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Three Commercial organic Acids for the Leaching of Metals from Tailings

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Abstract: The mining industry generates enormous volumes of mining wastes. Among these mine discharges, tailings are the most problematic given their very fine particle sizes and the chemicals used to process the ore. Moreover, if they contain iron and sulphides, their exposure to atmospheric agents, causes their oxidation and the production of acid mine drainage (AMD). Acid mine drainage is a concern for mining companies people and policy makers. It poses a threat to the environment and human health. The objective of this paper is to propose a technically and economically cost-effective method for recovering otherwise precious metals from tailings. To do this, various tests in flasks were carried out in the laboratory. The organic acids were used individually or as a mixture of the acids in pairs or a mixture of three acids. Selective sequential extraction (SSE) was performed to assess the geochemical distribution of metals. A statistical analysis was carried out through analysis of the variance (ANOVA) one-factor (type of acid, type of mixture, concentration or time) from the Tukey test. Citric acid (5.10^{-2} g/L) provides the highest solubilization percentages. The solubilization sequence of the metals is: Cu > Zn > Pb > Ni ~ Cd > Fe. All the metals in the exchangeable, carbonate, oxide/hydroxide geochemical fractions were solubilized (100%). In the case of commercial organic acids, the results confirm that the solubilization of metals contained in the tailings is not linked to extracellular enzymes but to the acidification of the medium. They show that leaching by commercial organic acids offers the possibility of recovering at attractive concentrations heavy metals retained in the large quantities of tailings released by the mining industry.

Keywords: Tailings, leaching, organic acids, heavy metals, environment

INTRODUCTION

Mining is a source of profit and wealth for states. It helps to fight against unemployment and poverty. However, mining activity has many impacts on the environment. It involves the production of large quantities of mining waste. These quantities depend on the type of ore mined, the type of operation, the grade and the size of the mine. The disposal of these large quantities of mine tailings presents considerable challenges for the mining industry and can have significant impacts on the environment. These effects are often more pronounced for open pit mines as for underground mines. Discharges which are generally no immediate economic value [1], represent the largest portion of the extracted material. This is explained by the low grade of metals in the rocks and the huge volumes of rock that must be extracted, treated and discharged. They are composed of discharges of stripping, waste rock dumps and residues stored in tailings parks. If a small portion of the waste is reused (landfill or construction material), much of it is stored. Tailings remain the most problematic because of their size and the chemicals they may contain (e.g., cyanide). They are composed of finely ground rocks and a high percentage of particles less than 80 microns [2]. In addition to aesthetic disturbance, when they contain metals or sulphide minerals, these residues are likely to produce acid mine drainage (AMD) and thus promote the mobilization (solubilization) of metals in the environment. Faced with these problems, many norms and laws have been adopted in several countries. The evolution of techniques of exploitation and management of tailings from mining companies also reduced impacts related to mining. Given the problems posed by the extractive industry and particularly those related to AMD, consequential demand increasingly growing in mineral raw materials, research is nowadays oriented towards the recovery of metals from low-grade ores and the recovery of tailings. Consequently, valorization techniques such as bioleaching have been developed. In bioleaching, the role of microorganisms, bacteria and fungi, is to promote the recovery of the metals contained in the solid residues, transforming them into soluble and extractable compounds. Bacterial leaching is used to recover metals in low-grade ores or for secondary recovery of metals from processing residues to prevent environmental pollution. However, bacterial leaching applies to acidic media and generally requires the presence of an energy source. In general, chemo-autotrophic bacteria of the genus *Thiobacillus* and *Sulfolobus* are used in sulphide media for the extraction of metals, unlike heterotrophic bacteria and fungi which are used both in the leaching of metal ores and non-sulphurous minerals [3]. Early work on fungal leaching has shown that it allows for the recovery of valuable metals at commercially attractive concentrations and represents environmentally friendly but not economically profitable biotechnology given the high cost of the substrate used [4-6]. Low-cost food residues available in large quantities can be used as a substrate source for the production of organic acids [7]. The use of whey permeate as a substrate in place of the commonly used sucrose with *Aspergillus niger* and *Penicillium simplicissimum* on residues from zinc and lead (New Brunswick) and nickel (New Caledonia) mines shows that Fungal leaching could be profitable depending on the type of mining residue and would protect the environment from a sustainable development perspective [3]. Thus, the fungal leaching applied to the different types of materials (acid, neutral, basic, presence or not of sulphides) appears as an alternative to environmental pollution problems related to AMD. Several studies on bioleaching have shown that other metabolism products besides the organic acids produced by microorganisms should be involved in the solubilization of metals [8, 9]. Enzymes secreted by fungi such as phosphatases would be responsible for the solubilization of metal phosphates [10]. The enzymatic reduction would be at the origin of the transformation of ferric iron (Fe^{3+}) into ferrous iron (Fe^{2+}) during bioleaching [11]. The recovery of metals contained in electronic residues by the using of *Aspergillus niger* shows that the solubilization of metals was not due to extracellular enzymes, but mainly due to the action of organic acids [12]. The citric, oxalic and gluconic acids produced by fungi were responsible for the bioleaching process in the removal of heavy metals. The results obtained by denaturing the enzymes by heat treatment in an autoclave were identical to those of the leaching of the metals from the original substrate by *Aspergillus niger* and *Penicillium simplicissimum* [13]. These results also confirm that extracellular enzymes were not responsible for metal solubilization. Where implementary bioleaching can poses problems and in order to evaluate the potential of organic acids, in this study, commercial acids are used.

