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Chemical Characterization and Leaching Kinetics of Metals From Iron Ores

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Abstract

The impact of mineral deposit on their host agricultural soil, available water bodies and near atmospheric environment is of great concern. In this study, mineralogical characterization and leaching kinetics of metals from iron ores in Kogi States, were reported. Physicochemical parameters namely; electrical conductivity, pH, bulk density and moisture content were also investigated. The SEM image of the iron ore appear compact with irregular shape. XRF analysis showed that, iron ore consist of 63.44 % Fe as major element, with the oxide composition of 90.71%. The XRD analysis of iron ore unveiled the presence of magnetite (88 %), hematite (9 %) and quartz (3 %) as associated mineral. Low concentration of iron (0.77-1.70 ppm) was observed to be leached from iron ore in the acidic medium, 0.35-1.10 ppm from basic medium and 0.32-0.88 ppm in the aqueous medium, The Shrinking core, Product-layer diffusion and leaching, controlled by diffusion were the three equations used to model the leaching parameters. The leaching experimental data of iron ore fit best into the diffusion- controlled model, with R2 = 0.94 for the acidic medium Hence, the rate determining step. The analysis shows good fit for the other kinetic models. Overall, result proved that, the environment around mining sites is chiefly contaminated by the metals leached from the ore (mineral) deposits. Hence, the need to monitor the pollution indices, the role of leaching, pollutant fate (transport and reaction) and the subsequent distribution of metals to neighboring environment.

Keywords: Magnetite; Leaching; Metals; Kinetics; Shrinking core; Product-layer diffusion.

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1. Introduction

Mineralogical characterization has the potential to improve risk assessment, guide appropriate mine planning for planned and active mines and optimize remediation design at closed or abandoned mines. In many natural and anthropogenic affected environments, secondary minerals control the mobility of the toxic heavy metal in the environment. Giving these environmental concerns, hydro-chemical process like dissolution and subsequent leaching may prove to be relevant in the contaminations.

Mineralogy and Environment: Mineralogy is an interdisciplinary science, in which the principles of physics and chemistry are applied to Earth materials [1]. Specific studies within mineralogy include the processes of mineral origin and formation, classification of minerals, their geographical distribution, as well as their utilization [2]. Environmental mineralogy is an interdisciplinary field dealing with systems at, or near, the surface of the Earth where the geosphere comes into contact with the hydrosphere, atmosphere and biosphere. One significant class of environmental pollutants is heavy metals such as Pb, As, Cd, Cr, and Hg, which are toxic, even at low concentrations, and may act as carcinogens. These metals may be naturally present but human activity has greatly increased the flux of biologically available forms of heavy metals in the environment [3].

Mining and Environment: The purpose of mining is to meet the demand for metals and minerals resources to develop infrastructure etc. and to improve the quality of life of the. These minerals can be, metalliferous minerals or metals, coal, or industrial minerals that are used in the chemical sector or for construction purposes. The environmental impact of mining includes erosion, formation of sinkholes, loss of biodiversity, and contamination of soil, groundwater and surface water [4].

Iron Ore Mining: Iron ore is a mineral substance which, when heated in the presence of a reductant will yield metalliferous iron (Fe). Iron ore is the source of primary iron for the world's iron and steel industries. The overburden in iron mines consists of weathered ore with clay particles and mainly lateritic layers along with low iron content [5]. Tailings are mixtures of crushed rock and processing fluids from mills, washeries or concentrators that remain after the extraction of economic metals, minerals, mineral fuels or coal from the mine resource [6, 7]. The chemical composition of tailings and ore mineralogy are linked. The chemical element, iron is the fourth most

common element in the Earth's crust and the second most abundant metal. About five percent of the Earth's crust is composed of iron. Iron occurs mainly in iron-oxide ores, while some are a mixture of minerals rich in iron. It is also present in many rock-forming minerals, including mica, garnet, amphibole, pyroxene and olivine. The forms are (i) magnetite (Fe_3O_4), (ii) hematite - hematite (Fe_2O_3) is a red iron ore, (iii) Goethite - Goethite ($Fe_2O_3.H_2O$), a brown ore, contains iron (iv) Limonite - Limonite ($Fe_2O_3.H_2O$) is a yellow-brown iron ore0020 [8]. Taconite contains low-grade iron in fine specks and bands.

