Equilibrium Modeling of Cu and Ni Removal from Aqueous Solutions: Influence of Salinity

Tomáš Bakalár, Milan Búgel, and Henrieta Pavolová

Abstract—This study deals with evaluation of influence of salinity (NaCl) onto equilibrium of Cu and Ni removal from aqueous solutions by natural sorbent – zeolite. Equilibrium data were obtained by batch experiments. The salinity of the aqueous solution was influenced by dissolving NaCl in distilled water. It was studied in the range of NaCl concentrations from 1 g.l^{-1} to 100g.l^{-1}. For Cu sorption there is a significant influence of salinity. The maximum capacity of zeolite for Cu was decreasing with growing concentration of NaCl. For Ni sorption there is not so significant influence of salinity as for Cu. The maximum capacity of zeolite for Ni was slightly decreasing with growing concentration of NaCl.

Keywords—Cu, Ni, sorption, zeolite.

I. INTRODUCTION

THIS study deals with the influence of salinity on the equilibrium concentration of Cu and Ni when removing by natural zeolites from aqueous solutions. The selective and quantitative separation of metal ions from aqueous solutions has been extensively investigated by applying several techniques. Amongst them, approaches where specific sorbents are used have been considered as one of the most promising techniques [1]. Metal ions in low quantities are difficult to remove from aqueous solutions. One of the possible solutions for such situations is adsorption. Nowadays, a number of low cost adsorbent materials are available to remove metal ions. These adsorbents include various materials. [2]–[6]

Zeolites are hydrated aluminosilicate minerals and have a micro-porous structure. The zeolites are framework silicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4. In order to be a zeolite the ratio (Si + Al)/O must equal 1/2. The alumino-silicate structure is negatively charged and attracts the positive cations that reside within. Zeolites have large vacant spaces in their structures that allow space for large cations such as sodium, potassium, barium and calcium and even relatively large molecules and cation groups such as water, ammonia, carbonate ions and nitrate ions. [7]

Zeolites have basically three different structural variations.

- There are chain-like structures where minerals form acicular or needle-like prismatic crystals.
- Sheet-like structures where the crystals are flattened platy or tabular with usually good basal cleavages.
- And framework structures where the crystals are more equate in dimensions.

Salinity is the presence of soluble salts in soils or waters. It is a general term used to describe the presence of elevated levels of different salts such as sodium chloride, magnesium and calcium sulfates and bicarbonates, in soil and water. [8]–[11]

II. EQUILIBRIUM MODELING

Isotherm models provide an adequate description of metal adsorption equilibria on wide range of adsorbent materials.

Equilibrium data, used for designing adsorption isotherms, are used for estimation of adsorption system. Three adsorption models were used to describe the equilibrium between adsorbed metal ions (Cu^{2+}, Ni^{2+}) on the adsorbent zeolite (q_{eq}) and metal ions in solution (c_{eq}) at a constant temperature and pH.

A. Langmuir Isotherm

The Langmuir equation [12]-[16], [18] that is valid for monolayer sorption onto a surface is given by equation

$$q_{eq} = q_{max} \frac{b_L c_{eq}}{1 + b_L c_{eq}}. \qquad (1)$$

B. Freundlich Isotherm

The Freundlich expression [13]-[18] is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases.

The empirical Freundlich equation based on sorption onto a heterogeneous surface is given by equation:

$$q_{eq} = k_F c_{eq}^{\frac{1}{n}}. \qquad (2)$$

C. Redlich-Peterson Isotherm

The Redlich-Peterson isotherm (R-P) [18] contains three parameters unlike the Langmuir and the Freundlich isotherms that contain two parameters. The form of R-P equation includes features of the Langmuir and Freundlich isotherms and is given by equation:

Symbol	Quantity	SI
b_L	adsorption constant defined by Langmuir isotherm (1)	$g^{-1}m^3$
b_R	adsorption constant defined by Redlich-Peterson isotherm (3)	$g^{-1}m^3$
c_0	initial metal concentration in solution	$g^{-1}m^3$
c_{eq}	concentration of metal in solution in equilibrium	$g^{-1}m^3$
d_{32}	Sauter mean particle diameter (5)	m
d_{50}	mean particle diameter at 50%	m
d_i	mean particle diameter in the interval i	m
k_F	adsorption constant defined by Freundlich isotherm (2)	$g^{-1}m^3$
k_R	adsorption constant defined by Redlich-Peterson isotherm (3)	$g^{-1}m^3$
n	adsorption constant defined by Freundlich isotherm (2)	-
n_i	number of particles in the interval i	-
q_{eq}	relative amount of metal adsorbed at given concentration per unit amount of dry adsorbent in equilibrium	$g \cdot g^{-1}$
q_{max}	maximum relative amount of adsorbed metal per unit amount of dry adsorbent	$g \cdot g^{-1}$

$$q_{eq} = \frac{k_R c_{eq}}{1 + b_R c_{eq}^{\beta}} . \tag{3}$$

This equation can be converted to a linear form by taking logarithms of both sides. The linear form is:

$$\ln\left(k_R \frac{c_{eq}}{q_{eq}} - 1 \right) = \ln b_R + \beta \ln c_{eq} . \tag{4}$$

Plotting the left-side of the equation against $\ln c_{eq}$ to obtain the isotherm constants is not possible because of the three unknowns b_R, k_R and β. Hence, the isotherm constants can be determined by minimizing the error between the experimental data and the calculation of values of q_{eq} by the R-P equation. The isotherms were determined using the solver add-in for Microsoft Excel [19].

III. MATERIALS AND METHODS

A. Zeolite

Zeolite used for the experiments is from the Nižný Hrabovec (SK) localization. The zeolite from the Nižný Hrabovec localization is a natural rock, which principal part is composed of crystalline hydrated aluminosilicate of alkaline metals and metals of alkaline soils (Ca, K, Na, Mg) so-called klinoptilolite. The structure of the klinoptilolite is based on the three dimensional skeleton consisting of $(SiO_4)^{4-}$ tetrahedrites interconnected via oxygen atoms, while a part of silicon atoms is replaced with $(AlO_4)^{5-}$ aluminum atoms.

The mean chemical composition of zeolites is presented in Table II [20].

The particle size distribution of zeolite was estimated by a particle sizer Analysette 22 (Fritsch, D). The particle size distribution of the adsorbents used is presented in Fig. 1. The Sauter mean diameter of zeolite particles, defined by equation

SiO_2	65.0 – 71.3 %
Al_2O_3	11.5 – 13.1 %
CaO	2.7 – 5.2 %
K_2O	2.2 – 3.4 %
Fe_2O_3	0.7 – 1.9 %
MgO	0.6 – 1.2 %
Na_2O	0.2 – 1.3 %
TiO_2	0.1 – 0.3 %

$$d_{32} = \frac{\sum_{i=1}^{m} n_i d_i^3}{\sum_{i=1}^{m} n_i d_i^2} \tag{5}$$

is $d_{32} = 2.170\mu m$. The mean diameter of zeolite particles at 50% is $d_{50} = 1.415\mu m$.
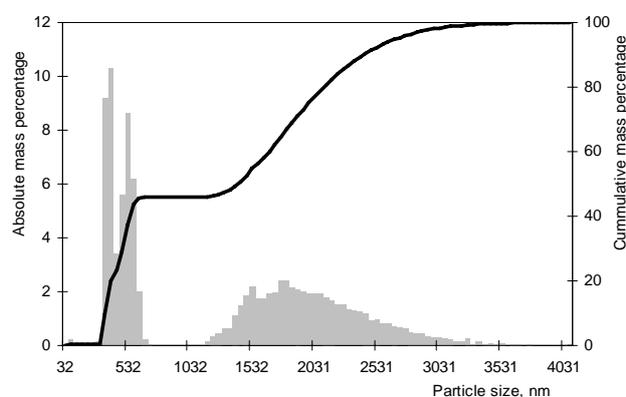
Fig. 1 Particle size distribution of zeolite particles

B. Batch Adsorption Equilibrium Studies

A series of flasks containing 200 ml of copper or nickel solutions of different concentrations prepared from copper or nickel sulphate and a fixed dosage of zeolite (1 $kg.m^{-3}$) together with a fixed dosage of NaCl (1, 2, 5, 10 and 100 $kg.m^{-3}$) were agitated for 3 hours in a rotary shaker at 200 rpm, with a temperature control at 25 ºC, what was sufficient for the copper and nickel adsorption to reach an equilibrium. After equilibration and sedimentation of suspensions the samples of aqueous phases were analyzed for copper or nickel content. The amounts of copper or nickel adsorbed q_{eq} in each flask were determined from the difference between the initial metal concentration c_0 and metal concentration at equilibrium c_{eq} in the solution.

