



**ASSESSMENT OF THE
PHOTOCATALYTIC
POTENTIALS OF
MAGAMAN-GUMAU
ILMENITE FOR USE IN HYDROGEN
GAS PRODUCTION**

**GUSHIT, J. S., ISRAILA J. J., JOCK A. A. AND
FRANCIS E. M.**

*Chemical/Petroleum Unit, Department of Science
Laboratory Technology, University of Jos, Jos
Nigeria*

Abstract

The photocatalytic potentials of Ilmenite ore for hydrogen gas production was studied by identifying and characterizing the pre-pulverised ore using X-Ray Fluorescence (XRF) Spectroscopy, Scanning Electron Microscopy (SEM), Bruneaur-Emmett-Teller (BET) and Fourier Transform Infra-Red (FTIR) Spectroscopy. The XRF result indicated the main constituents of the Ilmenite to be 49.53% and 9.16% of elemental titanium and iron respectively, while the BET provided the surface area of the raw Ilmenite to be 12.8164m²/g. Similarly, the SEM revealed that cleavage planes and fractured surfaces to be prevalent on the surface of the natural Ilmenite ore, which is known to provide much more active sites and slightly higher reactivity than that of its synthetic counterparts

with perfect crystal faces. FTIR Spectroscopy spectra showed strong spectral band between 1000 - 900 cm⁻¹ in ilmenite indicating relatively high

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(MO).

amount of surface oxygen than in other synthesized TiO₂ catalysts. The effect of the ilmenite photocatalyst in the degradation of Methyl Orange (MO) in the dark and under visible light irradiation at different selected times was used to assess the photocatalytic potential of the ilmenite. From the assessment, the

degradation of 200mL of 30mg/L MO solution using Ilmenite ore at varying quantities of 1.0g, 1.5g, 2.0g and 2.5g was carried out and it was clear that the degradation of MO under visible light irradiation by 2.0g of Ilmenite gave the highest degradation with 35.64%. Absorption test showed that the degradation was solely due to photocatalytic activity.

Introduction

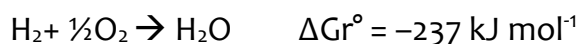
The increased concern on global warming, emission of pollutants and exhaustion of energy resources consequent to the rise of world energy demand, up till now mainly fulfilled by fossil fuels exploitation, urgently requires the development of alternative, environmentally friendly and totally renewable energy sources.

To replace or reduce the use of fossil fuels, several alternative energies have been developed. Alternative energies are renewable and have lower carbon emissions when compared to conventional energy sources. These energy sources include wind, hydropower, solar, geothermal, etc. (Dincer, 2011).

Solar energy is a free, inexhaustible resource from the sun that can be converted to electricity (photovoltaic power) or heat using devices such as solar cells or concentrators (Xie et al., 2011). Electricity produced from solar energy has advantages over wind power and hydropower, since the latter two need turbines with moving parts that are both noisy and require much maintenance. However, the major disadvantage of solar energy is its intermittent nature, i.e., the amount of sunlight a location receives varies greatly depending on the geographical location, time of day, season, and even clouds.

In this prospect, sunlight is the most promising renewable energy source of the future. Indeed, the amount of solar energy impinging on the earth's surface is estimated to be 3×10^{24} J per year (Mohammed, 2010), which is approximately 10^4 times greater than the worldwide yearly energy consumption. Moreover, increasing interest is addressed towards hydrogen, which is widely considered the clean energy vector of the future, because the chemical energy stored in the H-H bond formation is released

when it reacts with oxygen, yielding only innocuous water as a product, in a highly exothermic reaction (Fujishima and Honda, 1972),



Although the technologies of energy production from hydrogen, example fuel cells and internal hydrogen combustion engines, are already mature, hydrogen production remains a major problem. In fact, nearly all hydrogen production is still based on fossil raw materials and only 4% is produced via water electrolysis (Xie et al., 2011; Mohammed, 2010).

