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Kinetic studies of hydrochloric acid leaching of iron from agbaja clay

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Abstract

This study was carried out to extract iron oxide from Agbaja clay by dissolution of the clay mineral in aqueous solution of HCl and investigate the kinetic model of its dissolution. The raw and modified clay were characterized using X-Ray Florescence (XRF) for chemical composition. The modified clay was thermally activated at the temperature of 800 ºC and periods of 60minutes. The activated clay was ground and leached by varying particle sizes, acid concentration, liquid to solid weight ratio, stirring speed and leaching temperature. The dissolution kinetics was carried out and the data were analyzed using the various forms of shrinking core models. The characterization showed that Agbaja clay is kaolinitic in nature. Analysis of the dissolution data showed that the process increased with increased in leaching temperature, stirring speed, liquid to solid ratio and solvent concentration but decreased with decreased in particle size. The kinetic model that best fits the process is the Liquid film diffusion controlled process for the reaction kinetics of Agbaja clay dissolution in hydrochloric acid. Hence, the application of the simple and low cost modification techniques employed in this study has shown that Agbaja clay is rich source of iron oxide.

Keywords: Clay, leaching, iron oxide, calcinations, response surface methodology

1. Introduction

Iron has been known to be produced from hematite. Several clays have been found to contain considerable amount of iron in form of oxide. Numerous studies have been carried out by several researchers on some Nigerian clays and the results of their characterizations have shown that most Nigerian clays have rich content of iron oxide [1, 2, 3, 4]. Baral and Das, [5], Mukherji *et al*., [6], Veglio *et al*., [7], Ambikadevi and Lalithambika [8] and several other researchers have obtained iron from clay minerals using different acids both organic and inorganic acids in leaching processes.

The reaction kinetics is indispensable for the production process development and the reactor design operation and scale-up. The understanding of the reaction kinetics is also necessary for development of mathematical models describing the reaction rate and the product yield [9]. In the kinetic studies, the most important process parameters considered over the years by different researchers are; particle size, acid concentration, liquid-solid ratio, stirring speed and temperature. Therefore, this study aimed at kinetic studies of hydrochloric acid leaching of iron from Agbaja clay.

2. Materials and methods

2.1 Sample preparation

The local clay used in this work was obtained from Agbaja, Kogi State Nigeria. The mined clay was soaked in water for two days after which the impurities were removed and the clay sun-dried for 24 hours then oven dried at 60 ºC for 3hours. The clay was then subjected to a calcinations temperature of 800 ºC for a period of 1 hour.

2.2 Characterization

The X-ray fluorescence spectrometer (XRF: Phillips) was used to determine the chemical composition.

2.3 Leaching experiment of the kinetics studies

Leaching experiments were carried out using the calcined samples in a reflux system on a magnetic stirrer and temperature was noted using thermometer. 12g of the calcined sample was added to already determine volume of the acid and heated while stirring continuously. At the intervals of 15min, 1ml of leaching solution was taken out of the round bottom flask by a pipette. The collected sample of leach liquor was cooled, filtered with filter paper and used for iron estimation using AAS. The dissolution percentage of the iron in the slurry was calculated by:

$$X = \frac{\text{amount of } Fe^{2+} \text{ in the solution}}{\text{Total amount of } Fe^{2+} \text{ in original sample}} \times 100 \quad (1)$$

Experiments were performed using the calcined sample to investigate the effects of the following variables on the leaching process: Particle size, (mm): 0.045, 0.105, 0.25 and 0.54; Acid concentration, (M): 0.5, 1.5, 2 and 3; Liquid-solid ratio, (cm^3/g): 4, 8, 10 and 16; Stirring speed, (rpm); 150, 250, 350 and 450; Leaching temperature, (°C): 45, 65 and 85.

3. Results and Discussions

3.1 Characterization of the raw and activated clay

The XRF characterization was performed to know the chemical composition of the minerals that are present in the clay sample.

