

Study of Iron, Copper and Zinc Removal from Acidic Solutions by Sorption

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The attenuation of mining activity in the Slovak Republic which started in 1989 led to the extensive closing of deposits using wet conservation, i.e. flooding. Negative effects of acid mine drainage can be observed mainly in the localities where sulphide ores and sulphide-containing raw materials used to be mined. The treatment of acid mine drainage requires the study of using of physical–chemical methods in acidic conditions. Sorption belongs to the effective and economically acceptable methods to remove heavy metals.

The paper deals with the utilization of two sorbents: turf brush PEATSORB and zeolite for Fe, Cu and Zn removal from model sulphuric acid solutions (pH 4). The objectives of this work were to evaluate the effects of different parameters (ion concentration, pH) on sorption efficiency and the study of the mechanism of Fe, Cu and Zn removal in acidic conditions with the aim to use results for metals removal from acid mine drainage.

1. Introduction

The toxic metals, existing in high concentrations (even up to 500 mg.L^{-1}), have to be effectively removed from wastewaters. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment (Matis et al., 2004).

In recent years, the removal of toxic heavy metal ions from sewage, industrial and mining waste effluents has been widely studied. Their presence in streams and lakes has been responsible for several types of health problems in animals, plants and human beings (Clement et al., 1995).

There are various physical-chemical methods of such polluted water treatment e.g. neutralisation, ion exchange, precipitation, sorption, membrane processes, filtration. The choice of the suitable methods is based not only on the concentration of heavy metals in surface water but on economical factors, too. Sorption belongs to effective and economically acceptable methods to remove heavy metals (Petrilakova and Balintova, 2011). Zeolite, carbonate, clays, turf, oxide and hydroxide belong to the most often tested sorbents of heavy metals (Kumar et al., 2007). Unconventional materials such as spent tea leaves (Lavecchia et al., 2010) and turf brush are also low cost sorbent to remove Zn, Cu and Ni at low pH values (4.5-5.0) (Xirokostas et al., 2003).

Zeolite-based adsorbents have satisfactory adsorption capacity and low cost. They are abundant in nature, and they are not toxic (Argun, 2008). Since the original discovery of zeolitic minerals in a volcanogenic sedimentary rock, zeolitic tuffs have been found in several areas of the world (including Slovak Republic). In the past decades, natural zeolites have found a variety of applications in adsorption, catalysis, building industry, agriculture, soil remediation, and energy (Wang and Peng, 2010).

The present paper is focused on utilisation of the low cost sorbents: turf brush PEATSORB and natural zeolite to remove heavy metal ions such as Cu^{2+} , Zn^{2+} and Fe^{2+} from model acidic solutions. The removal efficiency and the sorption capacity were determined. The studied parameters were heavy metal ions concentrations, contact time and changes of the pH solution during the experiment.

2. Materials and methods

The model solutions of heavy metals were used with concentration of 50 mg.L^{-1} metal ions (Cu^{2+} , Fe^{2+} or Zn^{2+}) as the adsorbate. The initial pH of each solution was adjusted to the required value by adding H_2SO_4 solution (pH=4.2). It should be noted that sulphate anions are not forming precipitates or complexes with the corresponding metals at the test conditions and are considered to be inert.

For metal ions removal were used two different types of sorbents. A natural zeolite from Zeocem, a.s. (Bystre, Slovakia) with granularity 0.5 – 1mm, that was ground by planetary mill (Desk – top planetary ball Miller SFM-1) below 0.063 mm at 290 rpm (tray rotating) and 580 rpm (grinding jars rotating) for 18 min. As a second sorbent was used commercial turf brush PEATSORB (REO AMOS Slovakia), which was sieved through a 2 mm sieve.

The experiments were performed at laboratory temperature. The ion removal efficiency by sorptive materials was tested under static conditions. 1 g of sorbents: turf brush PEATSORB or zeolite were mixed at 500 rpm with 100 mL of model acidic solution (Cu^{2+} , Fe^{2+} or Zn^{2+}) for 1, 3, 5, 7, 10, 30 and 60 minutes, respectively. The samples were filtered and concentration of metal ions was determined by Colorimeter DR890 (HACH LANGE, Germany) and pH change was determined by pH meter inoLab pH 730(WTW, Germany). Maximum sorption capacity was determined for 24 h sorption time for all ions. Samples were filtered and the sorbents were then dried at $105 \text{ }^\circ\text{C}$ for 4 hours. IR spectra were measured by Alpha FT-IR Spectrometer with ALPHA's Platinum ATR single reflection diamond ATR module (Bruker, Germany).

