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RESEARCH ARTICLE

Dissolution behavior of metallic zinc in organic acid

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ABSTRACT

A series of experiments were conducted to examine the effect of citric acid on the dissolution of zerovalent zinc. The effects of citric acid concentration, the presence of anions and temperature were studied. The results have shown that zinc dissolution registered a maximum of 34% with 0.5M citric acid after 270 min and that the nature of anions present with citric acid affected differently the dissolution rate. In fact, the presence of 2M nitrates with 0.5M citric acid dissolved totally zinc after 30min while 91.85% and 13.15% were dissolved in the presence of 2M chlorides and sulfates respectively after 270min. SEM analyses have shown that the morphology of the corroded surface depended on the composition of the solution. The kinetic study has shown that zinc dissolution was controlled by the chemical reaction in all cases and that the activation energy was 39.3 kJ mol^{-1}.

Keywords: Zinc, citric acid, dissolution, concentrated conditions, nitrates, pollution

1. INTRODUCTION

The improper disposal of industrial, agricultural and municipal wastes is the major cause for soil contamination in developing countries [1]. In fact, population growth, the lack of awareness regarding the consequences of municipal solid wastes disposal and under-founded governments to prevent the efficient management of wastes participate in increasing the environmental pollution. Landfilling of municipal solid wastes is the most used method because of its simplicity and its low cost [2]. However, when huge amounts of organic wastes are daily placed in landfills as it is the case in Algeria "Mediterranean diet based essentially on the consumption of vegetables", then the anaerobic fermentation of the organic products occurred continuously leading to form leachates rich with organic acids such as formic, acetic, oxalic, citric and malic acids [3]. On the other hand, metals such as Fe, Pb, Cu, Zn, Mn, Cd, Ni and Cr are also found in landfills in Algeria [4]. This is problematic because various reactions can be occurring when these metals come into contact with these leachates enough acid to initiate the dissolution reactions and contaminate soil and groundwater [5] while they can be recovered in order to be reused as secondary raw materials [6-8]. In the literature, the dissolution of zinc by citric acid was studied in framework of its bioavailability in soils for agriculture. In fact, in soil plant system citric acid is often used because of its high efficiency in binding zinc cations (micronutrient) facilitating their absorption by the roots [9-11]. For this task only diluted citric acid is used (in mM). However, in landfills other conditions prevail where huge amounts of organic wastes continuously feed the discharge leading to increase the amount of the organic acids formed by anaerobic-digestion [12,13]. Citric acid is one of the most studied organic acids present in anaerobically-digested biosolids [14]. However, in the literature, the experimental data about the dissolution reaction of metallic zinc in concentrated citric acid is not available. The aim of this study is to investigate the extent of the dissolution process of zinc when exposed to highly concentrated citric acid. The effects of citric acid concentration, temperature, and the presence of anions were studied. The effect of the operation conditions on the resultant morphology was also investigated by SEM analysis and the kinetic parameters and the controlling step of the dissolution process were determined by using a heterogeneous model.

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2. MATERIALS AND METHOD

Zn (metal) (99.99% purity) in the form of spheres (3 mm of diameter) was supplied by Sigma-Aldrich. The composition of zinc is given in Table 1. The specimens were degreased in acetone and rinsed with deonized water, and were used without polishing as shown in Fig 1. Citric acid monohydrate (99.5 %, Riedel de Haën), NaCl (99.5 %, Biochem), $NaNO_3$ (99 %, Fluka) and Na_2SO_4 (99 %, Sigma-Aldrich) were used as received. Deonized water was used to prepare all aqueous solutions. Tests of Zn dissolution were performed in a Pyrex glass reactor heated in a water bath and equipped with a return-flow cooler. The experiments were performed by contacting 0.2 g of Zn with 200 mL of citric acid solution. After the leaching process, the reaction mixture was filtered and the Zn^{2+} specie was analyzed by complexometric titration with ethylenediamine tetraacetic acid disodium salt (EDTA), using NET as indicator [15]. The data presented are an average of three test replicates with an error of 5%. The percentage of dissolution was calculated from the following equation:

$$\frac{mol\ number\ of\ zinc\ in\ the\ solution}{mol\ number\ of\ zinc\ in\ the\ metal}\ X\ 100 \qquad (1)$$

