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Rinsed and thermally treated red mud sorbents for aqueous Ni^{2+} ions

S. Smiljanić [a,*], I. Smičiklas [b], A. Perić-Grujić [c], B. Lončar [c], M. Mitrić [b]

[a] University of East Sarajevo, Faculty of Technology, Karakaj bb, 75400 Zvornik, Bosnia and Herzegovina
[b] University of Belgrade, Institute of Nuclear Sciences "Vinča", P.O.B. 522, 11000, Belgrade, Serbia
[c] University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000, Belgrade, Serbia

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ABSTRACT

Red mud, an abundant industrial waste from alumina industry, represents a rich source of various metal oxides, mainly of Fe_2O_3, Al_2O_3 and SiO_2. In this study, the rinsed Bosnian red mud (RBRM) was evaluated as an economical, composite sorbent for aqueous Ni^{2+} ions. The process was investigated as a function of pH, contact time and initial metal concentration. The investigated mineral mixture exhibited a high acid neutralising capacity, and its most important role in cation immobilization was observed in the initial pH range 2–8. The initial metal ion concentration strongly influenced the sorption kinetics and equilibrium times. Addition of 5 g/L of RBRM caused 100% removal from the solutions of 10^{-4} to 5×10^{-4} mol/L, whereas with the further increase of Ni^{2+} concentration to 8×10^{-3} mol/L, the removal efficiency decreased to 26%. The maximum sorption capacity of 0.372 mmol/g, at initial pH 5, was determined using Langmuir theoretical model. The possibility of sorption efficiency improvement by annealing RBRM powder was investigated in the range 200–900 °C and the relationships between temperature, red mud physicochemical and sorption properties were established. The optimum heating temperature was found to be 600 °C, due to water exclusion from gibbsite and bayerite phases, leading to improved porosity and surface area, as well as increased pH value and sorption efficiency. The stability of the sorbed cation was assessed by leaching experiments in distilled water and acidic TCLP2 solution.

1. Introduction

Given that heavy metal ions are harmful to a variety of living species, issues of significant importance are their transport and distribution through the environment as well as their removal from contaminated water, soil and sediments. Industrial wastewaters that contain high levels of heavy metal cations are treated by different physicochemical processes, with the focus on chemical precipitation, coagulation–flocculation, flotation, ion-exchange, membrane filtration and sorption [1]. A survey of recent patents for water and wastewater treatments [2] showed that significant amount of patents related to sorption technologies still include only carbon based materials which are relatively expensive, act in a non-selective manner and exhibit unsatisfactory efficiency in the removal of inorganic contaminants. For that reason, there is an increasing trend in searching for new heavy metal sorbents among commercially available materials such as by-products of various industries. Recent comparison of composite sorbents which are accessible, inexpensive and effective for treating a variety of contaminants have emphasized the outstanding metal removal capabilities of materials originating from agricultural and industrial by-products [3]. The examples of stabilized industrial solid wastes that were evaluated as composite sorbents are red mud, fly ach, waste from electroplating industry and blast furnace slag [4–7]. One of the most promising sorbent was found to be red mud, a waste sludge obtained after processing the bauxite ore following Bayer's process. Iron in bauxite ores occurs in various minerals forming the principal component of the red mud waste. In addition, red mud usually contains Al-bearing phases boehmite (AlOOH) or gibbsite ($Al(OH)_3$), titania (TiO_2), quartz (SiO_2), sodalite ($Na_4Al_3Si_3O_{12}Cl$), and many residual minerals such as cancrinite-type sodium aluminum silicate (CAN), gypsum ($CaSO_4 \cdot 2H_2O$), calcite ($CaCO_3$), whewellite ($CaC_2O_4 \cdot H_2O$), etc [8].

