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 (Fe2+ and H2O2) 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 (FeSO4.7H2O). 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 H2O2, 3 mg/L Fe2+ 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 H2O2 and Fe2+ dosages (with ratios of PPD:Fe2+:H2O2::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 Phenylenedamines 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 dye. 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 (Blomke 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 Fe2+ to Fe3+. Fenton’s reaction generates hydroxyl radicals and photo-Fenton reactions reduce the Fe2+ to Fe3+; thus leading to production of additional OH radicals and continuous regeneration of Fe2+ 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 H2O2 (Laat et al., 1999).

Among all these advanced oxidation processes use combinations of oxidants, ultraviolet irradiation and catalysts to generate hydroxyl radicals (OH) in solutions and have attracted interest for the degradation of Phenylenediamines. Among all these Fenton reactions (mainly Fe2+/H2O2) generates hydroxyl radicals (OH) by means of the reaction of H2O2 with ferrous ion, which is
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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 H₂O₂ 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 (FeSO₄·7H₂O) are purchased from Merck. The
chemicals were used as received in the Fenton’s
Oxidation Process. Hydrochloric acid (HCl, 35% purity),
Sulfuric acid (H₂SO₄, 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°C.

Experimental Procedure

The oxidation experiments were carried out at ambient
temperature (27±3°C) in batch reactors. Initially, the
reaction conditions like pH, H₂O₂ dosage, and [H₂O₂]/
[Fe²⁺] 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
conducted 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,
and magnetic stirrer. A 1000 mL solution of required PPD
solution and Fenton’s reagent is stirred with
magnetic stirrer. A 1000 mL solution of required PPD
solution is maintained using 0.1 N HCl. The material
consisted of enclosed chamber comprising a
reactor and connected to AC power, covered with a quartz
jacket and connected to AC power, and magnetic stirrer.

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 233.4 nm. 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
due to the formation of more Fe(OH)₃ which has a
diphenylazo color which is used as in 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.

RESULTS AND DISCUSSION

In this present study laboratory scale experiments
were conducted for PPD using ferrous sulphate
(FeSO₄·7H₂O) 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, 2.5, 3, 3.5, 4.0 and 4.5. Experiments were
conducted by adding the ratio of H₂O₂: Fe::10:1 (H₂O₂:
Fe=56.6:6.6mg/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 Fe(OH)₃ which has much
higher activity than Fe²⁺ in Fenton’s oxidation (Badawy et
When pH >3, oxidation efficiency rapidly decreases due to auto-decomposition of H$_2$O$_2$ affecting the production of OH$^\cdot$ 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$_2$O$_2$ with Fe$^{2+}$ was seriously affected to reduce hydroxyl radical production and water is formed by the reaction of OH radicals with H$^+$ ions (Lucas and Peres 2006).

**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).

**Effect of Fe$^{2+}$ and H$_2$O$_2$ 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$_2$O$_2$ and 3 mg/L of Fe$^{2+}$.

**Figure 4:** Plot of PPD removal of initial concentration 10 mg/L against various doses of H$_2$O$_2$ and iron

**PPD and COD Removal at Different Initial Concentrations of PPD**

PPD concentration of 10 mg/L, maximum degradation was at 50 mg/L of H$_2$O$_2$ and 3 mg/L of Fe$^{2+}$ and UV dosage of 180 minutes. For initial PPD concentration of 10 mg/L, at a ratio of Fe$^{2+}$/H$_2$O$_2$: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$^{2+}$ 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).

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**Table 1:** Design of experiments for degradation of PPD

| C$_0$ (mg/L) | [pH]$_0$ | UV-Time (min) | [H$_2$O$_2$] (mg/L) | [Fe$^{2+}$] (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                 |
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$_2$O$_2$ and 6 mg/L of Fe$^{2+}$ 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 there lower concentration of OH$^-$ results from the increasing concentration of PPD while the dosage of H$_2$O$_2$ and Fe$^{2+}$ 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$^-$ 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$_2$O$_2$ 150 mg/L and Fe$^{2+}$ 9 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$^{2+}$:H$_2$O$_2$::1:16.67 as shown in the figure 9 which is same for all the initial concentrations of PPD.

This indicates that the PFO of Para phenylenediamines is best at lower concentrations, although there is an increase in Fe$^{2+}$/H$_2$O$_2$ 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.
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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