



Research Paper

A novel catalytic route to degrade paracetamol by Fenton process

Basavaraju Manu^{*}, Mahamood S, Vittal H, Shrihari S

Department of Civil Engineering, National Institute of Technology Karnataka, Surathkal, Mangalore, INDIA

Available online at: www.ijrce.org

Received 22nd June 2011, Accepted 4th July 2011

Abstract- The Fenton's Oxidation, which is efficient, reliable, eco-friendly and cost-effective over the other advanced oxidation processes, has not been reported for the treatment of paracetamol in water. In the present study, a novel iron catalyst source laterite soil was used to degrade paracetamol in aqueous solutions by Fenton oxidation process. Both $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and lateritic soil were studied as sources of iron for Fenton's reagent. Percent Paracetamol reduction and percent Chemical Oxygen Demand (COD) removal were measured as the objective functions to be maximized. Effect of influent pH, influent H_2O_2 concentration, and influent iron concentration on paracetamol degradation efficiencies were investigated by varying influent paracetamol concentration. At $[\text{H}_2\text{O}_2] : [\text{Fe}^{2+}] :: 60:1$ and $[\text{H}_2\text{O}_2] : [\text{Laterite iron}] :: 40:1$, pH 3 for the 10 mg/L initial concentration of paracetamol and for a reaction time of 60 minutes, the percent paracetamol reduction were 80 and 75 but the percent COD removal were 71 and 63. By HPLC analysis, 100% removal of paracetamol was observed at the above optimum conditions for both the sources of iron in 240 minutes. The use iron from laterite soil is a cost effective and eco-friendly method over other methods. The method can be applied in situ to treat the polluted soils and water bodies.

Key words: COD removal; Fenton's oxidation, Laterite soil, Paracetamol degradation etc.

Introduction

The presence of the Pharmaceutical compounds is observed in surface water^[1-3], Ground water, Sewage effluents^[4, 5], drinking water^[6], and also in solid waste^[7]. The drug concentrations detected in the environment were generally in the ng/L to µg/L range^[1, 2]. Pharmaceuticals retain their chemical structure long enough to do their therapeutic work and remain in the environment for a long time and is considered dangerous both at low and high concentrations^[8]. The effects like feminization in fish, inhibition of growth in microbes and plants, toxicity and Endocrine disruption in fish were reported^[9, 10]. The actual risk to the humans and to the ecosystem from trace quantities of the drugs and chemicals in drinking water sources is currently unknown^[1, 7]. Low concentrations of pharmaceuticals in water may not pose much risk to adult humans, but fetuses, infants or children and other organisms may be affected. Children may have an eight fold greater risk of adverse effects of pharmaceutical exposure^[11]. As the pharmaceuticals are bioactive and also when they have been continuously introduced into the environment, they would certainly affect the ecosystems.

As a precautionary measure, considering the potential adverse effects of pharmaceuticals, they should be removed

from the aqueous solutions. Advanced Oxidation Processes (AOPs) have proved capable of completely degrading the pharmaceuticals from aqueous solutions^[8]. These Processes are based on the generation of hydroxyl radical ($\text{OH}^\cdot$), which is a more powerful oxidant (E° 2.8V) than the other chemical reagents like ozone (E° 2.0V) or H_2O_2 (E° 1.8V)^[12]. Among AOPs, Fenton's Oxidation is emerged as the most promising method, in terms of cost effectiveness and ease of operation^[13]. In a comprehensive review, Neyens and Baeyens (2003)^[14] have indicated that the Fenton's Oxidation is very effective in the removal of many hazardous organic pollutants from water and wastewaters.

The presence of chloride and sulfate anions has a considerable influence on Fenton oxidation process^[15]. Free radicals, in solutions containing chloride, were scavenged to form chlorinated inorganic radicals among which the dichloride anion radical is the predominant^[16]. The overall effect of sulfates on degradation rates is much lower in comparison to chloride ions. Moreover, ferrous sulfate is more reactive towards hydrogen peroxide than ferrous ions alone

that can additionally balance inhibitory potential of the sulfate ions^[17].

Paracetamol (4-hydroxyacetanilide or 4-acetamidophenol or acetaminophen or Tylenol) is extensively used as analgesic and antipyretic drug, used as intermediate for pharmaceuticals and azo dyes, stabilizer for hydrogen peroxide, photographic chemicals and also used for the control of Brown Tree Snake population^[18]. Paracetamol was found to be present in sewage treatment plant (STP) effluents up to a concentration of 6 µg/L^[19], up to 10 µg/L in water samples from natural sources in USA^[2] and more than 65 µg/L in the Tyne River, UK^[20]. However, the concentrations of paracetamol in water and wastewater may rise due to increase in population and their modern life styles. Consequent to the steep increase in the usage, the production of paracetamol has also been increased manifold all over the world.