Dissolution of Fe from Iron Ore: Several chemical methods may need to be employed to dissolve a sample completely. Usually, the tracer is added to the sample at the time of sample dissolution. Initially the sample may be treated with acids yielding an insoluble residue [9]. Dissolution in hydrochloric acid (HCl) or nitric acid (HNO₃) is governed by protonation. The anions can promote the dissolution of iron oxides by replacing the surface OH groups and further facilitating the detachment of Fe atoms [10]

Dissolution Kinetics: The rate of dissolution has been described by different equations. Commonly used equations have been the cube root law [11], the Avrami-Erofe'equation, the first order nucleation and the shrinking core model. Leaching is a method where valuable minerals are selectively dissolved from a material by a lixiviant, normally aqueous solution, resulting in a rich solution with high concentration of valuable compounds [12]. All the equations could be applied to the dissolution of any solids, several of them have however, been shown to apply for numerous Fe oxides. The equations can be roughly divided into two categories: diffusion and reaction controlled. For diffusion, the rate determining phenomenon is the transportation of reactants products to or from the reaction site. Models, with high correlation coefficient values are termed as the best fit models. This is test of applicability [13]

Shrinking Core Model: SCM was developed [14], originally for gas-solid combustion system and has been successfully applied to non-combustion systems involving liquids and solids [14-16]. The SCM is based on the following assumptions: if the particles are spherical; if the particle shrinks uniformly and maintains its spherical shape; if the thickness of the layer around the core was attain constant during the leaching process and if the temperature remains constant during the process. Based on the aforementioned assumptions, reaction rate per unit surface of the core is related to dissolution rate of the solute as Safari, *et al.* [17].

$$R = -\frac{M}{s_e} \frac{dN}{dt}$$
(1)

$$R = -\frac{M}{(4\pi r_t^2)} \frac{d}{dt} (4\pi r_t^3 \rho | 3M)$$
(2)

With, M and N are the molar mass of the solute and the amount (moles) of the solute present in the solid, respectively. Se is the surface area of the unreacted solid. For particles assumed to be spherical, the equation becomes:

$$\frac{dN}{dt} = \omega \rho \, \frac{dr_c}{dt} = \, k^{\prime\prime} \, C_A \tag{3}$$

with ρ as particle density and r_t is the radius of the unreacted solid at time (t >0).

For a reaction progress unaffected by the presence of a product or "ash" layer, the process is best described as "chemical reaction controlled". According to Levenspiel [11], Eqn. (3) assumes (4) for dissolution to be a first order process.

$$t = \frac{\omega \rho r_i}{k'' c_A} \left[1 - \frac{r_t}{r_i} \right] \tag{4}$$

with k"and CA as the mass transfer coefficient between fluid and particle, concentration of the reactant in the reacting fluid respectively. Eqn. 4 can be solved to give 5.

$$t = \frac{w\rho r_i}{k'' c_A} \left[1 - \frac{r_t}{r_i} \right]$$
(5)
Other relevant equations are as follows [11, 18]

$$k_t = 1 - (X - 1)^{\frac{2}{3}} \tag{6}$$

$$1 - X = \frac{m}{\text{initial mass of particle}} = \frac{\frac{4}{3}\pi r_t^3 \rho}{\frac{4}{3}\pi r_i^3 \rho} = {\binom{r_t}{r_i}}^3$$
(7)

With m as mass of unreacted core at time, t; r_i is the initial radius of the unreacted solid and ω is the mass fraction of the solute in the bulk solid. k" is the first-order rate constant for the surface reaction.

Taking $k_r = \frac{k'' c_A}{\omega \rho r_i}$ where k_r is the "apparent" rate constant Where X is the fractional conversion, and

$$-\frac{1}{s_e}\frac{dN}{dt} = D_e \frac{dC_A}{dr}$$
(8)

$$1 - 3(1 - X)^{\frac{1}{3}} + 2(1 - X) = k_r t \tag{9}$$

$$1 - (1 - x)^{\overline{3}}$$
 (10)

$$1 + 2(1 - X) - 3(1 - X)^{\frac{2}{3}}$$
(11)

$$1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = k_{dif} \times t \tag{12}$$

