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LEACHING BEHAVIOUR OF NIGERIAN ILMENITE ORE IN ACID MEDIUM (HYDROCHLORIC ACID)

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Abstract: *This study was carried out to investigate the effect of hydrochloric acid on the dissolution of titanium present in ilmenite ore. The X-ray diffraction characterization of the ore reveals that it consists of iron, titanium and silicon oxide phases. Alkaline pretreatment of Nigeria ilmenite ore was carried out using 1.5M of sodium hydroxide. Leaching of the pretreated Nigeria ilemnite was carried out using hydrochloric acid (HCl) concentration of 2, 4 and 6moles, leaching temperature of 50,85,100, fixed leaching time of 150 minutes, fixed particle size of <0.5µm and fixed solid-liquid ratio of 0.1g/ml. Leaching of ilmenite ore with hydrochloric acid, the optimum leaching condition for ilmenite ore was at 6 M hydrochloric acid, leaching time of 150 minutes, solid-liquid ratio of 0.1gm/l, particle size of <0.5µm and leaching time of 85 °C, under these conditions, the optimum dissolution of Ti 81.01% was obtained.*

1.0 Introduction

Utilization of valuable minerals has become a very vital part of human lives. Existence of life without these minerals is almost unthinkable due to their vital contributions to industrial developments such as transportation, construction and manufacturing industries. Few minerals such as asbestos and talc can be utilized after mining without any processing. However, most of the minerals, especially the more important ones such as ores of aluminum, copper, titanium and iron need to be refined and reprocessed to produce usable materials.

Titanium is the fifth most abundant metal in the earth's crust following iron, aluminum calcium and magnesium. It occurs in a variety of titanium containing minerals such as ilmenite ($FeO \cdot TiO_2$ or $TiFeO_3$), rutile (TiO_2), pseudorutile (Fe_2Ti_3O) and leucoxene ($Fe_2O_3 \cdot nTiO_2$) (Mazzocchitti et al., 2009). Many researchers have focused on production of synthetic rutile using ilmenite, because known reserves of titanium oxides are reducing thus there is limited

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availability of natural rutile ores. Ilmenite which contains 40–65% TiO_2 is an alternative choice due to its abundance (Gambogi, 2011).

Ilmenite is also a common mineral found in igneous and metamorphic and rocks on earth and also on the surface of the moon. The structural, magnetic and electronic properties of ilmenite are of great interest in the materials and earth sciences. Ilmenite mineral constitutes about 90% of the known world titanium minerals It is a naturally occurring titanate of ferrous iron mineral ($Fe^{2+}Ti^{4+}O_3$) commonly used for the production titanium dioxide (TiO_2) and titanium metal (Zhang et al.,2011). Titanium is widely used in the fields of construction, aviation, biomaterials because of its corrosion resistance, high specific strength and bio-affinity whereas Titania (TiO_2) has been utilized in various applications such as pigment in pharmaceutical, paper, textile, paint and ceramics industries, due to its remarkable index of refraction and the ability to adjust the pore size, surface area (Abdel-Aal*et al.,* 2000, Diebold, 2003). Rich Ilmenite deposits are mainly mined from the alluvial deposits derived from these granites. Ilmenite produced in Nigeria is mined in the Jos, Bauchi, Zaria, Kano and Benue, Plateau, Kabba, Niger and Ondo zones.

The various acidic leaching processes for production of titanium dioxide pigment from ilmenite minerals: are the sulphate process and the chloride process. The sulphate process faces critical environmental challenges arising from generation of SO_2 and H_2S gases and release of waste acid during hydrolysis. In the Chloride Process, a high grade of TiO_2 grade is required like natural rutile mineral (94–98% TiO_2), synthetic rutile (92– 95% TiO_2), leucoxene (68% TiO_2), anatase (90–95% TiO_2), or titanium slag (80–90% TiO_2) because during chlorination process impurities of the ore can be chlorinated to form metal chloride. This gives rise to generation of chloride waste and chlorine gas loss (Baba *et al.,* 2013, Das *et al.,* 2013, Zhu *et al.,* 2014, Gireesh*et al.,* 2015, Kim *et al.,* 2021).

There are various factors affecting the properties of the titanium dioxide (synthetic rutile) produced from ilmenite such factors are ilmenite particle size, leaching time, reaction temperature, ilmenite to acid mass ratio, pulp density, and agitation, leaching agent concentrate, and also related parameters to kind of additive and mechanical activation conditions (Mahmoud *et al.,* 2004; Lasheen, 2005; El-Hazek*et al.,* 2007; Amer, 2002; Li *et al.,* 2006, 2007; Sasikumar*et al.,* 2007).

In all of the above mentioned researches, single input such as ilmenite particle size, leaching time, reaction temperature, ilmenite to acid mass ratio, pulp density, and agitation, leaching agent concentrate, and also related parameters to kind of additive and mechanical activation conditions at a series of experiments has been studied to understand the effectiveness of the input parameters on the preparation of synthetic rutile from ilmenite concentrate. The aim of the present study is to examine the effect of alkaline pretreatment, leaching temperature and leaching agent concentration on leaching performance of a Nigerian ilmenite ore.

