

A Study of the Kinetics of Dissolution of a Nigerian Laterite in Sulfuric Acid.

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ABSTRACT

A study of the kinetics of dissolution of a Nigerian laterite in sulfuric acid medium has been undertaken. The elemental characterization of the laterite sample was carried out by inductively coupled plasma mass spectrometry (ICP-MS) and the result showed that the major elements in the ore are Si (44.98%), Fe (13.93%), Ca (4.31%), Ni (2.43%), and Co (1.02%). Other parameters such as the loss of mass on ignition, moisture content, and pH of the material suspension in water were also determined. The effects of acid concentration, temperature, stirring rate, and particle size on the dissolution rate were investigated. Experimental results indicated that the laterite dissolution was greatly influenced by hydrogen ion concentration and the leaching data fitted a diffusion model. The activation energy of laterite dissolution in sulfuric acid obtained was 67.53 kJ/mol and the order of reaction was approximately one with respect to the hydrogen ion concentration.

(Keywords: laterite, activation energy, order of reaction, dissolution kinetics, sulfuric acid, sulphuric acid, loss of mass on ignition, moisture content, pH, ICP-MS)

INTRODUCTION

The term laterite was derived from the Latin word *Later* which means brick stone. The history of laterite monuments dated back to 200 B.C. with megaliths of Kerala, South India. Most of the third generation Khmer temples at Angkor (India) were built with laterite and have survived for 1,000 years. Later, world heritage sites such as churches of the old Gao (India) and the walls in G5 monuments of My Son in Vietnam were also built in laterite [1]. Until today, it is a common vernacular building material and profoundly used in road construction [2].

Laterite develops by intensive and long lasting weathering of the underlying parent rock [1]. It contains mainly minerals such as kaolinite, goethite, hematite, and gibbsite which form in the course of weathering. Moreover, many laterites contain quartz as relatively stable relic mineral from the parent rock. Lateritic soil may contain clay mineral; but they tend to be silica-poor, for silica is leached out by water passing through the soil [3]. The presence of goethite and hematite causes the red-brown color of laterites.

Laterite is still used in road construction, that is, laterite roads (also known as laterite pistes), especially in Africa. Such roads range from local roads to major highways, if well-constructed with attention to compacting the roadway base and drainage, and well maintained by grading, reasonably high average speeds and smooth travel can be achieved on them when dry.

Laterization is economically most important for the formation of lateritic ore deposits. Bauxite which is an aluminum-rich laterite variety can form various parent rocks if the drainage is most intensive, thus leading to a very strong leaching of silica and equivalent enrichment of aluminum hydroxides above all gibbsite. While laterization of igneous rocks often results in a considerable nickel concentration [4-5].

Solid lateritic gravel is readily put in aquaria where it favors the growth of tropical plants. The high concentration of iron provides an robust source of minerals for the plants. The oxidized Fe^{3+} can be turned to Fe^{2+} , (the form of iron most easily used by plant) by organic acids in the aquarium. It is also believed that the soft texture of the lateritic soil is conducive to plant root hairs and may be able to absorb other nutrients from the water [3].

In Nigeria, laterite is found in large proportion in Abia, Adamawa, Delta, Jigawa, Kano, Katsina,

Kwara, Lagos, Sokoto, Enugu, and Taraba States [6].

Little or no interest has been shown towards the kinetic study of this ore in Nigeria except by Olanipekun (2000) who reported the dissolution of laterite in HCl medium. This study thus represents a detailed study on the dissolution of cobalt-enriched Nigerian laterite in H₂SO₄ (sulfuric acid) medium.

EXPERIMENTAL

Material

Laterite used for this study was collected from a mining site in Idofian, Ifelodun Local Government Area of Kwara State, Nigeria. Elemental analysis was carried out by the use of ICP-MS. All reagents used were of analytical grade and were products of BDH. Doubly distilled water was used for all the analytical preparations.