If the reaction rate is controlled by chemical reaction, the integrated rate equation is expressed by following equation 10 [13, 19]. If the reaction is controlled by product-layer diffusion the equation 11 finds application while equation 12 is used if the reaction is controlled by diffusion. In his opinion [13], three major steps occur during leaching process. (i) diffusion or mass transfer through the liquid film surrounding a solid particle (ii) chemical reaction on the surface of the unreacted core, and (iii) diffusion through the ash/inert solid layer. The slowest step is

the rate limiting step. Their model assists in the derivation of the rate mechanism from sets of experimental data as follows

$$X = 3K_g M_s C_{At} / a\rho sro = K_{ft}$$
⁽¹³⁾

$$1 = \frac{2X_B}{r} - 1 - XB)^{\frac{2}{3}} = 2M_s DC_{At} / a\rho ro^2 = K_d t$$
(14)

$$1 - (-XB)^{1/3} = K'' M_s C_{At} / a\rho sro = K_f t$$
(15)

With M_s as molecular weight of the solid, C_A is the concentration of the dissolved lixiviant (such as acid), A in the bulk of the solution, "a" is the stoichiometric coefficient of reagent in the leaching reaction, r_0 = initial radius of the ore particle, ρs = density of the mineral ore, D = diffusion coefficient in the porous product layer, Kg = mass transfer coefficient between fluid and ore particle, "K" = first-order rate constant for the surface reaction and t is the dwell time.

XRD and XRF characterization: Characterisation of minerals has become an increasingly important part of Survey activities. X-ray diffraction analysis (XRD), image analysis, quantitative electron probe microanalysis (EPMA) and scanning electron microscopy (SEM) are becoming routine methods and supplement traditional microscopic studies and geochemical analysis. X-ray diffraction (XRD) is often used to identify chemical components based on how the targeted X-ray beam is reflected from the studied compounds. In general, XRD is a technique which requires the studied compounds to be in a crystalline form. The conditions needed for diffraction are determined by Bragg's law

 $n\lambda 2d \sin \theta$

(16)

with *n* as the order of diffraction, λ is the wavelength of the x-ray beam, *d* is the distance between the crystal planes, and θ is the diffraction angle. The output is called a diffractogram or a diffraction pattern, which describes the intensity of the diffracted beam as a function of the angle between the incident and the diffracted beam (2 θ), the diffractogram is then compared against known substances to identify the compound.

The primary objectives of leaching processes applied in mining are the selective dissolution of metals of interest in ores, segregate the loaded (pregnant) solution from solids and recover available metals either in metal compounds or in metallic forms through further hydrometallurgical treatment. Lixiviants such as Sulphuric acid and cyanide are chemical solutions used in leach mining to enhance dissolution of metals in ores. Thiourea and thiosulphate are common lixiviants for copper and gold but for their complicated chemical management issues and environmental concerns. The current study is aimed at the characterization and leaching kinetics of metals from iron ore obtained from Itakpe in Kogi States, Nigeria. Characterization of mineral ores was achieved, using non-destructive analytical techniques, including XRF for elemental and general ore composition study and XRD for diffraction pattern/crystallographic profile. Leaching kinetics of metals from ores was conducted in different media (acidic, natural and basic medium).

2. Materials and Methods

Iron ore was used as samples in this work. Analytical grade reagents were procured from certified vendors. They include nitric acid, sulphuric acid and sodium hydroxide. The instruments used in this study were energy dispersive x-ray fluorescence panatycal minipal 5, X-ray diffractometer (XRD), and Atomic absorption spectrophotometer (AAS).

2.1. Description of Sample Site

The sampling area (Itakpe iron ore depot of the Nigeria Iron Ore Mining Company) located in Okehi Local Government Area of Kogi States Itakpe is on the Latitude of $7^{\circ}36$ 'N; Longitude of $6^{\circ}16$ 'E. The people living in these areas are engaged in mining activities due to the existence of the ores at their disposal. Mining operational mode explored by these inhabitants is not a healthy type but rather at the expense the environment.

2.2. Sampling of the Ores

The mineral sample was handpicked randomly from the depots and stored in a nitric acid pre- treated dry polypropylene bag, well labeled, taken to the laboratory and stored under ambient condition [20]. The iron ore samples was pulverized and sieved into a target particle sizes [21].

2.3. Physicochemical Analysis

pH measurement, Particle size analysis, Bulk density, Conductivity measurement and Moisture content of the ore was carried out following documented procedures [22-24].

