



## Photocatalytic Degradation of Phenol using Nanosized Hematite under Visible Light Irradiation

\*<sup>1</sup>Abdulhamid Hamza, <sup>1</sup>Johnson Tunde Fatuase and <sup>2</sup>Alhaji Saleh Zanna

<sup>1</sup>Department of Chemical Engineering, Ahmadu Bello University Zaria, Nigeria.

<sup>2</sup>National Research Institute for Chemical Technology Zaria, Nigeria.

### ARTICLE INFO

#### Keywords:

Photocatalyst;  
Phenol;  
 $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>;  
Dosage;  
pH;  
Kinetics

#### Correspondence author:

#### e-mail:

abbamid@gmail.com

Phone: +2347051858728

### ABSTRACT

Photocatalysis is one of the most widely researched advanced oxidation processes for wastewater treatment. Phenol and its derivatives are found in the effluents of various industries. This work was aimed at investigating the effects of photocatalyst dosage, pH and initial concentration on the photocatalytic degradation of phenol using nanosized hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) synthesized via co-precipitation route. 94 % degradation of phenol was achieved in an irradiation time period of six hours. Photocatalytic degradation of phenol using  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> follows pseudo-first order kinetics. Highest photocatalytic degradation of phenol was observed in the acidic medium. The optimum dosage of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was found to be 1.5 gL<sup>-1</sup> under the experimental conditions employed.

### Introduction

Phenol is one of the most widely used chemicals produced at a rate of about 6 million tons per year worldwide. Phenol is used as a disinfectant, a solvent, a peptizing agent in glues, a blocking agent for blocked isocyanate monomers, and a reagent in chemical analysis (Ahmaruzzaman, 2008). Furthermore, phenol is a precursor to aspirin, xlenols, alkylphenols, chlorophenols, aniline and various polymeric materials such as phenol-formaldehyde resins, epoxy-resins, caprolactam, nylons, polyester polyols etc. Several chemicals produced from phenol serve as the raw materials for the production of surfactants, fertilizers, explosives, paints, textiles, antioxidants, etc. Therefore, phenol and its derivatives are found in the effluents of various

industries such as petrochemical, coal, pharmaceutical, wood, paint, pulp and paper industries (Busca *et al.*, 2008; Chiou *et al.*, 2008; Ahmaruzzaman, 2008). Phenol is easily absorbed through human skin causing skin and eye burns upon contact. Excessive exposure to phenol may cause convulsions, cyanosis and even death (Ahmaruzzaman, 2008; Pardeshi and Patil, 2008)).

Recently, there has been a lot of research interest in advanced oxidation processes (AOPs) for wastewater treatment (Oller *et al.*, 2011). AOPs are based on the generation of highly reactive oxidants for mineralizing various water pollutants and destruction of microorganisms present in water (Fujishima and Tryk, 2007; Konstantinou and Albanis, 2004). Photocatalysis is the most widely researched AOP for wastewater treatment.

Photocatalysis can achieve complete destruction of water pollutants and pathogens without generation of secondary pollutants under ambient temperature and pressure (Fujishima and Tryk, 2007). The photocatalytic activities of various semiconducting materials such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{CdS}$ ,  $\text{WO}_3$ ,  $\text{ZnS}$ , etc, and their composites to degrade a wide variety of water pollutants have been investigated by many researchers (Fujishima and Tryk, 2007).  $\text{TiO}_2$  is the most widely used photocatalyst due to its good photocatalytic activity, non-toxicity and low cost. However, the large band gap (3.2eV) of  $\text{TiO}_2$  makes it effective only in the presence of UV light with wavelengths shorter than 380nm, covering about 5% of the solar spectrum (Casbeer *et al.*, 2012).

Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) as a visible light active photocatalyst with a bandgap of about 2.2 eV has been applied for the photocatalytic degradation of some phenolic compounds (Zhang *et al.*, 2012; Bakardjieva *et al.*, 2007; Valenzuela *et al.*, 2002). Bakardjieva *et al.* (2007) synthesized iron oxides by calcination of ferrihydrite at different temperatures (200, 500, 800 and 1000 °C) and found  $\alpha\text{-Fe}_2\text{O}_3$  that was calcined at 1000 °C to be the best photocatalyst for the degradation of 4-chlorophenol. Valenzuela *et al.* (2002) reported that  $\alpha\text{-Fe}_2\text{O}_3$  is less active than  $\text{TiO}_2$ ,  $\text{ZnFe}_2\text{O}_4$  and  $\text{ZnO}$  for the photocatalytic degradation of phenol under ultraviolet light irradiation. To the best of our knowledge, the published literature reports on the photocatalytic degradation of phenol over  $\alpha\text{-Fe}_2\text{O}_3$  were aimed at testing the photocatalytic activity of  $\alpha\text{-Fe}_2\text{O}_3$  synthesized via different routes under ultraviolet light irradiation (Zhang *et al.*, 2012; Bakardjieva *et al.*, 2007; Valenzuela *et al.*, 2002). This is usually done by monitoring the effect of irradiation time on the photocatalytic degradation of phenol. The effects of various parameters on the efficiency of photocatalytic

degradation of phenol over  $\alpha\text{-Fe}_2\text{O}_3$  under visible light irradiation have not been reported in the literature. Therefore, the aim of this work was to investigate the effects of photocatalyst dosage, initial concentration of phenol and pH on the kinetics of phenol degradation using nanosized  $\alpha\text{-Fe}_2\text{O}_3$  photocatalyst synthesized via co-precipitation route.

## Materials and Methods

38.45g of iron nitrate was dissolved in 250ml of deionized water. 21ml of ammonium hydroxide was then added. The mixture was stirred at 50°C at a pH of 8.0 for three hours. The formed precipitate was aged for 24 hours, washed with deionized water and then filtered under vacuum. The product was dried overnight in an oven at 110°C. The dried product was further calcined in a furnace at 1000°C for four hours to yield  $\alpha\text{-Fe}_2\text{O}_3$ . Analytical grade reagents were used for the synthesis. Powder X-ray diffraction pattern of the synthesized  $\alpha\text{-Fe}_2\text{O}_3$  was recorded using an X-ray diffractometer (Shimadzu, model 6000) employing Cu K $\alpha$  radiation source ( $\lambda=0.154\text{nm}$ ). The specific surface area of the photocatalyst was obtained using a modified BET method which is based on the adsorption of water molecules on the surface of solid samples (Adefila *et al.*, 2003).

100ml of phenol solution of a given concentration (0.5g/L to 2.0g/L) was mixed with a fixed amount of the photocatalyst in a photoreactor and magnetically stirred for two hours in the dark in order to establish adsorption-desorption equilibrium of phenol on the photocatalyst. Thereafter, the mixture was exposed to visible light irradiation provided by a 500W halogen lamp under continuous stirring at room temperature ( $28\pm 2^\circ\text{C}$ ) for the required period of time. Periodically, samples were taken for analysis after separating the photocatalyst particles.

These samples were analyzed for residual concentration of phenol using a UV/Vis spectrophotometer (Jenway 6405). Experiments were repeated in duplicate for getting the reproducibility of the results. The percentage degradation of phenol was calculated using eq. (1):

$$\text{Percentage degradation} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

where  $C_0$  and  $C_t$  are the initial concentration of phenol and the concentration of phenol after irradiation time ( $t$ ) respectively.

### Results and Discussion

Displayed in Figure 1 is the XRD pattern of the synthesized  $\alpha\text{-Fe}_2\text{O}_3$ . Diffraction peaks

