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Unveiling the solubilization of potassium mineral rocks in organic acids for application as K-fertilizer

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Abstract

Organic acids produced by soil microorganisms can be useful to promote the release of potassium (K) from potassium mineral rocks (KR), but the complexity of low-reactivity minerals limits K solubilization and their use as fertilizer. Here, we investigate the ways that different organic acids (gluconic, oxalic, and citric) can affect the solubilization of potassium minerals, in order to propose process strategies to improve their solubility. For this, evaluations were performed using the model minerals $KR_{\text{polyhalite}}$ (sedimentary mineral), KR_{feldspar} (igneous mineral), and KCl (commercial fertilizer). For KCl and $KR_{\text{polyhalite}}$, complete solubilization was achieved using all the organic acids, while for KR_{feldspar} , the highest K^+ solubilization (34.86 mg L⁻¹) was achieved with oxalic acid. The solubility of KR_{feldspar} was further investigated under submerged cultivation with the filamentous fungus *Aspergillus niger*, as well as after a mechanochemical grinding treatment. The biotechnological route resulted in solubilized K^+ up to 63.2 mg L⁻¹. The mechanochemical route, on the other hand, increased the release of K^+ by about 8.6 times (993 mg L⁻¹) compared to the natural mineral, due to the greater fragmentation of the particles after the treatment (with a surface area about 2.5 times higher than for the *in natura* KR_{feldspar}). These findings demonstrated the potential of applying biotechnological and mechanochemical routes with organic acids to improve the solubilization of K present in low reactivity mineral rocks, contributing to the use of these minerals as fertilizers in more sustainable agricultural practices.

Keywords: Fertilizer; Potassium; solubilization; Organic acids; *Aspergillus niger*.

1. Introduction

The potential of microorganisms to solubilize low solubility mineral rocks for application as fertilizers has been explored by applying the microorganism together with the mineral in the soil, as well as *in vitro* using microbial cultivation techniques to promote solubilization (1–3). In this bioprocess, the production of low molecular weight organic acids is described as the main mechanism by which microbial agents, especially filamentous fungi, act to promote the solubilization of mineral rocks (4–7). The organic acids act directly in increasing the acidity of the medium, where the carboxyl and hydroxyl groups are responsible for chelating the metals present in the mineral and release of nutrients (8). Another important factor that affects the solubilization process is the particle size of the minerals (9, 10). In this case, the nutrient retained in the mineral structure can be released more easily due to the structural disorder of the system caused by the grinding process (11, 12). Therefore, knowledge about the effect of organic acids and properties of the mineral rock are essential to improve the nutrient solubilization process, especially for low reactivity potassium minerals.

Potassium (K) is an essential element for all living organisms. It is the seventh most common element in the earth's crust and the third most used macronutrient for plant nutrition in agriculture, after nitrogen and phosphorus (13, 14). Although potassium is abundant in the soil, the amount of K available for absorption by plants is very low, since about 90-98% of the potassium is in insoluble form (15). Therefore, the low concentrations of soluble K in the soil make it necessary to apply fertilizers to supply the nutritional needs of the plants. The direct application of potassium mineral rock (KR) as a natural fertilizer has been evaluated as an alternative way to supplement K for plants (16–18).

Sedimentary minerals such as polyhalite ($\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$), carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and langbeinite ($\text{KMg}_2(\text{SO}_4)_3$) can be applied to the soil and are gradually dissolved by the action of microbial organic acids, releasing nutrients to the plants (19).

However, about 95% of the minerals in the Earth's crust are igneous, formed from the crystallization of magma released during volcanic eruptions. The K-feldspars (KAlSi_3O_8) are among the most common igneous KRs, representing 60% of the oceanic and continental crust of the planet (20). They are formed by tetrahedral silica and aluminum groups, strongly linked together by cations, with the K inserted in the crystalline structure, making it difficult to extract (12). As a consequence, the dissolution process of this mineral in the soil involves complex reactions and mechanisms, which limits its application as a natural fertilizer once it does not meet the minimum nutritional demands required by plants (21, 22). A better understanding about the action of microbial organic acids on highly available minerals such as K-feldspar could contribute to promote their use as natural fertilizer.