Table 1: The XRF results of the raw clay samples

Chemical composition	% composition
Al_2O_3	34.50
SiO_2	40.20
Fe_2O_3	12.00
CaO	0.50
MnO	0.09
K_2O	4.12
TiO_2	3.50
Cr_2O_3	0.19
V_2O_5	0.15
NiO	0.57
CuO	0.20
Ga_2O_3	0.09
Rh_2O_3	2.99
BaO	0.49
Total	99.59

Table 2: The XRF results of the thermal activated clay sample

Chemical composition	% composition
Al_2O_3	34.00
SiO_2	43.00
Fe_2O_3	13.00
CaO	0.72
MnO	0.06
K_2O	5.20
TiO_2	2.00
Cr_2O_3	0.030
V_2O_5	0.054
NiO	0.086
CuO	0.00
Ga_2O_3	0.05
Rh_2O_3	0.90
BaO	0.47
Total	99.57

From Tables 1 and 2, it could be observed that both the raw and thermal activated clay have most of the essential metals. Table 2 shows that the essential metals in the raw clay increased after thermal activation and this could be as a result of increased in surface area of the clay which brought out the metals and made them easy for leaching**.**

3.2 Effects of dissolution parameters

The various process parameters that affect the yield of iron from the clay were investigated to study the reaction mechanism and kinetics. These process parameters include particle size of clay, acid concentration, stirring speed, acid-clay weight ratio and leaching temperature.

3.2.1 Effect of particle size and time on iron yield

Keeping the other parameters constant, the different particle sizes of 0.045mm, 0.105mm, 0.25mm and 0.54mm were used to study the effect of particle size and time on the yield of iron from the clay. Experimental result of the effect of varying particle size on iron yield (Figure 1) revealed that as the particle size of clay increased, the iron yield decreased with the highest yield at 0.045mm. This may be due to the fact that the smaller particle sizes have larger surface area that allows the iron ions embeded in the clay to easily contact the acid. Also, the rate of leaching decreased with time as the graphs appeared flatter with increase period.

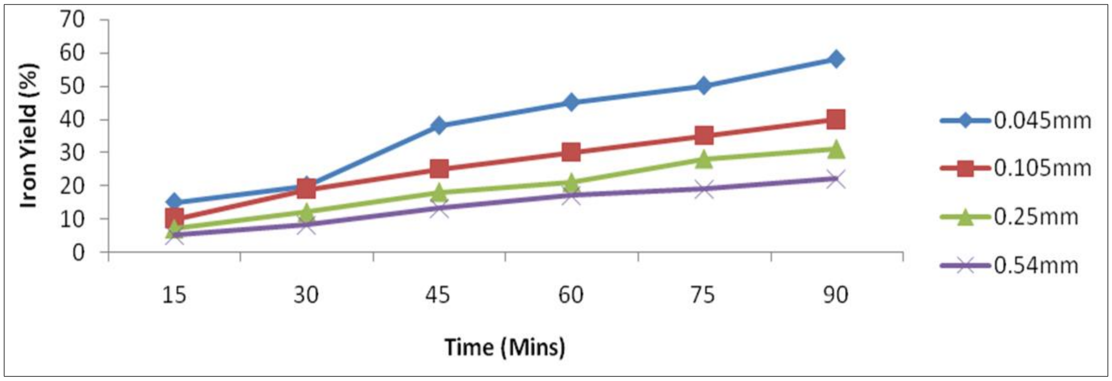

Fig 1: Effect of time and part.size on iron yield with HCl

3.2.2 Effect of acid concentration and time on iron yield

The optimum particle was used to study the effect of acid concentration on iron yield keeping the remaining parameters constant. The concentrations used were 0.5M, 1.5M, 2.0M and 3.0M. Experimental result on the effect of acid concentration on iron yield (Figure 2) revealed that that as concentration increased, the iron yield increased with the maximum yield recorded at the highest concentration of 3.0M. Increase in concentration increased the amount of hydrogen ion in the leaching liquor which enhanced the leaching efficiency. It can also be seen from the plot that increased in time decreased leaching rate as the graph appeared flat with time.

