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Mobility of Metals from Mine Tailings using Different Types of Organic Acids: Batch Leaching Experiment

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Abstract: The presence of toxic metals in mine tailings is a major concern because they are hazardous to ecological system and human health. Hence the mobility of heavy metals is an important factor to look at when assessing risk of pollution or contamination in tailing dump. This study was carried out in order to determine the effect of organic acids on the mobility of metals from mine tailings. Characterization of mine tailings was carried out using XRD and XRF. Batch leaching experiment under different initial pH, contact time, temperature, and concentration was carried out in this study. The results show that Fe and Al were the major elements, whereas quartz minerals were considered as the major constituents in the tailing. The batch leaching studies indicated high mobility of elements at low pH, short exposure time, high concentration of organic acids and high temperature. Increase of temperature resulted to faster release of metals, with maximum concentrations of Fe and Al recorded at 48 hours. Oxalic acid and citric acid were found as best leaching agents. The kinetic studies allowed to predict that the dissolution of metals from tailing samples was mostly diffusion controlled.

Keywords: Mine tailings, batch leaching, organic acids, mobility of metals, pH, temperature, concentration

1. Introduction

The exploitation of mineral resources provides strategic resources, but heavy metals contaminations in the soil and water has become one of the environmental problem within the vicinity of mines (Ding et al., 2014; Conesa and Schuling, 2010). Mining operations introduce various heavy metals into the soil and water. As chemical hazards heavy metals are non biogradable and can remain in the environment for a long period of time (Wuana et al., 2010). These metals are released from mine wastes. South Africa produce an estimated 468 million tons of mineral wastes (Oelefse et al., 2007), and most of it is produced by gold mines accountingfor221 million tons or 47% of all mineral wastes produced, making it the largest source of pollution. Among all the wastes, mine tailings are known to be the main environmental effect (Conesa et al., 2007; Dudka and Adriano, 1997) because of its low pHs (Wong et al., 1998; Conesa et al., 2007).

Decontamination of the mine tailings is required to protect the environment (Seh-Bardan et al., 2012). The conventional methods such as soil, venting incineration, physical treatment and chemical treatment are being used for the removal of metals from contaminated soil (Praburaman et al., 2015). This convectional mineral process recently used to recover metals, but these metals have disadvantages such as high costs, long repair cycle and low efficiency (Zhongbing et al., 2011; Dong et al., 2011). In comparison to the conventional methods, bioleaching is more effective to treat low-low grade tailings because many advantages such as low cost, low investment fast processing, simple equipment, wide range of applications, easy management and environment friendliness (Dong etal.,2011). Bioleachingis basically "the use of microorganisms to transform elements so that the elements can be extracted from a material when water is filtered through it" (Brandl, 2001; Mishra et al., 2005; Brandl and Faramarzi, 2006). Microorganisms can mobilize metals trough autotrophic and heterotrophic metabolites and siderophores and methylation which can result in volatilization (Mishra and Rhee, 2014). Microbes action on metals is based on three principles namely acidolysis, complexolysis and redoxolysis (Brandl and faramarzi, 2006). In these processes/ mechanisms microorganisms are able to mobilize metals by the formation of organic or inorganic acids (e.g. citric, oxalic acids and sulfuric acid (acidolysis). In the case of complexolysis processes, the metal solubilization is by ligand-induced mechanisms where microbial formation of complexing or chelating agents increases the metals mobility (Mishra and Rhee, 2014).

Organic acids can supply both protons and metal complexing anions (Gadd, 2004). Citrate form stable complexes with a number of metal ions, for example copper, zinc and highly mobile complexes may be resistant to biodegradation (Gadd, 2001). The reason why this low molecular weight (LMW) anion works as organic ligand, is because of its ability to promote the mobility of heavy metals from contaminated soil by (i) replacing adsorbed metals at the soil surface through ligand-exchange reactions, (ii) dissolving metal-oxides from surfaces that have adsorbed metals, and (iii) forming metal-organic complexes in solution (McColl and Pohlman, 1986; Pohlman, 1986; Stone, 1988; Banks et al 1994; Burckhard et al., 1995; Kim et al., 2013). Such anions increase the mobilization of metals from soil. Most studies have focused on the effect of organic acids on the mobility of metals from soils and sediments, however there is less information regarding their release from mine tailings and there is a need to confirm such findings in South Africa as this type of studies have been done in other countries. In this study batch leaching process was applied using organic acids in order to assess the mobilization of metals from mine tailings. Hence the objective of this study is to determine the effects of contact

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time, temperature, pH and concentration on the mobilization of metals from tailing dumps by organic acids.