Physico-chemical characterization

Loss of mass on ignition determination: Weighed crucible and 1g of laterite was put inside a muffle furnace and roasted at high temperature of about 500-600°C for about 2 hours. After roasting, the sample was withdrawn from the furnace and was allowed to cool in a dessicator. The cooled product was then reweighed.

The difference in mass represents the mass of organic present in the mineral [7]. The process was carried out in triplicate.

Moisture content determination: 1g of laterite was weighed and put in a crucible. This was then put inside an oven and heated to a temperature of 105°C for 5 hours. After heating, the sample was withdrawn and quickly transferred into a dessicator in order to prevent further moisture absorption from the atmosphere. The cooled product was then reweighed.

The difference in mass gives the mass of moisture content of the laterite [11].

pH determination: 10g of laterite was put inside a conical flask followed by the addition of 30ml distilled water. The mixture was stirred vigorously for 5 minutes and allowed to equilibrate. The pH of the suspension was taken by the use of a

pHep[®] HANNA pH meter. The measurement was monitored daily for two weeks [8].

Leaching Procedure

1g of laterite sample of 0.2mm particle size was put into a 100ml of 0.5M H₂SO₄. The magnetic stirrer introduced and the solution mixture heated at temperature of 55°C and stirred at a rate of 200 rpm for a particular contact time.

At the end of the contact time and for each concentration of the sulfuric acid, the solution obtained was filtered and the insoluble residue left in the filter paper was washed thoroughly with distilled water.

The residue in the filter paper was oven-dried at about 60°C and was reweighed. The difference in the amount of the laterite left from the original mass was then noted. This was then used to determine the percentage of the laterite dissolved in a given leachant [11].

The same procedure was repeated for other concentrations of sulfuric acids: 1.0M, 2.0M, 4.0M, and 8.0M. Each concentration of acid was contacted with 1g of laterite for 5, 10, 30, 60, and 120 mins. [8].

RESULTS AND DISCUSSION

Loss of Mass on Ignition

The results obtained on loss of mass on ignition of the dry sample are put together in Table 1.

The average percentage of loss of mass on ignition of laterite ore was approximately 21.57%. The loss of mass could be accounted for by the presence of volatile or organic/decayed substances.

Moisture content

Table 2 shows the result obtained from the moisture content determination.

Moisture content determination of the mineral enables us to find out the state of dryness or otherwise of the mineral. The result obtained for the moisture content of the laterite was 8.7%.

Table 1: Loss of Mass on Ignition of Laterite.

	Crucible 1	Crucible 2	Crucible 3
Mass of laterite used (a)	1g	1g	1g
Mass of crucible + laterite before roasting (b)	16.918	16.348	73.158
Mass of crucible + laterite after roasting (c)	16.703	16.132	72.942
Loss of mass on ignition (b-c)	0.215	0.216	0.216
% loss of mass on ignition	21.50%	21.6%	21.6%

Table 2: Moisture Content Determination of Laterite.

	Crucible 1	Crucible 2	Crucible 3
Mass of laterite used	1g	1g	1g
Mass of crucible + laterite before drying	16.918	16.348	73.158
Mass of crucible + laterite after drying	16.832	16.261	73.070
Mass of laterite left	0.914	0.913	0.912
Mass of moisture content	0.086	0.087	0.088

pH

The pH of the laterite-water suspension was 8.5. This value suggests that the surface of laterite is basic. This is in support of the predominant chemical form of laterite, which is oxide.

ICP-MS analysis

The results of the ICP-MS analysis showed that Si (44.98%), Fe (13.93%), Ca (4.31%), Ni (2.43%), and Co (1.02%) formed the major element in the laterite sample. Other minor elements include Cu, Zn, S, Ti, Mn, and Ag. However, elements such as Al, Mg, Nb, W, Cd, and Cr are recorded at trace levels.

Leaching Studies

Effect of Acid Concentration: The effect of acid concentration was studied over the concentration range of 0.1M-8.0M. The result of the fraction of laterite dissolved at different contact time in various concentrations of sulfuric acid medium is illustrated in Figure 1.