SEM images were taken with the Environmental Scanning Microscopy instrument (XL 30, Philips, Netherlands). All analyses were performed in duplicate with an error of 5%. In this study, the results of zinc dissolution were analyzed using the shrinking core model. In this model the reactant is considered to be nonporous and is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk of the fluid. This model used the following expressions to describe the dissolution kinetics of the process [16]:

For liquid film diffusion control:

$$x = kt \qquad (2)$$

For film diffusion control through product layer:

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = kt \qquad (3)$$

For surface chemical reaction control:

$$1 - (1 - x)^{1/3} = kt \qquad (4)$$

where x is the fractional conversion of zinc at time t and k is the apparent rate constant (min^{-1}). The overall rate of dissolution is controlled by the slowest of these sequential steps.

Table 1. Composition of Zn used in this study

Element	As	Cd	Cu	Fe	Pb	Sn	Zn
%	0.0005	0.0005	0.001	0.002	0.005	0.001	99.99

3. RESULTS

3.1 Effect of citric acid concentration and temperature

The dissolution of zinc by citric acid may be written as follows:

$$3Zn + 2C_6H_8O_{7(aq)} \rightarrow 3Zn^{2+} + 3H_{2(g)} + 2C_6H_5O_7{}^{3-}{}_{(aq)} \quad (5)$$

Preliminary test was conducted with citric acid solution at 2M, ambient temperature, and without agitation. No dissolution of zinc was observed after 24h. The temperature was thus increased to 80°C and the solution was stirred under 350rpm to decrease the reaction time. Zinc was contacted with citric acid solution at different concentrations (0.2, 0.5, 1 and 2M) (Fig 2a). The results show that the dissolution of Zn passed through a maximum in the acid concentration range studied. In fact, 9.5% of zinc was dissolved with 0.2M citric acid after 270 min. It increased to 34% with 0.5M after the same period of time and decreased thereafter at higher citric acid concentration (1 and 2M) registering 31 and 16% respectively.

The effect of temperature was studied in range 30-80°C with 0.5M citric acid at 350rpm (Fig 2b). The results show that the dissolution of Zn increased with increasing temperature attaining 4.22-11.37-14.67 and 34% at 30-40-60 and 80°C respectively after 270min of reaction. The dissolution of Zn in citric acid was thus, thermally activated.

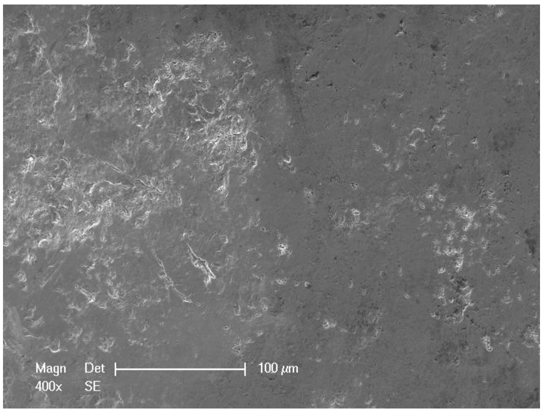


Fig 1. SEM analysis of Zn metal before dissolution experiments by citric acid

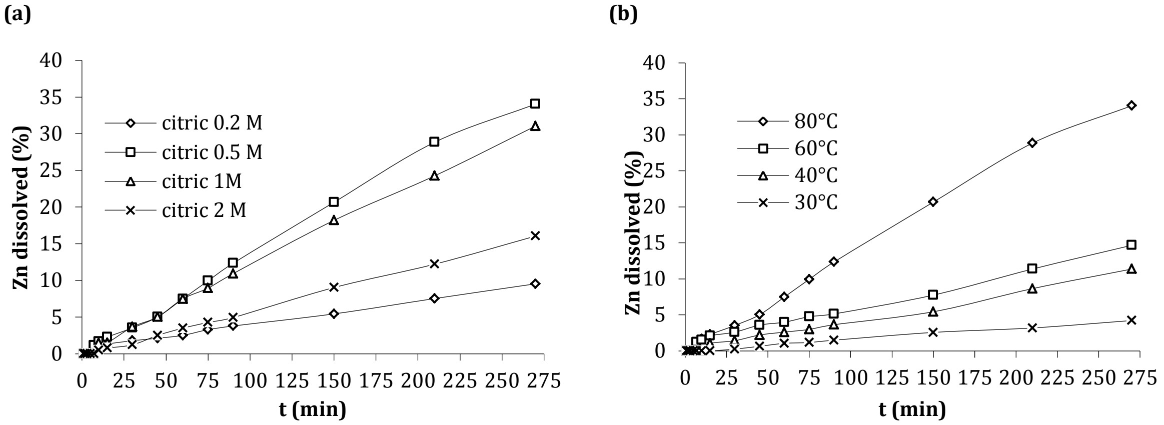


Fig 2. Effect of citric acid concentration (a) and temperature (b) on Zn dissolution

