

## Degradation of Para-Phenylenediamine in Aqueous Solution by Photo-Fenton Oxidation Processes

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### Abstract

In this research Photo-Fenton Oxidation of Para-Phenylenediamine (PPD) in aqueous solution by UV/Fenton's reagent (Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>) was investigated. Experiments were conducted in a batch reactor, at pH 3.5 and at 25°C with a source of UV-C light. The effects of different reaction parameters such as initial PPD concentration, pH of the solution, ferrous concentration, Hydrogen peroxide concentration, on the oxidative degradation of PPD were measured. Final concentration of PPD and COD of the solution after treatment were determined to know degree of degradation of the compound. Iron source used for photo-Fenton's oxidation were Ferrous Sulphate (FeSO<sub>4</sub>.7H<sub>2</sub>O). The optimum conditions established by Fenton's oxidation without UV, were considered for this investigation. Only the maximum removal conditions were tried with the UV for reaction time of 3 hours. The results showed that under optimum experimental conditions, the pH 3.5, 50 mg/L H<sub>2</sub>O<sub>2</sub>, 3 mg/L Fe<sup>2+</sup> and UV reaction time of 3 hours, the initial concentration 10 mg/L of PPD was reduced by 71.20% with 65.89% COD removal. Likewise the removal efficiencies for PPD concentration of 20, 30, 40 and 50 mg/L keeping the same proportion of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> dosage (with ratios of PPD:Fe<sup>2+</sup>:H<sub>2</sub>O<sub>2</sub>::10:1:16.7) were investigated and the results showed, PPD removal were 65.10, 61.23, 58.34 and 54.26% and COD removal was 61, 54, 52 and 50.32% respectively. From the results obtained it can be concluded that Fenton's reagent favours the lower concentration of Phenylenediamines and UV-C assisted photo-Fenton showed that the photo-Fenton process was very effective than the normal Fenton process.

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## INTRODUCTION

Para-Phenylenediamine (PPD) is a non-biodegradable organic chemical that is widely used as ingredient in various product including hair dyes. Sensitization to PPD is a well-known cause for Allergic Contact Dermatitis (ACD). Moreover, ACD because of PPD containing skin paints (temporary tattoos) are increasingly reported (Badawy *et al.*, 2006). Up to now, it is not completely understood why certain individuals are more likely to develop ACD after exposure to PPD than others. Genetic factors influencing the sensitization or reactivation process may have impact on the individual susceptibility (Blcmeke *et al.*, 2008). Many chemical treatment techniques have been emerged in the last few decades to degrade non-biodegradable organic pollutants. Among these treatment techniques, the Advanced Oxidation Processes (AOP) appears to be promising and reported to be effective for the degradation of non-biodegradable organic pollutants like PPD in water.

The AOP have proved capable of degrading the Para-Phenylenediamine from aqueous solutions (Klavarioti *et al.*, 2009). These Processes are based on the generation of hydroxyl radical, which is a powerful oxidant. Among AOPs, Fenton and Photo-Fenton Oxidation processes have emerged as the most promising methods for the

treatment of organic non-biodegradable pollutants (Manu *et al.*, 2011). In a comprehensive review, Neyens and Baeyens (2003) have indicated that the Fenton's Oxidation is very effective in the removal of many hazardous organic pollutants from water and wastewaters.

The photo-Fenton reaction involves irradiation with solar or UV light which significantly increases the rate of pollutant degradation by photo reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>. Fenton's reaction generates hydroxyl radicals and photo-Fenton reactions reduce the Fe<sup>3+</sup> to Fe<sup>2+</sup>, thus leading to production of additional OH radicals and continuous regeneration of Fe<sup>2+</sup> in a catalytic way (Sun and Pignatello, 1993). It is also observed that the additional amounts of OH radicals are also produced from the direct photolysis of H<sub>2</sub>O<sub>2</sub> (Laat *et al.*, 1999).

Among all these advanced oxidation processes use combinations of oxidants, ultraviolet irradiation and catalysts to generate hydroxyl radicals (OH<sup>•</sup>) in solutions and have attracted interest for the degradation of Phenylenediamines. Among all these Fenton reactions (mainly Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) generates hydroxyl radicals (OH<sup>•</sup>) by means of the reaction of H<sub>2</sub>O<sub>2</sub> with ferrous ion, which is

efficient and low cost method, taking place at room temperatures and at atmospheric pressure compared to all other advanced oxidation processes (Manu *et al.*, 2011).