It is evident that the percentage of laterite dissolved increased linearly with the concentration of sulfuric acid. Concentration of the leachant (sulfuric acid) thus has a significant effect on the leaching of laterite.

The pattern of the result obtained in Figure 1 is in agreement with the work reported by Olanipekun (2000) on a separate study involving leaching of raw and pre-roasted laterites by HCl.

Effect of Temperature: The effect of temperature on rate of laterite dissolution was studied over the temperature ranges of 28°C-80°C for 2M H₂SO₄.

As seen in Figure 2, an increase in temperature greatly accelerates the reaction rate and this leads to increase in the amount of laterite dissolved.

Effect of Particle Size: Table 3 shows the effect of particle size on the dissolution of laterite in 2M H₂SO₄ solution at 80°C, using four particle sizes: 0.2 mm, 0.3 mm, 0.4 mm, and 0.5 mm and at a stirring rate of 200 rpm.

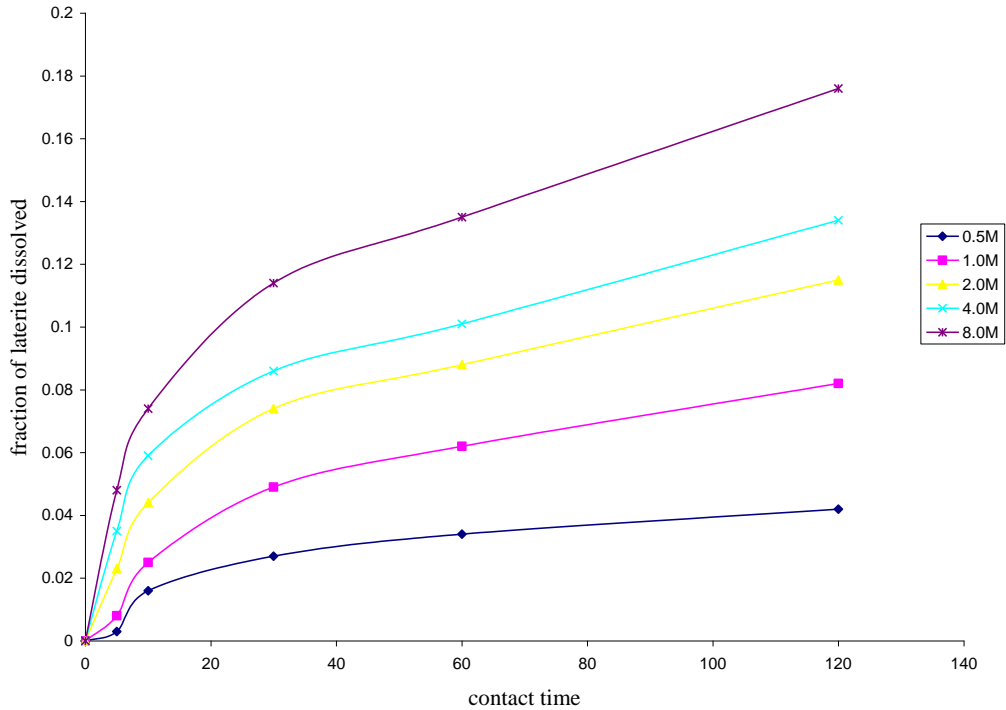


Figure 1: Fraction of Laterite Dissolved (X) versus Contact Time (min) at Different Concentrations of H₂SO₄. (Experimental conditions: temperature = 55°C, mass of laterite used = 1.0g, stirring rate = 200rpm, particle size = 0.2mm.)