In the present work we investigated the effects of different organic acids (gluconic, oxalic, and citric) on the solubilization of potassium rocks in order to develop strategies to improve the solubility of low reactivity potassium minerals. For that, $\text{KR}_{\text{polyhalite}}$ (sedimentary mineral), $\text{KR}_{\text{feldspar}}$ (igneous mineral), and KCl (commercial fertilizer) were used as model minerals. Full physical-chemical-morphological characterizations of the KRs were performed by X-ray diffraction, X-ray fluorescence, and scanning electron microscopy, in order to obtain a better understanding of the processes of solubilization of the KRs under the different conditions investigated. Biotechnological and mechanochemical routes were investigated for enhancing the solubilization of $\text{KR}_{\text{feldspar}}$. In the case of the biotechnological route, evaluation was made of the increase in potassium availability achieved using different strains of filamentous *Aspergillus* fungi as promoters of acidity in submerged cultivation. The mechanochemical route, on the other hand, consisted of the mechanical activation of KR by grinding, since the surface area and particle size significantly influence the structural characteristics of KR and, consequently, the solubilization of potassium ions. The findings

contribute to a better understanding of the kinetics of dissolution of these different K minerals in organic acids, contributing to their wider use in sustainable agricultural practices.

2. Materials and Methods

2.1. Materials

Potassium rocks were used as mineral potassium sources. The polyhalite potassium mineral ($KR_{\text{polyhalite}}$) was extracted from the Boulby mine (North Yorkshire, United Kingdom). The Feldspar potassium mineral (KR_{feldspar}) was extracted from a mine in Poços de Caldas (Minas Gerais, Brazil). The samples of $KR_{\text{polyhalite}}$ and KR_{feldspar} were supplied by ICL Specialty Fertilizers (Brazil) and Yoorin Fertilizers (Brazil), respectively. The KCl sample (commercial fertilizer) was supplied by Adubos Vera Cruz, Ltd. (Brazil). Citric and oxalic acids (≥ 99 wt.%) were supplied by Synth (Brazil). Gluconic acid (49-53 wt.%) and hydrochloric acid (37 wt.%) were supplied by Sigma-Aldrich (Brazil).

2.2. Solubilization experiments

Solubilization of the potassium minerals was evaluated using distilled water and 0.1 M solutions of gluconic, oxalic, and citric acids. Hydrochloric acid solutions (0.1 and 1.0 M) were also evaluated for solubilization of the feldspar potassium mineral. All the experiments were performed in 1 L beakers with 600 mL of solution (water or acid), at room temperature (25 °C), according to the methodology described by Bortoletto-Santos et al. (2016). The mineral mass was standardized so that the potassium mass added was equivalent to 100 ppm, under all conditions, requiring of 1.1046 mg $KR_{\text{polyhalite}}$ and 1.5064 mg of KR_{feldspar} .

In each experiment, aliquots of 1 mL were removed at 6, 12, 24, 36, and 48 h. After this period, aliquots were removed every 24 h, during 10 days, and then every 48 h, until the 20th day. Subsequently, further aliquots were obtained every 5 days, until the 40th day. All the assays

were performed simultaneously, in order to ensure identical laboratory conditions. These aliquots were used for the determination of K^+ solubilized from $KR_{\text{polyhalite}}$ and KR_{feldspar} . Solubilization tests using KCl as standard were performed under the same conditions.

The solubilized potassium (K^+) was determined by flame atomic absorption spectroscopy (FAAS), using a PerkinElmer PinAAcle 900T instrument. The analytical conditions for K^+ were wavelength of 766.49 nm, slit width of 0.7 nm, and flame gas mixture of synthetic air (10 L min^{-1}) and acetylene (2.5 L min^{-1}).

Interpretation of the curves and the dissolution behavior employed a kinetic model that enabled evaluation of the potassium dissolution rates in different acids. The dissolution kinetic constants (k) were calculated for each assay, assuming that the nutrient release kinetics followed a second order reaction, with the velocity (v) proportional to the product of the molar concentrations of reagents A and B (Equation 1). The reaction rate constant, k , is the dissolution constant, while $[A]$ and $[B]$ are the concentrations of reactants A (acids or water) and B (solubilized nutrient), respectively.