In order to obtain the sorption capacity, the amount of ions adsorbed per unit mass of adsorbent (q_e in milligrams of metal ions per gram of adsorbent) was evaluated using the following expression:

$$q_e = \frac{C_o - C_e}{m} \times V \quad (1)$$

where C_o is the initial metal ion concentration (mg.L^{-1}), C_e the equilibrium metal ion concentration (mg.L^{-1}), V the volume of the aqueous phase (L), and m the amount of the adsorbent used (g). To quantify the performance of the various adsorbents we evaluate the percentual metal ions removal efficiency as:

$$\text{Removal efficiency \%} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

3. Results and discussion

The results of the sorption capacities in dependence on the time are shown in Figures 1-3. For each monitored element has zeolite a higher sorption capacity as turf brush during the whole experiment.

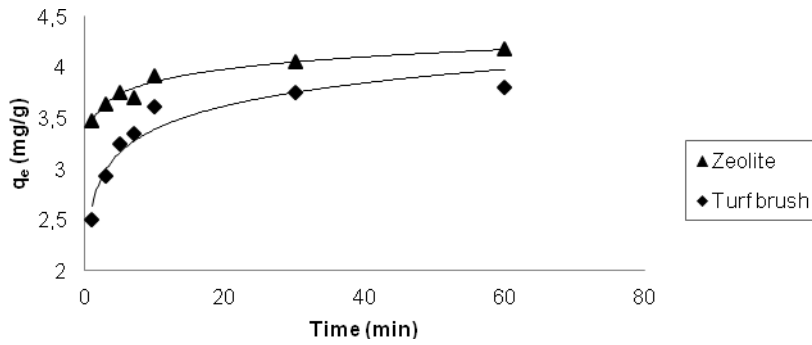


Figure 1: Determination of the sorption capacities of zeolite and turf brush for copper

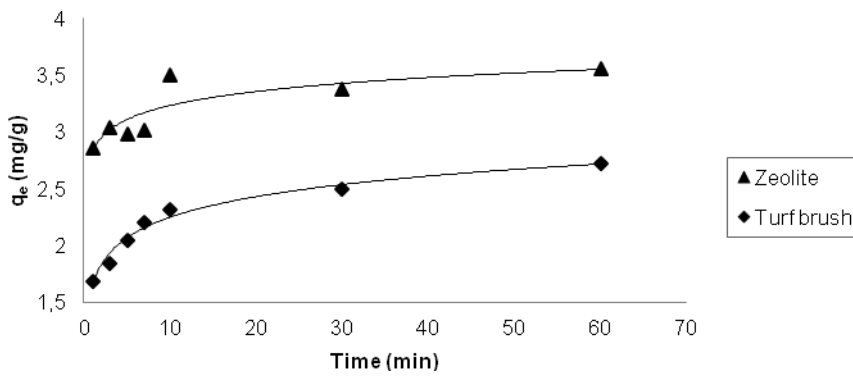


Figure 2: Determination of the sorption capacities of zeolite and turf brush for iron

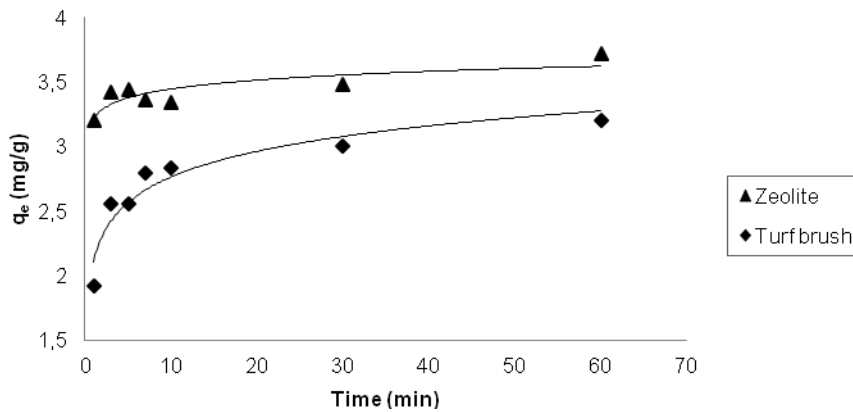


Figure 3: Determination of the sorption capacities of zeolite and turf brush for zinc

The solubility of Cu, Zn and Fe in model acidic solutions is a function of pH. According to the literature, Cu is precipitated at pH 4.5-6, Fe(II) is precipitated at pH about 8.5 and Zn at pH 5.5 - 7.0 (Balintova and Petrilakova, 2011). It was the main reason of the pH measurements in filtrates after sorption. The results of pH at different times of sorption are presented in Figures 4-6.