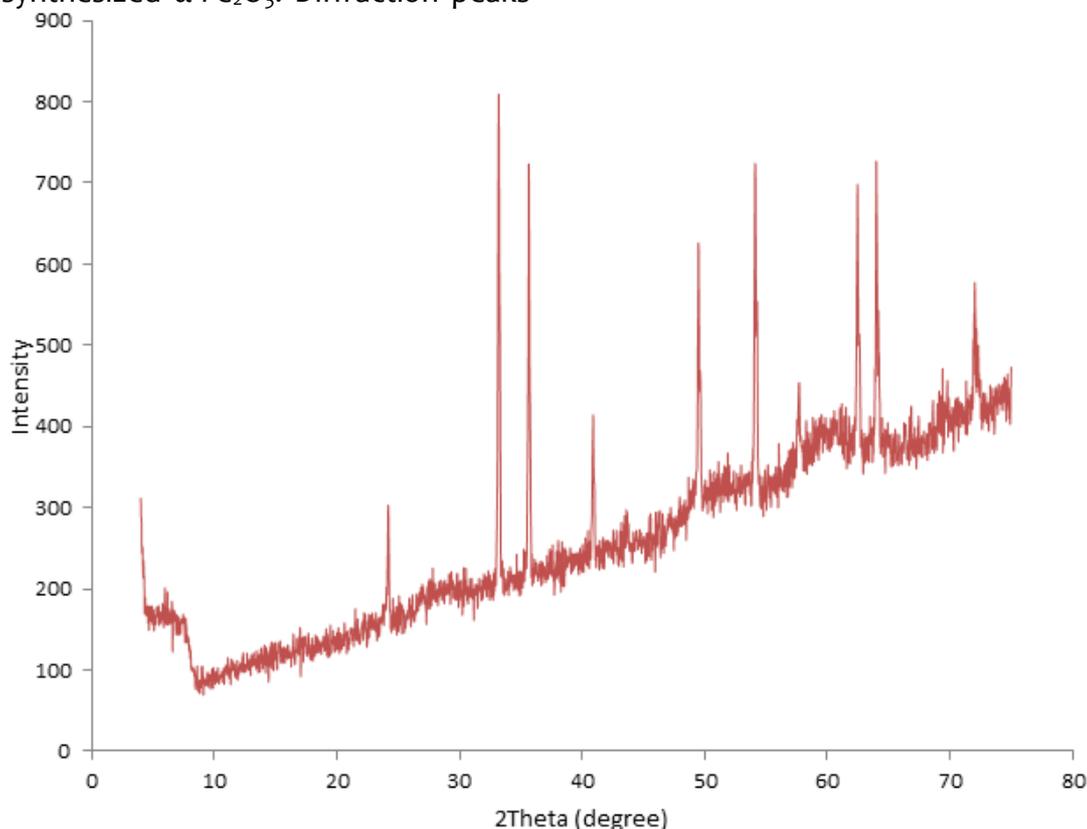


Figure 1. XRD pattern of the synthesized hematite

Control experiment was performed by mixing 0.1g of  $\alpha\text{-Fe}_2\text{O}_3$  with phenol (100ml, 0.5g/L) in the dark. The results show that six hours of adsorption of phenol in the dark over the surface of  $\alpha\text{-Fe}_2\text{O}_3$  lead to the removal of only 12% of phenol. The effect of irradiation time on the percentage

were observed at  $2\theta = 24.3^\circ, 33.3^\circ, 35.7^\circ, 40.9^\circ, 49.5^\circ, 54.1^\circ, 62.5^\circ$  and  $64.0^\circ$ . The peaks are due to hematite (JCPDS file No 33-0664). The crystallite size of  $\alpha\text{-Fe}_2\text{O}_3$  was determined using the Debye–Scherrer equation (eq. 2).