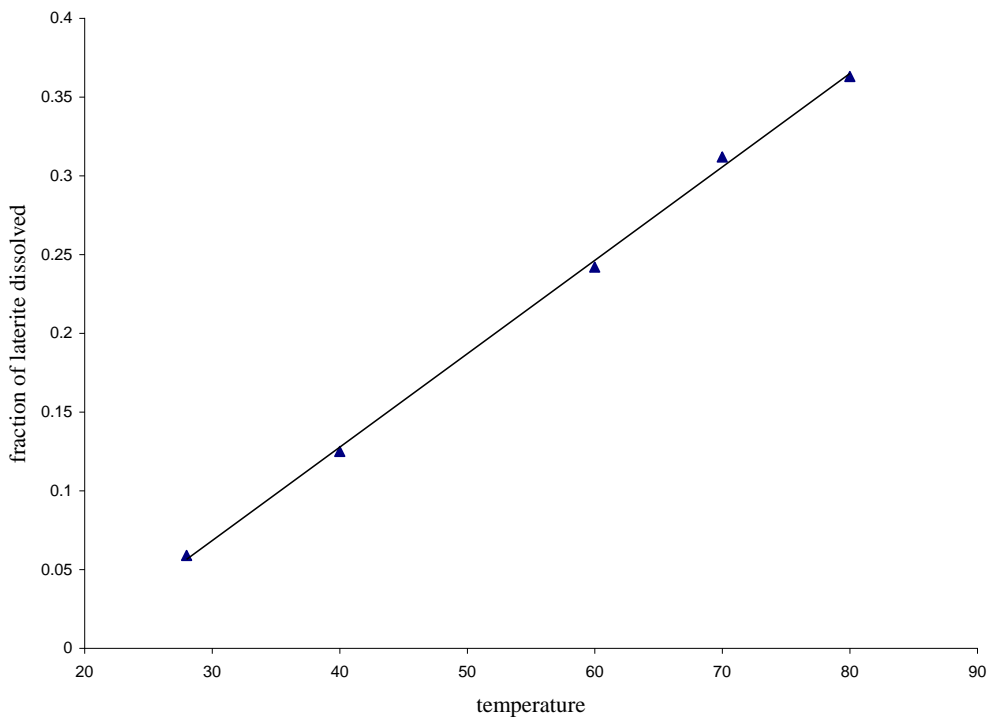


Figure 2: Fraction of Laterite Dissolved (X) versus Different Contact Temperature (°C). (Experimental conditions: mass of laterite used = 1.0g, stirring rate = 200rpm, contact time = 120min, particle size = 0.2mm.)

Table 3: Effect of Particle Size on Laterite Dissolution in 2M H₂SO₄ at 80°C.

Particle Size (mm)	Amount of Laterite Dissolved (%)
0.2	45.20
0.3	37.31
0.4	29.61
0.5	19.57

From Table 3, it is apparent that the fraction with the smallest particle size (0.2mm) gave the highest percentage (45.20%) of laterite dissolution. This was due to the highest surface area of the smallest particle size fraction. This particle size was then chosen for further investigation.

Effect of Stirring Speed: The effect of stirring speed on the dissolution of laterite was investigated in H₂SO₄ 4M solution with the 0.2mm size fraction of laterite at 80°C using stirring speeds of 0-540 rpm. The percentage of laterite dissolved (%) versus stirring rate (rpm) is shown in Figure 3.

It is clear from Figure 3 that the amount of laterite dissolved increases with the stirring speed between 0-360 rpm. The percentage dissolved appears to be practically constant afterwards. There is no appreciable gain from 360-540 rpm. Hence, increase in the percentage of laterite dissolved with increasing stirring speed demonstrates the importance of diffusion in the dissolution process.

