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Assessing the Photo Catalytic Activity of Rutile Ore from the Middle Belt Region of Nigeria on the Degradation of Phenol in Water

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Abstract: *The photocatalytic actitvity of Natural rutile collected from Bauchi State in the Middle belt region of Nigeria was assessed using Phenol as probe molecule with UV irradiation. The rutile, which contains substituting metal ions with* Fe^{3+} *as the predominant, was found to exhibit good photoactivity in UV light. The result showed that 51.7% of Phenol was photodegraded after 120min in UV light irradiation. Compared with P25* TiO_2 *degrading 71.8% of phenol, the effect of reusability of the rutile was also investigated, however under recycle, rutile surface was prone to oxidation of the substituting elements which led to relatively rapid deactivation of the ore. It was demonstrated that P25 was stable. The XRD, BET, SEM, DRS UV-Vis spectra and the TEM of the Nigeria rutile samples showed that the presence of trace element affects the photocatalytic properties of the sample.*

Keywords: *Degradation, Nigeria, Photocatalysis, Phenol, Rutile*

I. Introduction

Titanium dioxide is known to exist in three different phases: rutile, anatase and brookite that are naturally occurring in many parts of the world, also the rutile ore has been discovered in some region of Nigeria [1-2]. Titanium dioxide has several applications one of which it is used as a photoactive semiconductor in the photocatalytic mineralization of organic recalcitrant pollutant due to its stability to corrosion, nontoxicity, photostability and cost effectiveness. Titanium dioxide is the most commonly studied photocatalyst in the area of Advanced Oxidation process. Similar to pure anatase, pure rutile, a second polymorph of TiO_2, shows no photoactivity [3].

Fujishima and Honda in 1972 investigated the ability of TiO_2 to decompose water using visible light, after which anatase has been the most widely studied phase of Titanium dioxide in photocatalysis [4]. More also, investigation has recently been extended to rutile phase [5-6], although the reactivity of the rutile phase is fifth of anatase [6]. In contrast to rutile containing Vanadium and Iron, pure rutile shows no photoactivity [5].

However, depending on the type of elements presents in the rutile as impurity, it could show some photo activity. For example, naturally occurring rutile usually contains trace elements such as Vanadium and Iron and these elements enhance photocatalysis [7-8]. Since the mineral ore was only recently discovered in Nigeria [2], there is little information about its photo catalytic activity, which can be affected by the elemental characteristics of the rutile ore. To the best of our knowledge, this is the first effort at determining the photo catalytic properties of any rutile deposits in Nigeria.

II. Experimental

2.1 Material

All the reagents used for experimental studies were of analytical reagent grade. Dichloromethane, and Methanol (HPLC grade) where obtained from Sigma Aldrich UK, Titanium dioxide P25 was obtained from Degussa AG, Sodium Borohydride Powder was obtained from Lancaster Synthesis UK and Oxygen gas (99.5% Purity) was obtained from BOC UK.

2.2 Collections and Preparation of Sample

The rutile samples investigated were obtained from Bauchi-state in the Middle Belt region of Nigeria. The ore has a blackish color. Representative pieces of the mineral samples were collected, cleaned with acetone and made into powder using a Ball milling machine. All experiments were performed with particle size of 0.045-0.075mm.

2.3 Characterization of Rutile sample

Optical characterization of the Rutile ore and P25 was carried out using a UV-Vis spectrophotometer (Perkin Elmer Lambda 6505) in the wavelength range from 250 to 800 nm and a scanning speed of 300nm min^{-1}. Structural characterization was performed using x-ray diffraction. Measurements were made with Cu K∝ radiation (1.5405 Å) on a PANalytical X'PERT PRO MPD diffractometer equipped with reflection geometry, a NaI scintillation counter, a curved graphite crystal monochromator and a nickel filter. The scattered intensities were collected from 5^o to 80^o (2θ) by scanning at 0.017^o (2θ) steps with a counting time of 0.5 s at each step. The quantitative analysis of some selected elements in the rutile ore was determined using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, P-1000, Perkin- Elmer). The qualitative analysis of the rutile ore was determined using ED-XRF Spectrometer from Oxford Instrument X-Supreme 8000. Thermal characterization was performed by Mettler-Toledo TGA/DSC I STAR with a heating rate of 20°C min^{-1} under N_2. The surface area, total pore volume and average pore diameter were measured by N_2 adsorption-desorption isotherms at 77K using Micromeritics ASAP 2010. The pore size was calculated on the adsorption branch of the isotherms using Barrett-Joyner-Helenda (BJH) method and the surface area was determined using the Brunauer-Emmett-Teller (BET) method.