2. Materials and Methods

2.1 Sample Collection

Mine tailings used were collected from an abounded gold mine located in the Krugersdorp area, South Africa. Thetailings samples were taken from the top 30 cm of the surface using an auger drill.For this study tailing samples used were the representative from the top of the tailing dump (S2) and from the bottom of the tailing dump (S13). All samples were air dried in the laboratory for 2 days, ground in to fine form, sieved through 75 μ m to a powder form. The powder form samples were used in the entire batch leaching experiment, the remaining of samples were kept in plastics bags prior to use in the rest of experiment.

2.2 Batch leaching experiment

Batch experiments were conducted to determine the effect of organic acids (malic, gluconic, oxalic, and citric acid) on the mobilization of metals, such as Fe and Al from contaminated tailing at various concentrations of organic acids (1, 10, and 100 mM) and initial pHs (3.5, 4.5, 5.5, and 6.5) and temperatures (30°C,40°C and 50°C). In all the experiments, one representative sample from the top (S2) and one from the bottom (S13) of the dump, was used. The experiments were conducted as follows:

Effect of time

A mass of 2.5 g of tailing was added to 25 mL of 3 mM organic acid (malic, gluconic, oxalic, and citric acid). The experiment was conducted in duplicate. The mixture added into volumetric flasks was then shaken by hand for 1 minute to ensure full saturation of the tailing with the solution and then shaken on orbital shaker (200 rpm) at room temperature for 8, 20, 40 and 48 hours. The pH was measured after shaking and then the samples were centrifuged for 10 minutes at 4000 rpm, then the supernatant was kept in a fridge before analysis.

The samples kept in a fridge were then analysed for heavy metals using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Agilent Technologies, USA).

Effect of pH

A mass of 2.5g of tailing was added to 25 mL of 3 mM organic acid (oxalic, and citric acid) and initial pHs (3.5, 4.5, 5.5, and 6.5). The experiment was conducted in duplicate. The pH was controlled with HCl and NaOH. The mixture was added into volumetric flasks then shaken on orbital shaker at room temperature for 24 hrs at 200 rpm. The pH was measured after shaking, then the samples were centrifuged for 10 minutes at 4000 rpm, then the supernatant was kept in a fridge before analysis. The samples kept in a fridge were then analysed for heavy metals.

The effect of temperature

A mass of 2.5 g of tailing was added to 25 mL of 3 mM organic acid (oxalic and citric acids). The experiment was conducted in duplicate. The mixture was added into conical

flasks, then shaken on an orbital shaker at various temperatures (20, 30 and 40 °C). The experiment was conducted at various times for8hrs, 20hrs, 40hrs and 48hrs. The pH was measured after shaking and then the samples were centrifuged for 10 minutes at 4000 rpm and the supernatant was analysed as described above.

2.3 Analytical Method

The concentration of each metal in the supernatant was analysed by using inductively-coupled plasma (ICP-OES). The mineralogical study of the tailings samples were carried out by means of X-ray diffraction (XRD) analysis. The bulk composition was determined using the powder diffraction method, after grinding and homogenization of the samples to 75 µm particle sizes. Non-oriented powders were examined on a Philips X'pert MPD diffractometer, at a power of 1.6 kW operating at 40KV. Major and trace elements of the tailings were analysed using the X-ray- fluorescence spectrometer (XRF) which was done on the magiX PRO SuperQ Version 4. A rhodium (Rh) anode was utilized in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW.

3. Results

3.1. Characterization of mine talings

XRI

The mineralogical composition of the representative samples used in this study is summarized in Table 1. The mineralogical composition of tailing samples from the Krugersdorp mining area was determined by X-ray diffraction (XRD). The XRD pattern showed the dominance of quartz (SiO₂) minerals in the top and bottom of the tailing dump, while other minerals, such as iron catena-silicate & ferrosilite, sillimanate, and aluminium iron (III) oxide were detected in relatively high concentration in samples. A similar trend about the dominance of quartz in the tailings was reported in the study by Novhe et al.(2014).