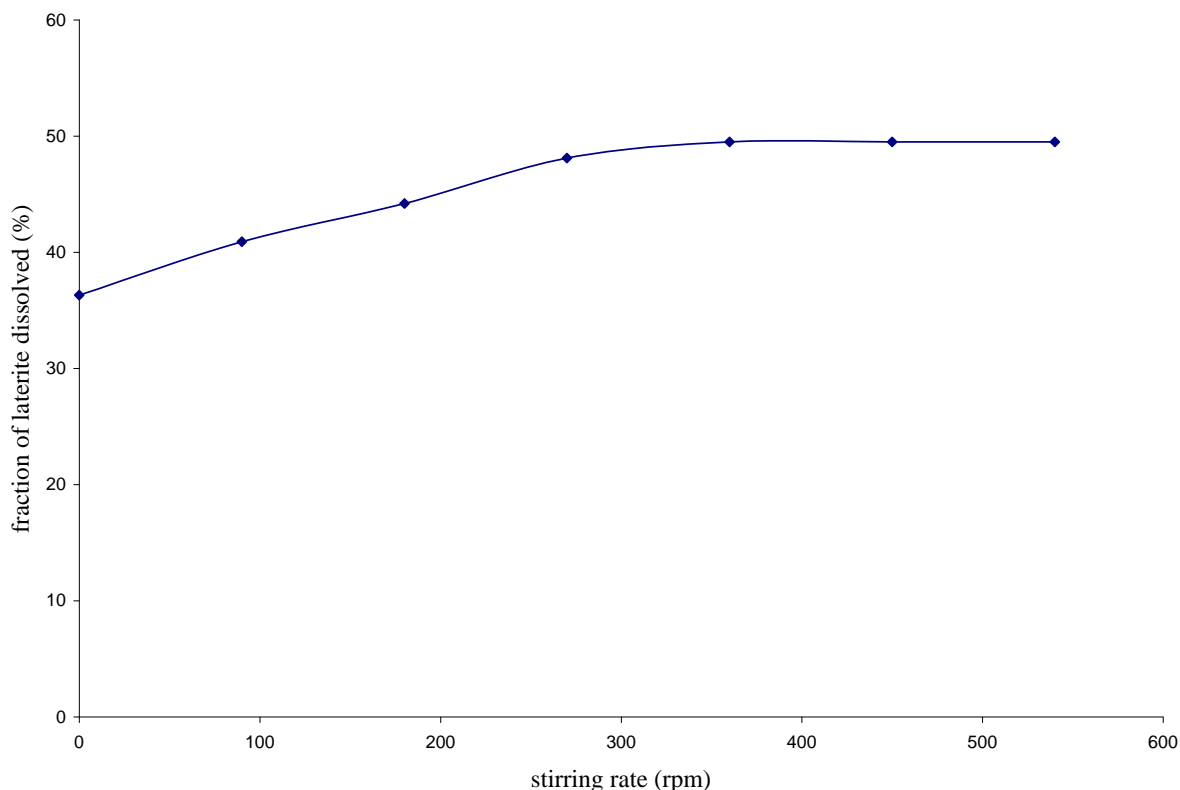


Figure 3: Percentage of Laterite Dissolved versus Stirring Rate (rpm).
(Experimental conditions: mass of laterite = 1.0g, contact time = 120min, particle size = 0.2mm).

Kinetic Analysis: The shrinking core model considers that the leaching process is controlled either by the diffusion of reactant through the solution boundary layer or through a solid product layer; or by the rate of the surface chemical reaction; or combination of surface chemical reaction and diffusion of reactant (mixed control mechanism).

For this study, two shrinking core models were investigated with respect to the linearization of the dissolution curve (Figure 1) as proposed by several investigators (9-10):

$$1 - (1 - X)^{1/3} = k_r t \quad (1)$$

$$1 - 2/3X - (1 - X)^{2/3} = k_d t \quad (2)$$

where: X is the fraction of laterite dissolved (g),
t is contact time (s), and
k_r, k_d and k_m are the reaction rate constants (kJ/mol).

Equation 1 is based on the surface chemical reaction as the rate controlling step and its slope corresponds to the apparent rate constant k_r.

Equation 2, on the other hand, is based on the assumption that the rate controlling step is diffusion through a semi-permeable product layer formed around the solid and its slope gives the apparent rate constant k_d.

The rate constant values k_r and k_d calculated from Equation (1) and (2), respectively, and their correlation coefficients for each concentration is given in Table 4.

The values of the correlation coefficients indicated that the dissolution rate of laterite is controlled by the diffusion of hydrogen ion and not by surface chemical reaction. The application of the diffusion kinetic model is shown in Figure 4 below.