2.4 Photocatalytic Activity

The Photocatalytic activity of the rutile ore was evaluated using phenol degradation experiments. The reactors used were closed Pyrex reactors with a diameter of 42.7 mm and a height of 210 mm. 100 mL of a solution containing 94.11 mg/L (1mMol L^{-1}) of phenol in deionized water from Barnstead Nanopure Diamond Machine and 0.2 g of the rutile ore was added to the reactor. The pH of the aqueous phenol solution was monitored during the reaction using the Jenway 3010 pH meter. The suspension was stirred magnetically using yellow line MST Basic magnetic stirrer at 650 rpm at ambient temperature for 2 h in the dark, and a small amount of the suspension was withdrawn to analyze equilibrium concentration of phenol in the solution. The mixture was then exposed to UV light using a Rayonet RMR-600 reactor. The reactor has 6 (8 Watt) UV lamps (350nm wavelength). The distance between the UV lamp and the surface of the solute was set at 63.5 mm. An oxygen balloon was connected to the reactor in order to assure a high oxygen saturation of the solution with a sparger. At selected time intervals of approximately 20 minutes over a typical 2hr reaction, 2.5 mL of the suspension was withdrawn and filtered using an Acrodisc CR 13mm syringe filter with 0.45µm PTFE membranes for HPLC analysis. The schematic of the system is presented in fig 1.

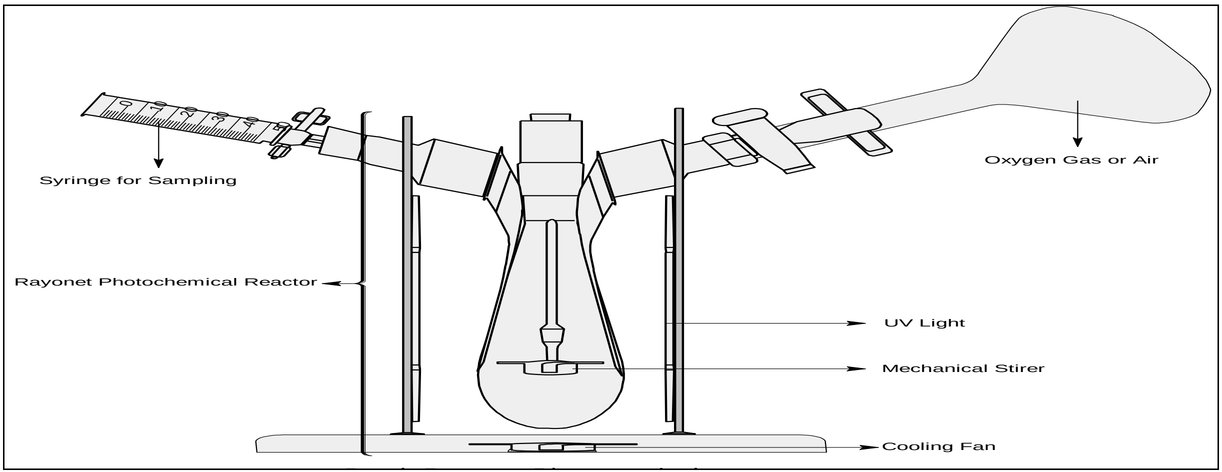

Figure.1. Diagram of the Photo catalytic Set-up

III. Results And Discussion

3.1 Rutile Ore Characterizations

3.2 Diffuse Reflectance UV-Vis of Rutile Ore

The optical properties of rutile ore collected from the middle belt region of Nigeria was compared with P25 Degussa due to the superior physicochemical properties of P25 Degussa and it wide application as a photocatalyst [9-10]. The DRS UV-vis absorption spectra of the rutile ore and P25 Degussa are presented in Fig 2. The absorption spectrum of the P25 Degussa appears to have a sharp absorption edge around 345nm, showing it will be photoactive mainly around the UV light region. Meanwhile, the rutile ore displayed wide absorption shoulder band around 358-569nm, meaning that a wider part of the visible light could be absorbed to generate electron-hole pairs [9]. The ability of the rutile ore to absorb Visible light explains the reason the rutile ore supported the photocatalytic oxidation of phenol in visible light.

