Kinetic Study on the Removal of Iron from Gold Mine Tailings by Citric Acid

T Mashifana[1], N Mavimbela[1] and N Sithole[1]

[1]University of Johannesburg, Department of Chemical Engineering, P.O. Box 17011, Doornfontein 2088, South Africa
E-mail: tmashifana@uj.ac.za

Abstract. The Gold mining generates large volumes of tailings, with consequent disposal and environmental problems. Iron tends to react with sulphur to form pyrite and pyrrhotite which then react with rain water forming acid rain. The study focuses on the removal of iron (Fe) from Gold Mine tailings; Fe was leached using citric acid as a leaching reagent. Three parameters which have an effect on the removal of Fe from the gold mine tailings, namely; temperature (25 ℃ and 50 ℃), reagent concentration (0.25 M, 0.5 M, 0.75 M and 1 M) and solid loading ratio (20 %, 30 % and 40 %) were investigated. It was found that the recovery of Fe from gold mine tailings increased with increasing temperature and reagent concentration, but decreased with increasing solid loading ratio. The optimum conditions for the recovery of Fe from gold mine tailings was found to be at a temperature of 50 ℃, reagent concentration of 1 M and solid loading of 20 %. Three linear kinetic models were investigated and Prout-Tompkins kinetic model was the best fit yielding linear graphs with the highest R^2 values.

1. Introduction

Africa is a mineral-rich country with metals such as gold, copper, and platinum group metals being exploited to a significant extent in the country's mining history. Mining generates large volumes of tailings, with consequent disposal and environmental problems. Research shows that the largest quantity of gold that has been mined in South Africa (98%) has come from the Witwatersrand goldfields. The cluster of gold mines located in the Witwatersrand Basin generates a significant amount of mine tailings, which have adverse effects on the environment and ecological systems. In addition, disposal costs are very high [1].

Un-reclaimed gold mining sites are a major problem in the entire world with tailings being a source of contamination for communities living close to these mine dumps. Tailings consist of ground rock and process effluents that are generated in a mine processing plant. Tailings storage is associated with ever increasing challenges. Innovations allow low grade ores to be exploited resulting in high waste volumes which require safe storage. Environmental laws are advancing, putting pressure on mining industries in handling of tailings. Due to this, mine operations are forced to treat tailings after recovering precious metals from ores prior to disposal. Rosner, [2] analysed heavy metal concentrations in stream sediments and rivers affected by gold mines in the Witwatersrand region and the Free State Province. Acid mine drainage and the leaching of toxic metals such as Co, Cu, Fe, Mn, Ni and Zn resulted in an increase in metal concentrations [2].

An investigation on the bioleaching of heavy metals from mine tailings by Aspergillus fumigatus showed that in the one-step bioleaching process where the fungi was cultivated in the presence of the tailings, concentration of oxalic acid was the highest and in the two-step process where the metabolic products of fungal growth, which have been separated from its biomass, were used, citric acid was

dominant [3]. In the one-step process, the highest removals of As, Fe, Mn, and Zn were observed at the lowest tailings concentration. In general, it was found that heavy metals removal efficiency decreased with increased tailings concentration in both bioleaching processes.
In 2014 Vapur et.al., conducted an investigation using oxalic, citric and glycolic acids as principal organic acids used in leaching slimes sized (-75 µm) feldspar ores in order to reduce iron amount [4]. The parameters investigated were; temperature, pulp density, leaching time and acid molarity. The overall test results showed that the highest iron removal was obtained as 67.90 % using oxalic acid. The toxic metals in gold mine tailings have a negative impact on human health and the environment and this necessitates the recovery of these metals [5].
The objective of this study was to find an optimal, cost effective treatment process for gold mine tailings (focusing on the removal of iron) and develop a kinetic model for the leaching of Fe from the gold mine tailings.

2. Experimental

2.1. Material
The mine tailing was collected from a gold mine and dried in the oven for 24 hours at 50 ^{o}C. Different concentrations (0.25 M, 0.5 M. 0.75 M and 1 M) of citric acid were prepared as the leaching reagents. The thermostatic shaker was used as a leaching equipment to leach Fe from the gold tailings at different temperatures (25 ^{o}C and 50 ^{o}C), at a constant speed of 200 rpm. Solid loading of 20 %, 30 % and 40 % we investigated.