Fenton oxidation systems have two limitations: (1) a large production of iron sludge, and (2) a slow reduction of ferric ions by  $\text{H}_2\text{O}_2$  in their application (Walling, 1975; De Laat and Gallard, 1999). However, Photo-Fenton Oxidation was suggested to overcome the limitations of the Fenton oxidation systems.

This study focused on the removal efficiency of Para-Phenylenediamine and to optimize the photo-Fenton's dosage, pH, with respect to PPD concentration. Photo-Fenton's reagent is reported to oxidize all kinds of organic contaminants and hence its evaluation could be a worthwhile effort.

## MATERIALS AND METHODS

### Materials

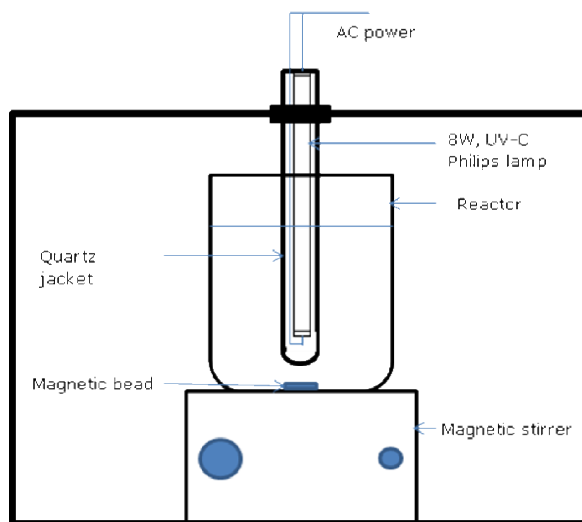
The materials include Para-Phenylenediamine was purchased from Merck manufacturer, India and was used as obtained. Hydrogen Peroxide (50%w/w) and Ferrous Sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) are purchased from Merck. The chemicals were used as received in the Fenton's Oxidation Process. Hydrochloric acid (HCl, 35% purity), Sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98% purity), Sodium hydroxide (NaOH, 98% purity), were also used in the experiments. PPD aqueous stock solution of 1000 mg/L concentration is prepared every week with Millipore Elix-3 deionized water and stored in the dark at  $4^\circ\text{C}$ .

### Experimental Procedure

The oxidation experiments were carried out at ambient temperature ( $27 \pm 3^\circ\text{C}$ ) in batch reactors. Initially, the reaction conditions like pH,  $\text{H}_2\text{O}_2$  dosage, and  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$  ratio were optimized in the Fenton oxidation of PPD and the further Fenton and photo-Fenton experiments were conducted with the optimum conditions. The effect of initial PPD concentration on the degradation and mineralization of PPD by both Fenton oxidation and UV-C Fenton oxidation were evaluated and the results were compared. PPD samples were analyzed using UV-VIS double beam spectrophotometer.

All the Fenton and photo-Fenton experiments were carried out in batch reactors. Figure 1 shows the photo-reactor, consists of enclosed chamber comprising a reactor (2L volume beaker), 8W UV-C Philips lamp covered with a quartz jacket and connected to AC power, magnetic stirrer. A 1000 mL solution of required PPD concentration is prepared from the stock PPD solution and was taken in the 2-liter reactor. The intrinsic pH of the wastewater was 6.32 and the Initial pH 3.5 of the solutions was maintained using 0.1 N  $\text{H}_2\text{SO}_4$  and 0.1N NaOH. Required amount of  $\text{H}_2\text{O}_2$  was added to the reactor bath to initiate the reaction. The mixture of PPD solution and Fenton's reagent is stirred with magnetic stirrer during treatment.

The PPD solution samples were taken out for analysis at pre-defined time intervals, filtered through 0.45- $\mu\text{m}$  Millipore filter membrane for COD analysis, and filtered through a 0.45  $\mu\text{m}$  Millipore Syringe filter for determination of PPD concentration by using UV-VIS spectrophotometer analysis.



