

PRELIMINARY CONSIDERATIONS ON THE REMOVAL OF Fe, Zn AND Mn IONS FROM ACIDIC MINE DRAINAGE USING HYDROXYAPATITE

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ABSTRACT. The present study aimed at evaluating at laboratory-scale the possibility of ability of a synthetic hydroxyapatite in the removal process of metallic ions (Fe, Zn and Mn) from acid mine drainage generated at the abandoned mining perimeter of "Gura Minei" from Rosia Montana (Alba County, Romania). The water drainage from "Gura Minei" is acidic (pH = 2.9) and contains high concentrations iron, manganese and zinc. The removal efficiency of metal ions from AMD by hydroxyapatite was determined at different sorbent dosages and contact times, during batch sorption experiments. The composition of the acid mine drainage from "Gura Minei" before and after the treatment with hydroxyapatite was determined by X-ray fluorescence spectroscopy. In the investigated experimental conditions, adsorption of heavy metal ions from acid mine drainage by hydroxyapatite lay in the following order: Fe > Zn > Mn. About 99.8%, 83.4% and 24.7 % iron, zinc and manganese, respectively were removed from acid water drainage after 300 minutes of contact with 1.5 g synthetic hydroxyapatite.

Key words: *acid mine drainage, heavy metals, sorption, synthetic hydroxyapatite*

INTRODUCTION

Acid mine drainage (AMD) is one of the most important environmental challenge facing the mining industry worldwide (Gupta, 2008). This type of pollution is commonly generated at the abandoned mines after the pumping was stopped and the water floods the underground sites. It occurs naturally within the environments containing an abundance of sulphide minerals, usually pyrite (FeS₂) which oxidizes and dissolves in contact with water and air.

The main sources for AMD occurrence into the environment are (Natarajan, 2008): waste rock and tailings; underground and open-cast mines; stock and spoil piles and spent heap leach dumps. Generally, the acidic mine drainage is characterized by low pH value, high concentrations of metals (iron is the most common), elevated sulfate level and excessive suspended solids and/or siltation (Gupta, 2008).

The release of acid mine water into the environment might cause toxicological effects on aquatic life, damage the ecosystem of receiving rivers and lakes, corrode the metal pipes and break down the concrete structures (Barrie and Hallberg, 2005). Furthermore, taking into consideration the predictions on the future loading of dissolved metals from abandoned mines which advise that sulphide oxidation and release of the dissolved metals into the environment could carry on for decades to centuries, it is evident that appropriate AMD treatments for heavy metals removal are necessary (Rios et al., 2008). Usually, the acid mine drainage waters are treated by adding alkaline materials (i.e. CaCO_3 , Ca(OH)_2 , CaO , Na_2CO_3 , NaOH etc.) to the source of AMD or directly to the polluted stream, in order to neutralize the water and to precipitate the metals as hydroxides. The main disadvantage of this method is the need for continuous operation and maintenance, low reaction rates, and the production of huge amounts of secondary wastes (Wingenfelder et al., 2005).

Several other methods have been also used for acid mine drainage treatment, including adsorption, ion-exchange, membrane separation, reverse osmosis, electrochemical remediation and solvent extraction (Nogueira da Silveira et al., 2009). Nowadays, adsorption is widely accepted in the environmental treatment applications and extensive research has been carried out in the last several years to find materials having high absorption capacity, low water solubility, high stability under reducing and oxidizing conditions, low costs and availability in order to be used as sorbents for the removal of metal ions from various wastewaters, including AMD (Moayyeri et al., 2013; Mohan and Chander, 2006).

In recent years, it was reported that apatite-group minerals with special crystal chemistry characteristics would become the most promising mineral materials for the treatment of wastewater containing fluoride and heavy metals (Y. Feng et al., 2010). Among them, hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] which is the main mineral constituent of human tissue (teeth, and bones) appears to be an ideal material for the disposal of long term contaminants from polluted soils or sewage and wastewaters.

