

EQUILIBRIUM STUDY OF COPPER IONS ADSORPTION ON THE NATURAL CLINOPTILOLITE-RICH ZEOLITIC TUFF

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ABSTRACT

In this study the influence of particle size on adsorption of copper ions on the natural clinoptilolite-rich zeolitic tuff was studied in batch reactor at the temperature of 25°C and with the stirring speed of 200 rpm. The appropriate amount of three different fractions (45-71 µm, 71-90 µm, and 90-125 µm) of the zeolitic tuff was placed into copper (II) nitrate solution of various concentrations and mixed until equilibrium was reached. The adsorbed amount of copper ions firstly increases with increasing of the initial copper concentration reaching its maximum at the copper concentration of 11.763 mmol dm⁻³ for all fractions of the zeolitic tuff. Langmuir and Freundlich isotherm models were used to fit the experimental adsorption data. Based on the correlation coefficient, the best fit of the experimental data was achieved with the Langmuir adsorption model, for all three particle sizes of the zeolitic tuff.

Key words: copper, natural untreated clinoptilolite-rich zeolitic tuff, adsorption isotherms, equilibrium.

INTRODUCTION

Due to rapid industrialization and globalization, the environment becomes more and more burdened by the emission of harmful substances, primarily heavy metals, especially when they are present in wastewaters. Most of them are highly soluble in water and show toxic and carcinogenic impacts on all living organisms [1]. For that very reason, it is important to reduce or, where it is possible, entirely remove heavy metals from contaminated wastewater prior to its discharge into the environment. One of the most applied treatment option is adsorption which represents a highly effective physicochemical process for removal of heavy metals from wastewater, especially at low initial metal concentrations [2-6]. Common adsorbents for removal of heavy metals are clays and zeolites.

Zeolites are microporous minerals whose structure mainly consists of alumino-silicates with SiO₄ and AlO₄ structures connected by shared oxygen atoms. Such structure generates cavities suitable for the exchange of various molecules or ions. Although natural zeolites are environmentally and economically friendly materials their effectiveness for removal of different pollutants in different technological processes mainly depends on their physicochemical properties that are closely related to their geological origin. The most widespread and studied natural zeolite is zeolite clinoptilolite due to its exceptional properties used in many industrial applications [7].

The objective of this study is to examine the effect of clinoptilolite particle sizes on the adsorption of copper ions. Experiments were performed with different initial copper concentrations and the obtained data were fitted according to two isotherm models – Langmuir and Freundlich.

EXPERIMENTAL

Starting material used in this study was the natural clinoptilolite-rich zeolitic tuff (Donje Jesenje site, Krapina, Croatia). The raw material was crushed and sieved to obtain three different particle sizes: 45-71 µm, 71-90 µm, and 90-125 µm. Solutions containing Cu ions were prepared by dissolving the appropriate amount of Cu(NO₃)₂·3H₂O (Kemika) in distilled

water. The initial concentrations (3.881, 7.780, 11.763, 19.305, 30.576 and 39.390 mmol dm⁻³) were confirmed by Perkin Elmer Lambda EZ 201 UV/VIS spectrophotometer.

The FTIR spectra of natural zeolite before and after the adsorption process was made on KBr pastille on a Shimadzu IRAffinity-1 in the range from 4 500 to 450 cm⁻¹.

The copper adsorption equilibrium studies were conducted by agitating 0.2 dm³ of copper solutions with 1.0 g of zeolitic tuff in batch reactors at the temperature of 25°C until the equilibrium was reached. In order to determine the time needed to reach the equilibrium, kinetic experiments were performed. Appropriate amount of each solution sample was taken out from reactors at certain time interval. Results showed that equilibrium was reached after 48 h regardless on the particle size of the zeolitic tuff. The equilibrium amount of copper adsorbed on the zeolitic tuff, q_e (g mmol⁻¹), was calculated by the Equation (1):

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

where c_0 is the initial copper concentration in the solution (mmol dm⁻³), c_e is the equilibrium copper concentration in the solution (mmol dm⁻³), V is the volume of copper solution in the batch reactor (dm³), and m is the mass of the zeolitic tuff (g).

The adsorption efficiency of copper ions on the zeolitic tuff, A_{eff} (%), was calculated by the Equation (2):

$$A_{\text{eff}} = \frac{c_0 - c_e}{c_0} \cdot 100 \quad (2)$$

RESULTS AND DISCUSSION

The chemical composition of zeolitic tuff is presented elsewhere [8]. The main oxide components (SiO₂ and Al₂O₃) present in the zeolitic tuff are SiO₂=64.93% and Al₂O₃=13.66%. XRD analysis showed that the zeolitic tuff contains predominantly clinoptilolite, while illite, quartz and feldspar are accessory minerals [8].

