CHEMICAL ENGINEERING TRANSACTIONS
VOL. 32, 2013
Chief Editors: Sauro Pierucci, Jiří J. Klemeš
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ISBN 978-88-95608-23-5; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1332094

Study of Sorption Properties of Zeolite in Acidic Conditions in Dependence on Particle Size

Marian Holub*, Magdalena Balintova, Petra Pavlikova, Lenka Palascakova

Technical University of Kosice, Faculty of Civil Engineering, Institute of Environmental Engineering. Vysokoskolska 4, 042 00 Kosice, Slovakia
marian.holub@tuke.sk

Discharges of acidic, highly mineralized water (acid mine drainage - AMD) belong to accompaniment of mining activities that have a negative impact on the environment in many countries of the World, especially where mining activities have had a long tradition. Generally, AMD is the product of sulphide minerals oxidation. The typical character of these discharges is low pH (about 3-4) and high concentration of heavy metals. This very low pH is limiting for many various treatment technologies, including sorption.
Sorption techniques are widely used to remove heavy metal ions from different water solutions, because they are highly effective and low cost. The use of natural or synthetic sorbents is closely linked to specific conditions. On the other hand the different sorption properties of adsorbents are also very important. These properties include porosity, specific surface area, ion exchange capacity, selectivity or modifiability.
The aim of this paper is to describe the influence of the particle size of zeolite on the heavy metals sorption process under acidic conditions. Natural clinoptilolite with various granularities were used for this purpose. Experiments were aimed to the study of the sorption equilibrium of zeolite for various concentrations of the cations (Cu^{2+} and Zn^{2+}) from acidic solutions.

1. Introduction

Pollution of water with toxic substances is of major concern for human health as well as for the environmental quality. One of these toxic substances, for example heavy metal ions are the most dangerous for the environment. Anthropogenic activities such as mining and smelting of metal ores have increased the prevalence and occurrence of heavy metal contamination at the Earth's surface. Specifically, opencast mining activities have a serious environmental impact on soils and water streams, having generated millions of tons of sulphide-rich tailings (Andras et al., 2012). Moreover, acidic drainage with pH ~ 3-4 resulting from the oxidation of sulphides leads to the leaching of large quantities of cations, e.g. Fe^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, etc. (Vega et al., 2006).
Different methods for the removal of heavy metal ions from aqueous solution such as chemical precipitation, ion exchange, filtration and membrane separation and reverse osmosis have been reported (Macingova and Luptakova, 2012). Sorption is considered as a very effective and economical process for metal ion removal from wastewaters. Among the different minerals which possess adsorbent properties, zeolite appears to be one of the most promising to perform metal purification function (Breck, 1974). Zeolites have a three-dimensional structure constituted by (Si, Al)O_4 tetrahedra connected by all their oxygen vertices forming channels where H_2O molecules and exchangeable cations counterbalance the negative charge generated from the isomorphous substitution. The advantage of zeolites, apart from their much lower cost, is their ion selectivity. Owing to zeolite's structural characteristics and their adsorbent properties, they have been applied as chemical sieve, water softener and adsorbents (Breck, 1974). Several researchers have studied the removal performance and selectivity sequence of heavy metal ions by natural zeolites (clinoptilolite and chabazite) (Blanchard et al., 1984).
The aim of this work is study of using of natural Slovak zeolite as a sorbent for copper and zinc removal from mining water. The experiments were carried out for the purpose of the follow parameters investigation: adsorption capacity of zeolite in dependence on initial concentration and granularity, pH

Please cite this article as: Holub M., Balintova M., Pavlikova P., Palascakova L., 2013, Study of sorption properties of zeolite in acidic conditions in dependence on particle size, Chemical Engineering Transactions, 32, 559-564 DOI: 10.3303/CET1332094

change and removal efficiency.To simulate acid mine drainage conditions experiments were realized with acidic solutions (pH 4).

2. Materials and methods

2.1 Zeolite samples preparation

Samples were prepared as follows: A natural zeolite from Zeocem, a.s. (Bystre, Slovakia) with granularity over 2 mm was ground by planetary mill (Desk – top planetary ball Miller SFM-1) at 290 rpm (tray rotating) and 580 rpm (grinding jars rotating) for 6 min. After that sieve analysis for the purpose of separation of 3 fractions (0.5 mm – 0.25 mm; 0.25 mm – 0.125 mm and below 0.125 mm) was performed. Sieves were shaken in a mechanical shaker for 10 minutes to provide complete separation. After this, the separated fractions of zeolite were dried at 105 °C for 2 h and then allowed to cool in the desiccators.

