# PHOTOCATALYTIC DEGRADATION OF CEPROFLOXACIN USING MAGNETIC IRON OXIDE

***Ezeibe A. U., Achilike J. B., Nleonu E. C. and Atuegbu O. M.**
Chemistry Department, Federal Polytechnic Nekede,
Owerri, Imo State, Nigeria
*Email: kingibe76@yahoo.com

**Abstract**

Magnetic Iron Oxide ($Fe_3O_4$) nanoparticles were synthesized by chemical co-precipitation method. The decomposition of ciprofloxacin under $Fe_3O_4$ and UV radiation was evaluated under contact time and catalyst dose using conductory method. The IR absorption band shows mineralization of the compound was not achieved and the result exhibited photocatalysis than photolysis.

**Keywords:** $Fe_3O_4$, Photocatalysis, Ciprofloxacin, Degradation.

## 1.0 INTRODUCTION

Several pharmaceutical compounds have been detected in domestic wastewater, natural aquatic systems and groundwater in many countries around the world [1]. In recent decades, very severe regulations have forced researchers to develop and evolve novel technologies to accomplish higher mineralization rate with lower amount of detectable contaminants [2].

Studies show that these substances have been detected in aqueous systems in concentrations of ng/L to μg\L [3]. Different physical, chemical and biological treatment processes have been employed to treat pharmaceutical waste.

The application of Advanced Oxidation Processes (AOPs) has shown promising results in removal of pharmaceutical pollutants in aqueous systems. The AOPs are chemical processes that have in common the generation of highly reactive hydroxyl radicals ($^{-}OH$) which is responsible to initiate the oxidation of several compounds found in wastewater [1].

The application of Magnetic Technology to solve environmental problems has received considerable attention in recent years. Studies have shown that magnetic $Fe_3O_4$ can be used for wastewater purification [4]. There are various ways of preparing $Fe_3O_4$ nanoparticles such as precipitation method, sol-gel method, emulsion technique, Mono chemical Processing, Hydro thermal precipitation and thermal plasma arc method, but chemical precipitation method has the potential to meet the increasing demand for the direct preparation of well dispersed (water-base) $Fe_3O_4$ nanoparticles and offer a low temperature alternative to conventional powder synthesis techniques [5].

The aim of this study is to synthesize $Fe_3O_4$ and assess the photocatalytic ability of $Fe_3O_4$ in degradation of ciprofloxacin.

## 2.0 EXPERIMENTAL

### 2.1 Chemicals

All the reagents used for the synthesis of $Fe_3O_4$ were of analytical grade and used without further purification. Ferric chloride hexahydrate ($FeCl_3.6H20$), ferrous chloride hexahydrate ($FeCl_2.4H_20$) and ammonium hydroxide ($NH_4OH$) solutions were prepared using double distilled water.

### 2.2 Synthesis of $Fe_3O_4$

Synthesis of $Fe_3O_4$ was prepared by co-precipitation of ferric and ferrous salts. 17.59g $FeCl_3$ and 7.59g $FeCl_2$ were dissolved in 200ml of distilled water, and the solution containing both ions was then heated up to 50°C for 10min. The two solutions were mixed together and the solution was precipitated using ammoniun hydroxide solution with continuous stirring at pH of 9.0. These particles were then separated from the solution using a filter paper. The black colored particles of magnetic iron oxide were further separated using a strong magnet and then washed many

times with distilled water. Finally $Fe_3O_4$ was washed with acetone and dried in hot air oven at 100°C for 12 hours.

### 2.3 Photodegradation Study

The photocatalytic process was carried out using a wooden box in which the inner wall was coated with aluminum sheet to prevent light dispersion. Also the photocatalytic box was supplied with 254nm 220V-15W UV-lamp.

In order to study effect of magnetic $Fe_3O_4$ loading, the experiments were performed by varying magnetic $Fe_3O_4$ concentration from (0.5g-2.5g) for 200mg/100ml solution of ciprofloxacin for 3 hours. The solution was separated by filtration using watman filter paper and the ciprofloxacin solution was analyzed using conductivity meter.

