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Synthesis and characterization of nanosized ZnO –α-Fe_2O_3, -ϒ- Fe_2O_3 composition from natural sphalerite

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ABSTRACT

Aim: This study was aimed to to assess the effect of chemical composition (altered via acid leaching and calcination) on its photocatalytic activity using MB as the model pollutant.

Method and Materials: Visible light active photocatalyst has been synthesized by leaching of a natural sphalerite (obtained from Abuni deposit, Nasarawa, Nigeria) using oxalic acid, drying of the obtained leachate, and subsequent calcination of the dried leachate to form ZnO –α-Fe_2O_3, -ϒ- Fe_2O_3 composite with trace amounts of MoO and MnO_2 . The natural spalerite and the ZnO –α-Fe_2O_3, -ϒ- Fe_2O_3 composite photocatalyst were characterized by X – ray fluorescence, X –ray difractiomery, and UV/Vis spectroscopy. The activity of the photocatalysts was tested by monitoring the kinetics of methylene blue degradation under visible light irradiation.

Results: The photocatalytic degradation of methylene blue dye follows pseudo first order kinetics on both natural sphalerite and the ZnO –α-Fe_2O_3, -ϒ- Fe_2O_3 composite. The experimental values of the apparent rate constant for the photocatalytic degradation of methylene blue on natural sphalerite and the ZnO –α-Fe_2O_3, -ϒ- Fe_2O_3 composite were 0.009min^{-1} and 0,012min^{-1} , respectively. Thus ZnO –α-Fe_2O_3, -ϒ- Fe_2O_3 composite obtained from natural sphalerite obtained from natural sphalerite can be used as a new cost effective and visible light – responsive photocatalyst.

Conclusion: It was concluded that calcined leachates are composed of ZnO α-Fe_2O_3,ϒ-Fe_2O_3 exhibited good photocatalytic property better than the leached residues and natural Sphalerite

CL90 was found to be the best catalyst for the photodegradation of MB dye under visible irradiation.

Keywords: Calcination, leaching, natural sphalerite and ZnO –α-Fe_2O_3, -ϒ- Fe_2O_3 composition.

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Introduction

Photocatalysis is the acceleration of a photochemical reaction in the presence of a catalyst. Photocatalysis can be compared with photosynthesis, in which chlorophyll captures sunlight and use it to convert water and carbon dioxide into oxygen and glucose. It creates strong oxidation agents (free radicals) that can breakdown any organic matter to carbon dioxide and water in the presence of photocatalyst, light and water. Both the technological and economic importance of photocatalysis has increased considerably over the past decade. Some of the major applications of photocatalysis are water and air purification, solar induced hydrogen production etc. (Stengl et al., 2007).

Extensive research continues to further develop this technology and to widen the spectrum of potential applications.

Recent research has reported that ZnO, which exhibits a direct band gap of about 3.2eV possesses higher photocatalytic efficiency than TiO_2. At the same time, the lower cost, biosafety and biocompatibility of ZnO indicate that it is suitable for large –scale water treatment operations. Therefore, different preparation methods have been used to synthesize ZnO and improve its photocatalytic activity. A significant draw back in the application of zinc sulphide and zinc oxide is their wide band gap of 3.6eV and 3.2eV respectively. Hence they cannot effectively absorb visible light. This has a consequent limitation for the use of zinc sulphide and zinc oxide as a solar light activated catalyst because about 50% of the solar spectrum is visible light, less than 5% is UV light (Alafara et al., 2010).

Natural Sphalerite (also Known as zinc blende)

is the principal primary ore of zinc (Aydogan et al., 2008). Sphalerite is a zinc ore mineral found in many sedimentary basins around the world. Its texture is described as a polycrystalline aggregate which results from the precipitation of metal-rich brines in a carbonate host rock. Sphalerite is mainly composed of ZnS with traces amount of Fe, S, Si, Mo etc. Zinc sulphide is a white to yellow colour powder or crystal. It is typically encountered in the more stable cubic form. Sphalerite composition varies widely depending on the origin, due to geochemical and environmental factors. Over 100 million tonnes of complex zinc sulphide minerals is available in Nigeria (Olubambi et al., 2008). Minor transition metals such as Fe, Pb, Cu, present in natural sphalerite can form polynary metal sulphide, which may lead to a visible light- driven photocatalytic activity (Bansal et al.,2009). In this work, natural Sphalerite obtained from Abuni, Nasarawa state, Nigeria has been investigated in order to assess the effect of chemical composition (altered via acid leaching and calcination) on its photocatalytic activity using MB as the model pollutant. The natural Sphalerite was characterized using XRF, XRD and surface area analysis. It was leached with organic acid (oxalic acid).