3.2 Effect of the presence of anions

The experiments were carried out in order to investigate the effect of nitrates, sulfates and chlorides on Zn dissolution by citric acid. Two concentrations of citric acid were used (0.5 and 2M) with the presence of NaCl, $NaNO_3$ and Na_2SO_4 at 2M (Fig 3a-c). The experiments were carried out at 80°C and 350rpm. The results show that zinc dissolution was greatly enhanced with both citric acid concentrations in the presence of nitrates (Fig 3a). In fact, the dissolution attained in both cases 100% after 90 min of contact with nitrates while with chlorides the results of dissolution depended on citric acid concentration. In fact, with 0.5M citric acid (Fig 3b) the dissolution attained 91.8% after 270min while with 2M citric acid the dissolution registered 16.5% after the same period of time. Zinc dissolution in the presence of sulfates was slight in both cases registering 13.15% with citric acid at 0.5M and 7.56% with citric acid at 2M after 270 min. Thus, the nature of the ions present with the organic acid may drastically affect the progress of the dissolution.

In order to determine the activation energy, Zn dissolution by citric acid at different temperatures was analyzed by using the shrinking core model. To determine the controlling step, the three expressions $[(x), (1 - 3(1 - x)^{2/3} + 2(1 - x)]$ and $[(1 - (1 - x)^{1/3})]$ were reported on the y axis as a function of time (t) which is reported on the x axis. The fit of the experimental data was tested by calculating the regression coefficients (R^2) for the three expressions. The equation $1 - (1 - x)^{1/3} = \text{kt}$ gave good linear fit as confirmed by the values of R^2 close to the unity (Table 2) indicating that the reaction was chemically controlled. The apparent rate constant is the slope of each line plotted. To determine the activation energy, Arrhenius equation $k = A \cdot e - Ea/RT$ was plotted as lnk vs. 1/T for each temperature and the activation energie was calculated from the slope $-Ea/R$. Ea value was determined to be 39.3kJ mol^{-1} corroborating the chemical reaction control. A chemically controlled reaction is generally a temperature dependent process and has an activation energy equal or higher than 40 kJ mol^{-1}.

