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SORPTION ISOTHERM STUDY OF MANGANESE REMOVAL FROM AQUEOUS SOLUTIONS BY NATURAL AND MnO2-COATED ZEOLITE

The applicability of the natural and MnO2-coated zeolite as sorbent for the removal of Mn(II) from synthetic solutions has been investigated. Batch experiments were carried out to determine the influence of pH and Mn(II) concentration on the sorption process. A maximum removal efficiency (98.9%) was observed for modified zeolite with the concentration of 10 mg/dm^3 of manganese in solution. The equilibrium data showed a very good correlation for both Langmuir and Freundlich sorption models and this suggests both monolayer adsorption and a heterogeneous surface existence. Maximum sorption capacity calculated from the Langmuir model constituted 5.57 mg/g for natural zeolite and 13.41 mg/g for modified zeolite.

1. INTRODUCTION

In recent decades, environmental pollution has increased exponentially due to rapid urbanization and industrialization. The side effect of the technological process such as electroplating, metal finishing, metallurgy, chemical manufacturing, mining and battery

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manufacturing is the discharge of wastewater, containing organic and inorganic substances in the environment [1–4]. Heavy metals defined as any metallic elements that have a specific gravity greater than 5.0 g/cm^3 and atomic weights between 63.5 and 200.6 u are considered pollutants. These elements enter the organism through air, food and potable water. They are non-degradable and dangerous because of their capacity to bioaccumulate. In small doses, some heavy metals are essential to the human metabolism but in large quantities could be poisoning [5–8].

Usually, manganese occurs in the environment together with iron in deeper wells or coal mining regions. The presence of high concentrations of Fe and Mn when exposed to air results in the formation of a dark sludge precipitate, which facilitate the development of ferruginous and manganese bacteria on walls of pipes increasing their corrosion. Mn is toxic to the brain developing a neurological disorder like Parkinson's disease. It is regularly used in the manufacturing of stainless steel, coins, metallic and superalloys, nonferrous metals, batteries, electroplating, etc. [7, 9–12]. Elimination of heavy metals from waters using nature-friendly methods is essential for environmental conservation and principles of sustainable development. Adsorption, the process, which occurs when a gas/liquid solute accumulates on the surface of a solid or a liquid to form a molecular or atomic film become popular in recent years due to its high efficiency, simple design, low cost and land required [2, 4, 13, 14].

Zeolites belong to low-cost materials used as filtration items to remove heavy metals from water. Natural zeolites are microporous, hydrated aluminosilicate minerals with a characteristic three-dimensional structure of tetrahedrons. The important property is their ability to exchange cations (such as Ca(II), Mg(II), Na(I) and K(I)) between aqueous solutions and intra-crystalline sites that provides their high sorption capacity for removal of contaminants. The formation of the new functional groups can influence the natural zeolites in process of modification and have a certain impact on their activity and selectivity on the removal of different pollutants [7, 10, 13–15].

Shavandi et al. [16] investigated the sorption capacity of natural zeolite for the removal of zinc, manganese, and iron. They tested the effects of contact time, agitation speed, pH, and sorbent dosage on the sorption process. The equilibrium was reached within 180 min and more than 50% of Zn(II) and Mn(II) and about 60% of Fe(III) were removed from the solution. The sorption capacities of zeolite ranged between 0.015 and 1.157 mg/g. The kinetics of heavy metal ion adsorption followed the pseudo-second order model, while the Langmuir isotherm fitted good the equilibrium data.

Taffarel and Rubio [4] investigated the sorption of Mn(II) ions from aqueous solution onto manganese oxide coated zeolite (MOCZ) as a function of contact time, solution pH and sorbent concentration. The sorption equilibriums have been described in terms of both the Langmuir and Freundlich isotherm models. The highest manganese uptake by MOCZ was achieved at pH 6.0 and was equal to 27.5 mg/g. The authors reported that the sorption process fitted the pseudo-second order kinetic model.

Irannajad and Haghighi [17] investigated the use of Mn-coated zeolite for the removal of cobalt, nickel and lead from aqueous solutions. The optimal initial concentration of metals, pH, contact time, and temperature were established. The maximum capacity was reached at pH of 5.5 for lead and 7–8 for cobalt and nickel. The results were found to fit sufficiently by both the Langmuir and Freundlich isotherm models. A thermodynamics study showed that the reaction was endothermic and the sorption of lead was more spontaneous than that of the other two ions. Good correlation coefficients were obtained for the pseudo-second order kinetic model.

This study aims to find out the effectiveness of natural and MnO₂-modified zeolite to be used as a sorbent for the removal of Mn(II) from synthetic solutions. In this work, the batch experiments were realized to determine the best sorption equilibrium model and the dependence of pH on Mn(II) removal.

