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Removal of Manganese from Water Using Modified Natural Zeolite

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ABSTRACT

The content of manganese in natural water is relatively high in Slovakia. For this reason research is concentrated on technologies which are efficient, low-cost and easy to use. In this study use of specific sorbents based on zeolite, ZeoCem Mn dark, light and mixed, were investigated to lower the high manganese level below the limit for drinking water. Zeolites are used for Mn(II) removal with different removal capacities. The modified zeolite was characterised, used in batch sorption experiments and evaluated using three isotherms. The samples were agitated for 2 hours at 200 min^{-1}, 25 °C, and the initial pH of the solution 7. The maximum sorption capacities of ZeoCem Mn dark, light and mixed were 3.057, 2.143 and 2.105, respectively, implying that the ZeoCem Mn grains separated by colour adsorbed higher amount of Mn than the original ZeoCem Mn grains. Dark zeolite grains adsorbed more Mn than light grains.

Keywords : zeolite, manganese, adsorption, isotherm, XPS.

I. INTRODUCTION (12 BOLD)

The drinking water quality is regulated by 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. The Decree has implemented the European Directives on the quality of water intended for human consumption and it also includes the limits for quality requirements. According to the decree the limit for manganese in drinking water is 50.0 µg per litre. According to the information from the Information System for Monitoring the Environment, partial monitoring system – water of the Slovak

Hydrometeorological Institute the limit values of manganese are exceeded in more than 50% of monitored sources of groundwater and surface water. For this reason new technologies have to be developed which are efficient, low-cost and easy to use.

This work was intended to investigate use of specific sorbents to lower the high manganese level below the limit. Although the investigated technology is not novel, the reason for the study was the high manganese concentration in most of natural water in Slovakia, based on the data of the Slovak Hydrometeorological Institute and to test the efficacy of manganese oxide coated zeolite in the removal of Mn(II) from aqueous systems reducing costs and improving the economic viability, though the economic aspect is not the merit of this study.

Zeolites are widely used for Mn(II) removal with different removal capacities. Chilean zeolite [1] used for removal of Mn(II) consisted of 36% of clinoptilolite, 33% of mordenite, 26% of quartz and 5% of montmorillonite and was used natural and treated with NaCl, NaOH, Na_2CO_3 and NH_4Cl. According to the results, under similar conditions, the adsorption capacity slightly decreases in the following order: activated zeolite with NaCl > activated zeolite with NaOH > activated zeolite with Na_2CO_3 > activated zeolite with NH_4Cl > natural zeolite. Manganese oxide coated Chilean zeolite [2] was tested for Mn(II) removal with a fairly good potential as an adsorbent and the equilibrium data showed excellent correlation for both Langmuir and Freundlich isotherm model and this implies both monolayer adsorption and a heterogeneous surface existence. Natural zeolite tuff from the Vranjska Banja deposit (Serbia) used for Mn removal consisted mainly of clinoptilolite (more than 70%) [3]. The Mn(II) removal was best described by the Langmuir-Freundlich isotherm. The intra-particle diffusion is not the rate-controlling step in the sorption of Mn(II) on clinoptilolite. Thermodynamic data suggest spontaneity of the endothermic ion-exchange process. A Ca-rich clinoptilolite with almost no Fe content from Thrace (North Greece) and its Fe-modified form were used for simultaneous removal of Cu(II), Mn(II) and Zn(II) from drinking water [4]. Based on the results order of selectivity was the same for both adsorbents: Cu > Zn > Mn. Natural zeolite from Sivas-Yavu (Turkey) and its modification by ion-exchange (NH_4NO_3) and addition of aluminum [$Al_2(SO_4)_3$] were used for Mn(II) removal [5]. All modifications increased the manganese adsorption capacity of natural zeolites two times. The Freundlich isotherm best fitted the data obtained implying a heterogeneous surface. Natural zeolite from the Manisa-Demirci region (Turkey) and its modification by NaOH were also used for Mn(II) removal [6]. The maximum sorption capacity was reached for the zeolite treated with $1.5 mol.L^{-1}$ NaOH. Higher NaOH concentrations lead not only to a decrease in sorption capacity, but also to a significant deformation of the zeolite structure. The experimental data of Mn(II) sorption on natural zeolite were best fitted with the Langmuir isotherm, while on NaOH modified zeolites were best fitted with the Freundlich isotherm. Natural zeolite from Enli Mining Company open pit mine in Manisa-Gördes in Western Anatolia (Turkey) was used to remove Mn(II) from aqueous solutions [7]. Based on the results the adsorption of Mn (II) cations match Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich isotherms. It was also found that the adsorption phenomenon depends on charge density and hydrated ion diameter.