The objective of this study is to verify the effectiveness of commercial organic acids (citric acid, gluconic acid and oxalic acid) which are cheaper and readily available, in recovering metals from tailings.

METHODOLOGY

Tailings from the Agnico-Eagle company's Laronde mine in the Abitibi region of northwestern Quebec were used. After tailings characterization, the leaching is carried out for 48 hours in 50 ml centrifuge tubes containing a certain mass of the mining residue and the organic acid (gluconic acid, citric acid, oxalic acid or mixture of the three acids). Tailings concentration is 5% (v / v). The organic acids were used individually or as a mixture of the acids in pairs or a mixture of the three acids. In order to respect this concentration, for leaching with a single organic acid or a mixture of two organic acids, 2 g of tailings were weighed using a balance to the nearest 0.001 g and then transferred to a 50 ml centrifuge tube. 40 ml of the organic acid or mixture of two organic acids (20 ml for each acid) are added thereto. In the case of the mixture of the three organic acids, 1.95 g of tailings are weighed with the balance to the nearest 0.001 g and then transferred to a 50 ml centrifuge tube. 39 ml of the mixture of the three organic acids (13 ml for each acid) are added thereto. The centrifuge tubes are sealed and then stirred for 48 hours on a stirrer plate at 110 RPM at room temperature. At the end of the leach period, the supernatant is filtered using 0.45 µm Whatman filters and then acidified with HNO_3 nitric acid and subsequently analyzed using an atomic absorption spectrophotometer to determine their metal content. Analyzed metals are: cadmium, copper, iron, nickel, lead and zinc. The solubilization potential of the various metals was evaluated by determining the percentage of solubilization for each.

A statistical analysis was carried out using version V.17 of the "Statistical Package for Social Sciences (SPSS, Inc.)" software. The mean values of solubilized metal contents (Cd, Cu, Fe, Ni, Pb and Zn) as a function of concentration, acid type (or mixture) and time were investigated using a the analyze of the variance (ANOVA) to one factor (type of acid, type of mixture, concentration or time) from a statistical test ie the Tukey test or the Tukey method which is a multiple comparison method. This method was used on raw data in conjunction with the analysis of variance (called post-hoc analysis) to find means that are significantly different from each other. It allows to compare all the possible pairs of averages and uses the "Student's T-test". A significance level of $p < 0.05$ was used for all comparisons at the end of the one-factor analysis.

RESULTS AND DISCUSSION

Characterization of tailings

Table 1 gives physic-chemical parameters and total metal content of tailings. Tailings have a heterogeneous and fine spreading size. Its sizes cover that of the fine sand to the clay passing by that of the silt. This is attested by the values of the coefficient of uniformity (5.78) and the coefficient of curvature (0.85). However, heavy metals tend to concentrate in the fine fractions, while the coarse fractions act more as diluents [14, 15]. The pH value of the order of 8.3 shows that the materials are not yet oxidized. The buffer capacity is very low around the initial pH of the tailings. The buffering capacity being the ability to oppose the pH changes induced by the addition of an acid or base, this means that these tailings capacity is very negligible when it is close to its initial pH. Tailings therefore have a high sensitivity to low additions of acid or base. The very low CEC value represents the amounts of cations that can be adsorbed by the negative charge sites of tailings. It seems to depend on the content of organic matter and fine particles. This property refers to the maximum level of adsorption of easily exchangeable cations [16, 17]. The main mineral phases identified by scanning electron microscope (SEM) and X-ray diffraction (XRD) are: pyrite, galena, feldspars and quartz. The metal contents, determined by spectrophotometry, are given in the following table. The concentrations of the heavy metals analyzed are high. The order of total concentration is Fe > Cu > Zn > Pb > Cd > Ni. The predominance of Fe concentration compared to other metals is related to the presence of pyrite and possibly other iron-magnesium minerals. Moreover, the concentrations of the heavy metals followed are in orders of magnitude, higher than the natural concentrations of trace elements in rocks and also for soils [18].

