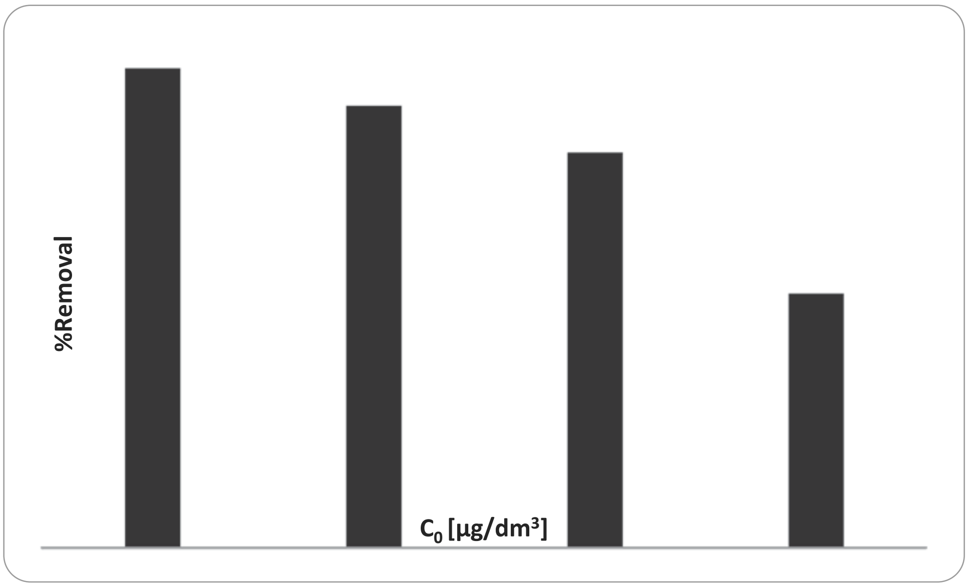

Figure 3. *Function of Co(II) removal from initial concentration*

Effect of amount of adsorbent

The effect of the amount of natural zeolite (0.1, 0.15 and 0.25 g/dm^3) on the removal of Co(II) was investigated at constant value of initial metal concentration of 450 µg/dm^3, at room temperature, pH 6, volume of the solution 2 dm^3, at 400 rpm and is given in Figure 4 and Figure 5. The Figure 4 shows that the amount of Co(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 as a result of aggregation of zeolite particles.

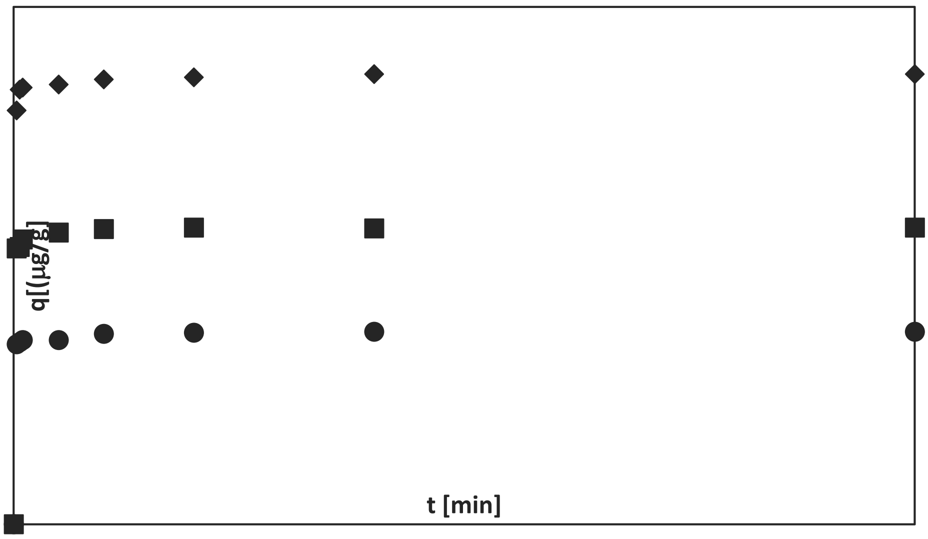

Figure 4. *Experimental equilibrium data for the system Co(II) - natural zeolite*

◆m=0.1 g/dm^3 ■ m= 0.15g/dm^3 ● m=0.25 g/dm^3

As shown in Figure 5, the removal of cobalt increased from 91% at 0.1 g/dm^3 to 93 and 99% at zeolite amount of 0.15 and 0.25 g/dm^3, respectively. However, this result was expected since as the dose of adsorbent increases, the number of adsorbent sites increases too. These amounts attach more ions to their surfaces.

