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MINERAL PRECIPITATES FROM MINE WATER AS ADSORBENTS: SITE SPECIFIC CHARACTERIZATION OF NATURAL DEPOSITS

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Introduction

Secondary minerals, mixtures of Fe-Al compounds such as oxohydroxy and hydroxosulfates can be naturally generated from mine water in response to processes such as oxidation /bio-oxidation, mixing, evaporation and neutralization. Deposits observed in significant quantities, with a very high iron content, from the mining perimeters of Certej-Coranda, Rosia Montana and Boita Hateg were sampled and characterized. Schwertmannite and Goethite can function as adsorbents after drying or further processing. In both cases, the chemical analysis of the product is important in order to promote it to potential users. A preliminary evaluation of the adsorption capacity for As(III) was performed for the original material and for products obtained after calcination.

Materials and methods

Iron rich precipitates were sampled from central Romanian mining area, from Rosia Montana Orlea Orizont714, Certej P1 Coranda-Galerie and Boita Hateg Orizont120 and stored in HDPE bags. These samples are referred further as *Orlea714*, *P1C* and *BH120*. Mineral samples were conditioned in the lab by removing vegetal debris and analyzed for elemental composition by X-ray fluorescence, metals and sulphur (SR-EN-15309:2008, Rigaku CG X-ray Spectrofluorimeter). After calcination (800°C), a second elemental analysis was performed. Thermal gravimetric (TG) and differential thermal analysis (DTA) were conducted on a Netzsch STA 409 thermal analyzer (air, linear heating rate 10°C/min). The adsorption capacity was studied in batch experiments on 1 g d.s. L^{-1} as mineral adsorbent suspensions for an initial concentration of 72.69 mg/L As(III) in distilled water, at neutral pH, contact time 180 min, temperature 24±1°C, orbital shacking, 175 rpm. Minerals were conditioned by drying and sieving (0.75 mm, passed). After the contact time, the samples were filtered through 0.45 µm membrane filters and the concentration of arsenic was determined using a Perkin Elmer PinaAcle 900T atomic absorption spectrometer.

Results and conclusions

All three precipitates have, as common characteristic, a very high iron content, about 500 g/kg d.s., the ratio Fe/S gram-atom / gram-atom is very different among the three minerals analyzed. Also was necessary to be studied mass loss values for the mineral bulk samples calcined at 300°C and 800°C (10°/min, 1h). The most significant Sulfur mass content variation by calcination at 800°C was observed for Orlea714 sample (-84%).

Thermal behaviour of the precipitates and of the calcined products
Natural precipitate from Rosia Montana Orlea714 shows a thermal decomposition with adsorbed and structural water loss occurring above 100°C and two transformations at approx. 580°C and 680°C respectively, with total mass loss due to thermal decomposition of about 38% up to 700°C. This thermal behaviour can be explained by the characteristic two-step decomposition of ferric hydroxosulfates, first at 560-580°C with water loss, producing Fe_2SO_4 and the second step being represented by the transformation to hematite, an endothermic reaction above 580°C with release of SO_3. The P1C precipitate has a somewhat similar TG curve, but with a higher final residual mass, about 80% of the initial and no observable decomposition at 500°C. The natural precipitate taken from Boita Hateg is rather goethite $Fe_2O_3 \bullet H_2O$, with a more modest mass loss than Orlea714, explainable also by the formation conditions, the mine water having in this case a circum-neutral character.

Adsorption capacity for As(III)
Among the products considered, the mineral with the highest As(III) adsorption capacity was the Schwertmannite type precipitate from Orizont 714 Orlea Gallery, followed by the natural precipitate obtained from P1-Coranda Gallery. It is interesting to observe that Orlea714 and P1C already had a relevant initial arsenic content of 1.87 g/kg d.s. and 2.96 g/kg d.s. respectively, sorbed from the mine water, these minerals being effective trace metals sinks as observed by some researchers.

For the calcined products, at a temperature of 300°C, the adsorption capacity of the initially Goethite or Schwertmannite containing minerals is preserved after calcination, with a certain decrease for the Orlea714 precipitate and with a certain increase in the case of Boita Hateg natural precipitate gallery. Porous hematite prepared from the calcination of goethite concentrate was found to have a good adsorption capacity for As(III) depending on equilibrium concentration (<12 mg/L, informative).

In the case of calcination at a temperature of 800°C, an effect of a significant decrease of the adsorption capacity (about 7 times for ORL714) was observed. Also, the adsorption capacity values became similar, close to a median value of 7.8 mg/g with a standard deviation of 0.51 mg/g as informative figure. The levelling effect of calcination may be explained due to the formation in all cases of a product containing mainly hematite.

Goethite (α-FeOOH) present in mineral samples or derived from Schwertmannite will be transformed in hematite (α-Fe_2O_3) by direct dehydration without an intermediate phase, *slit-shaped micropores* being formed. By increasing the calcination temperature to 800°C, the sinterization of hematite pores and the crystal growth will occur, but also the disappearance of pores and this could cause the decrease of the adsorption capacity as observed in this work.

Depending on calcination temperature, adsorption capacity decreasing and a leveling effect can be observed, most probably due to pore sinterizing and transformation to hematite, irrespective to the initial mineral.

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