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The influence of thermal treatment on bioweathering and arsenic sorption capacity of a natural iron (oxyhydr)oxide-based adsorbent

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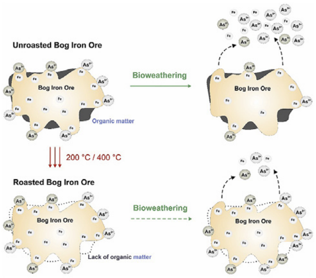
HIGHLIGHTS

- Applicability of bog iron ores (BIOs) can be limited by bioweathering.
- Removal of organic matter reduces BIOs' susceptibility to bioweathering.
- BIOs characterized by higher sorption capacity with regard to As(III) than As(V).
- As(III)-loaded BIOs are more susceptible to bioweathering than As(V)-loaded BIOs.
- Thermal treatment of BIOs increases their chemical stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption plays a significant role in remediation of waters contaminated with arsenic, but the efficiency of the process varies depending on the sorbent properties. Bog iron ores (BIOs), characterized by high sorption capacity and widespread availability, seem to be an optimal sorbent of arsenic. However, the use of BIOs for arsenic removal from waters may be limited by the high amount of organic matter, which may stimulate microbial activity, and thus decomposition of the sorbent. The aim of this study was to determine the effect of organic matter removal by thermal transformation (roasting) on the bioavailability of BIOs and their arsenic sorption capacity. For this purpose, the influence of bacterial growth and activity on untreated and treated BIOs, unloaded and loaded with arsenic, was studied. Moreover, the chemical and physical properties (including FTIR and desorption of arsenic) of BIOs were investigated as well. The results show that the removal of organic matter increases the stability of BIOs, and thus reduces the bioavailability of the immobilized arsenic.

1. Introduction

Among the numerous natural sorbents, bog iron ores (BIOs) are known to be a suitable material for the adsorption of many heavy

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metals (in the form of cations and anions) (Rzepa and Ratajczak, 2004). The adsorption process of BIOs is relatively fast and efficient in a wide range of metal concentrations and pH (Rzepa et al., 2009). Bog iron ores are widely available and have a high yield and low operating cost compared to other sorbents, so they can be applied in many remediation systems. Literature data indicate the high applicability of BIOs in soil and water remediation processes. The proposed application of BIOs for the stabilization of metals refers to sorption, precipitation or solidification processes (Müller and Pluquet, 1998; Mulligan et al., 2001; Rzepa and Ratajczak, 2004; Rzepa et al., 2009; Szrek et al., 2011; Tuchowska et al., 2016).

One of the limitations of using BIOs or other mineral sorbents for heavy metal removal may be their susceptibility to bioweathering caused by the microflora inhabiting the contaminated waters. BIOs contain large amounts of organic matter and nutrients (i.a. phosphorous) (Delvasto et al., 2009), which can be valuable growth substrates for various microorganisms (Uroz et al., 2009). Bacteria can use organic matter as a source of carbon and energy, leading to the dissolution of mineral deposits and the indirect release of metals. Moreover, microorganisms can directly contribute to the mobilization of metals adsorbed on the surface of BIOs and use it as a source of energy (Ahmann et al., 1997; Zobrist et al., 2000; Drewniak and Sklodowska, 2013; Drewniak et al., 2014). Heavy metals can also be released indirectly by bioleaching from various solids using secondary metabolites produced by bacteria (Mailloux et al., 2009). Therefore, before using BIOs or other mineral sorbent for heavy metals removal, it is important to minimize any microbial–mineral interactions and the bioavailability of BIOs to maximize their sorption efficiency.

A model example for studying the interactions between a metal/metalloid, a sorbent and microorganisms is arsenic sorption and desorption on BIOs under the influence of bacteria. Arsenic occurs in various chemical forms, two of which—As(III) and As(V)—are well absorbed by the BIOs. Many microorganisms are able to tolerate high arsenite and arsenate concentrations and may use this element in respiratory processes (oxidation and reduction) (Drewniak and Sklodowska, 2013). As previously mentioned, BIOs (like many other natural and mineral sorbents) contain a significant amount of organic matter, which can be used by microorganisms as a carbon and energy source. Therefore, microbial activity may lead to the destabilization of the structure of BIOs and release of the adsorbed elements.