2.2 Characterization

Zeolite used in experiments is clinoptilolite type with primary potassium cation, empirical formula of $Ca_{1.8}K_{1.8}Na_{0.2}Mg_{0.2}4Al_6Si_{30}O_{72}.24H_2O$. The chemical composition of the prepared zeolite declared by the manufacturer (Zeocem, a.s.) and results from X-ray fluorescence analysis (XRF) are listed in Table 1.

Table 1: Sorbent characterization

Constituent	Declared content (mass %)	XRF analysis (mass %)
SiO_2	65.00 – 73.00	64.10
Al_2O_3	11.50 – 13.10	9.89
CaO	2.70 – 5.20	2.99
K_2O	2.20 – 3.40	2.71
Fe_2O_3	0.70 – 1.90	1.34
MgO	0.60 – 1.20	0.73
Na_2O	0.20 – 1.30	-
TiO_2	0.10 – 0.30	0.15

2.3 Apparatus and instrumentation

- A Colorimeter DR890 (HACH LANGE, Germany) with appropriate reagents was used to determine amount of dissolved Cu^{2+} and Zn^{2+}.
- The basic chemical composition of zeolite was investigated by X-ray fluorescence analysis (XRF) using SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses.
- IR spectra were measured by Alpha FT-IR Spectrometer with ALPHA‘s Platinum ATR single reflection diamond ATR module (Bruker, Germany).
- pH were determined according to pH meter inoLab ph 730 (WTW, Germany) which was standardized using buffer solutions of different pH values (4.01, 7.00).

2.4 Adsorbate solutions preparation

Concentrated stock solutions of heavy metals (imitating AMD conditions) were prepared by dissolution of copper sulfate pentahydrate and zinc sulfate heptahydrate in deionized water. Working solutions were prepared by further dilution to the desired initial concentration of appropriate heavy metal. The initial pH of each solution was adjusted to the required value (pH=4.1 – 4.2) by adding 0.001M H_2SO_4. It should be noted that sulphate anions are not forming precipitates or complexes with copper and zinc cations at the test conditions and are considered to be inert.

2.5 Batch adsorption experiments

Batch experiments were carried out at room temperature (23±0.2°C) in beakers by adding of a constant mass of zeolite (1.0 g) in 100mL of metal solution (Cu^{2+} or Zn^{2+}) for 24 h contact time. To evaluate the effect of granularity and heavy metal initial concentrations influence, the various solutions with initial Cu^{2+} and Zn^{2+} concentrations ranging from 10 to 110 mg/L (10, 20, 30, 50, 70, 90 and 110) were prepared. Then 1.0 g zeolite of different granularity (0.5 mm – 0.25 mm; 0.25 mm – 0.125 mm and below 0.125 mm) to each solution was added. Measurement of pH at the beginning and at the end of process was done.

After 24 h contact time, the solid was removed by filtration through a laboratory filter paper for qualitative analysis.

In order to obtain the sorption capacity, the amount of ions adsorbed per unit mass of adsorbent (q_e in milligrams of metal ions per gram of adsorbent) was evaluated using the following expression:

$$q_e = \frac{c_o - c_e}{m} \times V, \qquad (1)$$

where C_o is the initial metal ion concentration ($mg.L^{-1}$), C_e the metal ion concentration after sorption (24 h; mg. L^{-1}), V the volume of the aqueous phase (L), and m the amount of the zeolite (g). To quantify the performance of the various fractions of zeolite, the percentage heavy metal removal was calculated using the following equation:

$$\%\ \mathrm{metal\ ion\ removal} = \frac{c_o - c_e}{c_o} \times 100\ \% \qquad (2)$$

3. Theoretical background

3.1 Adsorption isotherms

Two of the most commonly used isotherm theories have been adopted in this paper, namely, the Freundlich and Langmuir equilibrium isotherm theories.

The Freundlich equation has been widely used for isothermal adsorption. This is a special case for heterogeneous surface and her form can be represented by the following equations (3, 4):

$$q_e = k{c_e}^{1/n} \qquad (3)$$

or in the linear form:

$$\lg q_e = \lg k + \frac{1}{n} \lg c_e\ , \qquad (4)$$

where k represents the sorption capacity when metal equilibrium concentration equals to 1, C_e is the equilibrium concentration of remaining metal in the solution ($mg.L^{-1}$), q_e, the amount of adsorbed per unit weight ($mg.g^{-1}$) and n, Freundlich constants related to adsorption intensity.

