

THE SORPTION AND RETENTION CAPABILITY OF NATURAL AND IRON-MODIFIED ZEOLITES TOWARD MANGANESE IONS

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ABSTRACT

In this paper, the sorption and retention capability of natural (NZ) and iron-modified (FeZ) zeolites was tested. A 5-fold higher sorption capacity was observed on FeZ compared to NZ, under optimal experimental conditions of pH_0 and solid/liquid ratio. Moreover, the standard leaching test confirmed FeZ as more effective sorbent for retaining Mn^{2+} ions in a wide pH range compared to NZ.

Key words: manganese, natural zeolite, iron-modified zeolite, sorption, retention.

INTRODUCTION

Manganese is a naturally occurring element in rocks, soils and groundwater in the form of various minerals. It is essential in small amounts since it enables the maintenance of various biological functions in the human body. Overexposure to Mn(II) (> 0.1 mg/L) leads to neurotoxic effects such as Parkinson's disease. For this reason, the World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA) set the permissible limit of manganese in drinking water at 0.05 mg/L [1]. According to the Croatian legislation, the permissible limits of manganese in treated wastewater are 2 mg/L for discharge into water bodies and 4 mg/L into the sewage system [2]. Since manganese is used in the production of non-ferrous metallurgy, steel, batteries, etc., it is necessary to adequately treat wastewaters. Existing techniques currently researched and applied are oxidation, precipitation, sorption and other physical, chemical and biological techniques. Our research focuses on the investigation of the sorption and retention capability of natural (NZ) and iron-modified (FeZ) zeolites with respect to the Mn^{2+} ions.

EXPERIMENTAL

Sample preparation

The starting sample, natural zeolite (NZ) is collected from the Zlatokop deposit (Vranjska Banja, Serbia). The sample was milled, sieved and a particle size fraction of 0.6 – 0.8 mm was separated. Thereafter, sample was washed in ultrapure water and dried at 60 °C.

Iron-modified zeolite (FeZ) was prepared by treatment of NZ according to the procedure published previously [3]. Briefly, the procedure is consisted of three separated stages: firstly, sample was mixed with 1 mol/L $Fe(NO_3)_3 \cdot 9H_2O$ freshly prepared solution by dissolving iron(III) salt in acetate buffer at $pH=3.6$, followed by 1 mol/L NaOH and 4 % $NaNO_3$ solutions. The prepared sample was dried at 40°C and kept in a desiccator until use.

Sorption experiments

Aqueous solutions of Mn^{2+} ions were prepared by dissolving $Mn(NO_3)_2 \cdot 4H_2O$ salt in ultrapure water. The pH of the solution was adjusted by addition of a few drops of 0.1 mol/L HNO_3 and 0.1 mol/L KOH. All experiments were carried out in batch mode, at room temperature, at 230 rpm for 24 h. The concentration of Mn^{2+} ions was determined using atomic absorption spectrophotometer, AAS (PinAAcle 900F).

The effect of pH_0 was tested in the range $2.52 < pH_0 < 8.15$, at a solid/liquid ratio, $S/L = 10$ g/L and at initial concentration, $c_0 = 4.680$ mmol Mn/L. The effect of S/L ratio was studied at

$S/L = 2.5 - 17.5$ g/L, $pH_o = 5.8$, and at $c_o = 4.680$ mmol Mn/L. The effect of the c_o was tested in the range of 1.136 – 11.014 mmol Mn/L, at $S/L = 10$ g/L and $pH_o = 5 - 6$ (without adjustment of the pH).

Leaching experiments

The leaching of Mn^{2+} ions from the saturated NZMn and FeZMn samples obtained after saturation with $c_o = 6.390$ mmol Mn/L was examined according to the standard DIN 38414 leaching method [4]. A mass of 1.0 g of saturated samples was mixed with 10 mL of ultrapure water at different pH_o values in the 2.05 – 12.02, at room temperature and for 24 h.

RESULTS AND DISCUSSION

The effect of pH_o and S/L ratio on the removal efficiency, α of Mn^{2+} ions on NZ and FeZ is compared in Figure 1.