In nature, oxides of iron are important components of soils and sediments and represent the most important sink for toxic metal ions, released into the environment from a variety of anthropogenic sources [9]. Taking into account the main mineralogical phases of red mud, it is not surprising that samples from different parts of the world have revealed high removal efficiency for numerous heavy metal cations [8]. In addition, red mud was studied as an effective immobilization agent for various other pollutants such as fluoride [10,11], boron [12], phenol [13], dyes [14,15], etc. In the available scientific literature, temperature, acid and combined acid-heat activation procedures of red mud [13–18], were investigated. Temperature effect was thoroughly analyzed using phosphate [16,17] and arsenate anions as sorbates [18], but there it is hard to find a

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* Corresponding author. Tel.: +387 (0) 56260190; fax: +387 (0) 56260190.
E-mail address: slavkosm@gmail.com (S. Smiljanić).

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similar comprehensive study of the effect of annealing temperature on red mud removal properties in respect to heavy metals cations.

In this study, red mud supplied from the "Birač" Alumina Factory (Zvornik, eastern Bosnia), was evaluated in terms of heavy metal immobilization. At this location, rinsed red mud suspension, of a density between 1.2 and 1.3 g/mL and dry matter concentration 250–350 g/L is disposed as a waste in an open field – a natural dump area. The liquid phase of the suspension still contains about 7 g/L of Na_2O, therefore red mud waste is highly alkaline. As a heavy metal representative Ni^{2+} was selected, the cation most commonly found in wastewaters originated in metal plating operations and acid mine drainage. The results reported on Ni^{2+} removal by a sample from central Greece, indicated that heavy metal cations were efficiently removed from dilute solutions by red mud acting simultaneously as an alkalinity regulator, as an adsorbent of the formed nickel hydroxide and as a flocculant of the resulting fine particulate matter [19].

The objective of this work was: (i) to examine the physicochemical characteristics of rinsed red mud from Bosnia and influence of various experimental conditions on its sorption properties towards Ni^{2+} cations; (ii) to evaluate the effect of thermal treatment on red mud composition, pH and sorption properties, and to select optimal conditions for sorbent pretreatment.

2. Experimental

2.1. Preparation of red mud samples

Preliminary experimental results have shown that the original sample collected from the "Birač" Alumina Factory have pH around 10.5, and significant Ni^{2+} removal efficiency due to precipitation of insoluble $Ni(OH)_2$. Furthermore, thermal treatment had limited effect on Ni^{2+} removal by original red mud, because the effect of excess base covered other effects induced by annealing of the sample. In order to investigate the sorption properties of red mud mineral constituents, and produce environmentally benign sorbents, it was necessary to remove excess base by repeated washing. The sample was thoroughly washed with distilled water in the following way: in a 10 L plastic container, a 2.5 L of original red mud was mixed with approximately 6 L of distilled water; the suspension was stirred intensively by hand for a couple of minutes and then allowed to equilibrate and settle overnight. After decanting, a small solution aliquot was centrifuged and used for pH measurement. The fresh distilled water was then added to the red mad sample, and the whole procedure was repeated during the period of 2 weeks, i.e. until no further changes in pH were detected. The solution was decanted once more, the residual red mud was transferred to shallow pots, dried in an oven at 105 °C and, finally, powdered using mortar and pestle. Additional activation of the sample, denoted as RBRM, was carried out by annealing the 15 g portions in an electrical furnace, at 200 °C, 400 °C, 600 °C, 800 °C and 900 °C for 3 h. These samples were denoted as RBRM200–RBRM900.

2.2. Characterization of red mud samples

The chemical composition of RBRM sample was determined in the central laboratory of the "Birač" Alumina Factory. Additionally, the mineralogical composition of RBRM, as well as of temperature treated samples, was studied by X-ray diffraction (XRD) analyses using a Philips PW 1050 diffractometer, with Cu $K\alpha_{1,2}$ radiation and a step/time scan mode of 0.05°/1 s.