As shown in Figures 4-6, using of turf brush PEATSORB as a sorbent is connected with pH decrease of the tested samples, connected with releasing of hydrogen ions from turf brush into solution (Ho and McKay, 1999), whereas zeolite causes an increasing of pH, which can lead to precipitation of metals.

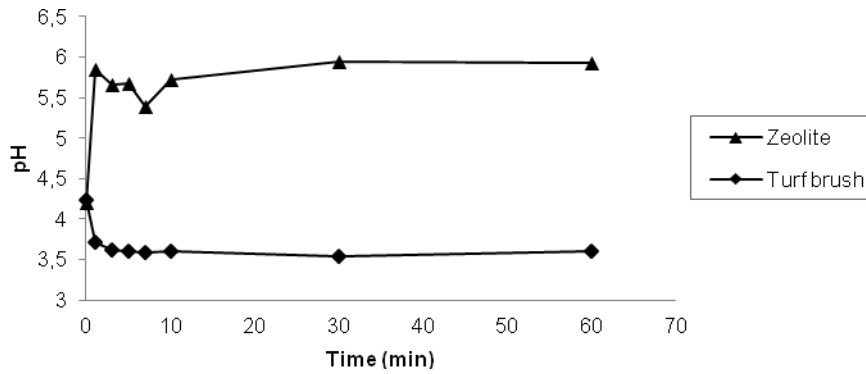


Figure 4: The pH changes of the filtrates after Cu²⁺ sorption

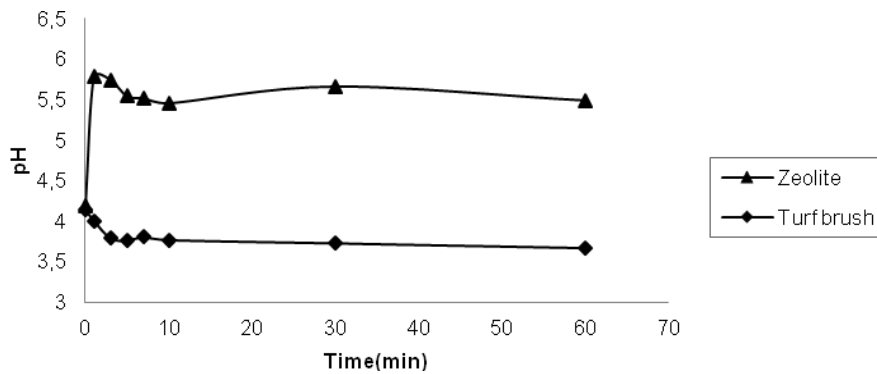


Figure 5: The pH changes of the filtrates after Fe²⁺ sorption

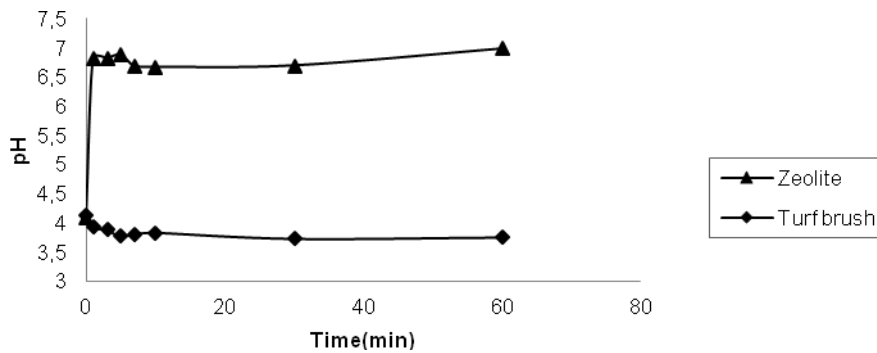


Figure 6: The pH changes of the filtrates after Zn²⁺ sorption

The precipitation of hydroxides was not confirmed by measuring the IR spectra. According to literature (Gadsden, 1975) for copper hydroxide is typical a broad band centred around 3320 cm⁻¹ which may be attributed to hydrogen bonded hydroxyl groups and an intense band is observed around 1382 cm⁻¹ which may be assigned to Cu-OH bond.

As it is seen in Figure 7, there is no difference between IR spectrum of zeolite before and after sorption of copper thus the mentioned bands were not observed. The same trend was confirmed for sorption of Zn²⁺ and Fe²⁺.