Similar experiments were carried out by varying time (1-5 hours) at drug concentration of 200mg/100ml and catalyst dose of 1.0g. All studies were conducted in triplicates and the results shown are the mean of the results.

### 2.4 Conductance Measurement

The conductance measurement was performed using Jenway 4510 conductivity meter. Conductance of ciprofloxacin before and after exposure was taken. The conductance measurement was used to measure the degradation of the drug.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Synthesis of Magnetic Iron Oxide ($Fe_3O_4$)

Black Magnetic Iron Oxide ($Fe_3O_4$) containing both Fe(II) and Fe(III) was synthesized by chemical co-precipitation method. The method produced fine stoichiometric particles of single and multi components of metal oxides. Magnetic Iron Oxide ($Fe_3O_4$) has been used to adsorb dye from wastewater by simple magnetic separation process. $Fe_3O_4$ nanoparticles have shown to possess super paramagnetic properties [4].

### 3.2 Photocatalytic Activity

The photocatalytic activity of $Fe_3O_4$ nanocomposite was studied by photodecomposition of ciprofloxacin by using UV-lamp of 254nm as the light source by taking into consideration contact time and catalyst weight.

$$\text{Percentage Drug Degradation} = \frac{\Lambda_1 - \Lambda_0}{\Lambda_1}$$

Where, $\Lambda_0$ is the initial molar conductance of drug before irradiation and $\Lambda_1$ is the molar conductance after irradiation.

### 3.2.1 Effect of Catalyst

Fig

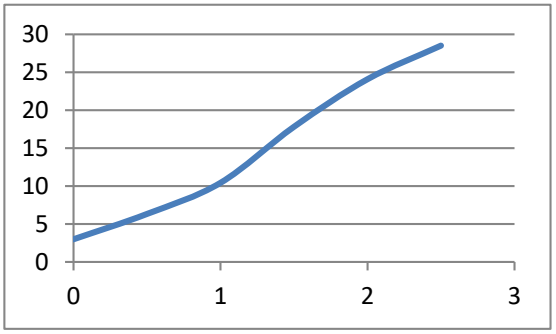


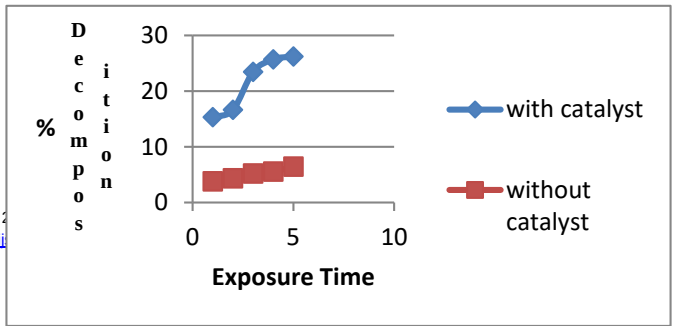

Fig. 1: Effect of Catalyst on Decomposition of Ciprofloxacin

Figure 1 shows effect of $Fe_3O_4$ catalyst dose on the degradation of ciprofloxacin solutions at natural pH. The result shows that increase in the weight of $Fe_3O_4$ from 0.5 - 2.5g increases the rate of degradation of ciprofloxacin solution, while the ciprofloxacin solution without $Fe_3O_4$ shows the least degradation. The result shows that the presence of active site on catalyst surface plays important role on the basis that the increase of the amount of $Fe_3O_4$ led to increase in the active sites on catalyst surface, as result in the number of adsorbed ciprofloxacin molecules on the surface of catalyst which leads to increase in the area of illumination. The increase in the amount of catalyst also leads to increase in the number of absorbed photons [2].

The limited degradation process obtained in this study may be due to higher concentration of $Fe_3O_4$ leading to light scattering that resulted in reducing the utilized light [6], [7].

