Enhanced degradation of paracetamol by UV-C supported photo-Fenton process over Fenton oxidation

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ABSTRACT

For the treatment of paracetamol in water, the UV-C Fenton oxidation process and classic Fenton oxidation have been found to be the most effective. Paracetamol reduction and chemical oxygen demand (COD) removal are measured as the objective functions to be maximized. The experimental conditions of the degradation of paracetamol are optimized by the Fenton process. Influent pH 3, initial H_2O_2 dosage 60 mg/L, $[H_2O_2]/[Fe^{2+}]$ ratio 60 : 1 are the optimum conditions observed for 20 mg/L initial paracetamol concentration. At the optimum conditions, for 20 mg/L of initial paracetamol concentration, 82% paracetamol reduction and 68% COD removal by Fenton oxidation, and 91% paracetamol reduction and 82% COD removal by UV-C Fenton process are observed in a 120 min reaction time. By HPLC analysis, 100% removal of paracetamol is observed at the above optimum conditions for the Fenton process in 240 min and for the UV-C photo-Fenton process in 120 min. The methods are effective and they may be used in the paracetamol industry.

Key words | COD removal, Fenton oxidation, paracetamol degradation, photo-Fenton oxidation, UV-C light

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INTRODUCTION

A number of chemical treatment techniques have emerged in the last few decades to degrade non-biodegradable organic pollutants. Among these treatment techniques, the advanced oxidation processes appear to be promising and are reported to be effective for the degradation of pharmaceuticals in water. Advanced oxidation processes (AOPs) have proved capable of completely degrading the pharmaceuticals from aqueous solutions (Klavarioti et al. 2009). These processes are based on the generation of hydroxyl radical (OH$^{\bullet}$), which is a more powerful oxidant. Among AOPs, Fenton and photo-Fenton oxidation processes have emerged as the most promising methods, in terms of cost–effectiveness, ease of operation and effective degradation of organic non-biodegradable pollutants. In a comprehensive review, Neyens & Baeyens (2003) have indicated that the Fenton 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 contaminant degradation by photoreduction of Fe^{3+} to Fe^{2+}. Fenton's reaction generates hydroxyl radicals and photo-Fenton reactions reduce the Fe^{3+} to Fe^{2+}, thus

leading to production of additional OH radicals and continual regeneration of Fe^{2+} in a catalytic way (Sun & Pignatello 1993). It is also observed that the additional amounts of OH radicals are also produced from the direct photolysis of H_2O_2 (Laat et al. 1999).

Paracetamol (4-hydroxyacetanilide or 4-acetamidephenol or acetaminophen or Tylenol) is extensively used as an analgesic and antipyretic drug. Paracetamol is found to be present in sewage treatment plant effluents up to a concentration of 6 μg/L (Ternes 1998), up to 10 μg/L in water samples from natural sources in USA (Buxton & Kolpin 2002) and more than 65 μg/L in the Tyne River, UK (Roberts & Thomas 2006). However, consequent to the steep increase in the usage, the production of paracetamol has also been increased manifold all over the world and hence the concentration of paracetamol may increase in the waters.

The aim of the present investigation is to study the paracetamol degradation and chemical oxygen demand (COD) removal efficiencies by Fenton and photo-Fenton processes. The oxidation experiments are carried out at ambient temperature (27 ± 3 °C) in batch reactors. Initially, the reaction conditions like pH, H_2O_2 dosage, and $[H_2O_2]/[Fe^{2+}]$ ratio

are optimized in the Fenton oxidation of paracetamol and the further Fenton and photo-Fenton experiments are conducted with the optimum conditions. The effect of initial paracetamol concentration on the degradation and mineralization of paracetamol by both Fenton oxidation and UV-C Fenton oxidation are evaluated and the results are compared. Paracetamol samples are analyzed using a UV–Vis spectrophotometer. It is observed that the UV-C light has enhanced both the degradation and mineralization of paracetamol in water over Fenton oxidation.

