

Potassium extraction from the silicate rock Verdete using organic acids

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Edited by: Tiago Osório Ferreira

Received June 02, 2020

Accepted January 15, 2021

ABSTRACT: Although Brazil is one of the world's leading exporter of agricultural products, the country is highly dependent on the importation of potassic fertilizers. K-bearing silicate rocks are reported as potential solutions to reduce external K dependency. This work evaluated K extraction from silicate Verdete rock, a glauconite-bearing rock containing 10 % of K₂O, by solubilization with organic acids. Firstly, Verdete rock was reacted during 3-120 h with solutions of citric or oxalic acid at 2 % (m/v) in Erlenmeyer flasks by shaking. Oxalic acid extracted 6.5 % of K in Verdete, while citric acid extracted 2.3 %. Another experiment was performed to evaluate the effect of various oxalic acid concentrations (2, 4, 6, 8, and 10 %) and differing reaction times (12, 24, 48, and 72 h) on K extraction from Verdete rock. Soluble K concentration nearly doubled with the increase of reaction time from 12 to 72 h, rising from 20 to 37 mg L⁻¹. Increments in K extraction were obtained by increasing oxalic acid concentrations up to 6 % and above this concentration, no significant gain was observed. The X-ray diffraction data showed that K extraction resulted from the formation of oxalate-metal complexes with metals in Verdete rock.

Keywords: glauconite, bioleaching, oxalate, fertilizer

Introduction

Potassium (K) is a critical nutrient for croplands worldwide. Although Brazil is considered a 'global farm' (Tollefson, 2010), most potash fertilizer applied in Brazilian agriculture is imported (ANDA, 2017). Therefore, freight costs greatly affect prices, an issue shared by other tropical countries in the southern hemisphere (Ciceri et al., 2017; Manning, 2018). The development of technologies that enable the exploration of local K sources to substitute imports can reduce costs.

Brazil has been depleting K reserves of potash ores of high solubility, such as sylvinite (KCl/NaCl mixture) and carnallite (KCl.MgCl₂.6H₂O) (DNPM, 2018). Nevertheless, there are large reserves of easily extractable K-silicate rock resources near the soil surface, such as Verdete rock, which contains around 10 % K₂O and its reserves are estimated at 10⁸ t (Luz et al., 2010; Safatle et al., 2020; Santos et al., 2015a). Since Brazilian deposits of soluble K sources supply less than 10 % of the demand for K, silicate rocks, such as Verdete rock, have been suggested as alternative K sources for agriculture (Luz et al., 2010; Santos et al., 2015a). However, due to the low solubility, these K-rich silicate rocks need physical, chemical, or biological treatment to make K available to plants in a short term (Ciceri et al., 2017; Matias et al., 2019; Santos et al., 2015b). Most of these treatments rely on high temperatures to achieve K solubilization (Ciceri and Allanore, 2020; Santos et al., 2015a), which is energetically unfavorable.

Microorganisms have been proposed as an alternative to produce soluble K fertilizer from K-rich silicate rocks (Lopes-Assad et al., 2010; Matias et al., 2019; Xue et al., 2019) or as soil inoculants to improve K availability to plants (Maity et al., 2014; Zhang and Kong, 2014). Citric and oxalic acids are microbial metabolites

involved in the biochemical weathering of rocks and minerals (Gadd, 1999, 2007, 2017a). These organic acids can weaken the mineral structure and release rock components through acidulation and complexation of cations (Gadd, 2017a; Stumm, 1986). There are reports on citric acid as a K extractor from K-bearing silicate rocks (Pessoa et al., 2015; Santos et al., 2015a); however, information on oxalic acid effectiveness is scarce. Citric and oxalic acid could possibly dissolve minerals in Verdete rock and thus release K. This research evaluated K extraction from Verdete rock using organic acids involved in mineral solubilization.

