COPPER REMOVAL FROM AQUEOUS SOLUTION USING NATURAL ZEOLITE AND ANTIBACTERIAL ACTIVITY OF THE COPPER-LOADED ZEOLITE

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ABSTRACT

The natural zeolite (Zlatokop mine, Serbia) is found to be effective in removal of the copper (II) ions from aqueous solutions, the sorption capacity at 298 K varies from 18.6 to 37.6 % for C_0 = 100 and 400 mg Cu dm^{-3}, respectively. The sorption isotherm is in accord only with the Freundlich model, a nonlinear equilibrium distribution relationship existing between the fluid and solid phases. The sorption kinetics is the best described by the pseudo-second-order model. Intra-particle diffusion of Cu^{2+} is present in the sorption process, but it is not the rate-limiting step. The copper-loaded zeolite exhibits an excellent antibacterial activity towards Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacteria suggesting that it could be a promising material in a final step of wastewater treatment.

Keywords: natural zeolite, copper removal, antibacterial activity, Freundlich isotherm, kinetics.

INTRODUCTION

Release of toxic heavy metals into environment can cause serious soil and water pollution. Industrial wastewaters often have a considerable content of heavy metal ions, and therefore such waters have to be appropriately treated before being discharged. Due to their adsorbent, ion-exchange and catalytic properties, zeolites attract a great attention. Adsorption using natural adsorbents is generally considered to be the most suitable method for wastewater treatment. Clinoptilolite, as the most abundant natural zeolite, can therefore be regarded as a cost minimizing choice of the adsorbent for the developing countries.

It has been found that the natural zeolitized tuff (NZ) from Zlatokop mine in Serbia contains more than 70 wt. % clinoptilolite [1] and therefore it was chosen in this work for studying as an adsorbent for potential use in wastewater treatment. In this paper we report in detail the kinetic and some biological aspects of the Cu^{2+} sorption by NZ at different temperatures and different Cu^{2+} solution concentrations. Since copper is among the metals which exhibit antibacterial activity [2], we have also investigated the copper-loaded zeolite CuNZ as an antibacterial material, having in mind a possible utilization of the exhausted zeolite.

EXPERIMENTAL

Natural zeolite (NZ) obtained from a large sedimentary Zlatokop deposit was used in the experiments. The particle size of the samples was in the range of 0.063–0.1mm. The sample (1.000 g) was pretreated with 100.00 cm^3 of 2.0 mol dm^{-3} solution of NaCl (p.a., Aldrich) in order to improve the tuff's exchange capacity of NZ. The suspension was shaken at about 100 rpm for 24 h in a thermostated water bath (Memmert WPE 45). The sample (NaNZ) was then washed by distilled water and dried in oven at 105 ºC. The Cu(II) sorption isotherms were determined at 298, 308, 318, and 328 K using the batch method. 1.000 g of

the NaNZ was placed in 100.00 cm^3 of the $CuSO_4$ (p.a., Aldrich) solution of chosen concentration. The Cu(II) concentrations were of 50 to 400 mg Cu dm^{-3}. The suspension was shaken at about 100 rpm for 24 h in a thermostated water bath (Memmert WPE45). The solid, Cu-loaded NaNZ (CuNZ), was then recovered by filtration.

The rate of sorption of Cu(II) by NaNZ was studied at temperatures of 298, 308, 318, and 328 K in solutions with an initial Cu(II) concentration of 100, 200, 300, and 400 mg Cu(II) dm^{-3}. The suspension was shaken at a rate of about 100 rpm for a time period from 20 min to 24 h. The solid was then separated by filtration.

Leaching test with the CuNZ was performed taking 1.00 g of CuNZ and 100.00 cm^3 of synthetic wastewater (pH adjusted to 7). The suspension was left for 24 h in a thermostated water bath at 37 °C. The Cu content in the filtrate was analyzed after filtration.Copper concentrations in solution were determined by AAS using Varian SpectrAA 55B; at least four measurements were done for each determination. All the experiments were carried out under controlled conditions: the temperature in the thermostated bath was maintained constant to within ±0.1 °C, the zeolite sample was weighted to four-digit accuracy using a Shimadzu electronic balance AX200, and the solution concentrations were determined with a four-digit accuracy by AAS.

The antibacterial activity of CuNZ was tested against representative pathogenic Gram-negative (*Escherichia coli*, DSM 498) and Gram-positive (*Staphylococcus aureus*, clinical isolate at Institute of Public Health, Zagreb) bacteria. The antibacterial assay was carried out with mass concentration of material of 1g/100 cm^3 in three different water media: Luria Bertani or LB medium, synthetic wastewater and real effluent water from the secondary stage of the biological wastewater treatment. The initial pH of the media was 7.0 and the chemical composition was as follows (in mg cm^{-3}): LB medium (bacto-tryptone 10,000; bacto-yeast extract 5,000; NaCl 10,000; COD 14,000), synthetic wastewater (Na-propionate 1,000; peptone 100; $MgSO_4$ 10; $CaCl_2$ 6; KCl 30; yeast extract 10; KH_2PO_4 20; COD 1,206), effluent water (T-N 28.3; T-P 2.27; COD 31.4). All media and materials were autoclaved prior to the experiments. The experiments were carried out at 37 °C. The number of bacteria was measured as colony forming units (CFU) grown on LB agar after 24h of incubation at 37 °C at the start and after 24h of experiment.