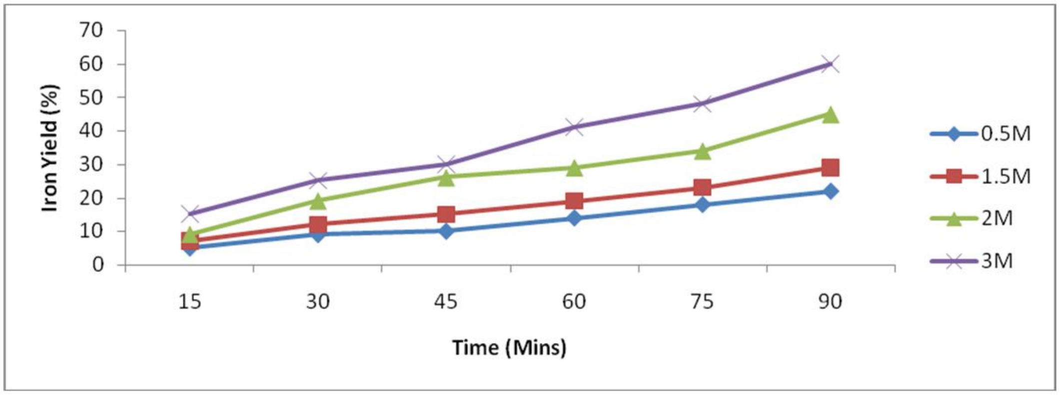

Fig 2: Effect of HCl conc. And time on iron yield

3.2.3 Effect of acid-clay ratio

Keeping stirring speed and leaching temperature constant and at the optimum particle size and acid concentration, the effect of acid-clay ratio on iron yield was studied using ratios of 4, 8, 10 and 16. Experimental result of the effect of acid-clay ratio on yield of iron (Figure 3) showed that iron yield increased with increase in acid-clay ratio. This may be due to the fact that the solute have more solvent to dissolve in as the ratio was increased. Maximum yield was recorded at the highest ratio of 16. Again, dissolution rate decreased with time.

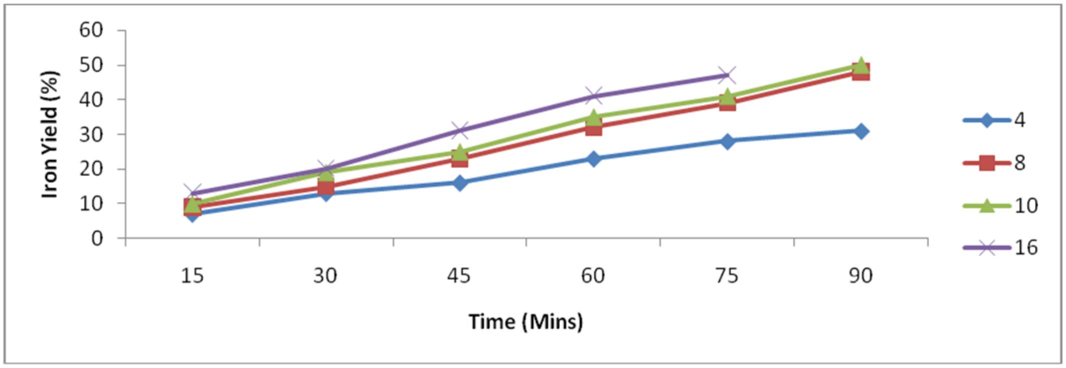

Fig 3: Effect of acid-clay ratio and time on iron yield with HCl

3.2.4 Effect of stirring speed and time on iron yield.

The particle size of 0.045mm, concentration of 3.0M, acid-clay ratio of 16 and a constant temperature of 65 ºC were mentained while varying the speed at 150, 250, 350 and 450rpm the experimental result of the effect of stirring speed on iron yield (Figure 4) showed that yield of iron was increased as stirring speed was increased.

