



Using of phosphatized dolomite for treatment of real mine water from metal ions



A.I. Ivanets^{a,*}, N.V. Kitikova^a, I.L. Shashkova^a, O.V. Oleksiienko^{b,c}, I. Levchuk^b, M. Sillanpää^b

^a Institute of General and Inorganic Chemistry of National Academy of Sciences of Belarus, St., Surganova 9/1, 220072 Minsk, Belarus

^b Laboratory of Green Chemistry, Lappeenranta University of Technology, Sammonkatu 12, 50130 Mikkeli, Finland

^c Institute of Sorption and Problems of Endoecology, NAS of Ukraine, 13 Naumova Str., Kyiv 03164 Ukraine

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ABSTRACT

The aim of this paper was to study the sorption properties of Ca–Mg phosphate sorbents using real mine water, containing bi- and trivalent metal ions such as Al^{3+} , Cr^{3+} , Ni^{2+} , Mn^{2+} , Co^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Fe^{3+} . The sorbents utilized in this work were prepared from dolomite and represent a mixture of Ca^{2+} and Mg^{2+} hydrogen phosphates (PD-1) and tertiary phosphates of Ca^{2+} and Mg^{2+} (PD-2). The synthesized sorbents were characterized by X-Ray diffraction, Fourier transforms infrared spectroscopy, differential-thermal analysis, thermogravimetric analysis, and low temperature adsorption-desorption of nitrogen methods. Sorption experiments were conducted in batch mode. Removal efficiency dependencies on sorbent dose, nature of the metal ion, contact time and temperature were established. For both tested materials the highest level of mine water purification was achieved at the sorbent dose of 25 g L^{-1} , leading to the elimination of all metal ions except Mn^{2+} when PD-2 was used and Cd^{2+} and Co^{2+} in the case of PD-1. The sorption kinetics of PD-1 and PD-2 were evaluated with a pseudo-second order kinetic model. It was observed that raising the temperature from 15 to 40°C leads to increased removal efficiency for all studied metal ions. The results of this study indicate that the prepared sorbents are highly effective for the treatment of multi-component mine water.

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1. Introduction

Purification of water from metal ions is one of the crucial tasks faced by researchers in the field of environmental engineering. This is due to the constantly increasing volumes of industrial wastewater containing significant amounts of metal ions such as Cr^{3+} , Ni^{2+} , Mn^{2+} , Co^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} etc., which threatens to pollute the soil, surface water and groundwater and can be toxic to the receiving environment [1–4].

Conventional methods for removal metal ions are chemical precipitation, ion exchange, membrane filtration, electrochemical treatment and evaporation. These methods have significant disadvantages, such as for instance incomplete removal, high-energy consumptions and production of toxic sludge or waste products. Adsorption methods are widely used for the purification of industrial wastewater from metal ions [5,6]. A great attention has

been contributed to develop new adsorbents, such as carbon nano tubes [7], magnetic sorbents [8], functionalized polymers and silica [9,10]. However, these materials have a low sorption capacity of $1\text{--}2 \text{ mmol g}^{-1}$, they can not always be used in acidic environments, and they are often very expensive.

Hydroxyapatite (HA) [11–14] and calcium phosphate with non-apatite structures [15–18] have been shown to be highly effective for removing various bi- and trivalent metal ions from aqueous solutions. To the best of our knowledge, there is no data reporting the use of magnesium phosphates for metal ion sorption. According to our previous studies, magnesium phosphates demonstrate superior adsorption efficiency to HA and calcium phosphate with non-apatite structures. Thus various Ca^{2+} and Mg^{2+} phosphates were studied for the sorption treatment of aqueous solutions from metal ions. These sorbents were also tested for the removal of stable and radioactive isotopes of strontium and a sorption mechanism was suggested [19,20]. In our previous research [20] an improved method of producing phosphatized dolomite was described, and studies of the adsorptive removal of different metal ions from model one-component aqueous solutions were performed. The extremely high adsorption capacity of phosphatized dolomite was

* Corresponding author.

E-mail addresses: Ivanets@igic.bas-net.by, andreiivanets@yandex.ru (A.I. Ivanets).

detected toward Co^{2+} and Pb^{2+} (15 and 12 mmol g^{-1} , respectively) and toward Zn^{2+} , Fe^{2+} and Cu^{2+} (about 8 mmol g^{-1}). Adsorption isotherms were built for each tested metal ions and were fitted to Langmuir, Freundlich and Redlich-Peterson models. Yet real industrial wastewaters contain a mixture of metal ions, resulting in lower sorption capacity in comparison with that from single component solutions [11,18].

The aim of this work was to study the effectiveness of sorbents of different chemical composition on the basis of phosphatized dolomite for the treatment of real mine water, containing a mixture of different bi- and trivalent metal ions (Al^{3+} , Cr^{3+} , Ni^{2+} , Mn^{2+} , Co^{2+} , Pd^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Fe^{3+}) depending on the dose of adsorbent and contact time.

2. Materials and methods

2.1. Chemicals

Laboratory glassware washed with concentrated HCl or HNO_3 and Milli-Q water (resistance 18.2 $\text{M}\Omega \text{cm}^{-1}$) was used for sorption experiments. Hydrochloric and nitric acids were of analytical grade and purchased from Sigma–Aldrich (Finland). Phosphoric acid of analytical grade was used for the modification of dolomite and purchased from Five Oceans (Belarus). All chemicals were used without further purification.