Recently, removal of paracetamol by electrochemical method^[21, 22], ozonation and H₂O₂/UV oxidation methods^[23, 24], oxidation with Diperoxydiphenylarsenate (II)^[18], TiO₂/UV^[25, 26] and sonolysis^[27] were reported. However, Fenton's oxidation (using FeSO₄·7H₂O and Lateritic soil as two different sources of iron), one of the most promising AOPs for the effective removal of hazardous organic pollutants, has not been reported for the oxidation of paracetamol in aqueous solutions. The Fenton's reagent is widely used in the wastewater treatment because of the fact that ferrous iron is a wide available and nontoxic element, and hydrogen peroxide is easy to handle and the excess is decomposed into eco-friendly products.

The aim of the present investigation was to explain the effect of operating parameters and reaction kinetics for the Fenton's Oxidation of paracetamol in aqueous solutions. The Oxidation runs were carried out at ambient temperature (27±3°C). Laterite soil is used as source of iron catalyst and the experimental results were compared with the use of FeSO₄·7H₂O as source of iron in Fenton's oxidation. The operating parameters were optimized for the maximum removal of paracetamol and the corresponding removal of Chemical Oxygen Demand (COD). Analysis of paracetamol samples using UV-Vis spectrophotometer and HPLC instrument were carried out.

Material and Methods

Chemicals

Paracetamol Extra pure (98% assay) were purchased from SD Fine Chem. Ltd. (India). Hydrogen Peroxide (H₂O₂) (50% w/w) and Ferrous Sulfate (FeSO₄·7H₂O) were purchased from Merck (India). The chemicals were used as received in the Fenton's Oxidation Process. Hydrochloric acid (HCl, Merck, India, 35% purity), Sulfuric acid (H₂SO₄, Merck, India, 98% purity), Sodium hydroxide (NaOH, Merck, India, 98% purity), were also used in the experiments. Methanol AR grade (Merck, India), Sodium Pentanesulfonate AR grade (Merck, India) and Formic acid AR grade (Merck, India) were used in HPLC analysis. The lateritic soil, for the extraction of iron, was acquired from the National Institute of Technology Karnataka, Surathkal (NITK, India) campus, which is located over laterite soil bed. The iron from laterite soil was extracted using procedure given by Olanipekun (2000)^[28].

Synthetic Paracetamol aqueous solution

The simulated paracetamol aqueous stock solution of 1000 mg/L concentration was prepared with Millipore Elix-3 deionized water every week and stored in the dark at 4° C.

Experimental Procedure

The experiments were conducted at ambient temperature (27±3° C) in batch reactors. A 1000 mL solution of required paracetamol concentration was prepared from the stock paracetamol solution and was taken in a 2 liter reactor. Initial pH of the solution was maintained using 0.1 N H₂SO₄ and 0.1N NaOH. Appropriate amount of Fe²⁺ concentration from the 1000 mg/L stock solution, freshly prepared from FeSO₄·7H₂O, was added to the reactor bath and stirred with magnetic stirrer. Required amount of H₂O₂ was added to the reactor bath to initiate the reaction. For the experiments with iron from laterite soil, pH was adjusted after adding appropriate iron solution, stirred with magnetic stirrer and then H₂O₂ was added. The mixture of paracetamol solution and Fenton's reagent was stirred with magnetic stirrer during treatment. The paracetamol solution samples were taken out for analysis at pre-defined time intervals and filtered through 0.45 µm Millipore filter membrane for COD analysis and also through a 0.45 µm Millipore Syringe filter for determination of paracetamol concentration by using UV-VIS Spectrophotometer and High Performance Liquid Chromatography (HPLC).

Analytical Methods

Paracetamol solutions of concentration 10, 20, 30, 40, 50 mg/L were prepared and UV-VIS spectra were recorded from 190 to 500 nm using UV-VIS double beam spectrophotometer (Systronics-2201). The absorbance peaks of Paracetamol for all the considered concentrations were at wavelength 243 nm. A standard absorbance versus paracetamol concentration calibration curve was prepared by single wavelength mode using 10, 20, 30, 40 and 50 mg/L paracetamol standards. This curve was used to determine the paracetamol concentrations in aqueous solutions during the subsequent experiments. Figure 1 shows the spectra and molecular structure of paracetamol used in this study. Figure 1

The concentration of paracetamol in the aqueous solution at wavelength 243 nm was measured immediately after removal of samples from the reactor using the standard curve, which has already been calibrated with UV-VIS Double beam Spectrophotometer. The pH was measured with a digital pH meter (Lovibond – pH 100). The COD of the samples was determined by closed reflux titrimetric method as per the procedure outlined in the Standard Methods (APHA 2005)^[29]. Final COD was quantitatively corrected for hydrogen peroxide interference according to the correlation equation given by Kang et al. (1999)^[30]. The Iron concentration was measured using Spectrocolorimeter (PC Spectroll, Lovibond) by Thiocyanate-colorimetric Method. The H₂O₂ concentration was determined by iodometric titration method^[31].

HPLC analysis was carried out with reversed-phase Jasco High Performance Liquid Chromatograph fitted with Microbonda 5 µm, 300 x 4.6 mm column at a temperature of 30°C and coupled with a Jasco UV-2075 plus intelligent UV-VIS Photodiode array detector selected at 243 nm, controlled through Jasco Chromatography data system. The mobile

phase employed for paracetamol was 0.1 mg/mL of Paired-Ion Chromatography reagent Sodium Pentanesulfonate (1.74g Sodium Pentanesulfonate + 2 mL Formic acid diluted to 1000 mL with double distilled water) at flow rate of 1.5 mL/minute. The paracetamol solution samples were injected at the rate of 15 μ L and acquisition time was set as 25 minutes.