2.2. Method
The sample was then milled to 80 % passing 75 µm. The leaching period of 24 hours was allowed, samples were taken in the interval of 2 hours. After 24 hours; the slurry was filtered, the solids were air dried for 24 hours and the effluent was taken for analysis. The prepared reagents with respective concentrations were mixed with the gold mine tailing in the solid liquid ratio of 20%, 30% and 40%, in a thermostatic shaker for the leaching of the material. The initial conditions (pH and temperature) of the slurry were recorded. The leaching period of 24 hours was allowed, with sampling in the interval of 2 hours. After 24 hours; the slurry was filtered, the solids air dried for 24 hours and the effluent taken for analysis.

2.3. Analysis
X-ray Fluorescence (XRF) was used for elemental composition of the material. X-ray diffraction (XRD) was used to study the mineralogy and Scanning Electron Micrograph (SEM) was utilized to study the crystal structure and morphology images of the materials. To analyze the solution samples, an atomic absorption spectrophotometer (AAS) was used.

3. Results and discussions
Table 1 shows that the tailings consisted highly of silica (Si 71.8444 mass %). This is of no surprise as the sample is from Gold Mine which is located in the West Rand and is known to be dominated by ores containing silica. The tailings also consisted of Fe (7.6945 %), Al (8.7896 %), Mg (4.5297), S (3.4468 %) and traces of other metals. Table 1 shows that the tailings consisted highly of silica (Si 71.8444 mass %). This is of no surprise as the sample is from Gold Mine which is located in the West Rand and is known to be dominated by ores containing silica. The tailings also consisted of Fe (7.6945 %), Al (8.7896 %), Mg (4.5297), S (3.4468 %) and traces of other metals.

Table 1. XRF results for raw gold mine tailings.

Element	Weight %	Element	Weight %
Mg	4.53	Mn	0.10

Al	8.79	Fe	7.69
Si	71.84	Ni	0.10
P	0.11	Cu	0.01
S	3.45	Zn	0.05
Cl	0.17	Rb	0.01
K	1.59	Zr	0.03
Ca	0.76	Pb	0.50
Ti	0.41	U3O8	0.01

3.1. XRD and SEM of gold mine tailing before treatment

Figure 1 shows that the gold tailings consisted highly of quartz (SiO_2), chalcocite (Cu_2S) and pyrite (FeS_2) complimenting the XRF results. Since Fe and Cu are both transition metals and tend to behave the same, it was concluded that only one of the two elements will be analysed. The study focused only on the leaching of Fe instead of Si and since Cu tends to behave in the same manner as Fe, it was assumed that it will give the similar results as those of Fe.

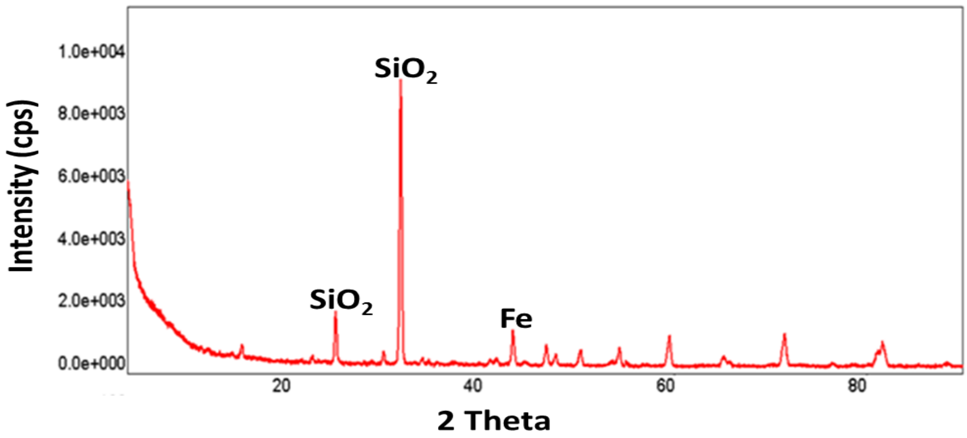

Figure 1. XRD of gold mine tailings.