Other material is used for Mn(II) removal also with different removal capacities:

- bentonite, mainly composed of clay minerals from the smectite group [8]. Langmuir isotherm described the adsorption of Mn(II) well. The removal of Mn(II) is achieved by an ion exchange mechanism with naturally occurring cations in bentonite, as well as by forming the inner- and outer-sphere complexes with bentonite surface.
- surfactant-modified alumina (with bilayer of sodium dodecyl sulphate) [9]. The experimental data were best fitted by Freundlich isotherm implying adsorption on a heterogeneous surface.
- white rice husk ash [10]. The obtained results showed that the removal is chemisorption, where the OH-groups of SiO_2 take part, releasing H^+ ions into the solution. The Langmuir isotherm well described the sorption process.
- carbonyl iron microparticles (MnO(x) coated magnetic particles) [11]. The advantages of using MnO(x) coated magnetic particles for Mn(II) ions removal are the absence of saturation up to initial concentrations of 500 mg Mn L^{-1}, the easy and efficient recovery of the adsorbents from the solution due to magnetic properties, minimizing alterations of water quality and the reusability of the adsorbents contributing to economic cost savings.
- sugarcane bagasse and activated carbon [12]. Freundlich and Langmuir isotherms for sugarcane bagasse and Freundlich isotherm for activated carbon described well the experimental data. Formation of hydrogen bonds and electrostatic attraction dominated the adsorption process for sugarcane bagasse by the FTIR analysis.
- granular activated carbon from coconut shell [13]. The Langmuir isotherm fitted the experimental data better as the ambient temperature was relatively high and allowed only monolayer adsorption as well as the chemisorption was more dominant.
- granular activated carbon and Amberlite IR-120H [14]. The Langmuir isotherm fitted the experimental data better than the Freundlich isotherm and the metal has higher affinity with the AIR-120H surface than the granular activated carbon.
- chitosan [15]. Among other parameters, the most significant effect on the adsorption capacity has pH in the range of 2.9-5.9. The Freundlich isotherm fitted the experimental data better than the Langmuir. Chitosan has also antibacterial properties [16].

II. MATERIALS AND METHODS

Mn(II) solutions were prepared from analytic grade $MnSO_4.H_2O$, obtained from ITES Vranov, Ltd. (SK). Analytic grade hydrochloric acid and sodium hydroxide were used to adjust the pH, both obtained from ITES Vranov, Ltd. (SK).

II.I Zeolite

Zeolites are naturally occurring minerals – aluminosilicates with an open crystal structure occupied by cations and water molecules. These components can be varied within large cavities, allowing ion exchange. Zeolite is composed of three-dimensional lattices of SiO_4 and tetrahedrons of AlO_4. Natural zeolites are relatively cheap, safe, and environmentally friendly adsorbents. They also have a large surface area. Zeolites have great potential for many applications, for example molecular sieves, catalysts, adsorbents, surfactants, and for removal of cations from acid mine water and industrial waste water. They have a strong affinity for heavy metals. The zeolite quarry is located in Nižný Hrabovec (SK). The basic characteristic of the zeolite is in Table 1. It is considered to be one of the largest and cleanest zeolite areas in Europe [17].

Modified natural zeolite ZeoCem Mn [17] with main component of clinoptilolite was used in the experiments. ZeoCem Mn was separated by colour to dark and light to create two new adsorbents, since it is assumed that the dark grains contain higher amount of MnO_2 on their surface, i. e. the adsorption capacity for Mn(II) ions will be higher than the light ones. Thus in the experiments 3 types of ZeoCem Mn were used – dark, light and mixed (original).