Results and Discussion

Effect of pH

The pH controls the production rate of hydroxyl radical and concentration of Fe^{2+} . To determine optimal pH, experiments were conducted at different pH values varying from 2 to 5.5 with initial paracetamol concentration of 10 mg/L, $[\text{H}_2\text{O}_2]_0$ 20 mg/L and $[\text{Fe}^{2+}]_0$ 2 mg/L. The maximum paracetamol reduction and COD removal were found to be 77.83% and 75.00% respectively at pH 3. The paracetamol removal efficiency was reduced for the other values of pH. Figure 2

Research findings indicate that the optimum pH of Fenton's Oxidation was independent from characteristics of water and the optimum pH was 3.5^[13] and 3^[32-34]. A similar result of optimum pH 3 was obtained by the present study on Fenton's oxidation of paracetamol solutions and was set for subsequent experiments.

At pH 3, Paracetamol removal was maximum and it may be due to the formation of more $\text{Fe}(\text{OH})^+$ which has much higher activity than Fe^{2+} in Fenton's oxidation^[33]. When pH > 3, oxidation efficiency rapidly decreases due to auto-decomposition of H_2O_2 affecting the production of OH radicals^[33] and deactivation of ferrous catalyst with the formation of ferric hydroxide precipitates^[35]. Also there was a decrease in oxidation potential of hydroxyl radical with increase in the pH value^[36]. When pH < 3, the reaction of H_2O_2 with Fe^{2+} was seriously affected to reduce hydroxyl radical production and water was formed by the reaction of OH radicals with H^+ ions^[36] and also there was an inhibition for the radical forming activity of iron^[35].

Effect of H_2O_2 and Fe^{2+} concentration

Hydrogen peroxide was the basis for the radical generation in Fenton's Oxidation. The hydroxyl radicals either oxidize the pollutant and other intermediates or react with the oxidant itself to cause reduction in pollutant removal efficiency. Hence, an investigation of H_2O_2 consumption and optimization in Fenton's oxidation was vital for using H_2O_2 efficiently and also for the other best possible conditions that were to be found in aforesaid process.

The investigation for optimization of hydrogen peroxide concentration was carried out by varying H_2O_2 concentration from 5 to 50 mg/L, keeping the iron concentrations constant (0 – 1.25 mg/L) for [paracetamol]₀ 10 mg/L at solution pH 3. The maximum paracetamol reduction was 87.98% and the corresponding COD removal was 79.17% at H_2O_2 concentration of 30 mg/L and $[\text{Fe}^{2+}]_0$ of 0.5 mg/L after a reaction time of 24 hours. Figure 3

Both the Paracetamol reduction and COD removal from the aqueous solution were significantly improved even with the addition of very low concentrations of Fe^{2+} to H_2O_2 . The maximum paracetamol reduction and COD removal were observed to be 9.10% and 8.33% respectively with oxidation

by H_2O_2 alone. But the paracetamol reduction and COD removal were increased up to 87.98% and 79.17% respectively with the addition of Fe^{2+} to the solution. Figure 3(a) -3(b) shows the variations in percent paracetamol reduction and COD removal under the different conditions of the Fe^{2+} and H_2O_2 maintaining pH of 3, reaction time of 24 hours. The max paracetamol reduction and COD removal were observed to be 87.98% and 79.17% respectively at 0.5 mg/L Fe^{2+} concentration. These results are in agreement with the literature, where in an increase in Fe^{2+} concentration of Fenton's reagent increases OH radical production and hence the degradation and mineralization^[34]. It has also been observed that at higher Fe^{2+} concentrations the paracetamol and COD removals were reduced. This may be due to the ferrous ion inhibition that occurs when high concentration of Fe^{2+} was present in the system and Fe^{2+} itself can react with OH radicals resulting the scavenging of OH radical.

The experiments were conducted to investigate optimum hydrogen peroxide concentration with laterite iron in Fenton's reagent. The hydrogen peroxide concentration was varied from 10 to 50 mg/L for Laterite iron concentration varying from 0.25 to 1.25 mg/L, initial paracetamol concentration 10 mg/L at initial solution pH of 3. It was observed that the maximum paracetamol reduction was 80.12% and the corresponding COD removal was 75.00% at H_2O_2 concentration of 30 mg/L and [Laterite iron]₀ of 0.75 mg/L after a reaction time of 24 hours. Figure 3(c) -3(d) shows the variations in percent paracetamol reduction and COD removal under the different doses of the Laterite iron and H_2O_2 maintaining pH of 3, reaction time of 24 hours.

The removal efficiency increases up to a maximum level with increase in H_2O_2 concentration and further increase in the H_2O_2 concentration decreases the removal efficiency. Similarly, both the paracetamol reduction and COD removal from the aqueous solution were increased with addition of iron extracted from the lateritic soil to a maximum level and then decreases with increase in iron concentrations. This may be due to the presence of maximum number of OH radicals at the optimum concentration of H_2O_2 and laterite iron.

