



Recovery of Gallium from Bauxite Residue Using Combined Oxalic Acid Leaching with Adsorption onto Zeolite HY

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Abstract

Bauxite residue, the byproduct of alumina production, may potentially be a valuable source of strategically important metals, e.g. Gallium. Ga is considered critical element for the EU. To ensure adequate supply of Ga for the future, secondary sources such as bauxite residue should be exploited with efficient extraction methods. Therefore, in this study, mineral acids (H₂SO₄, HCl, and HNO₃) and an organic acid (H₂C₂O₄—oxalic acid), were evaluated for their efficiencies to extract Ga from bauxite residue. Using H₂C₂O₄, the highest Ga leaching efficiencies were achieved, compared to other acids. The achieved leaching experimental results were considered for the construction of a design of experiment (DOE) model to achieve optimal conditions for Ga extraction using H₂C₂O₄. These values were validated by experiments which resulted in ~ 94% accuracy. In the second part of the study, using pure Ga solution, the adsorption of Ga onto zeolite HY was studied. The effects of adsorbent dosage, temperature, and contact time on the adsorption of Ga from solution by zeolite HY were studied. The obtained adsorption experimental results were used to construct a DOE model to achieve optimal conditions for Ga adsorption on to zeolite HY. The DOE-achieved optimal conditions were evaluated by experiments in pure Ga solution, which resulted in an efficiency of ~ 99.4 %. In the third stage, the bauxite residue was leached in H₂C₂O₄ under the optimal DOE conditions which resulted in 71% efficiency; thus the resulting bauxite residue solution was subjected to adsorption using zeolite HY under the optimal DOE conditions achieved. The Ga adsorption onto the zeolite was only 16% compared to the Ga adsorption of 99.4 % under the pure Ga solution, thus, representing the influences of the other leachates in the solution, which are minimizing the Ga adsorption onto the zeolite HY and providing an opportunity for future studies on the different mechanisms involved.

Keywords Bauxite residue · Critical raw materials · Extraction · Adsorption · Design of experiments · Oxalic acid · Zeolite

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Introduction

Recent studies by major economies [1–4] have identified strategically important elements, called critical raw materials (CRMs), for their economy. These are defined as materials with a high supply risk and an above average

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economic importance compared to other raw materials [5]. The European Commission (EC) is implementing a wide range of actions under the EU Raw Materials Initiative to help ensure their secure, sustainable and affordable supply [1]. One approach to reduce the supply risk of CRM is to utilize previously untapped primary and secondary sources [6].

Bauxite residue, a potential secondary source of CRM, can contain considerable amounts of strategically important metals depending on its geologic origin and processing [6, 7]. Bauxite residue is the byproduct of alumina production and is generated in the Bayer process when bauxite is digested in hot NaOH under elevated temperature and pressure. It is available at a multimillion ton scale worldwide as the global inventory of bauxite residue already reached an estimated 2.7 billion tons by 2011 [8] with an annual production rate of 150 million tons [9]. Numerous studies have focused on the utilization of bauxite residue as a source for the production of major elements (e.g., blast furnace for pig iron production [10–14]) or as a source of rare earth elements (REEs) [15–19] as well as the combination of these [20]. Fewer efforts have been made to use the bauxite residue as a secondary source of other CRMs such as V and Ga [18, 21, 22].

According to EC reports, Ga is considered as a strategically important metal for the EU since 2011 [1, 23, 24]. The Ga presence in the Earth's crust is small (< 19 mg/kg) therefore there is no primary Ga mine. Ga appears in trace amounts (< 50 ppm) as a salt in bauxite and zinc ores [25] and it is therefore extracted from bauxite as part of the bauxite–alumina–aluminum refining flow. Although some Ga is also derived from the processing of sphalerite ore for zinc, it is also recycled from the slag generated during the manufacture of gallium arsenide (GaAs)- and gallium nitride (GaN)-based devices [26]. Compounds of Ga such as GaAs, GaN, and copper–indium–gallium selenide (CIGS) possess semiconducting properties, and therefore, they are used for the production of microelectronic components [26]. World demand for GaAs- and GaN-based products increased during the past few decades, and it is expected to remain still high [27]. To ensure adequate supplies of Ga for the future, secondary sources such as bauxite residue should be exploited with efficient extraction methods.

The most widely used strategy for extraction of economically interesting elements from bauxite residue is direct hydrometallurgical leaching [16, 18, 28–30]. Technologies have been investigated for major metal (Al, Fe, and Ti) recovery by pyrometallurgical/mechanical operations (reductive smelting, roasting) and combinations of the latter with hydrometallurgical leaching [11, 12, 20, 31, 32]. Extraction of valuable elements requires the use of additional chemicals and energy: e.g., in direct hydrometallurgical leaching,

mineral acids such as H_2SO_4 , HCl, and HNO_3 are primarily used at high temperatures [6, 33–36].

Previous studies on extraction of Ga from bauxite residue have been based on mineral acids [18, 22] and on alkaline solutions from bauxite residue (hydrogarnet process) [21]. In the latter, the extraction of Ga from bauxite residue was carried out in high modulus alkaline solution (240 g/L Na_2O ; $\alpha_k = 30$) at high temperatures (240–260 °C) in the presence of lime followed by treatment of the leachate by CO_2 -enriched air [21].

Lu et al. [22] presented a method called acidic-leaching-ion-exchange process (ALIEP) to extract Ga from bauxite residue. The ALIEP method mainly consisted of three steps: extraction of Ga from bauxite residue by mineral acid (HCl), removal of Fe^{3+} from the leaching solution by chlorinated polystyrene macroporous (LSD-369) resin (adsorbent), and recovery of Ga from the leaching solution by LSC-500S resin. LSC-500S resin contained reactive groups of $[-\text{NH}-\text{CH}_2-\text{P}(\text{O})(\text{OH})_2]$ and was able to form stable complexes through reactive groups binding with metal ions. In Lu et al.'s [22] study, 94.8% Ga was extracted from bauxite residue at 4.4 M HCl, 4 h, 55 °C, 125 g/L slurry concentration; and 59.8% Ga was adsorbed from HCl leachate on the LSC-500S resin under conditions of 8 g/L resin dosage, 24 h, and 45 °C.

The extraction of CRMs such as Ga and REEs from bauxite residue by selective acid leaching was explored by Ujaczki et al. [18, 19]. After acidic extraction, CRMs were purified by liquid–liquid extraction using di-(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in kerosene. According to Ujaczki et al. [18, 19], 87.6% Ga was extracted from bauxite residue under conditions: 6.0 M HCl, 21 h, 50 °C, 56.7 g/L slurry concentration; and 29.0% Ga was extracted from HCl leachate to the organic solvent phase (D2EHPA in kerosene) under conditions: 0.1 organic/aqueous ratio, 0.78 M D2EHPA concentration in kerosene, 1 h, and 22 °C.