Table 1 Zeolite characteristics [17]

Chemical composition	**[%]**
SiO_2	65-71.3
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

Chemical composition	**[%]**
Si/Al	4.8-5.4
Mineral composition	[%]
Clinoptilolite	84
Cristobalite	8
Clay mica	4
Plagioclase	3-4
Rutile	0.1-0.3
Silica	Traces
Physical and mechanical properties :	
Bulk density	1600-1800 $kg.m^{-3}$
Specific surface	30-60 $m^2.g^{-1}$
Specific weight	2200-2440 $kg.\ m^{-3}$
Whiteness	70 %
Hardness (Mohs Scale)	1.5-2.5
Porosity	24-32 %
Ion-exchange properties	$[mol.kg^{-1}]$
Ca^{2+}	0.64-0.98
Mg^{2+}	0.06-0.19
K^+	0.22-0.45
Na^+	0.01-0.19
Total ion-exchange capacity	1.20-1.50

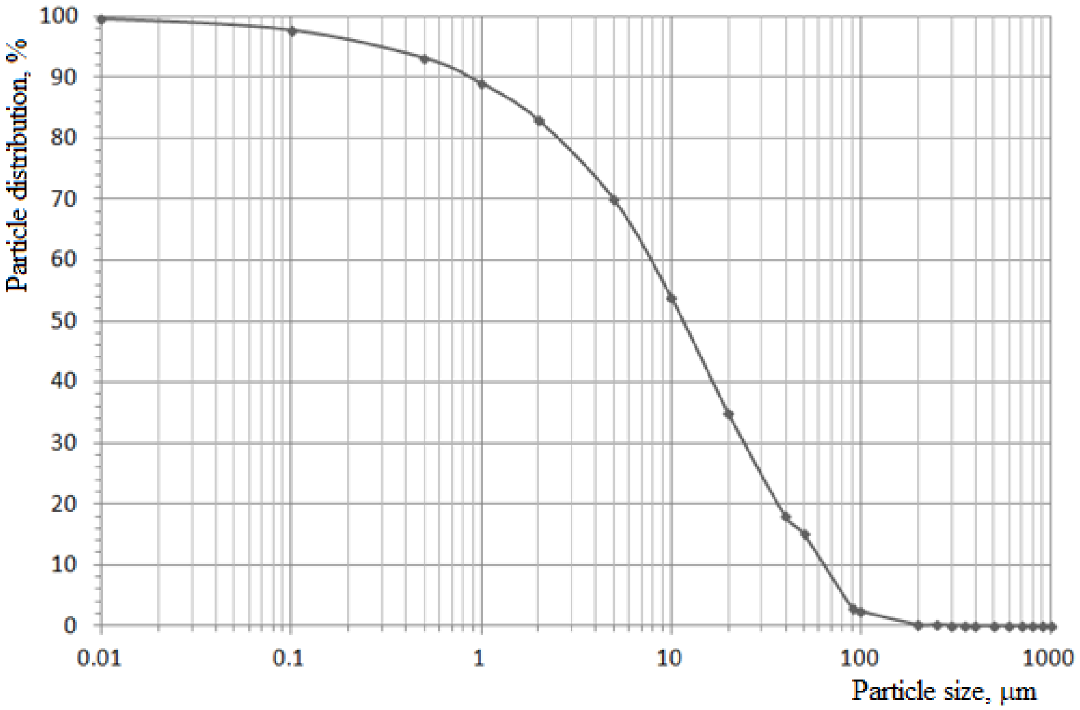


Fig. 1 Particle size distribution of ZeoCem Mn particles [17]

II.II Sorption experiments

The equilibrium experiments were carried out with a series of flasks containing 100 mL (V) of metal ion solution of different initial concentrations (C_0 = 0.001 to 1 g.L^{-1}) prepared from manganese sulphate and a fixed dosage of sorbent (C_a = 1 g.L^{-1}) which were agitated for 2 hours in a rotary shaker at 200 min^{-1}, with a temperature control at 25 °C, what was sufficient for the metal ions adsorption to reach an equilibrium. The initial pH of the solution was 7.

After equilibration and sedimentation of suspensions the samples were settled and the solutions were analysed for metal content by AAS as described below. The amounts of metal adsorbed q_e (kg.kg^{-1}) in each flask were determined from the difference between the initial metal concentration C_0 and metal concentration at equilibrium C_e (g.L^{-1}) in the solution and were calculated according to equation:

$$q_e = \frac{(C_0 - C_e)V}{m_a} \qquad (1)$$

m_a (g) is the weight of adsorbent, V (L) is the volume of solution.

All the experiments were performed in triples and the result was taken as the average value of each experiment.

