MANUFACTURING TECHNOLOGIES IN AUTOMOTIVE PRODUCTION AND WASTE WATER CLEANING ON ZEOLITE IN VIEW OF COPPER

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Industrial development in the 20th century brought environmental pollution, which includes also the water. Industrial activity, especially metallurgical and engineering industry brings pollution by heavy metals. These substances act on living organisms toxic, therefore the individual components of the environment are strictly monitored. Current research of heavy metals removal is intended for the use of low-cost methods such as the sorption on natural materials, as zeolites, and also their use as ion-exchangers. The paper presents research results of sorption properties of natural zeolite - clinoptilolite considering sorption of copper cations.

KEYWORDS
waste water, toxical metals, sorbents, zeolite, clinoptilolite

1 INTRODUCTION

The increasing contamination of aquatic ecosystems, the various forms of pollution is one of the key environmental challenges of our time. More than a third of freshwater reserves on earth is used for a variety of human activities, most of which causes water pollution in different foreign substances. Pollutants in an aqueous environment may receive a variety of ways. Most often, the pollution of aquatic ecosystems associated with the outlet of waste or process water from industrial plants. Despite significant technological advances and increasingly sophisticated approaches wastewater treatment and intensive monitoring of pollution sources to aquatic ecosystems are constantly under pressure pollutants of various types and origin. Insufficiently treated waste water bring to the surface and ground water with a substance of organic origin and also inorganic origin, such as heavy metals.In 2000 year, by the EU Framework Directive was acceptared 2000/60/EC, which provides a legal framework to protect and restore clean water across Europe. The Directive provides an innovative approach to water management, which is based on river basins, the natural geographical and hydrological units and sets specific deadlines for Member States to achieve the environmental objectives for aquatic ecosystems [Directive 2000/60/ES 2000]. The directive applies to inland surface water, groundwater, transitional and coastal waters. Decision 2455/2001/EC was acceptared list of priority substances to be monitored in the waters. The list shall also include heavy metals such as cadmium, mercury, copper, nickel, lead and others. Heavy metals and their compounds threaten the environment with no hope of them break down naturally. Some of them, such as copper, is in micro concentrations essential for life but in higher concentrations cause serious health problems. Conventional technology for the removal and elimination of heavy metals from waste water is e.g. chemical precipitation of metal, coprecipitation, filtration, membrane technologies, sorption, electrolysis, ion exchange, reverse osmosis, electrochemical process, metal evaporation, and others [Kubiniova 2000, Inglezakis 2002, Matiskova 2012, Flimel 2014, Chmielewska 2010, Panda 2011, Panda 2013, Panda 2016, Prislupcak 2016, Jurko 2016, Fabian 2013, Mrkvica 2012, Michalik 2014, Krehel 2013, Rimar 2014, Ragan 2012, Allo 2013, Cep 2014, Lesso 2010, Brezinova 2014, Gombar 2013, Monkova 2013, Janekova 2014, Zaborowski 2007]. Technological processes of water purification and treatment are constantly evolving, the newer methods may be mentioned ionization ultrasound, but still important role in wastewater treatment has a sorbent utilization. Significant is the role of sorbents in the final purification of ammonia and heavy metals pollutions. Especially for metals, which are persistent in the environment appropriate for reducing the adverse effects to the biota, and humans in addition to conventional oxidation-reduction processes, and precipitating adsorption [Korinekova 2006]. Between most heavy metal adsorbents tested are: zeolites, carbonates, clays, peat, lignite, activated alumina, and the like. Great number of experiments and modeling studies of the adsorption of heavy metal cations on the said material, described in references [Korinekova 2006, Chmielewska 2008, Peric 2004, Cejka 2000, Bailey 1999, Sabova 2010]. The sorbents in the adsorption of heavy metals proofed activated carbon, but at present, attention is paid to the use of natural zeolite in the field. Natural zeolites are highly affordable natural materials with absorption capacity. During the sorption of the emphasis is on high reaction surface sorption materials. Natural zeolites with 70% – 80% clinoptilolite content are often used in technological applications [Peric 2004]. Zeolites are defined as natural or synthetic crystalline aluminosilicates having a three dimensional structure consisting of the tetrahedron in the center of which is located ion Si+4 and Al+3. The basic of building blocks are tetrahedrons [SiO4]-4 and [AlO4]-5 in which the silicon and aluminum atom is saved centrally and in the corners of the tetrahedrons are disposed greazer oxygen atoms. Tetrahedrons are mutually connected by oxygen atoms linked to two adjacent tetrahedrons. The negative charge is compenstated by the grid inorganic or organic cations, which are located in outside grate positions. The most common the alkali metal cations and alkaline earth metal are located. Zeolites are considered as composite materials that are formed of two or more chemicals, if necessary. Structure of different components, among which one, known as the matrix the continuous phase and the other components form a discontinuous phase (dispersed in the matrix). Natural zeolite is defined in terms of the native form of the composite, based on high porosity, but also the multi-phase composition of the mineral. Zeolites are also considered macromolecular clathrates, respectively inclusive compounds which are microporosity and its network numerous channels capable of absorbing so visiting (guest), respectively others, also infrastructure clathrates, because these molecules integrated in contrast to an external skeleton subject only to weak intermolecular interactions [Cejka 2000]. In terms of water treatment are interesting sorption and ion-exchange ability of zeolite resulting from the structure. Their three-dimensional structure comprising regular arrangement of tetrahedrons

