PHOTOCATALYTIC DEGRADATION OF METHYL ORANGE BY IRON OXIDE (FE_2O_3) PARTICLE EXTRACTED FROM HEMATITE ORE

[1]MYAT LAY NWE, [2]SU HLAING PHYO, [3]KHINMYATHAN SEIN

[1]Associate Professor, Engineering Chemistry Department, Technological University (Kyaing Tong)
[2,3]Assistant Lecturer, Department of Chemistry, TaungGyi University

Abstract - In this research, Fe_2O_3 particle has been extracted from the iron ore by using simple acid digestion method. The extraction was performed at temperature 100 $\pm$ 5ºC. The hematite ore was collected from Kya-dwin-ye mine, PyinOoLwin Township, Mandalay Region in Myanmar. Mineralogical and chemical compositions of the raw material were investigated. Fe_2O_3 (68.20 %) was extracted from the raw material. The raw and extracted samples were characterized by using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) and Energy -dispersive X-ray fluorescence (EDXRF) techniques. The photocatalytic activities of extracted iron oxide were studied based on the degradation of methyl orange. Several experiments were used to optimize the experimental parameters. The effect of catalyst loading and reaction time on photodegradation rate was also investigated. It was inferred from control experiments that presence of both Fe_2O_3 and UV light is necessary for photodegradation.

Keywords - Photocatalytic Degradation, Hematite Ore, Iron (III) Oxide, UV Light

I. INTRODUCTION

Photocatalytic reactions have been widely used for environmental pollution control under mild conditions. Among the semiconductor photocatalysts, iron (III) oxide has been the foremost established material for degradation of organic pollutants [1][2]. The wastewater from textile industries with high aromaticity and low biodegradability are major environmental pollutants [3][4]. In printing, textile, paper and pharmaceutical industries, a large quantity of organic dyes are used. During these dying processes, a significant fraction of these dyes are lost and released into our environment especially water resources. In many situations, dye molecules are non-biodegradable, so it is important to mineralize them in aqueous solutions. The photocatalytic degradation of organic pollutants based on inorganic semiconductors has attracted considerable attention because they can solve the environmental pollution problems [5][6][7]. Nowadays, the decomposition of organic pollutants using various nano materials in the presence of sunlight or UV radiation has been a major topic for environmental problem. TiO_2 is a wideband gap semiconductor which is one of the most effective photocatalysts for the degradation of organic and inorganic pollutants. And that can degrade other toxic materials under ultraviolet (UV) light irradiation [8]. Nanocomposites can improve the visible light photocatalytic activities of wide band gap semiconductors. Although several types of visible light-active photocatalysts have been obtained, it is important to explore new types of photocatalysts under visible light irradiation [9]. Iron oxide (α-Fe_2O_3, hematite) is a promising material for photocatalytic applications owing to its narrow band gap of approximately 2.2eV, chemical stability and nontoxicity, which absorbs light up to 600 nm, collects up to 40% of the solar spectrum energy, and might be one of the cheapest semiconductor materials [10]. When the electron from α-Fe_2O_3 absorbs the visible light, these electrons are excited from the valance band to the conduction band. These excited electrons and the corresponding holes can activate the surrounding chemical species and promote the chemical reactions [10]. The band positions will move and higher redox potentials of the free electrons and holes will be achieved in this regime, which in turn enhance the charge-transfer rates in the materials. The increase in the charge transfer rates reduces the direct recombination rate of the charge carriers drastically, which may explain why smaller size particles show higher photocatalytic performance. Therefore, low-dimensional nanoscale materials may improve the photocatalytic properties for the degradation of organic pollutants owing to their special structure, morphology, size and spatial arrangement, and quantum confinement [11]. In this study, the Fe_2O_3 was extracted from Hematite, iron ore by the acid digestion process. The photocatalytic activity of the Fe_2O_3 was evaluated by degradation of methyl orange in aqueous solution using 200 WHg-Xelamp.