Table-1: Physic-chemical parameters and total metal content of tailings

Parameter	**Value**
pH	8.36
Conductivity (µS/cm)	732
Cation exchange capacity: CEC (Cmol/Kg)	0.035
Organic matter content (%)	7.55
Sulfate content (mg/L)	612
Metal contents (mg/Kg)	
Cadmium	71.48
Copper	1868.51
Iron	30375.40
Nickel	55.64
Lead	225.38
Zinc	431.90

Selective sequential extraction (sse)

The determination of the total concentration of the metals makes it possible to determine the degree of contamination but does not make it possible to distinguish between the various forms of metals, namely dissolved, adsorbed and complexed [19]. Selective sequential extraction also gives an indication of the bioavailability of metals and thus their apparent mobility. Therefore, selective sequential extraction (SSE) was performed to assess the geochemical distribution of metals in the tailings (Figure 1). It shows that the retention percentages of heavy metals in the residual phase are the highest for all metals. This retention in the crystalline phase is particularly remarkable for iron (85.8%) and copper (63.5%).

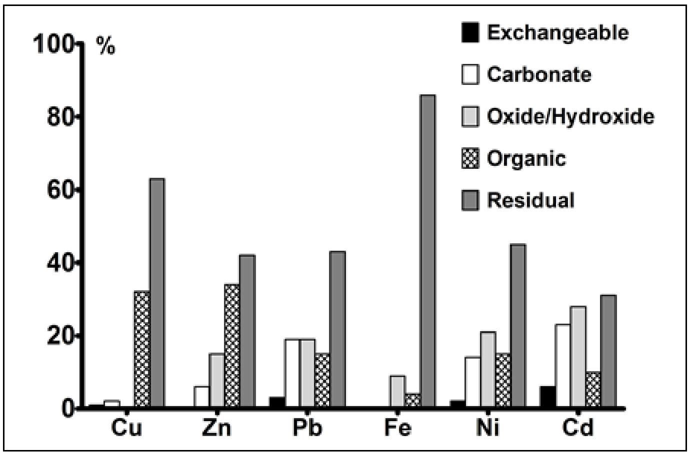

Fig-1: Geochemical distribution of metals in tailings

The relatively higher percentages in the residual fraction indicate the lithogenic nature, i.e., the natural origin of the metals [23]. In this fraction, the metals are bound to the crystal structure of the minerals and therefore difficult to extract. The initial alkaline pH (pH = 8.36) of the tailings indicates that it has not undergone oxidation which would have altered the geochemical distribution of the metals by geochemical fraction [3, 20].

Table-2: Selectivity sequence of metals in tailings

Fraction	**Selectivity sequence of metals**
Order of total concentration of metals	Fe > Cu > Zn > Pb > Cd > Ni
Exchangeable	Cd > Pb > Ni > Cu > Zn > Fe
Carbonate	Cd > Pb > Ni > Zn > Cu > Fe
Oxide - Hydroxide	Cd > Ni > Pb > Zn > Fe > Cu
Organic	Zn > Cu > Ni = Pb > Cd > Fe
Residual	Fe > Cu > Ni > Pb > Zn > Cd

Table 2 shows that for cadmium and lead, these metals are more retained in the carbonate fraction than in the organic fraction, unlike iron and nickel. Copper and zinc have different sequences in which the residual and organic phases are those which retain these metals more. The zinc retention sequence differs from that of iron and nickel, only in the retention of these metals in the oxide/hydroxide and organic phases. The zinc is retained in the residual and organic fraction, whereas for iron and nickel, the retention is essentially made in the residual and oxide/hydroxide phases. Copper is almost completely extracted in the fractions: soluble, oxide/hydroxide, exchangeable and carbonate. This is related to the fact that copper is the metal that is being exploited and the processing operations aimed at the highest possible recovery rates. The copper found in the tailings is the non-extractable portion (residual and organic phases) by the processing methods used.