MATERIALS AND METHODS

Materials

Paracetamol extra pure (98% assay) is purchased from SD Fine Chem. Ltd. (India). Hydrogen peroxide (H_2O_2) (50% w/w) and ferrous sulfate ($FeSO_4 \cdot 7H_2O$) are purchased from Merck (India). The chemicals are used as received in the Fenton oxidation process. Hydrochloric acid (HCl, Merck, India, 35% purity), sulfuric acid (H_2SO_4, Merck, India, 98% purity), sodium hydroxide (NaOH, Merck, India, 98% purity), are also used in the experiments. Methanol AR grade (Merck, India), sodium pentanesulfonate AR grade (Merck, India) and formic acid AR grade (Merck, India) are used in HPLC analysis. The simulated paracetamol aqueous stock solution of 1,000 mg/L concentration is prepared every week with Millipore Elix-3 deionized water and stored in the dark at 4 °C.

Experimental procedure

All the Fenton and photo-Fenton experiments are carried out in a batch reactor. The photo-reactor consists of an enclosed chamber comprising a reactor (2 L volume), 8W UV-C Philips lamp covered with a quartz jacket and connected to AC power, magnetic stirrer. A 1,000 mL solution of the required paracetamol concentration is prepared from the stock paracetamol solution and is taken in the 2 L reactor. The intrinsic pH of the wastewater is 6.32 and the initial pH 3 of the solutions is maintained using 0.05 mol/L H_2SO_4 and 0.1 mol/L NaOH. An appropriate amount of Fe^{2+} concentration from the 1,000 mg/L stock solution, which has been freshly prepared from $FeSO_4 \cdot 7H_2O$, is added to the reactor bath and stirred with a magnetic stirrer. The required amount of H_2O_2 is added to the reactor bath to initiate the reaction. The mixture of paracetamol solution and Fenton's reagent is stirred with a magnetic stirrer during treatment. The paracetamol solution samples are taken out for analysis at pre-defined time intervals, filtered through a 0.45-μm Millipore filter membrane for COD analysis, and filtered through a 0.45-μm Millipore syringe filter for determination of paracetamol concentration by using a UV–VIS spectrophotometer.

Analytical methods

The UV–VIS spectrum is recorded from 190 to 500 nm using a UV–VIS spectrophotometer and the absorbance peak of paracetamol is observed to be at wavelength 243 nm. The concentration of paracetamol in the aqueous solution at wavelength 243 nm is measured immediately after the removal of samples from the reactor using the standard curve, which has already been calibrated with a 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, AWWA & WEF 2005). Final COD is quantitatively corrected for hydrogen peroxide interference according to the correlation equation given by Kang *et al.* (1999). The iron concentration is measured using a spectrocolorimeter (PC Spectroll, Lovibond) by thiocyanate-colorimetric method. The H_2O_2 concentration is determined by iodometric titration method (US Peroxide Technologies). HPLC analysis is carried out with reversed-phase Jasco High Performance Liquid Chromatograph fitted with Microbonda 5 μm, 300 × 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 a Jasco chromatography data system. The mobile phase employed for paracetamol is 0.1 mg/mL of PIC B5 (1.74 g sodium pentanesulfonate + 2 mL formic acid diluted to 1,000 mL with double distilled water) at a flow rate of 1.5 mL/min. The paracetamol solution samples are injected at the rate of 15 μL and acquisition time is set as 30 min.

RESULTS AND DISCUSSION

Fenton oxidation process

Effect of pH

The experiments are conducted at different pH values varying from 2 to 5.5 with initial paracetamol concentration of 10 mg/L, $[H_2O_2]_o$ 20 mg/L and $[Fe^{2+}]_o$ 2 mg/L. The

maximum paracetamol reduction and COD removals are found to be 78 and 75% respectively at pH 3. The paracetamol removal efficiencies are less for the other values of pH. Figure 1 shows per cent paracetamol reduction and COD removal at different pH, [paracetamol]$_o$ = 10, [H$_2$O$_2$]$_o$ = 20 and [Fe^{2+}]$_o$ = 2 mg/L.

At pH 3, paracetamol removal is maximum and it may be due to the formation of more Fe(OH)$^+$ which has much higher activity than Fe^{2+} in Fenton's oxidation (Badawy & Ali 2006). When pH > 3, oxidation efficiency rapidly decreases due to auto-decomposition of H$_2$O$_2$ affecting the production of OH radicals (Badawy & 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+} is seriously affected to reduce hydroxyl radical production, and water is formed by the reaction of OH radicals with H$^+$ ions (Lucas & Peres 2006).

