



FENTON OXIDATION OF 3,4-DICHLOROANILINE IN AQUEOUS SOLUTION

MEENAKSHI VERMA

Department of Civil Engineering
National Institute of Technology Karnataka,
Surathkal
Mangalore, India
Email: vprachi29@gmail.com

Dr. BASVARAJU MANU

Department of Civil Engineering
National Institute of Technology Karnataka,
Surathkal
Mangalore, India
Email: bmanu8888@gmail.com

ABSTRACT

Degradation of aqueous 3,4-Dichloroaniline (3,4-DCA) using Fenton Oxidation was attempted in this study. Fenton oxidation is considered one of the cheapest advanced oxidation processes due to high availability of Fenton's reagents Fe^{2+} and H_2O_2 , wherein Fe^{2+} catalyses hydroxyl radical ($\cdot\text{OH}$) production from H_2O_2 . The low cost and locally available laterite soil was used as a source of iron rather than using iron salt (Ferrous Sulphate, Ferric Chloride etc.). 3,4-Dichloroaniline is a principal product of biodegradation of diuron and exhibits a higher toxicity.

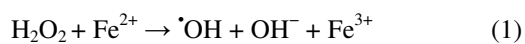
Keywords- 3,4-Dichloroaniline (3,4- DCA), Fenton Oxidation, Laterite soil

I. INTRODUCTION

3,4-Dichloroaniline (3,4-DCA) is widely used in manufacture of dyes, herbicides and pharmaceuticals. It indirectly possesses a significance amount of toxicity and could be a potential poisoning pesticide contaminant of ground water. Therefore, 3,4-Dichloroaniline should be removed before entering natural aquatic system. As the metabolite of liuron, diuron, phenylurea, acylanilide and carbamate pesticides, 3,4- DCA was also detected during the removal process of these pesticides[1–3]. It could be converted into 3,3',4,4'-tetra-chloroazobenzene, which was a carcinogen and potential genotoxin.

Many industrial processes, and agriculture and domestic activities leads to wastewater streams containing recalcitrant organic pollutant which need to be disposed off in a proper manner. Also the concentration of chemicals in the effluent streams should be kept at a certain minimum level in order to comply with the environmental laws, which are becoming more stringent these days.

Advanced oxidation processes (AOPs) are effective remediation methods based on the generation of reactive species, such as hydroxyl radicals ($\cdot\text{OH}$), which reacts rapidly and with low selectively with a variety of toxic and non-biodegradable compounds, yielding CO_2 and inorganic ions (pignatello et al., 2006). Among the (AOPs), processes using Fenton type reagent are relatively inexpensive and oxidizing agent is easily handled. It is the mixture of Fe^{2+} and H_2O_2 , capable to degrade all types of herbicides by generating highly reactive $\cdot\text{OH}$ radical (Arnold et al., 1995; Wang and Lemley, 2001) given in Eq. (1).



However, it is seen that the homogeneous Fenton's process generates high iron sludge and adds extra sulphates from FeSO_4 .

Therefore, the heterogeneous Fenton-like processes e.g. nano zero valent iron (nZVI) (Xu and Wang, 2011), iron supported clays (Hassan and Hameed, 2011), goethite ($\alpha\text{-FeOOH}$) (Ortiz de la Plata et al., 2010) and Fe_3O_4 (Zhang et al., 2009) have been successfully applied.

Laterite main composition is iron, aluminum, silicon oxides and Ti, Mg, Mn, Ca, K, Na in small traces (Gualtieri et al., 2015). Moreover, main privileges of laterite are: abundance, low cost, thermally stable, no toxicity in the environment and a proper alternative to the traditional iron. With all these advantages, few researchers were studied the natural laterite as Fenton's catalyst for the removal of sodium azide (Khataee and Pakdehi, 2014), azo dye (Khataee et al., 2015) and paracetamol (Manu and Mahamood, 2011).

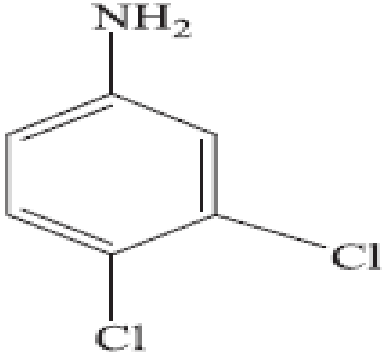
The aim of the present study is to determine the efficiency of Fenton's reaction in the process of 3,4-DCA removal from synthetic wastewater in an economical way.