Table 1: Mineralogical composition of tailing sample

Minerals	Top sample (S2)	Bottom sample (S13)
	Weight%	Weight%
Quartz	0.6	8.2
Fayalite	3.3	
Sillimanate	0.27	8.5
Iron catena-sillicate Ferrosillite	95.83	
Wustite		6.56

XRF

The major, minor and trace elements were determined by using XRF analysis, represented in Table 2. SiO₂ is the dominant oxide in all samples collected from the Krugersdorp mining area, which ranges from 40.49% to 89.15%. This confirms the result obtained using the XRD technique. Other studies also found SiO₂to be mostly abundant in mine tailings (Novhe et al., 2014). Elements such as Al, Cr, Ni, Zn, Cu, As, Pb,K,Mg,Na and Co were also identified in the tailings samples, but were not present in all samples. Those which were found in all samples include elements such as Ca, Cr,Fe,K, Mg, Na, Pb and Zn, however in the present study only Aland Fe remained as

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main focus because they were also detected in the results fort all parameters considered.

Table 2: Major and trace elements in tailing samples

Samples	Al2O3	Fe2O3	SiO ₂
Samples	Weight%	Weight%	Weight%
Top sample (S2)	13.6909	2.6767	81.3664
Bottom sample (S13)	7.9628	0.9971	89.1518

3.2 Batch leaching experiments

3.2.1. Effect of contact time

Table3 represents the effect of time on the leaching of metals considered in the study by using the different organic acids such as oxalic, citric, tartaric, and malic and gluconic acid. The metals obtained in high concentrations are likely to be easily mobilized under environmental conditions. Fe was effectively leached using oxalic, citric and gluconic acids. However leaching with gluconic has shown a slight fluctuation in concentration of Al and Fe from S2 and S13 respectively. The maximum leaching value of Fe from the sample S2achieved was 510.30 mg/L after 8 hours of contact and 31.12 mg/L from S13, which decrease later as both have attained lower concentration after 2 days, reaching lower

values of 40.74 mg/L and 1.38 mg/L respectively. Leaching of Fe from S2 and S13 using citric acid allowed to achieve maximum release at 8 hours equivalent to 232.70 mg/L and 18.71mg/L respectively, which decreased after some time. The leaching of Al from S2 was most effective and faster while using oxalic and gluconic acid, reaching maximum concentrations at 8 hours equivalent to 33.43 mg/L and 29.67 mg/L respectively. The same acids also performed better than other in extracting Al from S13 achieving a maximum release at 8 hours equivalent to 43.26 mg/l and 40.40 mg/L. It was however observed that the release of Fe and Al by tartaric acid, malic and gluconic acids fluctuates after some hours of leaching. These fluctuations of metal concentration maybe attributed to time consuming reactions which lead to metals hydrolysis and precipitation process (Guo et al., 2013). The results have shown a decrease in Fe concentration for top and bottom sample of tailing dump with an increase in leaching time, which indicate the very high leaching rate within the initial hours of leaching. Overall oxalic acid was very effective for the mobilization of Al and Fe from both samples while citric acid was mostly effective for the mobilization of Fe, both acids achieving high leaching rate within the initial hour of contact.

Table 3: Effect of leaching time on the extraction of Fe and Al using 3mM organic acids

Elements and leaching time Amounts leached by different organic acids (mg/L)					
Fe (S2)	Oxalic acid	citric acid	tartaric acid	malic acid	gluconic acid
8	510.3035	232.7045	108.73855	98.39625	544.316
20	185.363	208.8175	77.78065	294.218	118.679
40	80.0381	101.953	333.462	91.12525	61.7941
48	40.74305	21.69371	56.2005	32.1839	23.79085
Fe (S13)					
8	31.1162	18.71045	12.37895	9.224215	16.4782
20	7.53894	6.96971	7.238385	5.200845	3.80481
40	2.454205	1.85859	4.176355	2.53421	1.97174
48	1.37786	4.08308	2.61864	2.71176	2.02727
Al (S2)					
8	33.431	9.443835	5.205765	5.9941	29.6731
20	9.28663	7.841775	13.04776	20.9247	7.91692
40	6.14394	4.87031	22.36815	7.84034	5.33324
48	5.225145	3.3568	5.602945	6.89938	6.132435
Al (S13)					
8	43.26035	22.54065	15.09605	11.28685	40.39945
20	13.89515	10.5861	8.04997	20.93795	12.07935
40	6.28036	4.0194	19.4878	9.86768	6.951365
48	4.92678	12.0244	8.44536	9.05334	6.391465