2. MATERIALS AND METHODS

Preparation of sorbent and sorbate. Natural zeolite and MnO₂-coated zeolite (Klinopur-Mn) with a particle size of 0.5–1.0 mm were obtained from Slovak company ZeoCem a.s Byste [18]. The stock solution of Mn(II) with the concentration of 1000 mg/dm³ was prepared by dissolving manganese(II) sulfate tetrahydrate (MnSO₄·4H₂O) in deionized water. Solutions with concentrations of 10, 50, 100, 200, 350 and 500 mg/dm³ were prepared by diluting the stock solution with deionized water without pH adjusting.

Sorption study. Batch sorption experiments were carried out for removal of Mn(II) by mixing 0.5 g of zeolite or MnO₂-coated zeolite with 50 cm³ of manganese solution with different concentrations. The solutions were left for 24 h without mixing at laboratory temperature (22±2 °C) to reach equilibrium. Then the sorbent was separated by filtration and the residual concentration of manganese in the filtrates was determined by colorimetric analysis using the periodate oxidation method. Manganese in the sample was oxidized to the purple permanganate by sodium periodate (sodium periodate powder pillow), after buffering the sample with citrate (buffer powder pillow). The intensity of the purple color was linearly dependent on the manganese concentration. To determine the final concentration of Mn ions, the colorimeter DR 890 (HACH LANGE, Germany) was used [19, 20].

pH of solutions before and after the experiments was measured employing a pH-meter pH100 Waterproof ExStik (Extech Instruments, USA).

The sorption capacity of sorbents used (q_e) and the efficiency of the sorption process (E) were calculated according to the following general equations:

$$q_e = \frac{(c_0 - c_e)V}{m}$$ (1)

$$E = \frac{c_0 - c_e}{c_0} \times 100\% \tag{2}$$

where: E is the percentage of heavy metal removal from solution, q_e is the final amount of Mn(II) sorbed at equilibrium, mg/g, c_0 and c_e are the initial and final (equilibrium) concentrations of metal ions, respectively, mg/dm^3, m is the mass of the adsorbent, g, and V is the volume of the aqueous solution, dm^3 [16].

Isotherm models. Sorption isotherms indicated the relationship between the concentration of heavy metal ions in a solution and the amount of metal ions fixed per unit weight of the sorbent at a constant temperature. The most widely used isotherm models – Langmuir and Freundlich – have been examined.

The Langmuir isotherm [21] describes single monolayer sorption on homogenous surfaces. This model assumes the same affinity at all sorption sites and no interactions between the sorbed ions. The maximum adsorption capacity can be calculated by:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \tag{3}$$

where: q_e is the amount of metal ions sorbed at equilibrium, mg/g, c_e is metal concentration at equilibrium, mg/dm^3, q_m is the maximum capacity of monolayer sorption at equilibrium, mg/g, and K_L is the Langmuir equilibrium constant, dm^3/g.

The Freundlich isotherm [22] is an empirical equation applied to heterogeneous surfaces and describes the multilayer sorption process. Non-linear Freundlich isotherm is expressed as

$$q_e = K_F c_e^{1/n} \tag{4}$$

where: K_F is the Freundlich equilibrium constant and describes the relative sorption capacity related to the bonding energy, n is heterogeneity factor indicating the deviation from linearity of the model (for $n = 1$ the isotherm becomes linear).

3. RESULTS AND DISCUSSION

3.1. EFFICIENCY OF THE SORPTION PROCESS AND CHANGE OF pH

The efficiency of the sorption process in the removal of Mn(II) on the natural and modified zeolite is shown in Fig. 1. The modification improved the removal efficiency of the zeolite. Thus, Mn(II) removal efficiency of modified zeolite was higher than 50% at Mn(II) concentration of 200 mg/dm^3 in comparison with that of 21% obtained for natural one. The significant enhancement in removal efficiency on Mn-modified zeolite

can result from the microporous structure of manganese oxides supplying a higher surface area and also more available surface binding sites [4]. It was also reported [23] that MnO₂-coated zeolites have a very selective surface towards Mn sorption.
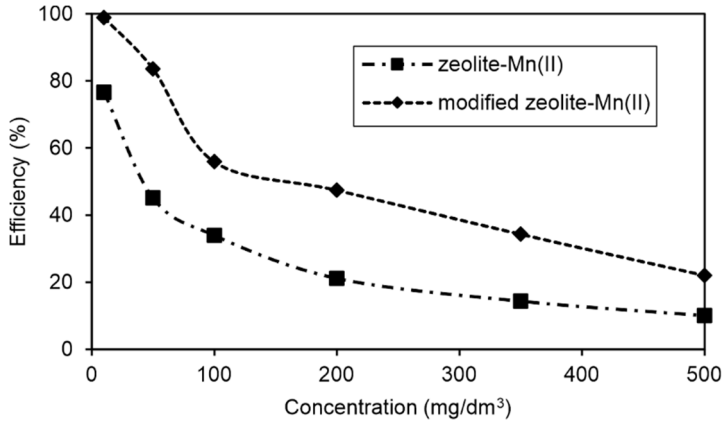

