Effect of Oxalic Acid Leaching on Photocatalytic Activity of Natural Sphalerite

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Abstract

Photocatalytic activity of the natural semiconducting sphalerite mineral from Abuni, Nasarawa State, Nigeria was studied for the degradation of methylene blue (MB). Natural Sphalerite as a visible – light responsive photocatalyst was characterized by X ray diffraction (XRD), X ray fluorescence (XRF) and surface area analysis. To further enhance the photocatalytic activity of natural Sphalerite, the chemical composition of the sphalerite was varied via leaching with oxalic acids. The photocatalytic activity of the Natural sphalerite, leached sphalerite and as well as the calcined leachates was tested for MB degradation under visible light illumination. The result shows a very high percentage of MB degradation by natural sphalerite after 60 minutes of light irradiation time. A composite of $\text{ZnO} - \alpha - \text{Fe}_2\text{O}_3 - \gamma - \text{Fe}_2\text{O}_3$ with traces amount of MoO_3 and MnO_2 was synthesized by calcination of the obtained leachates at 1000°C for 4 hours. The photocatalytic degradation of methylene blue dye follows pseudo first order kinetics.

1. Introduction

An ideal photocatalyst should be stable, inexpensive, non-toxic and, highly photoactive (Wagner et al., 2006). Several semiconducting metal oxides and sulphides are used as photocatalysts because their band gap energies are suitable for absorption of UV and visible light. The most studied photocatalysts are: TiO_2 , WO_3 , Fe_2O_3 , ZnO and ZnS (Huang et al., 2009). Recent research has reported that ZnO , which exhibits a direct band gap of about 3.2 eV 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 drawback in the application of zinc sulphide and zinc oxide is their wide band gap of 3.6 eV and 3.2 eV 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).

Zinc ores are widely distributed throughout the world. Zinc is the 24th most abundant element on earth crust (Ronald et al, 1993). 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 a mineral acid (hydrochloric acid) and organic acid (oxalic acid).

2. Experimental Section

2.1. Materials

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 106 μ m), Spatula, Beakers (100-500ml), Measuring cylinders (50 – 250ml), Crucibles, Laboratory mortar and pestle, Glass rod stirrer, Thermometer (0⁰C to 360⁰C), Sample bottles (glass and plastic), Petri dishes, Halogen Lamp (500W, 200W, 100W, 60W), Pipette, Burette, Retort stand, Pocket pH Indicator

2.2. Instruments

Magnetic Stirrer, Electric furnace.(Nabertherm; 30 – 1400⁰C), Electric Oven (NYC -101 ; 30 -400⁰C, Nabertherm; 30-650⁰C), 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).

2.3. Experimental Procedure

2.3.1 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 106 μ m was used to sieve the sample to the required particle size $\leq$ 106 μ m. The sample was analysed using XRF, XRD, UV – vis , and surface area analysis techniques.

2.3.2. 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 80⁰C (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 1000⁰C for 4hours and denoted with CL10, CL20, CL40, and CL90.

2.3.3. Calcination

The leachates obtained of air dried leachate were dried and then ground to powder form; the samples were then calcined at 1000⁰C for a constant time of 4hours

The oxalate precursor was annealed at 1000⁰ C for four hours to obtain ZnO powders. The decomposition of zinc oxalate dehydrate can be expressed as follows

2.3.4. 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, withstirring, 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.

$$S(\text{m}^2/\text{g}) = 32V - 25 \dots\dots\dots 6$$

3. Results And Discussion

3.1. XRF Analysis

Table 1: presents the summary of the XRF results obtained. As earlier observed from the XRD results of the natural Sphalerite, the XRF results further confirmed the presence of iron as an impurity; with concentration as high as 38.16 wt%in the raw mineral. Traces of other metals such as Al, Si, Ca, Sc, Mn, Cu, Mo, Ag, Cs, Eu, and Pb, were also detected by the XRF as shown in the results presented in the table.The effect of the acids that was used to leach the samples to vary its chemical composition was

observed from the XRF result of the leached samples, from the table as leaching time progress there is decrease in the percentage of iron, zinc, sulphur content which is as a result of the oxalic acids that was used for the leaching process.