2.0 Materials and methods

The particle size distribution was carried out with test sieves for this work, the mesh sizes were <0.5µm, 0.5-1.0µm and 1.0-1.5µm. 100 grams of sieved particle of the ore was poured into a 100ml conical flask containing sodium hydroxide (NaOH) of 1.5moles. After stirring thoroughly to ensure homogeneity, the content was allowed for

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60 minutes. At the end of pretreatment experiment, the slurry was filtered, washed with distilled water, oven dried at 150°C and the residue paste was taken for acid leaching investigations. 20 grams of sieved particle of the ore was poured into a crucible containing hydrochloric acid (HCl) of 2.-6moles. Analytical grade hydrochloride acid was used to make the feed solutions. After stirring thoroughly to ensure homogeneity, the content was allowed to leach between 50 to 150 minutes, particle size between 0.5μm-1.5μm, at temperature between 25-100°C and at constant liquid to solid ratio of 0.1g/ml, particle size of <0.5μm and leaching time of 150 minutes. At the end of each leaching experiment, leachant was then analyzed for iron and titanium to calculate their leaching efficiencies.

2.1 Preparation of standard solution

Steps

- Mapping out the various concentration of the leachants (acid) to be prepared and they are as follows: 2M, 4M and 6M
- Finding the volume that will be used to make up the 100ml solution. This is calculated as follows

Making of standard solution of sulfuric acid

chemical/physical data

37% w/w HCl_{aq} has a density of 1.19 kg/L

molecular weight of HCl = 36.5 g/mol
% to molar conversion

% w/w HCl to w/v HCl: 37% HCl x 1.19 kg/L density = 0.44 kg/L HCl

w/v to mol/v: 0.44 kg/L / 36.5 g/mol = 12 mol/L

Thus, concentrated HCl 37% is 12 molar (= M = mol/L).
diluted HCl from concentrated HCl.

- 1M HCl: add 1mol/12M = 83 ml conc. HCl to 1L of water or 8.3ml to 100ml
- 2M HCl: add 2mol/12M = 167 ml conc. HCl to 1L of water or 16.6ml to 100ml
- 4M HCl: add 2mol/12M = 332 ml conc. HCl to 1L of water or 33.2ml to 100ml
- 6M HCl: add 2mol/12M = 498 ml conc. HCl to 1L of water or 49.8ml to 100ml

3.0 Result and Discussion

3.1: Chemical analysis and Mineralogical analysis

The ilmenite ore used in the study was obtained from Jos- Nigeria. The X-ray diffraction (XRD) patterns show that major phases of ore were iron, titanium and silicon oxide phases (**Fig. 1**). **Table 1 and Figure 1** show data the chemical composition of ilmenite ore. Comparing with other ilmenite ore in the world, the ore used in this investigation had low titanium (Ti) content and high impurity contents such as iron(Fe) and silicon (Si).The XRF results show that the ore had major impurities such as iron (Fe), silicon (Si) and minor impurities such as aluminum (Al), tin (Sn), manganese (Mn), antimony (Sb), neodymium (Nb), calcium (Ca), molybdenum(Mo) and others.

3.2 Alkaline Pretreatment of Nigeria ilmemite ore

During the alkali pretreatment of ilmenite ore, (Baba et al.,2013) the following reactions will occur. High temperature decomposition of alkali was carried out in muffle furnace at 320°C, it can be represented by the following reactions:

$$2NaOH \rightarrow Na_2O + H_2O \quad (1)$$

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Sodium oxide formed from the reaction (1) will in turn react with the ilmenite phase.

$$4FeTiO_3+2Na_2O+O_2 \rightarrow 4NaFeTiO_4 \quad (2)$$

$$TiO_2+Na_2O \rightarrow Na_2TiO_3 \quad (3)$$

The possibility of formation of single titanate and ferrate through the breakdown of ilmenite structure is also not ruled out.

$$4FeTiO_3+6Na_2O+O_2 \rightarrow 4Na_2TiO_3+4NaFeO_2 \quad (4)$$

Ilmenite can also form a ferrate and a ternary phase simultaneously.

$$12FeTiO_3+6Na_2O+3O_2 \rightarrow 4NaFeTi_3O_8+8NaFeO_2 \quad (5)$$

The X-ray diffraction (XRD) patterns of pretreated ilmenite ore show that major phases of ilmenite ore were aenigmatite and quartz (**Fig. 4**). **Table 2 and Figure 3** show data the chemical composition of pretreated ilmenite ore. Comparing with ilmenite ore (table 4.1) alkaline pretreated resulted to increase in titanium and decrease in iron and silicon content, this is may be as a result of practically insolubility of the mineralogical phases of ilmenite ore in sodium hydroxide solution (Mazzocchitti et al.,2008). The XRF result shows that the pretreated ore had iron (Fe) and silicon (Si) as major impurities with other impurities such as aluminum (Al), tin (Sn), manganese (Mn), antimony (Sb), neodymium (Nb), calcium (Ca), molybdenum (Mo) and others.

3.3 Leaching Nigeria ilmenite ore with Hydrochloric acid

3.3.1 Effect of hydrochloric acid concentration on dissolution of titanium (Ti)

Several leaching experiments were performed keeping the following factors as constant, leaching time150 minutes, particle size of <0.5µm, solid-liquid ratio of 0.1g/ml and leaching temperature of 85 °C while varying hydrochloric concentrations from 2m to 6m as in **Tables 3 and Figures 6-9.** The results show that increasing acid concentration from 2M to 6M enhanced the dissolution of titanium. At 2M hydrochloric acid concentration, the Ti content was 65.1% and this value increased to 81.08% by increasing the HCl concentration to 6M. As the acid concentration increased, the leaching performance also increased. This was due to increased concentration