Materials and Methods

K source

Verdete samples were collected from a rock outcrop on the border between the municipalities of Quartel Geral and Serra da Saudade, in Minas Gerais State, Brazil (19° 17' 59.0" S, 45° 44' 16.9" W, altitude of 842 m) (Figure 1). Previous works have characterized Verdete as a sedimentary rock composed mainly by glauconite (40-80 %), whose origin may be related to marine transgression, resulting in diagenetic substitution with K⁺ into clay minerals (Moreira et al., 2016; Safatle et al., 2020).

The rocks were ground in a hammer mill and sieved to obtain particle size of ≤ 74 μm (200 mesh). The chemical composition of Verdete rock (Table 1) was previously determined by X-ray fluorescence (XRF) (Schimicoscki et al., 2020). Mineralogical characterization by X-ray diffraction (XRD) indicated that Verdete rock is composed mainly by aluminosilicates, with typical diffraction peaks of K feldspar, mica (muscovite and glauconite), and quartz (Safatle et al., 2020). The loss on ignition was 4 %.

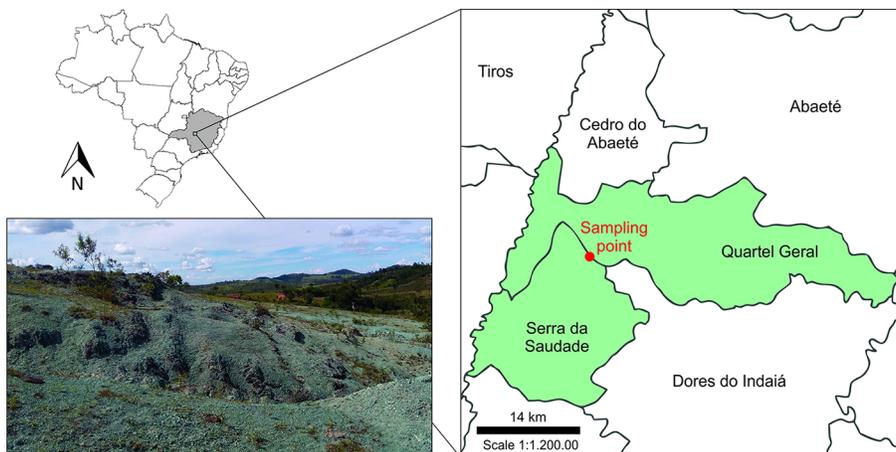


Figure 1 – Location map showing a detailed view of the municipalities where the Verdete samples were collected (red circle). The bottom left panel shows a picture of the outcrop.

Table 1 – Chemical composition of Verdete rock.

Compound	Mass fraction %
SiO ₂	60.29
Al ₂ O ₃	16.04
K ₂ O	11.28
Fe ₂ O ₃	7.36
MgO	3.10
Br	1.35
TiO ₂	0.93
V ₂ O ₅	0.12
P ₂ O ₅	0.09
Rb ₂ O	0.06
MnO	0.05
ZrO ₂	0.03
ZnO	0.02
Cr ₂ O ₃	0.02
NiO	0.01

Data obtained from Schimicoski et al. (2020).

K extraction from Verdete rock with organic acids

We performed a first experiment to compare the efficiency of citric and oxalic acids to extract K from Verdete rock. The reactions were carried out in 125-mL Erlenmeyer flasks containing 0.4 g of Verdete rock and 40 mL of 2 % (m/v) aqueous solutions of citric or oxalic acids. Acid concentration was based on Pessoa et al. (2015) applying 2 % of citric acid as an extractant for K-bearing ores. The flasks were sealed with parafilm and placed in an orbital shaker at 150 rpm and 30 °C. Three flasks were taken at 3, 6, 9, 12, 24, 48, 72, 96, and 120 h and the content was filtered through quantitative filter paper (pores 25 μm, 80 g m⁻²). The concentration of soluble K was determined by flame photometry. Controls consisted of flasks containing Verdete and distilled water. The initial solution was kept throughout the entire experiment.