Langmuir's isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites. This model is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface (Zheng et al., 2008). This model is represented as follows:

$$q_e = \frac{Q_{max} b c_e}{1 + b c_e} \qquad (5)$$

or in the linear form:

$$\frac{1}{q_e} = \frac{1}{Q_{max} b c_e} + \frac{1}{Q_{max}}, \qquad (6)$$

where q_e is the amount of a metal adsorbed per mass unit of sorbent at equilibrium ($mg.g^{-1}$), Q_{max} is the amount of adsorbate at complete monolayer ($mg.g^{-1}$) and b ($L.mg^{-1}$) is the Freundlich constant that relates to the heat of adsorption.

4. Results and discussion

4.1 Effect of granularity and initial concentration of metal ions

The results of the removal efficiency (%) in dependence on the initial concentration are shown in Figure 1 and Figure 2. Removal efficiency decreases with increasing initial concentration of appropriate metal. The sorption ability of metal ions (both) decreases in the following order of granularity: below 0.125 mm > 0.25 – 0.125 mm > 0.5 – 0.25 mm. Zeolite achieves better percentage removal of copper than zinc in all of three used fractions.

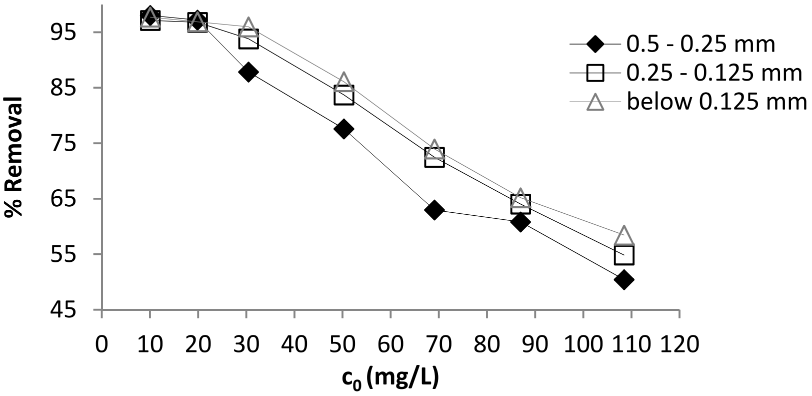

Figure 1: Effect of the initial concentration on removal of copper

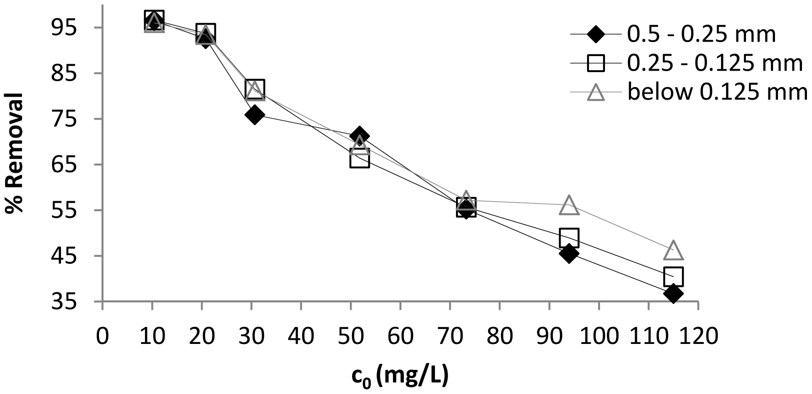

Figure 2: Effect of the initial concentration on removal of zinc

4.2 pH factor

pH is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions (Elliot and Huang, 1981; Dastgheib and Rockstraw, 2002). The solubility of copper and zinc in model acidic solutions is a function of pH. According to the literature, copper is precipitated at pH 4.5 – 6 and zinc at pH 5.5 – 7.0 (Balintova and Petrilakova, 2011). The main reason of the pH measurements in filtrates after sorption was that zeolite causes increasing of pH in all experiments. The pH values after sorption in dependence on the initial concentration of appropriate metal (c_0) are shown in Figure 3 and Figure 4.

