Citric, Ascorbic and Acetic Acids for Bauxite Residue pH Neutralization and their Effects on the Sodalite Phase

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Abstract

Bayer sodalite is the main desilication product (DSP) formed during the refining of alumina in the low temperature Bayer process and can represent 16 - 24 % of the bauxite residue (BR) composition. BR's sodicity and alkalinity, mainly due to soluble sodium salts and solid sodalite contents, can limit its use as a raw material for other applications (e.g. agriculture, building materials, and steel industry). Chemical, physical, and biological approaches have been developed to mitigate BR´s sodicity and alkalinity. Among them, treatment with organic acids, from chemical or biological sources, demonstrates great potential. However, more research is needed to understand the effects on sodalite dissolution and its impact on pH and other parameters over time. In this context, batch tests were carried out using citric, ascorbic, and acetic acids for the treatment of a Brazilian BR. The BR sample (20 % w/v) was mixed with organic acid solutions at different concentrations (50, 100, 200, and 400 mmol) and stirred at 100 rpm, at 28 °C. XRD, SEM, EC, and pH were evaluated up to the equilibrium factor $F \leq 0.5$. At 400 mmol, the equilibrium pH was lower using ascorbic and citric acids (pH ~ 7) than using acetic acid (pH ~ 8). SEM analysis showed small aggregates (< 5 μm), typical of sodalite mineral in the BRs treated with acetic and ascorbic acids. In the treatments with citric acid, these aggregates were less frequently seen. XRD peak intensities indicated a reduction in sodalite phase only at higher citric acid concentrations (> 200 mM). The result suggests that citric acid (≥ 200 mmol) is more effective in reducing BR pH and sodicity, indicating this as a promising pre-treatment for BR processing before use in other applications.

Keywords: Sodalite dissolution, Bauxite residue, Mineral biotechnology, Green mining.

1. Introduction

Bauxite residue (BR) is generated as a by-product of alumina production from bauxite by the Bayer process. BR alkalinity and sodicity result from bauxite ore digestion in a sodium hydroxide (NaOH) solution, at around 145 °C. The mineral phases in BR are mainly the primary bauxite minerals (e.g. hematite, quartz, anatase, rutile, boehmite), as well as secondary phases formed during the process, such as sodalite, cancrinite, hydrogarnet (generally referred as desilication products or 'DSP's), re-precipitated gibbsite, calcite, tricalcium aluminate and others [1].

Despite filtering and washing to reduce the soluble caustic and sodium in the solids, at discharge from the refinery BR still contains residual dissolved, and leachable sodium hydroxide, sodium carbonate, sodium aluminate, and other soluble substances. BR´s sodium content and alkalinity is mainly as soluble sodium salts and DSPs, where the latter can represent 16 – 24 % of the BR composition [2]. The DSPs, Bayer sodalite and Bayer cancrinite, have a common chemical formula $Na_6[Al_6Si_6O_{24}].2NaX.6H_2O$, where X represents OH^-, Cl^-, NO_3^-, ½ CO_3^{2-}, or ½ SO_4^{2-}, their crystal structures however, are different. Sodalite is cubic while cancrinite is hexagonal, and if calcium is present in the liquor, it can replace Na_2X in the cancrinite formula. Sodalite is formed in Bayer circuits designed for gibbsitic bauxite digestion at temperatures around 145 ºC, while cancrinite is formed at the higher reaction temperatures (> 220 ºC) used for boehmitic and diasporic bauxite digestion [3].

Due to the large and increasing annual global production, and BR´s large worldwide inventory [4], residue application research has increased in the last decade. Studies have reported potential BR application in waste-water and waste-gas treatment (for phosphorus adsorption and purification of acidic waste gases), as building materials, catalysts, as a secondary source of metal and rare earth elements, and in agriculture as a soil conditioner [5-8]. However, its physico-chemical characteristics limit wide application, and a dealkalization and sodium reduction step would facilitate its broader use [1-2]. Physical and biological approaches to mitigate BR´s alkalinity and sodium content, such as salt ion precipitation or displacement, pyrometallurgy and hydrometallurgy, acid neutralization, and microbial-driven remediation have been investigated [9-11].