3.2.2. Effect of pH

Figure 2 represents the results for leaching behaviour of Fe and Al at various pHs 3.5, 4.5, 5.5 and 6.5. From the figure it is clear that the leach ability profile of Al and Fe was a function of initial pH and the released amounts decrease with increasing pH value. Similar trend has been reported in other studies (Fan et al., 2016; Guo et al., 2013). The maximum removal of both Fe and Al appeared at pH 2. The maximum amounts of Al and Fe while leaching with oxalic acid for S2 sample are 11.92mg/L and 11.69 mg/L respectively and the maximum amounts of Al and Fe from S13 while leaching with the same organic acid is 19.17 mg/L and 33.71mg/L respectively. The amounts of Al and Fe leached with citric acid are as follow 24.81 mg/L and213.77mg/L respectively; for S2 and for S13 the

amounts leached out with citric acids for S13 sample are 26.32 mg/L Al and 24.99 mg/L. Fe from the top (S2) of the tailing dump has shown high mobility than the one released from the S13 sample when citric acids was used as a leaching agent, this might be due to the fact that sample S2is at high oxidation state compared to sample S13. The mobility of metals is high under acidic condition (low pH), according to Fan et al. (2016), the leaching of metals in such trend is due to the acidic attack. Al for top and bottom samples is released in high concentration while leached with citric acid than with oxalic acid. High concentration of Fe has been released from top sample than from bottom sample, this might be due to the fact that the oxidation at the top of tailing dump is higher than that of the bottom of tailing dump.

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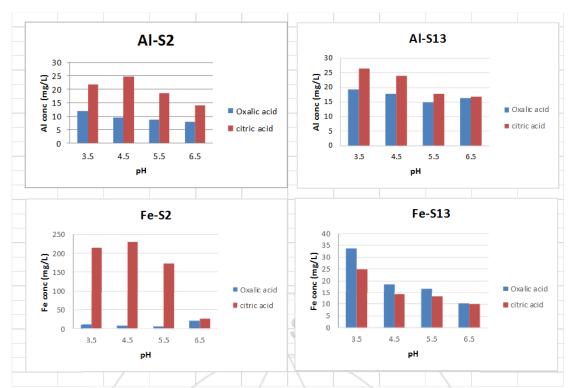


Figure 1: Effect of pH on release of Al and Fe from the top (S2) and bottom (S13) of tailing dump at 3mM oxalic acid and 48 hours contact time

3.2.3. Effect of Concentration

Figure 2 illustrates the effect of organic acid concentration on the mobility of metals at time interval 8, 20, 40 and 48 minutes. From the figure, it is evident that the mobility of metals depends on the organic acid concentration. For both S2 and S13 samples, the concentration of Fe and Al increases with the concentration of oxalic and citric acids from 1mM to 4mM. The higher the concentration of metals, the higher its mobility. Generally high oxalic and citric acids concentrations enhance the mobilization of heavy metals from the contaminated soil (Kim et al., 2013). The highest Al extraction for samples S2 and S13 are 25.96 mg/L and 18.86 mg/L respectively while using oxalic acid, and 17.61 mg/L and 25.96 mg/L for S2 and S13 respectively while

leaching with citric acid. Fe was extracted from S2 and S13 in high amount by using 4mM oxalic acid which is 157.45 mg/L and 17.41 mg/L respectively, while 310.30 mg/L and 22.13 mg/L of Fe were the highest amounts extracted by citric acid at 4mM from samples S2 and S13 respectively. The decreasing concentration of metals at increasing pH has been established in other studies (Kundu et. al., 2014; Fan et al., 2016).Fe from sampling site S2 has high mobility than that from S13, this might be due to the fact that the oxidation at the top of tailing dump is higher than that for bottom of the tailing dump, and this has been confirmed by the XRF findings