II. MATERIAL AND METHODS

A. Materials

3,4-DCA was purchased from Sigma Aldrich (99.5% pure) and the physico-chemical properties are listed in Table 1. The reagents, HCl (35%), H₂O₂ (50% w/w), NaOH were obtained from Merck manufactured in India. Laterite soil for the extraction of iron is taken from NITK, Surathkal campus.

Table1: Physical and chemical properties of 3,4-DCA

Properties	3,4-DCA
Structure	
Molecular formula	C ₆ H ₅ Cl ₂ N
Purity (%)	99.5
Vapour pressure (Pa)	1.3 (20 °C)
Molecular weight (g mol ⁻¹)	162
Melting point (°C)	72
Solubility in water (mg L ⁻¹)	580 (20 °C)

B. Wavelength scanning

For studying the wavelength of 3,4-DCA solutions of different initial concentrations (5, 10, 20, 30, 40 and 50 mg/l) were prepared in distilled water. Keeping the solution one by one in UV-Vis spectrophotometer, the wavelength of the compound was determined.

C. Calibration of the 3,4-Dichloroaniline

For obtaining the calibration curve of concentration versus absorbance, 3,4-DCA solutions of different concentrations in ascending order (5, 10, 20, 30, 40, and 50 mg/l) were placed in UV-Vis spectrophotometer maintaining the wavelength obtained during wavelength scanning. Thus a calibration curve was obtained for 3,4-DCA.

D. Extraction of Iron from laterite soil by leaching with HCL

Iron is extracted from laterite soil as per the procedure explained by Olanipekun (2000). Laterite soil for the extraction of iron is taken from NITK, Surathkal campus. The laterite soil is crushed to powder and is



passed through 50 micron sieve. 1.0g of the sieved soil sample is taken in a glass beaker and 20ml of 1:1 HCL is added. This solution is mixed and grinded till the entire sample is dissolved completely. The sample is kept on a hot plate for maximum evaporation till the residue is formed. The residue left is baked in an oven for 1 hour and 20ml of 1:1 HCL is added and it is heated for 1 minute, following which, 20ml of hot distilled water is added. The solution is filtered through a whatman 42 filter paper and the filtrate obtained is transferred to Nessler's cylinder and dilute up to 100 ml, the solution obtained is the iron extracted from the laterite soil.

E. Procedure for treatment

For the treatment of 3,4-DCA using Fenton reagent, initially a known concentration of 3,4-DCA solution was prepared (10 mg/l). The pH of the solution was tested. It was adjusted to the required pH by the addition of 0.1 N H_2SO_4 or NaOH as per requirement. Then extracted iron solution was added to the required dosage. Then immediately after the addition of H_2O_2 , the reaction was started. After the specific time (24 hours) of reaction, the solution is taken out and tested for concentration.

III. RESULTS AND DISCUSSIONS

A. Wavelength Scanning

The wavelength scanning of 3,4-DCA was conducted for 5mg/l, 10mg/l, 20mg/l, 30mg/l, 40mg/l and 50mg/l. The wavelength obtained for 5mg/l 10mg/l, 20mg/l and 30mg/l was 243nm and the wavelength obtained for 40mg/l and 50mg/l was 247nm and 250nm respectively. Shown in fig. 1(a), fig. 1(b), fig. 1(c), fig. 1(d), fig. 1(e), and fig. 1(f).

B. Iron extracted from the Laterite soil

Extracted iron solution from laterite soil was containing 2.6mg/l (in 0.1ml solution) concentration of Fe^{2+} , which could be used economically as a catalyst.

C. Calibration of 3,4- DCA

Different concentrations of 3,4-DCA in ascending order (5mg/l, 10mg/l, 20mg/l, 30mg/l, 40mg/l, and 50mg/l) were prepared and placed in UV-Vis spectrophotometer. A calibration curve was plotted with concentration versus absorbance.

