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The role of different minerals from red mud assemblage in Co(II) sorption mechanism

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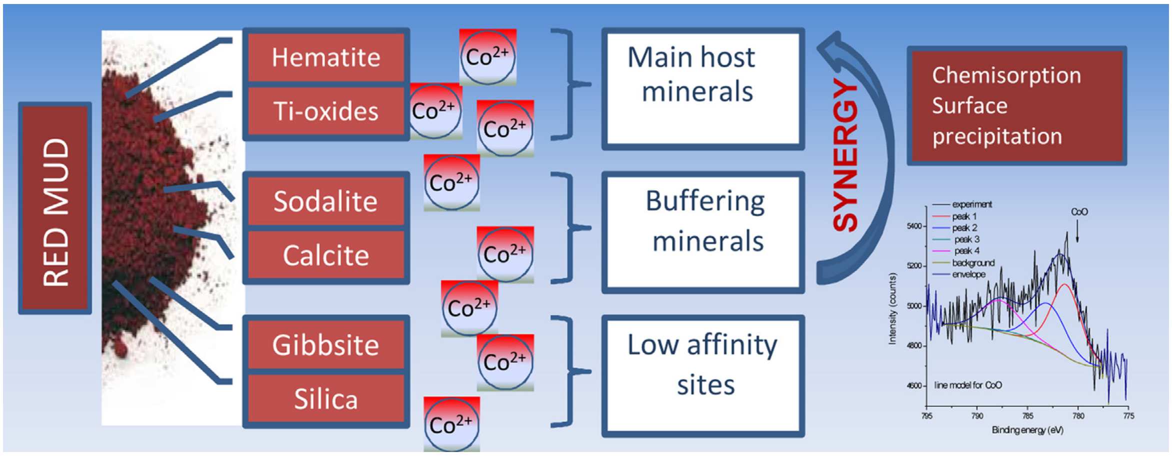
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Mechanism of Co(II) sorption by mineral assemblage of bauxite residue was studied.
- Sequential extraction of sorbed Co(II), SEM/EDS and XPS analyses were applied.
- Sorbed Co(II) was extracted mainly in operationally defined Fe,Mn-oxide fraction.
- Surface precipitation was detected on hematite and Ti-oxides.
- Synergistic effect of buffering and host minerals is crucial for cation sorption.

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ABSTRACT

A range of industrial by-products are currently under the consideration as cost-effective alternatives to conventional sorbent materials for environmental clean-up and remediation applications. Bauxite residue (red mud) has demonstrated exceptionally high potential for the immobilization of cationic pollutants. Due to heterogeneity of such material, determination of the role of individual mineral phases in the overall sorption mechanism is a challenging task. To enlighten the mechanism of Co(II) sorption by mineral

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assemblage of the red mud, sequential extraction analysis of Co-loaded sample was combined with the microscopic and spectroscopic studies performed by Scanning Field Emission Electron Microscope (FE-SEM), Energy Dispersive Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS). Sorbed Co(II) ions were found associated with operationally defined Fe,Mn-oxide and carbonate/acid soluble fractions. Binding of Co(II) by the red mud was achieved primarily by means of chemisorption/surface precipitation on Fe- and Ti-oxides. In coexistence with these highly selective surfaces, gibbsite and silica appeared to be low affinity sites for Co(II). Incongruent dissolution of sodalite phase was detected, indicating that its function was not to ensure sorption centers, but to increase the solution pH creating favorable environment for Co(II) binding by Fe- and Ti-oxides. The results demonstrate high stability of sorbed Co(II) and synergistic action of mineral constituents as essentially important property for red mud implementation as a purifying and remediation agent.

1. Introduction

Mining, mineral-processing and industrial by-products such as red mud, flue gas desulfurization gypsum, cement kiln dust, steelmaking by-products, heavy mineral processing residues, fly ash, calcined magnesia, water treatment residues, etc., demonstrate physico-chemical and sorption characteristics potentially beneficial for water purification and soil remediation purposes [1]. Utilization of such substantial resources as stabilization agents for heavy metals and radionuclides represents important alternative to synthetic sorbents and naturally occurring minerals, due to economic viability on one side and waste reduction on the other.

