SORPTION CHARACTERISTICS OF COOPER SORPTION ON THE CLINOPTILOLITE MEASUREMENT

IVETA PANDOVA, PETER ORAVEC, DARINA MATISKOVA

Technical University of Kosice

Faculty of Manufacturing Technologies with a seat in Presov
Presov, Slovak Republic

Natural zeolite has found important uses in environmental protection and water treatment.In term of chemical, the zeolites belongs to hydrate aluminosilicates and against the their structure they have unique physical-chemical properties. This atribute affords the zeolites utilisation at water cleaning from metal ions. The most offen method of removing metals from solutions is precipitation, which is particularly effective at higher concentrations. In this way, but it is not always possible to reach limits that are set by law and therefore the use of zeolite is an appropriate way to final purification waste water after processing, for example. precipitation. Adsorption is among the most used and most economical method for removing cationic and anionic pollution. The possibility to use zeolites for this purpose, desirable attributes, such as high ion exchange capacity, good kinetics of ion exchange and sorption at low temperature, non-toxicity, resistance to aggressive media. Contents of this paper are the results of research on natural zeolite - clinoptilolite originating from the site in NižnýHrabovec, due to the sorption of coppercations.

KEYWORDS

clinoptilolite, cooper, sorption, waste water

1 INTRODUCTION

The sources of toxic metals that enter into water are various human activities, such as operations in the automotive industry, engineering industry, mining and processing of ores, textileindustry, waste production [Panda 2014a, Panda 2016b, Panda 2016c, Prislupcak 2016, Rimar 2016, Straka 2013, Zelenak 2012, Olejarova 2016, Zaborowski 2007]. Many methods are used to reduce the metallic element in water, such as oxidation, reduction, chemical precipitation. Progress in science and technology is also evident in the field of water protection as modern, economically viable and environmentally acceptable cleaning processes and materials such as carbonaceous materials, dendrimers and zeolites are developed[Van Bekkum 2001]. All of them have very varied physicochemical properties which are particularly suitable for separating pollutants from water. Very promising for cleaning processes are specific nanometric nanomaterials applied as membranes or other structured materials [Lehman 2014]. These substances have a higher adsorption surface and may be modified by, for example, incorporating specific functional groups into a carrier. Natural zeolites also belong to such materials.

2 ZEOLITE PROPERTIES

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, Macala 2017]. 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, which corresponds to the ammonium ions of NH_4^+, H_2O, ^{134}Cs and ^{137}Cs. These substances have the greatest affinity for binding to clinoptilolite but which act as a selective adsorbent for a wide range of pollutants. As in other microporous materials, as well as in zeolites, the ion exchange sorption between the components of the liquid and solid phases is carried out according to the surface diffusion and the internal diffusion mechanism [Chmielewska 2014, Qiu 2009].

An important mineralogical and chemical parameter of each zeolite is the Si / Al ratio. This value indicates the acidity and alkalinity of the zeolites and also their thermal and chemical stability. Zeolites with a higher Si / Al ratio are more acidic and more stable. The thermal stability limits differ from the different types of zeolites. In addition to the Si / Al ratio, this is also affected by the cationic composition.Surface and ion exchange properties of natural zeolites can be influenced by structural modification. Dealumination is followed by modifying the zeolites by removing aluminum from the tetrahedral coordination of the zeolite grid, increasing the proportion of silicon to aluminum. For organic sorption, sorbent with a higher content of silicon, a sorbent with higher acidity, is more suitable. The action of dilute acids results in partial dealumination and alkali leaching, thereby increasing the number of active centers. This modification of the natural zeolites is carried out under conditions in which the zeolite is not destroyed. The possibility of improving the sorption properties of the zeolites is thus observed [Celiscev 1987].

