# Effect of zeolite particle size on Mn sorption capacity

TOMÁŠ BAKALÁR[1], HENRIETA PAVOLOVÁ[1] and IGOR MIŇO[2]

*1 – Technical University of Košice, Faculty of Mining, Ecology, Process Control and Geotechnologies, Letná 9, 042 00 Košice, Slovakia, tomas.bakalar@tuke.sk, henrieta.pavolova@tuke.sk*

*2 – Univesity of Veterinary Medicine and Pharmacy in Košice, Department of the Environment, Veterinary Legislation and Economy, Komenského 73, 041 81 Košice, Slovakia, igor.mino@uvlf.sk*

This work investigates the use of specific zeolite based sorbents to lower the high manganese level below the limit given by the Decree No. 247/2017 of the Ministry of Health of the Slovak Republic laying down details on drinking water quality, drinking water quality control, monitoring program and risk management of drinking water supply in Slovakia which is 50.0 μg per litre in drinking water. Unfortunately, this limit value of manganese is exceeded in more than 50% of monitored sources of groundwater and surface water based on the data from the Information System for Monitoring the Environment of the Slovak Hydrometeorological Institute. This is the reason why not only new technologies have to be developed but also the existing ones have to be evolved in order to make them more efficient, more low-cost and more easy to use. The investigated technology is not novel but the reason for the study was the high manganese concentration in most of natural water in Slovakia and to test the efficacy of Slovakia-based natural zeolite in the removal of Mn from aqueous systems – making it more efficient, reducing costs, improving the economic viability, though the economic aspect is not the merit of the study, and making it simpler.

Zeolites are aluminosilicates, naturally occurring minerals, with an open framework crystal structure. Zeolites are widely used in many applications, for example as molecular sieves, adsorbents, surfactants, as well as for removal of cations from acid mine water and industrial wastewater. Natural zeolites have high capacity in removing heavy metals from contaminated water, are relatively cheap, safe, and environmentally friendly adsorbents. The zeolite quarry, where the samples used for study were obtained from, is located in Nižný Hrabovec (SK) and is considered to be one of the largest deposits and cleanest zeolite areas in Europe (Zeocem, 2017).

Natural zeolite ZeoCem Micro 20 and Micro 50 (Zeocem, 2017) with mean particle size of 20 μm and 50 μm, respectively, and the main component of clinoptilolite were used in the experiments. Solutions of Mn were prepared from analytic grade manganese sulphate monohydrate (ITES Vranov, Ltd., SK). Analytic grade HCl and NaOH, used to adjust pH, were also obtained from ITES Vranov, Ltd. (SK).

The sorption experiments were realised with a series of flasks containing 100 $cm^3$ ($V$) of Mn solution at different initial concentrations ($C_0$ = 0.001 to 1 $g.dm^{-3}$) and a fixed dosage of sorbent ($C_a$ = 1 $g.dm^{-3}$), agitated for 2 hours in a rotary shaker at 200 $min^{-1}$, with a temperature control at 25 °C, sufficient for the metal ions adsorption to reach an equilibrium.

The initial pH of the solution was 7. The solutions were settled and analysed for Mn content by atomic absorption spectrometer (AAS) iCE 3300 Thermo Scientific (USA) with deuterium correction background. The amounts of metal adsorbed $q_e$ (kg.kg$^{-1}$) were calculated from the difference between the initial metal concentration $C_0$ and metal concentration at equilibrium $C_e$ (g.dm$^{-3}$) in the solution according to equation $q_e = (C_0 - C_e).V/m_a$, with $m_a$ (g) is the weight of adsorbent, $V$ (dm$^3$) is the volume of solution. All the experiments were performed in triples and the result was taken as the average value of each experiment.