3.3.2 Effect of leaching temperature on dissolution of titanium

The effect of leaching temperature was studied on the dissolution of major elements (titanium, iron and silicon) over a temperature range of 50 to 150 °C while 4 M hydrochloric acid concentration , particle size of <0.5µm, solid-liquid ratio of 0.1g/ml and reaction time of 150 minutes were kept constant as in **Table 3** and **Figures 9-13**. At temperature of 50^{o}C the dissolution of titanium was insignificant. However, with increase in temperature to 100^{o}C the dissolution of Ti reached 80%, further increase in temperature up to 150^{o}C resulted to decrease in dissolution of Ti. The decrease in dissolution of Ti at 150^{o}C might be as a result of volatility of hydrochloric acid. Thus, the optimum temperature is selected as 100 ^{o}C

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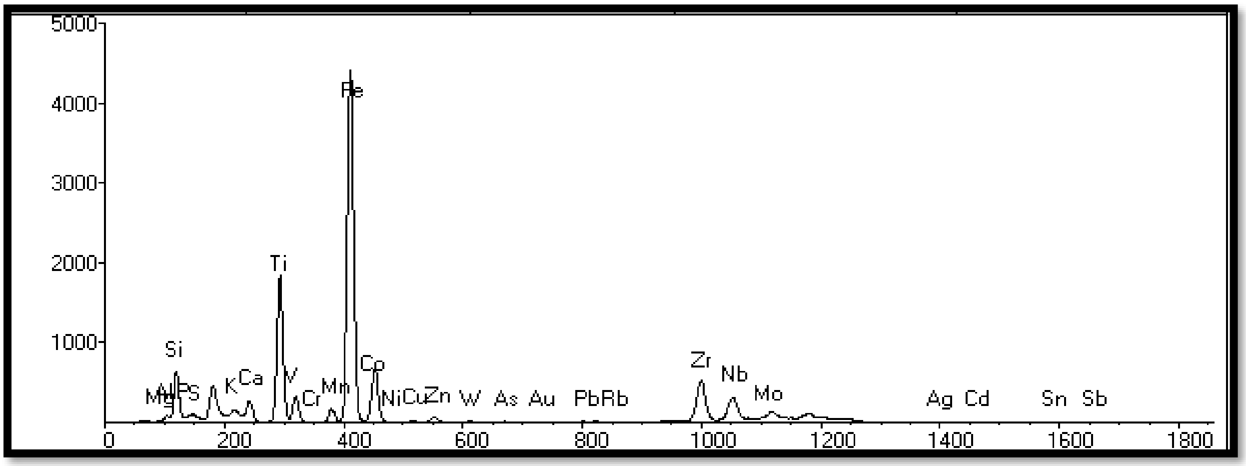

Fig. 1 XRF patterns of ilmenite ore

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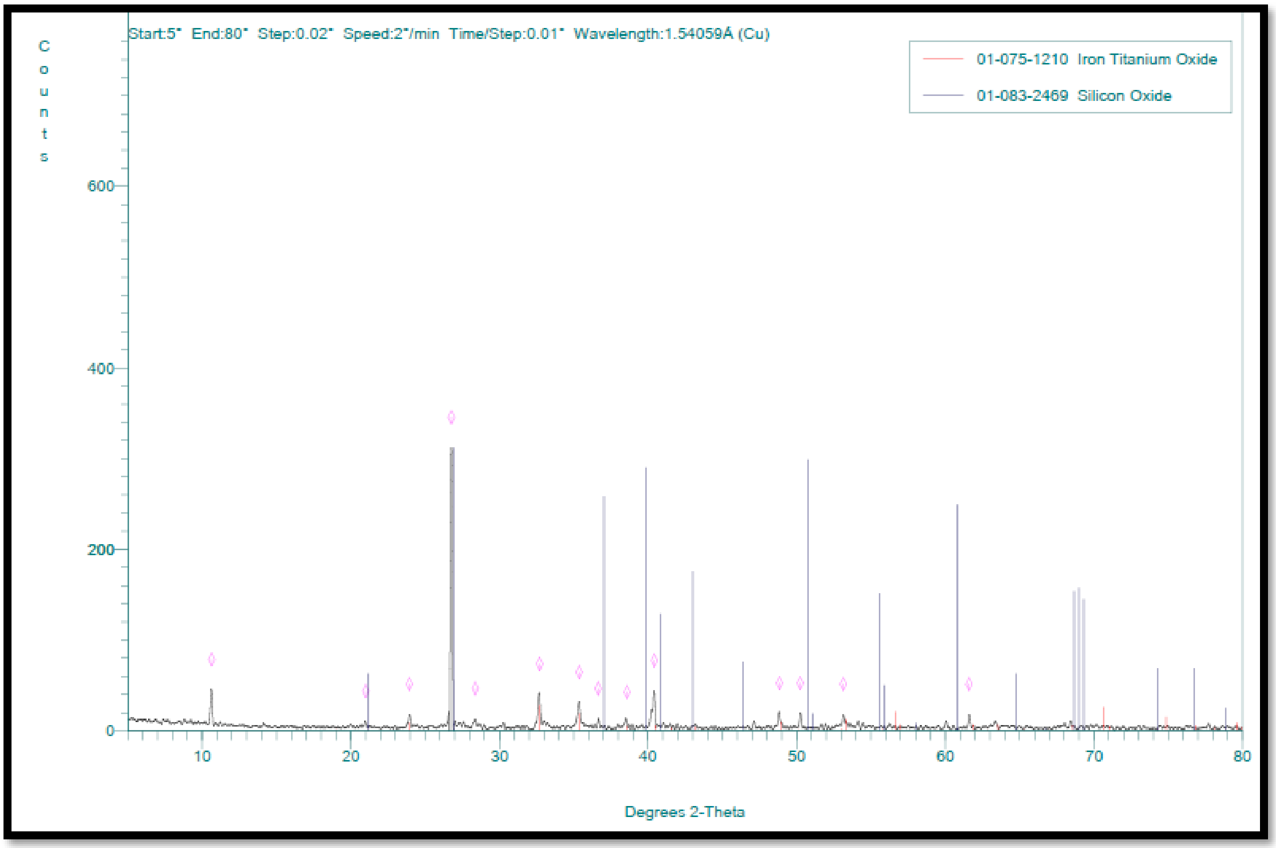