The action of dilute mineral acids leads to two stages of acid decatisation. The first step is the exchange of ions expressible by the following equation:

$$M^+[AlO_2]^-_x(SiO_2)_n]^x + x[H_2O+H^+] \rightarrow [(H_3O)^+_x (AlO_2)_x (SiO_2)_{n-x}]^x+$$

$$^- + xM^+ \quad (2.1)$$
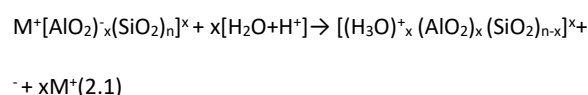
In the second stage, the dealumination is represented by the equation:

$$[(AlOOH)_x(SiO_2)_{n-x}]+3xH^+ \rightarrow [(H_4O_2)_x(SiO_2)_{n-x}]+xAl^{3+} \quad (2.2)$$
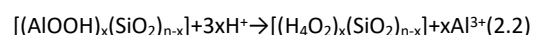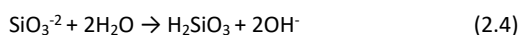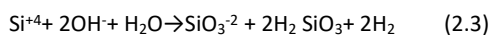
One of the other ways of modifying zeolites is boranation. The boranation is due to the fact that B_2H_6 has an electron deficit and the zeolite in its structure contains sites with increased

electron density. The most reactive sites in the H zeolite structure are:

a) hydroxyl group Si-O-H,

b) Si-O-Si oxygen bridges where oxygen has a high electron density.

Synthetic zeolites are produced as a primary product in the sodium form. Natural zeolite monoole sodium forms can be prepared by treatment with NaOH on the zeolite. Modification of the structure of the zeolites is based on the action of certain chemical solutions on the crystalline lattice of the zeolite. By diluting the alkali hydroxides, silicon is extracted from the structure of the zeolite. Depending on the concentration of the hydroxide-modifying solution, the surface or even internal pores of the zeolite may be partially altered. This change is based on the fact that silicon, which is part of the crystal lattice of clinoptilolite, reacts with the anions (OH) - which are formed by the equations [Főldesová 2003, Főldesová 2007]:

$$Si^{+4} + 2OH^- + H_2O \rightarrow SiO_3^{-2} + 2H_2 \ SiO_3 + 2H_2 \qquad (2.3)$$

$$SiO_3^{-2} + 2H_2O \rightarrow H_2SiO_3 + 2OH^- \qquad (2.4)$$

Silicon is passed into the solution in the form of soluble silicic acid.In the clinoptilolite increases the proportion of aluminum, and silicate extraction results in a new mesopore structure. At the same time ion exchange of cationic compensating cations in the original clinoptilolite (K^+, Ca^{2+}, Mg^{2+}) takes place under sodium cations. Monocatonic Na^+ form zeolite is formation.

3 EXPERIMENTAL

To observe the sorption kinetics, the natural zeolite clinoptilolite with the granuality 2,5 to 5 mm, weighing 30 g, was washed with deionized water and treated in to the mono-ion form with NaOH. This was covered by a model sample of copper cations with a volume of 0,20 dm³. The model sample contained copper cations with an initial concentration of 2,4 g·dm⁻³. At the exact time intervals, the same volume was taken from the model sample during the treatment with clinoptilolite, in which the content of copper cations was determined photometrically. When contacting the solid phase with the solution, the original copper concentration dropped to 0,95 g·dm⁻³. Measurement proceeded until equilibrium was reached. At the equilibrium state after the third hour, the concentration of copper cations in the solution was reduced to 0,95 g · dm⁻³. When measuring the copper cation adsorption to clinoptilolite, the values given in the Table no. 1.

t [min]	60	120	180	240
c [g·dm⁻³]	1,20	1,016	0,95	0,95

Table 1. Dependence of copper concentration in solution on time during sorption

The efficiency of clinoptilolite with respect to the copper cations reduction, was calculated according to formula (3.1), its value being 60,4%. The sorption capacity calculated according to (3.2) [Sabová 2010, Inglezakis 2002]was 9,7 mg · dm⁻³.

$$\eta = (c_0 - c_r / c_0) \cdot 100 \ (\%) \qquad (3.1)$$

$$a_0 = (c_0 - c_r / m) \cdot V \qquad (3.2)$$

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

$$K_R = c_S/c_r. \qquad (3.3)$$

The value of this parameter was 1,5.