Both studies showed a potential in extraction of Ga from bauxite residue by acidic leaching. Moreover, adsorption onto LSC-500S resin by Lu et al. [22] showed higher efficiency than separation by liquid–liquid extraction using D2EHPA dissolved in kerosene [19]. In addition, Ujaczki et al. [18] evaluated efficiencies of conventional extracting agents (mineral acids) and small molecular weight complexing agents (organic acids) to extract CRM such as Ga from bauxite residue. They found that the use of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) resulted in the most efficient extraction of Ga with, at the same time, lower extractions of Fe and Al.

In the present study, mineral acids (H_2SO_4 , HCl, and HNO_3) and organic acid ($\text{H}_2\text{C}_2\text{O}_4$) were evaluated regarding their efficiencies to extract Ga from bauxite residue. As a consequence of previous studies [18, 22] and the present comparison, $\text{H}_2\text{C}_2\text{O}_4$ was found to be the most efficient acid for the extraction of Ga from bauxite residue, and therefore,

parameters for the extraction by $\text{H}_2\text{C}_2\text{O}_4$ were also investigated. For the first time, experiments for adsorption onto zeolite for recovering Ga from $\text{H}_2\text{C}_2\text{O}_4$ leachate were conducted. The effects of adsorbent dosage, temperature, and contact time on the removal of Ga by zeolite HY from synthetic Ga solution were also studied. The optimization was achieved with the help of experimental design (DOE) software analysis which was validated with experiments. The residue left after the processing (post residue) was characterized to understand the influences of extraction process on the pH change, morphology, and chemical change.

Materials and Methods

Physicochemical and Mineralogical Characterization

The bauxite residue (pH 10.9, EC = 0.9 mS and 28% moisture content) used in this study was produced by the Bayer process, stored after dewatering by vacuum filtration and mud farming at the disposal area. Samples were dried at 105 °C for 24 h, pulverized using a mortar and pestle and sieved to a particle size of < 2 mm. The pH and electrical conductivity (EC) were measured using 5 g sample in aqueous extract at 1:5 ratio (solid:liquid) with an Aqualytic AL15 multimeter [37]. X-ray fluorescence (XRF) analysis was carried out using a Panalytical Axios XRF. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) was performed on Hitachi SU-70 microscope.

Elemental Analyses

Elemental analysis was performed after aqua regia digestion at 1:10 ratio (solid:liquid) in Multiwave 3000 (Rotor 8XF100) microwave digestion system at 200 °C and 1.25 MPa. The solutions after digestion were filtered with a 0.45 µm PVDF syringe filter and diluted in 1 M HNO_3 before analysis [18]. An Agilent Technologies 5100 inductively coupled plasma optical emission spectrometer (ICP-OES) was used for metal analysis. Standard solutions and samples were diluted with 1 M HNO_3 . The following analytical line (in nm) was used for calculations: Al 308.215, 394.401, 396.152; Ca 396.847, 422.673; Fe 234.350; Ga 294.363; Na 589.592; Si 250.690, 251.611, 288.158; Ti 334.188, 336.122, 368.520; V 268.796 [38].

Leaching Study

The comparative metal leaching tests were performed with equivalent normality acids (1 M H_2SO_4 , 2 M HNO_3 , 2 M HCl , 1 M $\text{H}_2\text{C}_2\text{O}_4$) at 60 °C, 24 h, 100 g/L slurry concentration in triplicate [18]. All tests were carried out in 100 ml conical flasks. These were shaken on an IKA KS

4000 i control incubation shaker at 250 rpm. Further leaching tests were carried out with $\text{H}_2\text{C}_2\text{O}_4$ by varying several parameters, i.e. acid concentration (0.05–3 M), contact time (1–24 h) temperature (20–80 °C) and slurry concentration (10–200 g/L). The acid concentration, contact time and temperature were extended for every extraction step to ensure that the leaching equilibrium (i.e. plateau of the kinetic) was reached.

The bauxite residue leachate solutions were centrifuged for 5 min at 3500 rpm and 20 °C (Sorvall TC-6), filtered, diluted in 1 M HNO_3 and analyzed by ICP-OES as described above. The extraction efficiencies were determined by the ratio of metal extracted to the aqua regia-accessible metal content (“Elemental Analyses” section).

Adsorption Study

Comparative experiments on Ga adsorption were conducted with three types of zeolites (HY, H-beta, ZSM-5) (see Supporting Information [SI], Table 1). Stock solution of 50 mg/L Ga was prepared by diluting 1000 mg/L Ga standard solution (certified reference material, matrix: 7% HNO_3). All tests were carried out in 100 mL conical flasks with constant shaking at 250 rpm. Further adsorption tests were carried out with zeolite HY by varying several parameters, i.e. adsorbent dosage (0.4–25.0 mg/mL), contact time (0–24 h) and temperature (20–80 °C). Following selection of optimum adsorption parameters the zeolite HY was investigated for adsorption of Ga from bauxite residue $\text{H}_2\text{C}_2\text{O}_4$ leachate. The adsorbent was separated from the solution by a 0.45 µm PVDF syringe filter and diluted in 1 M HNO_3 before analysis by ICP-OES as described above (“Elemental Analyses” section). The adsorption efficiencies were determined by the ratio of metal analyzed to the stock solution and to the $\text{H}_2\text{C}_2\text{O}_4$ leachate metal content, respectively. The adsorption isotherm was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{X},$$

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), C_0 is the initial adsorbate concentration (mg/L), C_e is the adsorbate equilibrium concentration (mg/L), V is the volume of the solution (L), and X is the mass of adsorbent (g).

Post Residue Characterization

The residue left after the processing (post residue) was characterized by pH and EC multimeter, XRD, and SEM–EDS as described in “Physicochemical and Mineralogical Characterization” section. Prior to the analysis, samples were dried at 105 °C for 24 h, pulverized using a mortar and pestle, and sieved to a particle size of < 2 mm.

Experimental Design and Statistical Analysis

Minitab 17 software was used for the development and analysis of experimental designs using the response surface methodology. In the leaching study, a linear model was fitted to the maximal extracted Ga which was recovered by extraction with $\text{H}_2\text{C}_2\text{O}_4$ under varied parameters. The effects of four factors were considered i.e. $\text{H}_2\text{C}_2\text{O}_4$ concentration, contact time, temperature and slurry concentration. In the adsorption study, a linear model was fitted to the removal of maximal Ga from solution under varied parameters. The effects of three factors were considered i.e. adsorbent dosage, contact time and temperature. Both models were subsequently reduced to only contain potentially significant factors ($p \leq 0.05$) and factors necessary to maintain model hierarchy using the stepwise automatic model regression of the software. The proposed optimal parameters were tested afterwards experimentally.

Results

Bauxite Residue Composition

The elemental composition of the bauxite residue was dominated by Fe (~ 43.3%), Al (~ 16.5%), Si (~ 9.4%), Ti (~ 8.9%), Ca (~ 6.2%) and Na (~ 6.0%) oxides as detected by XRF (SI, Table 2); the Ga concentration was 114.5 ± 5.2 mg/kg which was analyzed by ICP-OES (SI, Table 3). Additional characterization of physicochemical, elemental and mineralogical composition of bauxite residue in storage over a 12-year period was carried out by Cusack et al. [39] They found that the main mineralogical composition of the bauxite residue detected by XRD included haematite (Fe_2O_3), goethite [$\text{FeO}(\text{OH})$], perovskite (CaTiO_3), rutile (TiO_2), gibbsite [$\text{Al}(\text{OH})_3$], sodalite [$\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$], and cancrinite [$\text{Na}_6\text{Ca}_2(\text{CO}_3)$] (Cusack et al. [39]).