Fig. 2 XRD patterns of ilmenite ore

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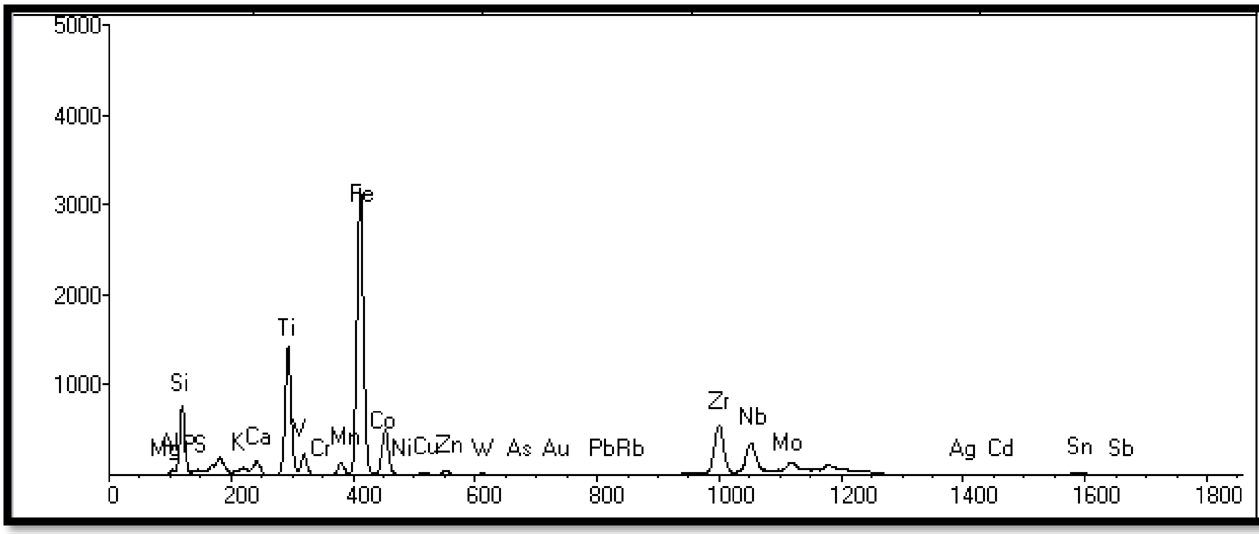

Fig. 3 XRF patterns of pretreated ilmenite ore

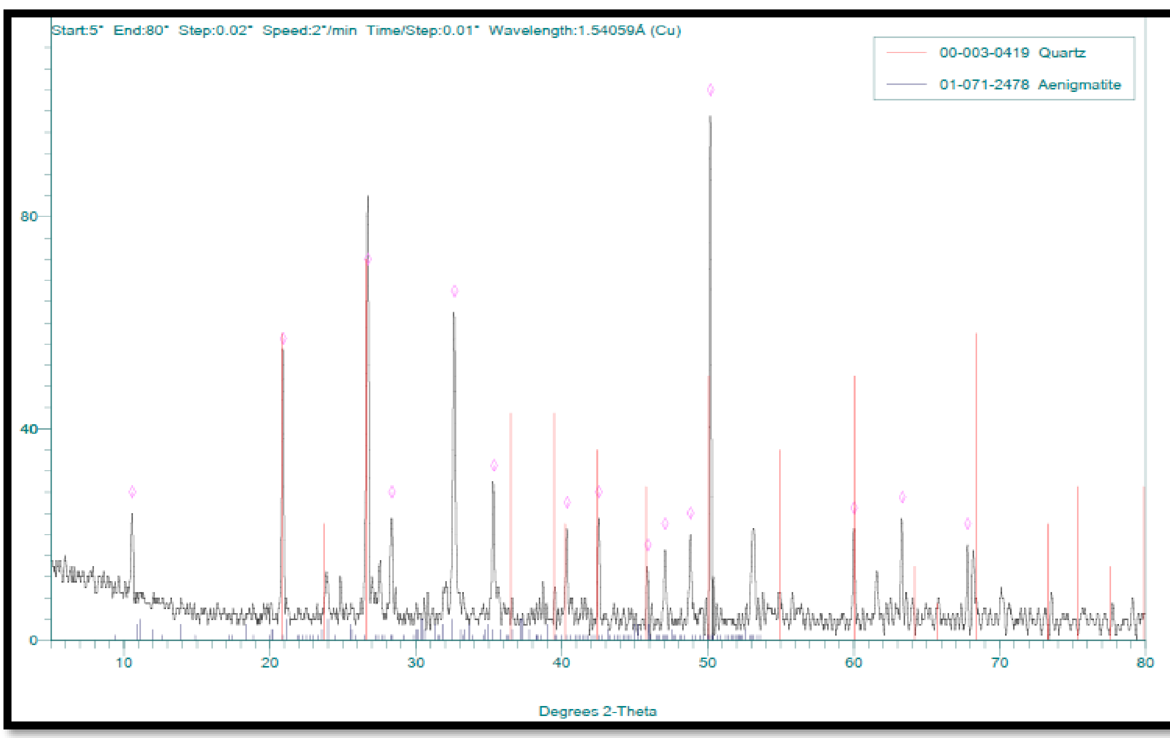

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Fig. 4 XRD patterns of pretreated ilmenite ore