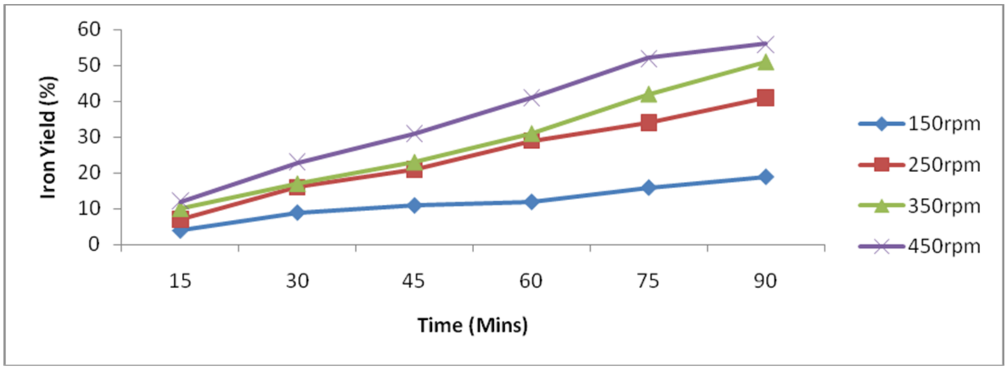

Fig 4: Effect of stirring speed and time on iron yield with HCl

3.2.5 Effect of temperature and time on iron yield

To determine the effect of temperature of leaching and time on the yield of iron, 0.045mm particle, 3M acid concentration, 16cm^3/g acid-clay ratio and 720rp stirring speed were used while varying the temperature at 45, 65 and 85 ºC. Experimental result on effect of leaching temperature on iron yield (Figure 5) revealed that as leaching temperature increased, the amount of iron dissolved in the solution increased and the highest yield was achieved at the highest temperature of 85 ºC.

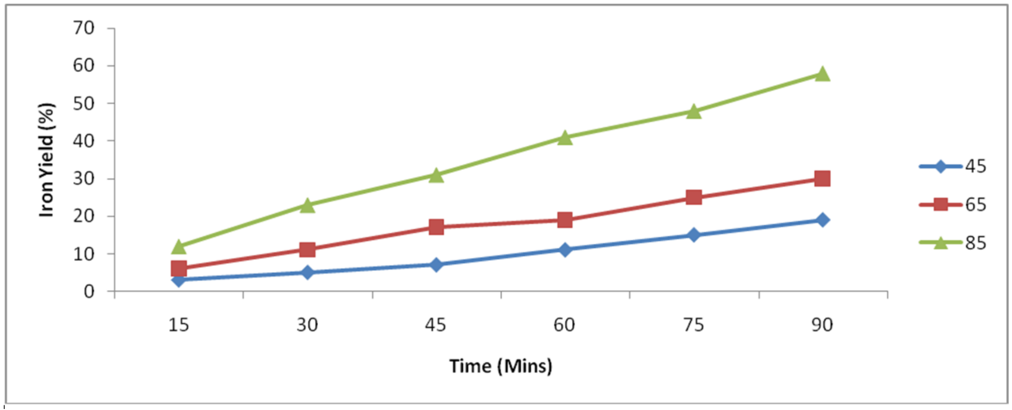

Fig 5: Effect of time and leaching temp on iron yield with HCl

3.3 Kinetic study

In the kinetics study, the different forms of the shrinking core model as proposed by several authors were considered to fit the experimental data obtained in order to identify the reaction mechanism for comparative analysis of the leaching kinetics of iron from the clay with sulphuric acid.

Chemical reaction controlled process $1-(1-X)^{1/3} = kt$ (2)

Liquid film diffusion controlled model $1-(1-X)^{2/3}=kt$ (3)

Product layer diffusion controlled process $1+2(1-X)-3(1-X)^{2/3}=kt$ (4)

Avremi Model $-\ln(1-X) = K_A t^m$ (5)

First-order pseudo-homogeneous model $-\ln(1-X) = kt$ (6)

Ginstling and Brounshtein model $1-2/3(X)-(1-X)^{2/3}=kt$ (7)

The experimental data (Figures 1, 2, 3, 4 and 5) were tested with the kinetic models in order to determine the rate controlling mechanism. The correlation coefficients was used as creteria to measure the fitness of the models to the experimental data. In all the process, liquid film diffusion controlled process gave the best fits (Figures 6, 7, 8, 9 and 10).

The activation energy for the process was calculated from (Figure 11) to be 34KJ/Mol.