D. Effect of pH value on the degradation of 3,4-DCA

The initial value of 3,4-DCA: H_2O_2 and 3,4-DCA: Fe^{+2} ratios were fixed to 1 and 100 respectively and pH value was varied fixing the total reaction time of 24 hours. The maximum degradation efficiency of 3,4-DCA was 81.9% at pH value of 2.0, at the pH value of 2.5, 3, 3.5, 4 and 5, the degradation efficiencies were 67.25%, 31.23%, 19.10%, 1.77% and 3.75% respectively.

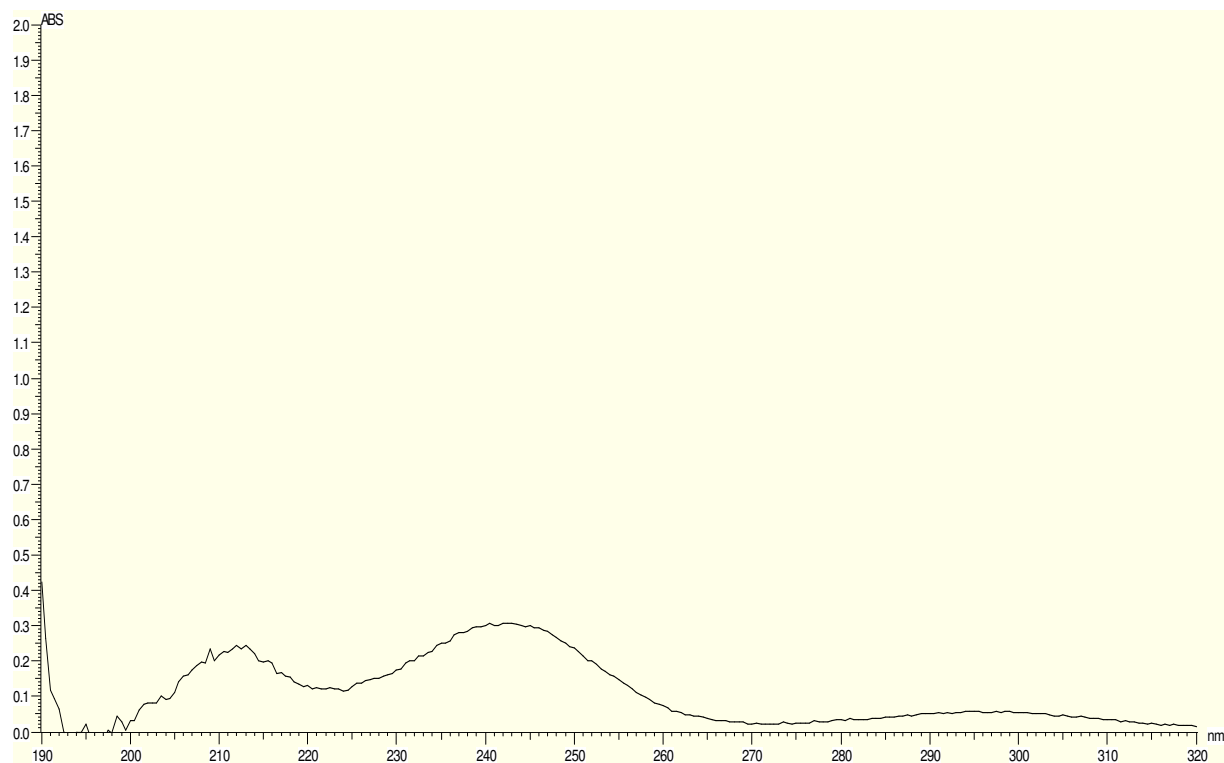


Fig.1(a): Wavelength scanning result of 3,4-DCA (5mg/l)

