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Fractionation study in bioleached metallurgy wastes using six-step sequential extraction

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ABSTRACT

The stored metallurgy wastes contain residues from ore processing operations that are characterized by relatively high concentrations of heavy metals. The bioleaching process makes use of bacteria to recover elements from industrial wastes and to decrease potential risk of environmental contamination. Wastes were treated by solutions containing bacteria. In this work, the optimized six-stage sequential extraction procedure was applied for the fractionation of Ni, Cr, Fe, Mn, Cu and Zn in iron–nickel metallurgy wastes deposited in Southern Poland (Szklary). Fractionation and total concentrations of elements in wastes before and after various bioleaching treatments were studied. Analyses of the extracts were performed by ICP-MS and FAAS. To achieve the most effective bioleaching of Zn, Cr, Ni, Cu, Mn, Fe the usage of both autotrophic and heterotrophic bacteria in sequence, combined with flushing of the residue after bioleaching is required. 80–100% of total metal concentrations were mobilized after the proposed treatment. Wastes treated according to this procedure could be deposited without any risk of environmental contamination and additionally the metals could be recovered for industrial purposes.

1. Introduction

Environmental pollution by heavy metals originated from abandoned mines and/or dump metallurgy waste are very important sources of soil and water contamination. In the Lower Silesia region of Poland there are a lot of dumps where various industrial wastes are deposited. One of such heaps is located in Szklary. An iron–nickel alloy was produced there until the end of 1970s. The mining and metallurgy wastes are characterized by relatively high concentrations of most of the elements, some of them are particularly toxic. There are many efforts to recover valuable elements from industrial wastes and to decrease potential risk of environmental contamination. One of the recently applied methods is bioleaching (the solubilization of metals from solid substrates either directly by the metabolism of leaching bacteria or indirectly by the products of their metabolism [4]) Bioleaching is a simple, economical and effective process for metal solubilization from industrial wastes or biosolids [1–3]. Metal solubilization from solid wastes or other solids is achieved through the activity of some chemolithotrophic bacteria for example autotrophic or heterotrophic bacteria. Autotrophic bacteria e.g. *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and *Thiobacillus thioparus* which can catalyze the oxidation of sulfur compounds to sulfuric acid causing pH lowering. Activity of heterotrophic bacteria e.g. *Pseudomonas fluorescens*, *Bacillus cereus* and *Bacillus thuringiensis* causes decomposition of organometallic compounds. Organic acids and phenols are the main products of bacteria metabolism [5]. These compounds may take part in decomposition of minerals available in industrial wastes.

The mobility and bioavailability of elements in the environment depends strongly on their chemical forms. Elements in soils, sediments and wastes occur in several different physico-chemical forms, i.e. as simple or complex ions, as easily exchangeable ions, as organically bound, as occluded by or coprecipitated with metal oxides, carbonates, phosphates and secondary minerals or as ions in crystal lattices of primary minerals [6]. The solid–liquid extraction is a useful tool to evaluate the elements binding. Many different sequential extraction procedures were applied to evaluate the contamination risk for soil [7–10] and sediment [11–13]. However, the number of proposed schemes for mining and metallurgy wastes was limited [14].

The aim of the study was to apply the optimized extraction procedure and to compare mobility of selected elements (Cr, Cu, Fe, Mn, Ni, and Zn) and their distribution between operationally defined phases in wastes before and after bioleaching processes. The sequential extraction was used to estimate the efficiency of mobilization of studied elements after application of bioleaching procedure. During preliminary studies the following fractions were defined: water-soluble, carbonate, Mn oxides, Fe oxides, organic and sulfide and residual. The concentration of selected extractants, temperature and duration of extraction procedure were optimized.

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Based on the obtained results the mobility of metals in residues and usefulness of bio-extracts for recovery of some valuable elements were assessed.

2. Experimental

2.1. Reagents

The following reagents were used: hydroxylamine hydrochloride and oxalic acid (puriss p.a.) (Fluka, UK); ammonium oxalate, hydrogen peroxide (puriss p.a.) (Sigma–Aldrich, Germany) and nitric acid, acetic acid, perchloric acid, hydrofluoric acid (supra pure) (Merck, Germany).

Standard solutions were prepared by dilution of Spectroscan solutions (1000 mg L^{-1}) of the appropriate element. Ultrapure water obtained form a Milli-Q-Water System (Millipore, USA) was used throughout the work.

2.2. Instrumentation

The total concentrations of Ca, Fe, Mg, Mn, Zn in samples and in extracts were measured using flame atomic absorption spectrometer 3110 (Perkin Elmer, USA). Total contents of Cr, Cu, Ni were measured using inductively coupled plasma mass spectrometer Elan 6100 DRC (Perkin Elmer SCIEX, Canada) with Meihard-type nebulizer and Scott-type spray chamber. Microwave Digestion System Ethos 1 (Milestone, Italy) was used for sample digestion. An Elpan 357 water bath shaker (Elpan, Poland) was used for sample extractions. Total concentrations of macroelements were measured using Scanning Electron Microscope equipped with Energy Dispersive Spectroscopy analyzer (Zeiss, LEO 435 VP) Röntec M1, Germany).

2.3. Sampling and sample preparation

Waste samples were collected in 2006 in Szklary in the Lower Silesia region of Poland. Waste samples were collected – using Zig-Zag method – from dump where metallurgy wastes were deposited. A total amount of samples of 1.5 kg were collected from 0 to 10 cm depth layer. Samples were air-dried, milled in agate ball mill and stored in polypropylene containers in room temperature.