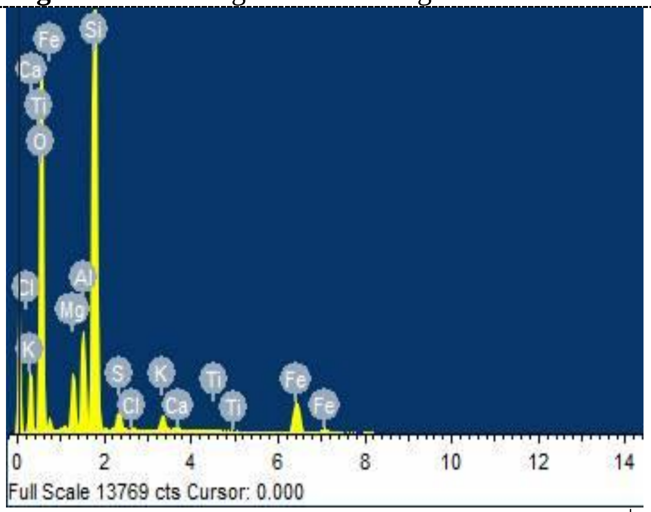

Figure 2(a). EDS of gold mine tailings.

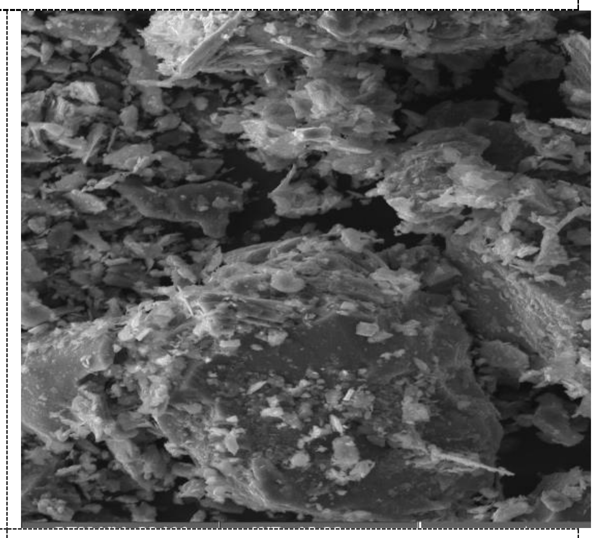

Figure 2 (b). SEM of gold mine tailings.

IOP Conf. Series: Earth and Environmental Science **120** (2018) 012025 doi:10.1088/1755-1315/120/1/012025

Figure 2(a) shows the elements present in gold mine tailings. The spectrum shows that the tailings were predominated by Si and Fe. The result correspond to the XRD results, the SEM, figure 2(b) , shows that the tailings consisted highly of silicon (greyish rock-like structure) which appeared as quartz in the gold tailings and Fe (black spaces in between the quartz).

3.2. Effect of citric acid concentration on leaching rate
The effect of citric acid concentration on the leaching rate of Fe from the gold tailings was studied at the reagent concentrations of 0.25 M, 0.5 M, 0.75 M and 1 M. The tests were conducted at a temperature of 25 ℃ and at a constant speed of 200 rpm. The percentage of the Fe leached is dependent on the concentration of the citric acid used to leach the gold tailings; the higher the citric acid concentration, the higher the recovery of heavy metals from the gold tailings. In Figure 3, the leaching temperature was kept constant at 25 ℃, and leaching at a speed of 200 rpm and 20 % solids. The results show that the recovery of Fe increases with increasing reagent concentration and time; the concentration of the iron leached is highest at 1 M compared 0.25 M, 0.5 M and 0.75 M.

3.3. Effect of temperature on leaching rate
Leaching is a chemically controlled process in which temperature mostly affects the reaction rate [6]. The rate of leaching is directly proportional to temperature; it increases with increasing temperature as molecules tend to gain more energy [6]. Although increasing the leaching temperature increases the solubility of the gold tailings and the leaching rate, the solvent's (citric acid) boiling point must not be exceeded as this might result in loss of solvent by evaporation and reduced metal recovery [7]. The effect of temperature on the recovery of gold tailings was studied at temperatures 25 ℃ and 50 ℃ at a constant speed of 200 rpm and reagent concentrations of 1 M. Figure 4 shows the leaching of Fe from gold tailings leached at 20 % solids. The figure shows that the recovery of Fe from the tailings increases with an increase in temperature. The recovery of Fe is significantly higher (47.08%) at 50 ℃ compared to the Fe leached at 25 ℃ (20.99%).