### 3.2.2 Effect of Contact Time

The effect of contact time with $Fe_3O_4$ on the degradation of ciprofloxacin is shown in Fig 2. Increasing the contact time led to a corresponding increase in the percentage degradation of ciprofloxacin

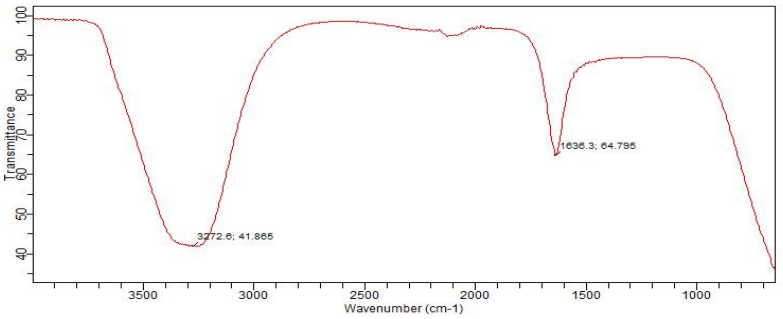


The percentage decomposition of the drug increased at a steady rate as contact time increased up to 5 hours. There was no significant change in the decomposition after 3 hours. The control experiments result showed that the presence of $Fe_3O_4$ played a major role in the decomposition of the compound. These results are in agreement with Mendez-Arriga *et al. (2008)* [8].

### 3.3 FT-IR Analysis

The FT-IR analysis of ciprofloxacin was studied using Fourier Transform Infrared Spectrophotometer (Happ-Genzol Model) to determine the functional group of the drug before and after UV irradiation in the absence and presence of $Fe_3O_4$.

The IR spectrum of non-irradiated ciprofloxacin is shown in Fig. 3(a) while irradiated ciprofloxacin in the absence and presence of $Fe_3O_4$ are shown in Fig. 3(b) and 3(c) respectively. The IR spectrum of non-irradiated and irradiated ciprofloxacin in the absence of $Fe_3O_4$ manifest prominent absorption band located at 3268.9 and 1636$cm^{-1}$ respectively showing N-H bending of quinolones and OH stretch of carboxylic acid respectively. The IR spectrum of irradiated ciprofloxacin in the presence of $Fe_3O_4$ absorption band 3272.9cm-1 and 1637.3$cm^{-1}$ showing no shift in the functional group of quinolones while OH group of carboxylic acid shifted to 3272.9$cm^{-1}$.




(c)

(a) (b)

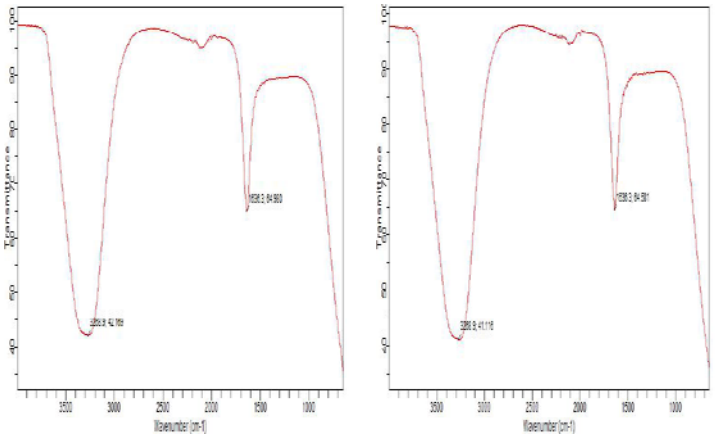


Fig.3: IR Spectrum of ciprofloxacin before exposure is shown (a), after exposure without $Fe_3O_4$ (b) and after exposure with $Fe_3O_4$ (c).