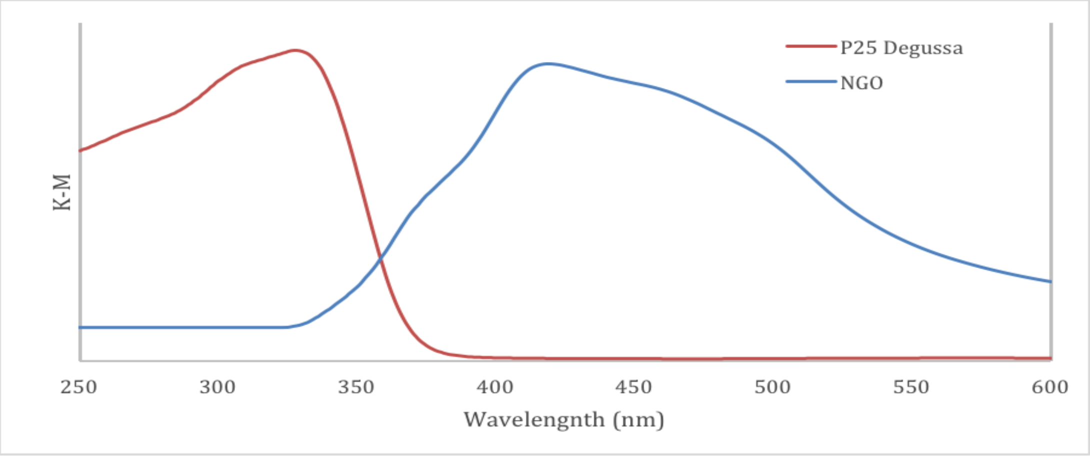

Figure 2: DRS UV-Vis of the Nigeria rutile (NGO) and P25 Degussa

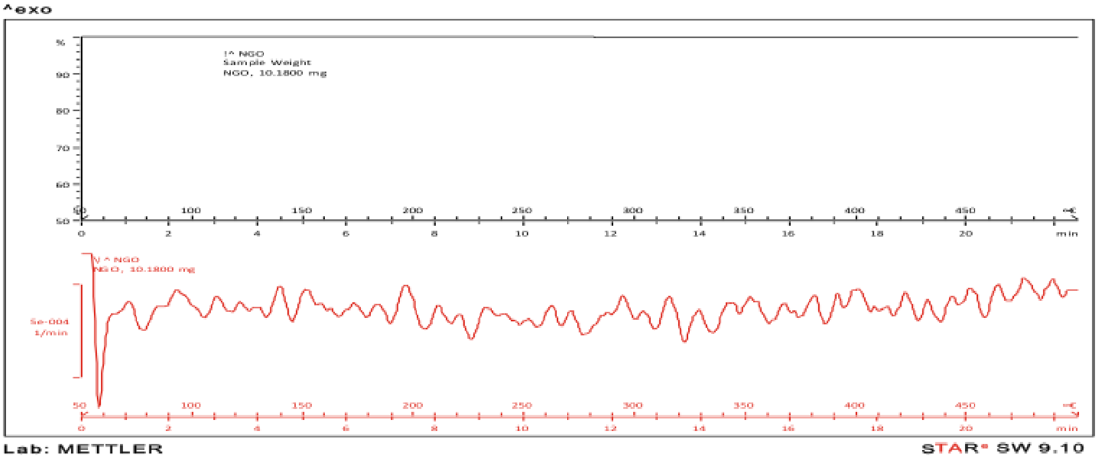

Figure 3. Thermal Gravimetric Analysis of the Nigeria rutile from the Middle belt region

3.3 Thermal gravimetric Analysis (TGA) of Rutile Ore

Thermal gravimetric Analysis (TGA) measures the mass of a sample as it is submitted to a selected temperature program in a defined atmosphere. The TGA curves show no remarkable weight loss. It has been reported that Rutile is a high-pressure and high-temperature polymorph and is Isostructural [11], which explain the stability of the Nigerian rutile in 500°C for 20mins as shown in Fig 4. Also this shows the thermodynamic stability of the rutile polymorph of TiO_2 at all temperatures, it is generally the primary titanium-bearing phase in most high-pressure metamorphic rocks [12].