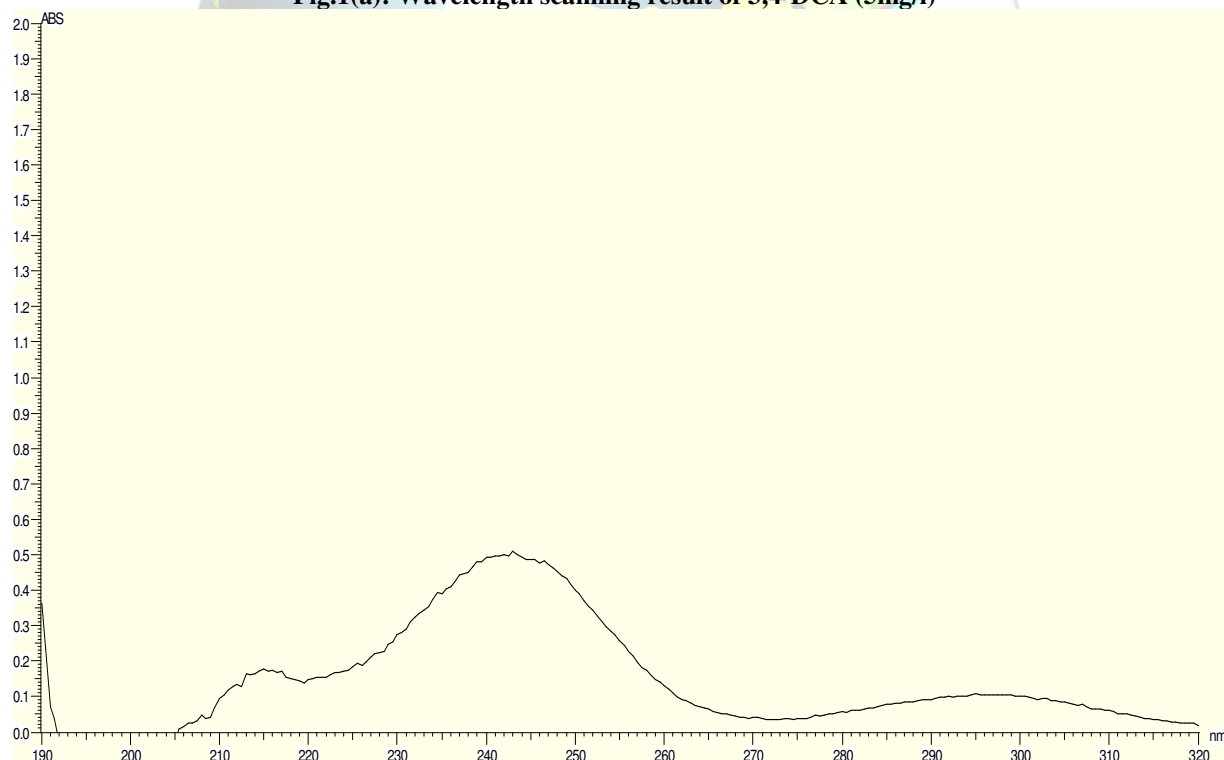


Fig. 1(b): Wavelength scanning result of 3,4-DCA (10mg/l)