Leaching with individual organic acids

The solubilization sequence of the metals is: Cu > Zn > Pb > Ni ~ Cd > Fe for all three organic acids and for the same concentrations (Figure 2). The solubilization of a metal varies from one metal to another. The solubilisation potential of the same metal also varies from one acid to another and from one concentration to another. The copper contents are the highest for the three organic acids; Iron being the least solubilized metal. For most metals, the solubilization percentages increase with the concentration. The highest solubilization percentages are obtained with citric acid for almost all metals. Citric acid has a much stronger complexing power than other organic acids (i.e. citric > oxalic > gluconic) [21]. Indeed, the effectiveness of citric acid in metal ion capture is mainly due to its relatively high acidity (pK1 = 3.13) [24] and the presence of three functional groups (COOH) which promote the formation of stable complexes. For these reasons, most metals are much more solubilized with citric acid. This is much more perceptible for copper and to a lesser extent for zinc and lead. On the other hand, cadmium levels are higher with gluconic acid.

In sum, copper is the most solubilized metal in these acids. The highest levels of copper were observed with citric acid at 5.10^{-2} g/L. In addition, the highest concentrations are observed for the concentration at 5.10-2 g / l for almost all metals. The ANOVA test shows that with the use of organic acids individually, for cadmium, nickel and copper there are no statistical differences irrespective of the acid used for leaching (citric acid or gluconic acid or oxalic). Statistical differences are found in leaching with citric acid only for lead, iron and zinc.

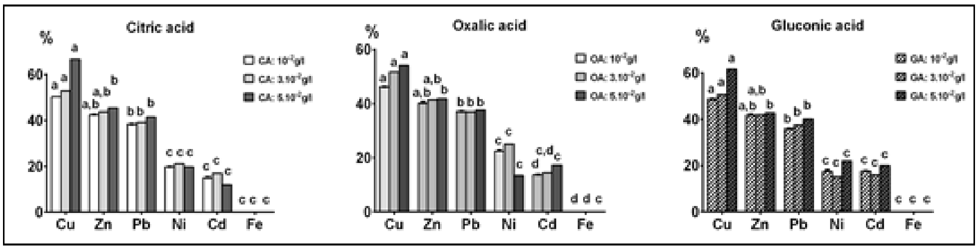

Fig-2: Percentages of metals solubilized from individual organic acids.

Lower case letters indicate the significant differences between the levels of the different metals at p < 0.05 from a 1-factor ANOVA.

Leaching with mixture of organic acids two by two

The same solubilization sequences as above can be observed with the mixture of the acids in pairs (Figure 3). As in the case of leaching with the acids used individually, copper is the most solubilized metal. The solubilisation of iron is very negligible. For copper and zinc, the highest percentages of solubilization are observed for the three concentrations with the mixture of citric and oxalic acid. As regards zinc, lead, nickel and cadmium, the observed percentages are substantially identical for the three concentrations with the mixture of citric and gluconic acid and that of oxalic and gluconic acid. The highest solubilization rates for lead are obtained with the citric and oxalic acid mixture at a concentration of 10^{-2} g/L. Considering the concentration of the mixture of the three acids two by two, the solubilization proportions are relatively higher for concentrations $5\text{-}10^{-2}$ g/L (more than 60% solubilisation for copper, in the case of organic acids used individually).

In the case of leaching with the mixture of acids in pairs, the statistical differences are found in lead, copper and zinc. For copper, leaching is different with the three mixtures: citric acid + gluconic acid; Citric acid + oxalic acid and gluconic acid + oxalic acid. As far as lead is concerned, leaching is identical with only the citric acid + oxalic acid mixture. It is therefore different for citric acid + gluconic acid and gluconic acid + oxalic acid mixtures. In the case of cadmium and zinc, an identical leaching is observed for citric acid + oxalic acid and citric acid + gluconic acid mixtures.