Table 1: Elemental Composition of the Developed Photocatalyst

Samples	Raw	S10 _{ox}	S20 _{ox}	S40 _{ox}	S90 _{ox}
Al	0.5	0.3	0.4	0.2	0.1
Si	0.75	0.70	0.64	0.53	0.75
S	6.6	4.0	3.3	2.90	2.0
K	0.05	0.03	0.02	0.004	0.03
Ca	1.07	1.00	2.05	3.07	4.15
Mn	4.14	6.19	7.40	9.40	11.53
Fe	38.16	39.15	37.30	34.01	28.94
Ni	0.02	0.025	0.03	0.034	0.4
Cu	0.057	0.040	0.057	0.03	0.03
Zn	44.5	43.9	42.8	44.2	42.0
Mo	3.9	2.2	2.4	0.39	2.2
Ln	0.1	NA	NA	NA	NA
La	0.06	0.13	0.89	1.17	1.32
P	NA	NA	1.05	1.87	2.14
Ag	NA	2.31	1.7	2.13	1.9
Yb	0.09	NA	0.06	NA	NA
Cs	NA	NA	NA	NA	NA
Sc	NA	NA	NA	NA	NA
As	NA	NA	NA	NA	NA
Ge	NA	NA	NA	NA	NA
Cl	NA	NA	NA	NA	NA
Eu	NA	NA	NA	NA	NA
Fe/Zn	0.857	0.892	0.871	0.769	0.689
Total	100	100	100	100	100

3.2. XRD Analysis

Figure 1 shows the XRD pattern of the natural Sphalerite sample. As observed in the figure, sharp peaks were obtained which shows that it is highly crystalline. The domination of the ZnS (Sphalerite) peaks is an indication that the mineral is mainly zinc sulphide based mineral. However, the prominent peak of FeS (siderite) indicated that the mineral contained reasonable amount of impurity. The three strongest characteristic peaks at 2θ of 28.4° , 47.3° , 56.1° correspond to (6.823nm), (5.777nm), and (7.495nm) crystallite size calculated. The average crystallite size of the raw sphalerite calculated using scherrers equation is 6nm. In addition, XRD data revealed the presence of associated minerals such as α -SiO₂, FeS₂, FeTiO₃. The Sphalerite in the ore occurs as ferrous Sphalerite. The iron in the Sphalerite might be probably due to availability of iron in the hydrothermal fluid as the Sphalerite crystal growths. This process occurs by a reaction of the diffusing zinc ions transported in hydrothermal solutions with iron (Baba et al., 2003). While X-ray diffraction can be very accurate in quantifying major components within a mixture, it is not very good at detecting constituents that are present in minor amounts (less than about 2%) (Walenta et al., 2004)

3.3. Surface Area Analysis

As mentioned earlier surface area for the sample were determined using sears method. Table 2: shows the results obtained.

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 specific surface areas of the photocatalysts are listed in 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. 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 – 1200⁰C from the result there was a sharp increase in surface area with the leachate that was calcined.

3.4. Photocatalytic Degradation of MB using NS and Product of Its Leaching

The raw natural Sphalerite and product of its leaching (S10,S20,S40,S90) with hydrochloric and oxalic acids were tested for their photocatalytic activity under visible light with varying intensity of light (500W,200W,100W,60W) at different time interval. Before then adsorption in the dark was done for each of the samples and it was discovered that there was mild removal of MB via adsorption in the dark.

Table 3: Effect of Irradiation Time on the Percentage Degradation of MB at Various Lamp Powers

Irradiation Time	N/S	S10	S20	S40	S90	CL90	CL40	CL20	CL10
<u>500W</u>									
0	0	0	0	0	0	0	0	0	0
20	19	13	10	8	5	24	14	12	9
40	33	28	22	18	16	35	25	23	12
60	44	41	35	33	27	50	44	27	24
<u>200W</u>									
0	0	0	0	0	0	0	0	0	0
20	10	9	7	6	5	14	13	10	8
40	22	20	18	17	16	24	20	14	10
60	32	28	26	20	19	38	30	25	21
<u>100W</u>									
0	0	0	0	0	0	0	0	0	0
20	9	8	7	5	4	14	13	10	8
40	20	19	18	16	14	24	20	14	10
60	29	26	25	22	19	38	30	25	21
<u>60W</u>									
0	0	0	0	0	0	0	0	0	0
20	5	7	6	5	5	13	11	8	7
40	14	16	14	11	9	22	18	14	9
60	27	24	21	19	17	35	29	22	20

3.5. Effect of Irradiation Time on the Degradation of MB Using Oxalic Leached Samples

The different graphs showing the rate of degradation of MB using different composition of oxalic leached Sphalerite at different intensity

From the graphs the raw sample gave a better degradation of the dye compared to different composition of oxalic leached sphalerite at different intensity which shows that natural sphalerite can be used as a visible light responsive photocatalysts. It was equally observed from the graph that sphalerite leaching using oxalic acid is very mild.