From Equation 1 and considering the concentration of solvent A (water, citric acid, gluconic acid, oxalic acid, or hydrochloric acid) to be infinitely higher than the concentration of solute B (nutrient) in the medium, it could be assumed that its variation as a function of time was constant (Equation 2) and that the derivative of the molar concentration of A ($d[A]/dt$) was approximately zero. Hence, the concentration of A ($[A]$) could be approximated as the initial concentration of A ($[A]_0$), obtaining a new rate constant k' (Equation 3).

$$v = k [A] [B] \quad \text{Eq. 1}$$

$$\frac{d[A]}{dt} \approx 0 \quad \text{Eq. 2}$$

$$k = k' [A]_0 \quad \text{Eq. 3}$$

Replacing Equation 3 in Equation 1 results in a pseudo-first order rate law (Equation 4)

which can be rewritten considering variation of the concentration of B over time and integrating the pseudo-first order rate law, resulting in the equation describing the kinetic model (Equation 5).

$$v = k [A] [B] = k' [B] \quad \text{Eq. 4}$$

$$\frac{(d[B])}{dt} = -k' [B]$$

$$\int_{[B]_0}^{[B]} \frac{d[B]}{[B]} = -k' \int_0^t dt$$

$$\ln\left(\frac{[B]}{[B]_0}\right) = -k' t$$

$$[B] = [B]_0 e^{-k' t} \quad \text{Eq. 5}$$

Finally, it can be considered that the concentration of B at a given time t is equal to the initial concentration of B ($[B]_0$) minus the concentration of solubilized nutrient, that is, $[B] = [B]_0 - [B \text{ solubilized}]$. Rewriting Equation 5 leads to a typical exponential curve, where at zero time, the amount of solubilized nutrient is zero, while the amount solubilized at infinite time is 100% of the nutrient initially present in the material.

$$[Product] = [B]_0 (1 - e^{-k' t}) \quad \text{Eq. 6}$$

2.3. Strategies to enhance the solubilization of $KR_{feldspar}$

2.3.1. Biotechnological route. A screening using four *Aspergillus* strains was performed to determine their capacity for solubilization of $KR_{feldspar}$. The isolates used in this work were *Aspergillus niger* C, *Aspergillus niger* 3T5B8, *Aspergillus niger* F12, and *Aspergillus* 763, from the Embrapa Food Agroindustry collection (Rio de Janeiro, Brazil). Spore suspensions of the fungal strains were maintained at -18 °C in a solution of glycerol (30 wt.%) and NaCl (0.9 wt.%). The spores were germinated at 30 °C in Petri dishes containing potato dextrose agar

(PDA). After 96 h, a suspension of the cultivated spores was collected by adding Tween 80 solution (1 wt.%). The spore concentration was measured using a Neubauer chamber.

Evaluation was made of solubilization of the potassium mineral under submerged cultivation in Aleksandrov liquid nutrient medium (24), at $\text{pH}_{\text{initial}}$ 7.0, supplemented with 2 wt.% of $\text{KR}_{\text{feldspar}}$. The biological solubilization was initiated by the addition of 10^7 spores L^{-1} of the microorganism to the culture medium, with agitation for 96 h in an orbital shaker-incubator at 30 °C and 220 rpm. After the required period, the resulting material was vacuum filtered using Whatman No. 1 filter paper and then centrifuged for 20 min at 7000 rpm and 4 °C. The supernatant was analyzed to determine the soluble potassium content (Section 2.2). All the experiments were performed in triplicate and the data were calculated as means $\pm$ standard deviations.

2.3.2. Mechanochemical route. The $\text{KR}_{\text{feldspar}}$ was submitted to a grinding process in a high-energy ball mill (Fritsch Pulverisette 7), using a vessel with 5 zirconia spheres (10 mm diameter), with rotation at 700 rpm for 6 h. The pretreated $\text{KR}_{\text{feldspar}}$ was characterized in terms of particle size and surface area, as described in Section 2.4. After the pretreatment, the $\text{KR}_{\text{feldspar}}$ was solubilized for 48 h in citric acid (2 and 10 wt.%) at 25 °C and 30 rpm. The supernatant was analyzed to determine the soluble potassium content (Section 2.2). All the experiments were performed in triplicate and the data were calculated as means $\pm$ standard deviations.

2.4. Chemical and physical characterization

2.4.1. X-ray diffraction (XRD). X-ray diffraction (XRD) analyses of the potassium mineral samples were performed using a LabX XRD-6000 diffractometer (Shimadzu, Japan) operated with Cu $\text{K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$), voltage of 30 kV, and current of 30 mA. The diffractograms were recorded for 2θ from 4° to 90°, using a scanning speed of 1° min^{-1} .