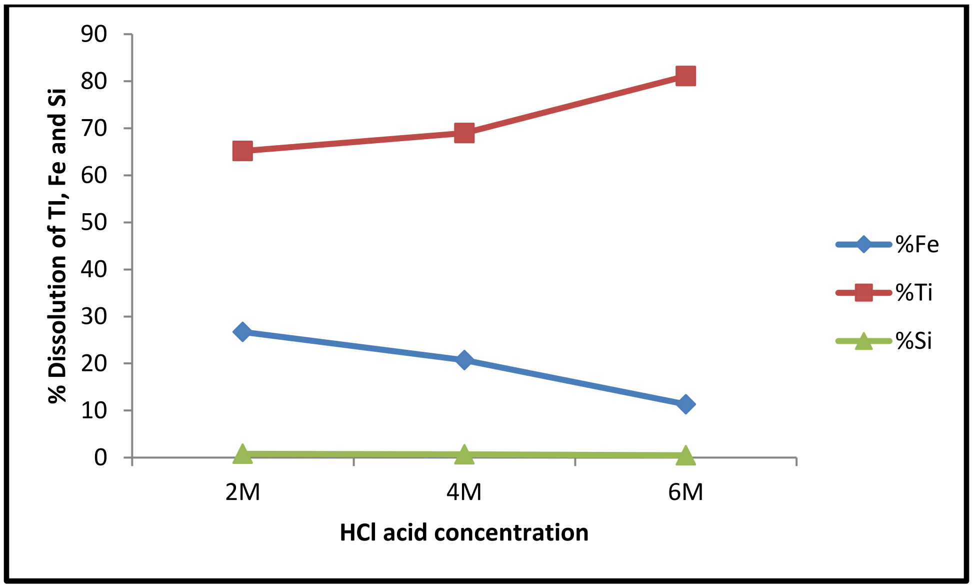

Fig 5: Effect of hydrochloric acid concentration on dissolution of titanium

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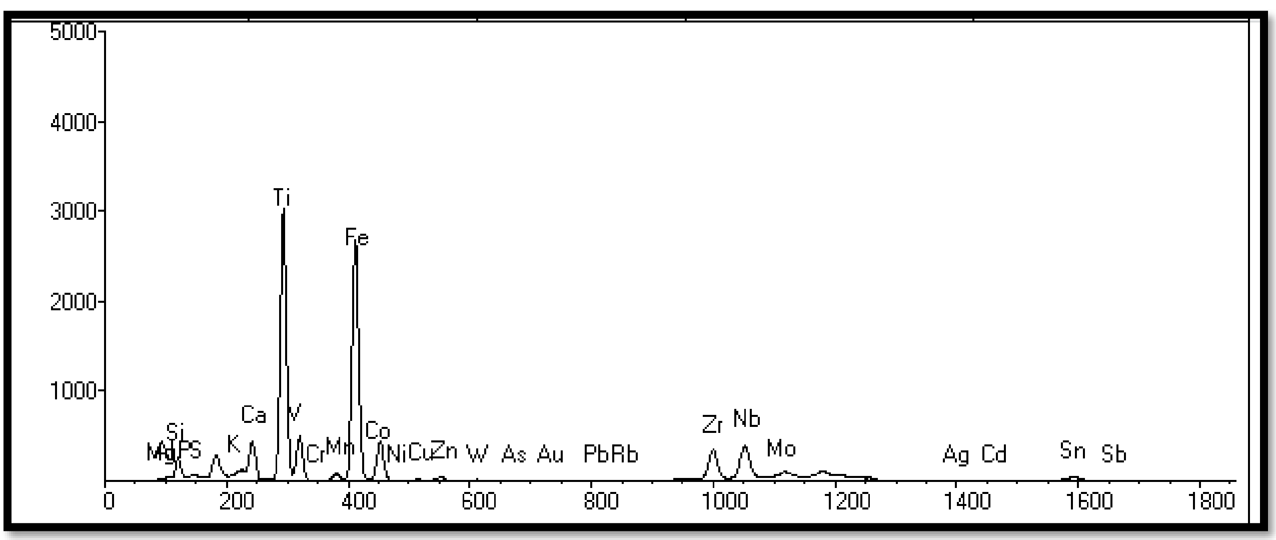

Fig. 6: XRF pattern (2M HCl)