II.III Data analysis

Adsorption isotherms are a critical piece of information on optimization of the use of adsorbents. Isotherm models provide an adequate description of Mn (II) adsorption equilibria on zeolites. The following isotherms were used:

- Freundlich [18]:

  $$q_e = K_f C_e^{1/n} \tag{2}$$

  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 [19],

- Langmuir [20]:

  $$q_e = \frac{q_m a_L C_e}{1 + a_L C_e} \tag{3}$$

  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 [21],

- Redlich-Peterson [22]:

  $$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{4}$$

  K_R ($m^3.kg^{-1}$) and a_R ($m^{3\beta}.kg^{-\beta}$) are constants, β (1) is exponent; the isotherm is used as a compromise between the Langmuir and Freundlich systems [19].

II.IV Regression analysis

The two-parameter adsorption isotherms were transformed into linear forms for obtaining adjustable parameters by linear regression analysis; though the three-parameter isotherm were not fitted to experimental data by linear regression means but in this case non-linear least squares analysis was applied.

For that reasons, a minimization procedure has been adopted to solve isotherms and kinetic equations by minimizing the sum of error squared between the predicted values and the experimental data using the solver add-in function of the Microsoft Excel. In order to quantitatively compare the applicability of isotherm equations in fitting to data, non-linear correlation coefficient (R^2) was calculated.

II.V Metal concentration analysis

The concentrations of metals in solutions were measured by the atomic absorption spectrometer (AAS) iCE 3300 Thermo Scientific (USA) with deuterium correction background. The samples were settled and the clear solution was used for the analysis. The samples were diluted, if necessary, using distilled water. The measurements were conducted at a wavelength of 279.5 nm with a detection limit of 0.020 mg.L^{-1}. The standards were prepared from Manganese standard solution for AAS, obtained from Acros Organics, Thermo Fisher Scientific Inc., Geel (BE) by dilution in distilled water.

II.VI Surface analysis

XPS (X-ray photoelectron spectroscopy) was used for surface analysis (SPECS, USA) equipped with PHOIBOS 100 SCD and non- monochromatic Al/Mg twin X-ray source. The survey surface spectrum was measured at 70 eV transition energy and high- resolution spectra at 50 eV, at room temperature. All spectra were acquired at a basic pressure of 2.10^{-9} mbar with AlKα excitation at 10 kV (100 W). The data were analysed by SpecsLab2 CasaXPS software (Casa Software Ltd). The spectrometer was calibrated against silver (Ag 3d). All samples showed variable degrees of charging due to their insulating nature. The energy scale has been calibrated by normalizing the C 1s line of adsorbed adventitious hydrocarbons to 285.0 eV. The method provided data on elemental composition of zeolite surface.

III. RESULTS

The parameters of the isotherms for Mn(II) adsorption onto ZeoCem Mn dark, light and mixed are presented in Table 2.

Table 2 Adsorption isotherm constants of Mn(II) on ZeoCem Mn dark, light and mixed

Adsorbent		ZeoCem Mn dark	ZeoCem Mn light	ZeoCem Mn mixed
Freundlich isotherm	k_f	0.0276	0.0064	0.0687
	n	1.9000	1.4700	2.7400
	R^2	0.9149	0.9698	0.8205
Langmuir isotherm	q_m	3.0571	2.1436	2.1057
	a_L	0.0007	0.0006	0.0030
	R^2	0.9510	0.9783	0.9493
Redlich-Peterson isotherm	k_R	1.6401	0.7906	1.7703
	b_R	46.2425	123.6432	19.6858
	β	0.4826	0.3269	0.5698
	R^2	0.9737	0.9667	0.9321

The maximum sorption capacity of Mn(II) onto ZeoCem Mn dark is 3.06 mg.g^{-1}. The equilibrium data and the fitted data of Mn(II) adsorption by isotherms are displayed in Figure 2. The correlation coefficients are in the range of 0.9149 to 0.9737. Based on the regression analysis and the fit in the graphics the best describing isotherm is Redlich-Peterson isotherm.

The maximum sorption capacity of Mn(II) onto ZeoCem Mn light is 2.14 mg.g^{-1}. The equilibrium data and the fitted data of Mn(II) adsorption by isotherms are displayed in Figure 3. The correlation coefficients are in the range of 0.9667 to 0.9783. Based on the regression analysis and the fit in the graphics the best describing isotherm is Langmuir isotherm.