**Figure 1:** Schematic representation of the photochemical reactor

### Analytical Methods

UV-VIS spectrum is recorded from 190 to 500 nm using UV-VIS spectrophotometer and the absorbance peak of PPD is observed to be at wavelength 233.4nm. The concentration of PPD in the aqueous solution at wavelength 233.4 nm is 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 is measured with a digital pH meter (Lovibond- pH 100). The COD of the samples is determined by closed reflux titrimetric method as per the procedure outlined in the Standard Methods (APHA, 2005).

The initial COD before treatment was due to PPD in synthetic wastewater and the COD after treatment was due to residual PPD if present and other reaction intermediates, if any, present in the aqueous solution. Final COD is quantitatively corrected for  $\text{H}_2\text{O}_2$  interference according to the correlation equation given by Kang *et al.* (1999). The Iron concentration is measured by Thiocyanate colorimetric Method using Spectrocolorimeter (PC-Spectroll, Lovibond). The  $\text{H}_2\text{O}_2$  concentration was determined by iodometric titration method (Kolthoff, 1920).

## RESULTS AND DISCUSSION

In this present study laboratory scale experiments were conducted for PPD using ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) as iron source in the Photo-Fenton's oxidation. Synthetic PPD solutions were prepared at different initial concentrations of 10, 20, 30, 40 and 50 mg/L.

### Effect of pH

Effect of pH with Fenton's reagent was studied for pH range of 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5. Experiments were conducted by adding the ratio of  $\text{H}_2\text{O}_2$ :  $\text{Fe}^{2+}$ :10:1 ( $\text{H}_2\text{O}_2$ :  $\text{Fe}^{2+}$ =66:6.6mg/L) to PPD concentration of 10 mg/L with a reaction mixture volume of 1000ml. The maximum PPD reduction and COD removal are found to be 56% and 71% respectively at pH 3.5 as shown in figure 2. The PPD removal efficiencies were less for the other values of pH.

At pH 3.5, PPD removal is maximum and it might be due to the formation of more  $\text{Fe}(\text{OH})^+$  which has much higher activity than  $\text{Fe}^{2+}$  in Fenton's oxidation (Badawy *et*

*al.*, 2006). When pH >3, oxidation efficiency rapidly decreases due to auto- decomposition of H<sub>2</sub>O<sub>2</sub> affecting the production of OH<sup>•</sup> radicals (Badawy and Ali, 2006) and deactivation of ferrous catalyst with the formation of ferric hydroxide precipitates (Luis *et al.*, 2009). When pH <3, the reaction of H<sub>2</sub>O<sub>2</sub> with Fe<sup>2+</sup> was seriously affected to reduce hydroxyl radical production and water is formed by the reaction of OH radicals with H<sup>+</sup> ions (Lucas and Peres 2006).

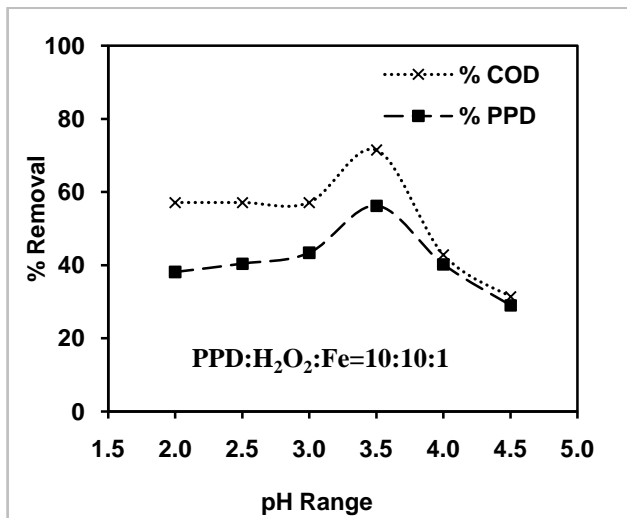


Figure 2: Effect of pH on PPD and COD removal during photo-Fenton's oxidation

**Effect of UV Radiation**

Kinetic studies for the degradation for removal of PPD were conducted for 24 hours and the reaction time was optimized. In the Figure 3, it is seen that PPD and COD removal increased till 180 minutes (3 hours) and there was no much degradation later on. Hence to optimize the photo degradation of PPD in photo-Fenton's oxidation the irradiation was taken as 180 minutes for the rest of the experiments. This proved to be economical and efficient than Fenton's Oxidation (Dark Fenton reactions).