2.4.2. X-ray fluorescence (XRF). XRF analyses of the two minerals were performed to identify the most common chemical components present in the structures, using the lithium tetraborate fusion technique.

2.4.3. Scanning electron microscopy (SEM). The morphologies of the minerals were observed by field emission gun scanning electron microscopy (FEG-SEM), using a Sigma microscope (Zeiss, Germany) operated at acceleration voltages of 2 and 4 kV, with a working distance of 10 mm and a secondary electron detector. The disc was coated with carbon in a Leica EMSCD050 chamber.

2.4.4. Determination of surface area. The specific surface areas of the two potassium minerals were determined by isothermal nitrogen adsorption, using a Micromeritics ASAP-2020 instrument, according to the 5-point B.E.T. (Brunauer-Emmett-Teller) method.

2.4.5. Determination of particle size. The average particle sizes of the potassium minerals were determined by dynamic light scattering (DLS), using a Zetasizer particle analyzer (Malvern Instruments). A portion of 10 mg of each sample was transferred to a 20 mL glass bottle containing 10 mL of distilled water. Prior to the DLS measurements, the solution was sonicated (Bransom, 450 W) for 10 min, in order to disperse the particles in the solution.

3. Results and Discussion

3.1. Chemical and physical characterization

The crystalline phases of KR_{polyhalite} and KR_{feldspar} were assessed using X-ray diffractometry (Fig. 1). The main crystalline phase of KR_{polyhalite} was K₂Ca₂Mg(SO₄)₄·2H₂O

(PDF2 diffractogram file #00-013-0526). It was also possible to observe minor phases such as halite (NaCl, PDF2 diffractogram file #00-005-0628), anhydrite (CaSO₄, PDF2 diffractogram file #00-037-1496), and gypsum (CaSO₄·H₂O, PDF2 diffractogram file #01-074-1904), as well as traces of quartz (SiO₂, PDF2 diffractogram file #01-070-3755). The identification of the KR_{polyhalite} phases was confirmed by X-ray fluorescence analysis (Table S1, Supplementary Material), which showed the presence of high quantities of K₂O (12.00 wt.%), SO₄²⁻ (40.84 wt.%), CaO (16.20 wt.%), and MgO (6.79 wt.%), which are the main constituents of polyhalite. These phases were consistent with the ones observed for similar polyhalite minerals by Xu et al. (2017).

The main crystalline phase observed for KR_{feldspar} was K-feldspar, with predominance of the potassium sodium aluminum silicate phase (K₅Na₅AlSi₃O₈, PDF2 diffractogram file #01-084-0710). The identification of the KR_{feldspar} phases was also confirmed by X-ray fluorescence analysis (Table S1, Supplementary Material), which showed the presence of high quantities of SiO₂ (55.10 wt.%), Al₂O₃ (20.04 wt.%), Na₂O (7.44 wt.%), and K₂O (8.35 wt.%), as well as significant quantities of Fe₂O₃ (3.88 wt.%) and CaO (1.70 wt.%). The presence of these species confirmed that this mineral was a K-feldspar. K-feldspar minerals, or tectosilicates, are important components of most felsic igneous minerals, pegmatites, low temperature hydrothermal veins, and many metamorphic minerals, especially those formed from the alteration of shale or felsic igneous minerals (26). The feldspar crystal lattice presents corner-sharing, with [SiO₄] and [AlO₄] tetrahedrally linked in an infinite 3D structure (12). This structure has high crystallinity, which makes the mineral hard and hinders solubilization of the potassium present. On the other hand, KR_{polyhalite} crystallizes in a triclinic symmetry, with the space group $P\bar{1}$ or $F\bar{1}$ (27, 28). The polyhalite structure consists of tetrahedral [SO₄²⁻], octahedral [MgO₆], and triangular [CaO₈] dodecahedra, with K located in an 11-oxygen-coordinated position (25). Although KR_{polyhalite} has a complex crystal structure, it is a mineral

of sedimentary origin, which makes its solubilization more favorable, compared to igneous minerals.

The morphological aspects and the physical and chemical characteristics of KR_{feldspar} and $KR_{\text{polyhalite}}$ are shown in Table S1 and Fig. 2. Table S1 also shows the chemical analysis for each KR, highlighting the K_2O contents of 8.35 and 12 wt.% for KR_{feldspar} and $KR_{\text{polyhalite}}$, respectively. As shown in Fig. 2, both potassium rocks presented smooth morphology with low roughness, which could explain their low surface areas. Both KR_{feldspar} and $KR_{\text{polyhalite}}$ also showed the presence of particle agglomerates around 2 μm in size.