The kinetic course of sorption is illustrated graphically in Figure 1.
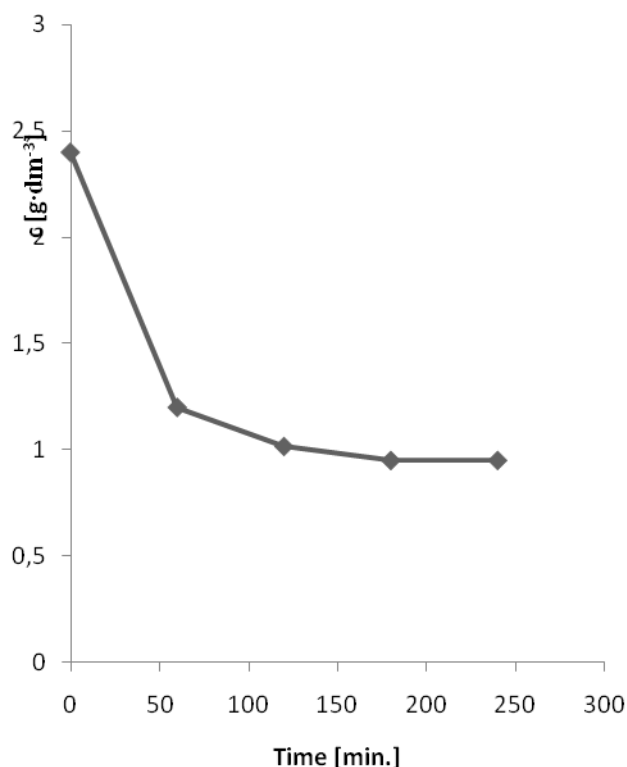

Figure 1. Dependence of copper cation sorption over time

Assuming adsorption takes place according to the Langmire mechanism, andthat the sorbed material is sorbed by molecular diffusion on the surface of the adsorbent, the concentration of the adsorbed substance at time t can be expressed by the equation [Pitter 1983]:

$$c = \frac{\lambda c_r - \beta e^{\overline{\rho t}}}{\lambda - e^{-\overline{\rho t}}} \qquad (3.4)$$

For the search relation c = f (t) we calculate the constants of equation (3,1) λ, β, ρ of the measured concentration values for individual time intervals.

According to equation (3,2)for the experimental values of concentration, the constant ρ and the average of the experimental values were calculated:

$$\overline{\rho} = \tfrac{1}{t}\ln\frac{(c_0 - c_r)(c - \beta)}{(c_0 - \beta)(c - c_r)} \qquad (3.5)$$

Measured and calculated ρ datas are listed in Table 2.

t [min]	c [g·dm⁻³]	ρ [min⁻¹]	c_v [g·dm⁻³]
60	1,20	0,02	2,3
120	1, 016	0,01	2,1
180	0,95	0,01	1,03
240	0,95	0,01	1,03
		ρ average 0,01	

Table 2. Values needed to calculate the equation constants

4 CONCLUSION

From the measured values we have calculated individual values ρ and ρ average for individual measurements according to equation (3,5). If the assumption is that the adsorbed material gets molecular diffusion on the surface of the adsorbent then the ρ values for all measured datas c (t) have approximately the same values, which is also confirmed.

Measured average value ρ average = 0,01min⁻¹.Search equation c = f(t) is then according to equation (3,4) using the calculated constants:

$$c_v = 0,95\,\lambda - 3,3\cdot e^{-0,01\,t} / \lambda - e^{-0,01}. \qquad (4.1)$$

Frequent methods of metals removing from solutions, such as precipitation processes, are effective especially at higher concentrations. In such a way, it is not always possible to achieve the limits set by law, and therefore the use of zeolite appears to be a suitable method for purifying waste water after treatment, e.g. precipitation. Natural zeolites are also more cost-effective than synthetic ion exchangers. The efficiency of natural zeolites as sorbents and ion exchangers as well as sorption capacity are influenced by modification.