In the Fenton's oxidation of paracetamol, the paracetamol reduction and COD removals were less for the laterite iron when compared with iron from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. This may be due to incomplete degradation and mineralization of paracetamol and the presence of intermediates in the aqueous solution. Further, the lesser removal efficiencies when laterite iron was used may be because of the presence of chlorides, which have scavenged the free OH radicals.

In accordance with the results obtained, the optimum ratio of $[\text{H}_2\text{O}_2]_0 : [\text{Fe}^{2+}]_0 :: 60:1$ (w/w) using iron from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and the optimum ratio of $[\text{H}_2\text{O}_2]_0 : [\text{Laterite iron}]_0 :: 40:1$ (w/w) using iron from lateritic soil were considered for subsequent experiments on Fenton's oxidation of paracetamol.

Effect of initial Paracetamol concentration

Experiments were conducted to study the effect of initial paracetamol concentrations (10, 20, 30, 40 and 50 mg/L) on the Fenton's oxidation process. For all the paracetamol concentrations, the optimum ratio of $[\text{Paracetamol}]_0 / [\text{H}_2\text{O}_2]_0$ was observed to be 1:3 (w/w) and the optimum ratio of $[\text{H}_2\text{O}_2]_0 / [\text{Fe}^{2+}]_0$ was observed to be 60:1 (w/w) at pH 3 after a reaction time of 24 hours (data not shown here). Further experiments were conducted with the optimized operating

conditions for a reaction time of 4 hours. The paracetamol reduction was increased and COD removal was decreased with the increase in initial concentration of paracetamol. This result is comparable with the literature, where COD removal of pharmaceutical wastewater by Fenton's Oxidation is more for the lower initial concentrations of drugs [13, 34]. Figure 3 (e)-3(f) shows the variations in percent paracetamol reduction and COD removals at $[\text{Paracetamol}]_0/[\text{H}_2\text{O}_2]_0$ ratio 1:3 (w/w), $[\text{H}_2\text{O}_2]_0/[\text{Fe}^{2+}]_0$ ratio 60:1 (w/w), pH 3 for 240 minutes of reaction time. 82.73% of Paracetamol reduction and 77.08% of COD removal were observed for 10 mg/L initial concentration of paracetamol, at H_2O_2 of 30 mg/L, Fe^{2+} of 0.5 mg/L in 240 minutes of reaction time.

A set of similar experiments were conducted using the laterite iron in Fenton's oxidation to study the effect of initial paracetamol concentration. The initial paracetamol concentration was varied from 10 to 50 mg/L. For all the initial paracetamol concentrations, the optimum ratio of $[\text{paracetamol}]_0/[\text{H}_2\text{O}_2]_0$ was observed to be 1:3 (w/w) and $[\text{H}_2\text{O}_2]_0/[\text{Laterite iron}]_0$ ratio was observed to be 40:1 (w/w) at pH 3 after a reaction time of 24 hours (data not shown here). The paracetamol removal was increased and COD removal was decreased with an increase in initial concentration of paracetamol. It has also been observed that paracetamol removals, after 60 minute of reaction time at all the initial concentrations of the paracetamol, the removal efficiencies reached the maximum level gradually. Figure 3(g)-3(h) shows the variations in percent paracetamol reduction and COD removals for $[\text{paracetamol}]_0/[\text{H}_2\text{O}_2]_0$ ratio 1:3 (w/w), $[\text{H}_2\text{O}_2]_0/[\text{Laterite iron}]_0$ ratio 40:1 (w/w) at pH of 3 in 240 minutes of reaction time. 77.23% of Paracetamol and 70.83% of COD were removed for 10 mg/L initial concentration of paracetamol, at H_2O_2 concentration of 30 mg/L, Laterite iron concentration of 0.75 mg/L in 240 minutes of reaction time.

By analyzing the results, it was observed that the removal efficiencies were less in the case of laterite iron when compared with iron from ferrous sulfate in the Fenton's oxidation of paracetamol process.

HPLC Analysis

HPLC analysis was carried out for the paracetamol samples of 10 mg/L concentration treated at optimum conditions pH 3, $[\text{H}_2\text{O}_2]_0$ 30 mg/L, $[\text{Fe}^{2+}]_0$ 0.5 mg/L and $[\text{Laterite iron}]_0$ 0.75 mg/L, UV irradiation time 240 minutes. The Figure 4 shows the chromatogram of paracetamol before and after treatment using ferrous sulfate and laterite iron. Paracetamol standard peak was absent after treatment in both the cases when ferrous sulfate and laterite iron is used. After treatment, one intermediate was observed in case of ferrous sulfate at 6.167 minutes but 10 intermediates in small quantities between 5 and 20 minutes were observed in case of laterite iron. At optimum conditions, it may be presumed that complete degradation of paracetamol was observed with both ferrous sulfate and laterite iron. Figure 4