C. Analysis of Concentration

The concentrations of unadsorbed copper were measured by the atomic absorption spectrometer (AAS) Perkin Elmer 3100 with deuterium correction background. Atomic absorption spectroscopy is an optical method based on absorption of electromagnetic radiation in the range of wavelengths 190 to 850 nm.

IV. RESULTS AND DISCUSSION

A. Copper Adsorption

The experimental equilibrium data for copper adsorption on zeolite for all dosages of NaCl were fitted by the isotherms (1), (2) and (3). Equilibrium data and the fitted isotherms for copper adsorption on zeolite for NaCl dosage 10 kg.m^{-3} (as an example) are presented in Fig. 2.
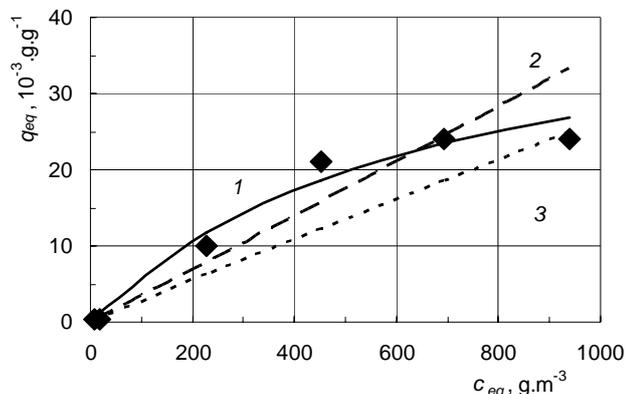
Fig. 2 Experimental data and adsorption isotherms of copper on zeolite for NaCl dosage 10 kg.m^{-3}. Dots represent the experimental data. Lines are fitted using *1* – Lagmuir (1), *2* – Freundlich (2) and *3* – R-P (3) isotherms

The best fitting isotherms according to the index of correlation were selected to describe the experimental data as presented in Fig. 3.

Fig. 3 Adsorption isotherms of copper on zeolite for the set of NaCl dosages
NaCl dosage: *0* – 0 kg.m^{-3}, *1* – 1 kg.m^{-3}, *2* – 2 kg.m^{-3}, *3* – 5 kg.m^{-3}, *4* – 10 kg.m^{-3} and *5* – 100 kg.m^{-3}

The best fitting isotherms for copper adsorption are presented in Table III.

According to the results presented in Fig. 3, there is a significant difference in copper adsorption in the presence of NaCl compared to the adsorption without NaCl. The maximum equilibrium capacity is the highest for NaCl dosage 1 kg.m^{-3} (65×10^{-3} g.g^{-1}) in comparison with the maximum equilibrium capacity for adsorption without NaCl (26.8×10^{-3} g.g^{-1}). Compared with the equilibrium capacity for lower initial copper concentration (0 – 250 g.m^{-3}) the equilibrium capacity for adsorption without NaCl is higher than with NaCl added.

TABLE III
BEST FITTING ISOTHERMS FOR COPPER ADSORPTION

NaCl dosage, kg.m^{-3}	Isotherm	Correlation index
0	Langmuir	0.9274
1	Langmuir	0.9889
2	Langmuir	0.9971
5	Freundlich	0.9758
10	Langmuir	0.9869
100	R-P	0.9509