2.2. Preparation of sorbents

Dolomite from the Ruba deposit with the following chemical composition (wt.%): SiO_2 1.1, Fe_2O_3 0.4, Al_2O_3 0.5, CaO 30.3, MgO 20.0, SO_3 0.4, K_2O 0.2, Na_2O 0.1 and calcination loss 47.0. For the synthesis of sorbent with a high content of calcium and magnesium phosphates and high sorption properties it was previously suggested to activate the natural dolomite by its calcination at 800 °C. This will allow to remove organic impurities contained in the natural dolomite, and also to decompose the dolomites to the magnesium oxide and calcium carbonate, which will significantly improve its activity in interaction with nitric acid. The first sorbent (PD-1) was obtained after 24 h of stirring dolomite with a 20% phosphoric acid at a dolomite: phosphoric acid weight ratio of 1:3; more details can be found elsewhere [19]. In order to prepare the second sorbent (PD-2), activated dolomite was dissolved in concentrated nitric acid, thereafter Ca and Mg phosphates were precipitated using ammonium phosphate at pH 10 as described in [20]. In contrast to previous work, the synthesis was realized by a slow controlled titration (5 mL s^{-1}), and after total addition of the ammoniumphosphate solution the suspension was mated during 24 h. After the aging and washing with distilled water the precipitate of Ca-Mg phosphate was rinsed with ethanol. Replacement of intermicellar liquid (water–ethanol) allows to obtain the sorbent with a more developed mesoporous structure, because ethanol has a lower value of the surface tension than water. By this means, sorbent PD-1 represents a mixture of Ca–Mg hydrogen phosphates with the approximate composition $(\text{Mg,Ca})\text{HPO}_4 \cdot x\text{H}_2\text{O}$ and PD-2 represents a mixture of Ca–Mg tertiary phosphates with the total formula $(\text{Mg,Ca})_3(\text{PO}_4)_2 \cdot y\text{H}_2\text{O}$.

2.3. Mine water

The adsorption studies of the removal of metal ions by phosphatized dolomite were carried out using real mine water from a Cu–Zn mine. The chemical composition of the mine water is given in Table 1. As this Table indicates, metal ions such as Al^{3+} , Fe^{3+} and Zn^{2+} predominate in the tested mine water leading to concentrations exceeding 300 mg L^{-1} . The concentrations of other

metal ions are significantly lower and vary from 0.2 to 34.7 mg L^{-1} . Anionic composition is represented by sulfate ions amounting to 7750 mg L^{-1} . The initial pH of the mine water was 2.42. The initial water was transparent with a bright orange color and a small amount of suspended particles.

2.4. Analytical methods

An X-ray diffractometer DRON-3 with $\text{CuK}\alpha$ radiation (2 θ 5–70°) was used for sorbent phase composition measurements. FTIR of the sample in a KBr pellet was recorded on a Midac FTIR field spectrometer at room temperature in the range of 400–4000 cm^{-1} . DTA and TGA were performed by means of a NETZSCH STA 409 PC/PG derivatograph system, heated at a speed of 10 °C/min from 20 to 1000 °C in an Ar atmosphere.

The porous structure of the sorbent were assessed by isotherms of low temperature (–196 °C) physical adsorption–desorption of nitrogen, measured by the volumetric method on an ASAP 2020 MP surface area and porosity analyzer (Micromeritics, USA). The surface area of pores per unit mass of the solid or the specific surface area was determined by the single point (A_{sp}), and BET (A_{BET}) methods. The single point method was used to calculate not only the specific surface area A_{sp} , but also the adsorption and desorption volumes ($V_{\text{sp,ads}}$ and $V_{\text{sp,des}}$) of pores and their average adsorption and desorption diameters D_{ads} and D_{des} . The relative error in determining the pore volume was $\pm 1\%$ for the surface area and $\pm 15\%$ for the pore size.

The concentration of metal ions presented in mine water in the course of the sorption experiments was analyzed using inductively coupled plasma optical emission spectrometer (ICP-OES) model iCAP 6300 (Thermo Electron Corporation, USA). The pH of the mine water before and after sorption tests was measured with a pH-meter 340i (± 0.02). The concentration of sulfates in the mine water was determined by means of a Shimadzu LC-20High Performance Liquid Chromatograph (HPLC). For this analysis an IC SI-50 4E column (4.0 \times 250 mm) and conductivity detector (CDD-10A_{VP}) were utilized. The analysis was performed at a temperature of 25 °C using 3.2 mM Na_2CO_3 + 1 mM NaHCO_3 solution as eluent at a flow rate of 0.7 mL min^{-1} .

2.5. Sorption and desorption experiments

The sorption properties of the prepared materials (PD-1 and PD-2) were studied using real mine water in batch mode. All experiments were repeated at least twice and the obtained mean values were used for all calculations.

In order to determine the optimal sorbent dose and provide maximum removal of metal ions from mine water, a series of experiments was performed varying the sorbent mass from 0.05 g to 2.5 g per 25 mL of water, corresponding to a sorbent dose of from 2 g L^{-1} to 100 g L^{-1} . A portion of sorbent was mixed with an aliquot of mine water for 24 h using a ST15 shaker (CAT, M. Zipperer GmbH, Staufen, Germany). Thereafter, the solutions were filtered through a 0.2 μm polypropylene filter and analyzed with ICP-OES.

To estimate the degree of metal ion retention by phosphate sorbents, desorption experiments were conducted. Desorption experiments were performed with the samples obtained in sorption experiments with sorbents PD-1 and PD-2 at a dose of 10 g L^{-1} . Desorption experiments were carried out similarly to the adsorption experiments at a dose of 5 g L^{-1} , shaking the samples in Milli-Q water with pH 7 for 24 h at room temperature. The degree of desorption ($\alpha, \%$) was calculated by the equation:

$$\alpha = \frac{C_d \times V_w}{q \times m_d} \times 100$$

where C_d —equilibrium concentration of metal ions after desorption, mg L^{-1} , V_w —volume of aliquot (20 mL), m_d —weight of sorbent, g, q —equilibrium capacity, mg g^{-1} .

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