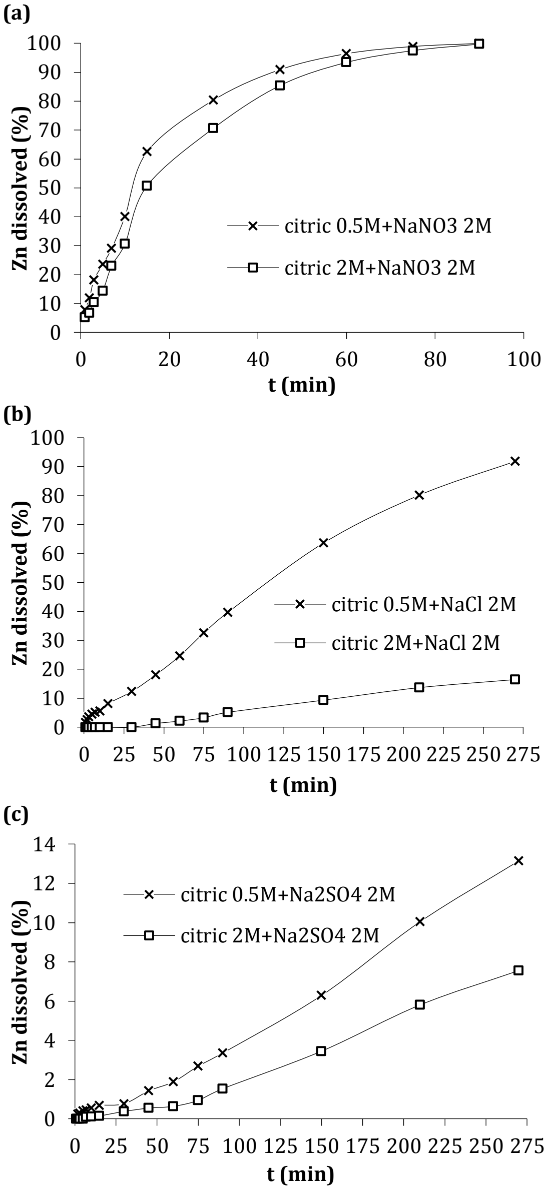


Fig 3. Effect of the presence of nitrates (a), chlorides (b) and sulfates (c) on Zn dissolution by citric acid

3.3 Special case of nitrates

Because of the remarkable effect of nitrates compared to those of chlorides and sulfates and in order to provide a better understanding of their role during zinc dissolution, other experiments were carried out in which Zn was contacted with citric acid at 0.5M to which nitrates were added at two concentrations (0.5 and 2M) at 80°C and 350rpm. The results (Fig. 4a) show a great effect of nitrates on Zn dissolution. In fact, citric acid alone at 0.5M dissolved 34% of Zn after 270 min while when mixed with nitrates at 0.5M i.e. (citric 0.5M + $NaNO_3$ 0.5M) it attained 100% after 30 min. At higher nitrates concentration i.e. (citric 0.5M + $NaNO_3$ 2M) the time needed to attain 100% was longer (90min). To assess the enhancing effect of nitrates on zinc dissolution, the temperature was lowered to 30°C and the dissolution was carried out with the mixtures (citric 0.5M + $NaNO_3$ 0.5M) and (citric 0.5M + $NaNO_3$ 0.2M) as shown in figure 4b. The dissolution of zinc at 30°C was still important since both mixtures dissolved respectively 95.4% and 83.4% of Zn after 60 min. Thus, the solubility of metallic zinc is increased in the presence of nitrates and the impact of temperature in this case was lowered.

