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REMOVING OF SELECTED METALS FROM MODELLED WASTEWATER BY SORPTION ON NATURAL CLINOPTILOLITE

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Abstract

Potential toxic metals (also called heavy metals) pollution constitutes one of the more compelling environmental problems. The present study describes sorption of toxic metal ions Ni^{2+}, Al^{3+}, Cu^{2+} and Cr^{6+} onto natural zeolitic tuff from Nižný Hrabovec deposit containing aluminosilicate mineral - clinoptilolite. A series of experiments were carried out in the same conditions with different initial concentration of metal ions. Used adsorbent seems to be a suitable adsorbent for removing of these elements from water.

Key words

Sorption, zeolite, clinoptilolite, copper, nickel, chromium, aluminum

Introduction

Potential toxic metals (PTM, e.g. Al, Ni, Pb, Cu, Cd, Cr) are important for the mechanical engineering, electrical engineering or various chemical industries and therefore they are intensively mined, treated and processed. These technologies will evolve PTM which at a certain concentration of a toxic effect on human health and as well as other biotic component of ecosystems. Their discharge into river or any aquatic environment can change both aquatic species diversity and ecosystem due to their toxicity and accumulative behavior. Aquatic organisms such as fish and shell fish accumulate metals to concentrations many times higher than present in water or sediment. Thus, PTM acquired through the food chain as a result of pollution are potential chemical hazards, threatening consumers. [1] Therefore, leaks of these elements and their substances to the environment must be restricted, wastewater must be treated. The most widely methods used in the industrial wastewater treatment from the engineering and electrical industries are precipitation, coagulation and neutralization. [2]

- Precipitation is an effective method to removal metals and cyanides from industrial wastewater. Addition of a suitable chemical agent (e.g. NaOH, $Ca(OH)_2$, Na_2S) to the wastewater forming the low solubility products (dissolved sulfides, hydroxides, carbonates or phosphates). Cyanides are usually precipitated by ferrous sulfate ($FeSO_4$). In some industrial wastewater is used adsorption precipitation. In this case, as the agent is a ferric or aluminum salt, which form a flocculent precipitate of ferric or aluminum hydroxide. During the creation and sedimentation of flakes additional substances, colloidal or very fine particles are captured by adsorption. [3]
- Coagulation is the process to destabilize suspensions or metals solutions. As coagulants are most used: aluminum ammonium sulphate, aluminum sulphate, calcium hydroxide, calcium oxide, chlorinated ferrous sulfate, ferric chloride; and other organic flocutant agents. [2]
- Neutralization is the process of adjusting the effluent pH. Simultaneously, metal ions are quantitatively precipitated in the form of hydroxides or alkali salts with low solubility. Fe^{3+}, Cr^{3+}, Cu^{2+} or Al^{3+} are quantitatively removed at lower pH, while the Zn^{2+}, Ni^{2+}, Cd^{2+} at the higher pH values. But increasing of pH can caught re-dissolution of Al^{3+} and Zn^{2+}. Soluble neutralizing agents are alkalis (lime, sodium hydroxide) and a soluble carbonates (soda). Low soluble neutralizing agents are oxides, hydroxides (magnesium oxide, magnesium hydroxide) and carbonates (calcium sulfate). Agents poorly soluble (or almost insoluble in pure water) must be crushed before use. [2]

In addition to these classical wastewater treatment methods, there are more progressive methods including electrochemistry treatment, membrane processes, ion exchange or adsorption processes.

- Electrochemical processes are used for extremely wasted and oily wastewater treatment. [1] The wastewater flows between the iron and the aluminum electrodes, which are fed by DC. Electrodes produce the iron and aluminum ions, which form hydroxide flakes assumed by fine suspended and colloidal impurities. They are coagulate and settle on the bottom of the tank and can be filtered in the filters. [4, 1] Sometimes is useful electroflotation for purified aqueous suspension, where fine bubbles of oxygen and hydrogen are formed by the electrolysis. [1]