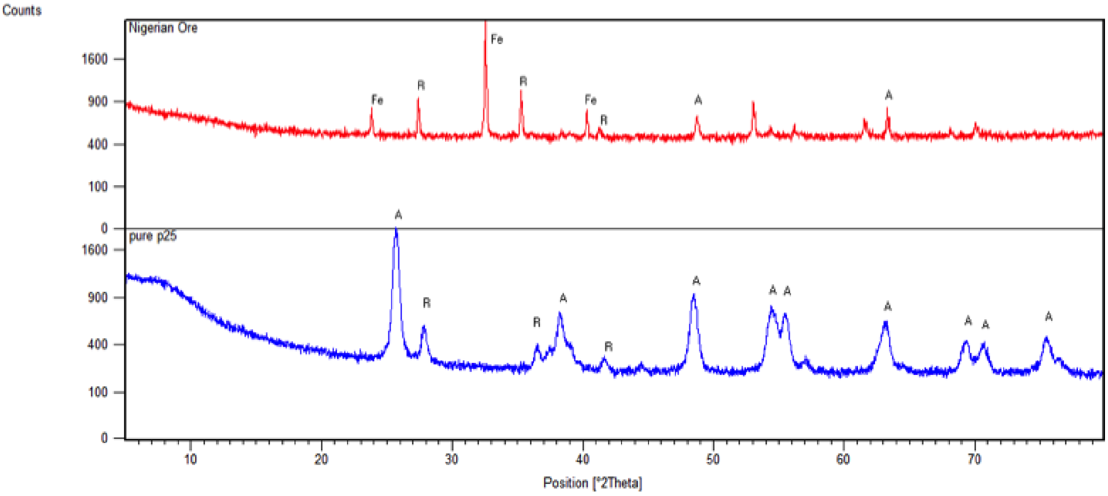

Figure 4. X-ray diffraction patterns of the Nigerian rutile and P25 Degussa

3.4 XRD of P25 Degussa and rutile sample

The phase structure, crystallite size, and crystallinity of TiO_2 plays an important role in its photocatalytic activity, and many studies have confirmed that anatase phase of titanium (IV) oxide shows higher photocatalytic activity than brookite or rutile phase [4]. The XRD pattern of P25 Degussa is shown in Fig 4. There existed diffraction peaks, which lay at 25.40°, 37.90°, 48.00° and 53.90°, corresponding to the anatase phase. The large surface area, high crystallinity, low crystallite size, and crystal structure are important properties that influence the photocatalytic activity of TiO_2. The average crystal size of P25 TiO_2 was determined to be 22.3 nm using the characteristic anatase peak at 2θ= 25.30 and 34.1nm for the rutile peak at 2θ= 27.40. The XRD patterns of the Nigeria rutile indicates that all prominent peaks are rutile phase and Iron peaks from present as ilmenite ($FeTiO_3$) in the sample. The comparison of the XRD peaks obtained from the Nigeria rutile ore and the JCPDS file 47-0421 and 29-1360 confirmed the presence of rutile as one of the major components of the mineral ore as shown in figure 4. For instance, the two peaks with the strongest intensities on the XRD Pattern at 27.58° and at 39.85° correspond respectively with the first and the last peaks in the diffraction pattern of rutile. Beyond that, all the other prominent peaks of rutile were also confirmed at 36.06°, 41.22° and 44.17°.

3.5 ED-XRF and ICP-OES analyses

The results of the elemental composition of the rutile ore collected from Bauchi state of Nigeria using the ED-XRF is presented in Table 1. From the qualitative analysis done using the ED-XRF three elements are predominant in the sample; Ti (39.96wt%), Fe (3.11wt%) and Si (16.35wt%) while Cu, Zn, Nb, Ta, Pb, Mo, V, Ca and W are present at trace level. For the quantitative analysis using the ICP-OES some selected elements were investigated, from the results obtained using the ICP-OES i.e. Nb (0.98wt%), Ta (1.06wt%), Pb (0.05wt%), V (0.93wt%) meanwhile Ca (1.93wt%), Ti (40.90wt%), Fe (3.54wt%) and Si (17.22wt%) appeared as the prominent element in the ore as confirmed by the ED-XRF. The slight difference in the concentration with the change in the technique used for the analysis is likely due to the orientation dependent of each sample, also the black-brownish color of the ore may be due to the reduction state of Ti in the ore and the brownish tint is probably due to the oxidation state of other elements like Fe, Cr, Co or Ni (Siyanbola et al., 2004) [2]