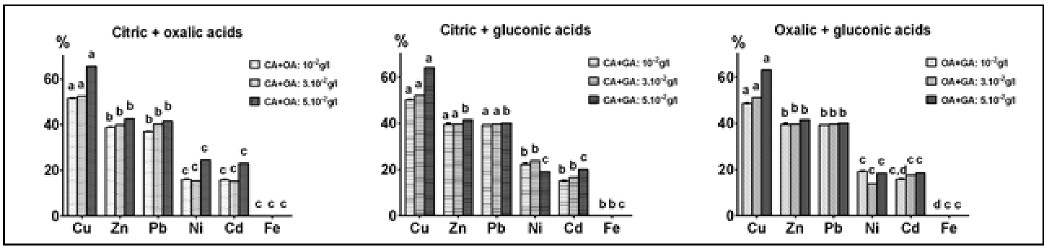

Fig-3: Percentages of metals solubilized from mixture of organic acids two by two.
Lower case letters indicate the significant differences between the levels of the different metals at p < 0.05 from a 1-factor ANOVA.

Leaching with mixture of the three organic acids

The proportions of solubilisation of the metals with the mixture of the three organic acids show a solubilization sequence identical to that of the two preceding situations: Cu > Zn > Pb > Ni > Cd > Fe with quasi-zero proportions for iron (Figure 4). An increase in the content of solubilized metals is observed when the concentration of the mixture of the three organic acids increases. The solubilization proportions of zinc and lead are almost identical for all concentrations. The evolution of the proportions according to the concentration is not very sensitive for all the metals outside the copper.

In the case of the mixture of the three organic acids, the variances are not homogeneous (absence of equality of the variances). It is therefore impossible to make an analysis of the variances. The ANOVA is therefore invalid.

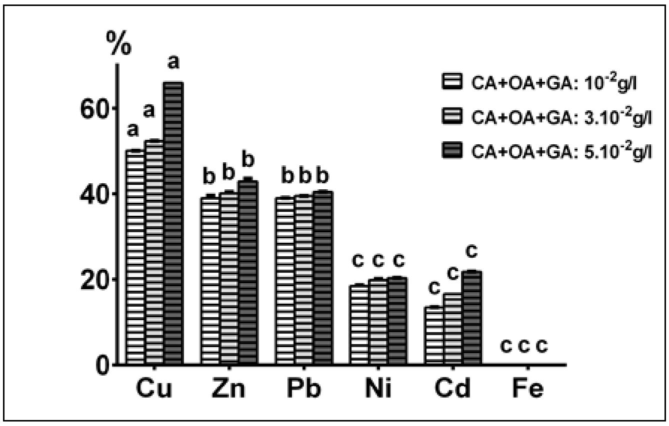

Fig-4: Percentages of metals solubilized from mixture of the three organic acids.
Lower case letters indicate the significant differences between the levels of the different metals at $p < 0.05$ from a 1-factor ANOVA.

With respect to the mixture of acids, there would be competition between organic acids in the capture of metals available for complex formation. Depending on the type of organic acid, the organic acids which produce the most complexes are respectively the tricarboxylic, di-carboxylic and hydroxyl acids. This is because the tricarboxylic acids have more functional groups to which the metals can be attached. Citric acid which is tricarboxylic, would produce more complexes than oxalic acid which is di-carboxylic. The pH of leaching would not have been high enough to allow complexation with, for example, the gluconic acid of which the pK1 was the highest among the organic acids present. Consideration should also be given to the affinity of organic acids for particular metals and the presence of competing metals in site occupancy (Cu, Zn, Pb, Ni, Cd, Ca, Mg, Fe, Al). According to [22], the stability constants of the complexes formed follow the order: Cu> Fe = Al> Mn = Co> Zn, which means that the complexes formed by copper are more stable than those formed by iron and zinc. This would explain the much higher copper solubilization levels of copper compared to other metals. In addition, other parameters such as ionic radius, ionic potential and the Misono parameter also influence the selectivity of metals [18, 23].

Solubilization of metals by geochemical fraction

The geochemical distributions of the metals were carried out after leaching with the various organic acids, the mixtures of the organic acids in pairs and with the mixture of the three organic acids and in the concentrations 10^{-2} g/L, 3.10^{-2} g/L and 5.10^{-2} g/L. The results are shown in Tables 3 to 9.