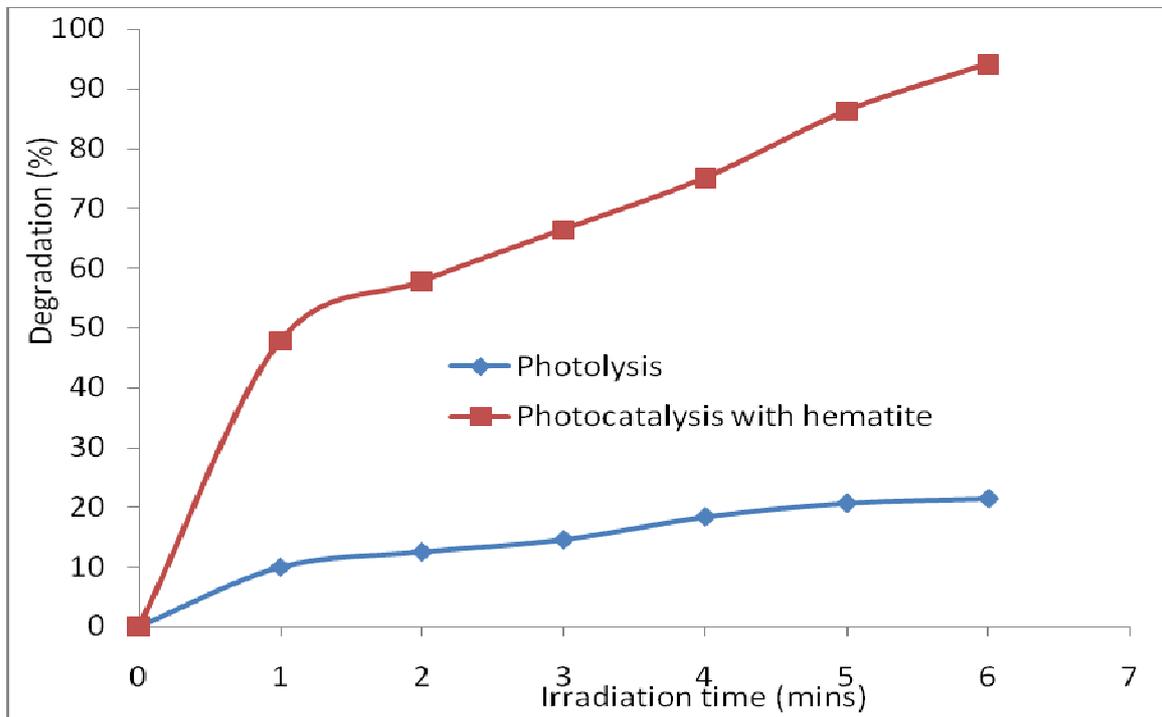
$$\tau = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where  $\tau$  is the particle size,  $\lambda$  is the wavelength of the X-ray radiation (Cu  $K\alpha = 0.1542$  nm),  $k$  is the shape factor ( $k = 0.94$ ),  $\beta$  is the full line width at half maximum height and  $\theta$  is the angular position of the peak maximum. The estimated crystallite size of  $\alpha\text{-Fe}_2\text{O}_3$  was 58.2nm. The measured specific surface area of  $\alpha\text{-Fe}_2\text{O}_3$  was  $162.3\text{m}^2/\text{g}$ .

degradation of phenol (100ml, 0.5g/L) over 0.1g of  $\alpha\text{-Fe}_2\text{O}_3$  as well as in the absence of photocatalyst is depicted in Figure 2. The percentage degradation of phenol increases with increase in the irradiation time, and reached 94 % within six hours.

In the absence of photocatalyst, the percentage degradation of phenol was only 21% in an irradiation time period of six hours. This result indicates that the

synthesized  $\alpha\text{-Fe}_2\text{O}_3$  has a good photocatalytic activity for the degradation of phenol.



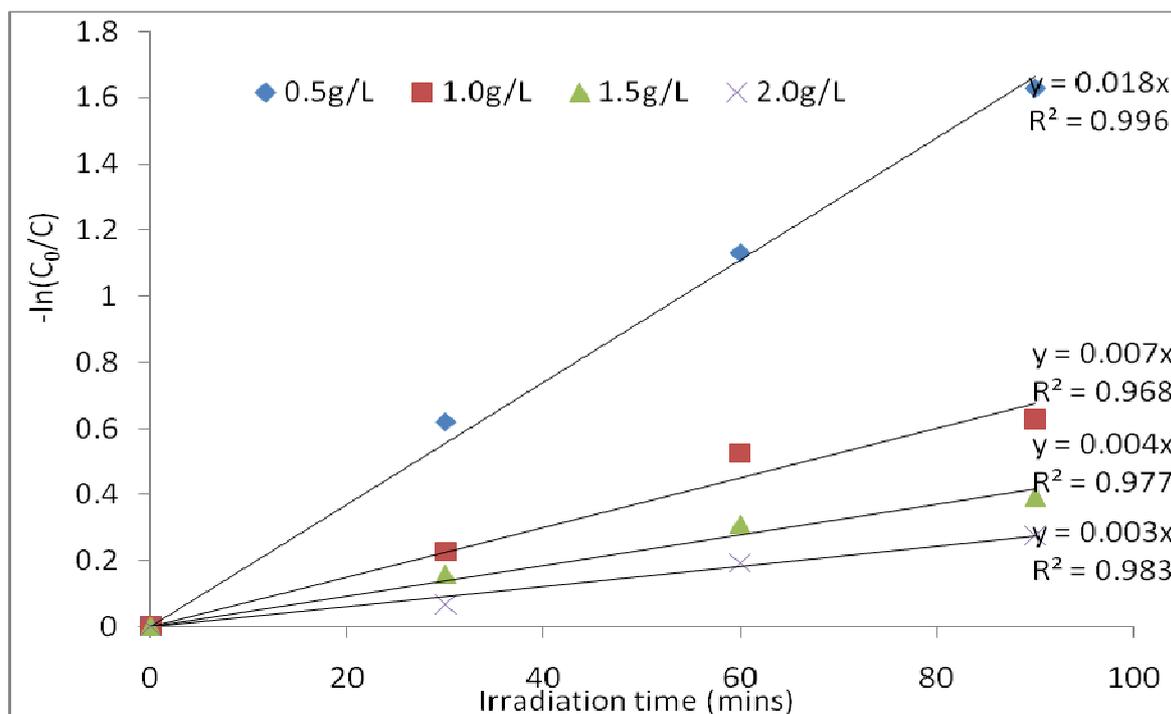
**Figure 2.** Effect of irradiation time on the percentage degradation of phenol via photolysis and photocatalysis using the synthesized hematite