BR transformation by mineral (hydrochloric and sulfuric) and organic (citric) acids at low concentrations, with and without gypsum amendment has also been studied [10]. All treatments were successful in decreasing total alkalinity and pH to some degree in experiments using cancrinite-rich bauxite residue. Citric acid reacts with cancrinite, promoting macro-aggregate formation, improving BR's physical properties [10]. Cancrinite was also leached using high concentrations of citric acid [11]. It is important to note that while inorganic acid leaching can neutralize and remove sodium from BR, it can also dissolve undesirable metals, making the option of organic acid treatment more interesting. Silica gel formation has also been described during sulfuric acid hydrometallurgical processing at pH < 7.0 [12].

Organic acid pretreatment (either from chemical or biological sources) offers the potential to boost BR use [13-14], further closing the aluminum circular economy loop. However, more research is needed to understand the effects over time on sodalite dissolution and on BR pH and other parameters. In this context, the present work reports batch tests carried out using citric, ascorbic, and acetic acids at different concentrations (50, 100, 200, and 400 mmol) for the treatment of a Brazilian BR, to determine their effects in reducing alkalinity and on sodalite dissolution. The study's results will contribute to a better understanding of the potential use of organic acids as a pre-processing step before BR use in various applications.

2. Experimental

The study was conducted at the SENAI Innovation Institute for Mineral Technologies (ISI-TM), in Brazil using a press-filtered BR sample obtained from an alumina refinery located in the state of Pará, Brazil. The BR´s chemical and physical characterization has been previously reported [15].

The experiment was carried out in batches (three replicates) using ACS grade acetic ($C_2H_4O_2$), citric ($C_6H_8O_7$), and L-ascorbic ($C_6H_8O_6$) acids, at concentrations of 50, 100, 200, and 400 mmol, according to an adapted methodology [14]. BR samples at 20 % (w/v) concentration were added into 60 mL clear capped polypropylene bottles and filled with the acid solutions to a final volume

of 40 mL. Distilled H_2O replaced the organic acids in a blank sample. The experimental procedure was carried out at room temperature and under constant agitation (100 rpm) using a benchtop orbital shaker (Gehaka, AO-370). The pH variation (Orion Star A211 pH meter, Thermo Scientific) and electrical conductivity (Hanna EC) of the supernatants liquids were monitored after 1 minute, 4 hours, 24 hours, and thereafter every 24 hours until the establishment of chemical equilibrium, evaluated by the pH value (equilibrium factor (F) ≤ 0.05). The reaction was completed after 18 days for the acetic and citric acid treatments, and after 11 days for ascorbic acid. At the end of the experiment, treatments were homogenized, and the remaining solid BR phase was collected and characterized.

The remaining BR solid phases after water and acid treatments were chemically characterized by energy dispersive X-Ray Fluorescence (EDXRF: Epsilon 3XLE, PANalytical Spectrometer) using an X-Ray Rhodium (Rh) tube, and anode at 1.5 W. Mineral phases were determined by X-Ray Diffraction (XRD: Empyrean PANalytical Diffractometer, Almelo, The Netherlands). Powder XRD patterns were obtained (5 ° – 80 °, 40 kV, 20 mA, Kα 1.78901 Å, step size 0.02 °, 55 s/step). Morphological micrographs were obtained by Scanning Electron Microscopy (SEM: Vega 3 LMU, Tescan), operated at 20 kV and 10 μA with a focal distance between 8 and 15 mm. Mineral samples were coated with a thin gold layer using a Desk V metallizer (Denton Vacuum) before SEM [15].

3. Results and Discussion

3.1 Effects of Treatments on pH and EC

Different concentrations (50 - 400 mmol) of ACS grade acetic, citric and ascorbic acids were evaluated as BR treatments (see Figure 1). All the organic acids at the tested concentrations were effective in reducing the pH of the liquid phase to below that of the control (only water, pH 11.4). An abrupt pH decrease, in as little as 1 minute, was observed due to the immediate consumption of the free anions in solution, such as OH^-, CO_3^{2-}/HCO_3^-, $(OH)_4^-/Al(OH)_3$. In general, pH buffering was observed after 24 hours of incubation at the organic acids' lower concentrations (50 – 200 mmol), persisting until the end of the experiment.

During the reaction time, until chemical equilibrium has been achieved, different acidic treatments showed a similar pH trend at the same concentration (Figure 1), except for acetic acid treatments at 50 mmol. The acetic acid treatment at 50 mmol exhibited a more pronounced buffer effect where it was not able to reduce pH (~ 12) as much as the other acids (~ 10) after 192 hours. Although, citric acid treatment at 400 mmol and up to 72 hours exhibited a pH value (< 4) lower than the others (> 5), after 168 hours the pH increased to values near to the other treatments at the end of the reaction time.