As oxalic acid performed better in the first experiment, another assay was carried out to evaluate the effect of oxalic acid concentration (2, 4, 6, 8, and 10 %) and the reaction time (12, 24, 48, and 72 h) on K extraction from Verdete rock. The two factors were combined in a 5 × 4 factorial scheme. The reactions were carried out in the same conditions described above. At each collection time, three flasks were taken and the content was vacuum filtered through a 0.45-μm membrane. The insoluble fraction retained on the membrane was collected and analyzed by XRD. The concentration of soluble K in the filtrate was determined by flame photometry.

XRD analyses

Powder samples of three repetitions were combined for the analyses. XRD was performed in a Shimadzu XRD 6000 X-ray diffractometer, applying Cu Kα radiation ($\lambda = 1.54056 \text{ \AA}$) and operated at 30 mA current and 40.0 kV voltage. Scans were performed continuously from 5° to 55° 2θ with a rate of 2° min⁻¹. Diffractograms of samples were compared to diffraction peaks of Verdete rock and to standard peaks obtained in the Inorganic Crystal Structure Database (ICSD) (K-feldspar 10270, muscovite 74608, and quartz 174) and to the American Mineralogist Crystal Structure Database (AMCSD) (glauconite 5026). XRD scans were shown in relative intensities; therefore, no quantitative estimates were carried out.

Chemical equilibrium modeling

We conducted a simulation in the software Visual MINTEQ 3.1 to estimate the concentration and activity of the main chemical species formed between metals in Verdete rock and oxalic acid. All chemical components of Verdete rock (Table 1) were included in the simulation at

amounts corresponding to the concentration of Verdete used in the experiments, that is, 1 % (m/v). Oxalate was included at 2 % (m/v). Visual MINTEQ was run using the following settings: pH calculated from mass balance, ionic strength fixed at 0.01, temperature 25 °C, activity correction by Debye-Hückel method, and oversaturated solids were allowed to precipitate, only after the final answer was reached. The other parameters were kept as software standards.

Statistical analyses

The experiments were conducted in a completely randomized design (CRD) with three repetitions per treatment. The data were subjected to the regression analysis. The significance of coefficients was analyzed by the *t* test ($p < 0.01$). A response surface model (RSM) was fitted using the experiment data with different oxalic acid concentrations and reaction times. RSM was performed to study the combined effect of both factors on K extraction and fit a multiple regression model (Myers et al., 2016). Non-significant coefficients ($p > 0.1$) were removed from the model (Mendes et al., 2013). The Minitab 18 software was used for the RSM analysis and for the creation of the contour plot.

Results

Oxalic acid provided the highest concentration of soluble K, reaching an extraction of 6.5 % (60.5 mg K L⁻¹) of K in Verdete rock (Figure 2). Citric acid, in turn, allowed only 2.3 % (22 mg K L⁻¹) of K extraction. The control with distilled water presented 3.6 mg soluble K L⁻¹. The kinetics of K extraction was different between the acids. The reaction with oxalic acid was faster, presenting an exponential rise of soluble K until reaching a plateau after 48 h. On the other hand, citric acid showed a linear increase in soluble K in the timeframe evaluated.

Oxalic acid was further investigated for its influence of the concentration and reaction time on K extraction from Verdete rock. Both variables significantly affected K extraction; however, the variables did not

interact significantly ($p = 0.73$). Regardless of oxalic acid concentrations, the longer the reaction time, the greater the amount of solubilized K (Figure 3A). On the other hand, increasing oxalic acid concentration was only efficient up to 6 %. Above this concentration, there was no more significant increment of the soluble K concentration (Figure 3B). The model fitted by RSM [$K \text{ (mg L}^{-1}\text{)} = 10.02 + 0.729 \text{ oxalate (\%)} + 0.2976 \text{ time (h)}$] had a determination coefficient (R^2) of 88.1 %. The contour plot clearly showed that the reaction time had more influence on the amount of solubilized K than the oxalic acid concentration (Figure 3C).