Heterogeneous photocatalysis involves two major steps: adsorption of the reactants on the photocatalyst surface followed by photooxidation or photoreduction of the adsorbed reactants with the photogenerated reactive intermediates (Konstantinou and Albanis, 2004). Unlike adsorption which merely concentrates phenol on the surface of the adsorbent, photooxidation of phenol generates intermediates (such as hydroquinone, catechol and benzoquinone) which are subsequently photooxidized

(mineralized) to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Chiou *et al.*, 2008; Valenzuela *et al.*, 2012). The pseudo first order kinetics equation (3) is often used to describe the kinetics of photocatalytic processes (Chiou *et al.*, 2008).

$$-\ln \frac{C_0}{C} = k_{app} t \quad (3)$$

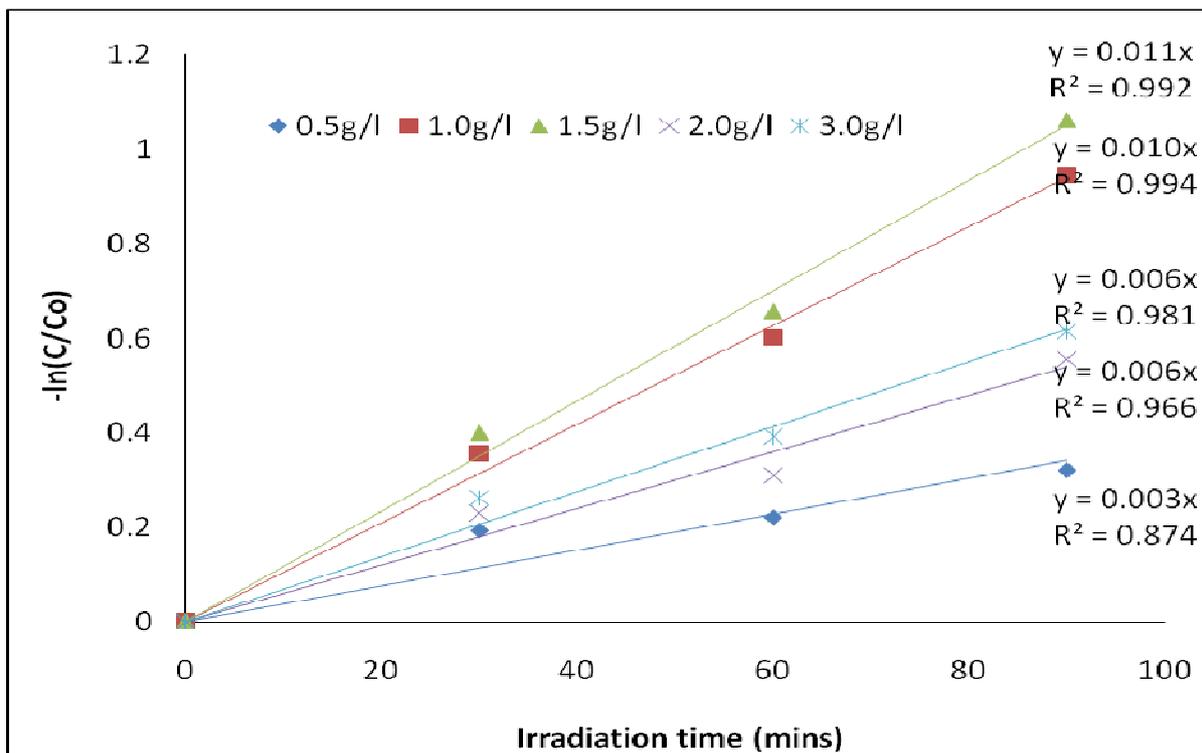
where  $k_{app}$  is the apparent rate constant of a photocatalytic process which is often used as a measure of the effectiveness of a given photocatalytic process.



