

SORPTION OF NICKEL CATIONS FROM THE WATER ENVIRONMENT ON THE CLINOPTILOLITE

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One of the world's biggest problems is the lack of drinking water. The most effective methods are sought for water treatment. The latest methods include sorption on the solid layer. In order to design the arrangement of the cleaning process, it is necessary to know the adsorption isotherm and the kinetic course of sorption. The article contains laboratory experiments designed to determine the sorption parameters of nickel cations sorption on natural zeolite - clinoptilolite, which is a low cost and environmentally friendly sorption material.

KEYWORDS

clinoptilolite, nickel, sorption, isotherm, kinetic, wastewater

1 INTRODUCTION

Methods as chemical precipitation, coagulation, ion exchange, liquid extraction, membran processes, reversible osmosis are the usual methods using at waste water cleaning contaminated by heavy metals. Some disabilities of them is high price, the need for a continuous supply of chemicals, toxic bilge water production. One of the waste water cleaning methods is biosorption, where brown algae (Sargassum) are used as adsorbent [Abu Al-Rub 2004]. Waste water contaminated with toxic metals can be purified by precipitation of metal ions from alkaline solutions containing divalent Fe to form ferrites [Alvarez 2003, Novakova-Marcincinova L. 2013, Balara 2018, Zaborowski 2007, Monkova 2013, Prislupcak 2014, Prislupcak 2016, Ragan 2012, Rimar 2016, Straka 2013, Panda 2013, Panda 2014, Panda 2016, Jurko 2011, Jurko 2016]. Another way of purifying wastewater is to use the ion exchange. Ion exchangers are inorganic or organic polyelectrolytes practically insoluble in water and in conventional solvents. Depending on their functional capabilities, they are divided into anion exchangers - cation anions and cation exchangers cations. In the purification of water mainly the synthetic ion exchangers are used, which are characterized by high capacity, sufficient chemical and mechanical resistance, by regulated grain processing during production and also by the possibility of introducing of various functional groups into the basic structure, so that the ion exchangers can be selective for certain ions [Sabova 2010].

2 THE SORBENTS UTILIZATION IN THE WASTEWATER PURIFICATION

Application of synthetic zeolites in industrial practice is limited their high price. Therefore big attention present to natural zeolite, as clinoptilolite, which has selective properties in consideration of cations some metals. Applications of the natural zeolites result from their specific physical-chemical facilities as ion - exchangeable properties, sorption and facilities

of molecular sites, dehydration and hydration and also by herself silicate structure and micron measurements quartz with very active measuring surface [Van Bekkum 2001]. There, where the claim specific crystallographic structural arrangement of zeolite is desired and tall purity the synthetic zeolites find application. Exemplify the catalytic, sorptive may be introduced and gridlines purposes at some branch of petrochemical industry and at organic synthesis. Natural zeolites are hydrated aluminosilicates characterized by their ability to adsorb heavy metals from aqueous solutions. In addition to chemisorption, the metal ions on the zeolite are also immobilized by an ion Exchange [Sabova 2010, Chmielewska 2010, Bailey 1999,]. The lattice structure allows the zeolite to act as ion exchange and selective adsorbent. Adsorption and ion exchange depend on their charge and size. The more the ion size coincides with the size of the input pores in the clinoptilolite grid, the easier it will be captured and maintained. The inlet pore diameter is 0.4 nm. Natural zeolites as minerals found in cavities of volcanic rocks have been known for more than 200 years. They were, however, considered more or less a mineralogical rarity without practical importance. Only after introduction of modern identification mineralogical methods, such as X-ray diffraction analysis and scanning microscopy, it was possible to determine the crystallographic arrangement of zeolites. The basic units of the hydrated aluminum silicate structure of zeolite minerals are $(\text{SiO}_4)^{4-}$ and $(\text{AlO}_4)^{5-}$ tetraheders linked together by oxygen atoms [Barloková 2014]. This gives rise to cavities in their crystalline structure interconnected with channels containing alkali metal and alkaline earth metal cations surrounded with molecules of water. Natural zeolites, due to their specific physical and chemical properties, are used as raw materials in various industries, in environmental protection and agriculture. The most frequently by applicable natural zeolite, including in the environmental area include clinoptilolite. Topology of the clinoptilolite is made up of 4 to 5 membered rings of tetrahedrons in parallel layers, which form right angles to each 8 to 10 ring members of tetrahedrons. In terms of IUPAC and IZA nomenclature, clinoptilolite is the structural type heulandite (HEU). Periodicity HEU zeolite structure is created according to the latest classification of construction IZA T9 units.