Materials and Methods

Natural Sphalerite sample from Abuni, Nassarawa State, Tap water, Distilled water, Oxalic acid AR (99.5%), Sodium chloride(99%), Sodium hydroxide (98%), Methylene blue (minimum assay 95%), Sieve (Mesh size 106µm), Spatula, Beakers (100-500ml), Measuring cylinders (50 – 250ml), Crucibles, Laboratory mortar and pestle, Glass rod stirrer, Thermometer (0^0C to 360^0C), Sample bottles (glass and plastic), Petri dishes, Halogen Lamp (500W, 200W, 100W, 60W), Pipette, Burette, Retort stand, Pocket pH Indicator

Instruments

Magnetic Stirrer, Electric furnace.(Nabertherm; 30 – 1400^{o}C), Electric Oven (NYC -101 ; 30 -400^{0}C, Nabertherm; 30-650^{o}C), Weighing Balances (Weda, T18; 0 – 100kg, Metler Toledo; AB204; 0 – 210g), Stop Watch, X-ray diffraction spectrometer (Shimadzu,6000), X-ray fluorescence spectrometer (Pananalytical,Minipal 4), Hot plate / magnetic Stirrer (Trieb, 73 -660 rpm).

Experimental Procedure

Raw Materials Collection: Natural Sphalerite also known as zinc blende which is the principal ore of zinc was collected from Abuni deposit of Nasarawa State Nigeria. The mineral was crushed to powder and a sieve of 106µm was used to sieve the sample to the required particle size < 106µm. The sample was analysed using XRF, XRD, UV – vis , and surface area analysis techniques.

Leaching of Natural Sphalerite Oxalic Acid

The X-ray fluorescence result of the Sphalerite under investigation showed that Sphalerite compose mainly of zinc sulphide with traces amount of Fe, S, Si, Cu, and Mo etc. Leaching experiments were performed in a 250 ml glass reactor equipped with a mechanical stirrer. The reactor was filled with 250 ml of 0.5M oxalic acid which was heated to 80^0C (Aydogan et al., 2005;). For every leaching experiment, the solution mixture was freshly prepared by dissolving 10g of the Sphalerite ore in 250Ml of oxalic acid at 80 °C. In all cases, the fraction of the Sphalerite dissolved was calculated from the initial difference in weight of the raw sample and the amount undissolved at various time intervals (10, 20, 40, and 90) mins, after oven-drying at about 60 °C. The residue obtained at various leaching times is denoted by. $S_{OX}10$, $S_{OX}20$, $S_{OX}30$, $S_{OX}40$, and $S_{OX}90$,corresponding to leaching times of 10, 20, 40, and 90 mins, respectively.

The filtrate was dried at room temperature, calcined at a temperature of 1000^0C for 4hours and denoted with CL10, CL20, CL40, and CL90.

Calcination

The leachates obtained of air dried leachate were dried and then ground to powder form; the samples were then calcined at 1000^{o}C for a constant time of 4hours

$ZnS + 2H_2C_2O_4 \rightarrow Zn(C_2O_4H)_2 + H_2S$ ……..…..1

$FeS + 2H_2C_2O_4 \rightarrow Fe(C_2O_4H)_2 + H_2S$ ……...2

The oxalate precursor was annealed at 1000^0 C for four hours to obtain ZnO powders. The decomposition of zinc oxalate dehydrate can be expressed as follows

$Zn(C_2O_4H)_2 \rightarrow ZnO + CO + CO_2$ ……..…..3

$Fe(C_2O_4H)_2 \rightarrow FeO + CO + CO_2$ ……..…..4

$FeO + O_2 \rightarrow Fe_2O_3$ ……..……..……5

Determination of Specific Surface Area of the Photocatalysts

The surface area for the natural Sphalerite was estimated according to Sears' method (Shawabkeh et al., 2004) by weighing 1.5g of natural Sphalerite, and acidifying with dilute hydrochloric acid to pH of 3 – 3.5. Then 30g of sodium chloride was added, with stirring, and the volume was brought to 150mL with distilled water. The solution was

titrated with 0.10N sodium hydroxide. The Volume, V, needed to raise the pH from 4 to 9 was recorded. The surface Area was estimated from the equation.