Several investigations have proved the ability of both, natural and synthetic hydroxyapatites in the removal process of various heavy metals, i.e. Pb, Zn, Cu, Cd, Co, As, Ni, Fe, Mn from solutions. [Chen et al., 1997; Gupta et al., 2011; Bazargan-Lari et al., 2012; Moayyeri et al., 2013]. The sorption mechanisms of heavy metals on hydroxyapatite are diverse and mainly include adsorption, ion-exchange, dissolution/precipitation, surface complexation, diffusion into the solid, coprecipitation or precipitation of amorphous phases (Mirhosseini et al., 2014). However, different sorption mechanism often work together and it is difficult to quantify the relative contribution from each process responsible for the metal uptake.

Despite various studies (Xiaobing et al., 1997; Sheha, 2007; Liao et al., 2010; Abdallah, 2014) attesting the effectiveness of several types of hydroxyapatite for heavy metal ions from synthetic aqueous solution under different experimental conditions, no research have been carried out to establish the sorbent's ability to eliminate the metals from authentic wastewaters.

The present study aimed at evaluating at laboratory-scale the possibility of using synthetic hydroxyapatite (sHA) (Saplontai et al., 2012) the removal process of the metallic ions (Fe, Zn and Mn) from the acidic mine drainage generated at the abandoned mining perimeter of “Gura Minei” from Rosia Montana (Alba County, Romania), under batch sorption experiments. The concentration of metals in the water drainage from “Gura Minei” before and after the treatment with synthetic hydroxyapatite was determined by X-ray fluorescence spectroscopy.

MATERIALS AND METHODS

Sampling site

The exploitation “Gura Minei” gallery is located in Rosia Montana mining perimeter, in the South Apuseni Mountains (Romania). Although the mining operation in Rosia Montana area were closed, currently the mine waters from “Gura Minei” are flowing unimpeded in the “Valea Roşiei” creek from nearby and then in “Abrud” river. The mine water drainage channel is arranged inadequately (figure 1) as it is a simple trench dug in the topsoil blankets from the abandoned platform.

Three samples of water drainage were collected from the abandoned mining perimeter of “Gura Minei” (figure 1) and their chemical composition was determined by X-ray fluorescence spectrometry using Quant’X ARL spectrometer (Thermo Scientific, USA). The water pH was measured on-site using portable pH meter (Hanna instruments).



Fig. 1. Water drainage at “Gura Minei” abandoned mining perimeter (23.05.2014, A. Lancranjan)

Characterization of sorbent material (Saplontai M. et al., 2012)

Hydroxyapatite powder was synthesized in “Raluca Ripan” Institute of Chemistry. Hydroxyapatite (sHA) was obtained by wet chemical methods (precipitation), from CaCl_2 (Sigma-Aldrich) and Na_2HPO_4 (Sigma-Aldrich) as raw materials. Precipitation reactions take place at the room temperature:



The resulted precipitate was maintained in the suspension at the ambient temperature, in the presence of crystallization admixtures, for 40 h, then filtered, washed with de-ionized water, dried at 110°C and thermally treated at 400°C for 2 h.

The granulation and specific surface area (BET) of the hydroxyapatite used in the present study were 10-70 µm and 50 m²/g, respectively.

Experimental

The efficiency of synthetic hydroxyapatite (sHA) in the removal of the metal ions from “Gura Minei” water drainage was investigated at the laboratory scale, using a batch reactor (250 ml) with continuous stirring at 300 rpm.

Various quantities (0.5, 1 and 1.5 g) of sHA were left in contact with 100 ml AMD solution. Aliquots of supernatant (1.5 mL) were collected at different time intervals (from 15 to 300 minutes) and the concentration of the metal ions in the aqueous phase was immediately determined by X-ray fluorescence spectrometry. It should be noted that the total sampling volume did not exceed 10% of the initial solution volume. All experiments were conducted at room temperature (22 ± 0.5°C), in duplicates to observe the reproducibility of the results and the mean values were used.

The removal efficiency, R.E. (%) of metallic ions by synthetic hydroxyapatite was calculated using the following equation:

$$\text{R. E. (\%)} = \frac{c_i - c_f}{c_i} * 100 \quad (1)$$

where c_i and c_f are the concentrations of the metal ions (mg L⁻¹) in the initial and final solutions respectively.