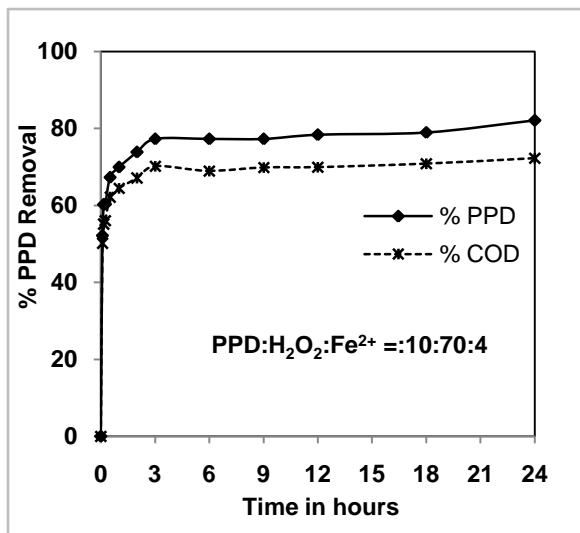


Figure 3: Kinetic studies for the degradation of PPD and COD for 24 hours UV radiation

**Photo Degradation of PPD with Ferrous Sulphate Iron as Catalyst in PFO**

After optimizing the favourable pH, a wide range of Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> ratios were investigated for the effective degradation of the compounds. The following table 1 shows the various doses of Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> designed for PFO of PPD

Table 1: Design of experiments for degradation of PPD

C <sub>0</sub> Mg/L	[pH] <sub>0</sub>	UV- Time (in min)	[H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> mg/L	[Fe <sup>2+</sup> ] <sub>0</sub> mg/L
10	3.5	180	50	3
20	3.5	180	100	6
30	3.5	180	150	9
40	3.5	180	200	12
50	3.5	180	250	15

**Effect of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> in Photo-Fenton's Oxidation of PPD**

The dosage of hydrogen peroxide and iron concentrations applied is shown in figure 4 and the respective PPD removal in the Fenton's oxidation. The figure 4 shows that for PPD concentration of 10 mg/L, maximum degradation was at 50 mg/L of H<sub>2</sub>O<sub>2</sub> and 3 mg/L of Fe<sup>2+</sup>.

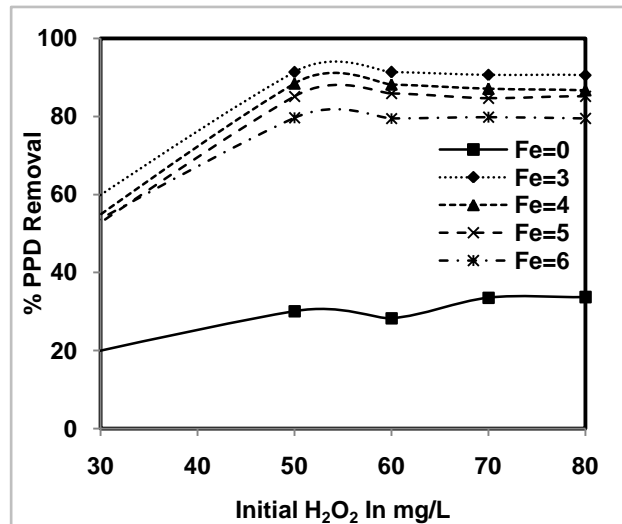
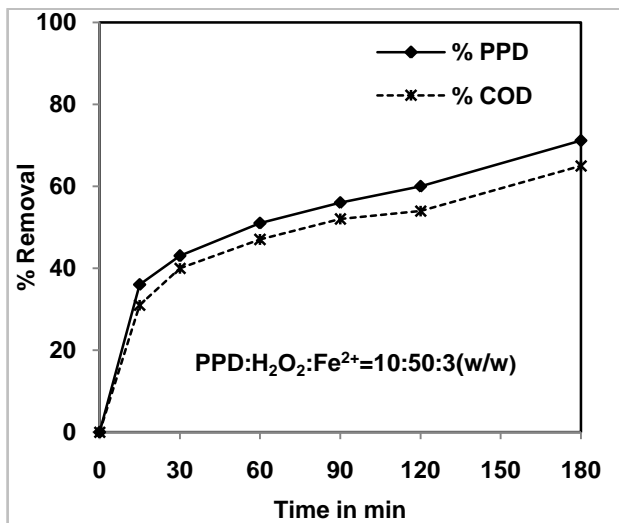