- The principle of membrane separation processes is based on the selective permeability of the membrane. [3] Separation works on the different mechanism, such as molecular filtration, ultrafiltration, inverse osmosis, dissolution or reaction one of the component from the separated mixture in the membrane, attraction and repulsion of some components by the membrane (electrodialysis). [5]
- Ion exchange lies in the ability of ion exchangers – substances that can exchange ions from their own molecules as ions from a solution. The various required performances in removing undesirable constituents from water is achieved by each type of catexes or annexes or a combination of thereof. [1]

There are also technologies using alternative treatment systems, which are based on the use of naturally occurring or chemically modified sorbents. One of these sorbents is clinoptilolite (type of natural zeolite), occurring in Slovakia in the area of Nizny Hrabovec. In generally, this material is mainly used for nutrients and toxic metals removal from specific types of industrial wastewater, respectively, as tertiary level in wastewater treatment. From the use of natural zeolites in wastewater management may be for example mentioned: Wastewater reclamation plant in Rosemont (Minnesota, USA), Richland (Washington, USA), Bari (Italy), Vác (Hungary) or tertiary level of wastewater treatment "Water Reclamation Plant "in Truckee (California, USA). [6] In the Czech Republic and Slovakia, there was built two pilot zeolite wastewater reclamation plant. The first was in a Water Research Institute in Bratislava - Vajnory field laboratory, which treated the modeled water with increased content of NH_4^+ ions (approximately 1 mg L^{-1}). The second project was planned as a tertiary deammonization unit installed in the Wastewater treatment plant – Otrokovice, aimed to removing ammoniacal pollution from mixed industrial and municipal wastewater. Wastewater contained an increased concentration of chromium from the leather tanning process. Both of these plants used domestic deposit of clinoptilolite in Nižný Hrabovec. [6]

Materials and methods

As adsorbent was used zeolite tuff from Nižný Hrabovec deposit containing 82 – 84 % of clinoptilolite, 9 % of cristobalite, 2 – 3 % clayey mica and traces of quartz. Grain size of the material was 0.3 - 0.8 mm, specific weight 2.39 g cm^{-3}, bulk density 0.84 g cm^{-3}, porosity 64.8 % effective pore diameter 0.4 nm and specific surface 36 m^2 g^{-1}. [7] Other physical and chemical properties are reported in Tab. 1.

Tab. 1 Chemical composition, physical and mechanical properties of zeolite tuff from Nižný Hrabovec. [8]

Chemical composition			
SiO_2	64.18 - 75.50 %	Al_2O_3	10.93 - 14.80 %
CaO	1.43 - 11.68 %	K_2O	1.24 - 4.24 %
Fe_2O_3	0.12 - 2.45 %	MgO	0.29 - 1.43 %
Na_2O	0.10 - 2.97 %	TiO_2	0.08 - 0.39 %
P_2O_5	0.01 - 0.18 %	FeO	0.29 - 1.43 %
SO_3	0.00 - 0.23 %	Si/Al	4.8 / 5.4
Physical and mechanical properties			
Softening point	1 260 °C	Density	70 %
Melting point	1 340 °C	A Mohs hardness	1.5 - 2.5
Compressive strength	33 MPa	Water absorption	34 - 36 %

All of the experiments were performed with modeled wastewater – water solutions prepared from p.a. chemicals. Stock solutions of Al^{3+}, Cu^{2+}, Ni^{2+} and Cr^{6+} were prepared using $Al(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and K_2CO_4, respectively. Batch mode experiments on adsorption and desorption of metals on zeolite were realized by this procedure: 1 g of zeolite sample (weighted to an accuracy of 0.1 mg) were added to 5.0 mL of metal solutions (initial concentration in range 0 – 100.0 mg L^{-1}) in glass bottles. The bottles were sealed and placed for 72 h to the orbital shaker. After that time, the suspension was centrifuged at 5000 rpm for 5 min. From the clear solution was taken the maximum volume and aliquot amount was used to determine the appropriate metal concentration. To the sorbent after sorption was added the same amount of desorption agent, how much of the solution was removed in the previous step. The desorption agent was $CaCl_2$ solution (0.01 mol L^{-1}) with small amount NaN_3 addition (to give a final concentration 0.0001 mol L^{-1}) to prevent biological activity. The bottles were sealed and following the procedure as in the case of adsorption experiments. All of experiments were realized in triplicates. The determinations of metals in solutions before and after experiments were realized by spectrophotometric methods reported in previous works. [9] The amount of heavy metal adsorption at equilibrium, q_e (mg g^{-1}), was calculated using equation:

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$$q_e = \frac{(c_0 - c_e) \times V}{m}$$

where, c_o = initial concentration of metal (mg L^{-1}); c_e = equilibrium concentration of the metal (mg L^{-1}); V = volume of the solution (L) and m = mass of adsorbent (g). Percentage expressing of heavy metal adsorption and desorption at equilibrium reporting the equation:

$$P_{sorb} = \frac{(c_0 - c_e)}{c_e} \times 100\ \%$$

$$P_{desorb} = \frac{q_{e\ desorb.}}{q_{e\ sorb.}} \times 100\ \%$$

Results and discussion

At the Fig.1 are shown the adsorption isotherms for the systems aqueous solution Cu^{2+} / zeolite, Ni^{2+} / zeolite, Cr^{6+} / zeolite and Al^{3+} / zeolite. In the first two systems are shown convex curves during adsorption. This shape is typical for the gradual occupation of adsorption positions on the surface of the adsorbent or the ion exchange. In our natural material this could be caused by exchange of monovalent or divalent ions present on the available adsorption positions by Cu^{2+} respectively Ni^{2+}. The opposite concave course of the curve in the case of the third system (Cr^{6+} / zeolite) suggests that there occur modification of the adsorbent surface or the formatting of the ionic double layer. Almost linear curve in the last case indicates a different way of adsorption. Clinoptilolite is a natural hydrated aluminosilicate with general formula: $(Ca,K_2,Na_2,Mg)_4Al_8Si_{40}O_{96} \cdot 24H_2O$. Linear course of the adsorption isotherm, typically for absorption or chemisorption might indicate processes like "embedding" of aluminum atoms on the surface and in the pores of the zeolite. How the ions are binding to the surface of clinoptilolite will be studied in the near future.