XRD patterns showed that Verdete rock was composed of K-feldspar, micas (muscovite and glauconite), and quartz (Figure 4). The main diffraction peaks attributed to K-feldspar (ψ) were located at 20.9°, 23.5°, 25.7°, 26.7°, 27.6°, 41.8°, and 50.8°. XRD peaks corresponding to muscovite (μ), phyllosilicate of the mica group, was found at 8.9°, 17.8°, 19.6°, 29.8°, 34.7°, 37.0°, 42.5°, and 45.5°. Most XRD lines for glauconite overlapped those of muscovite. However, the greenish color and softness, due to a laminar structural organization, indicate that the rock was also composed of glauconite (Safatle et al., 2020). XRD peaks at 20.7° and 26.5° (θ) demonstrated the presence of quartz.

The XRD patterns of the reaction products were very similar to the XRD pattern of Verdete rock (Figure 4). Characteristic peaks of K-feldspar, micas, and quartz were all present, with similar intensities and widths at half height. Peaks of 9°, 17.8°, and 45.5°, attributed to micas, showed a relative decrease compared to Verdete with increasing time and oxalic acid concentrations, suggesting a change in the crystal structure of these minerals. Perhaps the most interesting fact is the appearance of peaks at 18.7° and 28.9°, represented by α (upper right corner of Figure 4), and possibly related to formation on oxalate-metal complexes.

Discussion

In this research, oxalic and citric acids were tested as reactants for K extraction from Verdete rock. Reaction

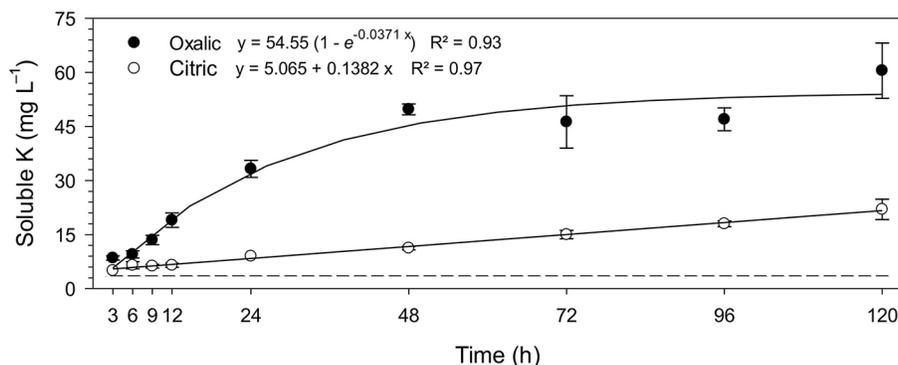


Figure 2 – Solubilized K from Verdete incubated during 120 h with a 2 % solution of oxalic or citric acid. The dashed line represents control with distilled water. Error bars represent standard deviation ($n = 4$). All regression coefficients are significant (*t* test, $p < 0.01$).