RESULTS AND DISCUSSION

Acid mine drainage characterization

The average chemical composition and pH of the water drainage samples collected from “Gura Minei” abandoned mining perimeter is presented in Table 1.

From Table 1 it could be observed that the water drainage is strongly acidic and contains significant levels of metal ions (Fe, Mn and Zn), whose concentrations substantially exceed the maximum consent limits established by Romanian Standard NTPA001/2002. It is clear that this water drainage introduces sulphuric acid and toxic metals into the environment that could damage the natural ecosystem, since AMD is disposed without any previous remediation treatment. On-site, the infiltration of the acidic water drainage into the soil which retains heavy metals and, therefore, causes constant pollution could be easily observed.

Table 1. Average chemical composition and pH of water drainage collected from "Gura Minei" abandoned mining perimeter

Parameter	AMD	Maximum consent limits*
pH	2.9 ± 0.1	6.5 - 8.5
Fe, mg L ⁻¹	594 ± 0.5	5
Mn, mg L ⁻¹	424.5 ± 0.7	1
Zn, mg L ⁻¹	21 ± 0.2	0.5

*According to Romanian Standard NTPA 001/2002

AMD treatment using synthetic hydroxyapatite

The removal of heavy metals from the acidic water drainage collected from "Gura Minei" abandoned mining perimeter onto sHA samples was investigated at different contact times and sorbent dosages.

The variations of iron, manganese and zinc ions concentration during the contact time between 100 mL acid water drainage and various amounts of sHA are illustrated in figure 2.

It can be observed from figure 2 that at a dosage of 0.5 g, the investigated synthetic hydroxyapatite was not able to treat any of the metallic ions from AMD solution to below the legal requirements. Although, the concentration of iron in the AMD solution decreases from the initial values of 594 ppm to 89 ppm during the first 15 minutes of contact with 0.5 g sHA, the manganese and zinc concentrations remained almost unchanged. At this sHA dosage, further increases of the contact time up to 300 minutes do not lead to an important enhancement of metal ions removal from AMD solution. However, the concentrations of the metal ions, especially iron and zinc in AMD solution significantly decrease by using higher amounts of adsorbent, when the removal rate is fast and the equilibrium is easily attained. This reveals that the instantaneous and equilibrium sorption capacities of the metal ions from AMD are functions of the sHA dosage. Since there is a higher total surface area at the higher adsorbent concentration, more adsorption sites are available causing higher removal of solution. For instance, the iron concentration in AMD sample decreases to 1 ppm after 60 minutes of contact with 1 g sHA and this value remains stable throughout the total contact time of 300 minutes. When an amount of 1.5 g sHA was used, the sorption equilibrium was attained after the first 15 minutes of contact and the value of the iron concentration in AMD solution was 1 ppm.

In the case of zinc and manganese, at a dosage of 1 g sHA, their concentrations remain at high levels, as could be observed from figure 2b and 2c. An increase of sHA dosage to 1.5 g/100 mL AMD solution resulted in substantial improvement of zinc removal. Hence, the zinc concentration in AMD solution decreases from 21 ppm to 9.1 ppm after the first 30 minutes of contact with sHA, while at the total contact time of 300 minutes, it reaches the value of 3.5 ppm.