Table-3: Percent solubilization of metals by geochemical fraction at 10^{-2} g/L with individual organic acids

Fraction % Metal	Exchangeable			Carbonate			Oxide – Hydroxide			Organic			Residual		
	CA	GA	OA	CA	GA	OA	CA	GA	OA	CA	GA	OA	CA	GA	OA
Cd	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Cu	100	100	100	100	100	100	100	100	100	37	33	32	0.00	0.00	0.00
Fe	100	100	100	100	100	100	100	100	100	20	17	15	0.00	0.00	0.00
Ni	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Pb	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Zn	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00

CA: citric acid; GA: gluconic acid; OA: oxalic acid

Table-4: Percent solubilization of metals by geochemical fraction at 3.10^{-2} g/L with individual organic acids

Fraction % Metal	Exchangeable			Carbonate			Oxide – Hydroxide			Organic			Residual		
	CA	GA	OA	CA	GA	OA	CA	GA	OA	CA	GA	OA	CA	GA	OA
Cd	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Cu	100	100	100	100	100	100	100	100	100	41	37	36	0.00	0.00	0.00
Fe	100	100	100	100	100	100	100	100	100	24	19	19	0.00	0.00	0.00
Ni	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Pb	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Zn	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00

Table-5: Percent solubilization of metals by geochemical fraction at 5.10^{-2} g/L with individual organic acids

Fraction % Metal	Exchangeable			Carbonate			Oxide – Hydroxide			Organic			Residual		
	CA	GA	OA	CA	GA	OA	CA	GA	OA	CA	GA	OA	CA	GA	OA
Cd	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Cu	100	100	100	100	100	100	100	100	100	51	45	41	0.00	0.00	0.00
Fe	100	100	100	100	100	100	100	100	100	32	21	19	0.00	0.00	0.00
Ni	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Pb	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Zn	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00

As regards leaching with individual organic acids (Tables 3,4,5), all the metals in the exchangeable, carbonate, oxide/hydroxide geochemical fractions were solubilized (100%), irrespective of the type of acid and the concentration. No metal retained in the residual (crystalline) phase was solubilized. In the organic fraction only copper and iron were solubilized. The solubilization of copper and iron in this geochemical fraction varies from one acid to another and from one concentration to another. In this fraction, depending on the type of acid, copper is much more solubilized in citric acid than in gluconic acid and oxalic acid, respectively. This observation can be made for the solubilization of iron, except for the solubilization with the concentration 10^{-2} g/L for which the solubilization percentages are equal (19%). Considering the acid concentration, an increase in the solubilization percentage of copper and iron is observed with the concentration in this geochemical fraction. For these two metals the percentage of solubilization increases as the concentration increases.

For the mixing of organic acids two by two (Tables 6,7,8), as in the case of leaching with the organic acids used individually, all the metals in the exchangeable, carbonate, oxide/hydroxide geochemical fractions were solubilized, irrespective of the type of acid and the concentration. Likewise, no metal retained in the residual (crystalline) phase was solubilized. In the organic phase, only copper and iron are solubilized as observed previously. Depending on the type of mixture of organic acids, solubilization of copper is more important in the mixture of citric acid and gluconic acid than in the mixture of gluconic acid and oxalic acid, and citric acid and oxalic acid except for concentration 3.10^{-2} g/L. In this latter case, the importance in the solubilization of the copper is respectively citric acid + gluconic acid; Citric acid + oxalic acid then gluconic acid + oxalic acid. Changes in the percentages of solubilization of iron are very small (1 to 3%) from one mixture to the next but with relatively higher values with the citric acid + gluconic acid mixture. for the three mixtures, the solubilization rates are identical (12%), at the concentration of 10^{-2} g/L. Taking into account the concentration, the following observations can be made. The copper solubilization percentages increase with increasing concentration of the mixture of organic acids. This variation is 32 to 43% with the mixture citric acid + gluconic acid. It is 28-39% and 31-42% for citric acid + oxalic acid and gluconic acid + oxalic acid mixtures, respectively. These variations are lower with regard to iron. They are 12 to 17% for the mixture citric acid + gluconic acid; 12 to 14% for the citric acid + oxalic acid and 12 to 16% for the mixture gluconic acid + oxalic acid. The type of mixture and the concentration influence the solubilisation of these two metals in this geochemical fraction.