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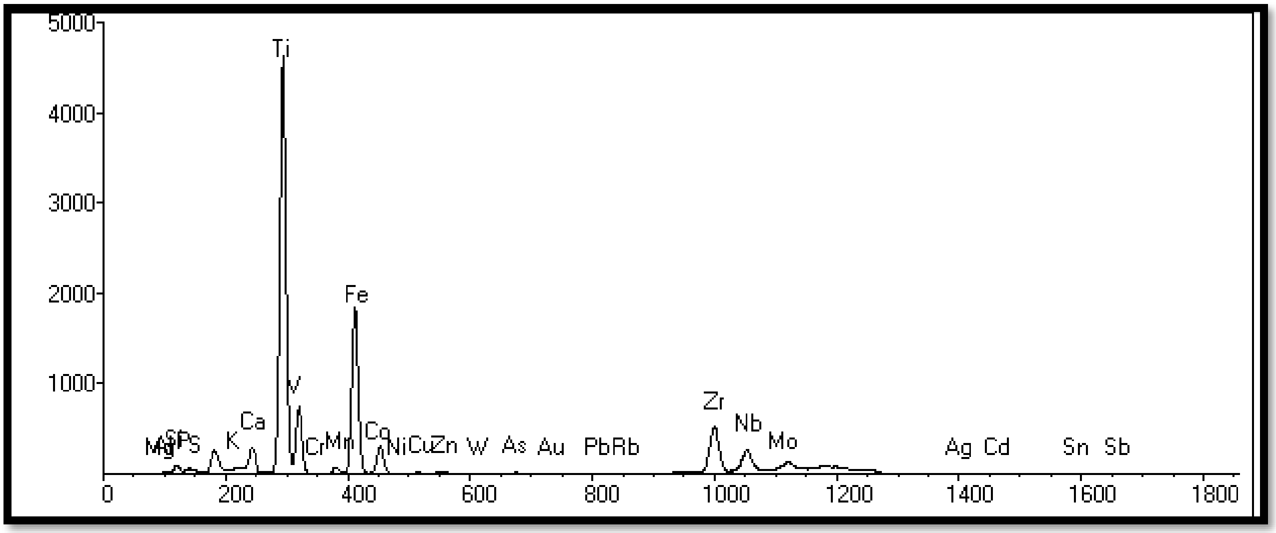

Fig. 7: XRF pattern of sample (4M HCl)

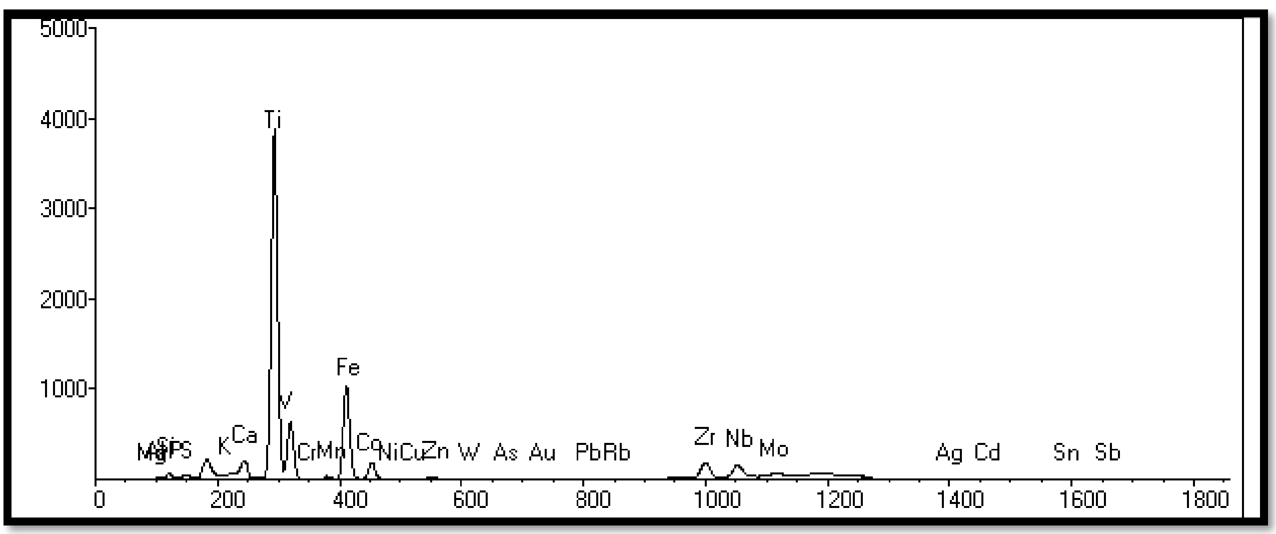

Fig. 8: XRF pattern of sample (6 M HCl)

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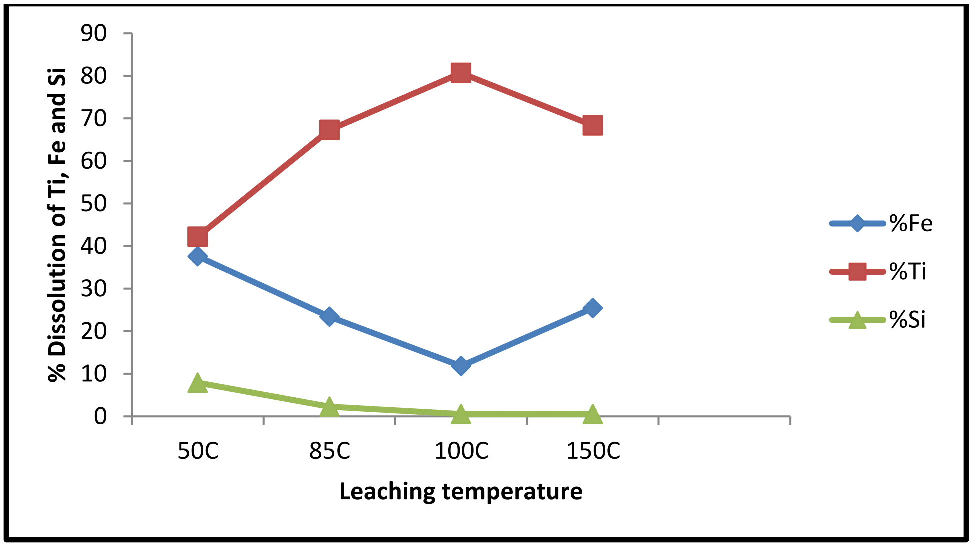