The residue of the alumina leaching from bauxite following Bayer process (red mud, RM) is among the most promising mineral sorbents which, by mass fraction, consists primarily of iron oxide (Fe_2O_3) 20–60%, alumina (Al_2O_3) 10–30%, silica (SiO_2) 2–20%, calcium oxide (CaO) 2–8% and titanium dioxide (TiO_2) trace-28%, whereas its high causticity comes from 2 to 10% Na_2O [2]. Due to the conditions of RM creation, it represents a heterogeneous mixture of nanocrystalline particles of metal-oxides and minerals, with the typical mineral assemblage comprised of hematite (Fe_2O_3), goethite (α-FeOOH), gibbsite ($Al(OH)_3$), boehmite (γ-AlOOH), rutile/anatase (TiO_2), quartz (SiO_2), sodalite ($Na_4Al_3Si_3O_{12}Cl$), cancrinite-type sodium aluminum silicate (CAN), and many others in small amounts [3].

Sorption properties of RM towards range of pollutants have been summarized in several review papers, where excellent performance in cation immobilization from contaminated aqueous solutions and the soil was highlighted [3–6]. Moreover, as application of selective sorbents plays an important role in nuclear waste management [7–9], various aspects of radionuclides (Cs, Sr, Co, Ra, U and Th) sorption by RM has been studied [10–15]. Besides its potential use in treatments of liquid radioactive waste (LRW), RM was recognized as suitable material for the construction of reactive barriers around the nuclear waste repositories, which minimizes impact of radionuclides to the environment caused by leaching of nuclear waste [16].

Since stability of sorbed heavy metals and radionuclides depends on the sorption mechanism, studying and understanding the phenomena taking place at RM/solution interface are crucial for practical applications and reliable prediction of the long-term fate of pollutants. Consequently, macroscopic sorption and desorption studies are necessary, as well as in situ surface characterization, to draw conclusions about the nature and the strength of bonds between RM and sorbates.

Bearing in mind Co toxicity, both as a heavy metal and important γ-emitting radionuclide (^{60}Co) in LRW, the possibility of its immobilization on selective carriers is of great relevance. As opposed to a number of papers related to Co(II) binding mechanism to individual metal oxides and minerals [17], there are almost no literature references on Co(II) binding by two or more metal oxides in the mixture. So far, sorption behavior of RM towards Co(II) ions was evaluated by sorption/desorption studies, using original (alkaline), water washed or acid modified RM [11,14,15]. High removal capacity of original waste is a result of its alkalinity. With regards to equilibrium pH values in the system containing untreated RM and Co(II) ions, precipitation of $Co(OH)_2$ was anticipated [14]. Water washed sample exhibited lower pH, and consequently lower sorption capacity [15], however, evidences of strong Co(II) sorption were numerous: sorption pH edge occurred below the isoelectric point of the sorbent, affinity towards Co(II) ions was high in the presence of other cationic species, and desorption rate was low [15]. Finally, acid treatment led to deterioration of RM sorption capacity towards Co(II), which was explained by partial loss of acid soluble RM minerals, such as cancrinite [11]. Nevertheless, the macroscopic studies of cations removal by heterogeneous sorbent such as RM are not indicative of dominant host minerals.

Recently, solid phases responsible for Mn(II), Cr(III), Co(II), Ni, Cu(II) and Zn immobilization by a modified (seawater neutralized) RM were evaluated by means of X-ray absorption spectroscopy (XAS) [18]. Surface analyses have revealed that the sorption mechanism of investigated metals is governed by mixtures of different minerals. In particular, Co(II) immobilization at pH 7.5, was attributed to formation of hydrotalcite-like, or layered double hydroxide precipitates, promoted by aluminum-containing minerals (sodalite, gibbsite and hydrotalcite). Seawater neutralization of RM converts free alkalinity to weakly soluble hydroxides, carbonates, and hydroxyl-carbonates of Ca and Mg, therefore, compared to the starting sample, modifications in respect to pH, chemical, mineralogical and surface composition are substantial.

Given that operating sorption mechanisms depend on the sorbent properties, the major goal of the present study was to deduce the role of different minerals originally present in RM, in the Co(II) sorption, by a combination of chemical and surface analyses. The Bosnian RM sample thoroughly rinsed with water (RBRM) was used as a sorbent. The excess free base (NaOH) from Bayer process was removed by this treatment, which lowers the sorbent's pH and prevents Co(II) removal from aqueous phase by bulk precipitation of $Co(OH)_2$. In that manner, the survey of the Co(II) removal mechanism by the mineral matrix of RM was enabled. The bonds between Co(II) ions and the RBRM were assessed by sequential extraction with selective leaching solutions of increasing strength, scanning electron microscopy (SEM), energy dispersive (EDS) and X-ray photoelectron spectroscopy (XPS).