**Figure 3.** Pseudo first order kinetic plot for the photocatalytic degradation of phenol using hematite at various initial concentrations of phenol

A series of photocatalytic experiments were carried out with different initial concentrations of phenol ranging from 0.5g/L to 2.0g/L with 1g/L of  $\alpha\text{-Fe}_2\text{O}_3$ . Figure 3 shows the effect of the initial concentration on the pseudo first order kinetics of the photodegradation of phenol using  $\alpha\text{-Fe}_2\text{O}_3$ . For the range of concentrations considered, the correlation coefficient ( $R^2 > 0.96$ ); hence, the kinetics of the photocatalytic degradation of phenol using  $\alpha\text{-Fe}_2\text{O}_3$  obeys pseudo-first order kinetic model. A decrease in the rate of phenol degradation with increase in the initial concentration of phenol was observed. The increase in the concentration of phenol causes saturation of active sites on the surface of hematite with phenol molecules, thus reducing light penetration and subsequent hydroxyl radical formation leading to lower photocatalytic activity. The apparent rate constants ( $k_{app}$ ) were found to be  $0.003\text{min}^{-1}$ ,  $0.004\text{min}^{-1}$ ,  $0.007\text{min}^{-1}$  and  $0.018\text{min}^{-1}$  for the initial phenol concentrations of 2.0g/L, 1.5g/L, 1.0g/L and 0.5g/L respectively. Similar kinetic behavior was observed by Chiou *et al.* (2008) for the

photocatalytic degradation of phenol using  $\text{TiO}_2$  under ultraviolet light irradiation. To study the effect of  $\alpha\text{-Fe}_2\text{O}_3$  dosage, various  $\alpha\text{-Fe}_2\text{O}_3$  doses ranging from 0.50 to 3.0g  $\text{L}^{-1}$  were used. Figure 4 shows the pseudo first order kinetic plot for the photocatalytic degradation of phenol at various dosages of  $\alpha\text{-Fe}_2\text{O}_3$ . The degradation rate increased with increasing  $\alpha\text{-Fe}_2\text{O}_3$  dosage up to 1.5g  $\text{L}^{-1}$ . The increase in the  $\alpha\text{-Fe}_2\text{O}_3$  dosage led to the increase in the active surface area of the  $\alpha\text{-Fe}_2\text{O}_3$  and enhancement of the photocatalytic activity. However, further increase in the  $\alpha\text{-Fe}_2\text{O}_3$  loading resulted in slower photodegradation. This observation can be attributed to the increased turbidity of the suspension, which leads to unfavourable light scattering and reduction of light penetration into the suspension thereby diminishing the photocatalytic activity (Jaafar *et al.*, 2012). Hence, the optimum dosage of  $\alpha\text{-Fe}_2\text{O}_3$  is 1.5 g/L under the experimental conditions employed. It shall be noted that the optimum photocatalyst dosage is dependent upon the size of the photoreactor as discussed recently by Sharma *et al.* (2013).