B. Nickel Adsorption

The experimental equilibrium data for nickel adsorption on zeolite for all dosages of NaCl were fitted by the isotherms (1), (2) and (3). Equilibrium data for nickel adsorption on zeolite for NaCl dosage 10 kg.m^{-3} (as an example) are presented in Fig. 4.
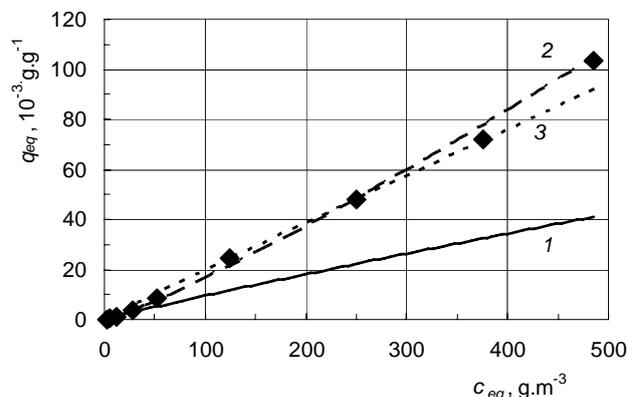
Fig. 4 Experimental data and adsorption isotherms of nickel on zeolite for NaCl dosage 10 kg.m^{-3}. Dots represent the experimental data. Lines are fitted using *1* – Langmuir (1), *2* – Freundlich (2) and *3* – R-P (3) isotherms

The best fitting isotherms according to the index of correlation were selected to describe the experimental data as presented in Fig. 5.

TABLE IV
BEST FITTING ISOTHERMS FOR NICKEL ADSORPTION

NaCl dosage, kg.m^{-3}	Isotherm	Correlation index
0	Langmuir	0.9991
1	R-P	0.9842
2	R-P	0.9931
5	R-P	0.9946
10	R-P	0.9975
100	R-P	0.9955

The best fitting isotherms for nickel adsorption are presented in Table IV.

According to the results presented in Fig. 5, there is not a significant difference in nickel adsorption in the presence of

163

NaCl and without NaCl for lower initial nickel concentration $0 - 200$ g.m^{-3}. The maximum equilibrium capacity is the highest for NaCl dosage 1 kg.m^{-3} (195×10^{-3} g.g^{-1}) the lowest for NaCl dosage 100 kg.m^{-3} (100×10^{-3} g.g^{-1}). The maximum equilibrium capacity for adsorption without NaCl is 156×10^{-3} g.g^{-1}.
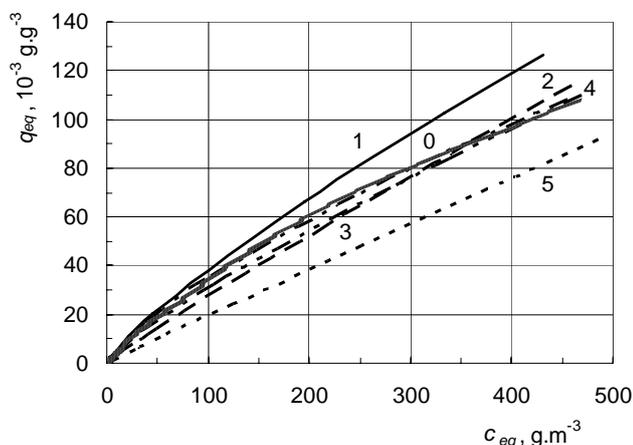
Fig. 5 Adsorption isotherms of nickel on zeolite for the set of NaCl dosages
NaCl dosage: $0 - 0$ kg.m^{-3}, $1 - 1$ kg.m^{-3}, $2 - 2$ kg.m^{-3}, $3 - 5$ kg.m^{-3}, $4 - 10$ kg.m^{-3} and $5 - 100$ kg.m^{-3}

V. CONCLUSION

The influence of salinity on copper and nickel adsorption was investigated. The presented results are partial. Further investigation will be concentrated on the influence of pH, temperature and also concurrent adsorption of heavy metals such as Cu, Zn, Ni, and Pb, etc.

REFERENCES

[1] B. Salih, A. Denizli, B. Engin, and E. Piskin, "Removal of cadmium (II) ions by using Alkali Blue 6B attached poly(EGDMA-HEMA) microspheres", *React. Funct. Pol.*, vol. 27, no. 3, pp. 199-208, 1995

[2] S. E. Bailey, T. J. Olin, R. M. Bricka, and D. D. Adrian, "A review of potentially low-cost sorbents for heavy metals," *Water Res,*, vol. 33, pp. 2469-79, 1999.