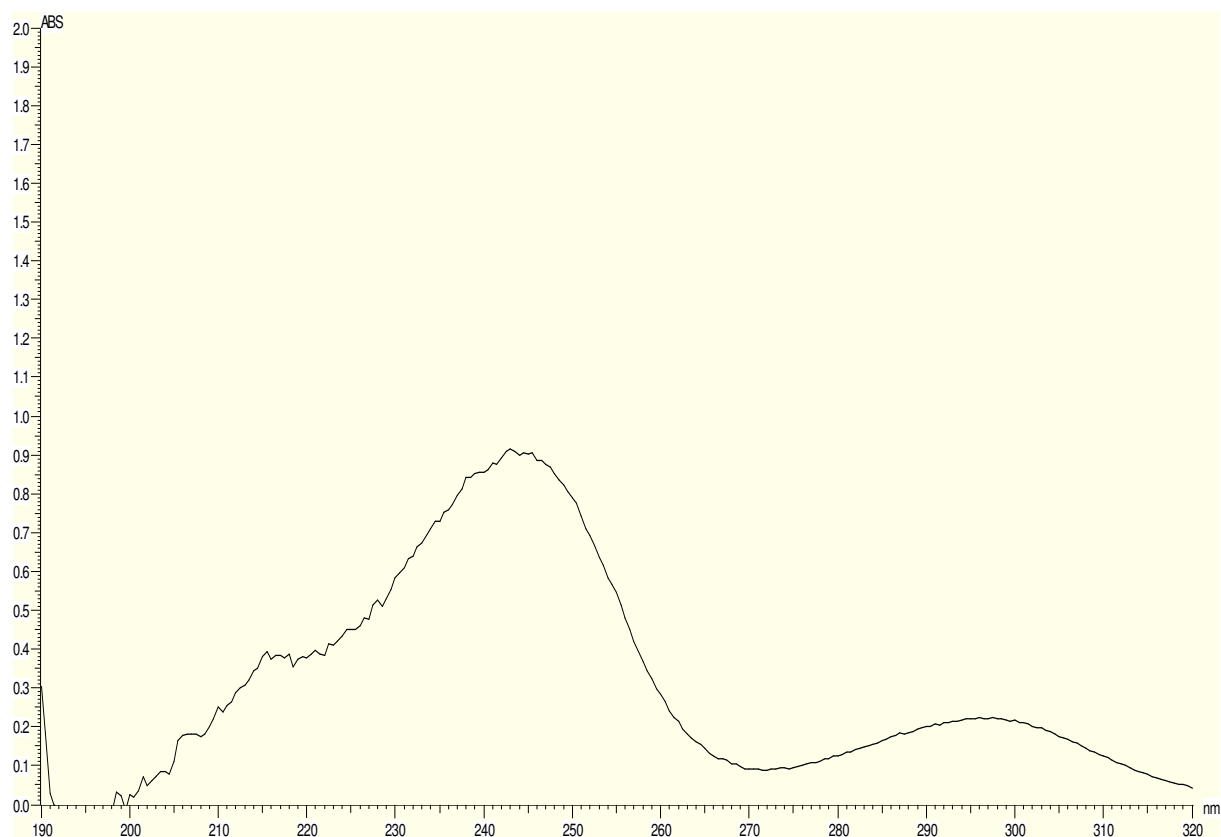


Fig. 1(c): Wavelength scanning result of 3,4-DCA (20mg/l)