Comparative Metal Acid Leaching Study

Three mineral acids (HCl , HNO_3 , H_2SO_4) and an organic acid ($\text{H}_2\text{C}_2\text{O}_4$) were used for the extraction of Ga from bauxite residue at normality = 2, 24 h, 60 °C, 100 g/L slurry concentration and 250 rpm. This comparative extraction study showed that the most efficient extraction for Ga was achieved by $\text{H}_2\text{C}_2\text{O}_4$ (39%–44.8 mg/kg) followed by acids in the order HCl (32%–37.2 mg/kg) > H_2SO_4 (27%–30.6 mg/kg) > HNO_3 (26%–29.8 mg/kg) (SI, Table 4). Therefore, $\text{H}_2\text{C}_2\text{O}_4$ was chosen for further investigation of leaching parameters. Al and Fe leaching were also investigated as they were major

elements in the bauxite residue and their leaching selectivity is an important factor. Using 1 M (2 N) $\text{H}_2\text{C}_2\text{O}_4$, 54% (~ 49,802 mg/kg) Al and 23% (~ 81,563 mg/kg) Fe were also coextracted under the above conditions (SI, Table 4).

Effect of Leaching Parameters

The effect of acid concentration, temperature, contact time and slurry concentration on the extraction of Al, Fe and Ga from bauxite residue were studied (Fig. 1) [40]. Increasing the $\text{H}_2\text{C}_2\text{O}_4$ concentration from 0.05 to 3 M increased extraction efficiencies of Ga from 3% (~ 3.6 mg/kg) to 44% (~ 50.9 mg/kg) at 24 h, 60 °C, 100 g/L slurry concentration and 250 rpm. 41% (~ 44.1 mg/kg) Ga extraction efficiency was already achieved using 1 M $\text{H}_2\text{C}_2\text{O}_4$, therefore, 1 M $\text{H}_2\text{C}_2\text{O}_4$ was chosen for the remaining leaching experiments. Increasing the contact time from 1 to 24 h increased extraction efficiencies of Ga from 12% (~ 13.8 mg/kg) to 38% (~ 44.1 mg/kg) using 1 M $\text{H}_2\text{C}_2\text{O}_4$, 60 °C, 100 g/L slurry concentration and 250 rpm. Also, elevating the temperature from 22 to 80 °C led to considerably increased extraction efficiencies of Ga from 18% (~ 19.5 mg/kg) to 40% (~ 42.7 mg/kg) using 1 M $\text{H}_2\text{C}_2\text{O}_4$, 24 h, 100 g/L slurry concentration and 250 rpm. The slurry concentration had a strong effect on extraction efficiencies similar to the acid concentration. Here, decreasing slurry concentration from 200 to 10 g/L resulted an increase in extraction efficiencies of Ga from 3% (~ 3.7 mg/kg) to 47% (~ 53.9 mg/kg) at 1 M $\text{H}_2\text{C}_2\text{O}_4$, 24 h, 60 °C and 250 rpm.

Similar trends were identified for Al and Fe extractions (Fig. 1). Using 1 M $\text{H}_2\text{C}_2\text{O}_4$ resulted in the extraction of 57% (~ 52,316 mg/kg) of Al and 22% (~ 75,447 mg/kg) of Fe at 24 h, 60 °C, 100 g/L slurry concentration, and 250 rpm. Elevated temperature increased the Al extraction efficiency to 63% (~ 58,102 mg/kg) of Al, while Fe still remained at 21% (~ 74,345 mg/kg) at 1 M $\text{H}_2\text{C}_2\text{O}_4$, 24 h, 100 g/L slurry concentration, and 250 rpm. The maximal Al and Fe extraction efficiencies were achieved by decreasing slurry concentration to 10 g/L resulting in 62% (~ 54,775 mg/kg) of Al and 62% (~ 21,6378 mg/kg) of Fe extracted using 1 M $\text{H}_2\text{C}_2\text{O}_4$, 24 h, 60 °C, and 250 rpm.

Design of Experiment Approach to Predict the Optimal Parameters for Leaching Experiments

In order to determine optimal extraction conditions to extract maximal Ga in bauxite residue, a design of experiment (DOE) approach was used to account for interaction effects between investigated factors regarding acid concentration (0.05–3 M $\text{H}_2\text{C}_2\text{O}_4$), contact time (1–24 h), temperature (50–80 °C), and slurry concentration (10–200 g/L) (SI, Table 5). The response surface-reduced linear model

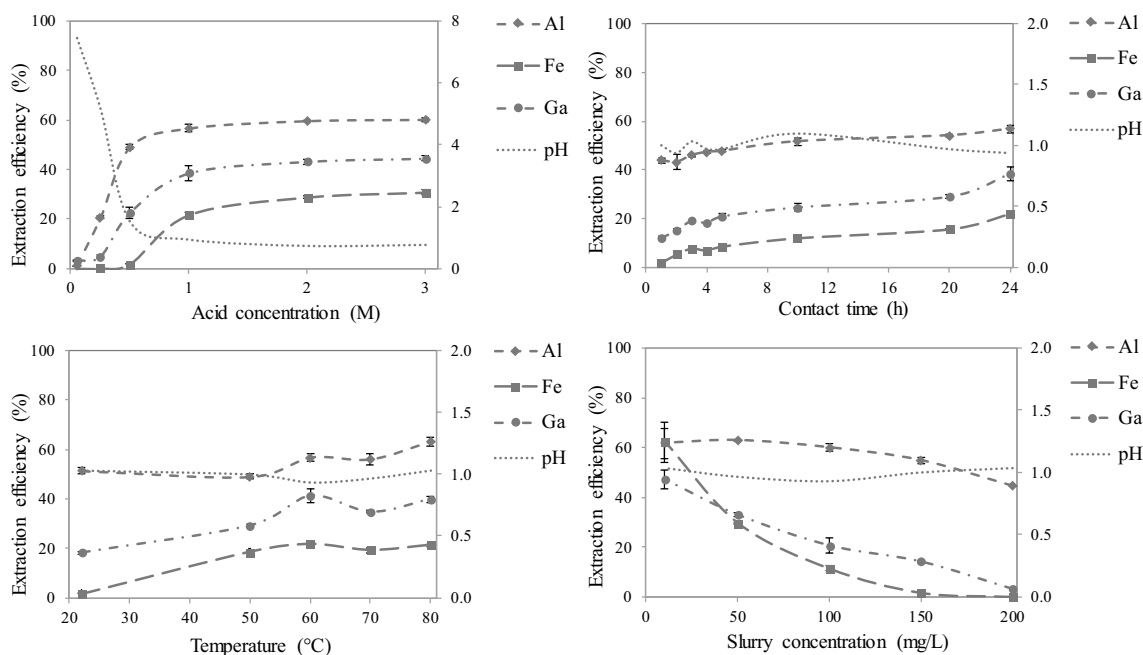


Fig. 1 Effects of leaching parameters ($\text{H}_2\text{C}_2\text{O}_4$ concentration, contact time, temperature, slurry concentration) on extraction efficiency (primary Y-axis) and pH (secondary Y-axis) of Al, Fe, and Ga. Single