II. MATERIAL AND METHODS

A. Sampling

The Hematite iron ore was collected from Kya-dwin ye mine, PyinOoLwin Township, Mandalay Region. The sample was washed with tap water to remove unwanted material on the ore surface. After that the sample was dried in the good ventilating place till no moisture content in the ore material. The ore sample was grounded with motor and pestle and then sieved

with 10 mm mesh size sieve. The sample size $\geq$ 10 mm was collected and stored in brown polyethylene bag.

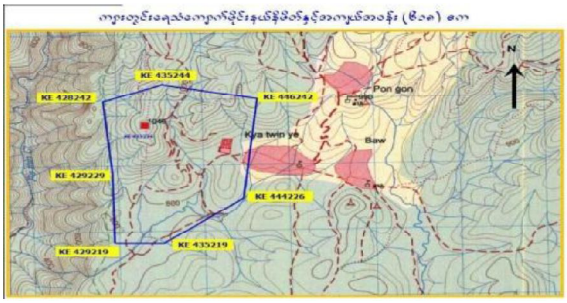


Figure (1) Map for Hematite Ore collecting area

B. Physicochemical Properties of Hematite Ore

The physicochemical properties such as moisture content, density and loss of ignition of hematite orepowder were determined. Moisture content of the sample was determined by oven drying method [12]. The density of the sample was measured by using density bottle (Web-1). In addition, loss of ignition of iron ore was also determined by using gravimetric method [13].Some physical properties of hematite ore such as hardness, color, and Luster/transparency were determined at Geology Department, University of Mandalay. The hardness of the hematite ore sample was determined by using a glass as a standard. The color of the hematite ore sample was measured by using streak plate. The hematite ore sample was rubbed over the streak plate (a piece of unglazed porcelain). Then, the color of the hematite ore sample on the streak plate was compared with the color of the sand the standard tungsten on it. The Luster of the hematite ore sample was determined by using microscope. Firstly, the hematite ore sample was placed under the eye piece of the microscope. Then, the luster of the hematite ore sample was watched using the natural light.

C. Characterization of Hematite Ore

The elemental analysis of the hematite ore sample powder was determined by EDXRF analyzer (EDX-700 spectrometer). It was measured at University Research Center, Taunggyi University. The crystalline nature of the sample was determined by X-ray diffractometer (XRD) at University of Research Center, West Yangon University. The FT IR spectrum of Hematite ore was measured at Sarkurai Lab, Division of Applied Chemistry, Graduate School of Engineering, Osaka University, Japan.

D. Extraction of Iron (III) Oxide

The dried Hematite powder was placed into the porcelain basin and mixed with 2 M sulphuric acid. Then, the basin was heated at 100℃ . This solution was heated until the insoluble residues were separated out. The remaining residue was washed with 100 ml (2 M) sodium hydroxide and heated again at 100℃ for 1 hr. In addition, it was also washed with distilled water three times. The brown precipitates was heated gently at first, and then ignited at 700℃ in the muffle furnace until the constant weight was attained. The dried powder was identified by SEM (JEOL-JSM-5610, Japan), EDXRF (EDX-700 spectrometer) and XRD techniques. All measurements were done at University of Research Center, West Yangon University, Myanmar.

E. Photocatalysis Activity

The photocatalytic activity of the Fe_2O_3 was tested for the removal of methyl orange under irradiation of UV light for 10-70 min. The photocatalyst (1-5mg) was dispersed in a methyl orange aqueous solution (110 M, 50 mL) and stirred for 1 h in the dark to achieve adsorption–desorption equilibrium. The photocatalytic reaction was then conducted under irradiation of a 200 WHg-Xe lamp (Hamamatsu, light intensity of 8mW/cm^2 at 365 nm) for 10-70 min at room temperature. During the full irradiation process, the suspension was stirred continuously. At a given time interval 3 mL of the suspension was removed and centrifuged immediately to eliminate the solid particles. The color intensity of methyl orange was determined using UV spectrometer, which was monitored at a wavelength of 462 nm. The degradation percentage of methyl orange was determined following Equation.

$$\%\ degradation = \frac{C_0 - C_e}{C_e}\ x\ 100$$

Where C_o is the initial concentration of methyl orange after reaching adsorption–desorption equilibrium under dark conditions, while C_e is the remaining concentration of methyl orange.