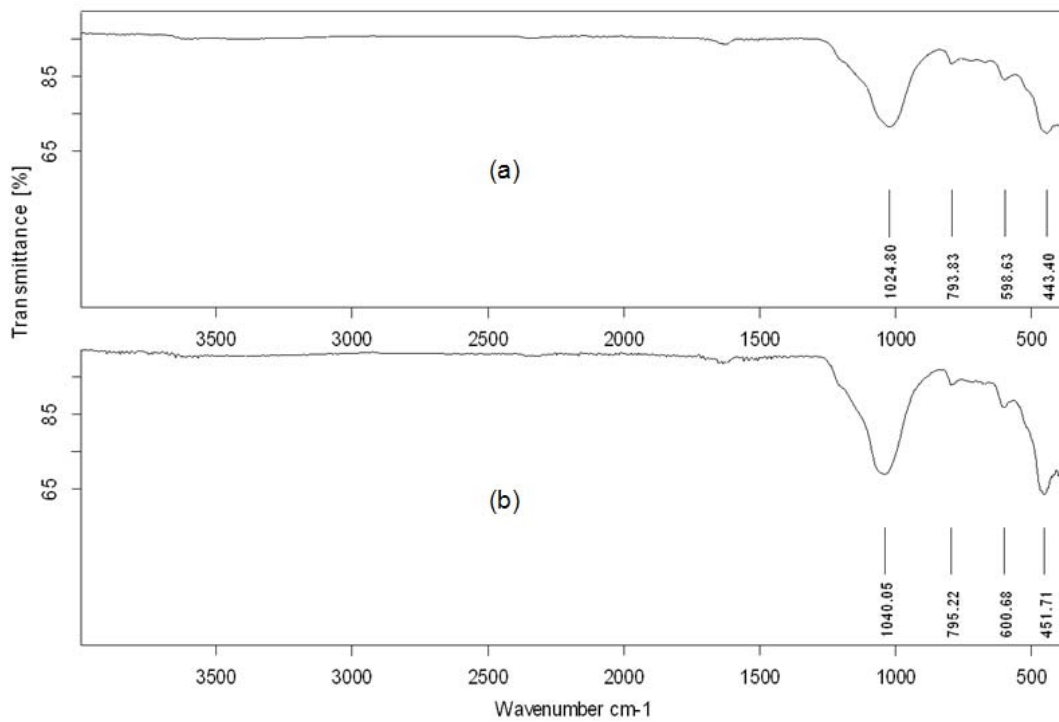


Figure 7: Infrared spectra. (a) natural zeolite; (b) zeolite after Cu^{+2} sorption.

The maximum sorption capacity of sorbents on Cu, Fe and Zn removal from model acidic solutions are presented in Figure 8.

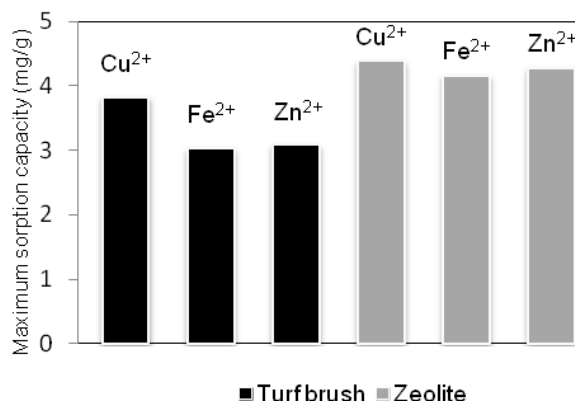


Figure 8: The maximum sorption capacity of turf brush PEATSORB and zeolite on Cu^{+2} , Fe^{+2} and Zn^{+2} removal from model acidic solutions

The efficiency of sorbents on Cu, Fe and Zn removal from model acidic solutions are presented in Table 1. As resulted from Figure 8 and Table 1, the sorption ability of these metal ions is in the following order: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Fe}^{2+}$.

Table 1: The efficiency of sorbents on Cu^{+2} , Zn^{+2} and Fe^{+2} removal from model acidic solutions

Sorbent	Efficiency %		
	Cu^{2+}	Zn^{2+}	Fe^{2+}
PEATSORB	78	69	61
Zeolite	89	85	83

4. Conclusion

This study showed the possibility of the selected sorbents (turf brush PEATSORB and zeolite) utilization for Cu, Fe, and Zn removal from model acidic solutions. Zeolite was the most efficient for Cu removal – decrease of Cu concentration is about 89 %. In general, the zeolite has better sorption properties than turf brush. Decrease of Fe concentration using zeolite is about 83 %, by turf brush PEATSORB is value about 61 %. Zinc cations were removed with efficiency rate about 85 % by using of zeolite and 69 % by PEATSORB. The results of this study will be used for adsorption of heavy metals from mixed solutions with the aim of their real using for acid mine drainage treatment.

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