[3] G. Crini, "Non-conventional low-cost adsorbents for dye removal: A review," *Biores, Tech.*, vol. 97, no. 9, pp. 1061-1085, 2006.

[4] E. L. Cochrane, S. Lu, S. W. Gibb, and I. Villaescusa, "A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media," *J. Haz. Mat.*, vol. 137, no. 1, pp. 198-206, 2006.

[5] X. G. Li, F. Hao, and M. R. Huang, "Natural sorbents for mercury-ion removal," *Prog. Chem.*, vol. 20, no. 2-3, pp. 233-238, 2008.

[6] K. Štefušová, M. Václavíková, G. P. Gallios, Š. Jakabský, I. Kozáková, L. Ivanovičová, and D. Gešperová, "Sorption of arsenic on synthetic akaganeite", in *Proc. 11th Conf. Environment and Mineral Processing, Part II*, Ostrava (CZE), 2007, pp. 71-74.

[7] S. H. Lee, G. K. Moon, S. G. Choi, and H.S. Kim, "Molecular-Dynamics Simulation Studies of Zeolite-A .3. Structure and Dynamics of Na+ Ions and Water Molecules in a Rigid Zeolite-A," *J. Phys. Chem*, vol. 98, no. 6, pp. 1561-1569, 1994.

[8] H. M. N. AlMadani, "Water desalination by solar powered electrodialysis process," *Ren. Energy*, vol. 28, no. 12, pp. 1915-1924, 2003.

[9] C. Green-Ruiz, V. Rodriguez-Tirado, and B. Gomez-Gil, "Cadmium and zinc removal from aqueous solutions by *Bacillus jeotgali*: pH, salinity and temperature effects," *Biores. Tech.*, vol. 99, no. 9, 2008.

[10] F. Di Natale, A. Lancia, A. Molino, and D. Musmarra,, "Removal of chromium ions form aqueous solutions by adsorption on activated carbon and char," *J. Haz. Mat.*, vol. 145, no. 3, 2007.

[11] M. Pansini, C. Colella, and M. De Gennaro, "Chromium removal from water by ion exchange using zeolites," *Desal..*, vol. 83, no. 1-3, pp. 145-157, 1991.

[12] R. Petrus, and J. K. Warchol, "Heavy metal removal by clinoptilolite. An equilibrium study in multi-component systems," *Water Res.*, vol. 39, no. 5, pp. 819-830, 2005.

[13] M. Akgul, A. Karabakan, O. Acar, and Y. Yurum, "Removal of silver (I) from aqueous solutions with clinoptilolite," *Mic. Mes. Mat.*, vol. 94, no. 1-3, pp. 99-104, 2006.

[14] N. Bektas, and S. Kara, "Removal of lead from aqueous solutions by natural clinoptilolite: equilibrium and kinetic studies," Sep. Purif. Technol., vol. 39, no. 3, pp. 189-200, 2004.

[15] A. M. El-Kamash, A. A. Zaki, and M. A. El Geleel, "Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A," *J. Haz. Mat.*, vol. 127, no. 1-3, pp. 211-220, 2005.

[16] M. Prasad, H. Y. Xu, and S. Saxena, "Multi-component sorption of Pb(II), Cu(II) and Zn(II) onto low-cost mineral adsorbent," *J. Haz. Mat.*, vol. 154, no. 1-3, pp. 221-229, 2008.

[17] G. P. C. Rao, S. Satyaveni, et al., "Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite," *J. Env. Manag.*, vol. 81, no. 3, pp. 265-272, 2006.

[18] A. Gunay, E. Arslankaya, and I. Tosun, "Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics," *J. Haz. Mat.*, vol. 146, no. 1-2, pp. 362-371, 2007.

[19] J. C. Y. Ng, W. H. Cheung, and G. McKay, "Equilibrium studies of the sorption of Cu(II) ions onto chitosan," *J. Coll. Int. Sc.*, vol. 255, no. 1, pp. 64-74, 2002.

[20] Zeocem, a.s., Bystré (SK) (February 10, 2007) [Online]. Available: http://www.zeocem.sk