The adsorption process is used to remove a wide range of organic and inorganic substances from contaminated water. It is most often used as a secondary or tertiary level of contaminated water treatment for the final cleaning of contaminated water. The gradual development and improvement of the adsorbent preparation technology has gradually increased their quality, in particular the sorption capacity, the specific surface, the abrasion resistance, the regeneration capacity or the selectivity in relation to certain types of contaminants. The adsorption process is based on the action of various types of forces on the phase interface resulting in the concentration of some components on the interface.

Adsorption is affected by many factors.

The most important thing is to be included:

- the size and character of the surface of the adsorbent,
- characteristics of the adsorbate (charge, size, molecular weight,
- concentration / activity of the adsorbate,

3 EXPERIMENTAL

The aim of this work was to study the removal of the nickel ions from the solutions by sorption on zeolites. The equilibrium

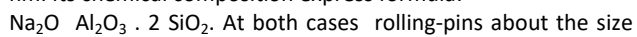
isotherm and adsorption kinetics are the most commonly used data.

4 MATERIAL AND METHODS

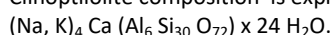
For experimental studies we used synthetic and natural zeolites, calsite, nalsite and clinoptilolite. Calsite is synthetic zeolite 5A type with size of the porous 0,5 nm. Its chemical composition express formula:



Nalsite is synthetic zeolite 4A type with size of the porous 0,4 nm. Its chemical composition express formula:



At both cases rolling-pins about the size 3,0 mm were testing. As natural zeolite was used clinoptilolite potassium-calcification type with the grain size 2,5 – 5 mm. Clinoptilolite composition is expression by formula:



Physical- chemical characteristics of the synthetic zeolites are placed in the table 1 [Čejka 2000].

Table 1. Physical-chemical characteristics of synthetic zeolites

Charakteristic	Nalsite	Calsite
Type	4 A	5 A
Modul	1,9 – 2,1	1,9 – 2,1
SiO ₂ : Al ₂ O ₃		
Efective porous diameter [nm]	0,4	0,5
Prevailing cation	Na ⁺	Ca ²⁺
The equilibrium adsorption capacity for water at 25 °C, (g/100g ads.),	19	18
Rate of exchange prevailing cation (%)	90 - 100	70 - 80

From a toxicological point of view, nickel is classified as a major poison. Acute poisoning causes damage to the digestive tract, vessels, kidneys and heart. As a result, the limit for this element was set for both drinking and waste water (Table 2).

Table 2. Limit values of the nickel cations in water

Cations	Concentration (wastewater)	Concentration (drinking water)
Ni ⁺²	1 mg · dm ⁻³	0,02 mg · dm ⁻³

For the analysis of the equilibrium experimental data for adsorption, the Langmuir or Freundlich isothermal model is used. The isothermal Langmuir model is based on the assumption that the surface areas of the adsorbent are homogeneous and that the maximum of adsorption is limited to covering the surface of the monolayer while the Freundlich isothermal model is based on the assumption of heterogeneous surface areas and multilayer surface coverage. The Freundlich isotherm assumes that the adsorbate concentration on the surface of the adsorbent increases with the increase in the adsorbate concentration [Inglezakis 2002, Korkmaz 2012, Chmielewska 2008].