$S(m^2/g) = 32V - 25$ 6

Where S = Surface Area, V = the volume needed to raise the pH from 4 to 9

Photocatalytic Experiments

Methylene blue has been used as the model pollutant to test the activity of the developed photocatalysts. Photocatalytic reactions were conducted at room temperature (30 ± 2^0C) and atmospheric pressure. 0.1g of photocatalyst powder was dispersed by a magnetic stirrer in an aqueous solution of methylene blue (50mg/L) . The pH value of the suspension was 7. Before Illumination, the suspension was stirred for 1hour in the dark to reach the adsorption- desorption equilibrium. Irradiation was provided by a 500W, 200W, 100W, 60W high pressure tungsten halogen lamps (Philips) which was placed 16cm away from the reactor. After a certain period of irradiation, samples were withdrawn from the suspension at different time intervals and filtered to completely remove the catalyst particles. The obtained filtrates were then analyzed using UV – vis spectroscopy by recording variations in absorbance at wave length 663nm of (λmax of MB).The percentage of degradation of MB was calculated using the equation.

$$\text{Degradation } (\%) = (C_O - C_t)/C_O \quad \text{.....7}$$

Where C_O is the initial dye concentration and C_t is the dye concentration at certain reaction time t (min)

The effect of variation of initial dye concentration, catalyst loading and pH of the solution on rate of photocatalytic degradation was also studied. The pH of solution was adjusted to desired level by adding NaOH and HNO_3 before the addition of the photocatalyst.

The effect of initial MB concentration on the phocatalytic degradation was studied by varying the concentration of MB from 0.050 down to 0.00625 g/L at a constant catalyst loading of 1g/L via different time interval.

To study the effect of catalyst loading on the photo degradation of MB, experiments were carried out by varying the amount of ZnO from 0.5 – 2.00g/L at a fixed dye concentration of 50mg at different time interval.

To study the role of pH on photodegradation of MB, experiment was carried out at pH of 4, 7, and 10 corresponding to acidic, neutral and alkaline, at 0.050g/L MB concentration and 1g/Catalyst loading for different time intervals

Results and Discussion

The Pseudo-First Order Kinetic Plots of MB Degradation of Calcine Filtrate of Leached Sphalerite With oxalic Acid at *1000^0C At* Different Intensity

Since the focus is on the oxalic acid leached, the leachate was calcine at a temperature of 1000^0C for four hours. The results of the photocatalytic experiment carried out showed that the Pseudo-first order kinetic plots of MB degradation of leachate that was calcined gave a higher values of Kapp and R^2(with R^2 values higher than 0.9) which attested that photodegradation on MB obeys first order kinetics with leachate that was leached for 90min having the best compared to those of the oxalic acid residue leached samples.

XRD analysis

It was showed the XRD pattern of the calcined leachate at 1000^oC (CL90mins) sample. It was a composite of ZnO, -α-Fe_2O_3, -ϒ-Fe_2O_3 peaks appear at Bragg angles: 24.25^o, 33.30^o, $35.7\ 7^o$, 41.02^o, and 54.20^o for -α-Fe_2O_3, 23.68^o, 15.39^o, 26.05^o, 30.73^o, 35.77^o, for ,-ϒ-$Fe_2O_3$and 31.75^o, 34.42^o, 47.53^o, 56.58^o, 62.84^o and 67.91^o. In all the catalysts, the expected components (ZnO, -α-$Fe_2O_3$and -ϒ-Fe_2O_3) were characterized by sharp and symmetric peaks, indicating high crystallinity and large particle size sharp and intense peaks were obtained which shows that it was highly crystalline. The average crystallite size was found to be 27nm by applying Scherrer equation. Adebayo et al (2006) also advocated to similar findings.

Effects of Operating Parameters on Photocatalytic Activity of CL 90

Effect of initial Concentration:

The effect of initial MB concentration on the photocatalytic degradation was studies by varying the concentration of MB from 0.050 to 0.00625g/L, at a constant catalyst loading of 1g/L for 1hour. It was found that degradation percentage was strongly influenced by the initial dye concentration and increases from 61.16 to 75.27% with decrease in concentration of dye from 0.050 to 0.00625. The rate of degradation is related to the available catalyst surface for the generation of electron – hole pair, which in turn generates hydroxyl radicals. Aydogan et al (2005) also corroborated with the findings of this study.