Table-6: Percent solubilization of metals by geochemical fraction at 10^{-2} g/L with mixture of organic acids two by two

Fraction % Metal	Exchangeable			Carbonate			Oxide – Hydroxide			Organic			Residual		
	CA+GA	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**
Cd	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Cu	100	100	100	100	100	100	100	100	100	32	28	31	0.00	0.00	0.00
Fe	100	100	100	100	100	100	100	100	100	12	12	12	0.00	0.00	0.00
Ni	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Pb	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Zn	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00

Table-7: Percent solubilization of metals by geochemical fraction at 3.10^{-2} g/L with mixture of organic acids two by two

Fraction % Metal	Exchangeable			Carbonate			Oxide – Hydroxide			Organic			Residual		
	CA+GA	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**
Cd	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Cu	100	100	100	100	100	100	100	100	100	41	39	37	0.00	0.00	0.00
Fe	100	100	100	100	100	100	100	100	100	16	14	15	0.00	0.00	0.00
Ni	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Pb	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Zn	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00

Table-8: Percent solubilization of metals by geochemical fraction at 5.10^{-2} g/L with mixture of organic acids two by two

Fraction % Metal	Exchangeable			Carbonate			Oxide – Hydroxide			Organic			Residual		
	CA+GA	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**	**CA+GA**	**CA+OA**	**GA+OA**
Cd	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Cu	100	100	100	100	100	100	100	100	100	43	39	42	0.00	0.00	0.00
Fe	100	100	100	100	100	100	100	100	100	17	14	16	0.00	0.00	0.00
Ni	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Pb	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Zn	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00

Finally, with respect to the mixture of the three organic acids (Table 9), all metals monitored which were contained in the exchangeable, carbonate, oxide / hydroxide geochemical fractions were solubilized. No metal from the residual fraction was solubilized. In the organic fraction, copper, iron and zinc were solubilized. In this fraction, the solubilization of copper increases with the concentration of the mixture (36%, 49% and 52%). It is the same for the iron (16%, 24% and 27%). The zinc solubilization percentages, although relatively smaller, also follow this trend (6%, 7% and 11%). In the organic fraction, zinc has only been solubilized with the mixture of the three organic acids in contrast to the leaching with the organic acids taken individually and with that with the mixture of the organic acids in pairs.

Table-9: Percent solubilization of metals by geochemical fraction with mixture of the three organic acids

Fraction % Metal	Exchangeable			Carbonate			Oxide – Hydroxide			Organic			Residual		
	C1	C2	C3	C1	C2	C3	C1	C2	C3	C1	C2	C3	C1	C2	C3
Cd	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Cu	100	100	100	100	100	100	100	100	100	36	49	52	0.00	0.00	0.00
Fe	100	100	100	100	100	100	100	100	100	16	24	27	0.00	0.00	0.00
Ni	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Pb	100	100	100	100	100	100	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Zn	100	100	100	100	100	100	100	100	100	6.00	7.00	11	0.00	0.00	0.00

C1: concentration 1: 10^{-2}g/L; C2: concentration 2: 3.10^{-2}g/L; C3: concentration 3: 5.10^{-2}g/L

In sum, all these observations confirm that the metals associated with the exchangeable, carbonate, and oxide / hydroxide geochemical fractions are most readily extractable. Those associated with the residual fraction are practically non-extractable. These metals are therefore of lithogenic origin. In the organic fraction only copper, iron and zinc (only with the mixture of the three organic acids) are solubilized. In general, in this fraction, copper has the highest solubilization percentages. Solubilization of metals depends on the type of acid or mixture and concentration.

Technical-economic analysis of leaching by citric acid

In order to evaluate the cost-effectiveness of tailings leaching with commercial organic acids, a technical-economic analysis was carried out using leaching with citric acid at 5.10^{-2} g/L results. Metal prices of 2015 – 2016 are used for analysis.

Copper: $4.56USD / Kg
Nickel: $ 10.34 USD / Kg
Zinc: $ 1.79 USD / Kg
Lead: $ 1.70 USD / Kg
Iron: $ 52.15 USD / ton

The Canadian dollar - US dollar exchange rate on May, 2016 was 0.7623 [25]. Considering the production costs proposed in Table 10 [7], the cost of production can be estimated at CAN $ 1.26 since the tailings are not crushed (CAN $ 0.25) because they already have a very fine granulometry.

Nutrient costs that are higher than the other components of the process (CAN $ 5.27) are not considered to be that the organic acids used are commercially available and have not been produced from microorganisms (mushrooms). By discounting these 1999 costs (CAN $ 1.26) from the 20 August 2015 discount rate using the Bank of Canada's inflation rate spreadsheet, they are valued at CAN $ 1.75. The average annual rate of inflation, i.e. the fall in the value of money (%) over 17 years, is estimated at 1.94 and the percentage change is 38.70%. The consumer price index for Canada in 2002 (CPI 2002) is equal to 100.00 with the first year's CPI (April 1999) estimated at 92.50 and that of 2016 (CPI April 2016) to 128.30.