Table 1. Qualitative Analysis using ED-XRF

Metal	Ti	Fe	Cu	Zn	Nb	Ta	Pb	Mo	Si	V	Ca	W
Wt%	39.96	3.11	0.04	0.81	0.74	1.05	0.07	0.03	16.35	1.00	1.33	0.04

Table 2. Quantitative analysis of some selected elements using ICP-OES

Metal	Ti	Fe	Nb	Ta	Pb	Si	V	Ca
Wt%	40.90	3.54	0.98	1.06	0.05	17.22	0.93	1.93

3.6 Scanning Electron Microscopy (SEM) of the Nigerian Rutile from the Middle Belt region

In general, the rutile powders from the Middle Belt of Nigeria consist of nano-sized primary particles with a spherical shape of agglomerated powder particles, which are packed on layers of cubic flakes as shown on Fig 5, also a close look into these powders' micrographs reveals that a degree of rod like shape are also formed. A patchy rusty brown veneer Iron oxide commonly coats the rutile ore. The Backscatter SEM images shown Depicts the zoning of the texture of the rutile ore is produced by concentrations of heavy metals.

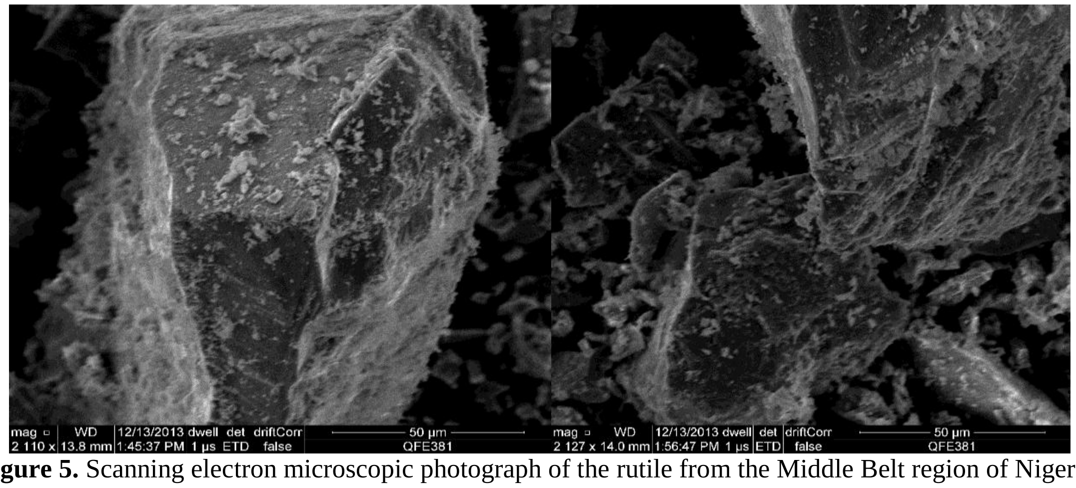

Figure 5. Scanning electron microscopic photograph of the rutile from the Middle Belt region of Nigeria.

3.7 Transmission Electron Microscopy of rutile from the middle belt region of Nigeria

Transmission electron microscopy was applied to investigate the microstructure of the rutile in Methanol solution. Fig 6 shows a typical TEM image of the ore. The sample mostly consists of cubic like particles of different sizes packed in layers, in good agreement with the SEM data.