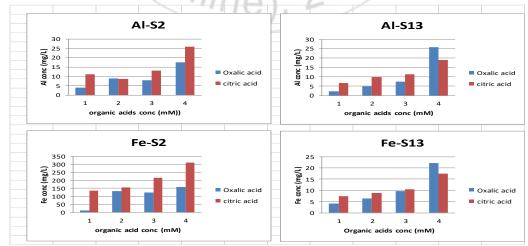


Figure 2: Effect of concentration on the release of Al and Fe from the top (S2) and bottom (S13) of tailing dump at 3mM oxalic and citric acid during 48 hours of contact time

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3.2.4. Effect of temperature

Figure 3 is showing the effect of temperature on the mobilization Fe and Al when leached with oxalic acid and citric acid over temperature range of 30 to 50°C. As shown in the figure, the leaching of Al and Fe examined depend on the temperature and contact time. Leaching with oxalic acid reveals that the concentration of Fe is high at temperature 50°C than at 30°C and 40°C. The mobility of Al and Fe increases with an increase in leaching time, which means that more time is required to mobilize higher amounts of these metals. Metals were highly removed after 48 hours with oxalic acid, as Fe from sample S2have shown the

following removal pattern 0.89 mg/L at 30°C, 0.98 mg/L at 40°C and 1.36 mg/L at 50°C. Whereas Al from S2 has shown the following releasing pattern at 48 hours; 0.30 mg/L. at 30°C, 0.41 mg/L at 40°C and 0.44 mg/L at 50°C when leached out by oxalic acids. The same metals show the same leaching behaviour for sample S2 when oxalic acid is used, and when both metals from S2 and S13 are leached with citric acid. The trend where by metals are removed in higher concentration at higher temperature than at low temperature has been reported in other studies (Guo et al., 2013; Habache et. al., 2009)).

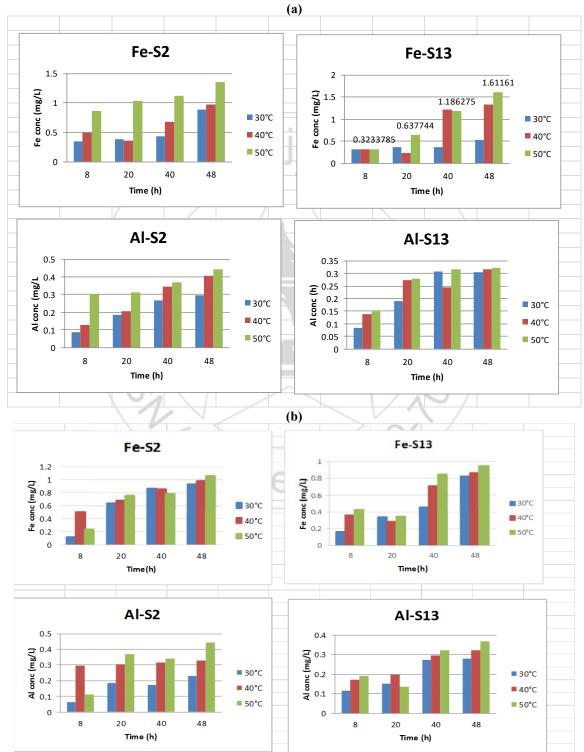


Figure 3: Effect of temperature on the release of Al and Fe from the top (S2) and bottom (S13) of tailing dump at 3mM (a) oxalic and (b) citric acid during 48 hours of contact time.

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3.2.5 Effect of temperature - Synergy of organic acids

Figure 4 exhibits the effect of the combination of organic acids (oxalic, citric, tartaric, malic and gluconic) on mobility of metals in various contact time of 8, 20, 40 and 48 hours. The results show that the concentration of Fe decreases with leaching time, which illustrates that when this organic acids are combined together, they are more effective in leaching the metals at the initial leaching time than when each organic acid is used. At initial hours of leaching the mobility of metals is high for sample S2, when leaching with synergic organic acid. The concentration of Fe decreases from 1.5mg/L to 0.56 mg/L at 8 to 20 hours for 30°C, at 40°C it decreases from 2.09 mg/L to 0.67 mg/L and in S13, the decrease from 8 to 20 hours at 30°C is 3.09 mg/L to 1.86 mg/L and remained undetected at 40 and 48 hours, the increase in leaching time from 8, 40 and 48 hours at 40°C has shown the attenuation of amounts released from 3.29 mg/L, 1.20 mg/L to 1.47 mg/L. Al was released in high amount from sample S2 at 8 hours and temperatures of 30°C, 40°C and 50°C, yielding to concentrations equivalent to 12.48 mg/L, 20.42 mg/L and 22.09 mg/L respectively, which further decrease after 48 hours to the following concentrations 4.92 mg/L, 5.49 mg/L and 8.80 mg/L. The maximum amount of Al was leached at 8 hours at of30°C, 40°C and 50°C, temperatures yielding concentrations equivalent to 21.01 mg/L, 25.22 mg/L and 25.97 mg/L, then a decrease was recorded in the following hours to 6.29 mg/L, 6.35 mg/Land 7.88 mg/L respectively. Fe from samples S2 and S13 exhibit similar trend for Al, however in some cases Fe is not detected. The synergy of all organic acids, allows mobilizing more metals in the first hours of leaching time under the influence of temperature; this is favourable for high leaching rate.