Figure 4: Plot of PPD removal of initial concentration 10 mg/L against various doses of H<sub>2</sub>O<sub>2</sub> and iron

**PPD and COD Removal at Different Initial Concentrations of PPD 10, 20, 30, 40 and 50 mg/L against Various Dosages of UV Radiation in PFO**

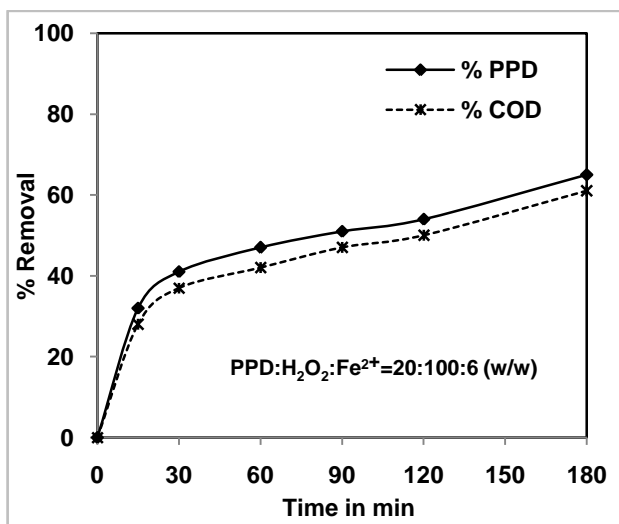
PPD concentration of 10 mg/L, maximum degradation was at 50 mg/L of H<sub>2</sub>O<sub>2</sub> and 3 mg/L of Fe<sup>2+</sup> and UV dosage of 180 minutes. For initial PPD concentration of 10mg/L, at a ratio of Fe<sup>2+</sup>:H<sub>2</sub>O<sub>2</sub>::1:16.67 removal achieved was 71.20% with 65.89% of COD removal. This was the highest removal achieved in PFO of PPD. The other high ranges of Fe<sup>2+</sup> did not prove to be efficient, because excessive ferrous ions can be dominant scavengers of hydroxyl radicals generated during PFO (Tang *et al.*, 1996 and Walling, 1975).



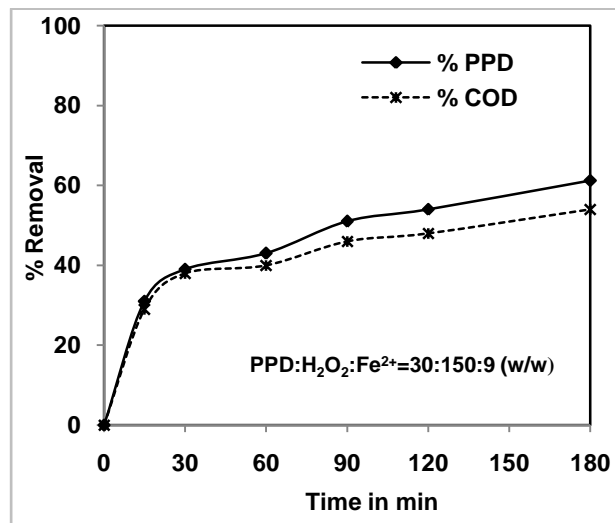
**Figure 5:** Plot of PPD and COD removal for 10 mg/L PPD concentration against various dosages of UV radiation

For PPD concentration of 20 mg/L, maximum degradation was at 100 mg/L of H<sub>2</sub>O<sub>2</sub> and 6 mg/L of Fe<sup>2+</sup> and UV dosage of 180 minutes resulting in 65.10% PPD with 61.8% of COD removal as shown in Figure 6.

The Figure 7 shows that the increase in initial concentration of PPD, degradation rates decrease. This is because a relatively lower concentration of OH<sup>•</sup> results from the increasing concentration of PPD while the dosage of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> remains the same, which leads to a decreasing of the degradation efficiency of PPD. A higher concentration increases the number of pollutant molecules, but not the HO<sup>•</sup> radical concentration, and so the removal rate diminishes (Marco, 2009). A maximum of 61.23% PPD removal and 54.59% COD removal were achieved at H<sub>2</sub>O<sub>2</sub> 150 mg/L and Fe<sup>2+</sup> 9 mg/L and UV dosage of 180 minutes.