From the correlation coefficients obtained from the different plots for each of the process variables the liquid film diffusion model had the best fit (Table 3). This revealed that the leaching of iron from Agbaja clay with HCl followed the product layer diffusion model.

The reaction order was determined from the plot of the natural logarithm of the apparent rate constants against the natural logarithm of each process variable according to the following equation:

$$\ln(-r) = \ln k + n \ln C_A \qquad (9)$$

A semi-empirical model was developed from the analysis given above as follows

$$1-(1-x)^{2/3} = AC^{a}_{[HCl]}\,(dp)^{b}\,(L/S)^{c}(sp)^{d}\exp(-E_a/RT)t \qquad (10)$$

The variables a, b, c, d were determined from the slopes of the plots as 0.552, -0.482, 0.491 and 0.6388 respectively. The value of A was obtained as 0.0075 and E was 34. Substituting these values in the equation, the dissolution of iron in Agbaja clay in HCl could be described by the following equation

$$1-(1-x)^{2/3} = 0.0075\ {}^{0}C^{.55\ 2}{}_{[HCl]}\,(d_p)^{-0.482}\ (l/s^{1.19}\ (sp)^{0.491}\exp(-34/RT)\ (11)$$

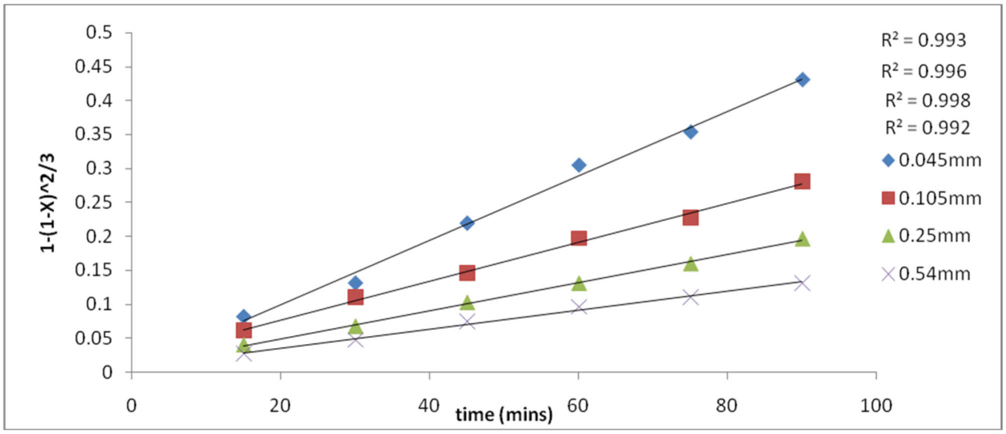

Fig 6: Plot of $1-(1-X)^{\wedge 2/3}$ Vs time at different part. Size with HCl

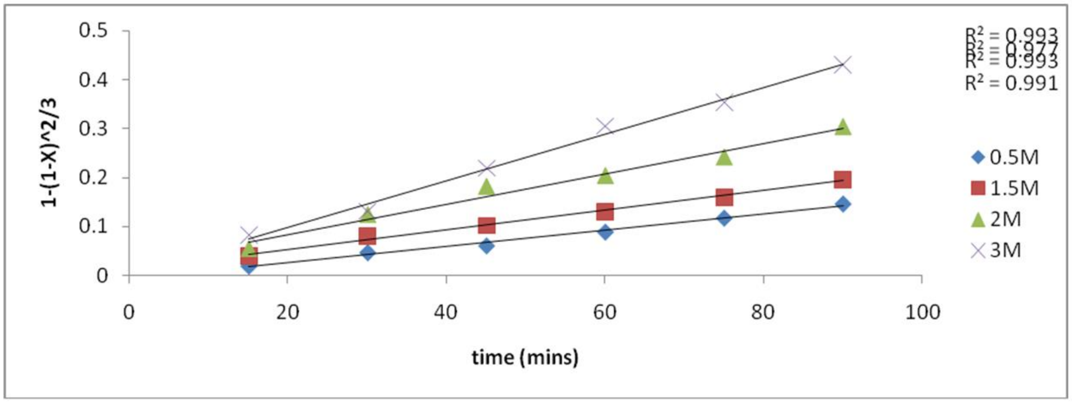

Fig 7: Plot of 1-(1-X) ^2/3 Vs time at different HCl conc

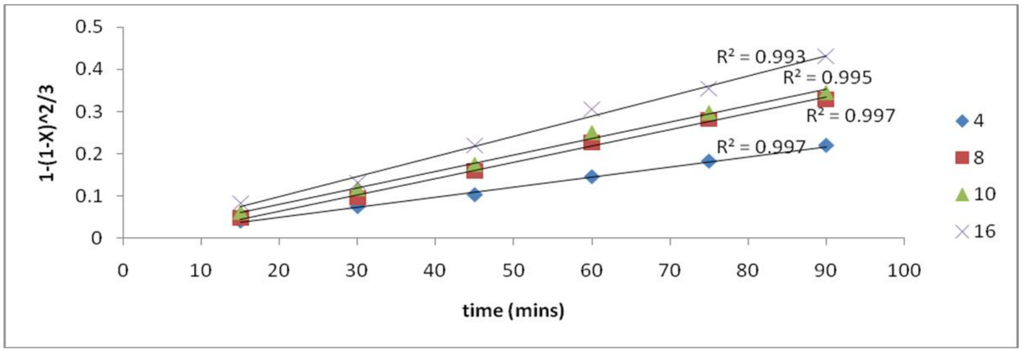

Fig 8: Plot of 1-(1-X)^2/3 Vs time at different liquid-solid ratio with HCl

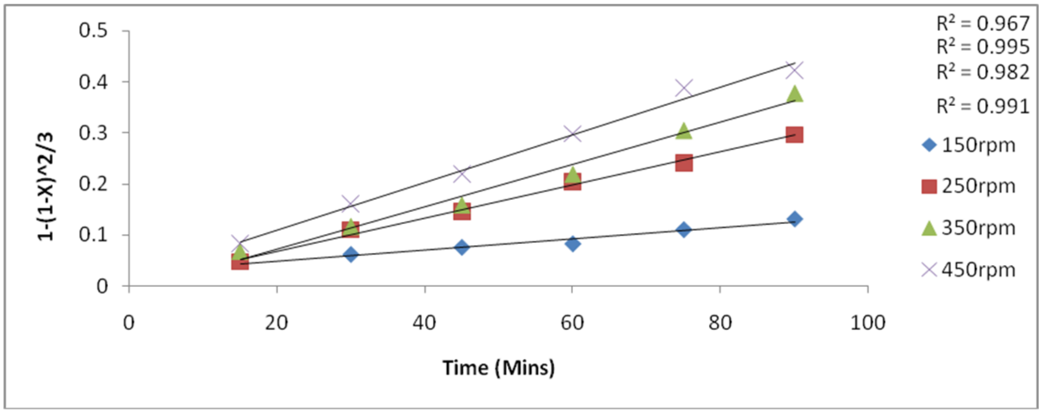

Fig 9: Plot of 1-(1-X)^2/3 Vs time at different stirring speed with HCl

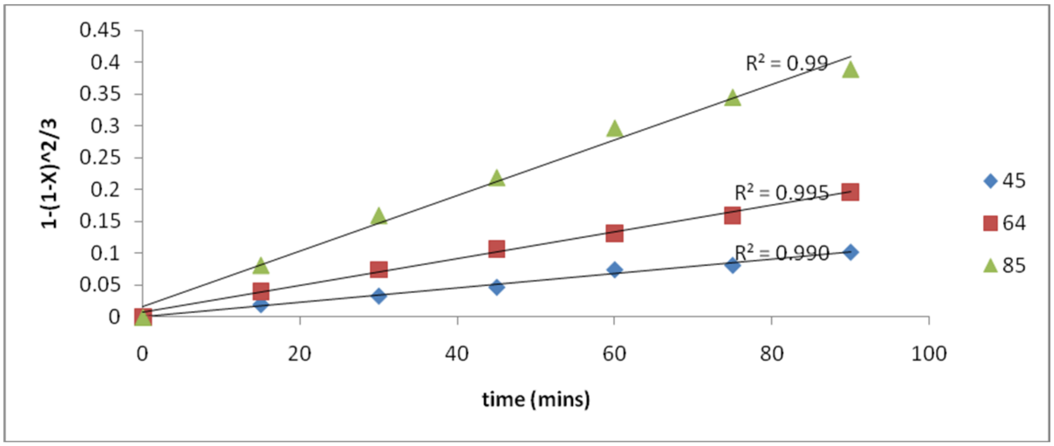

Fig. 10: Plot of 1-(1-X) ^2/3 Vs time at different temperature with HCl

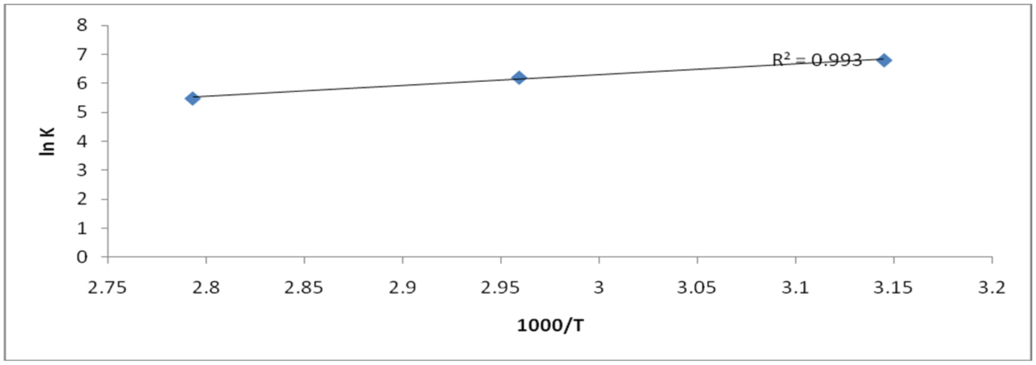

Fig 11: Plot of ln K Vs 1000/T with HCl.

Table 3: values of correlation coefficients for the different process parameters for each tested models for iron yield with HCl.

Process parameter	**Models**				
	Chemical reaction	**Liquid film diffusion**	**Product layer diffusion**	**Avremi**	**Pseudo first order**
	R^2	**R^2**	**R^2**	**R^2**	**R^2**
Particle size					
0.045mm	0.872	0.993	0.911	0.768	0.882
0.105mm	0.883	0.996	0.945	0.812	0.812
0.25mm	0.881	0.998	0.934	0.754	0.831
0.54mm	0.891	0.992	0.921	0.871	0.823