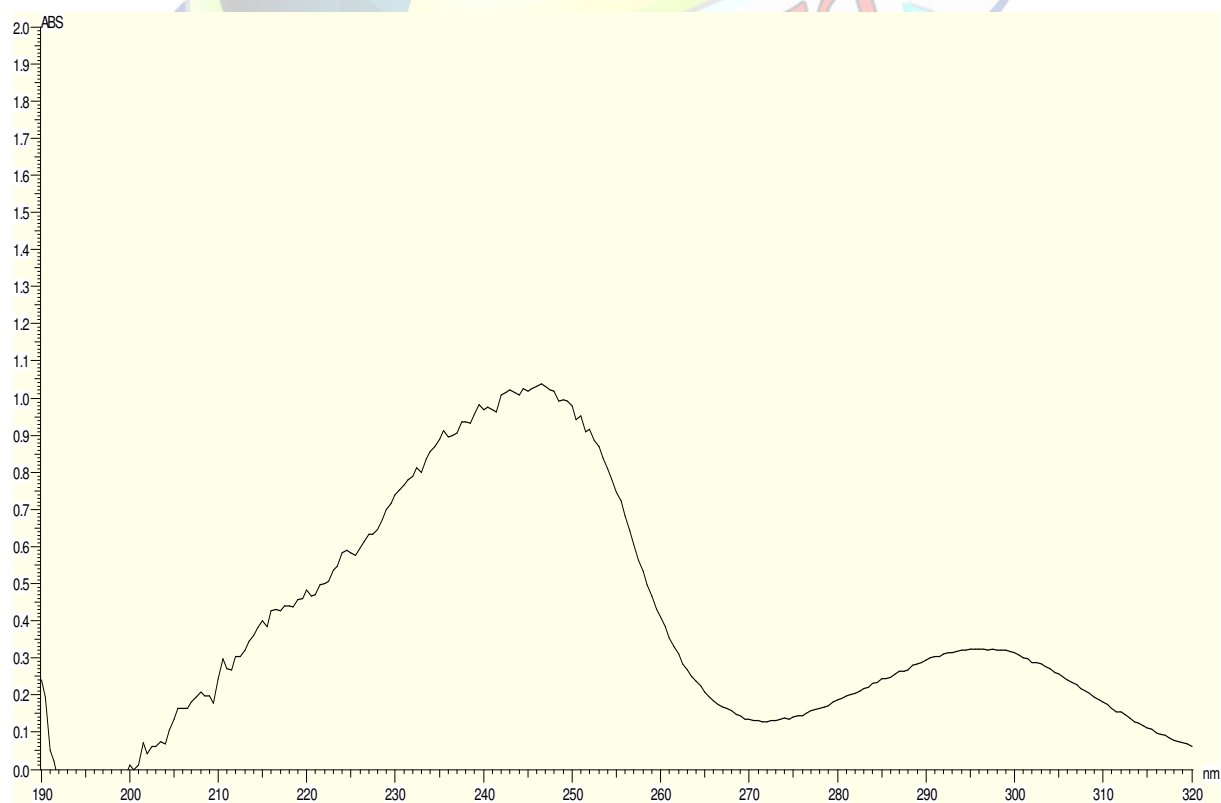


Fig.1(d): Wavelength scanning result of 3,4-DCA (30mg/l)

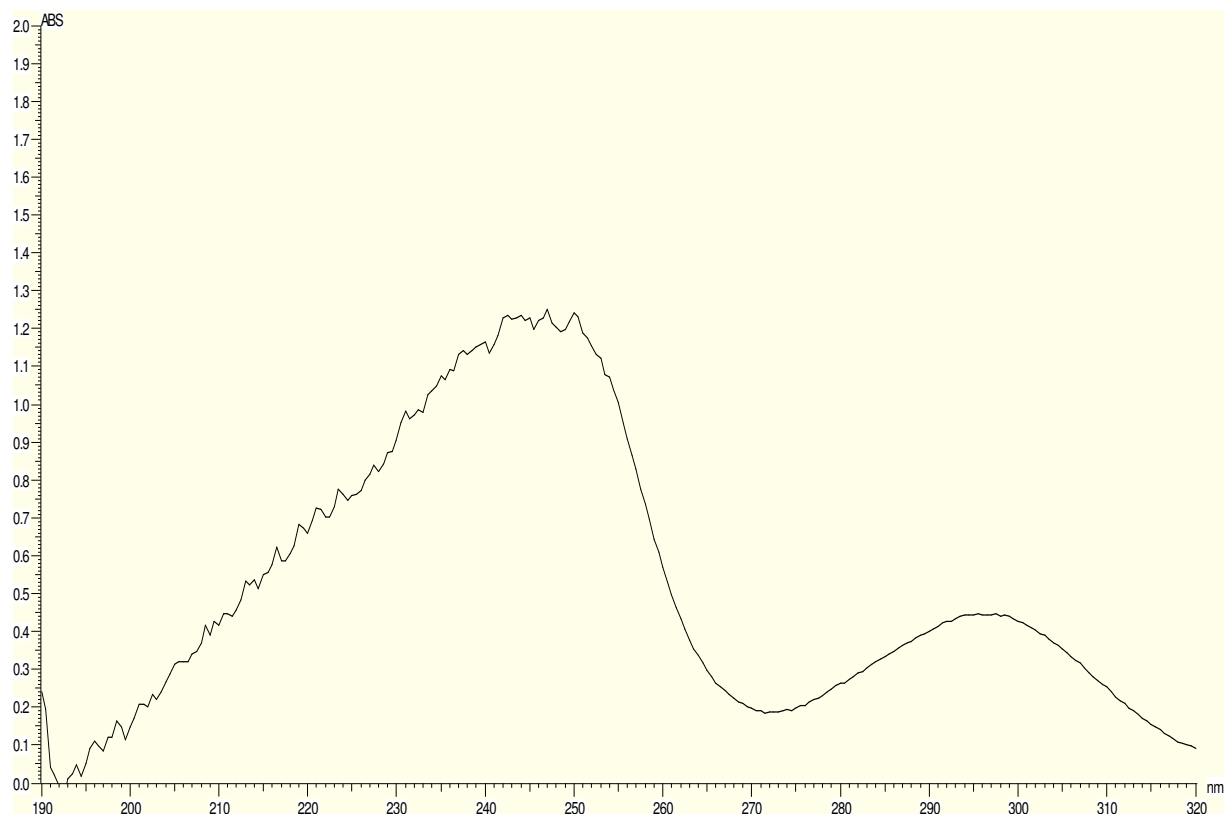


Fig. 1(e): Wavelength scanning result of 3,4-DCA (40mg/l)