5 RESULTS AND DISCUSSION

An important feature of the zeolite minerals is their ability to sorption. The aim of this work was to study the acquisition of

nickel ions from solutions by sorption on zeolite. The experiments were aimed at removing nickel ions from model solutions. In our experiments, we used the method of static sorption. The kinetic course of sorption was observed on the natural zeolite of clinoptilolite and on the two synthetic zeolites calsite and nalsite. At regular intervals, during the sorption, a change in the concentration of nickel cations in the solutions was recorded until the system reached the equilibrium state. For the experiments we used a model sample with a content of nickel ions of 1,93 g·dm⁻³. The experiments were performed at the same time on all three sorbents at temperature 24°C. Analytical determination of the concentration of nickel ions was performed by spectrophotometry. The results at the individual time intervals are shown in the table 3.

Table 3. Kinetic course of the sorption

Time [min.]	60	120	180	240
	nickel concentration [g · dm ³]	nickel concentration [g · dm ³]	nickel concentration [g · dm ³]	nickel concentration [g · dm ³]
Calsite	0,03	0,1	0	
Nalsite	0,01	0		
Clinoptilolite	1,5	1,4	1,1	1,1

In the course of the second hour of nickel cations solution treatment on nalsite, a zero value of nickel cations was achieved. The calsite occurred during the third hour. By clinoptilolite the equilibrium state was achieved to a level of 1,1 g·dm⁻³ over a third hour. In other experiments, clinoptilolite was tested for its potential for use in reducing nickel cations in water. We used clinoptilolite with a grain size of 2.5 - 5 mm. We studied the adsorption isotherm at 24 ° C. For this we used model samples of nickel cations with an initial nickel concentration of C₀ 2.1 g·dm⁻³, 1.93 g · dm⁻³ and 6.6 g · dm⁻³.

To determine the time required to achieve equilibrium in the system, we monitored the dependence of the adsorbed amount from the time of contact of the sorbent with the adsorbate. The results were graphically processed using adsorption isotherms and mathematically evaluated using Freundlich adsorption isotherm.

The equilibrium concentration value for aqueous solutions depends on the properties of the sorbent used. Different values of equilibrium concentrations are obtained for different initial concentrations of solute and different sorbent quantities.

Based on the measured values of the monitored parameters we have constructed an adsorption isotherm. The amount of nickel cations absorbed to clinoptilolite was calculated according to equation (1) as the difference between the initial concentration c₀ and the concentration in solution at the equilibrium state c_r, where a is the sorption capacity [mg · g⁻¹], V is the volume of the solution and m expresses the sorbent weight [Inglezakis 2002]. Measured and calculated values are placed in the table 4.

$$a = (c_0 - c_r / m) \cdot V \quad (5.1)$$

Table 4. Measured and calculated parameters

c ₀ [g · dm ⁻³]	c _r [g · dm ⁻³]	a [g · g ⁻¹]
6,6	1,21	0,033
2,1	0,5	0,02
1,9	0,3	0,01

The most commonly used quantitative sorption marker is the K_D partition coefficient, which is defined as the proportion of the sorbed amount of the cations to be examined in the fat matrix (sorber) to their concentration in the aqueous solution during the equilibrium state. The significance of detecting the partition coefficients is that they are the basic input data in the mathematical models of transport of the monitored substances in the waters. The equilibrium concentration of nickel cations in the aqueous solution was determined by the spectrophotometry method. From the difference of the known initial and equilibrium concentration (C_0 and C_r ($\text{mg}\cdot\text{dm}^{-3}$)) in the aqueous solution, the sorbed quantity of nickel ions (C_s [$\text{mg}\cdot\text{g}^{-1}$]) was calculated. The table 5 states the partition coefficients.