**Figure 4.** Pseudo first order kinetic plot for the photocatalytic degradation of phenol at various dosages of hematite

Photocatalytic reactions occur on the surface of photocatalysts most of which are amphoteric in aqueous media. As apparent in Figure 5, the highest photocatalytic activity was obtained at the pH of 4. Increase in the pH of phenol solution resulted in lower photocatalytic activity. This may be attributed to the reduction in the amount of positive charges on the surface of  $\alpha\text{-Fe}_2\text{O}_3$  with increasing pH. Reduction in the amount of positive charges on the surface of  $\alpha\text{-Fe}_2\text{O}_3$  decreases the attraction of phenol towards the surface. Electric charge properties of both the photocatalyst and the substrate play an important role in photocatalysis. The zero point charge

(pHzpc) of  $\alpha\text{-Fe}_2\text{O}_3$  is  $8.68 \pm 0.12$  (Smith and Salman, 1966). At pH values lower than pHzpc, the surface of  $\alpha\text{-Fe}_2\text{O}_3$  is positively charged and above pHzpc, the surface of  $\alpha\text{-Fe}_2\text{O}_3$  is negatively charged. The  $\text{pK}_a$  of aqueous solution phenol is 9.95 (Chiou *et al.*, 2008). If  $\text{pH} < \text{pK}_a$ , then phenol is in the molecular form ( $\text{C}_6\text{H}_5\text{OH}$ ) and if  $\text{pH} > \text{pK}_a$  the phenolate anion ( $\text{C}_6\text{H}_5\text{O}^-$ ) dominates. At the pH of 11.0, the photocatalytic activity of  $\alpha\text{-Fe}_2\text{O}_3$  is minimal because both  $\alpha\text{-Fe}_2\text{O}_3$  and phenol are negatively charged at that pH level. Hence they repel one another thus decreasing phenol adsorption on  $\alpha\text{-Fe}_2\text{O}_3$  and subsequent photooxidation.

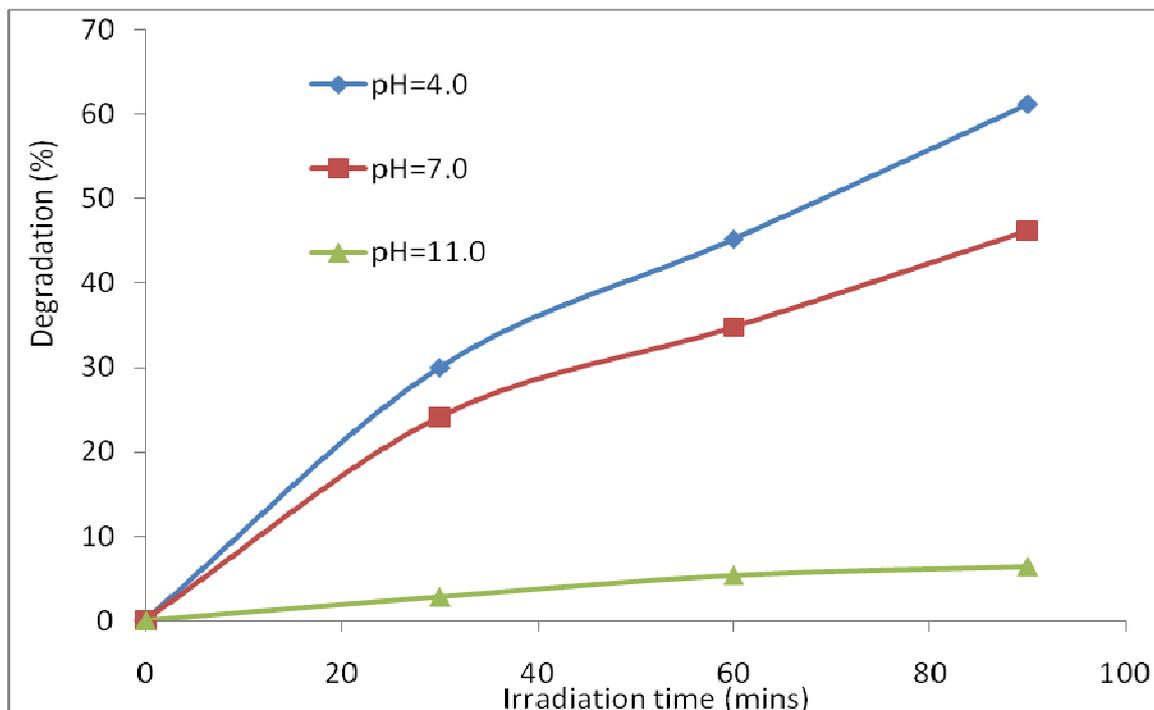


Figure 6. Effect of pH on the photocatalytic degradation of phenol using hematite

### Conclusion

94 % photocatalytic degradation of phenol was achieved in an irradiation time period of six hours using the synthesized hematite. In the absence of hematite, six hours of irradiation resulted in the

degradation of only 21 % of phenol. Photocatalytic degradation of phenol follows pseudo-first order kinetics. The optimum dosage of  $\alpha\text{-Fe}_2\text{O}_3$  was found to be  $1.5 \text{ g L}^{-1}$ . Highest photocatalytic degradation of phenol was observed in the acidic medium.