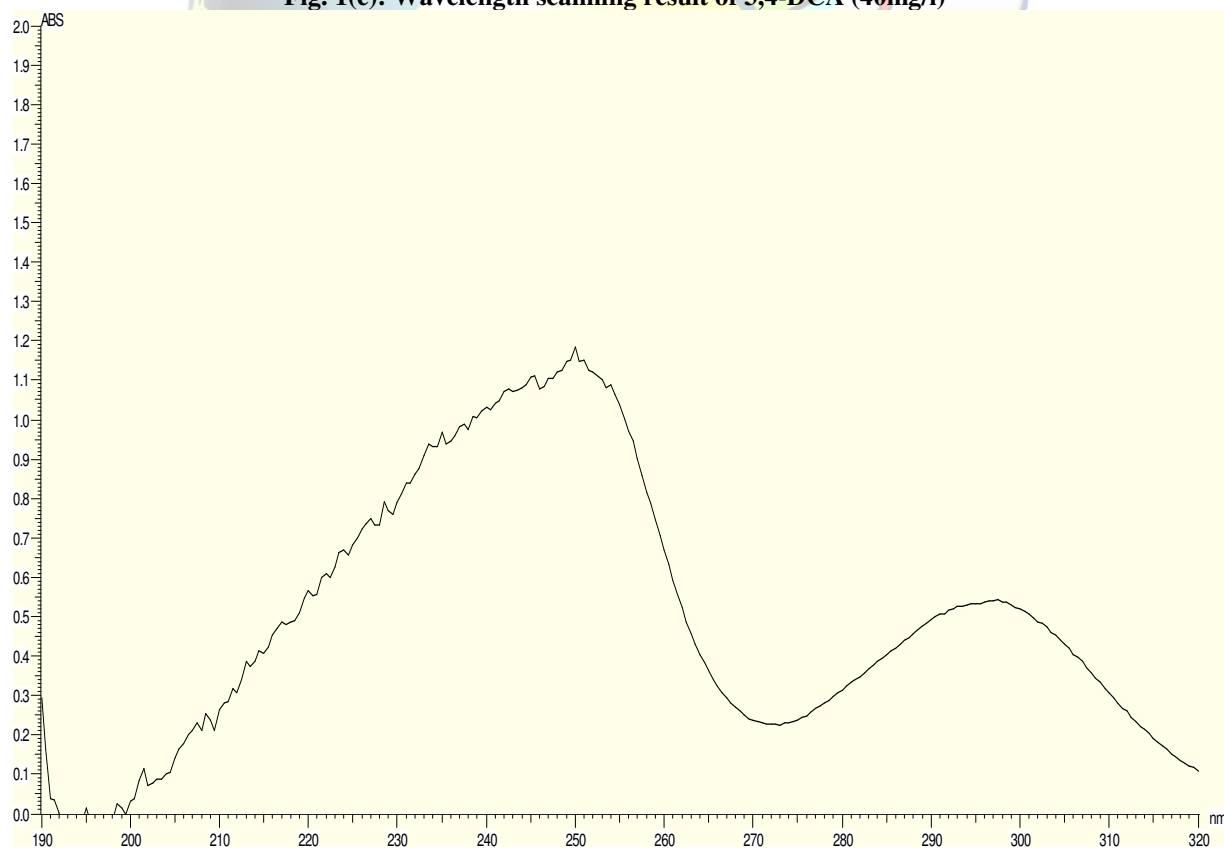


Fig. 1(f): Wavelength scanning result of 3,4-DCA (50mg/l)



IV. CONCLUSIONS

Aqueous 3,4-DCA could be degraded effectively by Fentonoxidation in an economical way. The degradation efficiency of 3,4-DCA decreased with increased pH value and the maximum efficiency for the removal of 10mg/l concentration 3,4-DCA was at pH value 2. So the optimum value of pH 2 could be used for the degradation of different concentration of 3,4- DCA. The addition of extracted iron from laterite soil was beneficial and very economical to improve the degradation efficiency of 3,4-DCA.