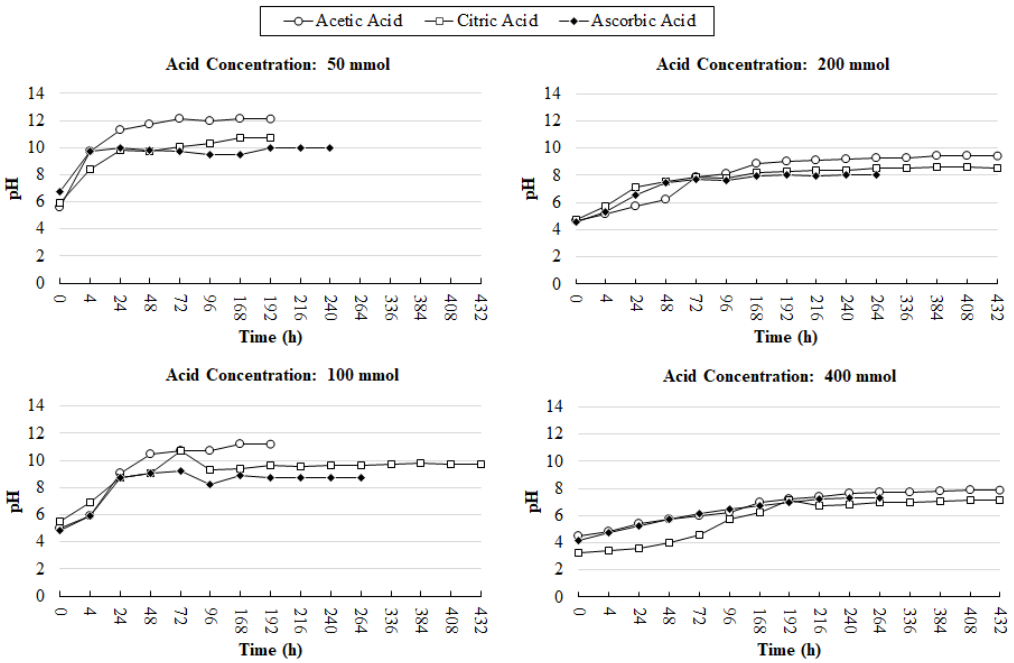

Figure 1. pH evolution of BR treated with acetic, citric and ascorbic acids at concentrations of 50, 100, 200 and 400 mmol.

Figure 2 shows the EC values of each organic acid treatment as a function of the reaction time. Treatments containing either 50 or 100 mmol of organic acid showed similar EC curves. Higher EC values were observed in the BR treated with citric and acetic acids at higher concentrations (200 and 400 mmol), indicating an increased concentration of ions in the solution, probably derived from BR´s solid phase leaching or dissolution. The type of organic acid added, mostly at higher concentrations (200 - 400 mmol), showed a pronounced influence on the EC values, as observed in Figure 2.

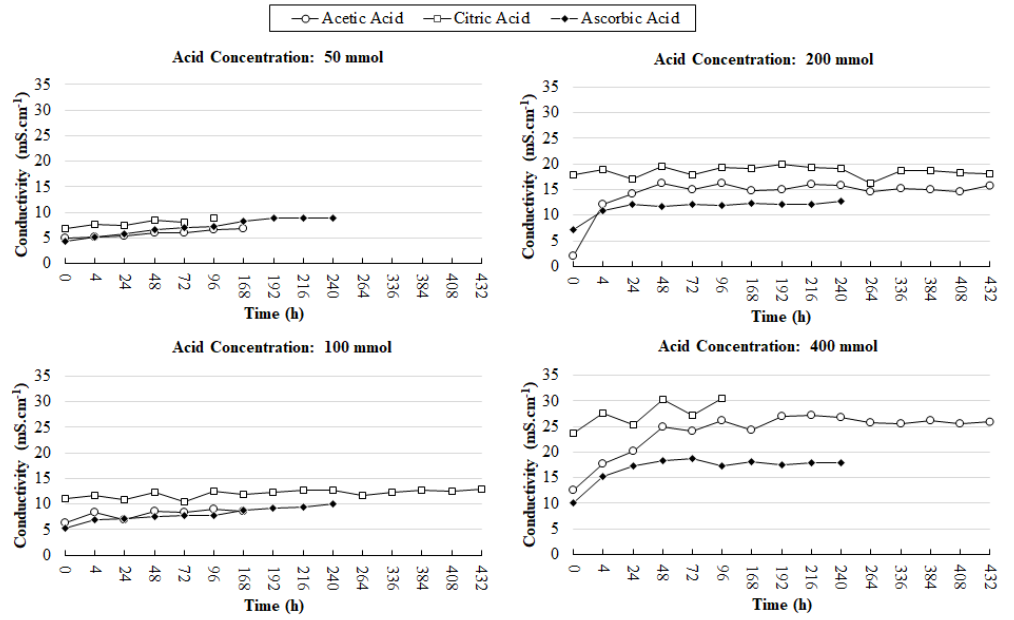

Figure 2. EC evolution (in hours) of BR treated with acetic, citric and ascorbic acids at concentrations of 50, 100, 200 and 400 mmol.