3.2. Effect of organic acid type on potassium solubilization

The solubilization of potassium (K^+) from KCl, $KR_{\text{polyhalite}}$, and KR_{feldspar} in water and different organic acids (gluconic, oxalic, and citric acids) is presented in Fig. 3. These organic acids were chosen because they are commonly produced by many microorganisms found in soil and can act to promote the solubilization of potassium rock (29). KCl is the most common source of K^+ used in agriculture, given its high K^+ solubilization (30). Therefore, this fertilizer was used as a K^+ release control, for comparison with $KR_{\text{polyhalite}}$ and KR_{feldspar} . The rapid release of K^+ from KCl can be seen in Fig. 3a, which shows the solubilization profiles in water and organic acids. The type of organic acid did not appear to significantly influence the solubilization of K^+ from KCl, with high K^+ dissolution rate constants obtained using all these acids (Table 1).

The solubilization profiles of $KR_{\text{polyhalite}}$ are shown in Fig. 3b. The K^+ release reached 100% in water and all the organic acids, after 6 days. The solubilization temporal profiles were similar for all the organic acids, showing that the nature of the organic acid did not influence the K^+ release (Table 1). The high solubilization of K^+ from $KR_{\text{polyhalite}}$ could be explained by the structural characteristics of this mineral of sedimentary origin. Nonetheless, $KR_{\text{polyhalite}}$ has

a complex crystal structure, making it less soluble in water, compared to traditional potassium sources, such as KCl (31).

In contrast, KR_{feldspar} showed K^+ solubilization lower than 30% for the different conditions (Fig. 3c). This could be explained by the structural characteristics of the KR_{feldspar} , since the cation is contained in a highly stable and resistant crystalline aluminum silicate structure, which makes its release more difficult (20). The igneous origin of KR_{feldspar} results in lower reactivity, compared to the sedimentary rock ($KR_{\text{polyhalite}}$).

Interestingly, different from the results observed for $KR_{\text{polyhalite}}$, the organic acids significantly influenced the solubilization of K^+ from KR_{feldspar} , compared to the solubilization in water, which was too low to permit kinetic calculations (Table 1). In addition, the kinetic parameters (Table 1) showed that the solubilization rate was not directly associated with the maximum amount of K^+ solubilized. Although the highest K^+ solubilization rate was observed using citric acid, the order of maximum K^+ solubilization from KR_{feldspar} was oxalic acid (34.86 mg L^{-1}) > gluconic acid (23.06 mg L^{-1}) > citric acid (17.63 mg L^{-1}) > water (7.51 mg L^{-1}). This difference in the potential of organic acids to solubilize the KR_{feldspar} could be mainly attributed to their physical and chemical properties, such as their different acidification capacities. The maximum K^+ solubilization using oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) could be explained by its high acidification capacity and high acid dissociation (low pK_{a1}), as shown in Table 2. Oxalic acid has a structure containing two neighboring carboxylic groups, so that the interaction of these carboxylic groups favors their dissociation, making the acid relatively strong ($\text{pK}_{\text{a1}} = 1.27$) (32, 33). It is possible that the solubilization process could also be influenced by other mechanisms, such as chelation or complexation processes involving these organic acids.

The solubilization results obtained for citric acid and gluconic acid were also related to the acidification capacities of these acids, with the supply of protons (H^+) being the main factor driving solubilization (33). Despite their different chemical structures, gluconic acid

(monocarboxylic) and citric acid (tricarboxylic) showed similar performance for the solubilization of K^+ from $KR_{feldspar}$. These acids showed lower solubilization potential than oxalic acid, due to their lower acidification capacity, which could be explained by their lower dissociation constants (higher pK_a), with pK_{a1} values of 3.13 and 3.62 for citric acid and gluconic acid, respectively (Table 2) (33–35).