2.4. Mineralogical Characterization

X-ray Fluorescence Analysis (XRF): Quantitative analysis of the major oxides and elements within the ore was determined by X-ray Fluorescence Spectroscopy.

X-ray Diffraction Analysis (XRD): XRD analysis was conducted for the qualitative (phase identification) and quantitative analyses of the minerals in the ore. Diffraction pattern was presented and crystalline sizes was computed using the Debye-Scherrer equation given as:

$$B(2\theta) = \frac{\kappa\lambda}{Lcos\theta}$$
With k as 0.94
(17)

2.5. Leaching Experiment

Effect of pH: Iron ore dissolution experiment was carried out in 5 Erlenmeyer flask, containing 0.5 g of the ore in 50 mL distilled water. For acidic medium, 0.1 M H_2SO_4 was added to adjust pH to acidic range (2 and 4). The filtrate was analyzed for iron (Fe). Then 0.1 M NaOH was added to adjust to basic range (9, 11 and 13). The filtrate was analyse for elemental.

Effect of time: Iron ores (0.5 g) was placed in five well labeled 250 mL Erlenmeyer flasks, each containing 50 mL of mineral acid solution. The flasks was placed on mechanical shaker for 30, 60, 90 120, 180 and 240 minutes resulting mixture was filtered using Whatman filter paper and stored in a well labeled glass bottles at normal room temperature for sample digestion and further analysis [25] for iron, Fe, using AAS.

Leaching Kinetics for Ores in Acidic Medium: Four different sizes fraction (0.5, 1, 1.5 and 2 mm) was obtained by sieving through ASTM standard sieves. For kinetics studies, sulphuric acid concentration was varied (0.1, 0.2... 0.6 M). In a classic analysis, 150 mL of sulphuric acid solution was poured into a thermostatic vessel, 1.0 g of iron ore (0.5 mm fraction) was introduced and stirred mechanically. After the desired reaction time, the leached solution was withdrawn at time intervals, digested and the iron content was determined spectrometrically by means of AAS [20].

The dissolution fraction (α) of Fe and Fe oxide was calculated by the given equation

$$\alpha \text{ (Fe/Fe-oxide) exp} = \frac{\text{Amount of Fe in dissolve sample}}{\text{Total amount of Fe in the original sample}}$$
(18)

The same procedure was repeated with sodium hydroxide and water (0.1, 0.2.....0.6M) for basic and aqueous medium respectively [20].

2.6. Digestion of Leached Iron (Solution)

Withdrawn iron leachate (10 mL solution) from the dissolution experiments was measured into 250 mL teflons beakers which was previously washed by soaking in dilute nitric acid (0.001 M) overnight and dried in oven at 50 °C. 10 mL nitric acid and 30 mL H_2SO_4 of analytical grade reagent was added to each beaker and heated in boiling water in a water bath for 2 hours. The resulting digest was filtered into 50 mL volumetric flasks and made up to 50 mL mark with distilled water. The blank was prepared by heating 15 mL (2 M) nitric acid in 50 mL distilled water for 2 hours, filtered and made up to 100 mL mark with distilled water.

2.7. Heavy Metal (Fe) Analysis

The digest, containing iron is quantified for heavy metals (Fe), using Atomic Absorption Spectrometry. The instrument was set according to the manufacturer's instruction. Sample solution was aspirated into the AAS and absorbance was recorded.

3. Results and Discussion

3.1. Physical Inspection of Samples

Plate 1 is a photograph showing iron ore sample, used in this study. The sample was physically examined and observed to contain small-size stones after grinding and prior to screening.



3.2. Physicochemical Characteristics of Mineral Ores

The results of the physicochemical parameters of the mineral ores; pH, Conductivity, Bulk density and Moisture content were presented in Table 1.

pH: The pH of Iron ore analyzed was 8.27. This is slightly higher than the pH value reported as 7.01 to 7.99 Akpovata, *et al.* [26]. pH is an important soil property, having great effects on solute concentration and absorption in the ore.

Electrical conductivity: Results of conductivity measurements of iron ore was 139 μ S.cm⁻¹. The conductivity measurement of 165 - 210 μ S.cm⁻¹ was previously reported [26]. The observed conductivity measurement was lower than result reported in the previous work. The conductivity observed may be due to increase in the concentration of some soluble salt in the ore [26].