3.2 BR Solid Phase Characterization after Acid Treatments

Table 1 shows the XRF elemental composition of the BR solid phase at the final reaction time. The organic acids used in this experiment showed little effect on BR chemical composition considering either type or concentration of organic acid evaluated, except for Na_2O, Al_2O_3, SiO_2, and Fe_2O_3 at 400 mmol citric acid treatment. While the content of sodium, silicon, and aluminium decreased considerably, iron (Ti and Zr) increased, almost certainly due to the overall mass loss with DSP dissolution. Acid leaching of bauxite residue´s DSP occurs in two stages: $Na^+ - H^+$ ion exchange (with a minimal reaction of Al and Si) and hydrolysis of the Al−O−Si framework (dissolution of DSP) [16], consistent with the XRF results.

Table 1. XRF elemental composition (%wt) of the remaining BR solid fractions after treatment with acetic (AA), citric (CA) and ascorbic (AS) acids.

	Concentration												
	-	50 mmol			100 mmol			200 mmol			400 mmol		
%	BR	AA[1]	CA[2]	SA[3]	AA	CA	SA	AA	CA	SA	AA	CA	SA
Na_2O	9.7	9.7	8.2	9.0	8.41	7.5	8.4	8.0	6.0	8.1	7.0	3.70	7.2
Al_2O_3	17.3	16.3	19.8	20.8	20.9	19.3	20.7	20.6	17.6	20.4	20.3	13.7	19.6
SiO_2	14.0	11.3	14.1	14.6	14.7	13.5	14.5	14.4	12.5	14.4	14.3	9.1	13.7
P2O5	0.1	0.3	0.4	0.4	0.4	0.4	0.3	0.4	0.4	0.4	0.4	0.3	0.3
CaO	1.4	1.5	1.1	1.3	1.0	1.0	1.2	0.8	0.9	1.1	0.6	0.7	0.9
TiO_2	5.9	6.4	5.1	5.0	5.0	5.2	4.9	4.5	5.5	5.0	5.2	6.2	5.0
V_2O_5	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Fe_2O_3	40.8	44.8	41.8	39.6	40.2	43.2	40.2	41.2	46.3	40.0	42.7	53.3	41.3
ZrO_2	0.9	0.84	0.7	0.7	0.6	0.7	0.7	0.6	0.7	0.6	0.7	0.9	0.7
LOI[4]	9.1	8.6	8.5	8.2	8.5	8.9	8.6	8.4	9.7	9.6	8.3	12.0	10.8

[1] AA: Acetic Acid. [2] CA: Citric Acid.[3] SA: Ascorbic Acid.[4] LOI: Loss on Ignition.

Mineralogical analyses of the solid BRs remaining after treatment with water and the different concentrations of acetic, citric, and ascorbic acids (50, 100, 200, and 400 mmol) after reaching chemical equilibrium are shown in Figure 4. XRD diffractograms revealed the presence of hematite, anatase, sodalite, gibbsite, quartz and aluminous goethite as the main phases in water treated BR, and all acid-treated BR. Despite XRD being only a semi-quantitative method, sufficient peak intensity variations were detected in some treatments to indicate a significant change in phase concentration.

In the citric acid case (Figure 3), with increasing concentration (200 and 400 mmol), a reduction in the main peak corresponding to sodalite (°2θ = 16.03, d = 6.41 Å) was observed. Variations in the intensities of the main quartz peak were also detected in acetic and citric acid treatments. In the case of ascorbic acid treatment at 200 and 400 mmol, diffractograms showed novel peaks (°2θ = 16.59, d = 6.19Å; °2θ = 37.43, d = 2.78 Å) associated with weddellite, a calcium oxalate dihydrate ($Ca(C_2O_4).{}_2H_2O$). The formation of weddelite can be explained by the partial conversion of ascorbic acid into oxalate, forming calcium oxalate. The XRD diffractogram of water treated BR was similar to a previously analysed raw BR sample [15].