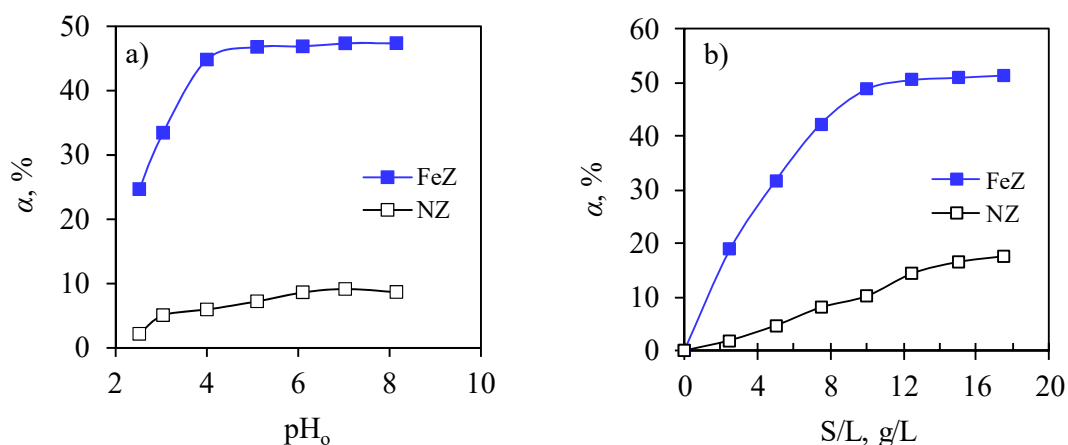


Figure 1. Effect of: a) pH_o and b) S/L ratio on manganese removal efficiency on NZ and FeZ.

Firstly, it should be pointed out that the precipitation of Mn^{2+} in the form of hydroxide occurs at $pH > 8.6$ [5]. Thus, the pH_o range was chosen in order to enable Mn removal by sorption, without the occurrence of precipitation. The absence of precipitation was confirmed by the equilibrium pH_e values, which were lower than 8.6, and were in the range 2.8 – 6.21 for NZ and 3.62 – 7.64 for FeZ (results are not shown). As can be seen from Figure 1a, contrary to the NZ for which Mn^{2+} removal efficiency increases slightly with increase of the pH_o up to 5.1, significant increase in removal efficiency was observed for FeZ in the same pH range. For both sorbents, at higher pH values there is no change in Mn^{2+} removal efficiency. The results suggest that the optimal pH range is 5.10 – 8.15 for the sorption of Mn^{2+} ions on both zeolite samples. Enhanced sorption of Mn^{2+} ions on NZ, especially on FeZ at the specified optimal pH_o range, is probably the result of undisturbed sorption of Mn^{2+} ions, since the competition effect with H^+ ions is more pronounced in more acidic solutions.

The results of effect of the S/L ratio (Figure 1b) indicate a continuous increase in removal efficiency up to $S/L = 12.5$ g/L for NZ, while for FeZ the removal efficiency increases sharply up to $S/L = 10$ g/L, after which it reaches a constant value. The increase in removal efficiency with an increase in the S/L ratio is the result of a higher amount of active sorption sites, whereby their amount is obviously greater for FeZ. The optimal S/L ratio for FeZ is 10 g/L (1g FeZ in a volume of 100 mL), while for NZ the optimal value of the S/L ratio has not been established.

In order to compare the results of the effect of initial concentration on the sorption of Mn^{2+} ions on NZ and FeZ, the experiments were carried out at the optimal S/L ratio for FeZ.

The influence of the initial concentration on the amount of sorbed Mn^{2+} ions, q_e as well as the removal efficiency, α on NZ and FeZ is shown in Figure 2.

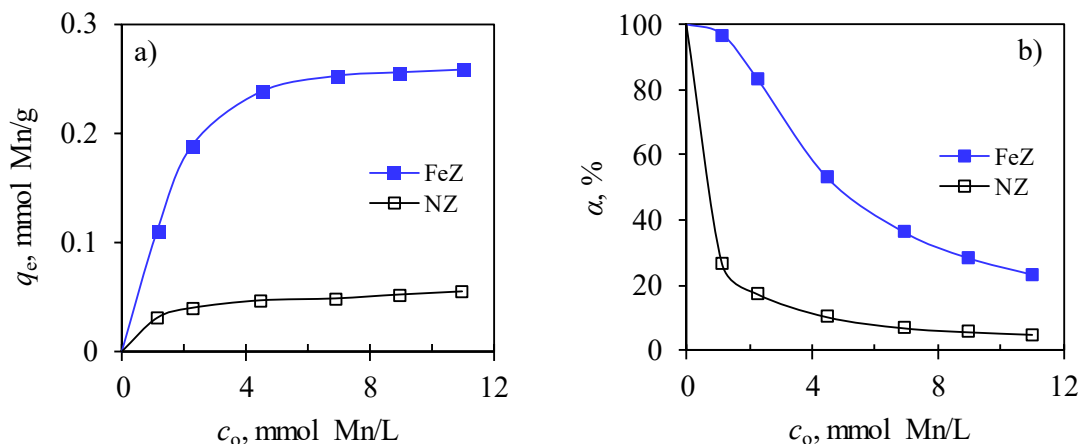


Figure 2. Effect of initial concentration on: a) amount of sorbed Mn^{2+} ions and b) removal efficiency on NZ and FeZ.