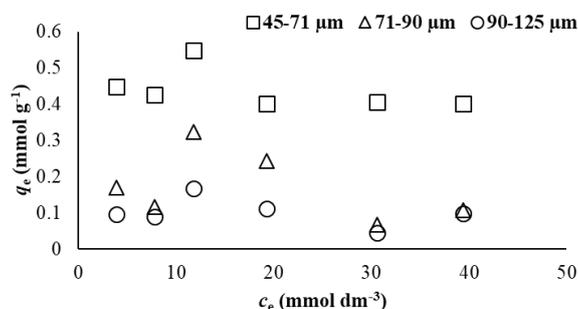


Figure 1. Equilibrium amount of copper ions adsorbed on zeolitic tuff depending on the equilibrium concentration of copper ions in solutions.

Copper adsorption isotherms of the three different fractions of the zeolitic tuff are presented in Figure 2. It is evident from Figure 1 that the adsorbed amount of copper ions increases with increase of the initial copper concentration reaching its maximum at copper concentration of 11.763 mmol dm⁻³. After this, small decrease in copper adsorption to lower values is observed for all three particle sizes. The reason for this effect is most likely related to the presence of various impurities in the zeolitic tuff as well as to the composition and exchangeability of cations in the zeolite structure, distribution and amount of clinoptilolite in different fractions of the zeolitic tuff [9-10].

The adsorption efficiency is also determined and according to the data obtained for the adsorbed amount of copper ions on the zeolitic tuff it can be observed that it decreases as the

initial concentration of copper ions in solution increases (Table 1). It is also evident that the adsorption efficiency decreases as the particle size of zeolitic tuff increases, as the result of decrease of surface area of adsorbent.

Table 1. Adsorption efficiency of zeolite clinoptilolite.

Initial concentration of copper solutions (mmol dm ⁻³)	A _{eff} (%) 45-71 μm	A _{eff} (%) 71-90 μm	A _{eff} (%) 90-125 μm
3.881	57.766	21.824	11.985
7.780	27.312	7.065	5.535
11.763	23.327	12.653	5.977
19.305	10.370	5.854	2.561
30.576	6.616	1.062	0.630
39.390	5.083	1.295	1.200