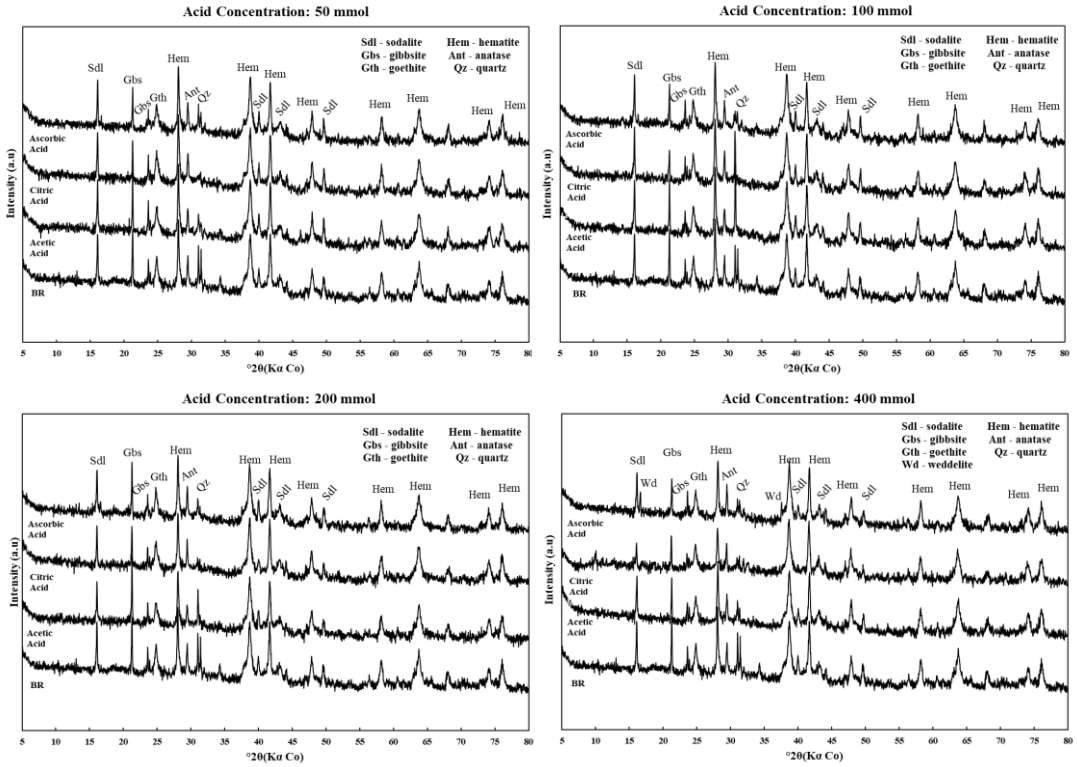

Figure 3. XRD diffractograms of remaining BR solid fractions after acid treatments.

3.3 BR Morphological Analyses after Acidic Treatments

Figure 4 shows SEM micrographs of the remaining BR after treatment with water (Figure 4.1) and the organic acids at the end of the experiment (Figure 4.2-4). Several micrographs show the presence of a thin layer of small aggregates (around 5μm) considered to be Bayer sodalite, over the entire viewed area of the BR, without observing regular crystals and/or with defined shapes. BR treatment with acetic acid (50, 100, 200, and 400 mmol) exhibited similar morphology, with a predominance of sodalite aggregates in all treatments (Figure 4.2A - D). Over the 100 mmol BR citric acid treatment (Figure 4.3B - D), a reduction in sodalite aggregates and an appearance of larger grains with an undefined shape were observed. In the treatment with ascorbic acid (Figure 4.4A - D), sodalite aggregates also remained, however, crystals with ordered planes and dimensions close to 5 μm were detected (Figure 4.4D).