Bulk density: The bulk density of Iron ore is 4.33 g.cm⁻³. This agrees with other studies [27], which gave bulk density ranging from 2.0 to 3.12 g.cm⁻³. High bulk density (> 1.5 g/cm⁻³) reduces water infiltration and plant root penetration resulting in increase in surface water pollution [28]. It is also widely believed that soil BD declines with an increase in soil organic matter because of the increase in porosity volume [29]

3.3. Morphology of Mineral Ores (SEM Characterization)

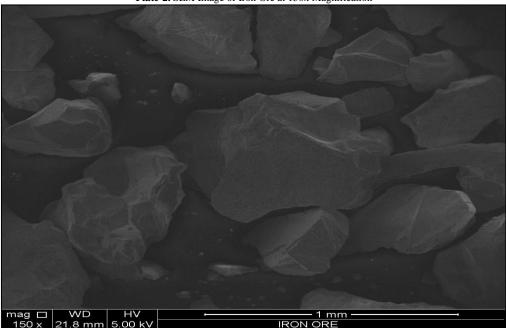
The result shows images that are grain-like micro aggregates, this could support easy delamination and subsequent leaching of metals from ore into surrounding soils. The images of the iron ore appear compact with irregular shape, unlike an observed image [30], which has irregular, bulkier and agglomerated particles. leaching of metals may result after weathering or blasting of ore.

Table-1. Physicochemical parameters of iron Ore			
Parameters Values			
Conductivity (µS/cm)	139±0.00		
рН	8.27±0.00		
Bulk density (g/cm ³)	4.33±0.00		
% moisture	2.25±0.00		

3.4. Mineralogical Characterization of the Mineral Ores

Ore Surface Morphology: Scanning electron microscopy was carried out to determine the surface morphology of the mineral ore. Images of the iron ore is presented in plate 2. Images appear rocky, compact with irregular shape. Similar to this observation is in a recent report [24]





3.5. Chemical Composition of Mineral Ores (XRF Characterization)

The XRF was applied to analyze element/oxide of the iron ore. It detects the major, minor and the trace elements in the mineral ores. The results (Table 2) of the elemental composition of ore by X-ray fluorescence technique showed that the iron ore exist mainly as FeO₃. The X-ray fluorescence data revealed that iron ore exists mainly as FeO₃ (90.71 %) with 63.44% iron. The amount of iron here was similar to that of Alafara, *et al.* [31] ,whose result was (66.7 %). The minor element are Al (0.51 %), Si ((0.39 %), K (0.66 %), Ca (0.40 %), Ti (0.59 %), P (0.93 5), Cr (1.14 %), V (1.35 %) etc. The mineral ore contains metallic ores (with heavy metals), essential elements and. The metallic ore in iron ore include: Al₂O₃ (0.56 %), SiO₂ (7.00 %), TiO₂ (0.18 %), Cr₂O₃ (0.17 %),

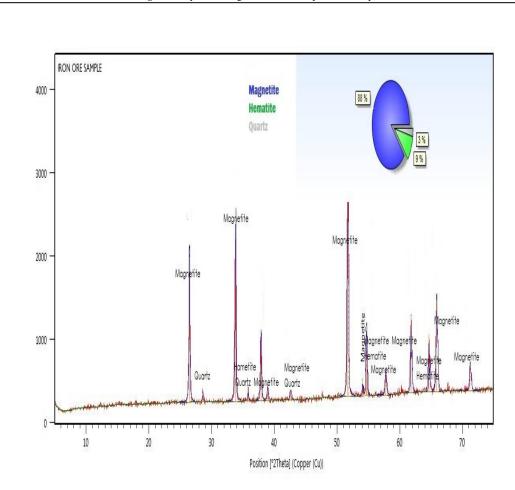
 V_2O_5 (0.04 %), MnO (0.10 %), Fe (63.44 %), CuO (0.03 %) and (0.16 %): the essential elements present are K_2O (0.08 %), CaO (0.11 %) and P_2O_5 (0.07). No radionuclide is detected in the iron ore.