parameters were varied, whereas all other parameters were kept constant at (1 M $\text{H}_2\text{C}_2\text{O}_4$, 24 h, 60 °C, and 100 g/L slurry concentration)

considered linear effects between the investigated parameters (SI, Eq. 1) when all linear effects of the four tested factors had a significant ($p \leq 0.05$) effect on the extracted Ga (SI, Table 6). Figure 2 shows the two-factor-interaction effects between contact time and $\text{H}_2\text{C}_2\text{O}_4$ concentration (Fig. 2a); temperature and $\text{H}_2\text{C}_2\text{O}_4$ concentration (Fig. 2b); and slurry concentration and $\text{H}_2\text{C}_2\text{O}_4$ concentration (Fig. 2c).

$\text{H}_2\text{C}_2\text{O}_4$ concentration, contact time and temperature had the most pronounced effect on the extracted Ga (ranging from 3.0 to 63.1 mg/kg while leaving the other factors at optimal values) and are, therefore, the most important factors to optimize. Slurry concentration had a considerably lower impact.

Optimal conditions predicted by the model regarding extraction of maximal Ga from bauxite residue were 2.5 M $\text{H}_2\text{C}_2\text{O}_4$ acid concentration, 21.7-h contact time, 80.0 °C temperature, and 10.0 g/L slurry concentration. The model predicted maximal extracted Ga of 85.8 mg/kg. The corresponding leaching experiment under these conditions was conducted, which yielded a maximal extracted Ga of 81.1 mg/kg. Since the experimentally determined and predicted maximal extractable Ga did not differ significantly (prediction was 93% of the obtained), the model was considered accurate. Using these optimal conditions, 71% of the aqua regia-accessible Ga content was extracted from bauxite residue.

Adsorption Study

For the first time this study showed a process combination of acid leaching and adsorption on zeolite for the recovery of Ga from bauxite residue, therefore process parameters were developed for the study in batch experiments using model solutions contain Ga.

In the batch study, the removal of Ga from Ga (50 mg/L) solution by three types of zeolites (HY, H-beta, ZSM-5) were compared (SI, Table 1). Among the investigated zeolite products, the zeolite HY showed the highest Ga sorption capacity from the solution with the 99% (~49.6 mg/L) Ga removal efficiency under the following conditions 10 mg/mL amount of adsorbent, 24-h contact time, and 20 °C (SI, Table 7).

The effect of adsorbent dosage, temperature and contact time on the removal of Ga by zeolite HY from Ga solution were studied (Fig. 3). Increasing the adsorbent dosage from 0 to 25 mg/mL increased removal efficiencies of Ga from 0% (~0.1 mg/L) to 100% (~49.9 mg/L) at 24 h and 20 °C. The Ga removal efficiency was already 90% at 5 mg/mL adsorbent dosage, therefore, it was used for investigating the effect of temperature and contact time. Temperature had no particular effect on the removal of Ga in the range of 20–80 °C. Increasing contact time increased removal efficiencies of Ga from 5% (~2.6 mg/L) to 90% (~44.8 g/L) using 5 g/mL amount of adsorbent at 20 °C. Ga adsorption

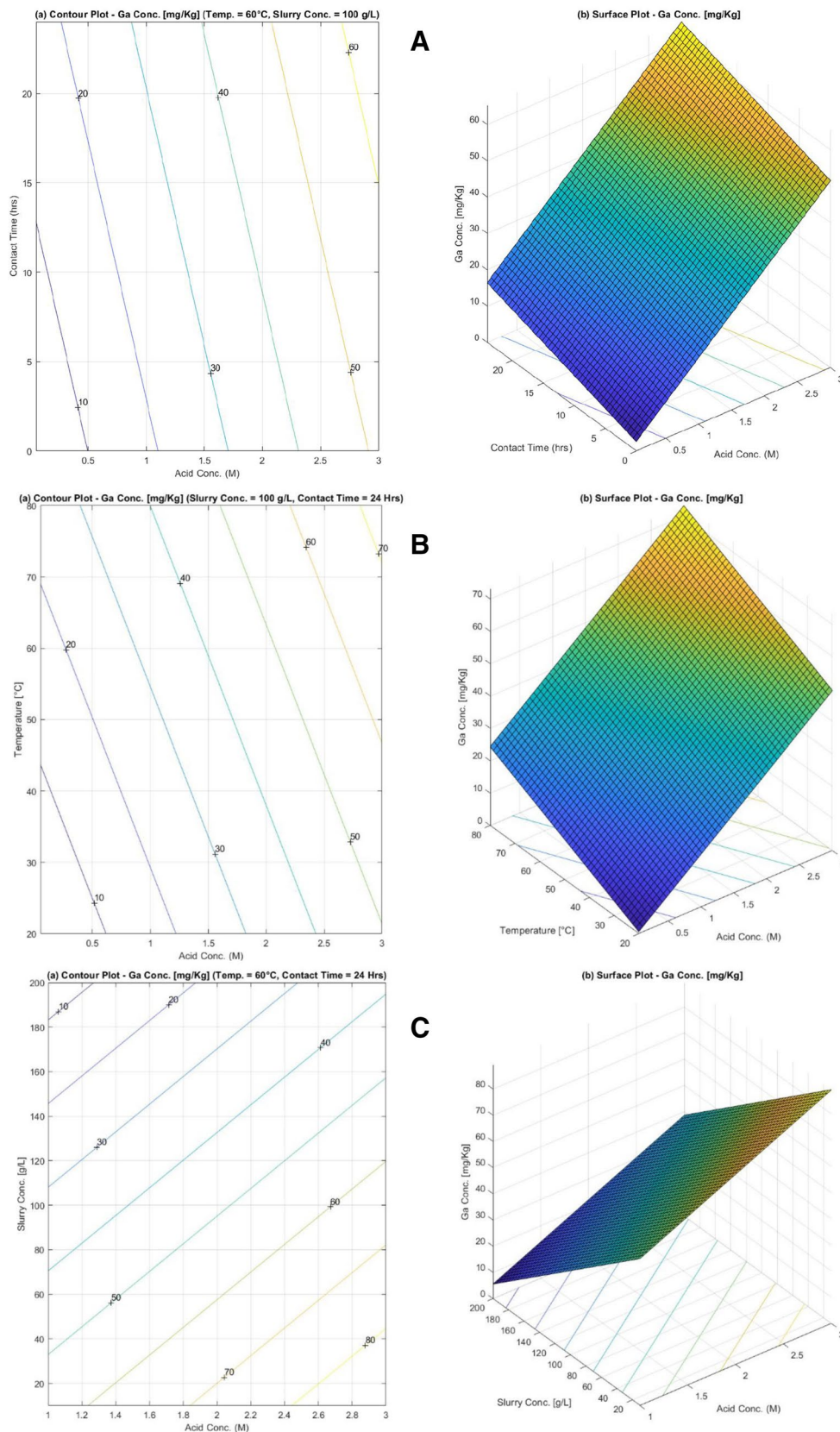


Fig. 2 Two-factor interactions (surface plot, left; contour plot, right) on the extracted Ga. Factors that are not shown in the graphs were held constant at the predicted optimal values (Color figure online)