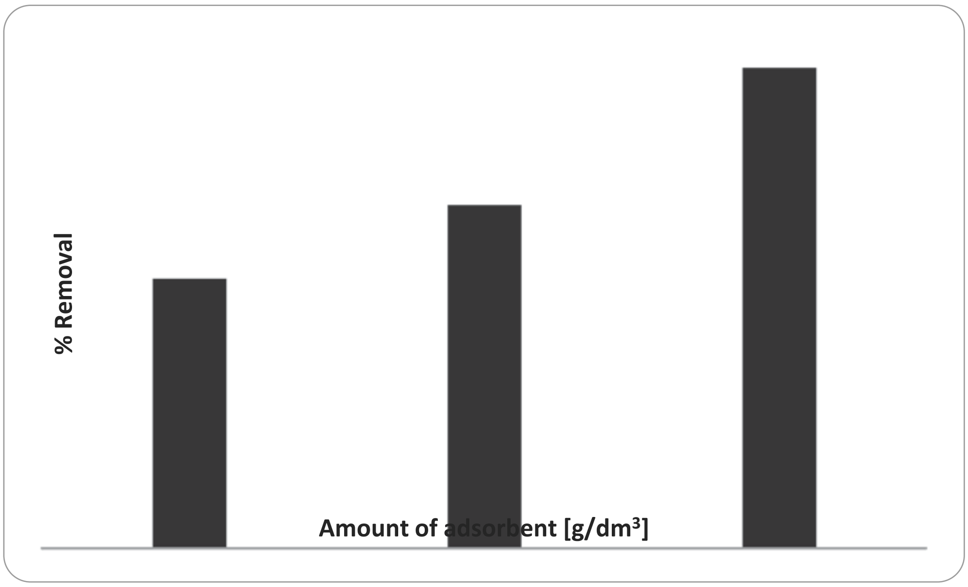

Figure 5. *Function of Co(II) removal from amount of adsorbent*

Effect of pH

The effect of pH on the metal adsorption by clinoptilolite was studied at pH 4, 6 and 8, conducting the experiment at room temperature, with constant value of initial metal concentration of 450 μg/dm^3, constant zeolite amount of 0.15 g/dm^3, volume of the solution 2 dm^3, at 400 rpm. Figure 6 represents the trend in the amount of Ni(II) ions adsorbed in respect of time at different pH of the solution. The effect of the pH on the percentage of removal is given in Figure 7. It is observed that best results for adsorption as well as for the removal of Co(II) ions are obtained at pH 6, which explains way pH 6 is used for other adsorption experiments in this study.