Effect of H$_2$O$_2$ and Fe^{2+} concentration

The investigation for optimization of hydrogen peroxide concentration is carried out by varying H$_2$O$_2$ concentration from 10 to 100 mg/L, keeping the iron concentrations 0 to 2 mg/L for [paracetamol]$_o$ 20 mg/L at solution pH 3. The maximum paracetamol reduction and COD removals are observed to be 89 and 75% respectively at [H$_2$O$_2$]$_o$ of 60 mg/L for a reaction time of 24 h.

The maximum paracetamol reduction and COD removals are observed to be 32 and 31% respectively with oxidation by H$_2$O$_2$ alone. However, the paracetamol reduction and COD removals are increased up to 89 and 75% respectively with the addition of Fe^{2+} to the solution. Figures 2(a) and (b) shows the variations in per cent paracetamol reduction and COD removal under the different conditions of the Fe^{2+} and H$_2$O$_2$ maintaining pH of 3
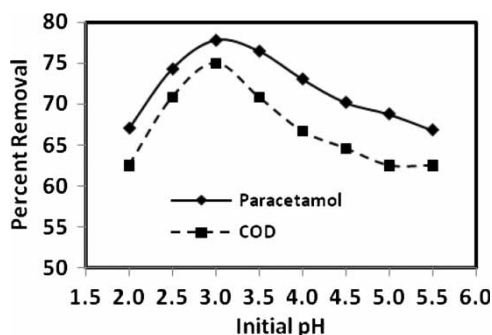

Figure 1 | Per cent paracetamol reduction and COD removal at different pH; [paracetamol]$_o$ = 10, [H$_2$O$_2$]$_o$ = 20 and [Fe^{2+}]$_o$ = 2 mg/L.

and reaction time of 24 h. The maximum paracetamol reduction and COD removals are observed to be 89 and 75% respectively at 1.0 mg/L Fe^{2+} concentration. These results are in agreement with the literature, wherein an increase in Fe^{2+} concentration of Fenton's reagent increases OH radical production and hence the degradation and mineralization (Yilmaz et al. 2010). It has also been observed that at higher Fe^{2+} concentrations the paracetamol and COD removals are reduced. This may be due to the ferrous ion inhibition that occurs when a high concentration of Fe^{2+} is present in the system and Fe^{2+} itself can react with OH radicals resulting in the scavenging of OH radical.

Effect of initial paracetamol concentration

Experiments are conducted to study the effect of initial paracetamol concentrations on the Fenton oxidation process by varying initial concentration from 10 to 50 mg/L for a reaction time of 240 min. The paracetamol reduction is increased and COD removal is decreased with the increase in initial concentration of paracetamol. The reduction in COD removal at high pollutant concentrations could be due to the formation of intermediate oxidation products, which trap the OH radicals. 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 (Yilmaz et al. 2010). Figures 2(c) and (d) show the variations in per cent paracetamol reduction and COD removals at [paracetamol]$_o$: [H$_2$O$_2$]$_o$: [Fe^{2+}]$_o$ :: 20 : 60 : 1 (w/w), pH 3 for 240 min of reaction time. Eighty four per cent of paracetamol reduction and 73% of COD removals are observed for 20 mg/L initial concentration of paracetamol, at H$_2$O$_2$ of 60 mg/L, Fe^{2+} of 1.0 mg/L in 240 min of reaction time.