As already mentioned, the supply of protons is one of the factors determining the solubilization and acidification capacities of organic acids. Therefore, additional tests were performed using hydrochloric acid (an inorganic acid) to assess whether increase of the concentration of an inorganic acid could enhance solubilization of K^+ from $KR_{feldspar}$. The K^+ solubilization results using HCl at two different concentrations (0.1 and 1 M) are shown in Fig. 3d. For both conditions, solubilization did not exceed 18.69 mg L^{-1} , indicating that the HCl concentration did not influence solubilization of K^+ from $KR_{feldspar}$. The findings also indicated that oxalic acid had a greater influence on K^+ solubilization, compared to the inorganic acid. Similar behavior was observed in the study by Mendes et al. (2020), who evaluated the solubilization of different phosphate minerals in sulfuric acid and in organic acids including oxalic, citric, gluconic, itaconic, and malic acids. Only oxalic acid and sulfuric acid solubilized 100% of the phosphate in all the minerals. However, the action of oxalic acid was stronger than that of sulfuric acid, solubilizing more phosphate per mmol of applied acid. This could be explained by the fact that in addition to the protonation effect and the high acidification power of oxalic acid, this acid has a powerful chelating effect on metals, especially aluminum (Al) (3, 33). Therefore, oxalic acid could act on the potassium mineral by acidification and proton exchange, binding to Al and removing it from the tetrahedral structure of the mineral, which destabilized the crystalline network and consequently increased the solubilization of potassium.

3.3 Characterization of residual KR materials

After the solubilization tests, the residual KR materials were separated and analyzed by XRD to identify the structures of the remaining phases. Fig. 4 shows the XRD patterns for the residual $\text{KR}_{\text{polyhalite}}$ and $\text{KR}_{\text{feldspar}}$ after solubilization in water and the different acids. The KCl was completely solubilized during the tests, so no residual material remained at the end of the experiment.

The XRD patterns of the $\text{KR}_{\text{polyhalite}}$ material (Fig. 4b-e) showed the formation of new crystalline phases in the mineral after the solubilization procedures, which were not present in the original $\text{KR}_{\text{polyhalite}}$, evidencing that solubilization had occurred. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, diffractogram file PDF2 #00-033-0311) was the main crystalline phase identified after the treatments using water (Fig. 4b), gluconic acid (Fig. 4c), and citric acid (Fig. 4e). This was due to the presence of gypsum in natural $\text{KR}_{\text{polyhalite}}$, as well as its possible formation during the solubilization process, since $\text{KR}_{\text{polyhalite}}$ has high contents of Ca^{2+} and SO_4^{2-} . Gypsum has low water solubility (36), so the phase did not dissolve during the experiment. However, the presence of gypsum was not observed in the residual material after the solubilization with oxalic acid, since oxalic acid has high capacity to chelate and complex calcium (Hannig et al., 2005; Mendes et al., 2020), forming $\text{C}_2\text{CaO}_4 \cdot \text{H}_2\text{O}$ (calcium oxalate, PDF2 diffractogram file #00-020-0231). These results corroborated the EDX analyses (Fig. S1, Supplementary Material) showing the main presence of Ca^{2+} and SO_4^{2-} in the residual materials after the treatments using water, gluconic acid, and citric acid, but only Ca^{2+} after the treatment using oxalic acid.

The residual materials from $\text{KR}_{\text{feldspar}}$ solubilized in water and the acids (Fig. 4g-l) presented crystalline phases similar to those of the XRD pattern of natural $\text{KR}_{\text{feldspar}}$ (Fig. 4f). However, greater dampening of the diffraction peaks characteristic of the K-feldspar phase was observed for the treatments using oxalic acid (Fig. 4i), 1 M HCl (Fig. 4l), and especially citric acid (Fig. 4j), for which around 50% dampening was observed. The EDX analysis (Fig. S1,

Supplementary Material) also showed the presence of K^+ , Na^+ , Al^{3+} , and Si, demonstrating that complete solubilization of $RK_{feldspar}$ was not achieved with any of the media evaluated.

3.4. Strategies to enhance the solubilization of $KR_{feldspar}$

The low solubility of $KR_{feldspar}$ has aroused interest in the study of possible strategies to enhance the release of K^+ from its structure. The dissolution process of this mineral involves complex reactions and mechanisms, such as the release of cations by ion exchange, adsorption/desorption of dissolved elements on the mineral surface, hydrolytic degradation of the tetrahedral bonds, and the protonation of Al^{3+} and Si present in the crystalline network of the mineral. High acidity of the medium, active inorganic binders, and the presence of defects in the mineral structure can contribute to the solubilization of this mineral (12). The results obtained in this work demonstrated that organic metabolites could positively influence the solubility of the mineral, although K^+ release remained low (34.86 mg L^{-1} in oxalic acid). However, the use of biotechnological and/or mechanochemical routes has previously been shown to be promising for the release of minerals from the soil (2, 9, 38). Fig. 5 shows the effects of these two strategies on the solubilization of K^+ from $KR_{feldspar}$. The biotechnological route uses microorganisms in a submerged culture process, while the mechanochemical route involves pretreatment of the mineral usually by grinding (Fig. 5a).