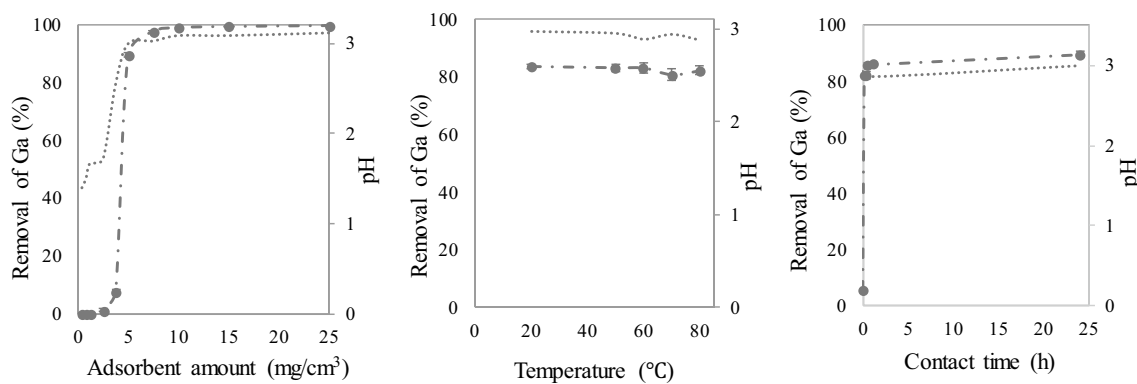


Fig. 3 Effects of adsorption parameters (adsorbent dosage, temperature, and contact time) on Ga removal efficiency (primary Y-axis) and pH (secondary Y-axis) from synthetic Ga (50 mg/L) solution by

zeolite HY. Single parameters were varied, whereas all other parameters were kept constant at (5 mg/mL amount of adsorbent, 24 h, and 20 °C)

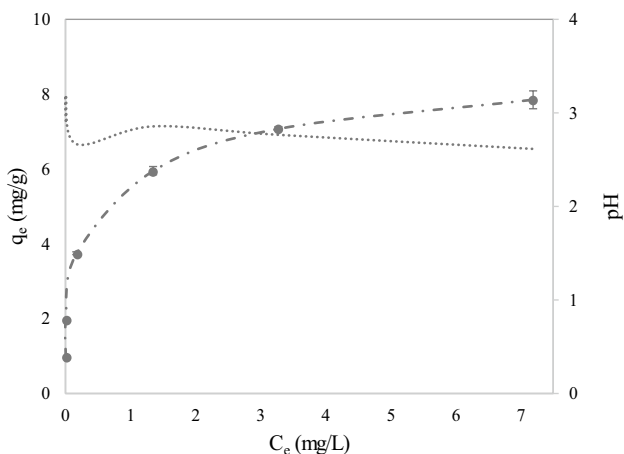


Fig. 4 Adsorption isotherm of Ga on zeolite HY under the following conditions: 10-min contact time, 20 °C (C_e adsorbate equilibrium concentration, q_e amount of adsorbate in the adsorbent at equilibrium)

on zeolite HY showed rapid kinetic as 82% (~40.0 g/L) of Ga was adsorbed from the solution after 10 min.

The adsorption equilibrium was correlated by a Langmuir-type equation; however, the curve did not reach any plateau (the adsorbent does not show clearly a limited sorption capacity) (Fig. 4) [41]. As shown in Fig. 4, the zeolite HY adsorbed Ga under the employed experimental condition, which shows that ion exchange can effectively remove Ga ion from acetic solution. The maximum amount of adsorbed Ga per zeolite HY was 7.9 (mg of Ga/g of zeolite HY).

Similar to the extraction study, in order to determine optimal removal conditions to remove maximal Ga from the solution, a DOE approach was used to account for interaction effects between investigated factors regarding adsorbent dosage (0.4–25 mg/mL), contact time (0–24 h), and

temperature (20–80 °C) (SI, Table 8). The response surface-reduced linear model considered linear effects between adsorbent dosage and contact time (SI, Eq. 2) as they had a significant ($p \leq 0.05$) effect on the Ga removal efficiency (SI, Table 9). The adsorbent dosage had the most pronounced effect on the Ga removal efficiency and was, therefore, the most important factor in the optimization (Fig. 5).

Optimal conditions predicted by the model regarding removal of maximal Ga from solution were 5 mg/mL adsorbent dosage and 1-h contact time, and 20 °C. The model predicted maximal Ga removal efficiencies of 99.8%. The corresponding adsorption experiment under these conditions was conducted, and it yielded a maximal Ga removal efficiency of 99.4%. Since the experimentally determined and predicted maximal Ga removal efficiencies did not differ significantly (prediction was 99.6% of obtained), the model was considered accurate.

The developed optimal adsorption parameters (5 mg/mL adsorbent dosage, 1-h contact time, and 20 °C) were applied to bauxite residue $H_2C_2O_4$ leachate (produced under optimal conditions, see “[Design of Experiment Approach to Predict the Optimal Parameters for Leaching Experiments](#)” section) to extract Ga from the leachate. In contrast to the batch study, 16.1% (~17.8 mg/kg) Ga was adsorbed with the presence of major elements onto bauxite residue (Al: 9.8%–13,419 mg/kg, Ca: 14.0%–2739 mg/kg, Fe: 11.7%–39,018 mg/kg, Na: 7.2%–5708 mg/kg, Ti: 17.7%–7045 mg/kg, V: 14.2%–210 mg/kg) (Fig. 6; SI, Table 3).

Study on the Byproduct of the Leaching

The pH of the post residue was 0.3 with the EC of 39.1 mS/cm. The SEM analysis showed that the bauxite residue powder had a size of < 10 μ m. Analyzing the exact size of