Table 1: Derived Values *of (kapp and R²)* @1000⁰CCalcine

	500W		200W		100W		60W	
	K	**R²**	K	**R²**	k	**R²**	K	**R²**
CL90	0.0117	0.9953	0.0098	0.973	0.0097	0.9688	0.0095	0.958
CL40	0.0099	0.9811	0.0095	0.9605	0.0095	0.9581	0.0094	0.9424
CL20	0.0093	0.9725	0.0094	0.9579	0.0092	0.9458	0.0088	0.9374
CL10	0.0088	0.9633	0.0093	0.9463	0.0085	0.9376	0.0082	0.9235

In this case, the amount of catalyst was kept constant and thus number of hydroxyl radicals generated remains same, while dye concentration was decreased (Ayinla, 2012). Thus the number of hydroxyl radical which attack dye molecule increases and thus rate of degradation decreased.

The plot of Ln (C_O/C_t) vs. time at different initial concentration of the dye at fixed catalyst loading 1g/L Linear plots were observed showing R^2value higher than 0.9 which attested that photo degradation of MB obeys pseudo – first order kinetics. Plotting the pseudo- first order rate constant and corresponding R^2 values, it was seen that with decrease in dye concentration from 0.050 to 0.00625 mM, degradation rate constant increased. Baba and Adekola (2010) was also discussed hydrometallurgical processing of a Nigerian sphalerite in hydrochloric acid.

Effect of Photocatalyst Loading

It was observed that percentage of MB degraded after 1hour increased from (49.88 to 63.28) % with increase in catalyst loading from 0.5 to 2.00g/L. The plot of Ln (C_O/C_t) VS time for different amount of photocatalyst. The change of rate constant with change in catalyst loading was shown. It was seen that the rate constant increases with increase in catalyst loading. However two regions of increase are there. First region from 0.5 to 1.00g/L where slope of cure is very steep and second region from 1.01 – 2.00g/L where increase in rate constant was relatively less. The increase in rate constant with constant with increase in amount of photocatalyst is due to an increase in number of active sites on photocatalyst surface. This results in an increase in generation of hydroxyl radicals and thus leads to an increase in the number of dye molecules degraded. However, increase in catalyst dosage also increases the turbidity of solution, and results in the decrease in UV light penetration due to increase in light scattering. This factor comes into existence at higher catalyst dosage (above 1g/L) and thus results in relatively smaller increase in rate constant with increase in catalyst dosage. Baba and Adekola (2012) reported a study of dissolution kinetics of a Nigerian galena ore in hydrochloric acid.

Effect of pH

A plot of Ln (C_O/C_t) VS time for different pH ranges. It was shown that degradation rate increases with increase in pH, exhibiting maximum at alkaline range (8–9). Further increase in pH resulted in decrease in degradation rate. Maximum degradation rate was observed in alkaline region. Alkaline facilitate the formation of OH^- ions which are responsible for the generation of OH radicals, which leads to increase in rate of photodegradation. The decrease in degradation rate at pH 11 may be due to the dissolution of ZnO. So optimum pH for photodegradation of MB was 9. Ginstling and Brounshtein (1950) and Liu et al (2010) reported kinetics of chemical reactions.

Surface Area Analysis

As mentioned earlier surface area for the sample were determined using sears method. The specific surface areas of the photocatalysts are listed (Table 2). As expected, the catalysts exhibited different surface areas. From the table there is a decrease in the specific surface area of the photocatalyst as leaching time increases which might be as a result of aggregation of the particles.

Table 2: Surface Area of the Developed Photocatalyst

Photocatalyst Sample	Specific Surface Area (m^2/g)
NS	54
S10	46
S20	45
S40	42
S90	40
CL90	81
CL40	78
CL20	75
CL10	71

The higher surface area of the calcine leachate could be explained in terms of the presence of small surface iron oxide particles whose core is the zinc ferrite. Typical literature values of surface areas for ZnO, ranges from 11-85 (Ismail *et al.,* 2012). The relatively higher surface area as compared to related works (Valenzuela *et al.,* 2002) might have resulted from combined effect of higher

temperature of calcination and amount of surface iron added. Surface area is a strong function of the calcination temperature, particularly in the ranges of 800 – 1200 ^{0}C from the result there was a sharp increase in surface area with the leachate that was calcined. Souza et al (2007) also advocated the Bioleaching and chemical leaching as an integrated process.

Conclusion

It was concluded that calcined leachates are composed of ZnO α-Fe_2O_3, ϒ-Fe_2O_3 exhibited good photocatalytic property better than the leached residues and natural Sphalerite and CL90 was found to be the best catalyst for the photodegradation of MB dye under visible irradiation. Photocatalytic reactions obey pseudo – first order kinetics model. For CL90, the optimal conditions for photodegradation of MB were found to be 1g/L catalyst at a solution pH of 9.

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