These results (Figure 4, Tables 4) clearly indicated that the mechanism of dissolution of laterite follows perfectly the diffusion through a semi-permeable product layer.

Activation Energy: Arrhenius diagram in Figure 5 was obtained by applying equation 2 to the leaching experimental data in Figure 2.

Table 5 summarizes the apparent rate constant values for 2M H₂SO₄ at various temperatures. The activation energy (E_a) for the dissolution of laterite calculated from the slopes in Figure 5 for H₂SO₄ is 67.53 kJ/mol.

The E_a value for laterite dissolution in sulfuric acid obtained (67.53kJ/mol) is close to the results obtained by Olanipekun (2000) who reported that the E_a for both raw and roasted laterite in HCl are 71.7 kJ/mol and 65.2 kJ/mol, respectively.

Order of Reaction: The results on the effect of sulphuric acid concentrations was applied to this kinetic model and k_d values for the hydrogen ion concentration are given in Table 6.

From the k_d and hydrogen ion concentration values in Table 6, a plot of lnk_d versus ln[H⁺] were constructed (Figure 6).

Table 4: Apparent Rate Constants k_r, and k_d and Correlation Coefficient Values at Various Concentrations of H₂SO₄.

Concentration of H ₂ SO ₄ (M)	Apparent Rate Constant (10 ⁻⁴ min ⁻¹)		Correlation Coefficient (R ²)	
	k _r	k _d	k _r	k _d
0.5	1.00	0,012	0.8205	0.9883
1.0	2.75	0.088	0.8305	0.9904
2.0	5.00	0.288	0.8372	0.9908
4.0	6.42	0.473	0.8427	0.9941
8.0	7.67	0.668	0.8470	0.9907