Table 4: Effect of synergic action of organic acids on the leaching of Al and Fe

Amounts removed per leaching time (mg/L)					
Elements and					
temperature	8	20	40	48	
Fe (S2)					
30°C	1.53945	0.558365	0	0	
40°C	2.08572	0.66585	0	0	
50°C	0	2.18158	1.781285	0.4938125	
Fe (S13)					
30°C	3.0861	1.862455	0	0	
40°C	3.287435	0	1.19705	1.465175	
50°C	0	3.16395	1.001295	0	
Al (S2)					
30°C	12.47578	7.405375	7.218395	4.920875	
40°C	20.42425	8.13586	7.53776	5.488085	
50°C	22.09275	8.44334	9.497185	8.796155	
Al (S13)					
30°C	21.0093	11.84515	8.63473	6.288015	
40°C	25.21515	14.59315	10.68065	6.354995	
50°C	25.96965	18.2287	3.9128952	7.88116	

Kinetic studies

Leaching kinetics is generally controlled either by diffusional mass transfer reactant through a liquid film or ash/product layer, the chemical reaction at the surface of the solid particles or a mixed diffusion and chemical reactions (Gharabaghi et al., 2013; Sahu et al., 2011; Gharabaghi et al., 2010, Levenspiel, 1998, Zafari, 2008). The reaction model between liquid and solid may be expressed as:

$$A(liquid) + B(Solid) \rightarrow products$$
 (1) In order to determine the kinetic parameters and the rate controlling step in the Iron and Aluminum leaching in oxalic acid solutions, the experimental data were analyzed based on the shrinking core model. The following equations can be used when either diffusion or the surface chemical reactions are the rate limiting step.:

$$x = kt$$
 for liquid film diffusion (2)

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

 $1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = kt$ for film diffusion control through ash layer (3)

$$(1-x)^{\frac{1}{3}} = kt$$

 $1 - (1 - x)^{\frac{1}{3}} = kt$ for surface chemical reaction control Where x is the fraction reacted, k is the kinetic constant (min^{-1}/h^{-1}) .

The rate limiting step is determined by looking at the high regression coefficients (R close to 1), which reveal a better fitting plot as shown in Figures 4.1 and 4.2. When the regression coefficients for kinetics controlled by different regimes were calculated, as shown in Table 5.1 and 5.2 the highest regression coefficient or the best fits for all the experimental results for tailing leaching using organic acids were found for rate expression controlled by diffusion through ash layer, but the fit was dependent of particle shape which varied among the two samples. Using oxalic acid as lixiviant, a better fit was mostly obtained when assuming particle of flat shape; it could be predicted that the dissolution of Fe was mostly controlled by ash layer diffusion when leaching took place at 30°C; while the dissolution of Al was controlled by film diffusion in S2 and ash layer diffusion in S13.

The fit of the experimental data for the leaching of tailing by citric acid revealed that Fe dissolution from S2 was better controlled by ash layer diffusion with assumption of spherical particle, while the dissolution from S13 was better controlled by ash layer diffusion but with assumption of flat particle. On the other hand, dissolution of Al revealed an inverse trend to that of Fe; as it was found to be controlled by ash layer diffusion with assumption of flat particle in S2, but in S13 the particle was spherical. Leaching using oxalic and citric acids allowed to obtain The different leaching patterns obtained while using oxalic and citric acids in this study is not only linked to the nature of the organic acids as found by Sahu et al. (2011), but the physico and geochemical difference among the samples may have played a considerable role. for the sample from the top (S2) and the bottom (S13) in terms of the rate limiting step, this implies that the release is based on the geochemical particles confirmed by the results of the XRF. The rate constant K was evaluated from the slope of the straight lines shown in Figure 4. Arrhenius equation $K = Ae^{(-Ea/RT)}$ was plotted as lnK vs (1/T) and Ea were calculated. The activation energies determined were found to be mostly lower 80, confirmed that the metal dissolution rate is predominantly diffusion controlled (Habashi, 1999; Aydogan et al., 2005).