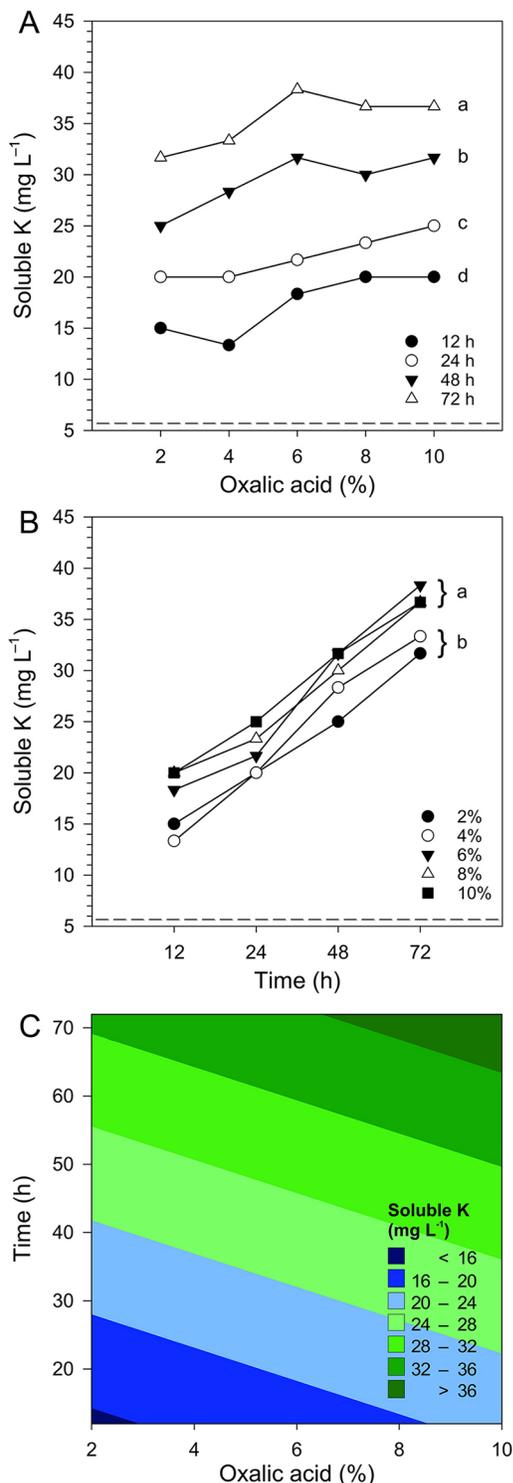


Figure 3 – Solubilized K from Verdete in terms of oxalic acid concentration and reaction time. A and B compare the reaction times and oxalic acid concentrations, respectively. Treatments with the same letter are not significantly different (Tukey test, $p < 0.05$). C) Contour plot showing the combined effect of the variables on solubilized K according to RSM. The dashed line represents control with distilled water.

with oxalic acid was faster and extraction of K was 275 % higher than citric acid after 120 h (Figure 2). The structure of oxalic acid ($C_2H_2O_4$) is composed of two adjacent carboxyl groups, which increases the dissociation constant (pK_{a1} 1.25, pK_{a2} 3.81) (Lide, 2004; Riemenschneider and Tanifuji, 2011) and facilitates the formation of oxalate-metal complexes and the precipitation of metal oxalates, depending on the metal and the chemical conditions (Gadd et al., 2014; Sarver and Brinton, 1927; Sayer and Gadd, 1997). Acidulation of micaceous minerals promotes K release due to the replacement of K^+ by H^+ ions in the interlayer space of the mineral (Schimicoscki et al., 2020; Varadachari, 1997). Additionally, the removal of Al, Fe, and Mg cations from the octahedral sheet disturbs the morphology of glauconite, loosening the mineral structure (Hassan and Baioumy, 2006; Schimicoscki et al., 2020). Al-, Fe-, and Mg-oxalate show very low aqueous solubility (Table 2) and, according to the chemical equilibrium model, more than 99 % of Al, Fe, and Mg were complexed by oxalate at the experimental conditions used (Table 3). Therefore, oxalic acid could provide H^+ to replace K^+ and remove cations from the structure of micas in Verdete rock. Indeed, our XRD data suggested the formation of metal-oxalate complexes with metals in Verdete rock (such as Al, Fe, Mg, Mn, Ni, and Zn) and a change in mica crystallinity (Figure 4). On the other hand, solubility of K-oxalate is higher, differently from most metal oxalates (Table 2); thus, K^+ was released into the solution. The chemical equilibrium model predicted that 72 % of K released was free K^+ and the remaining was complexed with oxalate (Table 3). However, the K-oxalate complex showed high activity (Table 3), suggesting that all K extracted from Verdete rock is available for plant uptake.