Table 5. Calculated partition coefficients

c_s [$\text{g}\cdot\text{dm}^{-3}$]	c_r [$\text{g}\cdot\text{dm}^{-3}$]	K_D
5,4	1,2	4,4
1,6	1,3	1,2
1,0	0,9	1,1

The quantitative distribution parameter of the substance between the solid and the liquid phase is the K_D partition coefficient [Korkmaz 2012].

$$K_D = c_s/c_r \quad (5.2)$$

For the analysis of the equilibrium experimental data for adsorption, the Langmuir or Freundlich isothermal model is used.

The isothermal Langmuir model is based on the assumption that the surface areas of the adsorbent are homogeneous and that the maximum of adsorption is limited to covering the surface of the monolayer while the Freundlich isothermal model is based on the assumption of heterogeneous surface areas and multilayer surface coverage. The Freundlich isotherm assumes that the adsorbate concentration on the surface of the adsorbent increases with the increase in the adsorbate concentration [Chmielewska 2008]. Assuming adsorption on a non-homogeneous adsorption surface, a Freundlich adsorption isotherm is used in shape [Chmielewska 2008, Bailey 1999, Chiou 1998, Sabova 2010, Pitter 1983].

$$a = K \cdot c_r^{1/n}$$

where K and n are Freundlich constant, which indicate the adsorption capacity of the adsorbent and the adsorbent affinity of adsorbate. On the base measured and calculated values the adsorption isotherm was constructed (Fig. 1).

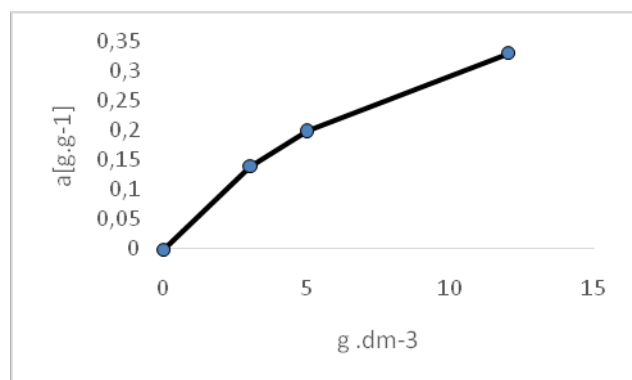


Figure 1. Sorption isotherm for sorption of nickel cations from solutions to clinoptilolite

Freundlich constants we obtained from the linearized Freundlich equation.

$$\log a = \log K + 1/n \log c_r$$

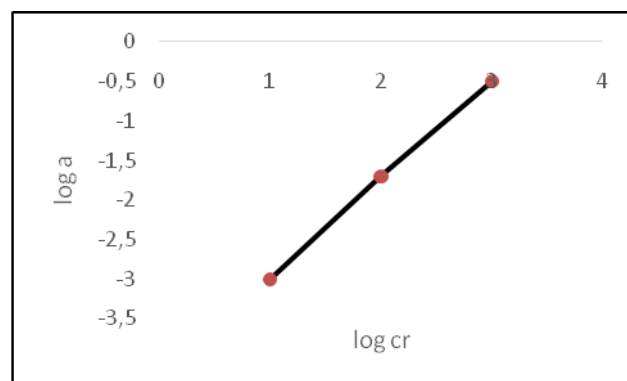


Fig. 2. Linearization of the isotherm

After the logarithm Freundlich isotherm, we translate the line with the experimental values plotted in $\log c_r$ and $\log a$. The Freundlich isotherm constants were calculated using the smallest squares method. In this way, we have reached the value of the constants $k = 0,072$ and $q = 2,2$. Based on these values we calculated the Freundlich constant $K = 1.99$.

Therefore the isotherm measured by us has taken shape $a = 1,99 c_r^{0,07}$.

6 CONCLUSION

Due to good availability and the low cost of its extraction, natural zeolites are still profitable and their mining has great potential in the future. There are still some reserves in their use for environmental protection. Ion exchange-sorption technology on clinoptilolite has the advantage of more distinctive selective properties and pricelessness compared to synthetic zeolites (cationites). These properties predetermine it for sewage treatment.

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