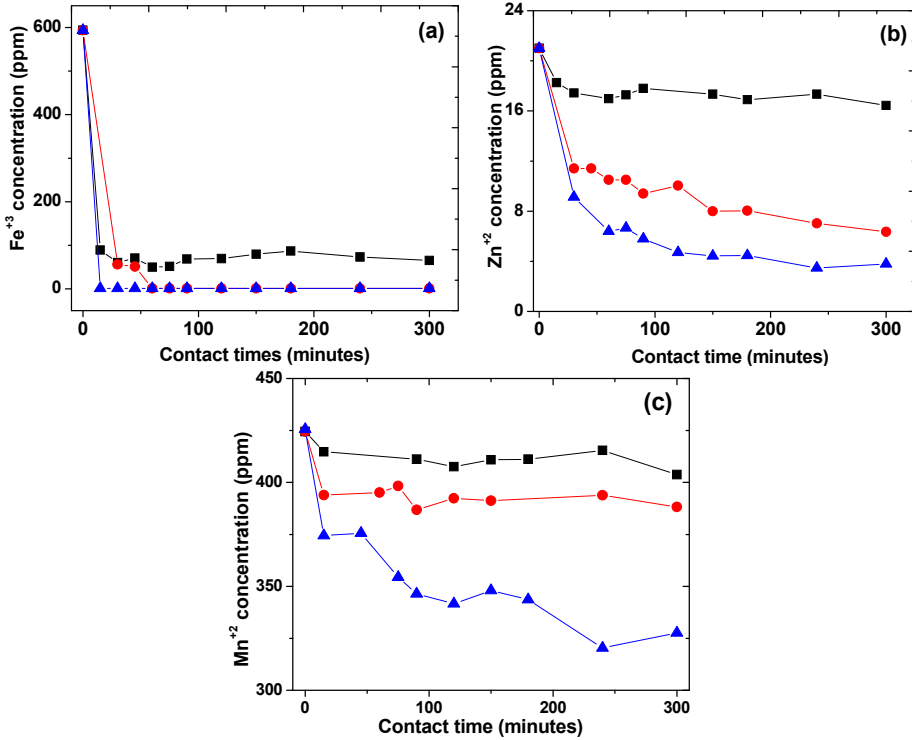


Fig. 2. Variation of iron (a), zinc (b) and manganese (c) ions concentration in AMD sample (100 mL) at different dosages of synthetic hydroxyapatite as a function of the contact time (■) 0.5 g; (●) 1 g; (▲) 1.5 g.

Disregarding the dosage of synthetic hydroxyapatite, the manganese concentration remains elevated in AMD solution and only a slight decreases from 424.5 ppm to 320 ppm took place after 300 minutes of contact with 1.5 g sHA.

From figure 2 it seems that the removal process of all metal ions from AMD solution took place in two steps. In the first step, the metal ions uptake is fast, while in the second one it happened slowly and exhibited a subsequent removal until equilibrium was reached (Zamani et al., 2013). The main reason for the appearance of rapid step could be correlated with the high number of the active sites on the sHA surface at the first stages of adsorption process. The gradual occupancy of these sites might cause an emerging of the lower step (Sheha, 2007).

The values of the removal efficiency of the synthetic hydroxyapatite calculated at different contact times, as a function of the adsorbent dosage are presented in figure 3.