At present, the annual world production of natural zeolite is about 3 million tons. Due to its 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.

REFERENCES

[Bailey 1999] Bailey, S.E. et al. A review of potentially low – cost sorbents for heavy metals. Water Research, 33, 1999, No. 11, p. 2469 – 2479.

[Celiscev 1987] Celiscev, N. F., Berenstein B. G., Volodin B. F. Zeolites – new type of minerals, NEDRA, Moskva, 1987.

[Foldesova 2003] Foldesova, M., Dillinger, P., Lukac, P., Svetik, S. Influenceof the calcination and chemical modificationon the natural zeolites structure. (In Slovak), Booklet of XVI. Conference on Thermal Analysis and Calorimetry TERMANAL 2003, PO-6, Stara Lesna, SR, oktober 2003.

[Foldesova 2007] Foldesova, M., Hudec ,P. Study of surface properties of Slovak natural zeolite – clinoptilolite by physicaladsorption of nitrogen. (In Slovak), In Petroleum & Coal 49(1), 34-40, 2007 .

[Frolov 1981] Frolov, J. G., Balajan, G. S., Nazarov, V. V. Koloid. z., 43, 726 (1981).

[Chmielewska 2008] Chmielewska, E., Sabova, L., Gaplovska, K. &Caplovicova, M., 2008: Functionally graded mesoporous zeolitic adsorbents in order to promote the pollutants removal, Kuwait. J. Sci. Eng. 35, 1 – 15.

[Chmielewska 2010] Chmielewska, E. Surface functionalized adsorbents based on natural zeolite. In: Mineralia Slovaca, 42 (2010), 467 – 472ISSN 0369-2086.

[Chmielewska 2014] Chmielewska, E. Natural resources to protect the environment. UK v Bratislave, Bratislava 2014.

[Inglezakis 2002] Inglezakis, V. J., Loizidou, M. D., Grigoropoulou, H. P. Equilibrium and kinetic ion exchange studies of Pb2+, Cr3+,Fe3+ and Cu2+ on natural clinoptilolite, Water Research 36 (2002) 2784–2792.

[Khunova 2007] Khunova, V. Polymer nanocomposites. (Polymerne nanokompozity). In: revealed the secrets of chemistry (Odhalene tajomstva chemie), Vyd. SAV VEDA, Bratislava (2007)

[Korkmaz 2012] Korkmaz, M., Ozmetin, C., Ozmetin, E. Copper sorption by clinoptilolite: Equilibrium and thermodynamic investigation.16-th international Water Technology Conference, IWTC 16, 2012, Istanbul, Turkey

[Pitter 1983] Pitter, P., Tucek, F., Chudoba, J., Zacek, I. et al. Laboratory methods in water technology. (In Czech) SNTL Alfa, Praha (1983).

[Lehman 2014] Lehman, S., Sarah, C., Larsen, S., C. Zeolite and mesoporous silica nanomaterials, greenersyntheses, environmentalapplications and biological toxicity ,*Environ. Sci.: Nano*,**1,** 200-213, 2014.

[Macala 2017] Macala, J., Pandova, I., Panda, A. Zeolite as a prospective material for the purification of automobile exhaust gases. In: Gospodarka Surowcami Mineralnymi, 2017, Vol. 33, p.125-138. ISSN 0860-0953

[Olejarova 2016] Olejarová, S., Krehel, R., Pollak, M., Kocisko, M. Research on impacts of mechanical vibrations on the production machine to its rate of change of technical state. In: Advances in mechanical engineering. Vol. 8, no. 7, 2016, p. 1-10. - ISSN 1687-8140.