The maximum sorption capacity of Mn(II) onto ZeoCem Mn mixed is 2.11 mg.g^{-1}. The equilibrium data and the fitted data of Mn(II) adsorption by isotherms are displayed in Figure 4. The correlation coefficients are in the range of 0.8205 to 0.9493. Based on the regression analysis and the fit in the graphics the best describing isotherm is Langmuir isotherm.

The XPS survey spectra of dark and light ZeoCem Mn in a wide energy range are shown in Figures 5 and 6, respectively.

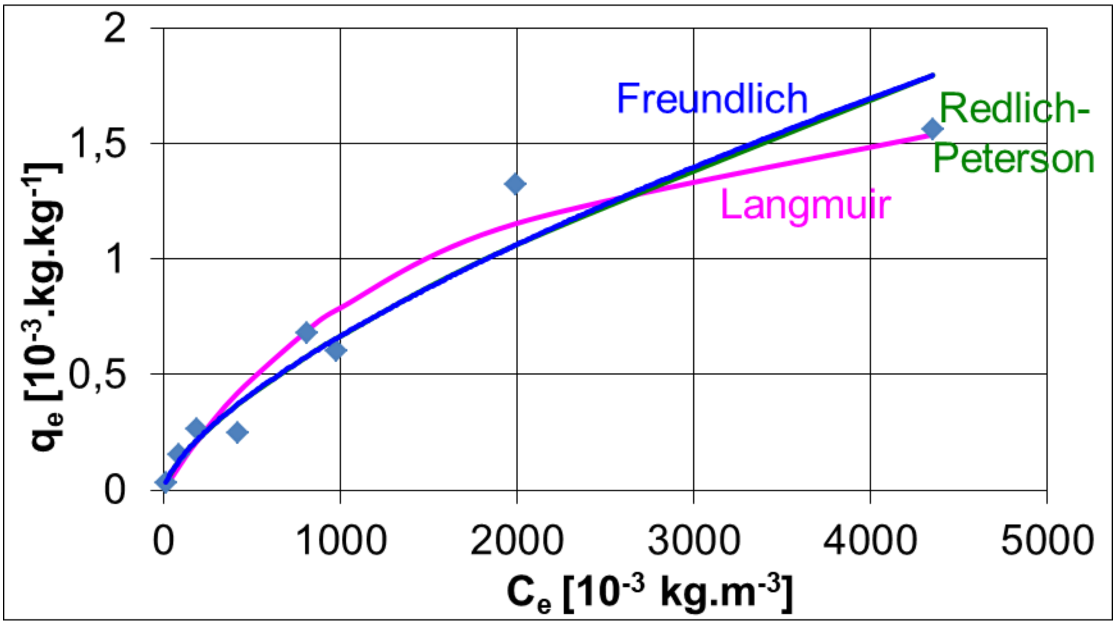


Fig. 2 Adsorption isotherms of Mn on ZeoCem Mn dark

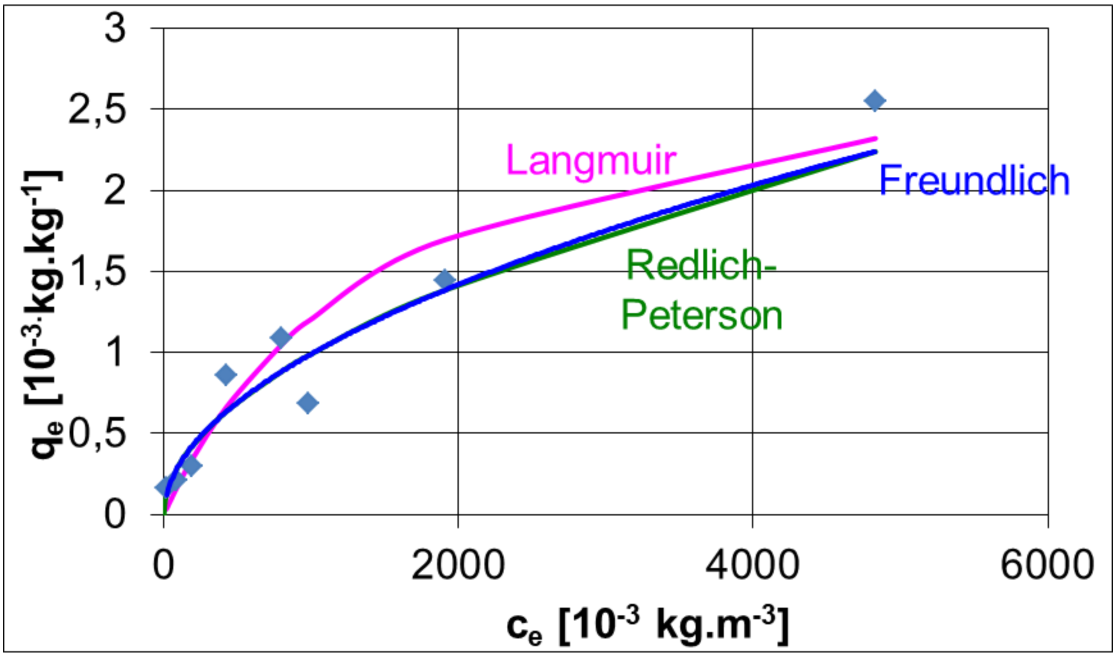


Fig. 3 Adsorption isotherms of Mn on ZeoCem Mn light

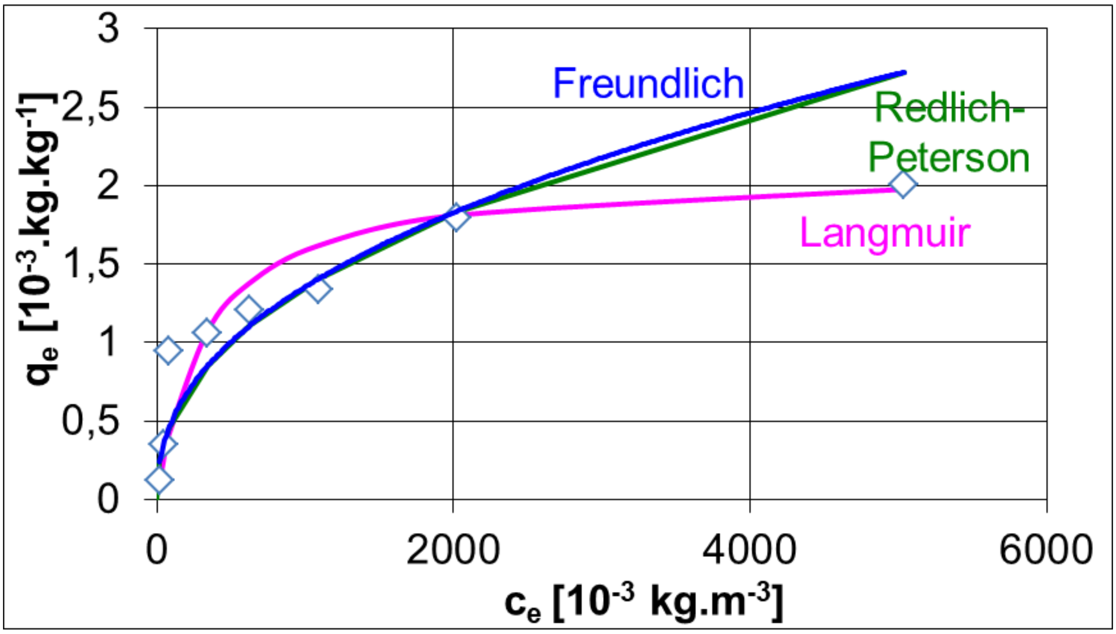
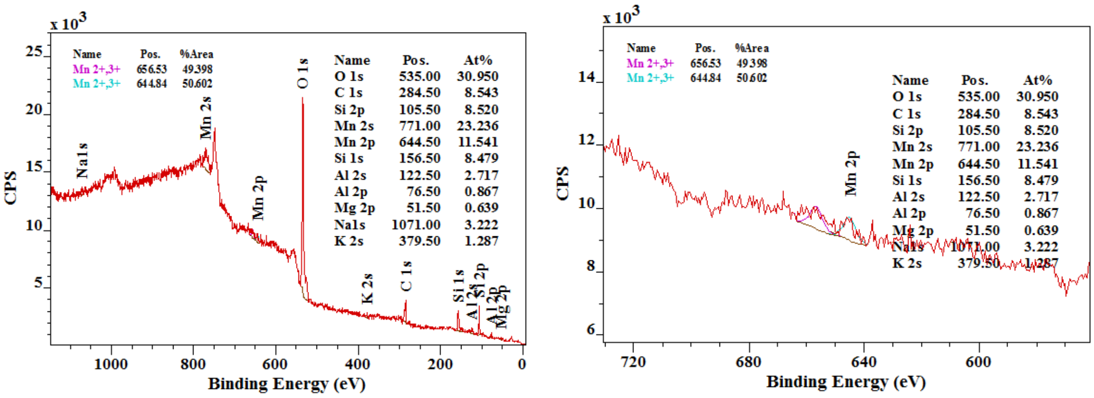