[SiO4]-4 and [AlO4]-5. The network of tetrahedrons [SiO4]-4 is part of the silicon atoms replaced by aluminum atoms isomorphic. The negative charges of zeolitic lattice entailed is compensated by cations, that are located in position outside the grid. The most common are the alkali metal cations and alkaline earth cations [Korinekova 2006, Chmielewska 2008, Cejka 2000]. These cations may be by means of sorption and ion exchange with other cations replace, for example, copper cation. Copper belongs to the essential elements, but at increased levels in the blood in the hepatic toxicity manifested by hepar breakage [Beseda 1999]. It is therefore important to monitor the concentration of this element in the waters and in the increased incidence of treatment concentrations.

2 EXPERIMENTAL

At the Faculty of manufacturing technologies currently being explored sorption and ion - exchange properties of natural zeolite - clinoptilolite coming from the quarry at Nizny Hrabovec in Slovakia. It is a hydrous potassium aluminum silicate - phosphate type having a pore size of 0.3 nm - 0.4 nm, which is characterized by the ability of sorption of heavy metal cations from aqueous solutions. These are on the zeolite immobilized by two mechanisms - ion exchange and chemisorption [Sabova 2010].

This natural product has been used for studies on uptake of cations of copper, and this property was compared with the ability of the synthetic zeolite - nalsite. Nalsite is the synthetic zeolite type 4A having a pore size of 0.4 nm. Its chemical composition in dehydrated state given by the formula: Na2O · Al2O3 · 2 SiO2.

For the experiments, the applied heat treated zeolite - clinoptilolite having a grain size of 1.0 - 2.5 mm. The chemical composition of the rocks is in the table 1.

Table 1. Chemical composition of the zeolite - clinoptilolite [Zeocem 2000]

Chemical substance species	Percentual composition [%]	Chemical substance species	Percentual composition [%]
SiO_2	65,0 - 71,3	Fe_2O_3	0,7 - 1,9
Al_2O_3	11,5 - 13,1	MgO	0,6 - 1,2
CaO	2,7 - 5,2	Na_2O	0,2 - 1,3
K_2O	2,2 - 3,4	TiO_2	0,1 - 0,3
P_2O_5	0,02	Si/Al	4,5 - 5,4

Table 2. Physical properties of the natural zeolite-clinoptilolite [Zeocem 2000]