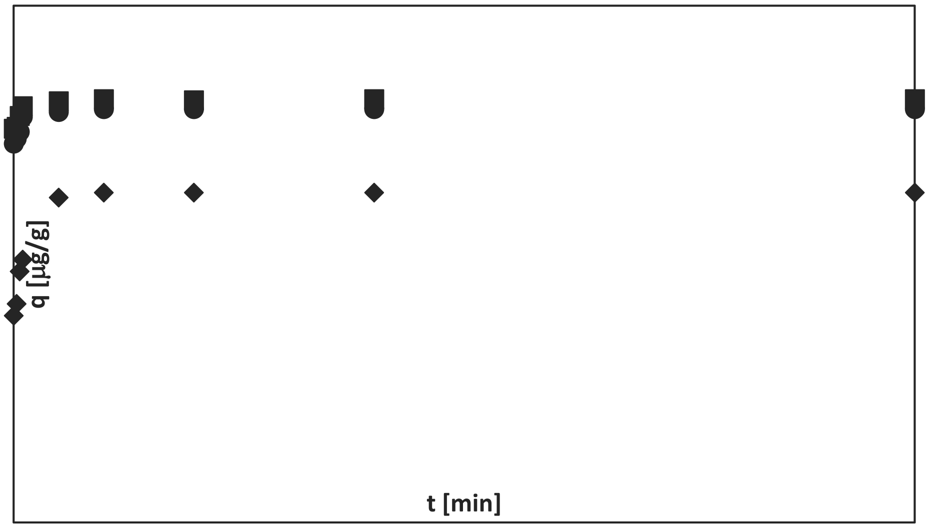

Figure 6. *Experimental equilibrium data for the system Co(II) - natural zeolite*

◆ pH = 4 ■ pH = 6 ● pH = 8

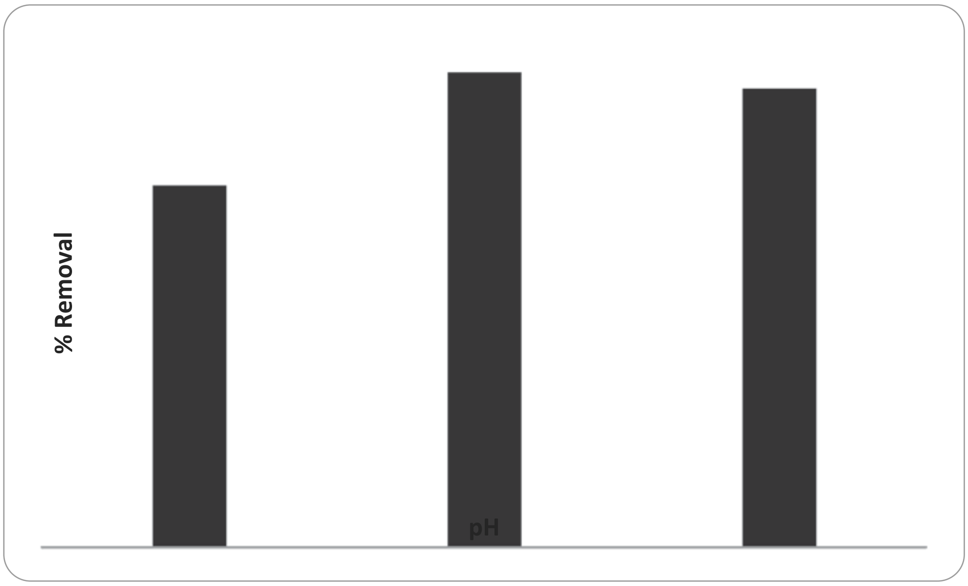

Figure 7. *Function of Co(II) removal from pH of the solution*

Adsorption isotherms

Adsorption isotherms are important for adsorption processes research. Figure 8 shows the plot of adsorbed amount of Co(II) ions at equilibrium versus equilibrium concentrations.

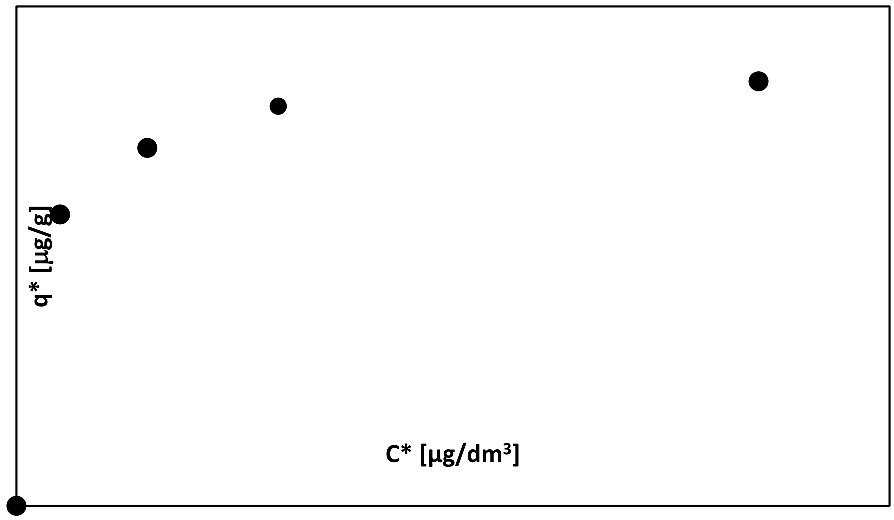

Figure 8. *Experimental adsorption isotherm for the system Co(II) ions - natural zeolite*