Minimizing the interaction between microorganisms and BIOs relies on the removal of organic matter from the ore. Among many possible methods, thermal treatment in an oxidizing atmosphere seems to be the simplest way to achieve this goal. Previous study (Rzepa et al., 2016) showed that organic matter may be removed from BIOs through thermal treatment at 200–600 °C. The question therefore arises as to how organic matter removal will affect the microbial weathering for nutrient acquisition, and, consequently, the bioavailability of natural BIOs (unloaded) and that containing arsenic (loaded). Thus, the main aim of this study is to verify how thermal transformation of BIOs, through treatment at 200 °C or 400 °C, affects (i) the ability of microorganisms to undergo sorbent colonization, and (ii) the amount of BIOs dissolution and/or arsenic released from saturated ores, caused by microbial activity.

Several studies on As sorption onto thermal-treated iron ores have been published (e.g. Ramirez-Muñiz et al., 2012; Yang et al., 2017). They concerned As(III) and As(V) sorption capacities, kinetics and thermodynamics, as well as possible mechanisms of adsorption. These studies, however, were carried out on highly-crystalline iron compounds from ore concentrates of relatively simple chemistry and devoid of organic matter. Our work focuses on bog iron ores which are natural sediments, containing organic matter and various admixtures, thus characterized by a more complex chemical structure than the previously studied iron compounds. Moreover, this study also includes three-step desorption analysis and explores microbial interactions with untreated and thermal-treated samples.

Realization of the previously mentioned aims (with the use of BIOs as an example of model Fe-based sorbent material) allows for a better understanding of the effect of the growth and activity of microorganisms on the biogeochemical properties of iron oxide- and hydroxide-based minerals containing high amounts of organic matter. The obtained results also enable conclusions to be drawn about the possibility of increasing the mineral stability by reducing its bioavailability.

2. Material and methods

2.1. Bog iron ore thermal treatment

BIOs used in this study were collected in Kolechowice, SE Poland. The applied sorbent is a fine sediment, which is characterized by very high surface area, measured using the BET model, and a high total carbon content (Rzepa et al., 2016). Ore samples were heated in a muffle furnace at 200 °C and 400 °C for 1 h. BIOs: natural and thermal-treated, as well as unloaded and loaded with As(III) and As(V), were analyzed by X-ray fluorescence spectroscopy (XRF), X-ray diffractometry (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). X-ray fluorescence analyses were performed using WDS spectrometer ZSX Primus II Rigaku equipped with a Rh lamp. Calculated LOD (wt.%) were as follows: SiO_2 – 0.006, TiO_2 – 0.006, Al_2O_3 – 0.003, Fe_2O_3 – 0.008, CaO – 0.002, MgO – 0.008, MnO_2 – 0.004, K_2O – 0.002, Na_2O – 0.010, P_2O_5 – 0.003, and SO_3 – 0.001. Relative standard deviations were <5% for all measurements. X-ray diffraction patterns were collected using the Rigaku SmartLab instrument equipped with a graphite monochromator, rotation Cu anode, 45 kV and 200 mA generator settings, 2–75°2Θ recording range, 0.05° step size, and counting time of 1 s per step. FTIR spectra were collected using Thermo Scientific Nicolet 7600 spectrophotometer in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. Prior to analysis, KBr pellets were obtained by homogenizing 200 mg of ground KBr with 4 mg of the sample. Scanning electron microscope analyses were carried out in low vacuum mode, using a FEI 200 Quanta FEG microscope equipped with an EDS/EDAX spectrometer. The acceleration voltage was 15–20 kV, and the pressure 60 Pa. The samples were not coated with a conductive layer. Zeta potentials were measured using a Zetasizer Nano ZS Malvern instrument at room temperature. Samples were dispersed in 0.1 M NaCl to maintain constant ionic strength. Automated titration was performed by MPT-2 titrator using 0.1 M HCl as titrant. The content of organic matter was determined using a Rock-Eval 6 Turbo apparatus (calculated LOD and RSD values were 0.01 wt%, and below 2%, respectively).

2.2. Arsenic sorption and desorption

To prepare As(III) and As(V)-loaded BIOs, a suspension of 50 g/L (2 g/50 mL) bog iron ore was reacted with 50 mM $NaAsO_2$ and 50 mM $Na_2HAsO_4 \times 7H_2O$ solution, respectively, at an initial pH of 7.0. This value corresponds to the pH range (5.7–8.0) of waters polluted with arsenic in the Zloty Stok area, SW Poland (Drewniak et al., 2016). Additionally, row (untreated) BIOs loaded with natural arsenic contaminated water (Zloty Stok, SW Poland) were used. These waters contained 4.0815 mg As/L and 0,0082 mg/L of iron. The use of high arsenic concentration solutions in BIOs-loading enabled the maximal loading of BIOs with arsenic, which, in turn, enabled the determination of the maximal degree of arsenic