In the study on oxidation of paracetamol by TiO_2/UV , Dalmazio et al. (2008) [25] reported a degradation of 90% in 160 minutes and Yang et al. (2008) [26] reported a degradation of 90% in 160 minutes. Brillas et al. (2005) [21] and Sires et al. (2006) [22], in the oxidation of paracetamol by electrochemical methods, reported a mineralization of 98% -

100% in 360 minutes and Skoumal et al. (2006) [24] reported 83% mineralization in 240 minutes. Andreozzi et al. (2003) [23] reported mineralization of paracetamol as 30% in 120 minutes by Ozonation and 40% in 120 minutes by $\text{H}_2\text{O}_2/\text{UV}$. Isriebl et al. (2009) [27] reported 39% mineralization of paracetamol in 480 minutes by Sonolysis. But in the present study, 100% of paracetamol degradation and 77% COD removal using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 100% of paracetamol degradation and 71% COD removal using laterite iron were observed in 240 minutes of reaction time. Hence, the Fenton Oxidation of paracetamol in water is efficient and reliable over the aforesaid methods. Fenton's process may effectively be applied to paracetamol industry and the process can also be applied in-situ for the treatment of paracetamol in surface water, ground water and earth at the geological strata containing lateritic soil.

Conclusion

Paracetamol degradation of 100% was observed with HPLC analysis in both the cases where ferrous sulfate and laterite iron was used in Fenton's reagent. The COD removal efficiency for iron extracted from laterite soil was marginally less than that of iron from ferrous sulfate. At optimum conditions, for the initial concentration of paracetamol 10 mg/L with a reaction time of 5 minutes, the percent paracetamol reductions were 72.96 and 69.15; the percent COD removals were 60.42 and 52.08 for the iron from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and Lateritic soil respectively. The degradation and mineralization of paracetamol for laterite iron in Fenton's oxidation of paracetamol was lower than that of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ due to the presence of chloride anions that inhibit the production of OH radicals in the system. Fenton's Oxidation Process is an effective treatment method for the removal of paracetamol in aqueous solutions and hence it may be successfully applied to treat paracetamol industrial effluent and also may be applied in-situ for the treatment of paracetamol in surface water, ground water and lateritic soils.

Acknowledgement

The authors gratefully acknowledge the esteemed pharmaceutical company, SeQuent Scientific Limited, 120 A&B, Industrial area, Baikampady, New Mangalore, India, for their HPLC analytical services.

References

- [1] Daughton C.G. and Ternes T. A., Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change?, *Environ. Health Perspect.*, **107**(6), 906-942 (1999)
- [2] Buxton H. and Kolpin D. W., Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, Fact Sheet FS-027-02, *United States Geological Survey*, (2002)
- [3] Vieno N.M., Harkki H., Tuhkanen T. and Kronberg L., Occurrence of Pharmaceuticals in River Water and Their Elimination in a Pilot-Scale Drinking Water Treatment Plant, *Environ. Sci. Technol.*, **41**(14), 5077-5084 (2007)
- [4] Ternes T. A., Joss A. and Siegrist H., Scrutinizing pharmaceuticals and Personal Care Products in Wastewater Treatment, *Environ. Sci. Technol.*, 392A-399A (2004)