Citric acid can also contribute to acidulation of rocks and minerals; however, its capacity to form

Table 2 – Aqueous solubility of selected metal oxalates.

Metal	Oxalates	Aqueous solubility ^c
Al	$Al_2(C_2O_4)_3^a$	Insoluble
Cr	$CrC_2O_4^b$	Soluble
Fe	$FeC_2O_4 \cdot 2H_2O^b$	0.078 ²⁵
	$Fe_2(C_2O_4)_3^b$	Soluble
K	$K_2C_2O_4 / K_2C_2O_4 \cdot H_2O^b$	36.4 ²⁰
	$K_3Fe(C_2O_4)_3 \cdot 3H_2O^b$	4.7 ⁰
	$K_2TiO(C_2O_4)_2^a$	Soluble
Mg	$MgC_2O_4 / MgC_2O_4 \cdot 2H_2O^b$	0.038 ²⁵
Mn	$MnC_2O_4 \cdot 2H_2O^b$	0.032 ²⁰
Ni	$NiC_2O_4^a$	Insoluble
Zn	$ZnC_2O_4 / ZnC_2O_4 \cdot 2H_2O$	0.0026 ²⁵

Data obtained from ^aO'Neil (2013) and ^bLide (2004). ^cSolubility is expressed as the number of compound grams (excluding any water of hydration) that dissolve in 100 g of water. The temperature in °C is given as a superscript. Qualitative information on the solubility in water is given if quantitative data was unavailable.

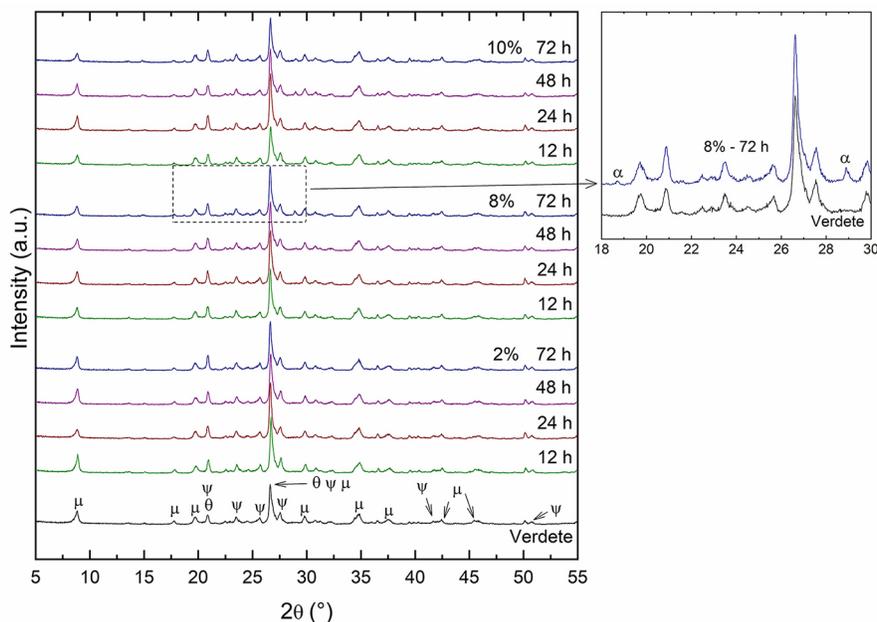


Figure 4 – X-ray diffractogram of Verdete rock and insoluble fractions of reaction products after attacking the rock with oxalic acid at 2, 8, and 10 %, for 12, 24, 48 and 72 h. ψ , μ , θ , and α identify peaks corresponding to K-feldspar, muscovite/glaucanite, quartz, and oxalate-metal complexes, respectively.