Acid conc.					
0.5M	0.832	0.993	0.912	0.876	0.823
1.5M	0.811	0.997	0.934	0.845	0.817
2M	0.834	0.993	0.901	0.865	0.851
3M	0.812	0.991	0.916	0.867	0.834
Liquid-solid ratio					
4cm^3/g	0.818	0.998	0.901	0.863	0.813
8cm^3/g	0.831	0.983	0.921	0.831	0.831
10cm^3/g	0.850	0.995	0.931	0.839	0.805
16cm^3/g	0.819	0.968	0.918	0.854	0.799
Stirring speed					
150rpm	0.826	0.967	0.910	0.832	0.802
250rpm	0.831	0.995	0.931	0.821	0.812
350rpm	0.831	0.982	0.912	0.827	0.824
450rpm	0.821	0.991	0.900	0.834	0.831
Leaching temperature					
45 ^oC	0.834	0.990	0.912	0.843	0.821
65 ^oC	0.813	0.995	0.917	0.876	0.823
85 ^oC	0.814	0.990	0.932	0.856	0.801

4. Conclusion

From the result obtained in this work, iron can be obtained from calcined Agbaja clay with hydrochloric acid. Increasing the acid concentration, stirring speed, liquid-solid ratio and leaching temperature increased iron yield while a decrease in particle size increase iron yield and the leaching process followed the liquid film diffusion controlled model and the activation energy was 34KJ/Mol.

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