Fig. 5b shows the K^+ solubilized from $KR_{feldspar}$ in the presence of different strains of *Aspergillus*. These filamentous fungi are known to be good producers of organic acids, with the potential to solubilize minerals present in the soil (39). Among the strains evaluated, *Aspergillus niger* C showed the highest showed the highest solubilization (63.2 mg L^{-1}), which was higher than the tests using organic acids. This fungal strain has also shown the potential to solubilize phosphate minerals (9, 10). The release of nutrients from minerals using the biotechnological route is directly influenced by the physical interaction between the microorganism and the mineral during cultivation. Microorganisms have the ability to bind to the mineral surface, as

well as to penetrate mineral particles by the growth of hyphae, exerting a physical force capable of fragmenting parts of the mineral, reducing the particle size and generating more reactive surfaces (38, 40). Another mechanism is the possible production of extracellular polysaccharides and other polymeric substances capable of creating microenvironments where organic acids can become concentrated and adhesion of the fungal hyphae to the mineral surface is facilitated (40). The results showed the beneficial effect of the biotechnological route for the solubilization of $\text{KR}_{\text{feldspar}}$. In addition, some variables of the cultivation process, such as the type and concentration of the carbon source, as well as the initial pH of the cultivation, could be further investigated to optimize the production of oxalic acid, since this organic acid presented the greatest solubilization potential, among the organic acids studied. The control of cultivation variables within specific ranges could induce the microorganism to produce the desired organic acid (in this case, oxalic acid) (41), which could further contribute to increased K^+ release.

Fig. 5c shows the results obtained for the solubilization of $\text{KR}_{\text{feldspar}}$ after 48 h, without and with application of the mechanochemical process. Under these conditions, the solubility of 2 wt.% $\text{KR}_{\text{feldspar}}$ increased 8.6 times after grinding (993 mg L^{-1}), compared to the natural material, while an increase of 2.6 times was observed for 10 wt.% $\text{KR}_{\text{feldspar}}$ (1329 mg L^{-1}). The increased solubility of the mineral was mainly due to particle fragmentation, with a surface area of $6.83 \text{ m}^2 \text{ g}^{-1}$ obtained after the pretreatment, which was around 2.5-fold higher than the surface area of the natural $\text{KR}_{\text{feldspar}}$. The K^+ retained in the $\text{KR}_{\text{feldspar}}$ structure could then be released more easily, due to the structural disorder of the system caused by the grinding process (11, 12). The higher surface area resulting from the reduction in particle size enabled greater interaction between citric acid and the mineral particles, consequently enhancing the physical and chemical processes on the surface of $\text{KR}_{\text{feldspar}}$, leading to greater solubilization. The high solubilization in citric acid of K^+ present in $\text{KR}_{\text{feldspar}}$ after grinding (up to 72%) showed that

use of the mechanochemical route is a promising strategy for increasing the solubility of low reactivity potassium minerals such as KR_{feldspar} . These results corroborated previous studies of the solubilization of low solubility phosphate minerals, where use of a grinding process for different times led to improved phosphorus release (10, 42). Therefore, these solubilization routes are promising strategies for potassium availability/release in organic acids, contributing to a better understanding and use of low reactivity potassium rocks as K-fertilizer in sustainable agriculture.

4. Conclusions

The results showed that the type of organic acid affected the extent of solubilization of low reactivity potassium rocks. Organic acids were more effective in solubilizing an igneous potassium rock (KR_{feldspar}), compared to inorganic acid. Oxalic acid showed the greatest potential for solubilization of K^+ from the two types of potassium rock investigated (KR_{feldspar} and $KR_{\text{polyhalite}}$). The solubilization strategies were shown to be promising routes for the release of K^+ . The biotechnological route, which involved direct physical interaction between the microorganism and the KR, improved the solubilization of K^+ when compared to the organic acid tests. In addition, application of a mechanochemical treatment significantly increased the surface area and decreased the size of the particles, changing the structural characteristics of the KR and increasing the solubility of KR_{feldspar} in citric acid around 8.6-fold, compared to the natural rock. These findings contribute to a better understanding of the solubilization in organic acids of potassium rocks from different sources, including a low reactivity potassium rock, which could improve the efficiency of these rocks used in more sustainable agricultural practices.