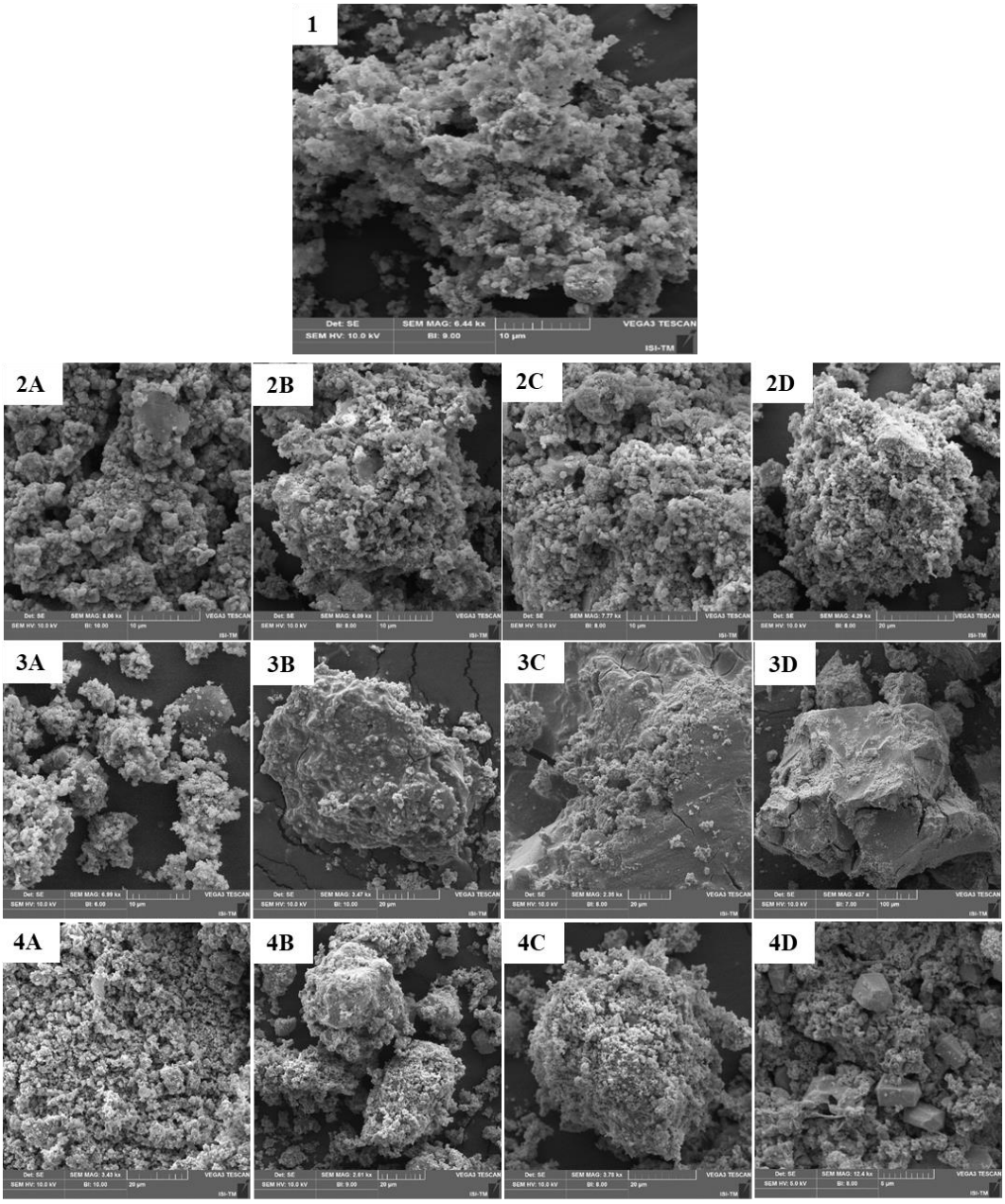

Figure 4. SEM micrographs of BR samples: 1) Blank (water); 2) Acetic Acid; 3) Citric Acid and 4) Ascorbic Acid at concentration of: A) 50 mmol, B) 100 mmol, C) 200 mmol and D) 400 mmol.

4. Conclusions

The BR sample's treatment with acetic, citric, and ascorbic acids resulted in pH reduction in all tested concentrations, whereas EC increased at higher organic acids concentrations (> 200 mmol). EC values were different according to the organic acid type and tested concentration. Acetic acid was less effective in reducing BR alkalinity at lower concentrations (50 - 200 mmol), while XRD and SEM analysis indicated persistence of Bayer sodalite. Citric acid showed promising results reaching the lowest pH (at 400 mmol) and significant sodium (XRF) and sodalite (XRD/SEM) reduction in the treated BR. Although ascorbic acid treatments presented similar final pH, a lower

sodium (XRF) and sodalite (XRD/SEM) removal capacity was observed compared with citric acid treatments. In conclusion, the results of this study indicates that citric acid, under the tested conditions, is effective as a BR treatment to reduce alkalinity and sodicity prior to BR's use in other applications which require lower pH and sodicity, and represents a promising route for pre-processing before large-scale commercial utilization.

5. References

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