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Comparison of sorption efficiency of natural and MnO₂ coated zeolite for copper removal from model solutions

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Abstract. Removal of heavy metals from the environment is important for living beings. The present work investigates the applicability of the natural and MnO₂ - coated zeolite as sorbent for the removal of copper from synthetic solutions. Batch experiments were carried out to identify the influence of initial pH and concentration in the process of adsorption. A maximum removal efficiency of Cu(II) was observed in 10 mg/L for natural (95.6%) and modified (96.4%) zeolite, where the values was almost identical, but at concentration of 500 mg/L was the removal efficiency of modified zeolite three times higher. Based on the correlation factors R^2, the Langmuir isotherms better describe the decontamination process than Freundlich. The optimum pH value was set at 5.0.

1. Introduction

For effective removal of heavy metals from wastewater was developed the various processes such as ion exchange, chemical precipitation, membrane separation, coagulation/flocculation, electrochemical operation, biological processes, filtration and others [1]. The disadvantage of these methods can be inefficiency in solution with low concentration of heavy metals, production of toxic sludge, expensive operation procedure. Sorption is considered as simple, cost effectiveness, eco-friendly, and ease of phase separation and availability of various materials. Some natural materials as clay, sawdust, zeolites and others are known as low-cost sorbents [2, 3].

Natural zeolites has been examined in a wide range of applications as low-cost sorbents in water treatment [3, 4, 5, 6]. Zeolites are porous crystalline aluminosilicates with three dimensional frameworks of SiO4 and AlO4 tetrahedrally connected together in different regular arrangements through the sharing of oxygen atoms. Negative charge on the framework is caused by substitution of Si(IV) and Al(III), which is balanced by positively charged cations such as exchangeable sodium, potassium, calcium, and magnesium cations. They have high sorption capacity and selectivity to exchange ions which determine their ability to remove heavy metals from industrial wastewater [6, 7, 8, 9].

Natural materials used as sorbents have lower removal efficiency towards synthesized one, but these materials could provide cheap alternation for the removal of heavy metal from environment. One possibility to solve this problem can be mechanical, thermal, or chemical treatments of low-cost materials which eliminate the impurities, due to improve the physicochemical properties and sorption capacity for heavy metal removal [3, 5, 6].

Manganese dioxides participate in controlling trace metal concentration in water environments through processes of sorption and co-precipitation. Manganese oxides posses a large surface area with microporous structure and high capacity for elimination of metal ions from soil, sediment, rocks and water, but it cannot be applied itself due to economic reasons and negative chemical and physical properties. The coating offers improve removal efficiency towards heavy metals [3, 4, 5, 10].

The aim of this paper is to compare the efficiency of natural and MnO_2 - coated zeolite as sorbent for copper removal from a model solution. The influence of initial and final pH was investigated, too. Copper was selected because of its widely used in various industries and negative effects on the aqueous environment in high dosages.

2. Materials and methods

Natural zeolite and MnO_2-coated zeolite (Klinopur-Mn) were obtained from Slovak company ZeoCem a.s Byste. In experiment the particle size in range of 0.5 – 1.0 mm was used. The stock solution with concentration of 1,000 mg/L of copper in distilled water was prepared from copper(II)sulfate pentahydrate.

The six solutions with concentration 10, 50, 100, 200, 350 and 500 mg/L were obtained by diluting the stock solution with distilled water. Batch sorption experiments were carried out for removal of copper by mixing 0.5 g of zeolite or modified zeolite with 50 mL of model solution. Sorption experiments run at laboratory temperature (22±2 °C) during 24 h with the purpose to determine equilibrium. After this time, the sorbent was filtered and the residual concentration of Cu(II) in the filtrates was determined by colorimetric method. The final concentration of copper ions was determined by colorimeter DR 890 HACH LANGE, Germany. The pH of solutions before and after the experiments was measured by pH meter- pH100 Waterproof ExStik (EXTECH INSTRUMENTS, USA).

