

Extended Abstract

# Evaluation of Zeolite Adsorption Properties for Cu(II) Removal from Acidic Aqueous Solutions in Fixed-Bed Column System <sup>†</sup>

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**Abstract:** The development of human society after 18th century is associated with metals. Technology of extraction and processing of heavy metals is essential for many areas of industry. Naturally, the extraction, processing and cleaning of impurities give the metals not only a new form, but also cause their intensive distribution in the environment, which represents a huge threat. Countries of the middle Europe, where extraction of mineral resources takes place a long period, have to solve the problems of mine wastewater. Finding of the new and cheap ways of these wastewater treatment can increase the quality of the environment in the affected areas. Sorption techniques belong to an effective and cost acceptable methods for remove of heavy metals from aqueous environment. The presented paper describes the adsorption behavior of Slovak natural zeolite in fixed-bed column system. In order to determine its applicability for mine drainage treatment, copper removal from model sulfuric acid solutions (pH 4) was studied.

**Keywords:** zeolite; sorption; copper; column

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## 1. Introduction

The hazard of environmental pollution as a consequence of anthropogenic activity has become a global problem [1]. Mining industries have taken a decisive part in the European history, being a significant aspect of economic and social development over the centuries. Without the mineral extraction of raw materials such as copper, iron, silver and coal, the look of the countries on continent would be very different. Central Europe has been in the middle of these progresses [2].

After the decline of mining industry in the 1990s, numerous old and abandoned mines stayed in Slovakia. The closed and unused places are mostly resulting of mining activities with waste-rock heaps, waste dumps and tailing impoundments. As an effect of intense mining for many decades, negative environmental influence of strong acidic waters (acid mine drainage—AMD) is clearly obvious in current time. According to nature of deposit, releases of waste waters from abandoned flooded mines affect the surface and subsurface waters with sulfates, heavy metals and other pollutants. [3].

Solubility of most heavy metals at low concentration can influence their access to essential elements of living organisms. At present time removal of heavy metals from contaminated waters has become a major priority because of its ability to causing health problems. The necessary of safe

and economical methods for the heavy metals removal from waste waters has begun concern towards the creation and production of low cost alternatives [1,4].

Sorption is recognized as a very efficient and economically acceptable technique for metal ion removal from aquatic solutions. The application of zeolites for this aim is used very frequent for precision process, selective adsorption and regeneration processes [5].

Sorption capacity onto natural zeolite was studied intensively [6–10] because of the ion exchange phenomena. Zeolites represent low cost material, hydrated aluminosilicates with a framework structure suitable for ion exchange due to isomorphous substitution of cations in the texture, lead to absence of positive charge in the structure [11]. After the large—scale application of x-ray powder diffraction in the second half of 20th century a huge reserves of zeolites began to appear and subsequently have been studied and utilized as adsorbents for the removal of heavy metals in many countries [12].

The aim of this study was to investigate application of Slovak natural zeolite for heavy metal ions removal under acidic conditions in column system. Copper was selected as a studied model ion due to its common presence in the AMD.

## 2. Materials and Methods

### 2.1. Samples Preparation

In this study a natural non—modified zeolite from locality of Nizny Hrabovec (Slovakia) was used. The samples were prepared by milling of commercial product (Zeocem, a.s.; Bystre, Slovakia) by planetary ball mill (Miller SFM-1) at 290 rpm (tray rotating) and 580 rpm (grinding jars rotating). Separation of different fractions was performed by sieve analysis.

### 2.2. Adsorbate

Synthetic solutions of Cu(II) were prepared from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (A.R.). Initial concentration of working solutions (50 mg/L) was adjusted by further dilution. The initial pH of each solution was adjusted to the required value ( $\text{pH} \approx 4$ ) by adding 0.001 M  $\text{H}_2\text{SO}_4$ .

### 2.3. Instrumentation

- A Colorimeter DR890 (HACH LANGE, Düsseldorf, Germany) with appropriate reagent was used to determine amount of dissolved Cu(II).
- pH values were determined according to pH meter inoLab ph 730 (WTW, Germany) which was standardized using buffer solutions of different pH values (4.01, 7.00)