III. RESULTS AND DISCUSSION

The density, moisture content and loss on ignition of the hematite ore was investigated by using respective methods. The density of the hematite ore sample is (5.24 g/cm^3). The hematite ore indicates the low moisture content. Its moisture content is 0.5%. The loss of ignition of the hematite ore was found to be 3.00%. It may be due to the volatilization of water and organic matter. It may also be the leave of carbon dioxide. The luster of hematite is metallic, submetallic and earthy. Its streak is red to reddish brown. Hematite ore occurs in many forms that include micaceous, massive, crystalline, fibrous, and others. Hematite is colored black to steel or silver-grey, brown to reddish brown, or red. It is mined as the main ore of iron. Hematite is harder than pure iron, but much more brittle. Its hardness is 5-6 and transparency is opaque. The feature of Hematite sample is irregular. Hematite ore was characterized by means of FTIR, XRD and EDXRF techniques. The most characteristic IR absorption bands of hematite are present in the low

frequency region (<600 cm^{-1}). Infrared vibrations of hematite formed from the Si-free ferrihydrite were observed by two intense bands at 471 and 548 cm^{-1}together with bands at 397, and 337 cm^{-1}[15][16]. Hematite is also present and identified by the presence of peaks at1036.55cm^{-1} (Fe–O–Fe), 1010.52 cm^{-1} (Fe–O–Al), 892.88 cm^{-1}, and 801.27 cm^{-1} (Fe–O–H) (Fig. 2). The IR bands at 543.82cm^{-1} (Fe–O–Al) and 474.403 cm^{-1} (Fe–O) are common in the hematite. When the diffractogram of the investigated sample was compared with the reference diffractogram, these two are nearly the same as like as the high Intensity and well resolution peaks. It means that the sample is the hematite ore. In addition, the XRD patterns show that the crystal structure of hematite ore sample is hexagonal structure. From the semi-quantitative results of EDXRF data, the largest constituents of hematite ore sample was found to be iron (61.00%), the second is manganese (1.09%) and the other constituents are Silicon, Aluminium, Magnesium, Copper, Titanium, Calcium, Phosphorus and Chromium. The extracted iron (III) oxide nanoparticles were characterized by using XRD, EDXRF and SEM analysis. The XRD diffractogram expresses the shape of the extracted iron (III) oxide is orthorhombic. All the observed peaks can be indexed in agreement with the expected orthorhombic structure of Fe_2O_3. The peaks appearing at 24.16°, 33.12°, 49.47°, 54.08°and 57.42°can be attributed to the 012, 104,024, 116 and 018 crystalline structures corresponding to Fe_2O_3 particles. The narrow sharp peaks indicate that the hematite products are highly crystalline, implying that the high purity of extracted hematite product is obtained by using this acid digestion method. The surface morphologies of the prepared samples were studied using Scanning Electron Microscope. All the particles are orthorhombic in shape. The average particle diameter of Fe_2O_3 was found to be various in sizes. According to the EDXRF results, 68.204 % of iron (III) oxide was extracted from the hematite ore by using 2M sulphuric acid. To evaluate the photocatalytic activity of iron (III) oxide, the optical property changes of a methyl orange aqueous solution in the presence of porous Fe_2O_3 particle under simulated solar irradiation for a constant time were measured. Without a catalyst, only a slow decrease in the concentration of MO was detected under the simulated solar irradiation. By monitoring the MO absorption peak at 462 nm, plots of the degradation ratio vs. reaction time were obtained in the absence/presence of a catalyst under identical conditions. The time and dosage dependent degradation spectra of the MO solution containing the Fe_2O_3 catalyst during the irradiation were shown in Figure (9). On the other hand, when different amount of Fe_2O_3 particles were added to the reaction system, the degradation of MO could be accelerated obviously. It was found the degradation percent is decreasing when the catalyst dosage is increased. After 70 min, the degrees of degrading were found to be 33.36 % (5 mg), 54.96% (4mg), 74.82% (3mg), 90.29% (2mg), and 89.25% (1mg). These experiments point out only a small amount of iron oxide need for photo degradation reaction. It was found that the color of iron oxide disturbed for determination of color of MO after degradation reaction when large amount of iron oxide is used. The gradually decreasing absorption peak intensities indicate that most of the MO had been degraded. The degrading of the solution can be due to the destruction of the dye chromogen.