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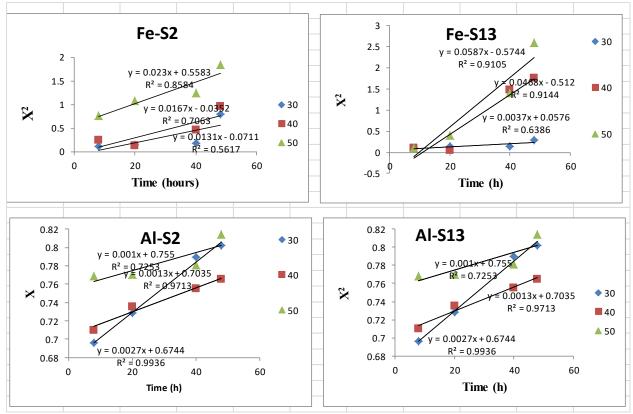


Figure 4.1: Plots of x vs. leaching time at different temperatures for the dissolution of Al and Fe from top (S2) and bottom (S13) of tailing dump with oxalic acid solutions.

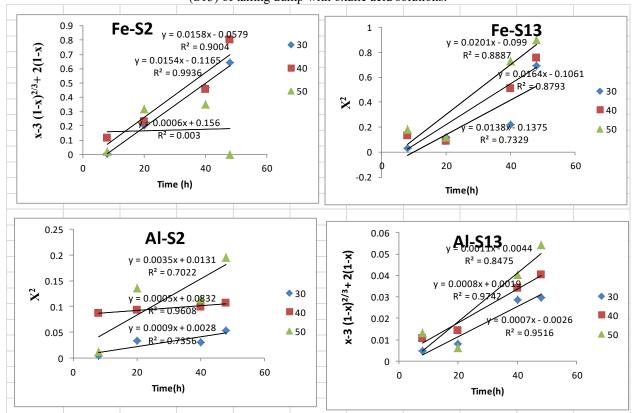


Figure 4.2: Plots of x vs. leaching time at different temperatures for the dissolution of Al and Fe from top (S2) and bottom (S13) of tailing dump with citric acid solutions.

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Table 5.1: Kinetics equations and their regression coefficient and activation energies when using oxalic acid as lixiviant

metals	Kinetic equation	$K(h^{-1})$	R^2	Ea (KJ/mol)
Fe- top	Y=-2.7559X+4.7401	-2.7559	0.9889	22.91296
Fe-bottom	Y=-13.699X+39.941	13.699	0.8251	113.8925
Al-top	Y=5.055X-21.542	5.055	0.9479	42.0271
Albottom	Y=1.8742X-11.468	1.8742	0.4852	15.5825

Table 5.2: Kinetics equations and their regression coefficient and activation energies when using citric acid as lixiviant

metals	Kinetic equation	$K(h^{-1})$	R	Ea
Fe- top	Y=-20.229+61.868	-20.229	0.7387	2.084651
Fe-bottom	Y=-1.8X+1.6992	-1.8145	0.9962	15.08584
Al-top	Y=0.1021X+3.3997	-0.102	0.9997	52.14982
Al-bottom	Y=-2.3765X +0.5316	-2.3765	0.9145	9.72893

4. Conclusion

It was found that the mobility of Al and Fe elements were highly influenced by environmental conditions. Citric and oxalic acids were found to be the most efficient leaching agents as both yielded fast dissolution rate of metals from both tailing samples. Fe and Al were mobilized efficiently in high acidic medium and high temperature conditions. It was also observed that when acting in synergy, organic acids were more efficient as lixiviant than when considered individually, this could be ascribed to the diversity of leaching mechanisms. The kinetic studies allowed to determine the rate limiting steps for the dissolution of metals which is critical for the improvement of the leaching rate; most of the rate expressions were diffusion controlled, implying that the physical properties of the tailing significantly influenced the leaching rate.

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