Table 3 – Estimated concentration and activity of the main chemical species formed by metals in Verdete rock in a solution of 2 % (m/v) oxalic acid. Data were obtained from a simulation in Visual MINTEQ with concentrations of elements based on the addition of Verdete rock at 1 % (m/v).

Metal	Species name	% of total metal Concentration	Concentration	Log activity
			mmol L ⁻¹	
Al	Al(Oxalate) ₃ ⁻³	99.80	31.405	-1.907
Fe	Fe(Oxalate) ₃ ⁻³	99.97	8.5937	-2.47
K	K ⁺¹	72.40	17.332	-1.808
	K-Oxalate ⁻	27.55	6.5956	-2.226
Mg	Mg-Oxalate	99.42	7.6468	-2.116
Mn	Mn(Oxalate) ₂ ⁻²	64.60	0.005836	-5.413
	Mn-Oxalate	35.30	0.003189	-5.495
Ni	Ni(Oxalate) ₂ ⁻²	99.43	0.01338	-5.053
Zn	Zn(Oxalate) ₂ ⁻²	98.38	0.0004	-6.397

sparingly-soluble metal complexes is lower than that of oxalic acid (Gadd, 1999, 2017b; Lide, 2004). Contrary to oxalates, Al, Fe-, and Mg-citrate complexes are water-soluble (Lide, 2004). Moreover, citric acid (pK_{a1} 3.13, pK_{a2} 4.76, pK_{a3} 6.40) is weaker compared to oxalic acid (pK_{a1} 1.25, pK_{a2} 3.81) (Lide, 2004). This explains the lower K extraction from Verdete rock by citric acid. Likewise, oxalic acid was superior to citric acid for phosphate extraction from various rock phosphates (Kpombrekou-A and Tabatabai, 1994, 2003; Mendes et al., 2020).

Oxalic acid is a key factor in microbial transformations of metals and minerals, playing an important role in element cycling, bioweathering, and formation of secondary minerals (Gadd, 2017a, b; Gadd et al., 2014). Fungal bioweathering of muscovite in laboratory and soil conditions has been observed, showing a network of channels formed by disruption of the mineral surface because of fungal hyphae growth, which was called fungal footprints (Wei et al., 2012). The authors attributed fungal footprints to a combination of physical and chemical mechanisms of mineral degradation, suggesting the participation of organic acids in the process. Our data support this observation, supplying evidence of the participation of organic acids, especially oxalic acid, in the dissolution of K-bearing silicate minerals.

K extraction from Verdete with oxalic acid was dependent on acid concentration and reaction time, which showed greater effect (Figure 2). At the intervals evaluated, the soluble K concentration nearly doubled by increasing reaction time from 12 to 72 h. The low dissolution rate is one of the main constraints to apply silicate rocks directly to soil as nutrient sources to plants (Manning, 2018; Santos et al., 2015a). The dissolution rate in the soil depends on the physicochemical conditions and the microbial community, which can accelerate mineral decomposition through bioweathering mechanisms (Manning, 2018; Wei et al., 2012). The K released from Verdete by oxalic acid after 72 h represents an increase in dissolution roughly 1,000 % over the control with distilled water (3.6 mg

K soluble L⁻¹). Fungus *Aspergillus niger* can produce 38 g L⁻¹ oxalic acid in only 10 days (Strasser et al., 1994), an amount greater than that used in this experiment (20 g L⁻¹). Therefore, the inoculation of oxalic acid-producing microorganisms to soils together with ground K-bearing silicate rock could improve K availability to plants. Soil inoculation of K-solubilizing microorganisms in combination with K-feldspar increased K uptake by plants (Maity et al., 2014; Zhang and Kong, 2014). Furthermore, the weathering of silicate minerals in soil tends to be faster than predicted by laboratory experiments, possibly due to the action of soil microorganisms (Ciceri and Allanore, 2015; Manning, 2018).