UV-C Fenton oxidation process

UV-Fenton experiments for the effect of initial paracetamol concentrations are conducted with paracetamol concentration varying from 10 to 50 mg/L, optimum ratio of [paracetamol]$_o$: [H$_2$O$_2$]$_o$: [Fe^{2+}]$_o$ :: 20 : 60 : 1 (w/w), which is observed in our studies with Fenton's oxidation, pH 3 and the UV irradiation time 120 min. Figure 3 shows the variations in per cent paracetamol reduction and COD removals at [paracetamol]$_o$: [H$_2$O$_2$]$_o$: [Fe^{2+}]$_o$ :: 20 : 60 : 1 (w/w), pH 3 and 120 min of reaction time. The paracetamol reduction and COD removals are observed as 82 and 68% respectively in 5 min UV irradiation time, whereas 91% of paracetamol reduction and 82% of COD
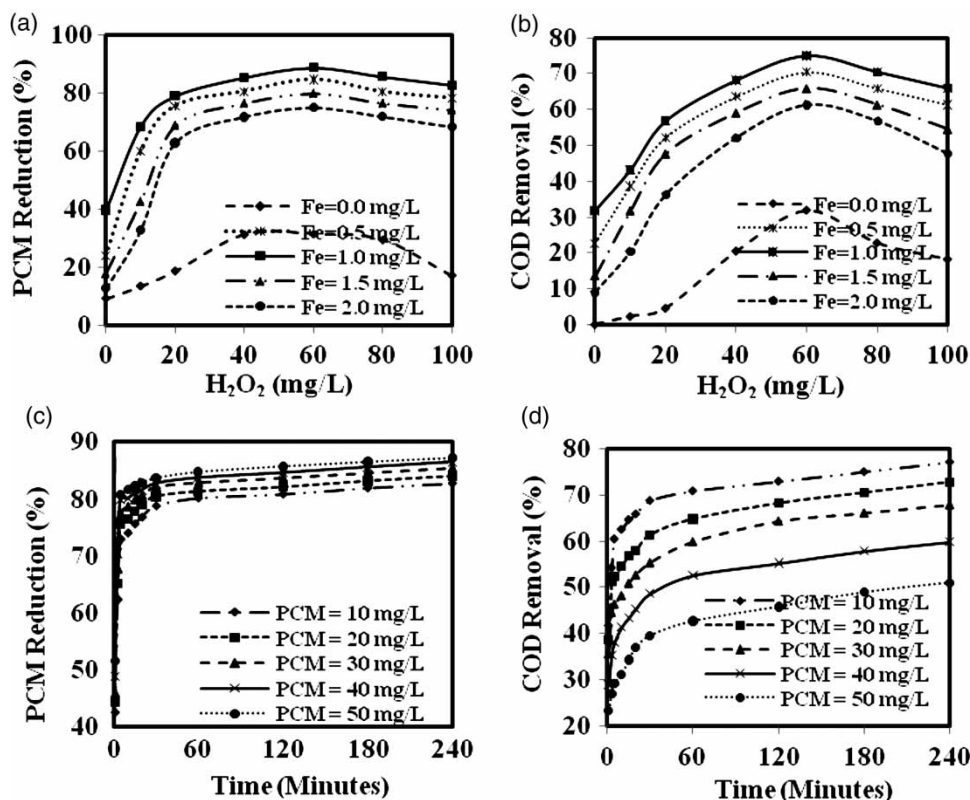
Figure 2 │ Variations in (a) per cent paracetamol reduction, (b) per cent COD removal for varying H_2O_2 dosage from 0 to 100 mg/L and varying [Fe^{2+}] from 0 to 2 mg/L, (pH 3, [paracetamol]$_o$ 20 mg/L) and (c) per cent paracetamol reduction and (d) per cent COD removal at [paracetamol]$_o$: [H_2O_2]$_o$: [Fe^{2+}]$_o$ = 20 : 60 : 1 (w/w), Fenton process.
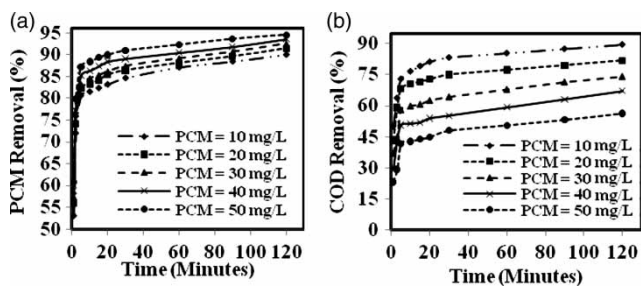

Figure 3 │ Variations in (a) per cent paracetamol (PCM) removal and (b) per cent COD removal, UV-C photo-Fenton process, [PCM]: 10–50 mg/L [paracetamol]$_o$: [H_2O_2]$_o$: [Fe^{2+}]$_o$ = 20 : 60 : 1 (w/w), pH 3.

removal are observed in 120 min of UV irradiation time for 20 mg/L initial concentration of paracetamol. With the increase in paracetamol concentration from 10 to 50 mg/L, the drug degradation is observed to be increased from 90 to 95% and the COD removal is decreased to 56 from 90%. This result is in accordance with the literature, where COD removal of pharmaceutical wastewater by UV-Fenton oxidation is more for the lower initial concentrations of pollutant (Devi *et al.* 2009). This phenomenon of decrease in COD removal with increase in initial

paracetamol concentration is associated with the characteristics of the UV–visible absorption spectrum of the paracetamol ($\lambda_{max} = 243$ nm), which is significant near 254 nm (UV-C light is used) and hence the solution with higher drug concentration absorbs a more significant fraction of the emitted UV light at 254 nm than that with a lower initial concentration. As a result, the number of available photons decreases leading to a decrease in the formation of OH radicals (Feng *et al.* 2003).