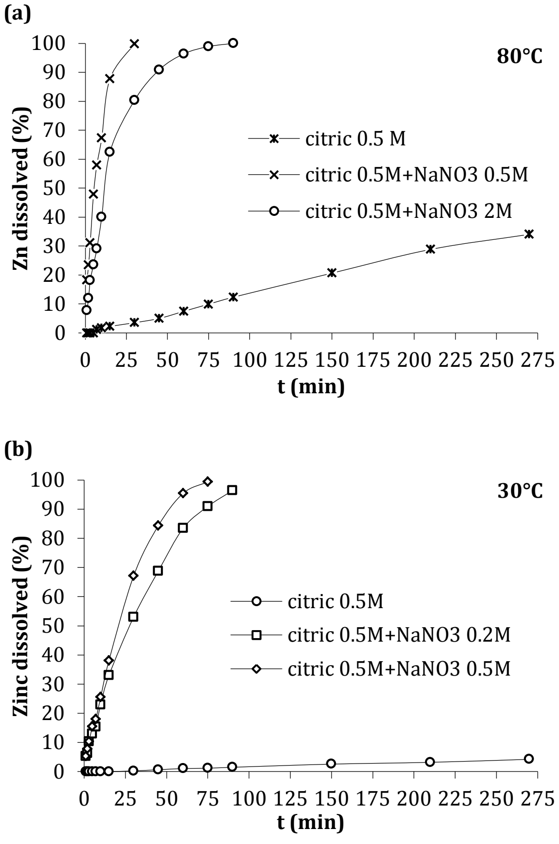


Fig 4. Effect of the presence of nitrates on Zn dissolution

3.4 SEM analysis

The surface of zinc was examined by scanning electron microscopy (SEM) analysis. The morphology of Zn surface obtained after contacting 0.5M citric acid at ambient temperature for 8 days and without agitation shows closed perpendicular sheets (Fig 5a). When Zn was contacted with the same solution heated at 80°C and stirred at 350rpm for 270 min, hexagonal pits (~5µm of size) were formed (Fig 5b). Thus, when the conditions are varied with the same solution the morphology of the pitted surface radically changed. The morphology of zinc surface was also studied in the presence of two nitrate concentrations. Figures 5c and d show Zn surfaces after contacting for 5 min the solutions (citric 0.5M + $NaNO_3$ 0.5M) and (citric 0.5M + $NaNO_3$ 2M) at 350rpm and 80°C. The images show that with the first solution a start of the corrosion was clearly observed while with the second one the surface was not pitted. Thus, increasing nitrate amount does not necessary increase the corrosion of Zn. Zinc surface was also analyzed after contacting the solutions (citric 0.5M + NaCl 2M) for 60 min and (citric 0.5M + Na_2SO_4 2M) for 270 min at 80°C and 350rpm. Figure 5f shows that despite the high temperature and the presence of stirring the corrosion of zinc in the presence of sulfates was very weak. In fact, small pits (~1-2µm of size) not uniformly dispersed on the surface were observed while with citric acid alone and under the same conditions the surface was clearly pitted (Fig 5b). This indicates that sulfates were greatly involved in the inhibition of Zn dissolution. On the contrary, clear corrosion was observed in the presence of chlorides (Fig 5e). In this case the crystallographic cubic shaped pits which are characteristics of chlorides attack were replaced by hexagonal pits (~5-10µm of size) already observed with citric acid alone. Thus, the presence of anions may have a decisive effect on the kinetic of zinc dissolution and the morphology of the pitted surface.

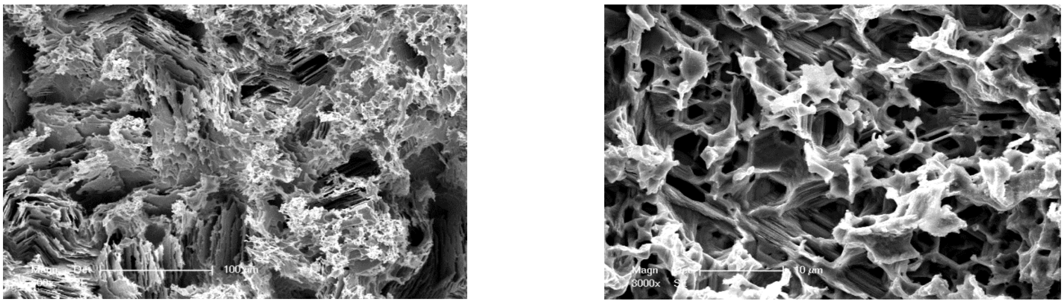
4. DISCUSSION

In this study it was found that among the 3 anions tested, nitrates increased remarkably Zn dissolution compared to chlorides and sulfates. In fact, the facility by which the dissolution of Zn occurred in the presence of nitrates regardless of the conditions used and the fact that it does not need high temperature to be initiated in their presence (as it was the case with citric acid alone) indicated that the mechanism involving nitrates during Zn release is different from those involving chlorides and sulfates.

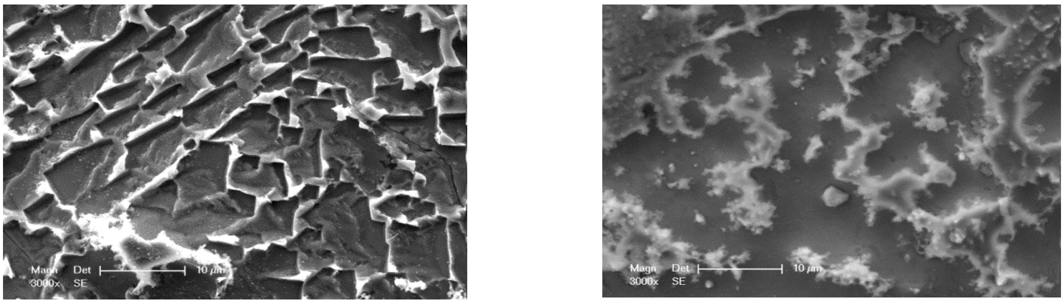
In the literature there is a lack in details about the reactivity of metallic zinc in the presence of concentrated citric acid and nitrates. However, studies dealing with its solubility in diluted organic acids were found in framework of phytoremediation of contaminated soil by metals. These studies were conducted on plants species such as Thalspi caerulescens and Arabidopsis halleri that have the ability to survive and reproduce on soils containing high concentration of zinc [17,18]. Mosant et al. for example added nitrogen in the form of NO_3^- and NH_4^+ to EDDS (Ethylenediaminedisuccinic acid) to study their effect on Zn phytoextraction by Thalspi caerulescens [17]. They observed that Zn phytoextraction was enhanced more with NO_3^- than with NH_4^+. They suggested that this uptake may be the consequence of physiology of NO_3^- assimilation by the plant which favors Zn uptake more than NH_4^+ or the variation of rhizosphere pH due to cellular cation-anion balance (NO_3^- uptake causes H^+ influx or OH^- efflux which may increase the pH of rhizosphere) leading to a favorable pH for Zn uptake. Other studies were also found dealing with the mixture nitrates+metal but in framework of water denitrification. In fact, it was reported that the presence of zerovalent metals with nitrates in an acidified medium leads to a reductive denitrification as follows [19,20]:

$$Zn + NO_3^- + H^+ \rightarrow Zn^{2+} + NO_2^- + OH^- \qquad (6)$$

(a) Zn-citric 0.5M-25°C-8days (b) Zn-citric 0.5M-80°C-4.5 h



(c) Zn-citric 0.5M+NaNO3 0.5M-80°C-5 min (d) Zn-citric 0.5M+NaNO3 2M-80°C-5 min



(e) Zn-citric 0.5M+NaCl 2M-80°C-60 min (f) Zn-citric 0.5M+Na2SO4 2M-80°C-4.5h

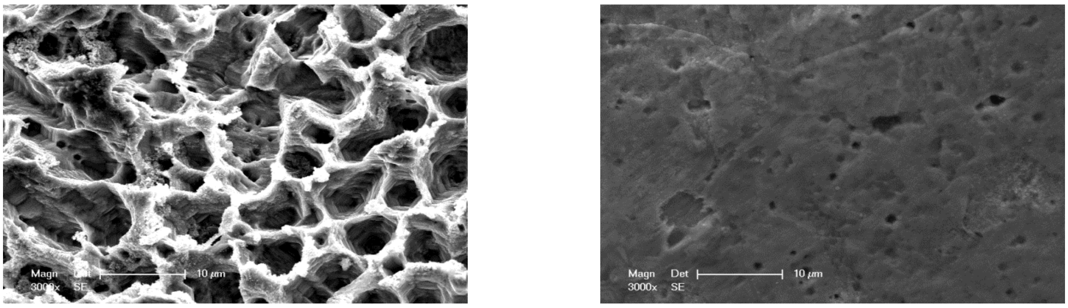


Fig 5. SEM analyses of zinc metal after contacting citric acid under different conditions

This denitrification is accompanied by the dissolution of the metal and the increase in pH of the medium. Alongside with the reaction (5) the dissolution of zinc in an acidified medium also occurs according to:

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_{2(g)} \qquad (7)$$

Thus, in our study the enhanced dissolution rate observed in the presence of nitrates was due to the occurrence of the reactions (6) and (7) simultaneously. This may explain also the finding reported by Mosant et al. [17]. In fact, since plants can extract Zn from soil only in soluble form, the enhancing Zn uptake by plants observed when nitrates were added was likely due to the reaction (6) leading to solubilize the metal. In this study another behavior was also observed when nitrates concentration was increased from 0.5M to 2M in the presence of citric acid. In fact, the dissolution of metallic zinc was lower at 2M NO_3^- than at 0.5M NO_3^- (Fig 4a).

In the literature it was reported that nitrates acted as oxidant that forms a protective oxide layer leading to decrease the corrosion of zinc [21]. Thus, when NO_3^- and H^+ are present, a competition between oxide film growth and metal dissolution occurred [22]. This was observed in our previous study [23]. Thus, at 2M NO_3^- it can be supposed that the oxide film growth on zinc surface was more important that at 0.5M NO_3^- leading to decrease Zn dissolution. On the other hand, the high dissolution rate observed in the presence of nitrates regardless of the conditions used may suggest that their involvement in zinc dissolution was mainly through the reaction (6) and when their concentration increased up to a certain value a part of them participates in developing the protective oxide film leading to decrease the dissolution rate of Zn.

The concentrations of citric acid used in this study (0.2-0.5-1 and 2M) corresponded to molar ratios (nca:nZn) of 13.5-33-66 and 132 respectively. Thus, in all cases the acid was in excess relative to zinc. However, the dissolution passed through a maximum located at 0.5M beyond which zinc dissolution decreased. This behavior is not usually observed; generally increasing the concentration of a leaching reagent leads to increase the dissolution of metals. In the literature, it was reported that citrate and protons are expected to react with metal surfaces [24]. Thus, the dissolution of zinc may be due to both the complexing action of citrate anions and the dissolution properties of protons released from citric acid.