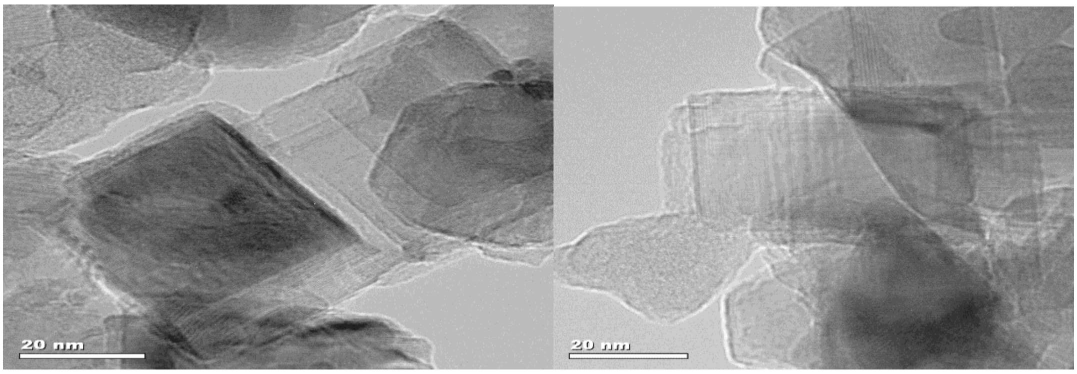

Figure 6: TEM Images of the rutile from the middle belt region of Nigeria

Table 3. BET Surface Area of P25 Degussa and Nigeria rutile

PARAMETERS	P25 DEGUSSA	Nigeria Rutile
BET Surface Area (m^2/g)	49.59510	0.455100
Pore Volume (cm^3/g)	0.072830	0.000591
Pore Size (Å)	70.79400	158.3240

The data obtained on the BET analysis are: surface area, pore volume and pore size of the catalyst as presented on Table 3. The surface area and pore volume of the P25 Degussa are 49.5951m2/g and 0.072830 cm^3/g, which are higher, compared to the Nigeria rutile having 0.4551m^2/g and 0.000591 cm^3/g. The presence of some elements on the rutile ore as listed in Table 1 may be responsible for the low surface area and pore volume observed. Larger surface area increased adsorption desorption capacity which can result to good photocatalytic activity [13-14].

3.8 Photocatalytic Activity

In order to assess the photo-response and the photocatalytic efficiency of the Nigeria rutile TiO_2 under UV light irradiation, the photocatalytic experiment was conducted using 0.2g of catalyst in 100ml of 0.001M phenol solution using the batch reactor as described in the experimental section. Based on these studies the results obtained as represented in Fig 6 and Table 4, which showed that 71.8% conversion of phenol to CO_2 and H_2O after 120 min was achieved in the case of P25 Degussa and for the Nigeria rutile TiO_2 the degradation is 51.7% respectively. The photocatalytic actitvity of the P25 in oxygen is as a result of the presence of the anatase phase in the P25. Also the photocatalytic performance of anatase generally is considered superior to that of the more stable rutile. One possible reason was that the particle size of P25 Degussa (20 nm) from the XRD results was significantly smaller than that of the Nigeria rutile sample (0.045-0.075mm), so P25 Degussa had a larger surface area to mineralize the phenol. Another likely factor was that the Nigeria rutile had more defects in the crystal structure. These defects acted as electron–hole recombination centers, and consequently suppressed the photocatalytic reaction [15]. Also the ratio of metal ions to oxygen ions is little less than 1:2 as depicted on the ED-XRF result, indicting that oxygen atoms are deficient in the Nigeria rutile sample. Which implies that oxygen defects are present in the crystal structure. These defect sites may be the recombination centers of photogenerated electrons and holes, resulting in the decrease of photoactivity of the Nigeria rutile.

Table 4: The rate of Phenol photocatalytic degradation in Oxygen Using the Nigeria Rutile and P25 Degussa

Catalyst	Rate X 10^{-7}(S^{-1})	Phenol Converted (%)
P25 Degussa	1.317	71.8
Nigeria rutile	1.024	51.7

In addition, the comparatively low reaction rate experienced with Nigeria rutile can be attributed to the dissolution of copper in aqueous solution when illuminated with UV light [16], another proposed reason for the decrease in the rate of reaction with the Nigeria rutile was the formation of surface complex structures of Cu^{2+} ions with phenol or its degradation products and the formation of some metals oxide on the surface of the TiO_2 in the presence of Oxygen in aqueous medium, which can act as surface poisons [17]. The rate of reaction of the P25 and Nigeria rutile are shown on Table 4.