Experimental data were processed by the three most commonly used isotherms: Langmuir, Langmuir - Freundlich and Ridlich - Peterson by using MATLAB/Simulink process software. The modeling of the experimental data for the investigated system applying these three models are given in Figure 9.

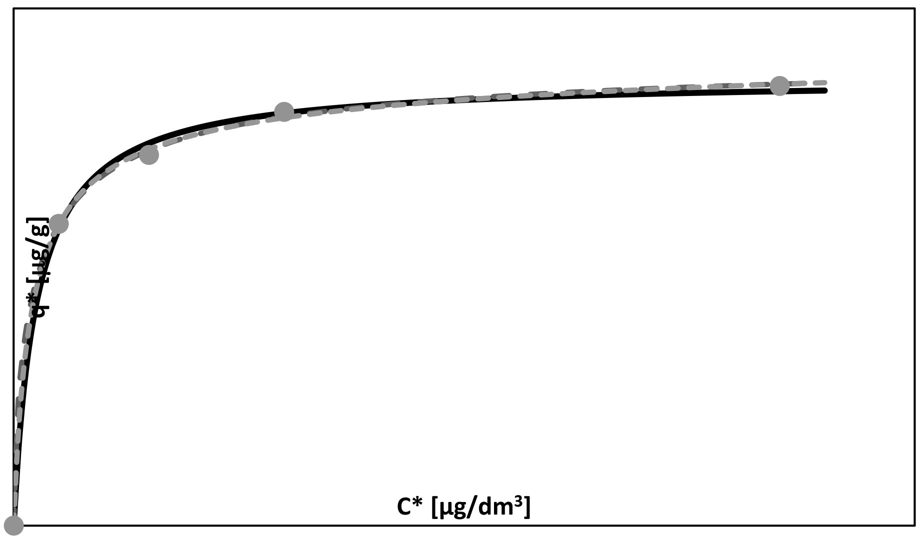

Figure 9. *Modeling of the experimental data for the system Co(II) - natural zeolite*

eksperimentalni podatoci; Langmuir;
Langmuir-Freundlich; Ridlich-Peterson

The data of model parameters of the applied adsorption isotherms for Co(II) ions adsorption on natural zeolite are listed in Table 2.

Table 2. *Model parameters of the applied adsorption isotherms*

	Langmuir	**Langmuir-Freundlich**	**Ridlich-Petrson**
q_m[μg/g]	3459.735	3691.14	
K_L[dm^3/μg]	0.1962		
K_C[dm^3/μg]$^{1/n}$		0.3419	
n		1.433	
A[dm^3/g]			0.3249
K_{RP}[dm^3/μg]$^{1/n}$			919.9
β			0.9593
R^2	0.9984	0.9996	0.9995

The maximum adsorption capacities of natural zeolite for Co(II) removal, determined by Langmuir and Langmuir - Freundlich isotherms are 3460 and 3691 μg/g, respectively. The values of the coefficients of correlation reveal that experimental results better fit with Langmuir - Freundlich and Ridlich - Peterson isotherm models than with Langmuir model.

Conclusion

In this study, the adsorption of Co(II) ions on natural zeolite - clinoptilolite, was investigated. Batch experiments were conducted with aim to find the optimal conditions for maximum removal of Co(II) ions, investigating the effects of the initial concentration of Co(II) ions in the aqueous solution, the dose of the nano-porous adsorbent and the pH of the solution on the adsorbed amount of metal ions and on percentage of removal. Using MATLAB/Simulink process software it was found that experimental results correspond well to the Langmuir - Freundlich and Ridlich - Peterson isotherm models.

The results indicate that the natural zeolite - clinoptilolite has the potential to be applied as an effective adsorbent material for cobalt removal from water resources.

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