Increasing oxalic acid concentration improved K extraction; however, a significant increase of soluble K was not observed above 6 % of oxalic acid in the timeframe evaluated (Figure 3B). The equilibrium was not apparently reached at 72 h; thus, predicting the effect of oxalic acid concentration after 72 h was not possible. During acid attack of rocks, high acid concentration can cause precipitation of reaction products on the surface of mineral particles, creating a layer that impairs solubilization reaction (Hatfield, 1964). Oxalic acid forms low-solubility complexes with metals in Verdete, such as Al, Fe, Mg, Mn, Ni, and Zn (Table 2). XRD of the remaining solids after attacking of Verdete rock with oxalic acid suggested the formation of metal oxalates (Figure 4), which could impair the reaction, if they accumulate on the surface of mineral particles at high oxalic acid concentrations.

After 72 h of reaction, an extraction of up to 6.5 % of K was reached in Verdete. Similar extraction rate was achieved in a chemolithotrophic bioleaching system after 49 days of cultivation of *Acidithiobacillus thiooxidans* (Matias et al., 2019). Thus, a chemoheterotrophic bioleaching based on oxalic acid-producing microorganisms could likely reach similar extraction rates in a shorter time. Biogenic oxalic acid has been used to recover several chemical elements from rocks, minerals, and wastes (Gadd, 1999, 2017a; Gharieb et al., 1998; Kang et al., 2019, 2020; Liang and Gadd, 2017; Sayer and Gadd, 1997; Suyamud et al., 2020; Vakilchapp et al., 2016). Bioleaching can be performed in systems with direct contact between the microorganism and the rock or by applying microbial products as leaching agents (Goldstein et al., 1993; Johnson, 2014; Vakilchapp et al., 2016). This research shows that oxalic acid is a promising microbial metabolite for such schemes, presenting the possibility of using microorganisms for K extraction in reactors or directly in the soil. K extraction in reactors could benefit from optimized conditions to reach high yield production of oxalic acid by microorganisms using carbohydrates as renewable energy sources (Strasser et al., 1994). On the other hand, K solubilization in the soil could produce additional benefits for plants due to other microbial mechanisms of plant-growth promotion, such as the production of phytohormones, phosphate solubilization, and stress

relief (Araújo et al., 2020; Batista et al., 2018; Gupta and Pandey, 2019; Lubna et al., 2018; Zhang and Kong, 2014). Nevertheless, this strategy requires the development of formulations to allow efficient colonization and activity of the inoculated microorganism in the highly competitive soil environment (Herrmann and Lesueur, 2013; Malusá et al., 2012; Vassileva et al., 2020).

Conclusions

Oxalic acid can extract K from Verdete rock more efficiently than citric acid, possibly due to the formation of oxalate-metal complexes with metals in Verdete. The reaction is affected by oxalic acid concentration and time, which affects the amount of solubilized K.

Acknowledgments

The authors wish to thank Dr. Edmar Isaías de Melo for his assistance in the K analyses. This work was supported by the Brazilian National Council for Scientific and Technological Development (CNPq 401485/2016-1), the Minas Gerais State Agency for Research and Development (FAPEMIG APQ-01842-17), the Coordination for the Improvement of Higher Level Personnel (CAPES, Finance Code 001), and the University Support Foundation (FAU 02/2018).

Authors' Contributions

Conceptualization: Duarte, L.M.; Mendes, G.O.; Ávila Neto, C.N. **Data acquisition:** Duarte, L.M.; Xavier, L.V.; Rossati, K.F.; Oliveira, V.A.; Schimicoscki, R.S. **Data analysis:** Duarte, L.M.; Mendes, G.O.; Ávila Neto, C.N. **Design of methodology:** Duarte, L.M.; Mendes, G.O.; Ávila Neto, C.N. **Writing and editing:** Duarte, L.M.; Mendes, G.O.; Ávila Neto, C.N.

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