The non-shift in the absorption band of quinoline indicated non mineralization of the drug [9],[10] while the shift in the absorption band of the OH group in the presence of $Fe_3O_4$ shows the decomposition of ciprofloxacin through the carboxylic group, demonstrating ciprofloxacin solution degradation through photocatalytic reaction. The result shows that the mechanism of reaction lies in the production of OH free radical facilitated by use of $Fe_3O_4$ which increases the surface area of ciprofloxacin solution to exposed UV light. Its mechanism is similar to that of $H_2O_2$/UV and $O_3$/UV but $Fe_3O_4$ is more suitable compared to the others due to its stability under various conditions, its high potential to produce radicals and its ease of synthesis at low cost [11],[12]. This study shows that both UV light and catalyst are important factors in ciprofloxacin degradation. However, the result showed a photocatalytic rather than a photolytic process.

## 4.0 CONCLUSION

Magnetic iron oxide ($Fe_3O_4$) was synthesized by co-precipation method and its photo-catalytic ability in degradation of ciprofloxacin solution was studied under UV radiation. The result shows that the percentage decomposition of the drug increased at a steady rate and presence of $Fe_3O_4$ played a major role in the decomposition of the compound.

## COMPETING INTEREST

Authors have declared that no competing interest exists.

## REFERENCES

[1] Braz, F. S., Silva, M. R. A., Silva, F. S., Andrade, S. J., Fonseca, A. L. and Kondo, M. M. (2014). Photocatalytic degradation of ibuprofen using $TiO_2$ and ecotoxicological assessment of degradation intermediates against *Daphnia similis*. *Journal of Environment Protection*, **5**:620-626.

[2] Alaa, J. A., Muthana, S. M., Amer, M. J. and Hanaa, A. A. (2016). Photocatalytic degradation of paracetamol and procaine. *Internationl Journal of ChemTech Research*, **9**(1):412-425.

[3] Santos, J. L., Aparico, I. and Alonso, E. (2007). Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants, a case study: Seville City (Spain). *Envirnoment International*, **33**:596-601.

[4] Poeji, L. H., Muhammad, F., Ridwa, M. and Dedi S. (2013). Synthesis and properties of $Fe_3O_4$ nanoparticles by co-precipitation method to removal procion dye. *International Journal of Environmental Science and Development*, **3**(4):336-340.

[5] Kulkarni, S. A., Sawadh, P. S. and Kokate, K. K. (2012). Synthesis and characterization of $Fe_3O_4$ Nanoparticles for engineering applications. *International Journal of Computer Application*, 17-18.

[6] Derksen, J. G. M., Rijs, G. B. J. and Jongbloed, R. H. (2004). Diffuse polution of surface water by pharmaceutical products. *Water Sci. Technol.*, **49**:213-221.

[7] Golet, E. M., Alder, A. C. and Giger, W. (2002). Environmental exposure and risk assessment of flouroquinolone antibacterial agents in wastewater and river water of the Glatt Valley Watershed, Switzerland. *Envrion Sci. Technol.*, **36**:3645-3651.

[8] Mendez-Arriga, F., Esplugas, S. and Gimenez, J. (2008). Photocatalytic degradation of non-steroidal anti-inflammatory drugs with $TiO_2$ and simulated solar irradiation. *Water Research*, **42**:585-594.

[9] Da Silva, J. C. C., Teodoro, J. A. R., Afonso, R J. C. F., Aquinom S. F. and Augusti, R. (2013). Photolysis and photocatalysis of ibuprofen in aqueous medium: characterization of by-products via liquid chromatographycoupled with high resolution mass spectrometry and assessment of their toxicities against *Salina*. *Journal Mass Spectrometry*, **49**:145-153.

[10] Choina, J., Kosslick, H. Ficher, C., Flechsig, G. U., Frunza, L. and Schulz, A. (2013). Photocatalytic decompostion of pharmaceutical ibuprofen pollutions inf water ove titaniacatalyst. *Applied Catalysis B: Environment*, **129**:589-598.

[11] Wu, W., He, Q. G. and Jiang, C. Z. (2008). Magnetic iron oxide nanoparticles: synthesis and surface Functionalization strategies. *Nanoscale Res Lett*, **3**:397.

[12] Verma, A. "Advanced oxidation technologies for wastewater treatment". M.tech Seminar, 2004.