Fig. 4 Adsorption isotherms of Mn on ZeoCem Mn mixed



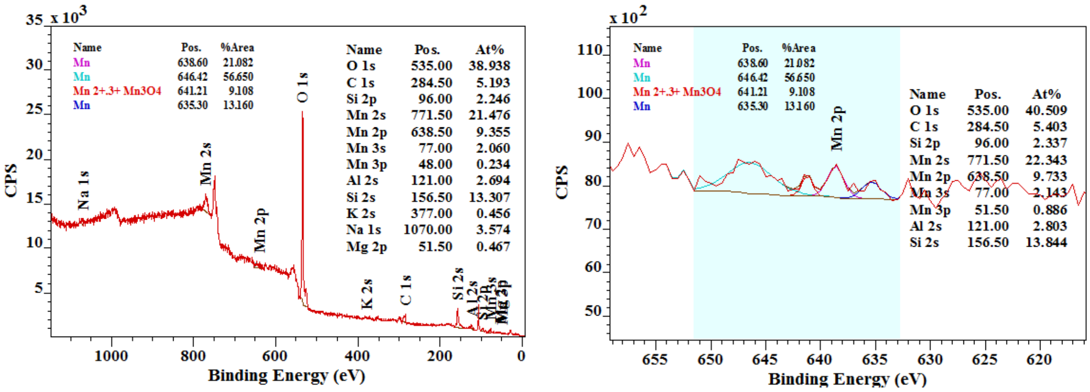
Name	Pos.	%Area
Mn 2+,3+	656.53	49.398
Mn 2+,3+	644.84	50.602

Name	Pos.	At%
O 1s	535.00	30.950
C 1s	284.50	8.543
Si 2p	105.50	8.520
Mn 2s	771.00	23.236
Mn 2p	644.50	11.541
Si 1s	156.50	8.479
Al 2s	122.50	2.717
Al 2p	76.50	0.867
Mg 2p	51.50	0.639
Na1s	1071.00	3.222
K 2s	379.50	1.287

Name	Pos.	%Area
Mn 2+,3+	656.53	49.398
Mn 2+,3+	644.84	50.602

Name	Pos.	At%
O 1s	535.00	30.950
C 1s	284.50	8.543
Si 2p	105.50	8.520
Mn 2s	771.00	23.236
Mn 2p	644.50	11.541
Si 1s	156.50	8.479
Al 2s	122.50	2.717
Al 2p	76.50	0.867
Mg 2p	51.50	0.639
Na1s	1071.00	3.222
K 2s	379.50	1.287

Fig. 5 XPS characteristics of ZeoCem Mn dark



Name	Pos.	%Area
Mn	638.60	21.082
Mn	646.42	56.650
Mn 2+.3+ Mn3O4	641.21	9.108
Mn	635.30	13.160

Name	Pos.	At%
O 1s	535.00	38.938
C 1s	284.50	5.193
Si 2p	96.00	2.246
Mn 2s	771.50	21.476
Mn 2p	638.50	9.355
Mn 3s	77.00	2.060
Mn 3p	48.00	0.234
Al 2s	121.00	2.694
Si 2s	156.50	13.307
K 2s	377.00	0.456
Na 1s	1070.00	3.574
Mg 2p	51.50	0.467

Name	Pos.	%Area
Mn	638.60	21.082
Mn	646.42	56.650
Mn 2+.3+ Mn3O4	641.21	9.108
Mn	635.30	13.160

Name	Pos.	At%
O 1s	535.00	40.509
C 1s	284.50	5.403
Si 2p	96.00	2.337
Mn 2s	771.50	22.343
Mn 2p	638.50	9.733
Mn 3s	77.00	2.143
Mn 3p	51.50	0.886
Al 2s	121.00	2.803
Si 2s	156.50	13.844