Table-10: Updated Production Costs for 1999 [7]

Process	Price (1999) ($Can/kg Cu)	Updated cost (2017) ($Can/kg Cu)
Crushing	0.25	0.35
Nutrients	5.27	7.31
Electricity	0.72	1.00
Workforce	0.30	0.42
Solvent extraction	0.03	0.04
Reagents (solvent extraction)	0.04	0.06
Dehydration	0.04	0.06
Electrolysis	0.13	0.18
Total	6.78	9.40

In order to explore the impact of certain parameters on the recovery of metals from commercial organic acids, a sensitivity analysis was performed (Figure 5). This analysis took into account the following parameters: the price of the metal, the cost of production, the capital cost and the exchange rate. Net present values (NPV) were calculated for copper, nickel, lead and zinc using a discount rate of 1.38 as of August 2015 according to the bank's inflation rate spreadsheets of Canada and a tax rate on the profit of

0.4. The cost of production of iron being higher than the price of the metal on the market, it was not taken into account in the sensitivity analysis. The net present values calculated for the four metals considered (copper, nickel, lead and zinc) are not zero and all greater than zero, which means that the recovery of metals by commercial organic acids is viable and profitable.

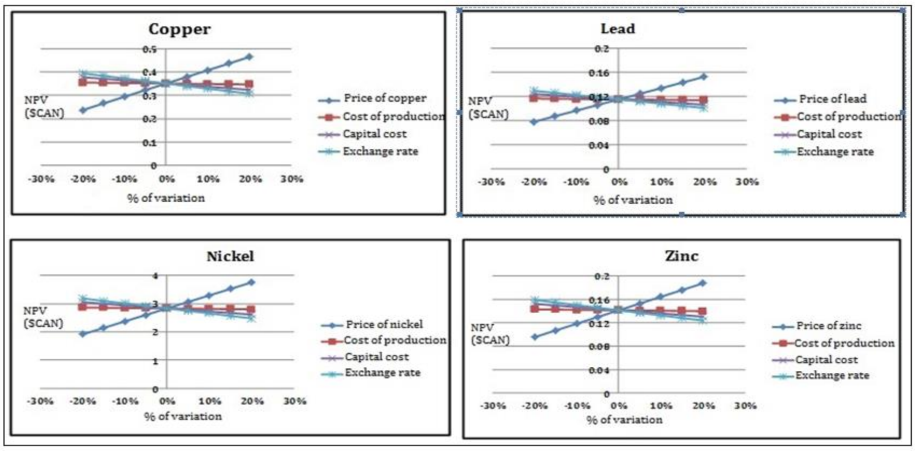

Fig-5: Sensitivity analysis

The evolution of the different parameters taken into account in the sensitivity analysis is almost similar because the initial cost of production is identical (Figure 5). The sensitivity analysis shows that factors such as the cost of production are virtually invariable and therefore not very influential on the viability of a potential recovery project for metals contained in the tailings by commercial organic acids (particularly citric acid). The most critical parameter is the price of metals, which shows a net increase in net present value as a result of the increase in metal prices (Figure 5). The prices of metals are therefore a parameter that considerably influences the viability of such a project. The capital cost and the exchange rate are also critical, but to a lesser degree than the price of metals.

In summary, the technical-economic analysis of citric acid leaching shows through the evaluation of production costs, the net present values and the sensitivity analysis that the recovery of metals by leaching with organic acids is technically and economically profitable. Therefore, it can be considered as a technique that preserves the environment from a perspective of sustainable development.

CONCLUSION

Variations in the solubility potential of metals or metal are attributable to various factors such as leaching pH, geochemical distribution of metals in tailings, the nature and concentration of organic acids in the leach solution, As well as their complexing capacity, their affinity with metals and the presence of competing metals. Among the three commercial organic acids, the citric acid which is a tricarboxylic acid gives the highest levels and solubilization ratios. These results confirm that the solubilization of the metals contained in the tailings is not linked to extracellular enzymes but to the acidification of the medium. Leaching by commercial organic acids therefore allows the recovery of the metals contained in the tailings. It can therefore be applied to deposits of low grades or for the recovery of metals contained in electronic wastes. It therefore avoids the use of nutrients and the cultivation of microorganisms. It is technically and economically cost-effective, saves time and preserves the environment. It is thus a method that integrates with sustainable development not only by preserving the environment and public health from the harmful consequences of the presence of heavy metals but also by allowing the latter to be valued as a secondary source of raw materials.

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