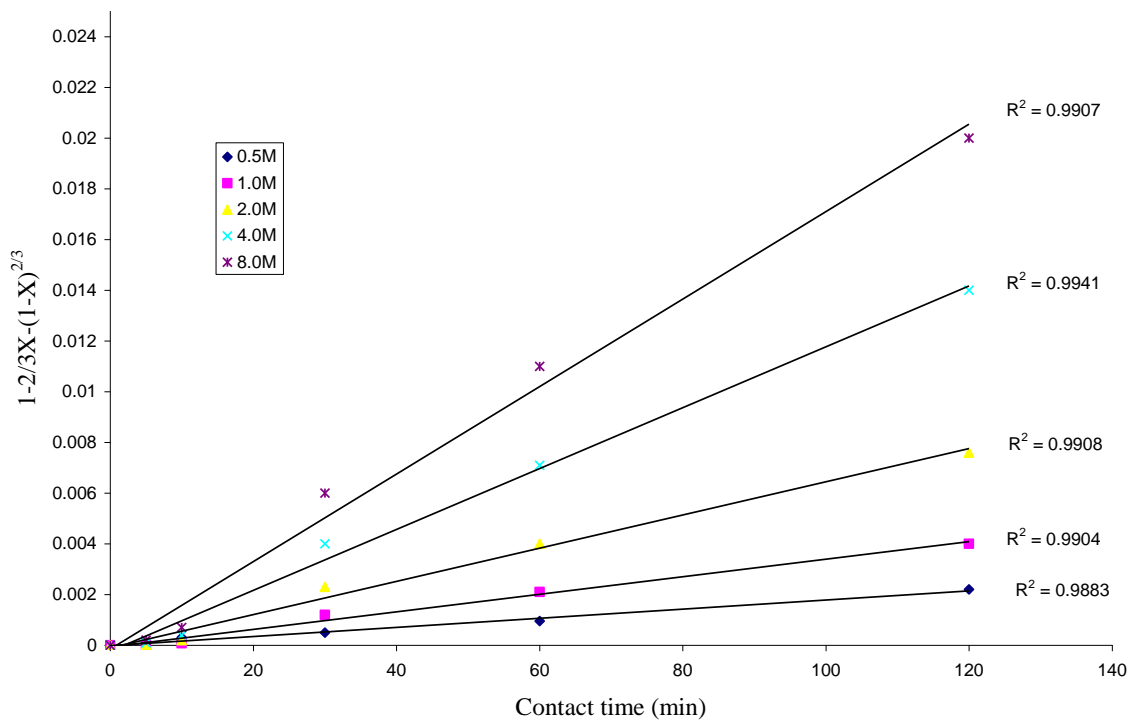


Figure 4: Plot of $[1-2/3X-(1-X)^{2/3}]$ versus Contact Time at Various Concentrations of H_2SO_4 .

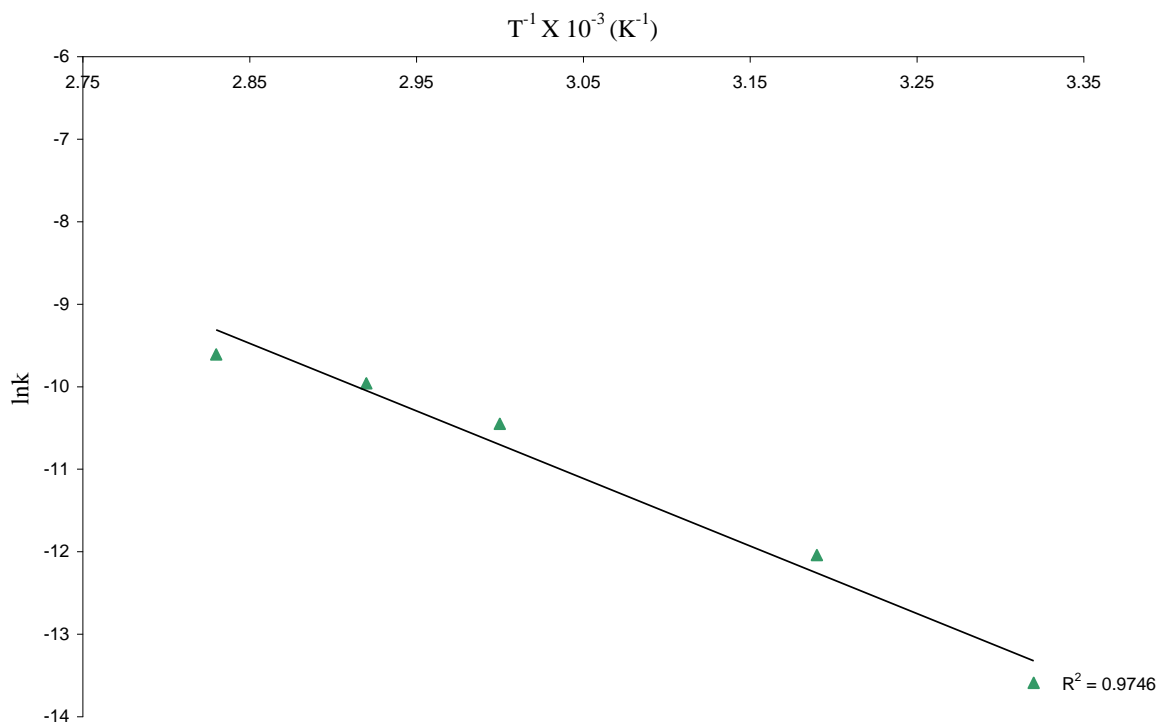


Figure 5: Arrhenius Plot for Laterite Dissolution in H_2SO_4 .

Table 5: Apparent Rate Constant values k_d for 2M H_2SO_4 at Different Temperatures.

T°C	1/T (K ⁻¹)	2M H ₂ SO ₄ k _d (h ⁻¹)
28	3.32 X 10 ⁻³	1.25X 10 ⁻⁶
40	3.19 X 10 ⁻³	8.83 X 10 ⁻⁶
60	3.00 X 10 ⁻³	2.88 X 10 ⁻⁵
70	2.92 X 10 ⁻³	4.73 X 10 ⁻⁵
80	2.83 X 10 ⁻³	6.68 X 10 ⁻⁵

Table 6: Apparent Rate Constant Values k_d for Different Concentrations of H₂SO₄.