The sorption efficiency (E) was determined according to the following general equations Eq. 1:

$$E(\%) = \frac{(c_0 - c_e)}{c_0} x100 \tag{1}$$

where: E is the percentage of heavy metal removal from solution [%],
          C_e is the final concentration of metal ions in solution [mg/L],
          C_0 is the initial concentration of metal ions [mg/L]

The sorption capacity of copper ion (q) was calculated by Eq.2:

$$q(mg / g) = \frac{(c_0 - c_e)}{m} xV \tag{2}$$

where: q is the final amount of copper sorbed at equilibrium [mg/g],
          m is the mass of adsorbent used in the experiment [g]
          V is the volume of aqueous solution [L].

Langmuir isotherm was calculated according to the following equation (3):

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

where: q_e is the amount of sorbed matter per unit mass [mg/g],
q_m is the amount of ions needed to form one monolayer per unit mass of sorbent [mg/g] and
K_L is the Langmuir constant associated with the apparent energy of the process [L/mg] [11].

Freundlich equation is given by equation (4):

$$q_e = K_F . C_e^{1/n} \qquad\qquad (4)$$

where: K_F is the relative sorption capacity of the zeolite [$L^{1/n}.mg^{1-1/n}/g$],

n is the heterogeneity factor or Freundlich coefficient representing the deviation from the linearity of sorption, and

q_e represents the amount of sorbed substances per unit weight [mg/g] [17].

3. Results and discussion

The efficiency of sorption process in removal of copper on the natural and modified zeolite is shown on Table 1. As can be seen in table 1, the modification with manganese oxide improved the removal efficiency of copper sorption. In low concentration (10 mg/L), both sorbents reached high removal efficiency (> 95%). With the higher concentration of copper in solution, the efficiency decrease due to occupation of free sorption sites. But, the modified reached the triple removal efficiency even in high concentration of 200, 350 and 500 mg/L of Cu (II).

The same results were obtained by Irannajad et al. [4]. The authors observed in the concentration bellow 100 mg/L that the sorption was rapid and more than 90% of heavy metals (zinc, copper and cadmium) were eliminated.

Table 1. Removal efficiency of natural and modified zeolite.

Initial values	Final values					
	Natural zeolite			Modified zeolite		
C_o [mg/L]	C_e [mg/L]	E [%]	q [mg/g]	C_e [mg/L]	E [%]	q [mg/g]
10	0.44	95.6	0.96	0.36	96.4	0.96
50	15.7	68.6	3.4	6.5	87.0	4.4
100	67.4	32.6	3.3	16	84.0	8.4
200	157	21.5	4.3	80	60.0	12.0
350	296	15.4	5.4	184	47.4	16.6
500	454	9.2	4.6	349	30.2	15.1

The higher removal efficiency in case of manganese oxide coated zeolite can be explicated by the microporous structure of MnO_2 providing greater and selective surface area and binding sites together [10, 12].

The values of pH at the beginning and at the final of experiments in copper removal on natural and MnO_2 coated zeolite are shown in Table 2.

Table 2. Change of pH during the experiment.

Concentration [mg/L]	Initial pH	Final pH	
		Natural zeolite	Modified zeolite
10	5.68	6.97	9.19
50	5.46	5.53	8.74
100	5.11	5.11	6.13
200	5.49	4.83	5.13
350	5.36	4.46	5.02
500	4.98	4.34	4.54

The removal of heavy metals from model solutions depends on the pH value which has impact on the surface charge on the solid particles and the solubility of the heavy metal ions [1]. In case of modified zeolite, it can be observed increased values of pH compared to the natural one.

The MnO_2 coated zeolite present a hydroxylated surface which has a high effect on change of pH in model solution. At a lower pH, sorption of Cu(II) was reduced because of competition with hydrogen ions for active sorption sites that results in a net positive surface charge that prevent the cation sorption. With the increasing of pH, the surface negative charge increases due to deprotonation of – OH functional groups and cations which are caught to the surface by electrostatic forces [4, 10, 12].