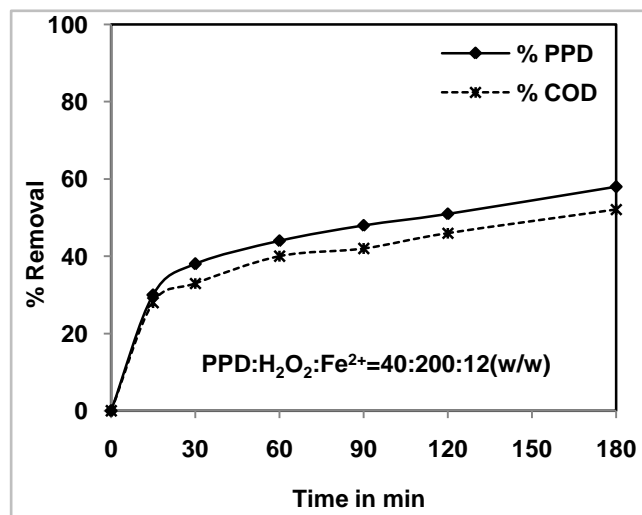
**Figure 6:** Plot of PPD and COD removal for 20 mg/L PPD concentration against various dosages of UV radiation.



**Figure 7:** Plot of PPD and COD removal for 30 mg/L PPD concentration against various dosages of UV radiation

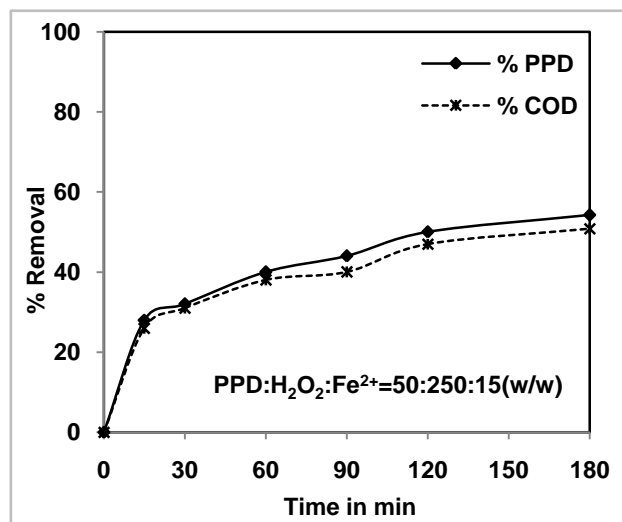
Degradation studies for the PPD concentration 40 mg/L resulted in decrease in removal rates. At low concentration of pollutants, the percentage conversion is higher compared to that at higher concentration (Rathi *et al.*, 2003). A maximum of 58.12% PPD removal and 52.84% COD removal were achieved at H<sub>2</sub>O<sub>2</sub> 200 mg/L and Fe<sup>2+</sup> 12 mg/L and UV dosage of 180 minutes as shown in figure 8. However there was no significant improvement in removal efficiencies.

Similarly for PPD initial concentrations of 50 mg/L, PPD removal was decreased to 54.26% with COD removal of 50.60%. The ratio of Fe<sup>2+</sup>:H<sub>2</sub>O<sub>2</sub>::1:16.67 as shown in the figure 9 which is same for all the initial concentrations of PPD.



**Figure 8:** Plot of PPD and COD removal for 40 mg/L PPD concentration against various dosages of UV radiation.

This indicates that the PFO of Para phenylenediamines is best at lower concentrations, although there is an increase in Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> concentrations in equal proportion to the initial concentration. Also the presence of excess of Fenton's reagent itself is a hindrance to effectiveness of Photo Fenton Oxidation for pollutant removal. The results obtained for higher concentrations of PPD were not encouraging.



**Figure 9:** Plot of PPD and COD removal for 50 mg/L PPD concentration against various dosages of UV radiation

## CONCLUSIONS

From the results obtained from the study, it can be concluded that Fenton's reagent favours at the lower concentration of PPD. UV-Fenton process is observed to be an effective treatment method over Fenton process for the removal of Para Phenylenediamines in aqueous solutions. Photo Fenton's oxidation process may be applied *in-situ* for the treatment of Para Phenylenediamines in surface and ground water.

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