3.4. Effect of solid liquid ratio
The effect of solid-liquid ratio on the amount of Fe leached is shown in figure 5. The results show that the amount of the Fe leached decreases with an increase in the solid-liquid ratio. For the same amount of the reagent used at the same temperature and reagent concentration, it is expected that the concentration of the Fe leached decreases at a higher solid loading than at lower solid loadings. A higher volume of the reagent is needed to leach the 40 % solids compared to the 20 % solids. In the 20 % solids, molecules can move freely, resulting in high recovery.

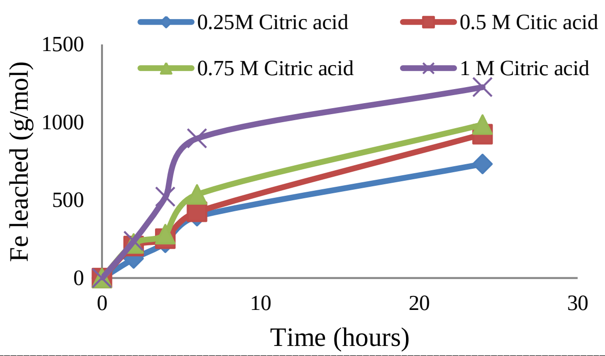

Figure 3. Comparison of Fe leached at different concentrations.

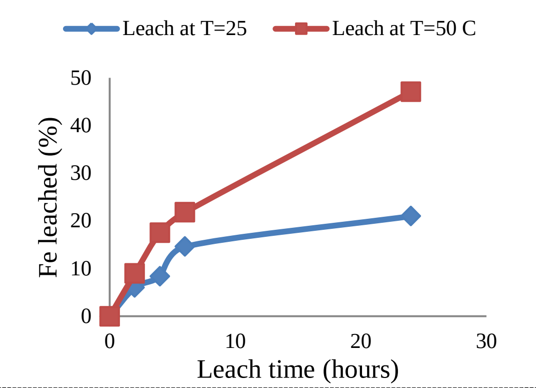

Figure 4. Comparison of Fe leached at different temperatures..

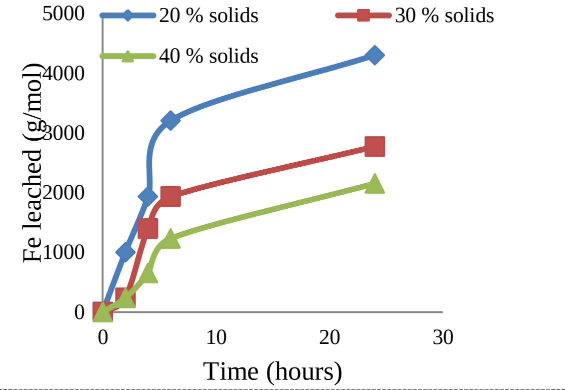

Figure 5. Comparison of Fe leached at different solid loading.

3.5. Leaching kinetics

Different kinetic models were drawn. Of all the kinetic models studied, only three models with the highest R^2 values are discussed. Based on the effect of temperature, reagent concentration and solid-liquid ratio, kinetic models were drawn. Figure 6 shows the results obtained with the Prout-Tompkins kinetic model. The Prout-Tompkins kinetic model gives linear graphs with an R^2 value of 0.9957 at a temperature of 50 ℃ and an R^2 value of 0.9968 at a temperature of 25 ℃.

Figure 7 shows results obtained with the Interface kinetic model. Figure 7 shows that the Interface kinetic model had an R^2 value of 0.9856 at a temperature of 50 ℃ and 0.9928 at a temperature of 25 ℃. Figure 8 shows the results obtained with the Second Order kinetic model. The results show that the Second Order kinetic model had an R^2 value of 0.9249 at a temperature of 50 ℃ and 0.882 at a temperature of 25 ℃.

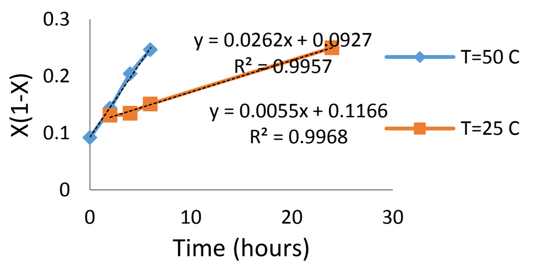

Figure 6. Prout-Tompkins kinetic model.