In Figure 1 is shown application of Freundlich and Langmuir isotherm. The coefficients of isotherms are shown in Table 3.
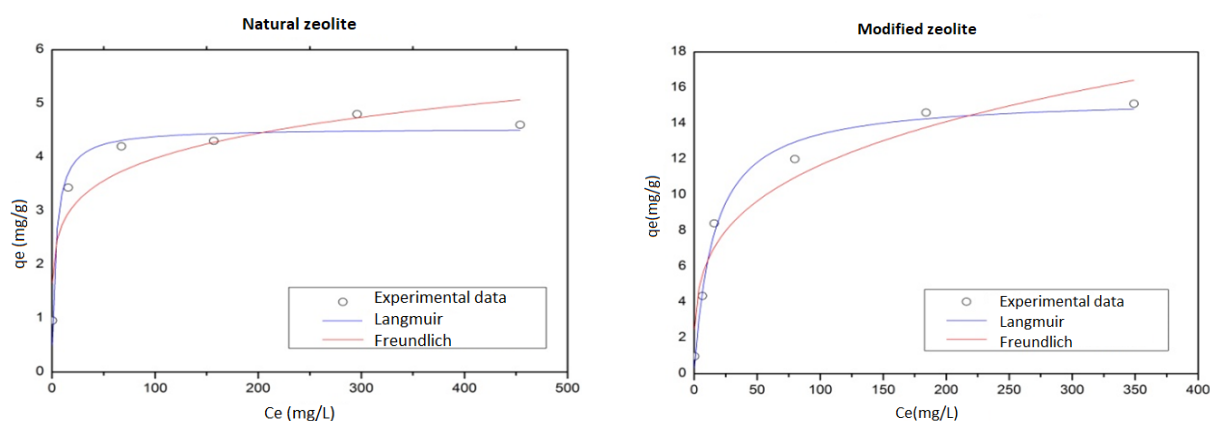

Figure 1. Langmuir and Freundlich sorption isotherm.

Based on higher correlation factor (R2) of Langmuir isotherms (0.95 for natural zeolite and 0.99 for modified one) than Freundlich (0.86 for natural zeolite and 0.93 for modified one) we can conclude that the Langmuir isotherms better describes the decontamination process. Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is open while desorption is proportional to the fraction of the adsorbent surface that is covered [13].

Table 3. Constants of isotherms for natural and modified zeolite.

Zeolite	Langmuir constants			Freundlich constants		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F (L $^{1/n}$.mg$^{1-1/n}$/g)	n	R^2
Natural	4.54	0.28	**0.95**	1.90	6.25	0.86
Modified	15.45	0.07	**0.99**	3.32	3.66	0.93

In the Table 4 are presented the comparison with similar studies in removal of copper from model solutions. From the Table 4, we can observe that the best pH value for copper sorption is about 5.0. The values of maximum sorption capacity are very different due to region where they appeared.

Table 4. Comparison with results of other studies.

Type of zeolite	q_{max} [mg/g]	pH	Literature
Turkish clinoptiolite	0.21	5-6	[7]
MnO_2 - modified zeolite	6.92	5.5	[4]
FeO – modified zeolite	8.82	5.5	[4]
Croatian zeolite clinoptiolite	3.083	5.5-7.0	[14]

Zeolite from Kamchatka region	0.023	-	[15]
Slovak zeolite	1.48	-	[16]
Natural zeolite	5.4	4.46	This study
Manganese coated zeolite	16.6	5.02	This study

4. Conclusion

In the present study natural and MnO_2 - coated zeolite was used as a sorbent for the removal of copper from aqueous solutions through the series of the batch experiments. The sorption efficiency of modified zeolite was 1.5-3-times higher than natural one in all cases except low concentration, where removal efficiency was almost identical. The value of pH was higher in case of MnO_2 - coated zeolite like in natural one. The optimum pH value for maximum sorption capacity was observed around value 5.0. The reason could be hydroxylated surface of modified sorbent. The commercial applications of MnO_2 for water treatment can be the object of the further study.

Acknowledgments

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