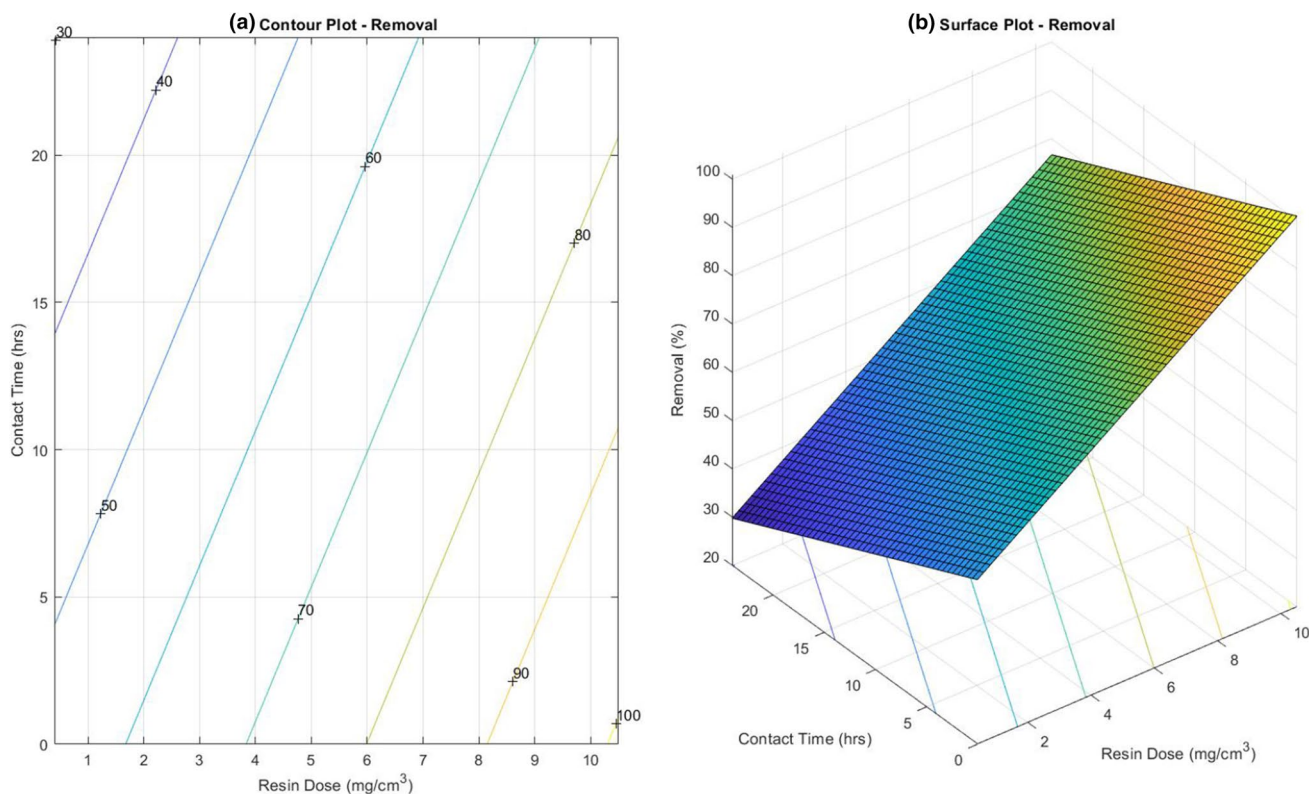


Fig. 5 Two-factor interactions (surface plot, left; contour plot, right) on the removal of Ga (%). Factors that are not shown in the graphs were held constant at the predicted optimal values (Color figure online)

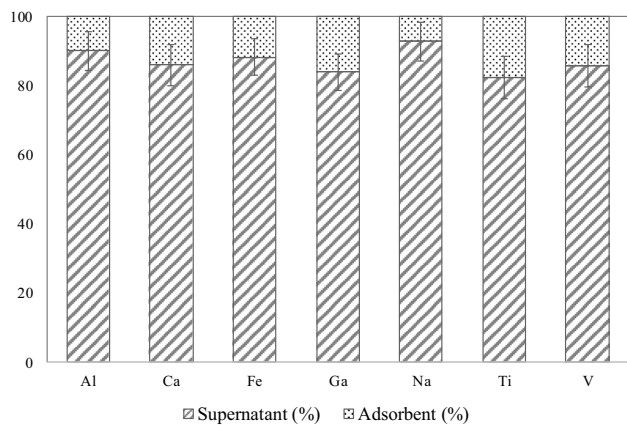


Fig. 6 Bauxite residue leachate compounds partitioning into supernatant and adsorbent during adsorption onto zeolite HY under the following conditions: 5 mg/mL, 1-h contact time, 20 °C (pH 0.5)

particles was not possible because of particles agglomeration (Fig. 7a). EDS mapping showed the presence of major components such as Al, Fe, Na, Si, Ca and Ti. Measuring the composition of the bauxite residue with EDX data was also limited due to the concentration of components. The detected dominance of elements by EDX: Fe, Al, Na, Si,

Ca, and Ti oxides (SI, Table 10) corresponds to composition detected by XRF and ICP-OES.

SEM analysis showed that post residue formed large aggregates (Fig. 7b). EDS mapping showed that elements remained in acidic solid residue accumulated on the surface of the large aggregates. The EDX mapping of the post residue showed the presence of Fe, Al, Si, Ti, Ca and Na oxides (Fig. 7b; SI, Table 11).

Discussion

The typical order of elemental abundance in bauxite residue is Fe > Si ~ Ti > Al > Ca > Na [42]. In this study, the elemental composition of the bauxite residue was dominated by (expressed as oxides) Fe (~43.3%), Al (~16.5%), Si (~9.4%), Ti (~8.9%), Ca (~6.2%), and Na (~6.0%) (SI, Table 2), and the aqua regia-accessible Ga concentration was 114.5 ± 5.2 mg/kg (SI, Table 3). Similar Ga contents were described, for instance 89 mg/kg, in Australian bauxite residue [43], as well as 91 mg/kg in Indian bauxite residue [44].

Similarly to Ujaczki et al. [18] in this study the extraction efficiency of Ga was higher using $H_2C_2O_4$ in comparison to HCl, HNO_3 and H_2SO_4 under normality = 2, 24 h, 60 °C and 100 g/L slurry concentration (SI, Table 4). Lu et al. [22]