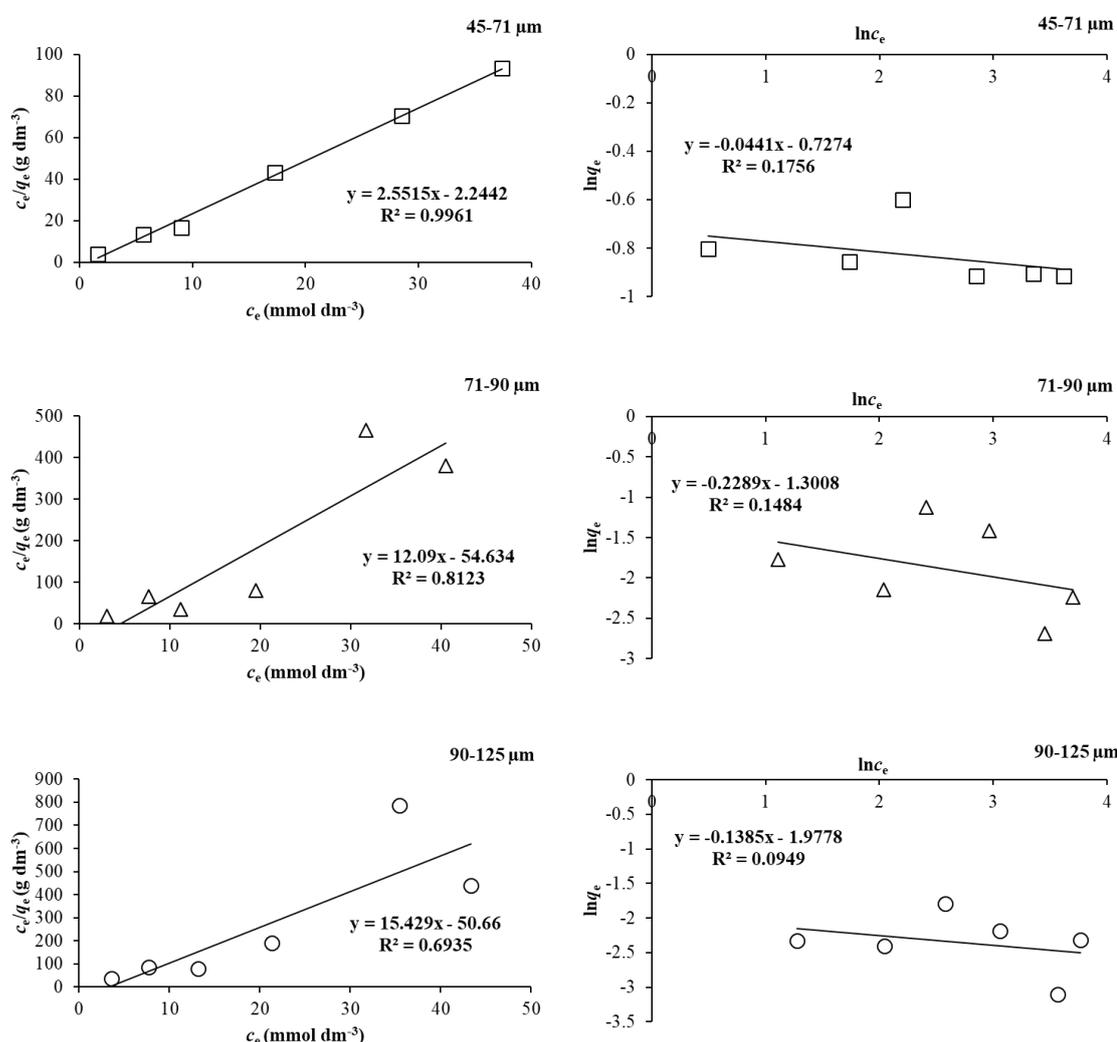


Figure 2. Correlation of experimentally obtained data (symbols) with the selected isotherm models (lines): Langmuir (left) and Freundlich (right) for various particle sizes of adsorbent used.

The experimental data were fitted to two selected isotherm models, Langmuir and Freundlich. Linear forms of both isotherms are presented in Figure 2. The Langmuir isotherm model fits the experimental data much better than the Freundlich isotherm model for all particle sizes which is confirmed with the R² value. From Figure 2 it is also evident that the best correlation of the Langmuir isotherm model with the experimental data is achieved when the

adsorbent with a lowest particle size was used, 45-71 μm , because smaller adsorbent size offered comparatively larger available surface area for adsorption of copper ions.

In Figure 3 the FTIR spectra of the zeolitic tuff before and after the adsorption of copper ions are shown. The widest band at 1043.49 cm^{-1} is attributed to the asymmetric stretching vibrations of the Si–O–Si and Al–O–Si. The bands, located at 794.67 and 466.77 cm^{-1} , correspond to the bending of Si–O–Si and O–Si–O bonds, indicate the presence of quartz in the system. The band at 1645.28 cm^{-1} , as well as bands at 3631.96 and 3442.94 cm^{-1} corresponding to the bending vibrations of the H–O–H bond and stretching vibrations of –OH, H–O–H can also be observed. These bands indicate the presence of water trapped in the cavities within the zeolite structure [11].

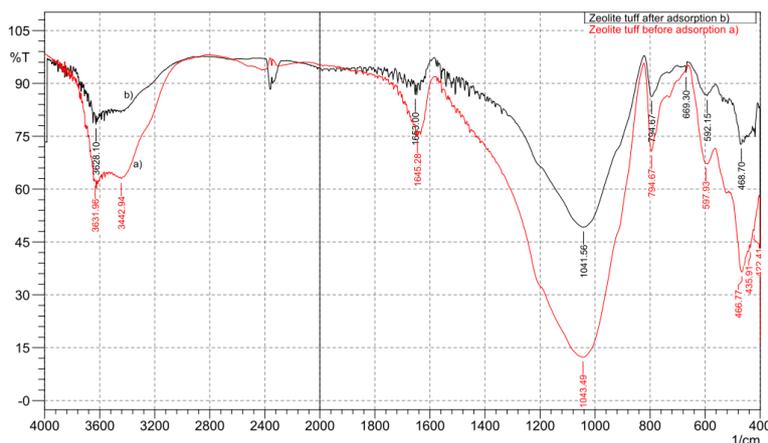


Figure 3. FTIR spectra of the zeolite tuff before and after the adsorption of copper ions.

CONCLUSION

In this study the effect of clinoptilolite particle size on the equilibrium adsorption of copper ions was investigated. The adsorbed amount of copper ions reaches its maximum at the initial copper concentration of $11.763\text{ mmol dm}^{-3}$. Adsorption efficiency decreases as the particle size of zeolitic tuff increases as a result of decrease of surface area of adsorbent. FTIR spectra revealed no changes of the structure of adsorbent after adsorption of copper ions. The correlation of the data obtained with the Langmuir and Freundlich isotherm models revealed that the Langmuir isotherm model fits the experimental data better for all the particle sizes of zeolite tuff, in particular for particle size $45\text{--}71\text{ }\mu\text{m}$.

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