Furrer and Stumm [25] explained the dissolution process by low molecular weight organic acids as follows: the adsorption of chelating anion (citrate in our case) will transfer a considerable electron density into the coordination sphere of the metal cation (citrate contains several donor atoms that are able of forming mononuclear bi- and polydentate surface chelates). As a result, the metal-oxygen bonds are polarized and weakened lowering consequently the energy barrier for the dissolution of the metal atom.

The explanation given above indicates clearly the importance of the anionic specie of organic acid (ligand) in the dissolution process. However the decrease in dissolution rate observed at 2M citric acid is not easy to explain since this organic acid is known as an enhanced-dissolution compound. One study was found dealing with the inhibiting effect of a dissolution-promoting chelating agent when its concentration increased. In fact, it was reported that increasing the concentration of maleate beyond a certain value caused a decrease in the dissolution rate of corundum [26]. This behavior was explained by the fact that at high concentration the strong adsorption of this anion sterically protects corundum surface sites against attack by dissolution promoting species such as protons at low pH. The results obtained in our study may be due to the same phenomenon. Thus, the adsorption strength of the ligand -which is dependent on the organic acid concentration- occurring prior to detachment process of the metal from the surface, orients toward a retarding dissolution process in the case of concentrated acid.

Table 2 shows the rate constants (k) calculated with the equation (4) for all the operation conditions tested in this work.

The rate constant of Zn dissolved at 30°C by 0.5M citric acid was 5.10^{-5} min^{-1}. The same solution but containing nitrates (citric 0.5M + $NaNO_3$ 0.5M) at 30°C increased the dissolution rate to 0.0107 min^{-1} which represents ~214 times the value obtained with citric acid alone while increasing the temperature to 80°C with citric acid alone increased the dissolution rate to 0.0005 min^{-1} which represents only 10 times the rate constant obtained at 30°C. Thus, Zn dissolution was more sensitive to the presence of nitrates than to temperature.

It is known that when several anions contacted a solid in aqueous solutions they compete for the adsorption on surface sites [27]. The initial pH values of acid solutions at 2-1-0.5 and 0.2M were 1.09- 1.39- 1.61 and 1.89. In these cases the metal was positively charged attracting electrostatically the anions present in the solution. Thus, two kinds of positive species (protons and the positively charged surface of zinc) and two negative species (citrates and anions (Cl^-, NO_3^- and SO_4^{2-})) may react together and simultaneously in several ways: 1)- H^+ attack (protons with zinc surface species), 2)- Anions reactions (Cl^-, NO_3^-, SO_4^{2-} with zinc surface species), 3)- Citrate complexation with zinc surface species, 4)- H^+ combination with citrates to form molecular citric acid. This shows the complexity of the system studied.

Chlorides were involved remarkably in the dissolution process when used with 0.5M citric acid (Fig 3b) while with 2M citric acid they had no effect. It should be noted that citric acid alone dissolved 34% of Zn when used at 0.5M and 16.05% when its concentration increased to 2M after 270 min (Fig 2a). In the presence of chlorides Zn dissolution registered 91.85% with the solution (citric 0.5M+NaCl 2M) and 16.46% with the solution (citric 2M+ NaCl 2M) after 270min. The high dissolution rate obtained in the first case was probably due to chlorides attack favored by the presence of the suitable acid concentration [28,29]. This behavior indicated that chlorides favored the dissolution when the latter is already initiated. The absence of their effect when present with 2M citric acid may confirm the fact that pitting process of chlorides - which begins generally with their adsorption on the solid surface - was absent because of the saturation of zinc surface with citrates forming strongly bonded complexes and avoiding consequently chlorides attack. This is in accordance with the explanation given by Johnson et al. [26]. In this study sulfates were found to inhibit the dissolution of Zn registering 13.15% with the solution (citric 0.5M+Na_2SO_4 2M) and 5.81% with the solution (citric 2M+ Na_2SO_4 2M) after 270min. In both cases the dissolution percentages were lower than those obtained with citric acid alone at both concentrations. This behavior was reported to be due to the strong adsorptive affinity of sulfates (doubly charged) on solid surfaces that may hinder the progress of the dissolution [30].