The pH value of RBRM was measured following the EPA 9045D method for soil and waste pH [20]. According to this method, waste is continuously stirred with reagent water for 5 min, and after settling for another 15 min, aqueous phase used for pH measurement is separated from the suspension by filtration or centrifugation. The 1:1 solid to solution ratio is preferred, but the method allows additional dilutions, if working with hygroscopic or other problematic matrices. Since investigated RBRM powder tends to absorb water and form dense mud, different solid/solution ratios in the range 1:200 to 1:1 (5–1000 g/L) were investigated. For the comparison, the pH values of thermally treated samples were determined at selected 1:2.5 solid/solution ratio.

The point of zero charge (pH_{PZC}) of RBRM was determined by batch equilibration technique [21]. The sample was agitated for 24 h with the electrolyte solution of known initial pH, at solid/solution ratio of 1:200. As an electrolyte 0.1 mol/L, 0.01 mol/L and 0.001 mol/L NaCl solutions were applied. Initial pH values were adjusted in a wide pH range (from ~1 to ~11) by adding minimum quantities of variously concentrated HCl and NaOH solutions. Final pH values were plotted against initial pH and the pH_{PZC} was determined from the plateau of the graph.

2.3. Ni^{2+} sorption/desorption tests

In general, sorption tests were carried out in closed PVC bottles by agitating suspensions containing 0.1 g of a sorbent and 20 mL of $NiCl_2$ solution. Experiments were conducted on a horizontal laboratory shaker for 24 h at room temperature (20 ± 1 °C). Variously concentrated NaOH and HCl solutions were used for the adjustments of initial pH values. After equilibration, the solid residues were separated from the liquid phase by both centrifugation and filtration, and the remaining metal concentrations were determined by a flame Atomic Absorption Spectrometer (Philips Pye Unicam SP9) at 232.0 nm. The detection limit for Ni^{2+} ions was 0.059 mg/L. The amounts of Ni^{2+} removed from the solution were calculated as difference between initial and final metal concentrations. The initial and final solution pH values were measured by InoLab WTW pH-meter.

The effect of pH on Ni^{2+} uptake by RBRM was screened using solution with initial cation concentration of 10^{-3} mol/L and adjusting the initial pH values in the range from ~1 to ~12.

The effect of contact time on the amount of heavy metal cations removed was determined by equilibrating the RBRM powder with 10^{-4} mol/L and 8×10^{-3} mol/L $NiCl_2$ solutions, at initial pH 5. For each system, nine identical batches containing sorbent and appropriate $NiCl_2$ solution were prepared and placed on the shaker. At different time intervals (from 5 min to 48 h) one of the batches was taken for solid/liquid separation. Along with the determination of residual Ni^{2+} concentrations, solution pH changes were monitored.

The effect of initial cation concentration was analyzed using initial Ni^{2+} concentrations in the range 10^{-4} to 8×10^{-3} mol/L. pH values of all solution were adjusted to five prior to addition of sorbent, whereas equilibrium pH values were recorded.

The desorption of Ni^{2+} ions, previously sorbed from differently concentrated solutions, was examined in acidic conditions, by equilibrating dried solid residues with 20 mL of solution. Leaching solution was prepared from acetic acid, following Toxicity Characteristic Leaching Procedure (TCLP) [22] for more aggressive extraction media (TCLP2, pH 2.88 ± 0.05).

In order to evaluate and compare sorption properties of RBRM and products obtained at different annealing temperatures, Ni^{2+} solutions of 2×10^{-3} mol/L was applied, whereas initial pH values were adjusted in the range 2–5. For the assessment of final pH changes sorbents were additionally equilibrated for 24 h with distilled water, at 1:200 solid/solution ratio.

The stability of obtained Ni-loaded products was also estimated. The red mud residues loaded with Ni^{2+} at initial pH 2, 3 and 4 were dried at 105 °C overnight, resuspended in 20 mL of distilled water and shaken for another 24 h. For the estimation of leaching characteristics in acidic media, sorption products obtained at initial pH