Fig. 6 XPS charakteristicks of ZeoCem Mn light

IV. DISCUSSION

The fact that dark grains contain higher levels of MnO_2 on their surface is demonstrated by the XPS analysis of the samples. In the case of the dark zeolite peaks belong to Mn^{2+}, Mn^{3+}, and the presence of oxygen confirms the presence of $KMnO_4$ (Fig. 5). In the case of the light zeolite there is a clear shift in the position of Mn 2p peak which confirms the presence of elemental Mn. Mn 3p has the position of Mn^{6+} cation, i.e. pure elemental Mn predominates in this sample (Fig. 6).

Table 3 A comparison of sorption capacities of different Mn(II) adsorbents

Adsorbent	q_{max} [mg.g^{-1}]	Temperature [°C]	Initial pH	Source
ZeoCem Mn dark	3.057	20	7	
ZeoCem Mn light	2.143	20	7	
ZeoCem Mn mixed	2.105	20	7	
Natural Chilean zeolite	7.114	25	6	[2]
Manganese oxide coated Chilean zeolite	30.216	25	6	[2]
Natural zeolite tuff from the Vranjska Banja deposit (Serbia)	8.610	25	6	[3]
Natural zeolite from Sivas-Yavu (Turkey)	7.680	25	6	[5]
Aluminium modified natural zeolite from Sivas-Yavu (Turkey)	25.120	25	6	[5]
NH_4^+ exchanged natural zeolite from Sivas-Yavu (Turkey)	24.330	25	6	[5]
Natural zeolite from the Manisa-Demirci region (Turkey)	31.200	25	6	[6]
NaOH modified natural zeolite from the Manisa-Demirci region (Turkey)	66.100	25	6	[6]
Natural zeolite from Manisa-Gördes in Western Anatolia (Turkey)	8.241	25	6-7	[7]
Unmodified bentonite (no further details)	12.410	20	5.49	[8]
Surfactant-modified alumina	1.480	30	8.05	[9]
White rice husk ash	18.010	35	*	[10]
Carbonyl iron microparticles	0.600	25	7	[11]
Sugarcane bagasse	0.676	23	4.5	[12]
Activated carbon	1.897	23	4.5	[12]
Granular activated carbon from coconut shell	2.545	30	*	[13]
Granular activated carbon	7.630	20	7	[14]
Amberlite IR-120H	8.710	20	7	[14]

*no pH adjustment

It was confirmed that the separation of ZeoCem Mn by colour mattered because it confirmed a higher sorption capacity for Mn^{2+} ions as originally. The light grains contained less MnO_2 on their surface than the dark ones, thus the adsorption capacity of the light grains was also lower than the adsorption capacity of the dark grains.

The results of this study presented similar sorption capacities to the results of other study [14], though they used different sorbents. The adsorption capacity was 4.9 $mg.g^{-1}$ and the pH and temperature were the same as in the experiments of this study. In Table 3, other zeolite- and non-zeolite-based sorbents and modifications of sorbents are disclosed. Based on the study of the literature and data presented in Table 3, it can be concluded that the highest efficacy for Mn^{2+} removal had NaOH modified natural zeolite from the Manisa-Demirci region (Turkey) [6] but, unlike our conditions, these experiments were carried out at different pH and temperature.

V. CONCLUSION

The modified zeolite has a layer formed on the surface to increase the sorption capacity for Mn. The formed surface layer of the modified zeolite has a major role in removing Mn from water. The adsorption study was conducted with three sorbents, two of which were formed by separation based on colour. Based on the correlation coefficients we evaluated the equilibrium and selected the most suitable isotherm. The study confirmed that the ZeoCem Mn grains separated by colour adsorbed higher amount of Mn than the original ZeoCem Mn grains. Dark zeolite grains adsorbed more Mn than light grains. Based on a comparison with studies that also used natural zeolite, it can be concluded that the adsorption capacity of ZeoCem Mn samples were lower. However, the experiments were not performed under the same conditions, i.e. temperature and pH were different. Further studies will concentrate on searching for other sorbents, especially those based on natural materials form Slovakia and their comparison under different conditions, especially varying pH and temperature as well as their modifications.

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