### References

1. Busca, G., Berardinelli, S., Resini, C. and Arrighi, L. (2008). Technologies for the removal of phenol from fluid streams: a short review of recent developments, *Journal of Hazardous Materials* 160:265-288.
2. Chiou, C.H., Wu, C.Y. and Juang, R.S. (2008). Influence of operating parameters on photocatalytic degradation of phenol in UV/TiO<sub>2</sub> process, *Chemical Engineering Journal* 139:322–329.
3. Ahmaruzzaman, M. (2008). Adsorption of phenolic compounds on low-cost adsorbents: A review, *Advances in Colloid and Interface Sciences* 143:48–67.
4. Pardeshi, S.K. and Patil, A.B. (2008). A simple route for photocatalytic degradation of phenol in aqueous zinc oxide suspension using solar energy, *Solar Energy* 82: 700-705.
5. Oller, I., Malato, S. and Sánchez-Pérez, A. (2011). Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review, *Science of Total Environment* 409:4141-4166.
6. Sarwan, B., Pare, B., Acharya, A.D., and Jonnalagadda, S.B. (2012). Mineralization and toxicity reduction of textile dye neutral red in aqueous phase using BiOCl photocatalysis. *Journal of Photochemistry and Photobiology B.* 116:48-55.

7. Fujishima, A.Z. and, Tryk, D.A. (2007). Heterogeneous photocatalysis: From water photolysis to applications in environmental cleanup, *International Journal of Hydrogen Energy* 32:2664–2672.
8. Konstantinou, I.K. and Albanis, T.A. (2004). TiO<sub>2</sub>-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations - A review, *Applied Catalysis. B. Environment* 49:1-14.
9. Casbeer, E., Sharma, V.K. and Li, X.I. (2012). Synthesis and photocatalytic activity of ferrites under visible light: A review, *Separation and Purification Technology* 87:1–14.
10. Zhang, G., Feng, Y., Xu Y., Gao, D. and, Sun, Y. (2012). Controlled synthesis of mesoporous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorods and visible light photocatalytic property. *Material Research Bulletin*. 47:625-630.
11. Bakardjieva, S., Stengla, V., Subrta, J., Houskova, V. and Kalend, V. (2007). Photocatalytic efficiency of iron oxides: Degradation of 4-chlorophenol, *Journal of Physical Chemistry Solids* 68:721-729.
12. Valenzuela, M.A., Bosch, P., Jimenez-Becerrill, J., Quiroz, O. and Paez, A.I. (2002) Preparation, characterization and photocatalytic activity of ZnO, Fe<sub>2</sub>O<sub>3</sub> and ZnFe<sub>2</sub>O<sub>4</sub>. *Journal of Photochemistry and Photobiology B*. 148:177–182.
13. Adefila, S.S., Aderemi, B.O., Ajayi, O.A. and Baderin, D.A. (2003) Comparative surface area determination using water adsorption method. *Nigerian Journal of Engineering* 11:88-95.
14. Jaafar, N., Abdul Jalil, A., Triwahyono, S., Muhid, M., Sapawe, N., Satar, M. and Asaari, H. (2013) Photodecolorization of methyl orange over  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-supported HY catalysts: The effects of catalyst preparation and dealumination, *Chemical Engineering Journal* 191:112-122.
15. Sharma, S., Ameta, R., Malkani, R.K. and Ameta, S.C. (2013). Photocatalytic degradation of Rose Bengal using semiconducting zinc sulphide as the photocatalyst. *Journal of the Serbian Chemical Society* 78:897-905.
16. Smith, G.W. and Salman, T. (1966). Zero-Point-of-Charge of Hematite and Zirconia, *Canadian Metallurgical Quarterly* 2:93-107.