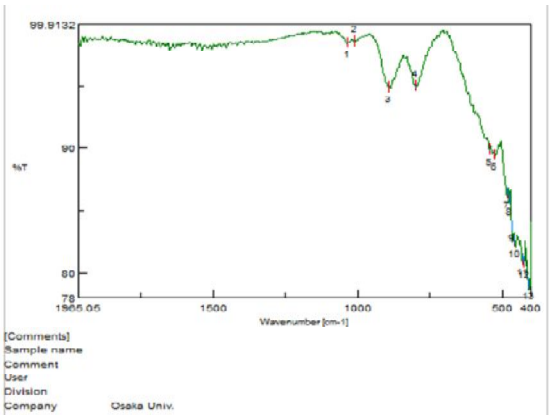


Figure (2) FT IR spectrum of Hematite Ore

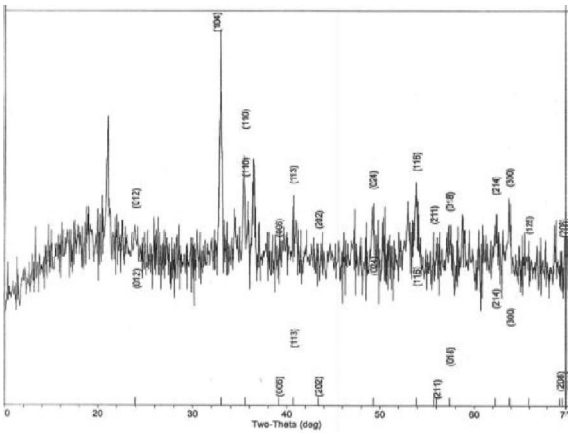


Figure (3) XRD pattern of Hematite ore

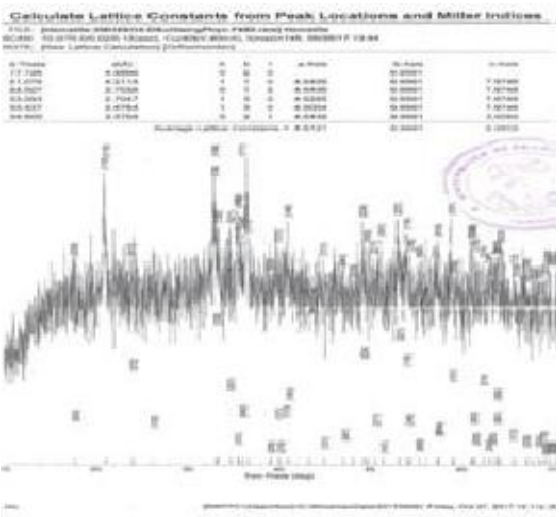


Figure (4) XRD pattern of Iron (III) oxide

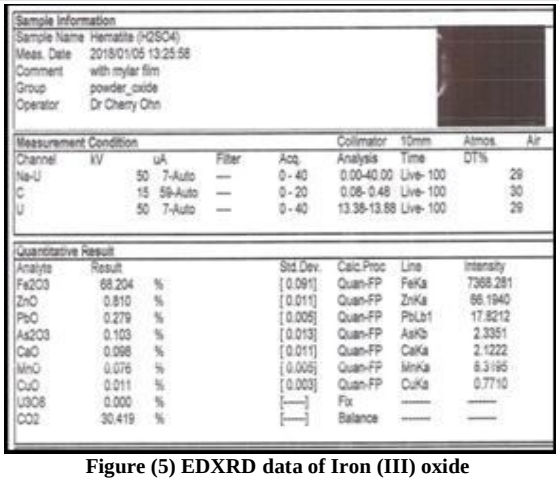


Figure (5) EDXRD data of Iron (III) oxide

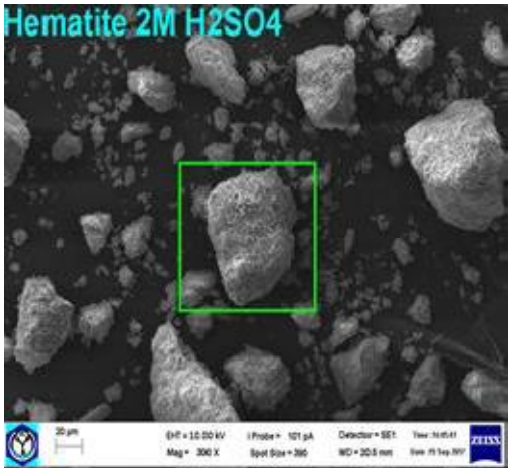


Figure (6) SEM image of Iron (III) oxide

Reaction time (min)	% Degradation
0	0
10	0.76
20	1.45
30	1.62
40	2.22
50	2.65
60	2.66
70	2.74

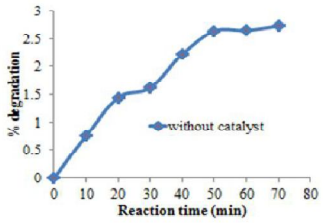


Figure (7) UV–Vis spectroscopic changes of the MO solutions without □-Fe_2O_3particles with variationirradiation time

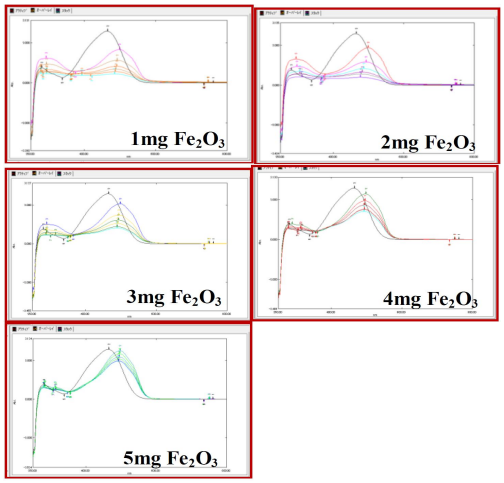


Figure (8) UV–Vis spectroscopic changes of the MO solutions with □-Fe_2O_3particles with variationirradiation time

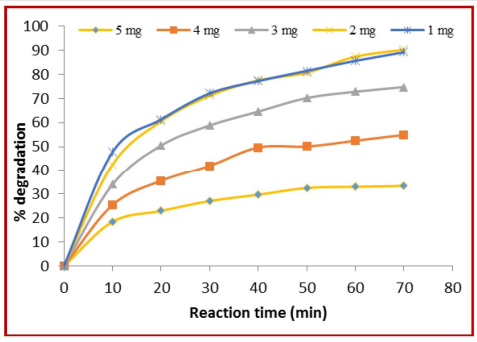


Figure (9) % degradation Vs reaction time

IV. CONCLUSION

Photocatalysis has been attracting much research interest because of its wide applications in environmental remediation especially to treat organic dye contaminating waste water. There are many materials that are found to show good photocatalytic activity in the presence of ultraviolet (UV). Fe_2O_3 particle was successfully extracted from Hematite by acid digestion method. The extracted iron (III) oxide was used as photocatalysts for the removal of methyl orange dye from its aqueous solution. The photocatalytic process was found to be dependent on dosage of the photocatalyst and the irradiation time. Fe_2O_3 can be used for effective removal of dyes from textile and paper effluents.

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