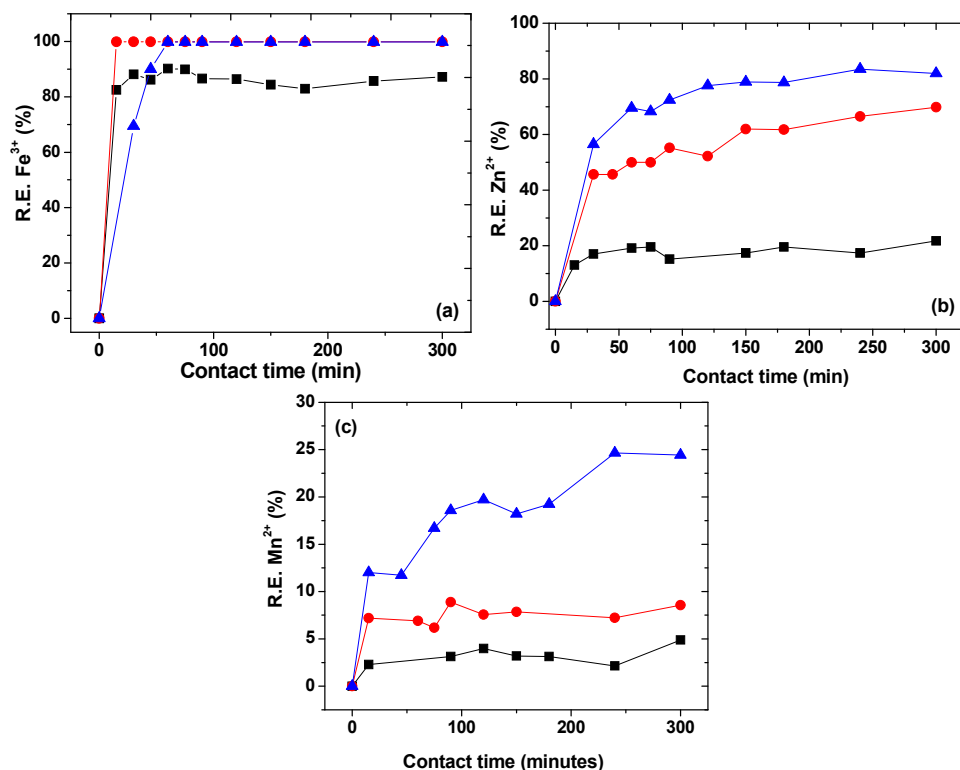


Fig. 3. Effect of sHA dosage on the removal efficiency of the metal ions from AMD: (■) 0.5 g; (●) 1 g; (▲) 1.5 g.

As it can be seen in figure 3, in the investigated experimental conditions, sHA was able to remove significant amounts of metal ions, especially iron and zinc from the water drainage collected from “Gura Mine” abandoned mining perimeter.

At a sorbent dosage of 0.5 g/100 mL AMD, the iron removal efficiency was 88.1% after 30 minutes and reached the value of 99.2 % by increasing the contact time to 60 minutes. At a sorbent dosage of 1.5 g/100 ml AMD, the percent of iron removal was 99.8 and the final concentrations of iron were reduced to levels less than the maximum consent limit for wastewater discharges after only 15 minutes of contact with sHA.

In the case of zinc, the maximum value of the removal efficiency was 21.7 % when an amount of 0.5 g sHA was used, but it enhanced to 69.7 % by increasing the sorbent dosage to 1 g. The removal efficiency of zinc attains the maximum value of 83.5 % after 240 minutes of contact with 1.5 g sHA/100 mL AMD solution.

As seen in figure 3c, in the investigated experimental conditions, the removal efficiency of manganese is only 24.5% after 300 minutes of contact with 1.5 g sHA. This low removal rate of manganese from AMD solution may be the result of the

weak interaction between Mn^{2+} and sHA caused by the fact that the volume of hydrated manganese ions is high and the ions are more likely to be in solution rather than adsorbed. Another possible explanation could be related to the low value of water drainage pH, since it is known that the solution pH greatly affects metal sorption mechanism by apatite and metal-apatite reaction products (Wright et al., 1997).

In the investigated experimental conditions, adsorption of heavy metal ions from acid mine drainage by synthetic hydroxyapatite lay in the following order: $Fe > Zn > Mn$. The high removal rate of iron and zinc ions from AMD solution is most probably attributed to the adsorption of metal ions on the solid surface followed by their diffusion into hydroxyapatite structure and the release of cations originally contained within the sorbent. This hypothesis was supported by the increases of the calcium concentration into the solution after the first moments of contact of AMD solution with sHA (results not shown).

CONCLUSIONS

The present paper examined the effect of a synthetic hydroxyapatite in the removal process of metal ions from the acid water drainage collected at "Gura Mine" abandoned mining perimeter in Rosia Montana (Romania).

The preliminary results indicated that the used synthetic hydroxyapatite was able to remove significant amounts of metal ions, especially iron and zinc from acidic mine drainage. The removal effectiveness of the metal ions by the investigated sorbent is strongly dependent on its applied dosage and contact time with AMD solution.

In the investigated experimental conditions, about 99.8%, 83.4% and 24.7 % of iron, zinc and manganese, respectively were removed from AMD solution in contact with 1.5 g synthetic hydroxyapatite.

The preliminary results showed that synthetic hydroxyapatite have the potential to be used for treating actual acid mine drainage.

The rapid sorption rates of iron and zinc on hydroxyapatite allows the consideration of their removal by column filled setup which generally has a short contact time between the polluted solutions and the adsorbent.

Further investigations are needed to investigate the mechanisms of adsorption in relation to the ion exchange process and to determine the optimum conditions for the use of synthetic hydroxyapatite for cleaning-up industrial wastewaters. The possibility of metals recovery and the regeneration of the sorbent used for AMD treatment using various eluting agents (i.e. hydrochloric acids, double distilled water, calcium chloride, barium hydroxide) is another issue to be further investigated.

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