Fig. 1. Efficiency of sorption process in function of the initial Mn(II)concentration

The removal of heavy metal ions from water is strongly dependent on the pH value of the solution. The pH value has impact on the surface charge of solid particles and solubility of the heavy metal ions [11]. In Table 1 are indicated the changes of pH at the beginning and at the end of experiments. The final pH in case of modified zeolite increase more significantly than for natural zeolite. The manganese oxides present a hydroxylated surface that has a high effect on change of pH of aqueous solution. With the increase of pH, the surface negative charge increases due to deprotonation of hydroxide functional groups and cations are captured to the surface by electrostatic forces. On the other hand, at the low pH, dominant H^+ ions in solution conquer the binding-sites of sorbent resulting in a net positive surface charge that prevent the cation sorption [4, 20, 23, 24].

Table 1

pH at the beginning and the end of the experiment

Initial Mn(II) concentration [mg/dm³]	Initial pH	Final pH	
		Natural zeolite	Modified zeolite
10	6.85	6.54	9.09
50	6.63	6.32	7.89
100	5.98	6.28	7.25
200	5.76	6.36	7.30
350	5.48	6.20	6.30
500	4.73	5.62	5.79

3.2. EQUILIBRIUM STUDY

The equilibrium data provide important information about the sorbent capacity or the amount needed to eliminate a certain amount of a contaminant under the system conditions. This data is necessary for its application in water and wastewater treatment design. Figure 2 shows the Mn(II) sorption isotherms onto natural and modified zeolite.
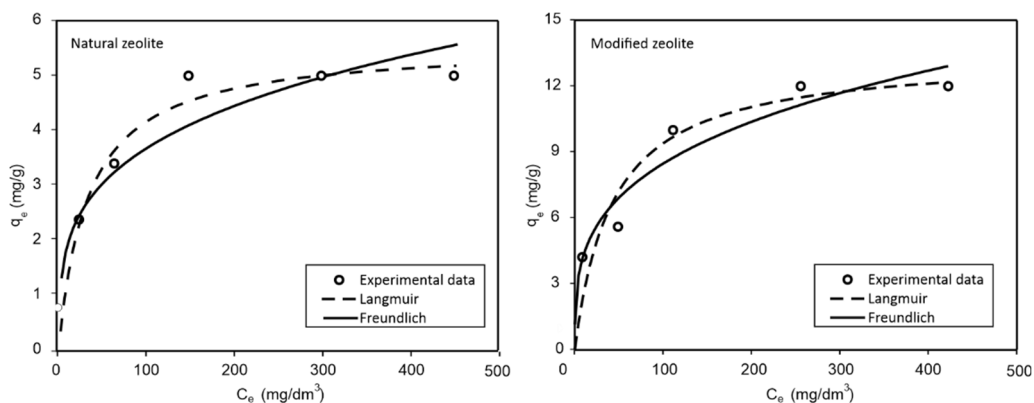

Fig. 2. Sorption isotherms of natural and modified zeolite loaded by Mn(II)

Table 2

Isotherm parameters for sorption of Mn(II) on natural and modified zeolite

Sorbent	Langmuir model			Freundlich model		
	q_e [mg/g]	K_L [dm^3/mg]	R^2	K_F [dm$^{3/n}$·mg$^{1-1/n}$·g^{-1}]	n	R^2
Natural zeolite	5.57	0.03	0.96	1.04	3.65	0.89
Modified zeolite	13.41	0.03	0.91	2.28	3.42	0.94

High correlation coefficients (>0.89) were found for both the Langmuir and Freundlich models (Table 2). The applicability of two isotherm models for Mn(II) removal predicts the existence of a heterogeneous surface and even monolayer sorption at the surface of tested zeolites [25]. The sorption capacities of sorbents for Mn ions are in line with the results of other studies of manganese adsorption [26].

4. CONCLUSION

The pollution of the water environment by heavy metals is a worldwide problem due to their toxic and bio-accumulative characters. Sorption has been widely applied to remove heavy metal ions from wastewater since is an economical and efficient technology.

In the present study, the sorption efficiency of modified zeolite was 1.5–3.6 times higher than that of natural one. Correlation coefficients (R^2) corresponding to the Langmuir model were higher those of the Freundlich model. The amount of Mn ions sorbed onto modified zeolite at equilibrium was 2.7 times higher than that of the natural zeolite.

The results of this study demonstrate that the MnO₂-coated zeolite showed good potential as a sorbent for Mn(II) removal from synthetic solutions.

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