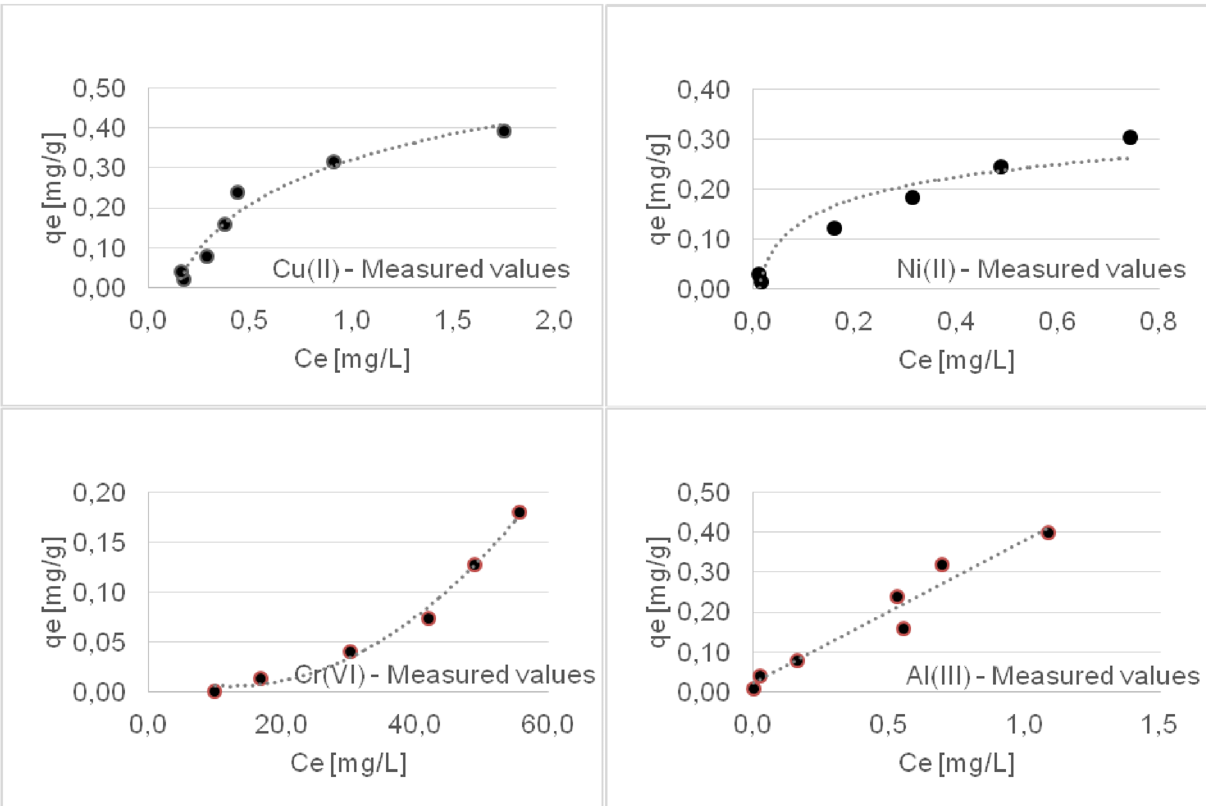

Fig.1: Adsorption isotherms of studied metals on clinoptilolite.

Comparison of the adsorption capacity in percentage of the various initial concentrations is shown in Figure 2. Adsorption efficiency for natural clinoptilolite is in the following order: Ni^{2+}> Al^{3+}> Cu^{2+}> Cr^{6+}. Natural clinoptilolite is good adsorbent for removing Ni^{2+}, Al^{3+} and Cu^{2+} from water solutions. Desorption of metals are also high; there is good potential for recovery metals and regeneration of zeolite. Clinoptilolite is also suitable removing toxic Cr^{6+} in higher initial concentration. The percentage of desorption is lower, it would be appropriate to use a stronger desorption agent or change the other conditions of desorption.

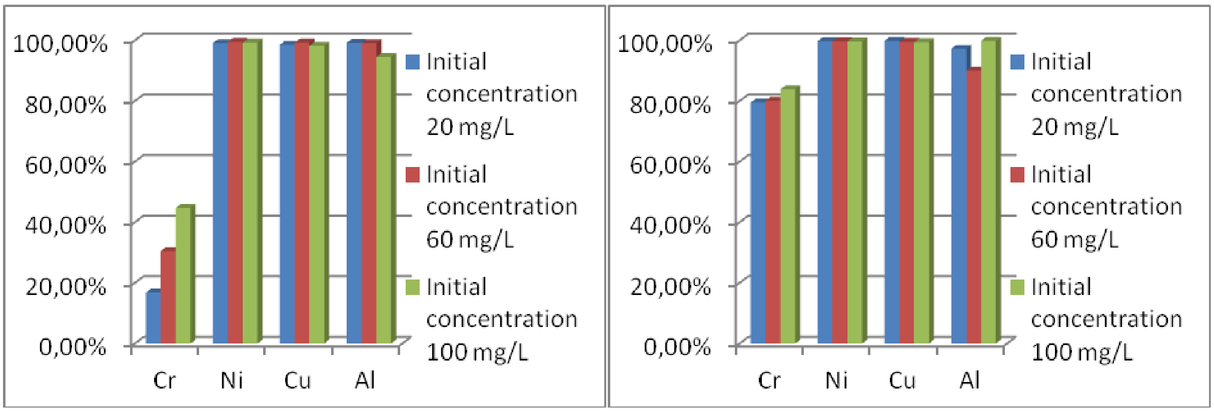

Fig. 2: Adsorbed (left) and desorbed (right) amount of metals expressed as a percentage in the adsorption systems with initial concentrations of metals 20, 40 and 60 mg L^{-1}.

Conclusions

Natural zeolite tuff from Nižný Hrabovec deposit is an effective adsorbent of studied metals (Al^{3+}, Cu^{2+}, Ni^{2+} and Cr^{6+}) and has potential for use in wastewater treatment. In future work, we will focus on increasing the efficiency of this material by various chemical methods.

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