- [5] Zhou J. L., Zhang Z. L., Banks E., Grover D. and Jiang J. Q., Pharmaceutical residues in wastewater treatment works effluents and their impact on receiving river water, *J. Hazard. Mater.* xxx, in press (2008)
- [6] Westerhoff P., Yoon Y., Snyder S. and Mert E., Fate of Endocrine-Disruptor, Pharmaceutical and Personal Care Product Chemicals during Simulation Drinking Water Treatment Processes, *Environ. Sci. Technol.*, **39**(17), 6649-6663 (2005)
- [7] Musson S.E. and Townsend T. G., Pharmaceutical compound content of municipal solid waste, *J. Hazard. Mater.*, **162**, 730-735 (2009)
- [8] Klavarioti M., Mantzavinos D. and Kassinos D., Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes - Review article, *Environ. Int.*, **35**, 402-417 (2009)
- [9] Boxall A.B.A., The environmental side effects of medication, *EMBO reports*, **5**(12), 1110-1116 (2004)
- [10] Bolong N., Ismail A.F. and Matsura T., A review of the effects of emerging contaminants in wastewater and options for their removal, *Desalination*, **239**, 229-246 (2009)
- [11] Collier A.C., Pharmaceutical contaminants in potable water: Potential concerns for pregnant women and children, *Eco. Health*, **4**, 164-171 (2007)
- [12] Zazo J. A., Cases J. A., Mohedano A. F., Gilarranz M. A. and Rodriguez J. J., Chemical Pathway and Kinetics of Phenol Oxidation by Fenton's Reagent, *Environ. Sci. Technol.*, **39**, 9295-9302 (2005)
- [13] Tekin H., Bilkay O., Ataberk S. S., Balta T. H., Ceribasi I. H., Sanin F. D., Dilek F. B. and Yetis U., Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater, *J. Hazard. Mater.*, **136**, 258-265 (2006)
- [14] Neyens E. and Baeyens J., A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.*, **98**, 33-50 (2003)
- [15] Siedleck E.M. and Stepnwski P., Phenols degradation by Fenton Reaction in the presence of Chlorides and Sulfates, *Polish J. Env. Studies*, **14** (6), 823-828 (2005)
- [16] Troung G.L., De Laat J. and Legue B., Effect of chloride and sulfate on the rate of oxidation of ferrous ion by H₂O₂, *Water Res.*, **38**, 2383 (2004)
- [17] Laat J. D., Troung G. L. and Legue B., A comparative study of the effects of chloride, sulfate and nitrate ions on the rates of decomposition of H₂O₂ and organic compounds by Fe(II)/H₂O₂ and Fe (III)/H₂O₂, *Chemosphere*, **55**, 715 (2004)
- [18] Hiremath D. C., Hiremath C.V. and Nandibewoor S.T., Oxidation of Paracetamol Drug by a New Oxidant Diperiodatoargentate (III) in Aqueous Alkaline Medium, *E-J. Chem.*, **3**(10), 13-24 (2006)
- [19] Ternes T. A., Occurrence of drugs in German Sewage Treatment Plants and Rivers, *Water Res.*, **32**, 3245-3260 (1998)
- [20] Roberts P. H. and Thomas K. V., Occurrence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment, *Sci. Total Environ.*, **356**(1-3), 143-153 (2006)
- [21] Brillas E., Sires I., Arias C., Cobot P. L., Centellas F., Rodriguez R. M. and Garrido J. A., Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode, *Chemosphere*, **58**, 399-406 (2005)
- [22] Sires I., Garrido J. A., Rodriguez R. M., Cabot P. L., Centellas F., Arias C. and Brillas E., Electrochemical Degradation of Paracetamol from Water by Catalytic Action of Fe²⁺, Cu²⁺, and UVA Light on Electro generated Hydrogen Peroxide, *J. Electrochem. Soc.*, **153** (1), D1-D9 (2006)
- [23] Andreozzi R., Caprio V., Marotta R. and Vogna D., Paracetamol oxidation from aqueous solutions by means of ozonation and H₂O₂/UV system, *Water Res.*, **37**, 993-1004 (2003)
- [24] Skoumal M., Cabot P. L., Centellas F., Arias C., Roderiguez R. M., Garrio J. A. and Brillas E., Mineralization of paracetamol by ozonation catalyzed with Fe²⁺, Cu²⁺ and UVA light, *J. appl. Catal.*, **66**, 228-240 (2006)
- [25] Dalmazio I., Alves T. M. A. and Augusti R., An Appraisal on the Degradation of Paracetamol by TiO₂/UV System in Aqueous Medium, Product Identification by Gas Chromatography-Mass Spectrometry (GC-MS), *J. Braz. Chem. Soc.*, **19** (1), 81-88 (2008)
- [26] Yang L., Yu L. E. and Ray M. B., Degradation of paracetamol in aqueous solutions by TiO₂ photocatalysis, *Water Res.*, **42**, 3480-3488 (2008)
- [27] Isariebel Q. P., Carine J. L., Javier J. H. U., Marie W. A. and Henri D., Sonolysis of levodopa and Paracetamol in aqueous solutions, *Ultrason. Sonochem.*, **16**, 610-616 (2009)
- [28] Olanipekun E. O., Kinetics of leaching laterite, *Int. J. Miner. Process.*, **60**, 9-14 (2000)
- [29] APHA, AWWA, WEF, Standard methods for the Examination of Water and Wastewater, 21st ed., Washington, DC. USA, (2005)
- [30] Kang Y. W., Cho M. J. and Hwang K. Y., Correction of Hydrogen Peroxide interference on Standard Chemical Oxygen demand test. *Water Res.*, **33**(5), 1247-1251 (1999)
- [31] Kolthoff. I. M., *Chem. Weekblad.*, **17**, 197(1920)
- [32] Hsueh C. L., Huang Y. H., Wang C. C. and Chen C. Y., Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, *Chemosphere*, **58**, 1409-1414 (2005)
- [33] Badawy M. I. and Ali M. E. M., Fenton's peroxidation and coagulation processes for the treatment of combined industrial and domestic wastewater, *J. Hazard. Mater.*, **136**, 961-966 (2006)
- [34] Yilmaz T., Aygun A., Berkay A. and Nas B., Removal of COD and colour from young municipal landfill leachate by Fenton process, *Environ. Technol.*, **31**(14), 1635-1640 (2010)
- [35] Luis A. D., Lombranda J. I., Varona F. and Menendez A., Kinetic Study and hydrogen peroxide consumption of phenolic compounds oxidation by Fenton's reagent, *Korean. J. Chem. Eng.*, **26**(1), 48-56 (2009)

[36] Lucas M. S. and Peres J. A., Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton

oxidation, *Dyes and Pigm.*, **71**, 236-244 (2006)