[H ⁺] (M)	ln[H ⁺]	H ₂ SO ₄ k _d (h ⁻¹)
0.5	-6.93 X 10 ⁻¹	6.14 X 10 ⁻⁶
1.0	0	1.13 X 10 ⁻⁵
2.0	6.73 X 10 ⁻¹	2.05 X 10 ⁻⁵
4.0	1.39	2.63 X 10 ⁻⁵
8.0	2.08	4.70 X 10 ⁻⁵

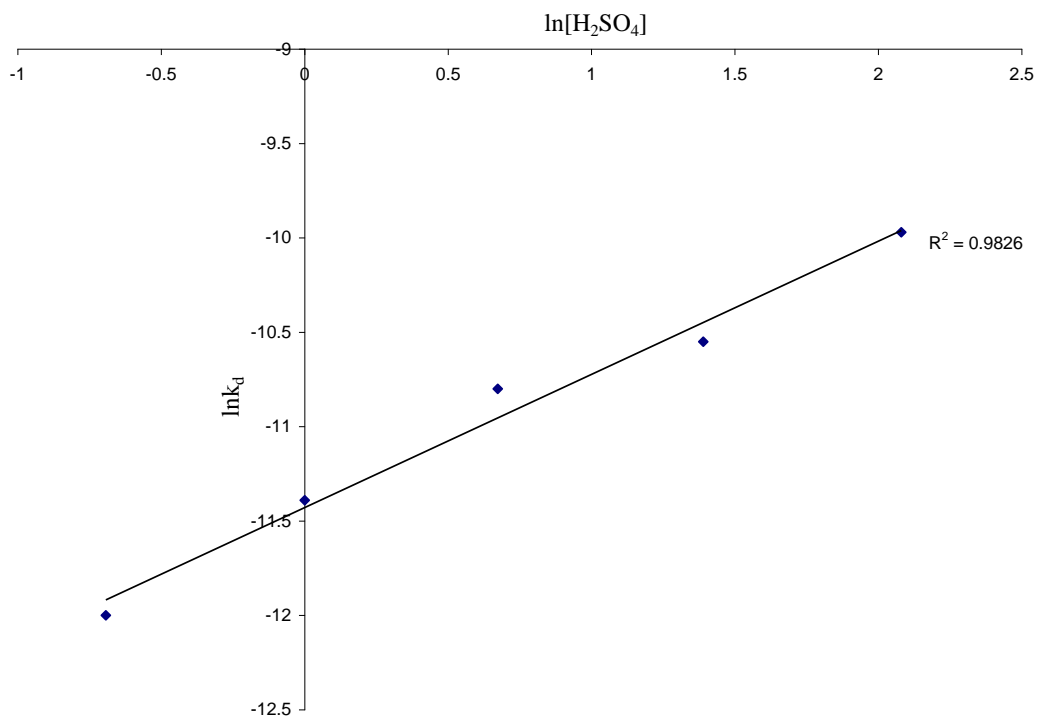


Figure 6: Plot of $\ln k_d$ vs $\ln[H_2SO_4]$ Concentrations.

As seen from Figure 6, the estimated order of reaction for the system was 0.73 with respect to H₂SO₄ concentration.

Furthermore, the activation energy and the order of reaction values with respect to the various acids concentration, temperature and particle size confirm the shrinking core model for a diffusion controlled process.

CONCLUSION

In the present study, the dissolution of laterite in sulfuric acid solutions was studied. It was found that the rate of laterite dissolution increases with acid concentration, temperature, stirring speed, and decreases with particle size. The dissolution of laterite was found to be controlled by the shrinking core model for a diffusion-controlled process. A value of 67.53 kJ/mol was obtained for the activation energy of laterite dissolution in sulfuric acid and the order of reaction was approximately one.

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