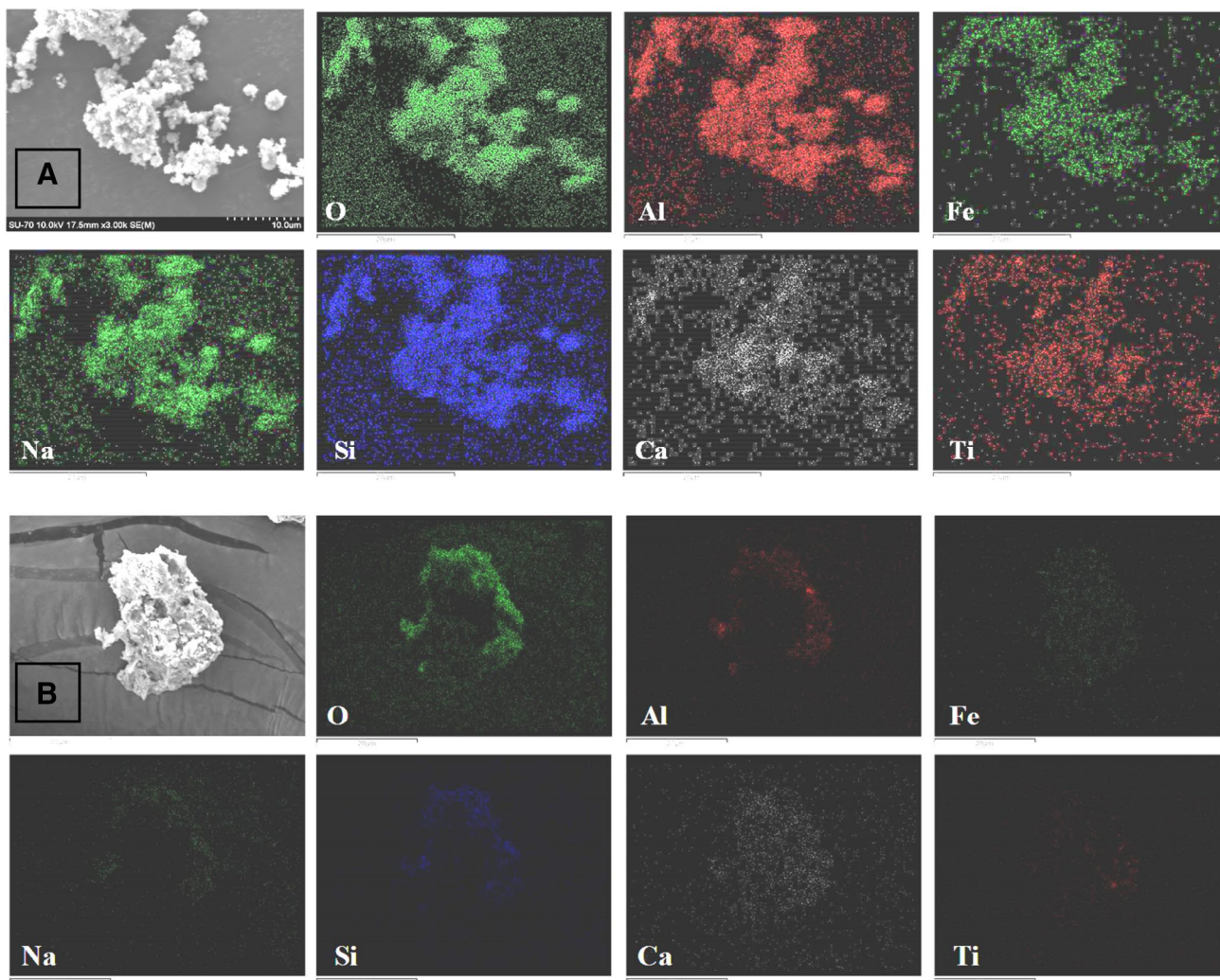


Fig. 7 Morphology and chemical composition of bauxite residue (a) and post residue (b) detected by SEM–EDS (10.0 kV, 17.5 mm, $\times 3.00$ k) (Color figure online)

also evaluated the effects of different mineral acids (4.4 M HCl, 2.2 M H_2SO_4 , 4.1 M HNO_3) on the Ga extraction from bauxite residue at 4 h, 60 °C, 125 g/L slurry concentration. In their study leaching with HCl resulted greater efficiency than leaching with H_2SO_4 or HNO_3 in accordance with the present and Ujaczki et al. [18] investigations.

Considering leaching parameters such as acid concentration, contact time, temperature and slurry concentration, general trends were observed. The extraction efficiencies depend largely on the acid concentration with more extraction achieved at higher acid concentrations [18, 22]. For instance, Lu et al. [22] reported a significant increase in Al and Ga extraction efficiency from 81 to 95% when the HCl concentration increased from 4.4 to 6.5 M at 4 h, 100 °C and 125 g/L slurry concentration. They found a slight improvement in Al and Ga extraction efficiency from 4.4 to 5.8 M HCl, then both Al and Ga extraction efficiency increased

remarkably from 5.8 to 6.5 M HCl. They attributed this to the initial extraction of only the most easily digested Al (Ga) phases in bauxite residue e.g. kaolinite at lower acid concentrations. Here, increasing the $\text{H}_2\text{C}_2\text{O}_4$ concentration from 0.05 to 3 M increased extraction efficiencies of Al and Ga from 3 and 1 to 44 and 60%, respectively at 24 h, 60 °C, 100 g/L slurry concentration (Fig. 1).

Other studies showed similar effects of contact time on extraction of Ga from bauxite residue. For example, Lu et al. [22] reported that increasing the contact time from 1 to 5 h led to increased extraction efficiencies from 82 to 95% at 4.4 M HCl, 55 °C and 125 g/L slurry concentration. They found an increase Ga extraction efficiency from 94 to 95% at 4–5-h contact time, therefore 4 h was chosen as the optimal extraction time in their study. In Ujaczki et al. [18] the best results regarding contact time was achieved at 3 h, showing 63% Ga extraction efficiency at 4 M HCl,

60 °C and 100 g/L slurry concentration. Ujaczki et al. [18] found relatively low Fe extraction efficiency (21%) at 3 h but the Al extraction efficiency was already high after the first hour (72%). In this study, increasing the contact time from 1 to 24 h increased extraction efficiencies of Ga from 12 to 38% using 1 M $\text{H}_2\text{C}_2\text{O}_4$, 60 °C and 100 g/L slurry concentration. A slight increase was detectable at increasing contact time from 1 to 24 h for Al (from 44 to 57%) (Fig. 1).

According to Davris et al. [45] and Pepper et al. [46] temperature plays a crucial role in the bauxite residue dissolution. The extraction of aluminosilicate (Ga) phases in bauxite residue has been shown to increase with the increasing reaction temperatures. In Lu et al. [22] study, the extraction efficiency of Ga increased from 89 to 94% when the temperature increased from 40 to 55 °C, while they found a slight increase from 55 to 100 °C. In the present study, elevating temperature from 22 to 80 °C led to considerably increased extraction efficiencies of Ga from 18 to 40% using 1 M $\text{H}_2\text{C}_2\text{O}_4$, 24 h, 100 g/L and slurry concentration (Fig. 1). Elevated temperatures increased Al extraction efficiency for 63% Al while Fe still remained 21%.

Slurry concentration had a strong effect on extraction efficiencies similar to acid concentration. Here, decreasing the slurry concentration from 200 to 10 g/L resulted in an increase in extraction efficiencies of Ga from 3 to 47% using 1 M $\text{H}_2\text{C}_2\text{O}_4$, 24 h and 60 °C (Fig. 1). The maximal Al and Fe extraction efficiencies were also achieved with decreasing slurry concentration at 10 g/L when 62% Al and 62% Fe were extracted. This is in accordance with Ujaczki et al. [18]. However, Lu et al. [22] did not find significant improvement in the Ga and Al extraction efficiency. They found that the slurry (bauxite residue and HCl acid solution) filtration was quite difficult when the slurry concentration was below 125 g/L, which could be attributed to a high concentration of formed silica gels in the slurry [47, 48]. Kinetic studies performed by Rivera et al. [17] with HCl and H_2SO_4 demonstrated that, at ambient temperatures, silica dissolution increases with increasing acid concentration, which leads to the formation of silica gel.