Heterogeneous photocatalysis has received much attention and has been an active research area over the last four decades. Titanium dioxide has become the state-of-the-art material for photocatalytic reactions due to its relatively high efficiency under UV irradiation, abundance, low cost, photo-corrosion resistance and biocompatibility (Jina, 2010).

However, a fatal disadvantage for most photocatalysts is their large band gap, which makes them effective under UV light irradiation (Pankaj, 2010). So, their application is constrained to only the UV light range which makes up only 4-5% of the solar spectrum, whereas approximately 40-50% of solar photons are in the visible light region (Pelaez et al., 2012). To extend their application into the dominant visible light range in solar light, many efforts have been made but challenges still remain in finding new materials that can effectively utilize the visible light irradiation. Therefore, effective utilization of visible light has become one of the most difficult challenges in photocatalysis, and it is highly desirable to develop a photocatalyst that can use visible light in high efficiency under solar irradiation.

Various strategies have been adopted for improving the photocatalytic efficiency of photocatalysts. They can be summarized as either morphological modification, such as increasing surface area and porosity, or as chemical modifications, by incorporation of additional components in the photocatalyst structure. Although visible light active (VLA) photocatalysts require chemical modifications, their overall efficiencies have been significantly enhanced by controlling the semiconductor morphology.

Chemical modifications by non-metal doping of photocatalysts has shown great promise in achieving VLA photocatalysis, with nitrogen being the most

promising dopant due to its comparable atomic size with oxygen, small ionization energy and high stability (Linsebigler and Yates, 1995).

Experimental

Materials

The natural Ilmenite ore used in this work was collected from the National Metallurgical Development Centre (NMDC), Jos, Plateau State, Nigeria; sourced from an Ilmenite deposit hosted at Magaman-Gumau, Bauchi State, Nigeria. The sample was pulverized, after which it was sieved using 63 μ m (63 x 10⁻⁶m) mesh size sieve, i.e. the size of particles obtained were below 63 μ m. Analytical reagent grade methyl orange (MO) crystals and deionized water were used for preparing all the solutions without further purifications.

Characterization

Elemental composition of the natural Ilmenite was obtained using an X-ray Fluorescence (XRF) analyzer at the Centre for Minerals Research and Development, Kaduna Polytechnic. Microstructures and morphologies were investigated using a PHENON PRO-X Scanning Electron Spectrophotometer in Chemical Engineering, ABU Zaria. Frequencies and intensities of absorptions were obtained using a SHIMADZU FTIR-8400s Fourier Transform Infrared Spectrophotometer and the Surface area and pore size were obtained using V-Sorb 2800P Surface Area and Porosimetry Analyser at the National Research Institute for Chemical Technology, Zaria. The concentration of MO was measured spectrophotometrically using a JENWAY spectrophotometer (Model 6405) in Postgraduate Laboratory, Chemistry Department University of Jos.

Measurements of Photocatalytic Activity

Photocatalytic activity of the pulverized and sieved natural Ilmenite ore was evaluated by the degradation of aqueous Methyl Orange (MO) solution. Various quantities (1.0g, 1.5g, 2.0g and 2.5g) of the photocatalyst was added each to a 200ml MO solution (30mg/L) and stirred for 20 minutes in the dark

to reach the absorption equilibrium, then exposed to Visible light (1000W high pressure Halogen lamp). To minimize the influence of temperature emanating from the lamp, the photoreactor was placed in a water bath. The degradation time was varied from 0 to 100 minutes at 20 minutes interval. Samples at the various degradation times were then taken and their absorbances were measured using a JENWAY UV-Vis spectrophotometer to monitor the degradation of MO molecules by converting each absorbance to concentration. The characteristic absorption peak of MO at (463nm) was chosen to monitor the photocatalytic degradation. The photocatalytic degradation efficiency was calculated using the expression

$$\text{Degradation (\%)} = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

Where C_o is the initial concentration (mg/L) of MO, C_t is the MO concentration (mg/L) at a certain reaction time, t in minutes.