The effect of photocatalyst activity of the leached samples of the oxalic leached samples gave a better degradation as shown from the graphs of their percentage degradation against irradiation time. The graph of their liner plots $-\ln(C/C_0)$ Vs time were observed (with R^2 values higher than 0.9) which attested that photo-degradation on MB obeys first order kinetics. It can equally be seen that photocatalytic activity is a function of the intensity as the intensity increases a better photocatalytic activity was observed making the 500W lamp the best intensity among every other lamp used for the experiment. Another observation is that as the time of leaching increases photocatalytic degradation decreases and degradation rate constant decreases thereby making the raw sample the best among all the samples. It was noticed that the leached samples from oxalic acid gave a better photo catalyst activity because of its mild nature and its gradual leaching process. When the solution of MB in the absence of catalyst was irradiated by sun light for different time interval, it was noticed that degradation was increasing as time of exposure increases. This continued until after 1hour reaction time, 30.4% degradation was observed.

3.6: The Pseudo-First Order Kinetic Plots of MB Degradation of Oxalic Acid Leached

The graphs showed a high activity for MB degradation with the different photocatalyst with the natural sphalerite having the best value of k_{app} and R^2

The kinetic of photocatalytic degradation of MB was calculated using the first order equation

$$\ln (C_0/C_t) = K_{app}t.....42$$

Where $K_{app}t$ is the pseudo – first order rate constant (min^{-1}),

C_0 =is initial concentration,

C_t = is the concentration of MB at time t (min).

Table 4: Derived Values of k_{app} and R^2 for Oxalic Leached Sample

	500W		200W		100W		60W	
	k_{app}	R^2	K_{app}	R^2	k_{app}	R^2	k_{app}	R^2
NS	0.01	0.9989	0.0083	0.9933	0.0078	0.9986	0.0075	0.9875
S10	0.0091	0.9926	0.0079	0.9989	0.0076	0.9903	0.0072	0.9943
S20	0.0089	0.9867	0.0076	0.9900	0.0074	0.9899	0.0071	0.9978
S40	0.0081	0.9582	0.0075	0.9642	0.0072	0.9707	0.0068	0.9791
S90	0.0078	0.9583	0.0073	0.9576	0.0069	0.9822	0.0067	0.9693

3.6. The Pseudo-First Order Kinetic Plots of MB Degradation of Dalcine Filtrate of Leached Sphalerite With oxalic Acid at 1000°C At Different Intensity

Since the focus is on the oxalic acid leached, the leachate was calcine at a temperature of 1000°C for four hours. The result 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

Table 5: Derived Values of (*kapp and R^2*) @ 1000°C Calcine

	500W		200W		100W		60W	
	K	R^2	K	R^2	k	R^2	K	R^2
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

3.8. UV/ Vis Analysis

The absorption edge of the pure Sphalerite sample is at 365nm, corresponding to the band gap of 3.4eV. This implies that the pure Sphalerite sample could not utilize visible light to generate electron – hole pairs (Yan et al., 2008). However, the absorption spectra of the natural Sphalerite sample and calcine leachate shows both a steep absorption edge at about 450nm and a broad absorption shoulder band in the vicinity of 400–600 nm. The absorption spectra of natural Sphalerite based photocatalyst suggest they can serve as a visible light – responsive photocatalytic reaction.

4. Conclusion

1. A series of photocatalyst were prepared by treating raw Sphalerite with oxalic.
2. The prepared photocatalysts were characterized by XRF, XRD, UV-Vis spectroscopic techniques.
3. The leached samples (residues) exhibit lower photocatalytic activity than the natural Sphalerite.
4. The photocatalytic reactions obey pseudo – first order kinetics model.
5. The calcine leachate at 1000°C of the leached samples gave a better photocatalytic activity compared to the residue
6. Pseudo-first order kinetic plots for MB photodegradation showed a good regression because of the mild nature of oxalic acid during reaction.

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Figures

Figure 1

XRD pattern for the natural Sphalerite

Figure 2

rate of degradation of MB using different composition of oxalic leached Sphalerite using 500W halogen lamp
 rate of degradation of MB using different composition of oxalic leached Sphalerite using 200W halogen lamp
 rate of degradation of MB using different composition of oxalic leached Sphalerite using 100W halogen lamp
 rate of degradation of MB using different composition of oxalic leached Sphalerite using 60W halogen lamp

Figure 3

Pseudo-first order kinetic plots for MB photodegradation using 500W halogen lamp
Pseudo-first order kinetic plots for MB photodegradation using 200W halogen lamp
Pseudo-first order kinetic plots for MB photodegradation using 100W halogen lamp
Pseudo-first order kinetic plots for MB photodegradation using 60W halogen lamp

Figure 4

Pseudo-first order kinetic plots for MB photodegradation using 500W halogen lamp
Pseudo-first order kinetic plots for MB photodegradation using 200W halogen lamp
Pseudo-first order kinetic plots for MB photodegradation using 100W halogen lamp
Pseudo-first order kinetic plots for MB photodegradation using 60W halogen lamp

Figure 5

UV/ VIS Absorption Spectra of the developed Photocatalyst