For both zeolite samples, with an increase in concentration up to $c_0=6.917$ mmol/L, an increase in the q_e value is observed, after which a plateau is established (Figure 2a). A further increase in c_0 has no effect on the increase in q_e , since all available sorption sites are saturated with Mn^{2+} ions. Comparing the maximum amount of sorbed Mn^{2+} ions on NZ (0.05 mmol Mn/g) in relation to FeZ (0.26 mg Mn/L), a 5-fold higher amount of sorbed Mn^{2+} ions on FeZ is obtained. This observation is consistent with the results shown in Figure 1a. The significantly increased sorption ability of FeZ is a consequence of the modification, i.e. the increase of active sorption sites available for the sorption of Mn^{2+} ions which justifies the implementation of zeolite modification. This is supported by the results shown in Figure 2b. Namely, at the lowest initial concentration of 1.136 mmol Mn/L, almost complete removal of manganese was achieved on FeZ (96.96%) than that on NZ (26.27%). At the mentioned c_0 , the remaining Mn concentration after treatment with FeZ was 1.906 mg/L, which is below the limit for the discharge of treated wastewater into water bodies according to Croatian regulations. This indicates the applicability of FeZ for single-stage Mn removal for concentrations below 1.136 mmol Mn/L (62.408 mg Mn/L). For higher concentrations, it is necessary to design a two-stage system.

The percentage of Mn^{2+} ions leached, $\alpha_{leached}$ from saturated NZMn and FeZMn according to the standard DIN 38414 leaching procedure is shown in Figure 3. In the case of saturated NZMn, leaching of Mn^{2+} ions occur $<1\%$ in the pH_o range 4 – 10, $pH_o \geq 11$ about 1 – 2%, and in $pH_o \leq 3$ about 5 – 14%. On the other hand, for the FeZMn sample, in the wide pH_o range 4 – 12, Mn^{2+} ions leaching occurs only up to 0.62%, while at $pH_o \leq 3$ about 2 – 8%. The results clearly indicate that regardless of pH_o , FeZ shows a more pronounced ability to retain Mn^{2+} ions in its structure compared to NZ. In extremely acidic conditions, $pH_o \leq 3$, the percentage of leached Mn^{2+} ions from NZMn is almost twice higher than from FeZMn, while the amount of sorbed Mn^{2+} ions is 5 times higher on FeZ than on NZ. The more pronounced leaching of Mn^{2+} ions in highly acidic conditions is a consequence of dealumination and, consequently, partial degradation of the zeolite structure [3].

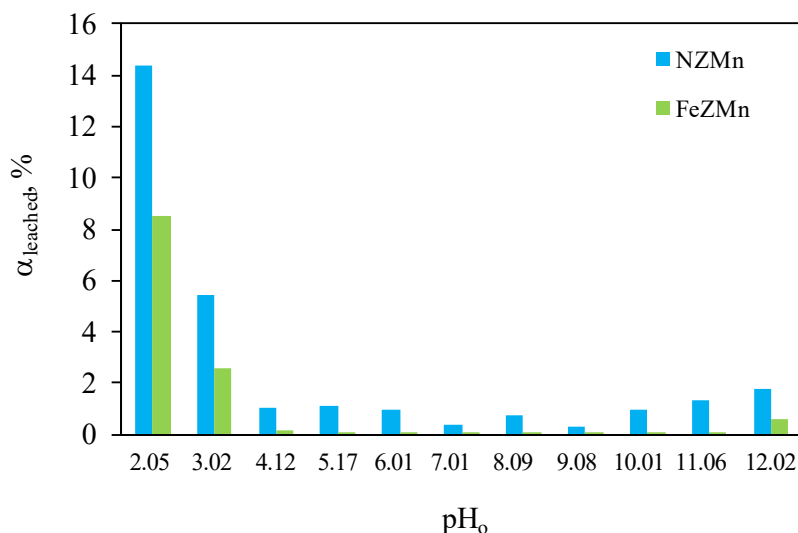


Figure 3. Percentage of Mn^{2+} ions leached from saturated NZMn and FeZMn as a function of pH_0 .

Taking all the results into account, FeZ showed a significant ability of sorption and retention of Mn^{2+} ions in its structure compared to the NZ, which justifies the implementation of modification. Therefore, this opens the possibility of its eventual application for manganese removal and the relatively safe disposal of saturated FeZMn in the environment.

CONCLUSION

The research showed that at optimal sorption conditions ($pH_0=5 - 8$, $S/L=10$ g/L) a 5 times higher sorption capacity was achieved on FeZ than on NZ (0.26 mmol Mn/g FeZ vs. 0.05 mmol Mn/g NZ). Almost complete Mn^{2+} ions removal is achieved at $c_0=1.136$ mmol Mn/L (62.408 mg Mn/L) whereby the limit for the discharge of treated wastewater into the water bodies according to Croatian regulations is met. The leaching results showed an exceptional ability of FeZ in retaining the Mn^{2+} ions in its structure. Therefore, the results showed that FeZ imposed as a good sorbent material for removal of Mn^{2+} ions.

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