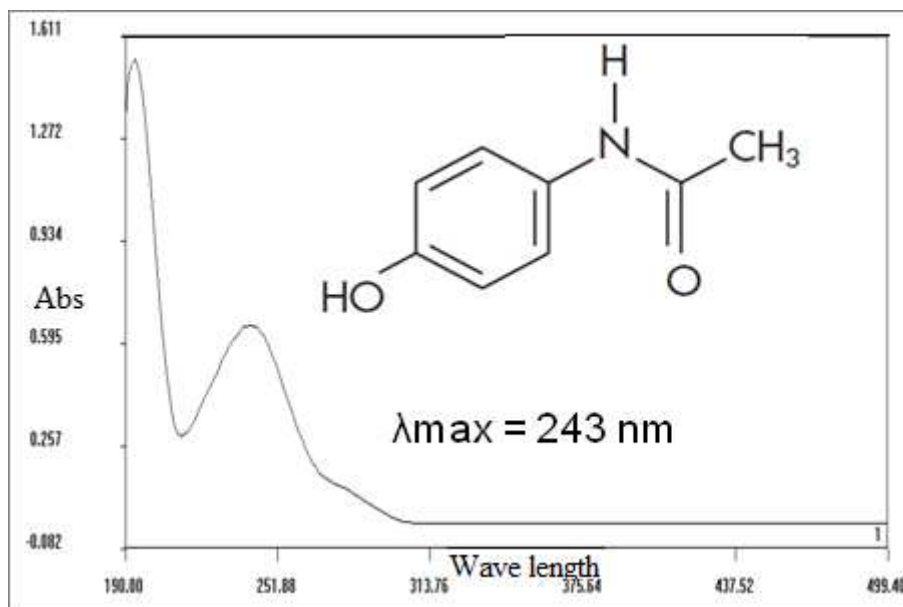


Figure 1: UV-VIS spectra with chemical structure of paracetamol compound

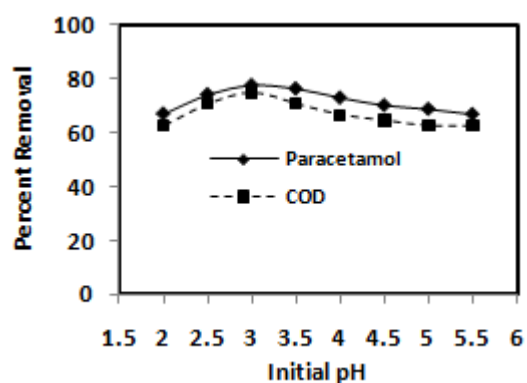


Figure 2: Percent paracetamol reduction and COD removal at different pH; $[\text{paracetamol}]_0 = 10 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 20 \text{ mg/L}$ and $[\text{Fe}^{2+}]_0 = 2 \text{ mg/L}$