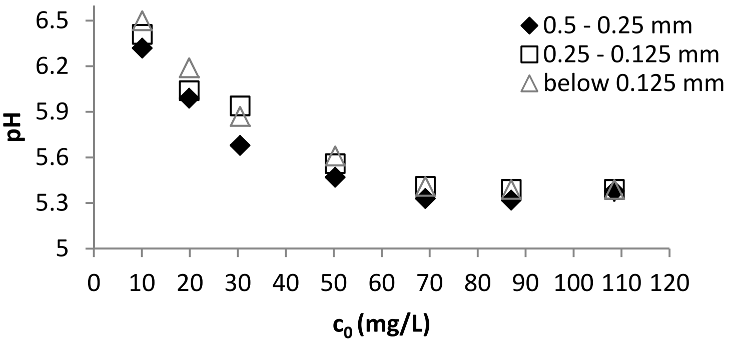

Figure 3: The pH values after cooper sorption

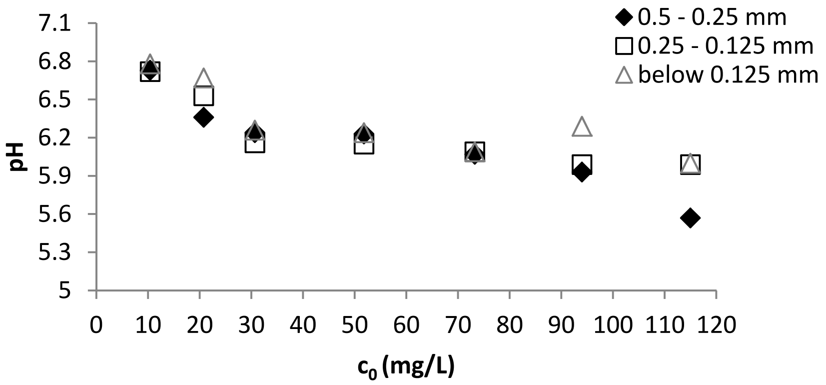

Figure 4: The pH values after zinc sorption

The precipitation of hydroxides was not confirmed by measuring the IR spectra. According to literature (Gadsden, 1975) for copper and zinc hydroxide is typical a broad band centered around 3320 cm^{-1} which may be attributed to hydrogen bonded hydroxyl groups and an intense band is observed around 1382 cm^{-1} which may be assigned to Cu–OH bond.

As it is seen in Figure 5, there is no difference between IR spectrum of zeolite before and after sorption of copper or zinc thus the mentioned bands were not observed.

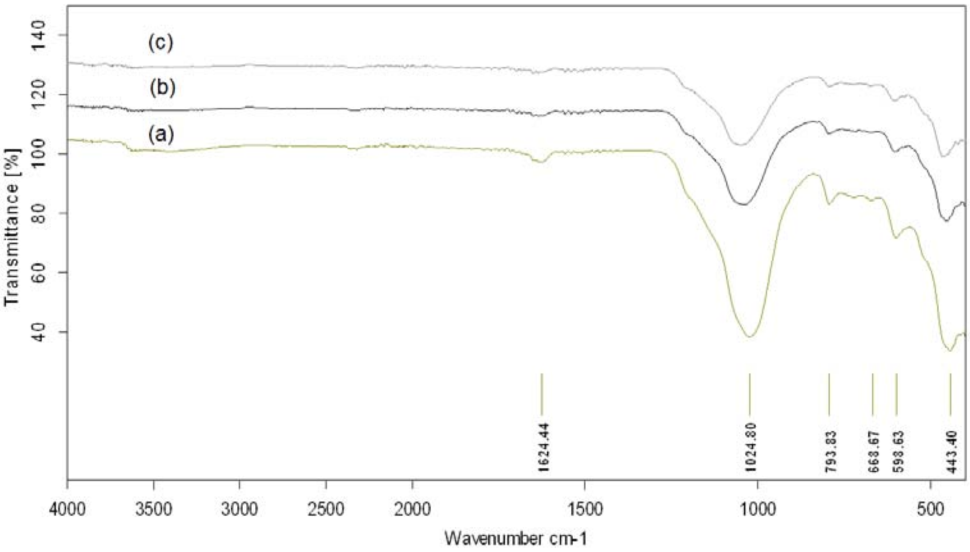

Figure 5: Infrared spectra. (a) natural zeolite; (b) zeolite after Cu^{2+} sorption; (c) zeolite after Zn^{2+} sorption

The characterization of zeolites by FTIR technique is based on the presence of bands in three regions. A higher one corresponds to the OH stretching modes (3,650 – 3,450 cm^{-1}) with an additional band at 1,620-1,640 cm^{-1} (Lewis sites). This region is assigned H-O-H bending of the water molecules (zeolitic water) in channels of the samples (Zhao et al., 2006). The middle zone (1,200 – 900 cm^{-1}) is characterized by strong bands attributed basically to the TO_4 (T=Al, Si) stretching modes whereas the corresponding bending modes of the 3D covalent arrangement are observed below 700 cm^{-1} (Van der Marel and Beutelspacher, 1976).