Softening temperature	1260˚ C
Melting temperature	1340˚ C
Pour temperature	1420˚ C
Porosity	24 az 32 %
Effective pore diameter	0,4 nm
Compresive strenght	33 MPa
Specific weight	2200 - 2440 kgm^{-3}
Volume weight	1600 - 1800 kgm^{-3}

Sorption characteristics

The sorption process of a substance from a solution to a solid can be expressed as a result of the reversible reaction, sorption and desorption, which equilibrium for a final concentration of the chemical in both phases. This is generally studied by evaluation of the equilibrium concentration of the chemical in the sorbent as a function of the total of the equilibrium concentration in the solution at a given temperature. Expression of this addiction are isotherms. Often used for comparison characteristic sorption properties of the sorbents is the partition coefficient KR. Partition coefficient KR, which is the slope of the linear adsorption isotherm indicates the ratio between the concentration of the substance to the sorbent cS (g / g), and the concentration of Cr in the solution (g / dm3) during the steady state. It is a quantitative indicator of the distribution of substances between the solid and liquid phase.

$K_R = C_S/C_r$ [Korkmaz 2012].

$$K_R = \frac{c_0 - c_r}{c_r} \cdot \frac{V}{m} \qquad (1)$$

To express sorption is most commonly used Freundlich isotherm in a non linear state

$a = K_R \cdot c_r^{1/n}$, (2)

where a = sorbed quantity K_R = partition coefficient, c_r = equilibrium concentration of the solution, n = sorption exponent characterizing the surface quality. The sorption index is in the range of 0.2 - 0.9. After the logarithm isotherm takes the form [Peacock 2000]:

$\log a = \log K_R + 1/n \log c_r$ (3)

3 EXPERIMENTAL

To define the time required to reach equilibrium in the system we watched addiction adsorbed amount of adsorbent contact time with the adsorbate. Kinetic experiments were carried out so that the glass containers have weighed 40 grams of the clinoptilolite and 40 grams of the nalsite and 0,1 dm3 model samples with analytical precision. The three samples of the model, in a concentration of copper cations 4.95 g· dm-3, 6.72 g · dm-3 and 7.05 g · dm-3. In time intervals one hourse, we analytically determine the sampling solution contains of the copper cations by method calibration curve with the help of photometry. We established equilibrium concentration cr after the equilibration obtained from the kinetic dependence at 22ºC establish. The amount of copper cation adsorbed on the adsorbent was calculated by the equation [Subramanyam 2009, Ragnarsdottir 2016]:

$$a = \frac{c_0 - c_r}{m} \cdot \mathrm{V} \qquad (4)$$

where V is the volume of solution and m is the weight of the adsorbent. Measuring datas of copper equilibrate concentrations at solutions and copper concentrations on the sorbents were used to calculate of the partition coefficients.

Clinoptilolite samples were prior to measurement washed with distilled water and heat treated at 250º C for one hour. For sorption of copper cations we were used clinoptilolite samples with grain size 1 mm - 2.5 mm. Sorption characteristics were calculated using the formula No.1 and No.4. At table 3 are shown the sorption characteristics for sorption of copper, calculated on the clinoptilolite cations at different starting concentrations of model samples.

Table 3. Sorptive characteristics of the Cu^{+2} cations sorption on the clinoptilolite

c_0 [g·dm^{-3}]	c_r [g·dm$^{/3}$]	K_R	a[mg·g$^{/1}$]
4,95	0,66	0,02	12,87
6,72	0,755	0,023	17,87
7,05	0,762	0,025	18,9