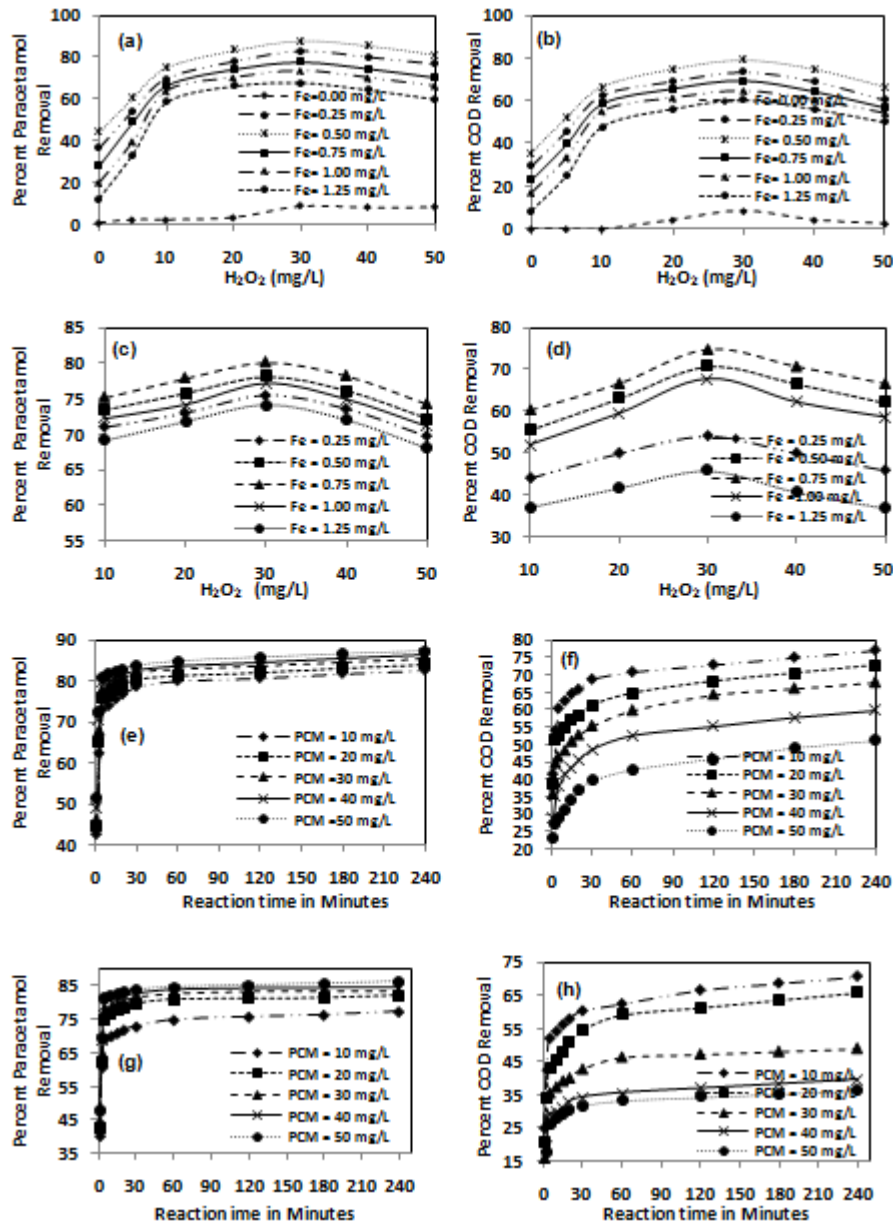


Figure 3: Variations in (a) $[Fe^{2+}]$ - percent paracetamol reduction, (b) $[Fe^{2+}]$ - percent COD removal, (c) [Laterite iron] - percent paracetamol reduction and (d) [Laterite iron] - percent COD removal for $[H_2O_2]_0$ 10-50 mg/L; (e) percent paracetamol reduction and (f) percent COD removal at $[Paracetamol]_0 / [H_2O_2]_0$ ratio 1:3 (w/w) and $[H_2O_2]_0 / [Fe^{2+}]_0$ ratio 60:1 (w/w) (g) percent paracetamol reduction and (h) percent COD removal at $[paracetamol]_0 / [H_2O_2]_0$ ratio 1:3 (w/w) and $[H_2O_2]_0 / [Laterite\ Iron]_0$ ratio 40:1 (w/w) for 240 minutes of reaction time (pH 3, $[paracetamol]_0$ 10 mg/L)

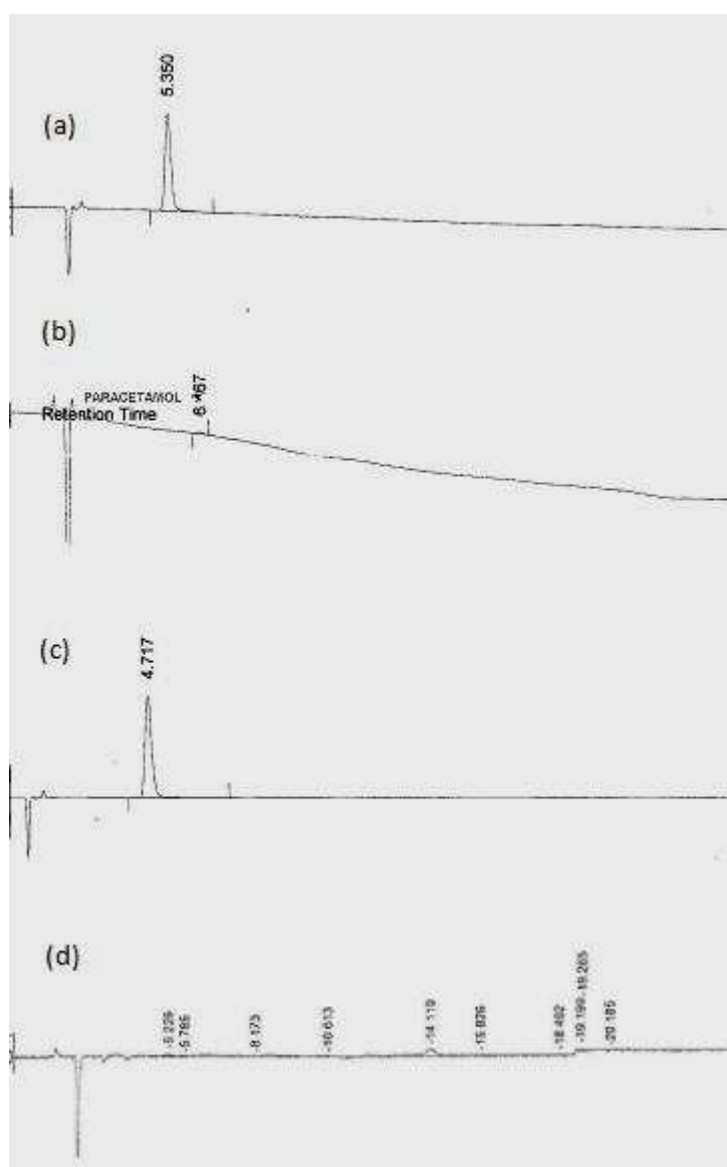


Figure 4: HPLC chromatogram for [Paracetamol]₀ 10 mg/L, pH 3, [H₂O₂]₀ 30 mg/L, and (a) paracetamol standard before treatment - [Fe²⁺]₀ = 0.5 mg/L (b) Sample after treatment- [Fe²⁺]₀ = 0.5 mg/L (c) paracetamol standard before treatment - [Laterite iron]₀ 0.75 mg/L (d) Sample after treatment- [Laterite iron]₀ 0.75 mg/L , reaction time 240 minutes