[Panda 2014a] Panda, A., Duplak, J. Comparsion of Theory and Practice in Analytical Expression of Cutting Tools Durability for Potential Use at Manufacturing of Bearings. In: Applied Mechanics and Materials. 2014, Vol. 616 (2014), p. 300-307. ISSN 1660-9336

[Panda 2016b] Panda, A., Jurko, J., Pandova, I. Monitoring and Evaluation of Production Processes. An Analysis of the Automotive Industry. Monograph, Springer International Publishing, Switzerland, 2016, (8.4.2016), 117 pages, ISBN 978-3-319-29441-4

[Panda 2016c] Panda, A., Jurko, J., Valicek, J., Harnicarova, M., Pandova, I. Study on controller bearing surface roughness improvement and the effect of surface roughness on tape red roller bearing service life. In: The International Journal of

Advanced Manufacturing Technology. Springer London Ltd, pp. 1099-1106, Volume 82, Issue 5-8, 2016, ISSN 0268-3768

[Prislupcak 2016] Prislupcak, M., Panda, A. Comparsion and Analysis of the flow Rate. In: Key Engineering Materials. 2016, Vols. 663-696 (2016), p. 197-204. ISSN 1013-9826

[Qiu 2009] Qiu, W., Zheng, Y. Removal of lead, copper, nickel, cobalt, and zinc from water by a cancrinite-type zeolite synthesized from fly ash. Chemical Engineering Journal, Vol.145, No.3, 483-488, 2009.

[Ragan 2012] Ragan, E., Dobransky, J., Baron, P., Kocisko, M., Svetlik, J. Dynamic of taking out molding parts at injection molding. Metallurgy No.4/2012, vol.51, Zagreb, Croatia, Croatian Metallurgical Society, 567-570 p.

[Rimar 2016] Rimar, M., Smeringai, P., Fedak, M., Kuna, S. Technical and software equipment for the real time positioning control system in mechatronic systems with pneumatic artificial muscles. In: Key Engineering Materials, Operation and Diagnostics of Machines and Production Systems Operational States 3. Vol. 669 (2016), p. 361-369. ISSN 1662-9795

[Sabova 2010] Sabova, L., Chmielewska, E., Gaplovska, K. Preparation and utilization of combined adsorbents on zeolite base for removal of the oxyanion pollutants from water. Chem.Listy 104, 243 – 250 (2010).

[Straka 2013] Straka, L., Corny, I., Krehel, R. Evaluation of Capability of Measuring Device on the Basis of Diagnostics. In: Applied Mechanics and Materials, Trans Tech Publications, Zurich, Switzerland, vol. 308, 2013, p. 69-74.

[Valicek 2016] Valicek, J., Harnicarova, M., Panda, A. Mechanism of Creating the Topography of an Abrasive Water Jet Cut Surface. In: Advanced Structured Materials. 2016, Vol. 61 (2016), p. 111-120. ISSN 1869-8433.

[Van Bekkum 2001] Van Bekkum, H., Flanigen, E. M., Jansen, J. C. ed.: Introduction to Zeolite science and Practice. Elsevier Science Publishers, Amsterdam, 2001.

[Vitikac 2016] Vitikac, P., Bateskova, E., Panda, A. Elimination of pressure cylinder deflection on two cylinder bending machine. In: Key Engineering Materials. 2016, Vols. 663-696 (2016), p. 253-261. ISSN 1013-9826

[Zaborowski 2007] Zaborowski, Ekowytwarzanie. Gorzow, pp.100

[Zelenak 2012] Zelenak, M. et al. Comparison of mechanical properties of surface layers with use of nanoindentation and microindentation tests. Metalurgija, 2012, Vol. 51, pp 309-312, ISSN 0543-5846

CONTACTS:

RNDr. Iveta Pandova, PhD.
Technical University Kosice with seat in Presov
FVT, Department of Manufacturing Technologies
Bayerova 1, Presov, 080 01, Slovak Republic
e-mail: iveta.pandova@tuke.sk