Fig 9: Effect of leaching temperature on dissolution of titanium

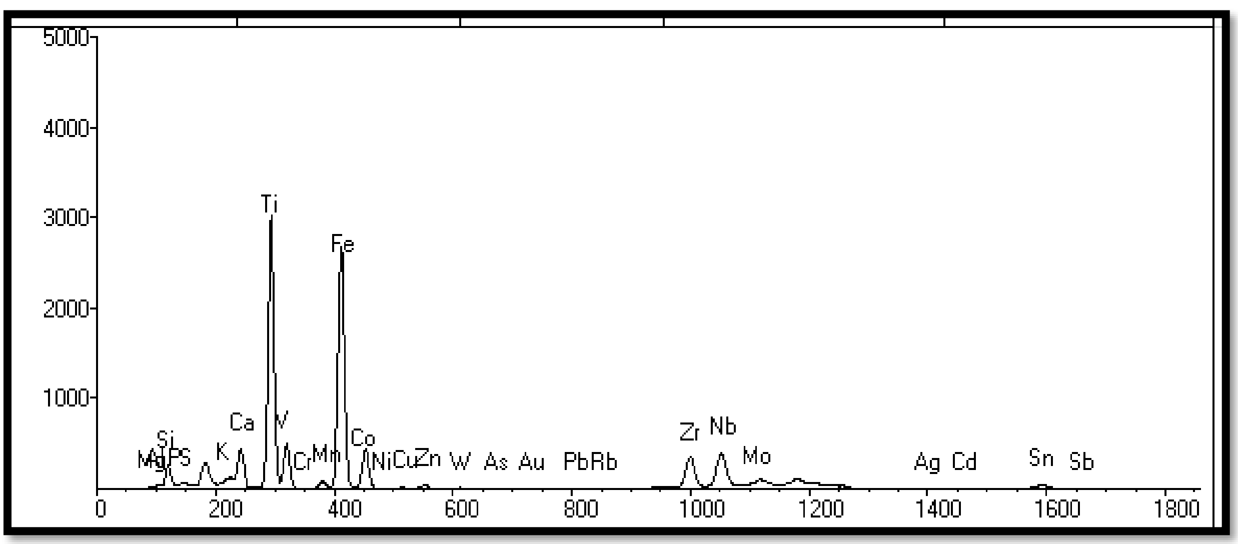

Fig. 10 XRF pattern of sample (at 50°C)

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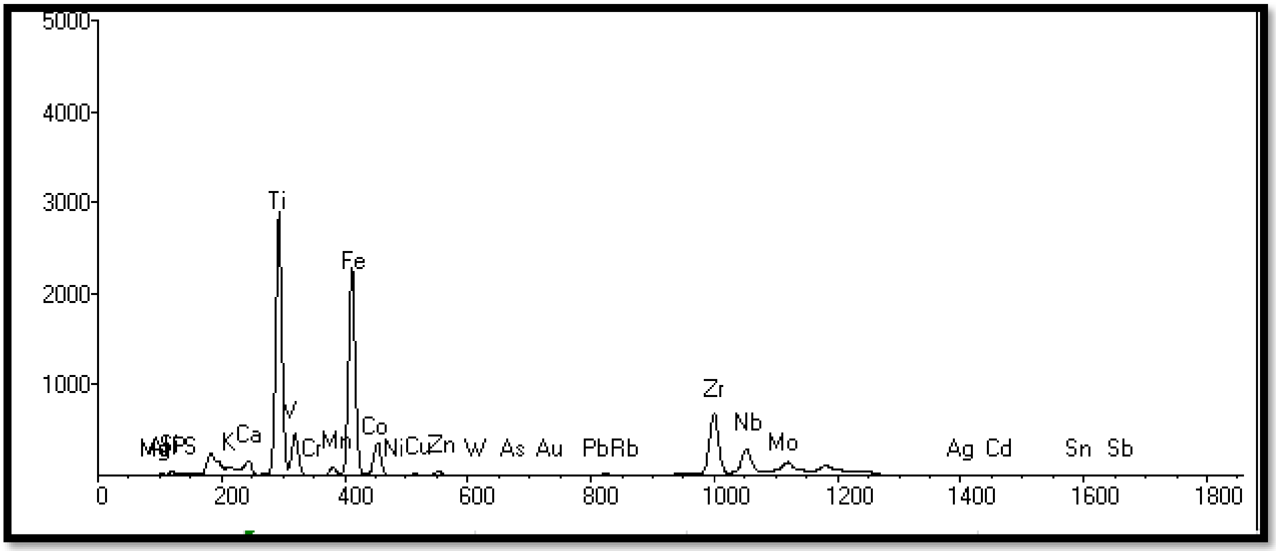

Fig.11: XRF pattern of sample (at 85^{o}C)