REFERENCES

- [1] Fava, L., Orrú, M.A., Businelli, D., Scardala, S. and Funari, E., 2006. Leaching potential of some phenylureas and their main metabolites through laboratory studies. *Environmental science and pollution research*, 13(6), pp.386-391.
- [2] Herrera-González, V.E., Ruiz-Ordaz, N., Galíndez-Mayer, J., Juárez-Ramírez, C., Santoyo-Tepole, F. and Montiel, E.M., 2013. Biodegradation of the herbicide propanil, and its 3, 4-dichloroaniline by-product in a continuously operated biofilm reactor. *World Journal of Microbiology and Biotechnology*, 29(3), pp.467-474.
- [3] Wang, S., Poon, K. and Cai, Z., 2013. Biodegradation and removal of 3, 4-dichloroaniline by *Chlorella pyrenoidosa* based on liquid chromatography-electrospray ionization-mass spectrometry. *Environmental Science and Pollution Research*, 20(1), pp.552-557
- [4] Pignatello, J.J., Oliveros, E. and MacKay, A., 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical reviews in environmental science and technology*, 36(1), pp.1-84.
- [5] Arnold, S.M., Hickey, W.J., Harris, R.F., 1995. Degradation of atrazine by Fenton's reagent: Condition optimization and product quantification. *Environ. Sci. Technol.* 29, 2083–2089.
- [6] Wang, Q.Q., Lemley, A.T., 2001. Kinetic model and optimization of 2,4-D degradation by anodic Fenton treatment. *Environ. Sci. Technol.* 35, 4509–4514
- [7] Xu, L., Wang, J., 2011. A heterogeneous Fenton-like system with nanoparticulate zerovalent iron for removal of 4-chloro-3-methyl phenol. *J. Hazard. Mater.* 186, 256–264.
- [8] Hassan, H., Hameed, B.H., 2011. Fe-clay as effective heterogeneous Fenton catalyst for the decolorization of reactive blue 4. *Chem. Eng. J.* 171, 912–918.
- [9] Ortiz de la Plata, G.B., Alfano, O.M., Cassano, A.E., 2010. Decomposition of 2- chlorophenol employing goethite as Fenton catalyst. I. Proposal of a feasible, combined reaction scheme of heterogeneous and homogeneous reactions. *Appl. Catal.*, B 95, 1–13.
- [10] Zhang, S.X., Zhao, X.L., Niu, H.Y., Shi, Y.L., Cai, Y.Q., Jiang, G.B., 2009. Superparamagnetic Fe₃O₄ nanoparticles as catalysts for the catalytic oxidation of phenolic and aniline compounds. *J. Hazard. Mater.* 167, 560–566.
- [11] Gualtieri, M.L., Romagnoli, M., Pollastri, S., Gualtieri, A.F., 2015. Inorganic polymers from laterite using activation with phosphoric acid and alkaline sodium silicate solution: Mechanical and microstructural properties. *Cem. Concr. Res.* 67, 259–270
- [12] Khataee, A.R., Pakdehi, S.G., 2014. Removal of sodium azide from aqueous solution by Fenton-like process using natural laterite as a heterogeneous catalyst: Kinetic modeling based on nonlinear regression analysis. *J. Taiwan Inst. Chem. Eng.* 45, 2664–2672.
- [13] Khataee, A., Salarpour, F., Fathinia, M., Seyyedi, B., Vahid, B., 2015. Iron rich laterite soil with mesoporous structure for heterogeneous Fenton-like degradation of an azo dye under visible light. *J. Ind. Eng. Chem.* 26, 129–135.
- [14] Manu, B., Mahamood, S., 2011. Enhanced degradation of paracetamol by UV-C supported photo-Fenton process over Fenton oxidation. *Water Sci. Technol.* 64 (12), 2433–2438.
- [15] Huang, D., Wang, Z., Zhang, J., Feng, J., Zheng, Z. and Zhang, J., 2016. Gamma radiolytic degradation of 3, 4-dichloroaniline in aqueous solution. *Separation and Purification Technology*, 170, pp.264-271.
- [16] Olanipekun, E.O., 2000. Kinetics of leaching laterite. *International Journal of Mineral Processing*, 60(1), pp.9-14.