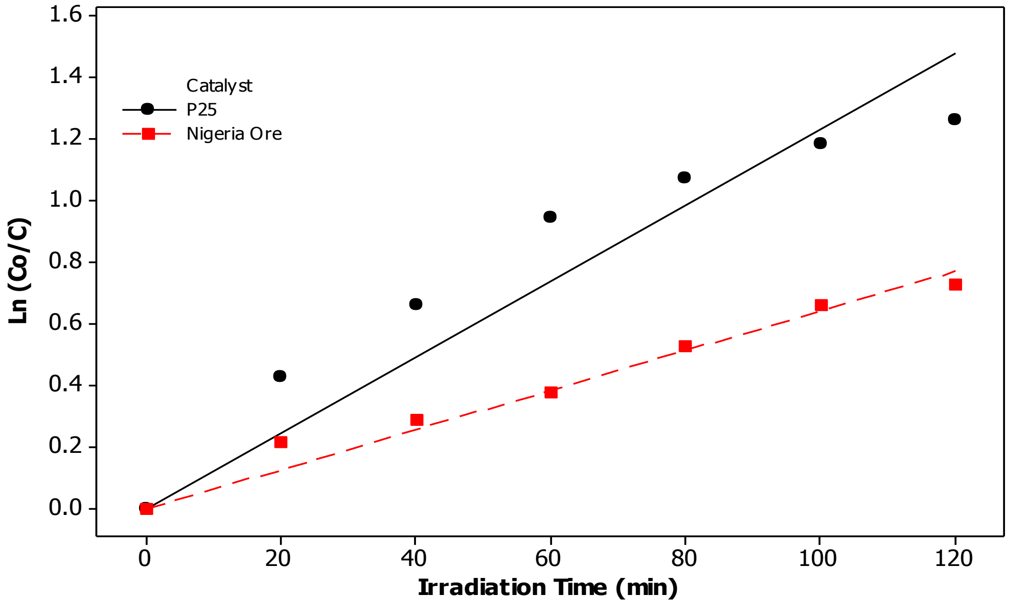

Figure 7. The Linear fit to the data represent Pseudo-first-order degradation kinetics of P25 and Nigeria rutile.

The kinetics of the photocatalytic degradation of phenol on solid surface has been reported in terms of Langmuir- Hinshelwood (L-H) equation [18]. The Langmuir-Hinshelwood expression is widely used in semiconductor photocatalysis to determine the rate and order of the photocatalytic degradation of organic pollutants [19-20].

$$\mathbf{1/k_{obs} = 1/(k_c\, K_{LH}) + [Ph]_o/k_c} \qquad (1)$$

Were [Ph]o is the initial concentration of phenol (mgL^{-1}), K_{LH} is the Langmuir- Hinshelwood adsorption equilibrium constant (Lmg^{-1}) and kc is the rate constant of the catalyst surface reaction ($mgL^{-1}min^{-1}$). Fitting of the experimental data into the Langmuir-Hinshelwood model has been shown to work only for organic pollutant of single component. The photocatalytic degradation of phenol follows pseudo-first-order kinetics with respect to the concentration of the bulk solution of phenol.

$$\mathbf{r = dC/dt = k_{obs}\, C} \qquad (2)$$

Integrating the equation with the following restriction C = Co at t = 0, with Co being the initial concentration of the phenol solution and t the reaction time. The following expression is obtained

$$\mathbf{\ln(C_0/C) = k_{obs}\ C} \qquad (3)$$

From the expression, k_{obs} is the apparent pseudo-first-order rate constant and is affected by the concentration of phenol. The plot of $\ln(C_o/C)$ versus irradiation time for the photocatalysis experiment using the batch reactor in oxygen with the P25 and Nigeria rutile in UV light is presented in Fig 7. The presence of other trace metallic elements on the rutile ore alters the adsorption of water and diminishes the population of surface hydroxyl group bonded to the titanium (IV) oxide (titanol). Therefore, in this regard, these elements can play a negative effect, decreasing the photocatalytic activity of the rutile under UV illumination. This negative effect is expected to occur when the trace element are not playing any active role in the process and simply masks and covers the surface titanol groups. It has been reported that in photocatalytic reactions, it is considered that the presence of metals, such as gold, palladium, iron and copper, on TiO_2 increases the charge separation efficiency and inhibits recombination of electron and hole produced by UV absorption [21-23]. The increase in charge separation efficiency will enhance the formation of active oxygen species, from these considerations, it is expected that the presence of these metallic ions on the rutile will enhance its interaction with phenol and the formation of active oxygen species, which improved the degradation of phenol as can be observed in our investigation. It has also been reported that Fe-doped TiO_2 was found to have very high photocatalytic activity under visible light irradiation than P25 Degussa. Fe^{3+} cations acted as shallow traps in the TiO_2 lattice which leads to increase of photoactivity [24].