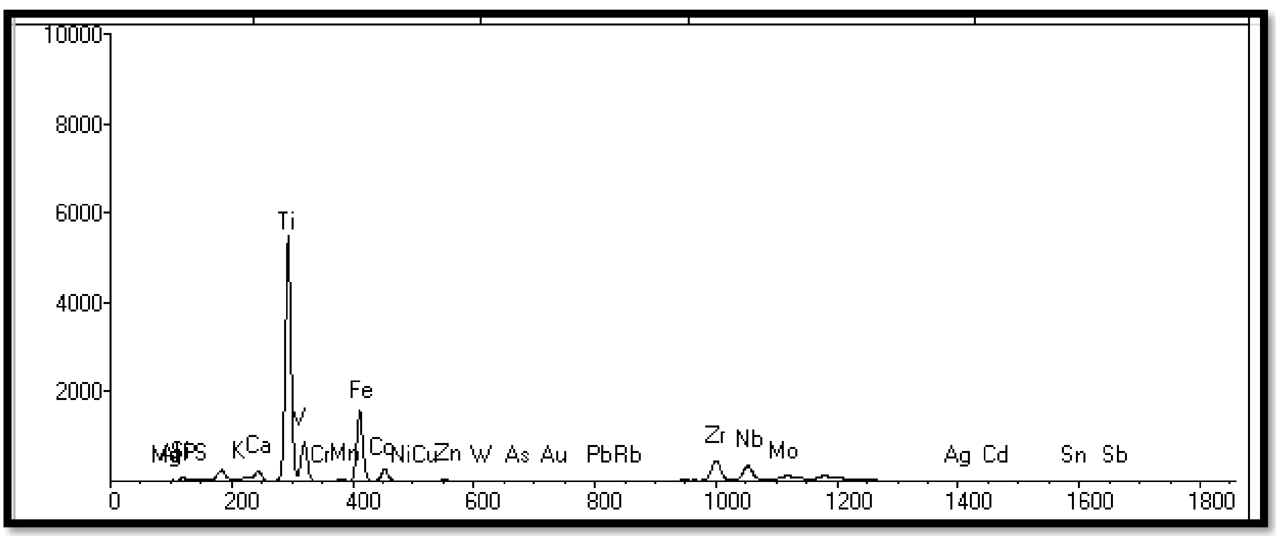

Fig. 12: XRF pattern of the sample (at 100^{o} C)

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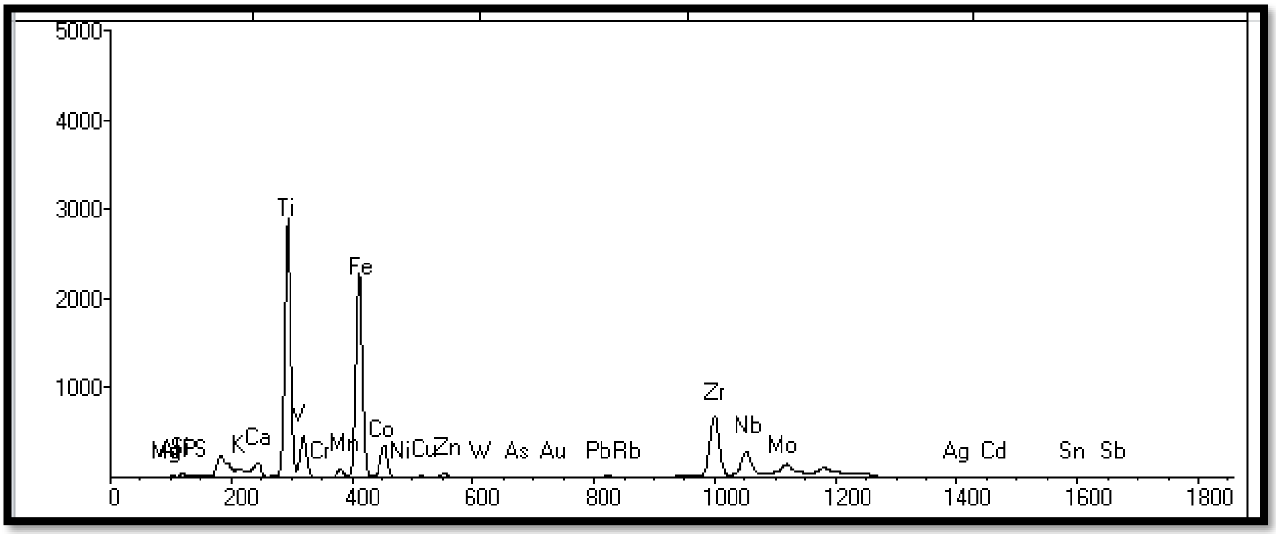

Fig. 13: XRF pattern of sample (at 150° C)

Table 1: Elemental composition of ilmenite ore (%)

Fe	Ti	Si	Al	Mn	Sn	Nd	Sb	Ca	Mo
51.671	32.582	6.217	2.075	1.995	0.5103	0.4664	0.2895	0.472	0.252

Table 4.2: Elemental composition of pretreated ilmenite ore (%)

Fe	Ti	Si	Al	Mn	Sn	Nd	Sb	Ca	Mo
42.902	37.637	8.147	3.264	1.910	1.144	0.3354	0.236	0.344	0.269

Table 3: Effect of hydrochloric acid concentration and leaching temperature on dissolution of titanium, iron and silicon

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Effect of hydrochloric acid concentration on dissolution of titanium, iron and silicon			
Factor	**Response**		
Concentration of hydrochloric acid	%Fe	%Ti	%Si
2M	26.7036	65.1642	0.803
4M	20.6894	68.9813	0.7282
6M	11.3274	81.0881	0.5001

Effect of leaching temperature on dissolution of titanium, iron and silicon			
Factor	**Response**		
Leaching temperature	%Fe	%Ti	%Si
$50^{o}C$	37.5854	42.238	7.9122
$85^{o}C$	23.3739	67.2848	2.2737
$100^{o}C$	11.8281	80.6678	0.5384
$150^{o}C$	25.4164	68.3820	0.525

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Conclusion

The acid leaching of ilmenite ore was carried out using concentrated hydrochloric and sulfuric acid, from the study, conclusions can be drawn as follows:

1. The XRD characterization of the ore reveals that it consists of iron, titanium and silicon oxide phases
2. For leaching using hydrochloric acid, the optimum leaching condition for ilmenite ore was at 6 M hydrochloric acid, leaching time of 150 minutes, solid-liquid ratio of 0.1gm/l, particle size of <0.5µm and leaching time of 85 °C, under these conditions, the optimum dissolution of Ti was 81.01%

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