Absorption Test

Table 1 show the absorption test carried out on the Ilmenite sample. The absorption of Methyl Orange (MO) by dissolving 2g of the Raw Ilmenite Photocatalyst in 50ml of the prepared solution was carried out to ascertain the differences in the degradation of MO by the Photocatalytic Activity of Ilmenite and degradation due to Absorption.

Table 1: Absorption Test of Ilmenite

Initial concentration (C_o) (mg/L)	Absorbance	Final Concentration (C_t) (mg/L)	Uptake (q_e) $\left[\frac{m}{v}(C_o - C_t) \right]$
5.00	0.353	4.702	0.0119
10.00	0.713	9.507	0.0197
15.00	1.073	14.307	0.0277
20.00	1.392	18.560	0.0576
25.00	1.766	23.893	0.0581
30.00	2.1405	28.540	0.0584

Results and Discussion

Table 2 shows the elemental composition of the natural Ilmenite. The X-Ray Fluorescence (XRF) result of the Ilmenite sample indicated that the main constituents are elemental titanium (49.53%) and iron (9.16%) as shown in Table 2.

Table 2: Elemental Composition of Ilmenite Sample using X-Ray Fluorescence (XRF)

Element	Concentration (Wt%)	Element	Concentration (Wt %)
Si	1.07	Zn	0.01
S	0.04	Nb	0.13
Ca	0.14	Cr	0.01
Ti	49.53	Ba	0.03
V	0.28	Al	2.13
Mn	0.32	Mg	6.34
Fe	9.16	P	0.12

The degradation of 30mg/L solution of MO using Ilmenite at different dosages of 1.0g, 1.5g, 2.0g and 2.5g was carried out and represented in Figure 1. It is clear that the degradation of MO under visible light irradiation by 2g of Ilmenite gave the highest degradation percentage of 35.64%. This is attributed to the fact that at low concentration region (1g/200ml and 1.5g/200ml of MO solution of TiO₂), the amount of electron-hole pair generated is also low and this will lead to low degradation of MO. On the other hand, “screening” effect is produced when TiO₂ concentration is high (above 2g/200ml). The reaction rate diminishes due to the excessive opacity of the solution, which prevents the catalyst farthest in from being illuminated. Also, when catalysts concentration is high, after travelling a certain distance on an optical path length, turbidity impedes further penetration of light in the reactor. The effect of irradiation time on the photocatalytic degradation of methyl orange is presented in figure 1.

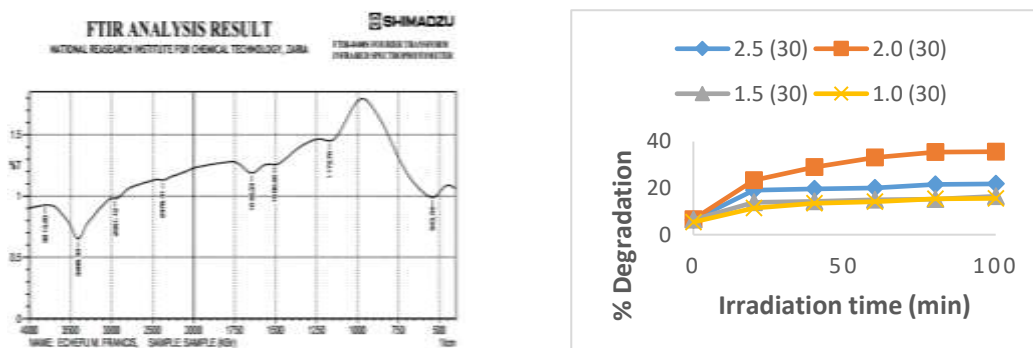


Figure 1: Effect of irradiation time on the photocatalytic degradation of methyl orange using natural Ilmenite ore as photocatalyst

The absorption test was carried out to ascertain the differences in the degradation of MO by the Photocatalytic Activity of Ilmenite and degradation due to Absorption. This was due to the relatively high degradation of MO in the dark; which was assumed to be as a result of absorption. The absorption test shows that the sharp decrease in concentration was not due to absorption, but Photocatalytic Activity and the presence of light in the dark, which could not be shielded completely. The trend in the absorption increases with an increase in the concentration of MO. But this increase tends to reduce at a higher concentration of the MO.