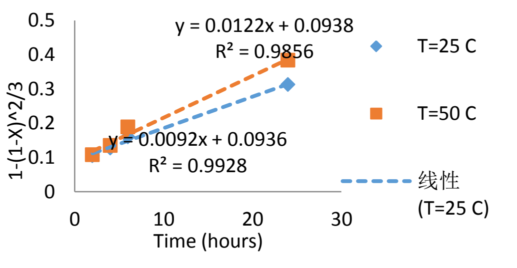

Figure 7. Interface kinetic model.

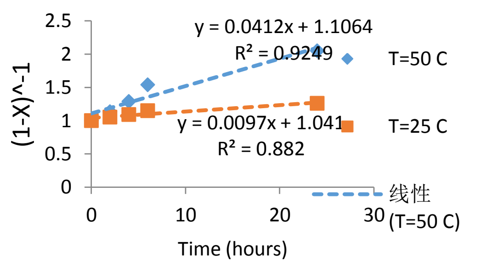

Figure 8. Second order kinetic model.

Table 2 gives a summary of the three models that gave the best fit.

Table 2. Summary of R^2 values for three kinetic models

Kinetic model	R^2, T= 25 °C	R^2, T=50 °C
Prout-Tompkins	0.9968	0.9957
Interface	0.9928	0.9856
Second order	0.8820	0.9246

The Prout- Tompkins gave the best line of fit with an R2 of 0.9957 at a temperature of 50 ℃ and an R^2 of 0.9968 at a temperature of 25 ℃. All three models show that the rate of reaction depends on the Fe leached and the amount of citric acid used. The higher the concentration of the reagent used, the higher the conversion.

4. Conclusion

The effect of citric acid concentration on leaching of the Fe was investigated at concentrations: 0.25 M, 0.5 M, 0.75 M and 1 M at a temperature varying from 25 ℃ to 50 ℃ and a solid loading of 20 %, 30 % and 40 % at a constant stirring speed of 200 rpm. It was found that the concentration of the metals leached from the gold tailings increased with increasing reagent concentration and temperature, but decreased with increasing solid-liquid ratio. The highest concentration of the iron leached was found to be at a reagent concentration of 1 M at 20 % solids and a temperature of 50 ℃. This is because when increasing the leaching temperature, solubility of the tailings also increases, resulting in high recovery of the metal being leached. Increasing the solid-liquid ratio had a negative effect on the leaching rate of the metals being leached. The leaching rate decreased with an increase in solid loading at a constant slurry volume. The kinetic model that was found to be fit for the overall investigation at all temperatures was found to be the Prout-Tompkins model. Since citric acid is an organic that is biodegradable and nature friendly and inexpensive, it is highly recommended for the removal of iron from gold tailings.

5. References

[1] Malatse S and Ndlovu M 2015 The viability of using the Witwatersrand gold mine tailings for brickmaking *Journal of the Southern African Institute of Mining and Metallurgy*, 115G.

[2] Rosner T 1999 The environmental impact of seepage from gold mine tailings near Johannesburg South Africa. Pretoria : University of Pretoria, pp 3-7.

[3] Seh-Bardan BJ, Othman, Wahid S, Husin A and Sadegh-Zadeh F 2012 Column bioleaching of arsenic and heavy metals from gold mine tailings by Aspergillus fumigatus". *CLEAN–Soil Air Water*, 40(6), pp.607-614.

[4] Vapur H, Demirci H., Top. S and Altiner M 2014 Removal of feldspar ores by leaching with organic acids *Turkey: Department of Mining Engineering*, pp.761.

[5] Phetla TP, Ntuli F and Muzenda E 2012 Reduction crystallization of Ni, Cu, Fe and Co from a mixed metal effluent *Journal of Industrial and Engineering Chemistry*, 18, pp. 1171–1177.

[6] Eksteen J and Oraby E 2015 The leaching and absorption of gold using low concentrated amino acids and hydrogen peroxide: Effect of catalyst ions, sulphide minerals and amino acid type *Minerals Engineering,* pp. 309-315.

[7] Zhong SP 2015 Leaching kinetics of gold bearing pyrite in H_2SO_4-$Fe_2(SO_4)_3$ system *Transition of Nonferrous Metals Society of China*, pp. 3461-3466.

Acknowledgments

The authors would like to thank the University of Johannesburg for providing resources to conduct the study and for financial assistance.