



## The influence of citrate anion on Ni(II) removal by raw red mud from aluminum industry

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### HIGHLIGHTS

- ▶ The influence of citrate anion on Ni(II) removal by raw red mud has been evaluated.
- ▶ High red mud alkalinity positively influenced Ni(II) immobilization.
- ▶ Coexisting citrate anion suppressed Ni(II) removal efficiency.
- ▶ Removal diminished the most in acidic media and for Ni/Citrate molar ratios  $\geq 1:1$ .
- ▶ Ni(II), Ni/Citrate and citrate sorption by red mud was confirmed by FTIR.

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### ABSTRACT

The removal of Ni(II) from aqueous solutions by raw red mud powder was studied in the absence and in the presence of citrate ligand, as a function of process parameters. Using lower initial Ni(II) concentration ( $10^{-3}$  mol/L) detectable amounts were found only at initial pH 3, whereas for higher concentration ( $2 \times 10^{-3}$  mol/L) removal increased simultaneously with pH in the range 3–4 and at pH > 8. Process efficiency was suppressed in the presence of citrate. However, at Ni/Citrate molar ratios 1:0.25 and 1:0.5, 10–20% decrease was noticed in acidic media, while the negative influence diminished with the rise of pH. At higher ligand rates, formation of stable aqueous complex between Ni(II) and citrate significantly reduced metal removal in the whole tested initial pH range (3–10). Due to instantaneous pH rise above 8, removal of Ni(II) from  $10^{-3}$  mol/L solution was completed in 5 min. Kinetic data demonstrated slower Ni(II) uptake using both solutions of higher initial Ni(II) concentrations and Ni/Citrate solutions. At initial pH 5, estimated capacity towards Ni(II) was found to be 27.4 mg/g, without citrate. For Ni/Citrate molar ratios 1:0.25 and 1:0.5, capacities decreased slightly to 25 mg/g and 21 mg/g, whereas at equimolar and higher concentrations, citrate significantly inhibited Ni(II) immobilization (7.6 mg/g and 2.5 mg/g, respectively for Ni/Citrate ratios 1:1 and 1:2). The results demonstrated beneficial effect of red mud high alkalinity on Ni(II) removal. The sorbent satisfactorily immobilize nickel from solutions having initial Ni/Citrate molar ratios lower than 1:1, and neutral to alkaline initial pH. FTIR analysis confirmed that red mud can act as a removal agent for Ni(II), Ni/Citrate complex and free citrate ligand.

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### 1. Introduction

The red mud (RM) is a widely accepted name for a solid waste residue formed during the production of alumina, after the caustic digestion of bauxite ore. Due to the presence of large quantities of hydroxides, red mud is highly alkaline, but otherwise not a particularly toxic material [1,2]. It contains many residual minerals from the starting bauxite ore, however, oxides of Fe, Al, Si and Ti usually

represent the main mineral phases. Considering the excessive amounts of bauxite residue generated all over the world, as well as the fact that most of the red mud is disposed in landfills or dumped at sea, this material exhibit a large environmental impact. As a consequence, resource recovery of red mud was a subject of numerous scientific papers over the last 10–15 years. Strong alkalinity presents a potential risk for further red mud applications, therefore, in order to obtain the products more friendly to the environment methods like seawater washing and acid neutralization have been proposed for its neutralization [1].

Recently reported developments in the field of red mud exploitation include a range of industrial, environmental and engineering

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