2.4. Bioleaching procedures

Bioleaching process was performed using two different procedures. Each process was performed in Erlenmeyer flasks. The first bioleaching process with autotrophic bacteria was carried out for 65 days, while the second one consists of 35 days heterotrophic pretreatment and then 35 days autotrophic bioleaching (in sequence). In the first process 250 mL of leaching medium, containing some inorganic ions such as: Fe^{2+}, Ca^{2+}, K^{+}, Mg^{2+}, NH_4^{+}, NO_3^{-}, SO_4^{2-}, HPO_4^{-}, Cl^{-}, was added to each of three flasks containing 50 g of pretreated solid waste. The leaching medium was inoculated with a mixture of autochthonic bacteria strains *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* [former name *T. ferrooxidans* and *T. thiooxidans*] before addition to the flasks. The process was carried out for 65 days at 25 °C, pH 2. Both bacterial systems as well as control one were aerated and stirred with magnetic stirrers. pH was adjusted daily to the value 2 using 5 mol L^{-1} H_2SO_4.

In the second bioleaching process, with heterotrophic bacteria, 250 mL of mineral solution (pH 7) containing some inorganic ions such as: K^{+}, Mg^{2+}, NH_4^{+}, SO_4^{2-}, HPO_4^{-}, $H_2PO_4^{2-}$ was added to each of three flasks, containing 50 g of solid waste. After that, flasks were inoculated with a mixture of active, autochthonic bacteria strains (*P. fluorescens*, *B. cereus* and *B. thuringiensis*). The process was performed for 35 days at 25 °C. All solutions were stirred with magnetic stirrers. Solid phase after first step of bioleaching procedure (with heterotrophic bacteria) was flushed, dried and treated with autotrophic bacteria. The dried material was flushed with H_2SO_4 solution and pH was adjusted to value 2. After that operation, autotrophic bioleaching was started using leaching medium with autochthonic bacteria strains *Acidithiobacillus ferrooxidans* and *Acidithiobacillus* mixed in the ratio of 1:1. All solutions were stirred on magnetic stirrers. Bioleaching process was performed for 35 days at 25 °C, pH of the solutions was adjusted to value 2 and controlled throughout the experiment.

Control sample were prepared only in autotrophic and sequential bioleaching procedures. It contained only solid waste and leaching medium without bacteria. Thymol as a bacteriostatic substance was added to the both control flask. After all described bioleaching processes samples were rinsed with Milli-Q water, air-dried and homogenized by grinding in agate mill.

2.5. Total metal determination

Approximately 200 mg of dried material and a mixture of concentrated acids (2 mL of HNO_3 and 1 mL $HClO_4$) were placed in PTFE vessels and digested in a microwave digestion system. A three-stage program with a maximum temperature of 200 °C and maximum microwave power of 1000 W was used. In the second step 0.5 mL HF was added and the same three-stage program was applied (5 min: 20–90 °C; 10 min: 90–170 °C; 50 min: 170–200 °C). Digested samples were transferred into 50 mL volumetric flasks and diluted to the volume with Milli-Q water. Digestion of all samples was triplicate. Digested samples were diluted and the concentrations of studies elements were measured using FAAS and ICP-MS. ICP-MS was used for determination of Cr, Cu and Ni. ICP-MS measurements were performed under following conditions: sweep 5, replicates 5, dwell time 100 ms, ICP RF power 1100 W, lens voltage 8 V, plasma gas flow 15 L min^{-1}, auxiliary gas flow 1.2 L min^{-1}, nebulizer gas flow 0.9 L min^{-1}, measured isotopes: ^{52}Cr; ^{63}Cu; ^{58}Ni. FAAS was used to determine Ca, Mg, Fe, Mn and Zn. The air-acetylene flame was adjusted according to the manufacturer's recommendations. The following parameters of measurements were applied—HCL wavelength, current and slit width respectively: Ca – 422.7 nm, 7 mA, 0.5 nm; Mg – 202.6 nm, 7 mA, 0.7 nm; Fe – 248.3, 13 mA, 0.2 nm; Mn – 279.5, 10 mA, 0.2 nm; Zn – 213.9 nm, 10 mA, 0.7 nm. Quantitative determination of elements in both techniques was performed using calibration plot. Elementary analysis of main components of solid samples was performed using Scanning Electron Microscope equipped with EDS analyzer.

2.6. Extraction procedure

The six-step sequential extraction was applied to compare the mobility of Mn, Fe, Ni, Cr, Zn, and Cu in waste samples before and after bioleaching treatment. Extractions were carried out in triplicate. 1 g of dried solid waste sample was extracted with 50 mL of the extractant in 120 mL polyethylene container (steps 1–5). Extracts were centrifuged at 2000 rpm during 30 min and filtered through 0.45 μm cellulose acetate filter into a polyethylene container. Extracts after filtration were acidified with 50 μL of concentrated HNO_3 (to pH about 2) and stored at 4 °C before analysis.

Step 1. (Water-soluble fraction) Samples were shaken with Milli-Q water for 3 h in room temperature in horizontal position in a water bath shaker.

Step 2. (Carbonate fraction) 0.43 mol L^{-1} (24.6 mL of glacial acetic acid was diluted with water in 1 L volumetric flask) acetic