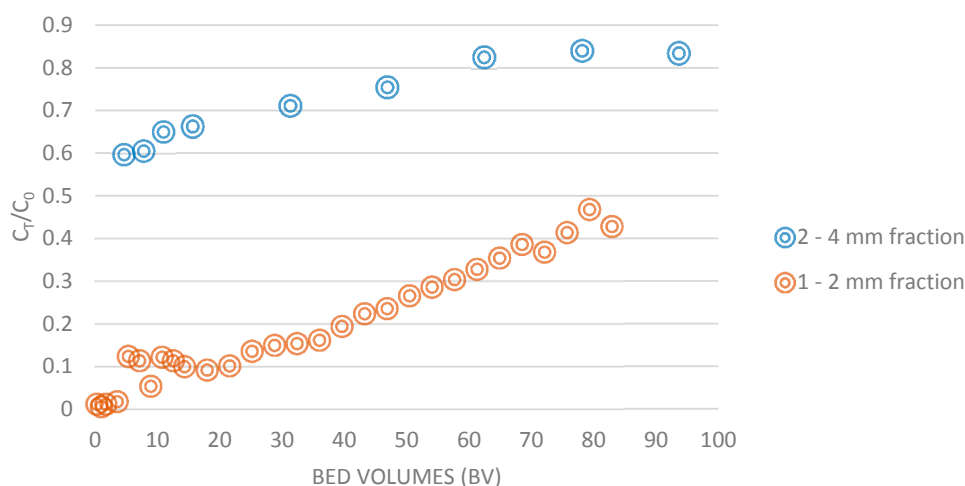
### 2.4. Column System

Fixed-bed column system used in this study was made of Pyrex glass tube with the inner and outer diameters of 4.0 and 4.5 cm, respectively ended by coarse porosity fritted glass disc. Column was filled by a known quantity (50 g) of the zeolite (two fractions: 1–2 mm and 2–4 mm) which yield a bed height of 4 cm. Working solution flowed by gravity downward through the column at a filtration velocities of 0.3 and 1.3 mL/s (for 1–2 mm and 2–4 mm fraction, respectively), controlled by a couple of valves. The effluents at the outlet of the column were collected at regular time intervals and the Cu(II) concentrations were measured. All experiments were performed at room temperature ( $23 \pm 0.2$  °C).

## 3. Results and Discussion

### Column System

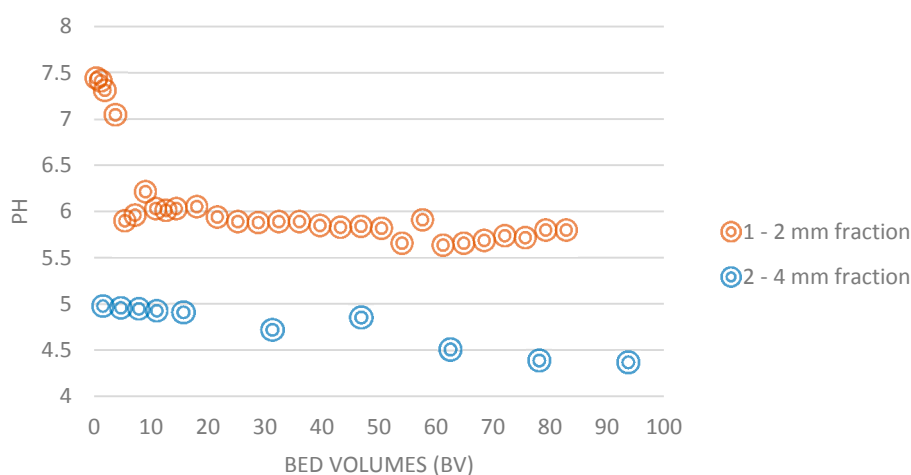
Adsorption of copper by zeolite is presented in the form of breakthrough curves (Figure 1).



**Figure 1.** Breakthrough curves of column experiments for Cu(II) (initial concentration—50 mg/L;  $C_t$ —concentration in specific time,  $C_0$ —initial concentration).

According to the results of experiments with 2–4 mm fraction, flow rate of 1.3 mL/s is too high, since breakthrough occurs faster and the boundaries are less sharpened. It was necessary to reduce the flow rate using the smaller fraction of zeolite which has proved as successful approach (see Figure 1). Lower flow rate results in higher contact times in the system. According to the relatively slow loading kinetics of zeolites, long contact times are needed [13]. In addition, the decreasing in particle size improves the efficiency of adsorption and ion exchange due to the extension of surface area and better access to easily removable exchangeable cations in the zeolite structure [14].

The pH values of the effluent are shown in Figure 2. Generally, natural zeolites tend to increase the pH in acidic conditions due to the hydrogen cations exchange with exchangeable cations.



**Figure 2.** pH measurement of column experiments for Cu(II) (initial pH = 4.0).

On the basis of Figure 2, it is clearly evident that the pH of the effluent decreases from 7.4 to 5.3 and from 5.0 to 4.5 according to fraction used. At the beginning of the reaction the strong ion exchange takes place, resulted to complete copper cations removal, thus, the pH increases from its initial value (4) to 7.4 and 5.0 (according to zeolite fraction). Increasing is caused by the absence of hydrolysis due to the complete removal of copper cations together with the removal of hydrogen cations from the solution. As the zeolite is gradually loaded with copper cations, the solution concentration increases in the bed and, thus, with increasing time, the pH is decreased due to hydrolysis. In this stage, zeolite causes elevation of the solution pH (by removing of hydrogen cations from solution); however, the

effect of hydrolysis is stronger, so increase in pH decreases with increasing concentration with copper concentration in effluent [13].

#### 4. Conclusions

In this study, the natural zeolite (clinoptilolite) from Slovakia (Nizny Hrabovec) was used for copper removal from acidic solutions. A fixed-bed system was used to describe the adsorption properties. The efficiency of Cu(II) sorption was at satisfactory level (60% after 80 batch volumes in the dynamic conditions), in addition the competitive adsorption in the process of ion—exchange between copper and hydrogen cations was observed.

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