The surface area of the Ilmenite sample was evaluated on a 0.3752g using the Multi-Point Brunauer-Emmett-Teller (BET) method pre-treated for 5hrs at ambient temperature. The specific surface area of the natural Ilmenite was found to be low with a value of 12.8164m²/g. The low activity of the Ilmenite was due to several factors like low surface area, pore size and volume, surface morphology and low band gap for light absorption.

Figure 2 shows the FTIR spectra of the natural Ilmenite sample along the wave number region of 4000 – 700cm⁻¹. It measures the sample's frequencies and intensities of absorption. The frequencies for the FTIR were helpful for the identification of the Ilmenite chemical make-up. High spectral band between 1000-900cm⁻¹ in Ilmenite indicates the presence of higher amount of surface oxygen than in other synthesized TiO₂ catalysts.

However, this constraint can be remediated by modification of the photocatalyst, hereby improving its photoactivity.

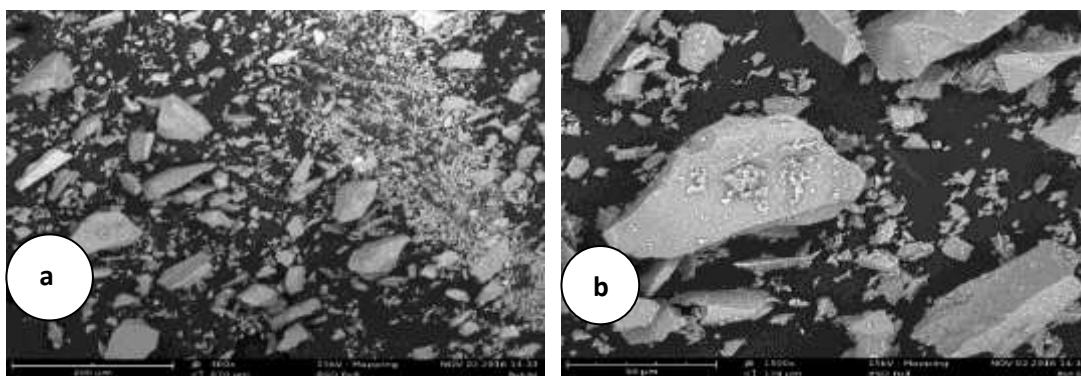


Figure 2: FTIR spectra for Ilmenite

The images of the SEM results shown in Plate 1 (a, b, c) depict the morphology and different crystal sizes of the Ilmenite sample at $\leq 63\mu\text{m}$. The photoactivity of a photocatalyst depends on the specific surface area of the particles, such that a high specific surface area of the particles promotes high photoactivity. Specific surface area however, decreases with increase in crystal sizes of the particles and increases with decrease in the crystal sizes of the particles. Cleavage planes and fractured surfaces were prevalent on the surface of the natural Ilmenite, which were probably produced by the mechanical grinding. Since cleavage planes and fractured surfaces are known to provide much more active sites than flat crystal faces [9], the slight reactivity of natural Ilmenite was observed to be higher compared to that of its synthetic counterparts with perfect crystal faces.

Plate 1: Scanning Electron Microscopy Images at different magnifications (a: 400x, b: 1500x, c: 2500x).

Conclusion

Natural Ilmenite as a visible light-driven photocatalyst was characterized and its photoactivity was successfully tested for the degradation of MO under visible light irradiation. The natural Ilmenite was seen to provide much better photocatalysis reactions as the cleavage planes and fractured surfaces it possess are known to provide much more active sites than flat crystal faces of its synthetic counterparts with perfect crystal faces (Zhao et

al., 1998). It was also seen from the absorption test that the degradation of MO by the natural Ilmenite was solely due to Photocatalytic Activity. The natural Ilmenite used in this work further exhibited its best activity at 2.0g dosage in 200mL of 30mg/L MO solution at 12.8164m²/g specific surface area, making this a promising photocatalyst in hydrogen gas production.

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