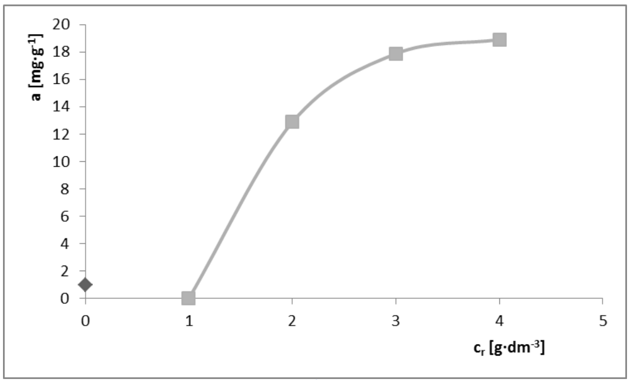

Figure 1. Sorptive isotherm for Cu^{+2} cations sorption on the clinoptilolite

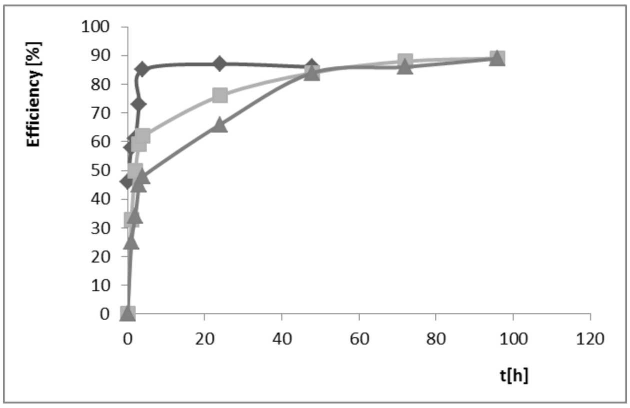

Figure 2. Temporal change of sorption efficiency on the clinoptilolite 1mm – 2,5mm

4 DISCUSSION

Figure 2 shows curves of efficiency in view of the clinoptilolite cations of copper uptake as a function of time using samples of various concentrations of Cu+ 2. The graph shows that the long-term effect on the sorbent with solution, the activity in terms of sorption of copper cations increases. The efficiency of clinoptilolite has grown with time during 96 hours in all three samples. Maximal efficiency of sorbent was achieved in the operation of model samples with an initial concentration of 7.05 mol dm^{-3} · 6.72 mol·dm^{-3}, namely 89%. The results of the experiments conducted on natural and synthetic samples, it is found that clinoptilolite has to sorption of copper cations, the efficiency of sorption increases with increasing initial concentration. The efficiency of the natural clinoptilolite was compared with synthetic zeolites nalsite. Sorption of this zeolite takes place in the same the laboratory conditions as near clinoptilolite and in this case was recorded 100% efficiency.

To define the time required to reach equilibrium in the system we watched dependence of adsorbed amount on contact time of the adsorbent with adsorbate. In the case of copper cations in nalsite was required shorter time to reach equilibrium. When copper cations in nalsite was applied within one hour of 100% efficiency. Clinoptilolite at steady state was achieved after 96 hours in all experiments.

The rate of sorption of copper cations has been expressed through the partition coefficient calculated using the formula No. 1. Partition coefficients KR are shown in table. 3. For copper sorption partition coefficients are almost identical regardless of the initial concentration of the model solution. With increasing initial concentration ratio of the amount of sorbed copper cations grows.

5 CONCLUSIONS

Results show that over the nalsite sorption speedier as clinoptilolite. In contrast, however, the natural zeolite is more favorable in the view of economic indicator. Considering to rich deposits of this natural non-toxic natural material cost less challenging. For comparison, the prices of both sorbents are shown: clinoptilolite - € 0.078 / kg, nalsite - € 4.813 / kg. As the cost of removal of heavy metals from water are relatively high near classic technologies, looking for the cheap but effective cleaning methods. One way is by an ion exchange and sorption. Frequently used active carbon over a zeolite unfavorable abrasive properties, it is expensive to manufacture, which corresponds to a relatively high price on the market. Natural zeolites are readily available, natural materials. Experimental results indicate the potential use of clinoptilolite for reducing the content of copper cations in water. Currently, teams of researchers are working on preparing a new generation of environmental sorbents that prefer natural matrices, including natural zeolite as carriers for functional groups to obtain usable sorbents for the purification of water and due to impurities in the waters in the form of anions.

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