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Declarations

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Availability of data and materials

Data will be available upon request.

Code availability

Not applicable.

Authors' contributions

Ludimila A. Lodi: Writing - review & editing, Conceptualization, Methodology, Data curation, Formal analysis, Investigation, Roles/Writing - original draft; Rodrigo Klaic: Writing - review

& editing, Conceptualization, Data curation, Formal analysis, Roles/Writing - original draft; Ricardo Bortoletto-Santos: Writing - review & editing, Formal analysis, Roles/Writing - original draft; Caue Ribeiro: Writing - review & editing, Funding acquisition, Supervision; Cristiane S. Farinas: Writing - review & editing, Conceptualization, Funding acquisition, Supervision.

Competing interests

The authors declare that they have no competing interests.

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Figure Captions

Fig. 1 X-ray diffraction (XRD) patterns of a) $\text{KR}_{\text{polyhalite}}$ and b) $\text{KR}_{\text{feldspar}}$, together with the mineral phases identified and the corresponding XRD patterns

Fig. 2 High resolution electron microscopy (SEM-FEG) micrographs for a) $\text{KR}_{\text{polyhalite}}$ and b) $\text{KR}_{\text{feldspar}}$

Fig. 3 Temporal profiles of K^+ solubilization: a) KCl in water, gluconic acid, oxalic acid, and citric acid; b) $\text{KR}_{\text{polyhalite}}$ in water, gluconic acid, oxalic acid, and citric acid; c) $\text{KR}_{\text{feldspar}}$ in water, gluconic acid, oxalic acid, and citric acid; d) $\text{KR}_{\text{feldspar}}$ in 0.1 and 1 M HCl. The vertical bars are standard deviations. Dotted lines are only a guide to the eyes

Fig. 4 X-ray diffraction (XRD) patterns of the natural minerals and the materials remaining after solubilization: natural $\text{KR}_{\text{polyhalite}}$ (a) and $\text{KR}_{\text{polyhalite}}$ solubilized in water (b), gluconic acid (c), oxalic acid (d), and citric acid (e); natural $\text{KR}_{\text{feldspar}}$ (f) and $\text{KR}_{\text{feldspar}}$ solubilized in water (g), gluconic acid (h), oxalic acid (i), citric acid (j), 0.1 M HCl (k), and 1 M HCl (l)

Fig. 5 Potassium solubilization using different strategies: a) Representative scheme of the strategies used; b) Biological solubilization by different microorganisms in submerged culture in Aleksandrov medium for 4 days, using 2 wt.% $\text{KR}_{\text{feldspar}}$, $\text{pH}_{\text{initial}}$ 7.0, 30 °C, and 220 rpm; c) Solubilization of $\text{KR}_{\text{feldspar}}$ in its natural state and after mechanochemical treatment in citric acid for 2 days at 30 rpm

TABLES

Table 1 Kinetic parameters obtained using the pseudo-first order model

Dissolution	Water	Gluconic	Oxalic	Citric	HCl (0.1 M)	HCl (1 M)
KCl	452.8	1170.1	1170.1	224.8	Nd	nd
KR_{polyhalite}	35.3	20.4	25.9	24.8	Nd	nd
KR_{feldspar}	#	2.6	5.8	7.6	7.2	47.8

nd: Experiment not carried out.

#: Dissolution less than 1% (the proposed mathematical model could not be used).

Table 2 Molecular structures, acidity constants (pK_a), and numbers of carboxylic groups for oxalic, citric, and gluconic acids

Organic acid	Chemical Structure	Chemical formula	$pK_{a1}^{\dagger}$	pK_{a2}	pK_{a3}	-COOH groups
Oxalic acid		$C_2H_2O_7$	1.27	4.27	-	2
Citric acid		$C_6H_8O_7$	3.13	4.76	6.40	3
Gluconic acid		$C_6H_{12}O_7$	3.62	-	-	1

[†] pK_a : negative logarithm of the acid dissociation constant at 25 °C.

Fig. 1

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Fig. 2

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Fig. 3

Fig. 4

Fig. 5

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