On the contrary, Zn release was less parameter dependent in the presence of nitrates and a strong accelerating effect on the dissolution was observed regardless of the conditions used. This indicates their involvement in the dissolution of zinc through a chemical reaction. However, another reaction may also occur in their presence. In fact, Fanning [19] reported that nitrates may react with H_2 formed during zinc dissolution according to:

$$NO_3^- + 4H_2 \rightarrow NH_3 + 2H_2O + OH^- \qquad (8)$$

The reactions (7) is related to be the mechanism involving direct electron transfer between the metal and nitrates, whereas the reaction (8) is considered as an indirect electron transfer mechanism via H_2. Although there are controversies in the literature about the dominant process, the high dissolution rate of zinc obtained in this study in the presence of nitrates indicated that the reaction involving the direct exchange of electrons between Zn and NO_3^- was the dominant process.

Table 2. Kinetic parameters for Zn dissolution by citric acid

Parameters studied	$1-(1-x)^{1/3}=kt\pm b$	R^2
Effect of citric acid concentration		
Operations conditions : 80 °C, 350rpm, Zn=0.2 g, V=200 mL		
Citric acid 0.2M	0.0001t+0.0013	0.9858
Citric acid 0.5M	0.0005t-0.0015	0.9971
Citric acid 1M	0.0004t-0.0012	0.9992
Citric acid 2M	0.0002t-0.0010	0.9985
Effect of temperature		
Operation conditions: 0.5 M-350 rpm, Zn=0.2 g, V=200 mL		
30°C	0.00005t-0.0003	0.9935
40°C	0.0001t-0.00008	0.9895
60°C	0.0002t+0.0017	0.9912
80°C	0.0005t-0.0015	0.9971
Effect of the presence of anions		
Operation conditions: 80 °C-350 rpm, Zn=0.2 g, V=200 mL		
Citric acid 0.5M+$NaNO_3$ 2M	0.0101t+0.0543	0.9853
Citric acid 0.5M+ NaCl 2M	0.002t-0.0083	0.9913
Citric acid 0.5M+ Na_2SO_4 2M	0.0002t-0.0042	0.9973
Citric acid 2M+$NaNO_3$ 2M	0.0095t+0.022	0.9943
Citric acid 2M+ NaCl 2M	0.0002t-0.0065	0.9933
Citric acid 2M+ Na_2SO_4 2M	0.0001t-0.0037	0.9871
Presence of nitrates		
Operation conditions: 80 °C-350 rpm, Zn=0.2 g, V=200 mL		
Citric acid 0.5M+$NaNO_3$ 0.5M	0.0284t+0.0414	0.9956
Citric acid 0.5M+$NaNO_3$ 2M	0.0101t+0.0543	0.9853
Operation conditions: 30 °C-350 rpm, Zn=0.2 g, V=200 mL		
Citric acid 0.5M+$NaNO_3$ 0.2M	0.0073t+0.0085	0.9993
Citric acid 0.5M+$NaNO_3$ 0.5M	0.0107t-0.0046	0.9985

5. CONCLUSION

The results revealed that the mechanism through which zinc metal is dissolved by citric acid is complex. In this system several ionic species seem to interfere together leading to decrease or increase zinc dissolution. It was observed that increasing citric acid concentration up to 0.5M increased the dissolution of Zn to a maximum of 34% beyond which the dissolution decreased at higher citric acid concentrations. This can be interpreted in terms of sorption capacity of the solid surface where high amount of citrate anions may sterically protect the solid surface from proton attack and hinder the dissolution rate. The moderate conditions in which strong dissolution of zinc was observed in the presence of nitrates indicated that they were chemically involved in the reaction. The dissolution of zinc was accelerated when chlorides were present with 0.5M citric acid and was not impacted with 2M citric acid, while sulfate inhibited the dissolution of zinc in all cases. The kinetic study revealed that the dissolution process of Zn was chemically controlled and this was corroborated with the value of the activation energy which was found to be equal to 39.3kJ/mol.

Organic acids such as citric acid are prevalent in many natural settings and in discharges. Understanding the mechanism of metals dissolution in their presence alone or with mineral substances at a fundamental level is important in order to predict the environmental pollution risk.

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