Metallic Oxide	Composition (%) in the ore
Al_2O_3	0.56
SiO ₂	7.00
K ₂ O	0.08
CaO	0.11
TiO ₂	0.18
P_2O_5	0.07
SO ₃	ND
Cr_2O_3	0.05
V_2O_5	0.04
MnO	0.10
FeO ₃	90.71
Fe	63.44
CuO	0.03
ZnO	ND
BaO	0.16
ND: Not detected	

Table-2. Results of Cher	nical Composition of Iron Ore
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3.6. Diffraction Pattern of Mineral Ores (XRD Characterization)

XRD was used to identify the chemical composition of the mineral ores that were in the crystalline form. The analysis iron ore by X-ray diffraction gives a better description in terms of the mineral phases present in the ores. Figure 1 represents the XR-Diffractogram of the ore while Table 3 is a display of the crystallographic parameters. XRD technique was also used to show the phases of the iron present and provide the quantification of all the phases. The XRD analysis of the iron revealed Magnetite (88 %) as the major mineral with subordinate amounts of hematite (9 %) and Quart (3 %) as associated mineral, this has confirmed similar work [32]. The result from this work differ slightly from a study, which indicated the presence of associated minerals, such as a-quartz (SiO₂), sphalerite (ZnS), cassiterite (SnO₂), pyrite (FeS₂) and manganese oxide (MnO₂).



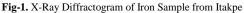


Table-3. Crystallographic Parameter of Iron Ore fro	m Itakpe
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Pos. [°2Th.]	Height[cts]	FWHMLeft [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Crystallite size (nm)
26.45	1565.69	0.15	3.37	36.78	32.05
28.57	98.13	0.15	3.12	2.43	32.19
33.81	1987.48	0.15	2.65	49.24	32.61
35.81	726.19	0.08	2.51	4.73	65.28
37.87	131.91	0.15	2.36	17.99	32.98
38.94	131.91	0.20	2.31	3.27	24.81
42.61	96.39	0.23	2.12	2.39	22.32
51.69	4036.51	0.12	1.77	100.00	46.64
51.84	1768.47	0.09	1.77	43.81	56.95
54.06	209.28	0.09	1.69	5.18	57.43
54.60	729.29	0.09	1.68	18.07	57.66
54.75	555.88	0.09	1.68	13.77	57.66
57.75	236.93	0.24	1.59	5.87	21.91
61.81	938.30	0.12	1.49	25.25	44.79
64.66	707.26	0.09	1.44	17.52	60.45
65.66	1123.66	0.19	1.42	27.84	30.48
71.21	336.72	0.19	1.32	8.34	43.12

3.7. Metal Leaching Profile

Tables 4 and 5 shows the results reported for the effects of some parametric factors. The results is a summary of the mean concentration of metallic iron (Fe) in mg/kg in the iron ore leached into the solution. The leaching profiles were presented as Figures 2 and 3. It was observed that the leaching of iron ore increases as the time increases but decreases as the particle size increases due to its decreasing surface area as earlier reported [33]. The concentration of the iron leached in the leaching media was observed to be very low. For the acidic medium it ranges from 0.77 - 1.70 ppm; 0.35 - 1.10 ppm for the basic medium and 0.32 - 0.88 ppm for the aqueous medium within the time frame of 6 to 36 hours. This is in accordance other report [34], on separate studies involving the leaching of sphalerite minerals. Proposed Leaching reaction include:

 $FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$

 $FeO + 2NaOH \rightarrow Fe(OH)2Na + Na2O$

(19) (20)

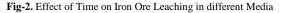
Table-4. Effect of Leaching Time (h) on the Mean Concentration (ppm) of Leached In	on
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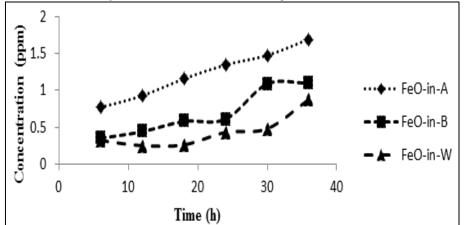
S/No.	Experiment	Time (h)	Conc (ppm)	SD	X (%)
1.	FeO-in-A	0	31.45	0.00	-
		6	0.77	0.00	97
		12	0.93	0.00	97
		18	1.16	0.00	96
		24	1.36	0.00	95
		30	1.48	0.00	95
		36	1.70	0.01	94
2.	FeO-in-B	0	31.45	0.00	-
		6	0.35	0.00	98
		12	0.44	0.01	98
		18	0.58	0.00	98
		24	0.61	0.00	98
		30	1.09	0.00	96
		36	1.10	0.00	96
3.	FeO-in-W	0	31.45	0.00	-
		6	0.25	0.00	99
		12	0.26	0.00	99
		18	0.32	0.00	98
		24	0.43	0.00	98
		30	0.48	0.00	98
		36	0.88	0.00	97