The experiments were analysed using adsorption isotherms which provide an adequate description of Mn adsorption equilibria on zeolites. The Freundlich (1906), Langmuir (1916), and Redlich-Peterson (1959) isotherms were used. The parameters of the isotherms for Mn adsorption onto ZeoCem Micro 20 and Micro 50 are presented in Table 1. The isotherms and parameters are as follows:

- Freundlich: $q_e = K_f C_e^{1/n}$, with $K_f$ (m$^{3/n}$.kg$^{-1/n}$) is adsorption capacity, $n$ is intensity (1); the isotherm represents sorption taking place on a heterogeneous surface with interaction between the adsorbed molecules (Albadarin et al., 2011),
- Langmuir: $q_e = q_m a_L C_e \big/ \left(1 + a_L C_e\right)$, with $q_m$ (kg.kg$^{-1}$) is maximum sorption capacity, $a_L$ (m$^3$.kg$^{-1}$) is adsorption energy; the isotherm represents sorption taking place on a homogenous surface within the adsorbent (Günay et al. 2007),
- Redlich-Peterson: $q_e = K_R C_e \big/ \left(1 + a_R C_e^{\beta}\right)$, with $K_R$ (m$^3$.kg$^{-1}$) and $a_R$ (m$^{3\beta}$.kg$^{-\beta}$) are constants, $\beta$ (1) is exponent; the isotherm is used as a compromise between the Langmuir and Freundlich systems (Albadarin et al., 2011).

The adsorption study was conducted with two sorbents based on zeolite. Based on the correlation coefficients we evaluated the equilibrium and selected the most suitable isotherm. The study confirmed that the experimental data are best described by Redlich-Peterson isotherm for both ZeoCem Micro 20 and Micro 50 and ZeoCem Micro 20 with smaller mean particle size has a higher sorption capacity for Mn, which might be caused by the particle size of the adsorbent. Further studies will concentrate on searching for other sorbents, especially those based on natural materials from Slovakia and their comparison under different conditions, especially varying pH and temperature as well as their modifications.

**Acknowledgement:** This work was supported by the Scientific Grant Agency of the Ministry of Education of Slovak Republic under the grant No. 1/0515/18.

## References

Albadarin, A.B., Al-Muhtaseb, A.H., Al-laqtah, N.A., Walker, G.M., Allen S.J. & Ahmad, M.N.M. 2011 Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts. *Chemical Engineering Journal*, 169, 1–3, 20–30.

Freundlich, H.M.F. 1906. Über die Adsorption in Lösungen. *Zeitschrift fuer Physikalische Chemie*, 57(A), 385–470.

Günay, A., Arslankaya, E. & Tosun, I. (2007). Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. *Journal of Hazardous Material*, 146, 1–2, 362–371.

Langmuir, I. 1916. The constitutuion and fundamental properties of solids and liquids. Part I. Solids. *Journal of American Chemical Society*, 38, 11, 2221–2295.

Redlich, O. & Peterson, D.L. 1959. A useful adsorption isotherm. *The Journal of Physical Chemistry*, 63, 6, 1024–1024.

Zeocem, 2017. Zeocem, a.s. Bystré [online], [cited 24.2.2017], available on-line: http://www.zeocem.com/sk/.

**Figure 1.** Sorption capacities of studied Mn sorbents.

| Adsorbent | | ZeoCem Micro 20 | ZeoCem Micro 50 |
|---|---|---|---|
| Freundlich isotherm | $k_f$ | 0.0922 | 0.0978 |
| | $n$ | 2.3523 | 2.8910 |
| | $R^2$ | 0.8701 | 0.9335 |
| Langmuir isotherm | $q_m$ | 4.6019 | 2.1588 |
| | $a_L$ | 0.0009 | 0.0015 |
| | $R^2$ | 0.9517 | 0.9390 |
| Redlich-Peterson isotherm | $k_R$ | 1.7166 | 1.4950 |
| | $b_R$ | 18.2342 | 15.0638 |
| | $\beta$ | 0.5778 | 0.656 |
| | $R^2$ | 0.9535 | 0.9728 |