RESULTS AND DISCUSSION

Sorption data revealed that the sorption capacity of the NaNZ increased both with temperature and with the initial Cu (II) solution concentration. The clinoptilolite was quite effective in removal of the copper (II) ions from aqueous solutions at ambient temperature: the sorption capacity at 298 K varied from 8.3 mg Cu g^{-1} (for C_0 = 100 mg Cu dm^{-3}) to 16.8 mg Cu g^{-1} (for C_0 = 400 mg Cu dm^{-3}), which corresponds to 18.6 – 37.6 % of cation exchange, respectively. In comparison with previosly studied Ni^{2+}, Mn^{2+} and Zn^{2+} ions [3] the NZ exibits an enhanced sorption capacity for Cu^{2+}.The equilibrium data have been analyzed by several empirical adsorption isotherm models. Satisfactory fits were obtained only with the Freundlich model.

The Cu(II) sorption dependence on time was investigated at 298-328 K for solutions with C_0 = 100, 200, 300 and 400 mg Cu dm^{-3}. The time dependence was followed until the sorption equilibrium has essentially been reached, the latter occurring in about 24 hours. The uptake values of Cu(II) from solution showed that at the beginning stages of sorption (i.e. approximately in the first 150-200 min) the Cu(II) uptake increased rather sharply from $q_t = 0$ at $t = 0$. Afterwards the sorption proceeded more gradually. This is presented in Figure 1 which shows the sorption kinetics for initial Cu(II) concentration of 100 mg dm^{-3}.

The data from Fig. 1 were analyzed using two reaction-based kinetic models and a diffusion-based model. It has been found that the sorption kinetics was best described by the pseudo-second-order model. Intra-particle diffusion of Cu^{2+} was present in the sorption process, but it was not the rate-limiting step.

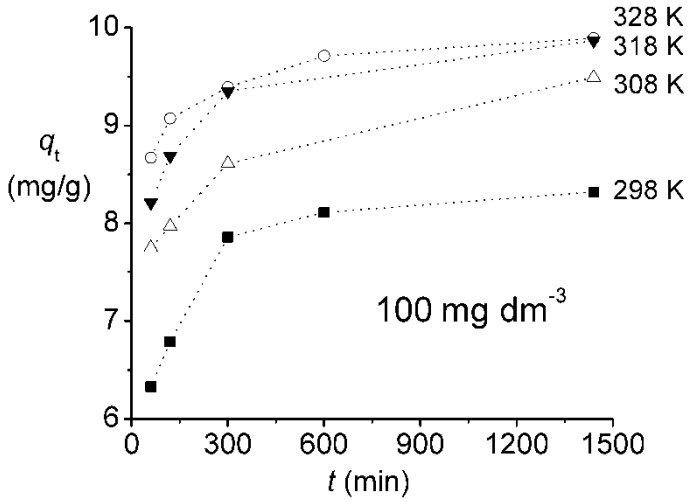

Figure 1. A typical sorption kinetics for Cu(II) on NaNZ; q_t is the amount of the sorbed Cu(II) (mg per 1 g of NaNZ) after time *t*.

The results of the antibacterial activity study of the CuNZ against *E. coli* and *S. aureus* are given in Table 1. The antibacterial activity of CuNZ was expressed as percentage of the log CFU reduction when compared to the control reactor without zeolite. The *E. coli* seems to be more resistant than *S. aureus*. The difference in final pH among control and experimental reactors was not higher than 1.11 units, indicating that the antibacterial activity is not caused by the change of pH. No significant antibacterial activity of materials was observed after 1h of contact with bacteria.

Table 1. Antibacterial activity of CuNZ against *E. coli* and *S. aureus* after 1h and 24h of incubation in different water media when compared to control. c_0 *E. coli* (10^6 CFU/mL) = 3.85±0.89; c_0 *S. aureus* (10^7 CFU/mL) = 1.42±0.24; significantly different when compared to ^{A}-LB medium, ^{B}-synthetic wastewater.

	E. coli reduction (%)	*S. aureus* reduction (%)
1 h	CuNZ	
LB medium	5.51	0.10
Synthetic wastewater	19.25 ^{A}	42.76 ^{A}
Effluent	39.93 ^{A,B}	54.97 ^{A,B}
24 h	CuNZ	
LB medium	5.44	10.69
Synthetic wastewater	95.67 ^{A}	90.77 ^{A}
Effluent	90.87 ^{A,B}	92.66 ^{A}

The leaching test suggests that the strong antibacterial activity obtained for the CuNZ towards *E. coli* and *S. aureus* in all water media could be assigned to Cu (II) ions released slowly from the zeolite to aqueous media. The concentration of Cu(II) found in the synthetic

water after 24 h was 33 mg Cu dm^{-3} (corresponding to 8.5 % of total amount of Cu bound in the CuNZ).

CONCLUSION

According to this study, the clinoptilolite from Zlatokop mine (Serbia) is quite effective in removing the copper(II) ions from aqueous solutions, the sorption capacity at 298 K varying from 18.6 to 37.6 % for C_0 = 100 and 400 mg Cu dm^{-3}, respectively; the investigation shows that it increases only slightly with temperature. The sorption isotherm is in accord only with the Freundlich model whereas the sorption kinetics is best described by the pseudo-second-order model. The results concerning antibacterial activity suggest that CuNZ could find further application since it exhibits an excellent antibacterial activity towards Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacteria. Therefore, the Cu-loaded clinoptilolite is a promising material in a final step of wastewater treatment.

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