Based on the conducted experiments, Lu et al. [22] determined optimum leaching conditions for Ga extraction from bauxite residue as the follow: 4.4 M HCl, 4-h contact time, 55 °C temperature, and 125 g/L slurry concentration. Under these optimal conditions, 95% average Ga extraction efficiency was reached. Here, an experimental design approach was used to determine optimal conditions for Ga extraction using $\text{H}_2\text{C}_2\text{O}_4$. Extraction of maximal Ga from bauxite residue was chosen as the application relevant response viable. Optimal conditions for extraction of maximal Ga from bauxite residue were predicted for 2.5 M $\text{H}_2\text{C}_2\text{O}_4$ acid concentration, 21.7-h contact time, 80.0 °C temperature, and 10.0 g/L slurry concentration. Indeed, experimentally determined

economic potential corresponded well (93% of predicted) with the predictions, allowing a maximum extracted Ga of 85.8 mg/kg. Using these optimal conditions, 71% of the aqua regia-accessible Ga content was extracted in bauxite residue.

Many strategies for valuable elements recovery from bauxite residue requires large amounts of energy and chemicals [15, 18, 20–22, 28–30, 45, 49]. However, the extraction of strategically important elements from bauxite residue is not only attractive from the financial point of view of recovered elements alone. It is also motivated by a number of factors such as economic, social, environmental and technological benefits [6].

For instance, extraction by $\text{H}_2\text{C}_2\text{O}_4$, can be biologically produced, showing a potential for bioleaching as a green alternative for the extraction. Bioleaching for valuable element recovery offers eco-efficient alternatives to classical pyro- or hydrometallurgical processes as it is an energy efficient process and the highly selective metal(loid) microbe interactions offer the possibility to unite bioremediation with resource recovery for many elements [5]. Bioleaching of Ga, Ge, V, Sc, La, Eu, and Yb from bauxite residue was investigated by Qu et al. [50]. In their study, *Aspergillus niger* showed almost the same metal leaching efficiencies as that by the commercial citric acid ($\text{C}_6\text{H}_8\text{O}_7$) at half its cost. In general, the growth of fungi in sugar-containing media results in the production of organic acids such as $\text{H}_2\text{C}_2\text{O}_4$, $\text{C}_6\text{H}_8\text{O}_7$, and gluconic acid ($\text{C}_6\text{H}_{12}\text{O}_7$) [51]. Studies also have shown that the alkaline medium favors $\text{H}_2\text{C}_2\text{O}_4$ production which is also beneficial in the application to an alkaline byproduct such as bauxite residue [51, 52].

Rivera et al. [17] showed high extraction efficiency of REE from bauxite residue in a two-step processing of bauxite residue by dry digestion and subsequent water leaching. They found that the low water consumption allows to increase the filtration efficiency of the leach liquor due to the avoidance of silica gel formation [17]. In this integrated multistage treatment, much more bauxite residue can be processed for REEs extraction without demanding too much water for the process [17]. Therefore, an increase in bauxite residue processing may help to reduce the inventories and costs associated with storing, which are major concerns for the alumina producers [17].

After extraction, dissolved Ga is mostly separated using solvent extraction [53–57]. Solvent extraction (liquid/liquid extraction) is based on the partitioning of the dissolved metal into a nonmiscible organic phase (extract), followed by recovery (stripping) of the metal from the solvent phase [58]. However, the solvents used during liquid–liquid extraction perform well technologically, certain processing steps have a comparably higher environmental impact [59].

Adsorption as a separation process is also available as another possibility due to its apparent lower environmental impact, high efficiency, easy operation and low price in

comparison to conventionally used solvents [60]. In recent years, zeolites have been investigated for the adsorption of metals owing to their net negative charge in the polymeric network and to the fact that zeolite exchangeable ions are relatively innocuous [61–63]. The structure of zeolite consists of a three-dimensional framework of SiO_4 and AlO_4 tetrahedra where the Al^{3+} is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice [61]. The net negative charge is balanced by the exchangeable cation (Na^+ , K^+ , NH_4^+ or Ca^{2+}), and these cations are exchangeable with certain cations [61]. In Zhao et al. [60], a magnetic cobalt ferrite (CoFe_2O_4)-coated zeolite was prepared using a hydrothermal method and was used for the adsorption of Ga and In. They investigated the effects of pH and adsorption time as the adsorption capacity was influenced by these parameters. In their experiments, the adsorption equilibria of Ga and In on CoFe_2O_4 -zeolite could be achieved very quickly. The optimum pH was chosen as 5.0 because at lower pH, more hydrogen ions exist, which can compete more effectively with Ga and In for active bonding sites, leading to lower adsorption capacity [60]. However, high pH also can lead to lower adsorption capacity, which is attributed to the formation of $\text{Ga}(\text{OH})_3$ and $\text{In}(\text{OH})_3$ [60]. According to Zhao et al. [60], the rapid and high adsorption efficiency was attributed to the presence of active sites on the adsorbent's surface in a large scale. In the present study, Ga adsorption onto zeolite HY showed rapid adsorption kinetic too, as 82% of Ga was adsorbed from the solution after 10 min (Fig. 5). The pH was kept low because the developed parameters in the batch experiments were applied on an acidic (pH 0.5) leachate to adsorb Ga. Identified future challenges to optimize Ga-adsorption techniques are (1) concentration of Ga in adsorbent from the leachate (2) improving selectivity of Ga against major components (e.g., Al and Fe) (3) developing recovery step from the adsorbent or finding a market where Ga bound to zeolite network can be utilized, and (4) regeneration of adsorbent. Moreover, challenges related to the post-residue production during Ga extraction from bauxite residue need to be also addressed. Due to the oxalic acid applied for the extraction of Ga, the byproduct produced is highly acidic (pH 0.3) compared to the original alkaline pH of the bauxite residue (10.9) (see in “Physico-chemical and Mineralogical Characterization” and “Study on the Byproduct of the Leaching” sections), which warrants further investigations for its disposal and/or utilization.

Conclusion

In the present study, the extractions of Ga from bauxite residue by mineral acids (H_2SO_4 , HCl , and HNO_3) and an organic acid ($\text{H}_2\text{C}_2\text{O}_4$) were evaluated regarding their

efficiencies which showed that the most efficient extraction for Ga was achieved by $\text{H}_2\text{C}_2\text{O}_4$ followed by the other acids in the order $\text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3$. Experimental design (DOE) software was used for the optimization of Ga extraction by $\text{H}_2\text{C}_2\text{O}_4$ from bauxite residue where the prediction was validated with laboratory experiments. Optimal conditions predicted by the model regarding extraction of maximal Ga from bauxite residue were 2.5 M $\text{H}_2\text{C}_2\text{O}_4$ acid concentration, 21.7-h contact time, 80.0 °C temperature, and 10.0 g/L slurry concentration. In the subsequent sections, the effects of adsorbent dosage, temperature, and contact time on the removal of Ga by zeolite HY from synthetic Ga solution were studied. Similar to the extraction study, DOE approach was used to predict optimal conditions for maximal Ga removal from the synthetic Ga solution when the optimal conditions determined were 5 mg/mL adsorbent dosage and 1-h contact time, and 20 °C. The corresponding adsorption experiments under these conditions from synthetic Ga solution were conducted, and they yielded a maximal Ga removal efficiency of 99.4%. However, adsorption, under optimal conditions, on zeolite HY for recovering Ga from $\text{H}_2\text{C}_2\text{O}_4$ leachate showed only 16% efficiency for Ga.

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Compliance with Ethical Standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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