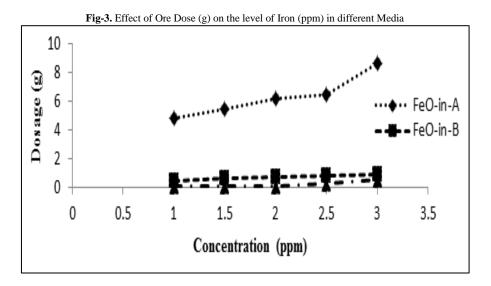
 \overline{Co} = initial concentration of iron in undissolved iron ore (31.459 ppm), X = fraction of leached metal, X (%) = leaching efficiency

S/No.	Experiment	Dosage (g)	Conc (ppm)	SD
1.	FeO-in-A	1.0	4.78	0.01
		1.5	5.47	0.01
		2.0	6.16	0.01
		2.5	6.45	0.00
		3.0	8.66	0.01
2.	FeO-in-B	1.0	0.44	0.00
		1.5	0.59	0.00
		2.0	0.75	0.00
		2.5	0.77	0.00
		3.0	0.91	0.00
3.	FeO-in-W	1.0	0.04	0.00
		1.5	0.06	0.00
		2.0	0.07	0.00
		2.5	0.29	0.00
		3.0	0.51	0.00

Table-5. Effect of Ore dosage (g) on the concentration of Leached Iron (ppm)







3.8. Iron (Fe) in Iron Ores

The XRF result of the iron ore showed that iron is the dominant metal with the composition of 63.44 % and the ore 90.71 % while that of the XRD showed that, magnetite is 88 %, hematite is 9 % and quartz as associated mineral with 3 %. The percentage of iron in the ore was previously reported [35] as 64.3% which is closely related to the experimental value of the XRF in this study.

3.9. Leaching Kinetics

The fraction of iron leached (X) obtained with respect to contact time was substituted in the following equations: Shrinking core model: $1 - (1 - X)^{\frac{1}{3}}$, Product-layer diffusion $1 + 2(1 - X) - 3(1 - X)^{\frac{2}{3}}$ and Leaching controlled by diffusion $1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}$, relating to the different media, the respective plots (Figures 4,5 and 6)

Shrinking core model, Product-layer diffusion and Leaching controlled by diffusion versus contact time give a comparative values of the rate constants K and their respective regression correlation coefficients (R^2) were shown. The results of the leaching studies indicated that the process is best controlled by diffusion (R^2 of 0.942 in acidic medium), shrinking core model (in basic; $R^2 = 0.865$) while leaching is best controlled by product layer diffusion in water (R^2 of 0.856). The analysis of the plots of all the kinetic curves, however, did not give a straight line, passing through the origin. This result differs with that of a similar report [35]. Low correlation coefficients were obtained for the shrinking core model (in acidic medium; $R^2 = 0.777$); diffusion control and product layer diffusion (in basic medium; both $R^2 = 0.685$); diffusion control is least applicable (in water ; $R^2 = 0.852$). Models, with high applicability values represent the rate-controlling step in the dissolution and metal leaching system [36]. For diffusion, the rate determining phenomenon is the transportation of reactants products to or from the reaction site [14]

Table-6. Shrinking Core Model Data for Iron Leaching from Iron Ore

Time (h)	$1 - (1 - X)^{\frac{1}{3}}$ (FeO-in-A)	$1 - (1 - X)^{\frac{1}{3}}$ (FeO-in-B)	$1 - (1 - X)^{\frac{1}{3}}$ (FeO-in-W)
0	-	-	-
6	0.31	0.73	0.79
12	0.31	0.73	0.79
18	0.34	0.73	0.73
24	0.63	0.73	0.73
30	0.63	0.66	0.73
36	0.61	0.66	0.69