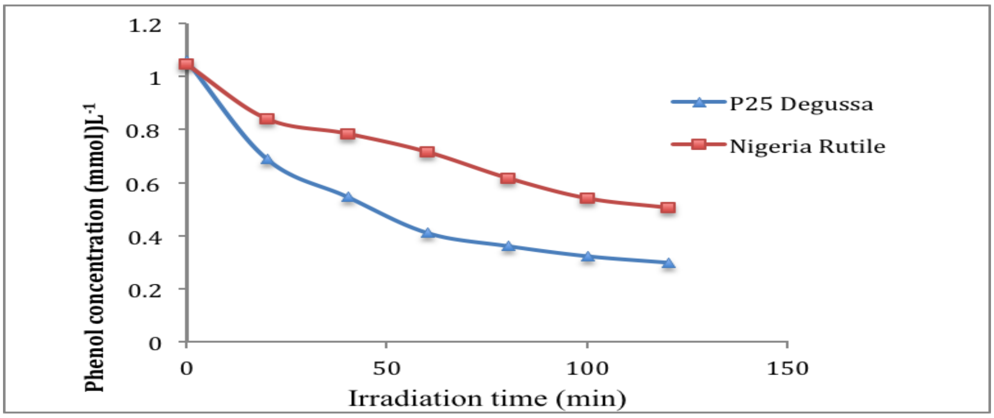

Figure 8: Phenol degradation in present of Nigeria rutile and P25 Degussa in UV light with Oxygen

3.9 Reusability of P25 and Nigeria rutile in Phenol degradation

In this experiment, the resulting solution from the photocatalytic degradation of phenols were filtered, and the catalyst washed and dried at 120°C overnight. The dried catalyst was subsequently used again under the same experimental conditions with a fresh phenol solution. The results obtained showed a loss in activity in both the P25 and the Nigeria rutile which is due to deactivation of catalyst by deposition of some polymeric species and intermediates, Fig 9 showed that the P25 catalyst lost 7% activity after the second run and 6% activity after the third run meanwhile, the Nigeria rutile sample lost 15% activity after the second run and 8% activity after the third. P25 Degussa samples showed considerably reproducible photocatalytic activity up to three runs for the degradation of all phenols. The loss in activity for the Nigeria rutile was more pronounced in the second and third run of reuse. The Nigeria rutile is prone to oxidations due to the presence of metallic elements, which are responsible to the lost of the activity.

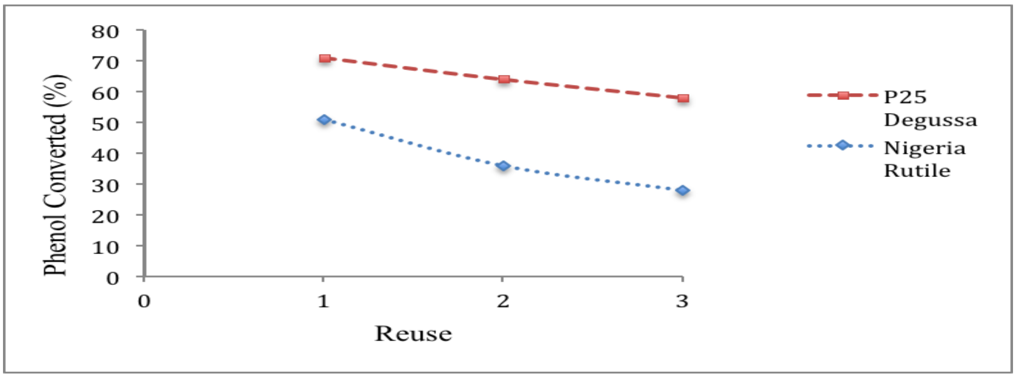

Figure 9: The reusability of Nigeria rutile compare with P25 Degussa in the Photocatalytic Degradation of Phenol

IV. Conclusion

Rutile sample collected from the Middle belt region of Nigeria was ball milled to a powder size of 72-75mm. The photocatalytic efficiency of the rutile was investigated by performing the photocatalytic degradation of phenol under radiation of UV light. The results showed that the efficiency of the rutile sample was relatively comparable with P25 Degussa. In particular, 71.8% destruction time of phenol was achieved in 120min for the P25 Degussa and 51.7% phenol was destroyed in 120min with the rutile sample. On the other hand, the Nigeria rutile showed a remarkable instability in its photocatalytic activity compared to the P25 when the reuseability study was done on the sample. Possible explanation could be due to the defects sites in the rutile sample and the presence of some trace elements that are acting as recombination center. This study also demonstrated that Nigeria rutile has some photocatalytic activity, which can be enhanced by the presence of some element like Iron and Copper.

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