4.3 Study of adsorption isotherms

The sorption data were analyzed using programs DataFit 9.0.59 and Origin 7.0. Results are shown in the Table 2. The equilibrium adsorption data better correlated with Freundlich isotherm model for all tested fractions of zeolite and both cations.

Table 2: Freundlich and Langmuir parameters

Metals	Fraction	Freundlich isotherm constants			Langmuir isotherm constants		
		k	1/n	R^2	Q_{max}	b	R^2
Cu^{2+}	0.5 – 0.25 mm	1.960	0.264	0.9783	5.153	0.473	0.8737
	0.25 – 0.125 mm	2.206	0.267	0.9699	5.720	0.572	0.9675
	below 0.125 mm	2.361	0.264	0.9679	5.876	0.722	0.9618
Zn^{2+}	0.5 – 0.25 mm	1.657	0.238	0.9319	1.283	0.375	0.8927
	0.25 – 0.125 mm	1.637	0.257	0.9847	4.483	0.383	0.8973
	below 0.125 mm	1.523	0.310	0.9757	5.351	0.205	0.8827

5. Conclusion

This study showed the possibility of zeolite utilization for Cu and Zn removal from model acidic solutions. The decreasing of granularity has positive influence on sorption capacity, which was confirmed by Q_{max} value from Langmuir model. The experimental data were well correlated to the Freundlich equation. Generally, zeolite was more efficient for copper removal than zinc removal. Increasing of pH values did not cause precipitation of the selected metal cations.

Acknowledgements

This work has been supported by the Slovak Research and Development Agency under the contract No.APVV-0252-10 and by the Slovak Grant Agency for Science (Grant No. 1/0882/11).

References

Andras P., Turisova I., Marino A., Buccheri G., 2012, Environmental hazards associated with heavy metals at Ľubietová Cu-deposit (Slovakia), Chemical Engineering Transactions, 28, 259 – 264. DOI:10.3303/CET1228044

Balintova M., Petrilakova A., 2011, Study of pH influence on the selective precipitation of heavy metals from acid mine drainage, Chemical Engineering Transactions, 25, 345-350. DOI: 10.3303/CET1125058

Blanchard G., Maunaye M., Martin G., 1984, Removal of heavy-metals from waters by means of natural zeolites, Water Resources, 18, 1501–1507.

Breck D.W., 1974, Zeolite molecular sieves: Structure, chemistry and use. New York, USA.

Dastgheib S.A. Rockstraw D.A., 2002, A model for the adsorption of single metal ion solutes in aqueous solution onto activated carbon produced from pecan shells, Carbon, 40, 1843 – 1851.

Elliott H.A. and Huang C.P., 1981, Adsorption characteristics of some Cu(II) complexes on aluminosilicates, Water Resources, 15, 849–855.

Gadsden J.A., 1975, Infrared spectra of minerals and related inorganic compounds. London: Butterworths, UK.

Macingova E. and Luptakova A., 2012, Recovery of metals from acid mine drainage, Chemical Engineering Transactions, 28, 109 – 114. DOI: 10.3303/CET1228019

Van der Marel H.W. and Beutelspacher H., 1976, Atlas of Infrared Spectroscopy of Clay Minerals and their admixtures. New York: Elsevier, USA.

Vega F.A., Covelo E.F. and Andrade M.L., 2006, Competitive sorption and desorption of heavy metals in mine soils: influence of mine soil characteristics, J. Colloid Interf. Sci., 298, 582 – 592.

Zheng W., Li X., Wang F., Yang Q., Deng P. and Zeng G., 2008, Adsorption removal of cadmium and copper from aqueous solution by areca – A food waste, Journal of Haz. Mat., 157, 490 – 495. DOI: 10.1016/j.hazmat.2008 .01.029

Zhao D., Zhou J. and Liu N., 2006, Preparation and characterization of Mingguang palygorskite supported with silver and copper for antibacterial behaviour, Applied Clay Science, 33, 161 – 170.