Table-7. Shrinking Core Model Constant for Iron Leaching from Iron Ore

Experiments	\mathbf{R}^2	Regression equation	Rate constant (k_f) (min^{-1})
FeO-in- Acid	0.777	y = 0.013x	0.013
FeO-in-Base	0.865	y = -0.002x	-0.002
FeO-in-Water	0.854	y =-0.003x	-0.003

Table-8. Product-layer Diffusion Data for Iron Leaching from Iron Ore

Time (h)	$\begin{bmatrix} 1+2(1-X)-3(1-X)^{\frac{2}{3}} \\ (FeO-in-A) \end{bmatrix}$	$1 + 2(1 - X) - 3(1 - X)^{\frac{2}{3}}$ (FeO-in-B)	$\begin{array}{c} 1 + 2(1 - X) - 3(1 - X)^{\frac{2}{3}} \\ \text{(FeO-in-W)} \end{array}$
0	-	-	-
6	0.86	0.89	0.93
12	0.86	0.89	0.93
18	0.84	0.89	0.89
24	0.82	0.89	0.89
30	0.82	0.84	0.89
36	0.80	0.84	0.86

Table-9. Product-layer Diffusion Constant for Iron Leaching from Iron Ore

Experiments	\mathbb{R}^2	Regression equation	Rate constant (k_f) (min^{-1})
FeO-in-Acid	0.827	y = -0.001x	0.031
FeO-in-Base	0.685	y = -0.001x	0.033
FeO-in-Water	0.856	y = -0.002x	0.034

Table-10. Leaching Controlled by Diffusion Data for Iron Leaching from Iron Ore

Time (h)	$\frac{1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}}{A}$ (FeO-in-	$1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}$ (FeO- in-B)	2
0	-	-	-
6	0.27	0.29	0.31
12	0.27	0.29	0.31
18	0.26	0.29	0.29
24	0.25	0.29	0.29
30	0.25	0.26	0.29
36	0.24	0.26	0.27

Table-11. Leaching Controlled by Diffusion Constant for Iron Leaching from Iron Ore

Experiments	\mathbf{R}^2	Regression equation	Rate constant (k_f) (min^{-1})
FeO- in-Acid	0.942	y = -0.001x	-0.001
FeO-in-Base	0.685	y = -0.001x	-0.001
FeO-in-Water	0.852	y = -0.001x	-0.001

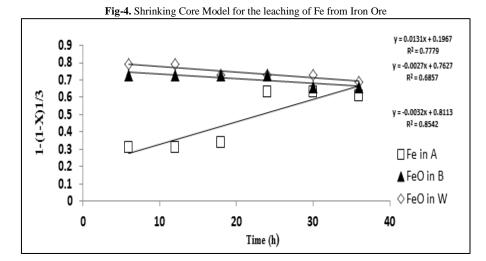
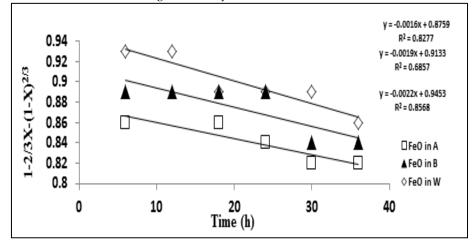


Fig-5. Product-layer Diffusion for Iron ore



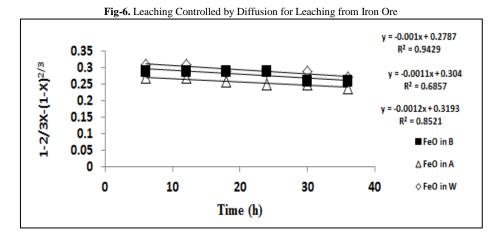


Table-12. Comparing Data Analysis in Different Media (p<0.05)				
S/N	Test	Statistical difference		
1.	FeO-in-W vs FeO-in-A	significant		
2.	FeO-in-W vs FeO-in-B	significant		
3.	FeO-in-A vs FeO-in-W	significant		

4. Conclusion

The mineralogical characterization and leaching kinetics of iron ores was successfully investigated. SEM analysis of the ore samples revealed compact aggregates with irregular shape. The XRD result of iron ore shows the presence of magnetite, hematite and quartz as associated mineral. The XRF showed various ores oxides chemical and elemental composition. The results of the leaching studies indicated that the process is best controlled by diffusion (in acidic medium), shrinking core model (in basic and aqueous media)

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