Comparison between Fenton and photo-Fenton process

By analyzing the results, it is observed that the paracetamol degradation efficiencies are more for UV-Fenton oxidation than the Fenton oxidation. Figure 4 shows the comparison of (a) per cent paracetamol reduction and (b) per cent COD removal between Fenton oxidation and UV-Fenton oxidation. Nine per cent more paracetamol reduction and 14% more COD removal are observed for UV-C photo-Fenton over Fenton oxidation. The reason for more degradation and mineralization of paracetamol may be due to regeneration of Fe^{2+} ions in

photo-Fenton oxidation and in turn production of more OH radicals, which mineralized more parent drug and the intermediates formed in the reaction.

There is a limited number of works reported on the advanced oxidation of paracetamol by different methods (Andreozzi *et al.* 2003; Sires *et al.* 2006; Skoumal *et al.* 2006; Dalmazio *et al.* 2008; Yang *et al.* 2008; Isariebel *et al.* 2009). Table 1 consists of a comparison of the present study with some important results in the literature. In the present study, 82% of paracetamol degradation, 68% COD removal in 120 min by Fenton process, 91% of paracetamol degradation, and 82% COD removal in 120 min by UV-C assisted photo-Fenton process are observed. By HPLC analysis, complete degradation of paracetamol is observed for the photo-Fenton process in 120 min and for the Fenton process in 240 min. As compared with previous studies, the extent of the degradation and mineralization in 120 min obtained in the present study are greater than that reported in most of the literature studies due to optimized conditions and UV-C light effectiveness in photo-Fenton oxidation.
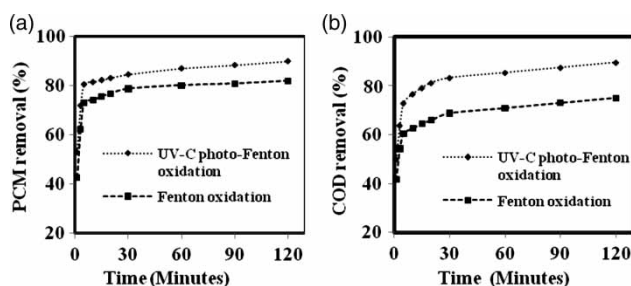

Figure 4 | Comparison for (a) per cent paracetamol (PCM) removal and (b) per cent COD removal between Fenton and photo-Fenton processes, [paracetamol]$_o$: [H_2O_2]$_o$: [Fe^{2+}]$_o$ = 20 : 60 : 1 (w/w), [PCM] 20 mg/L, pH 3.

Operational cost of Fenton and photo-Fenton processes

The operational costs of Fenton and photo-Fenton processes are calculated considering reagents used at optimum conditions and power requirements. For the maximum paracetamol degradation, it is observed that the Fenton oxidation process took 240 min reaction time and the photo-Fenton process took 120 min reaction time. It is also observed for the maximum removal of the paracetamol that the operational cost of the Fenton process is about US$0.36/$m^3$ more than that of the photo-Fenton process. Hence, overall operational cost for maximum pollutant removal is less in the case of the UV-C assisted photo-Fenton process.

CONCLUSIONS

UV-C light enhanced the photo-Fenton oxidation of paracetamol and the process is more efficient than Fenton oxidation. It is demonstrated by the Fenton process that the optimum conditions to treat 20 mg/L paracetamol concentration are pH 3, [H_2O_2] 60 mg/L, [Fe^{2+}] 1 mg/L corresponding to a [H_2O_2]/[Fe^{2+}] ratio of 60. At the optimum conditions, for 20 mg/L of initial paracetamol concentration, 82% paracetamol reduction and 68% COD removal by Fenton oxidation, and 91% paracetamol reduction and 82% COD removal by UV-C Fenton process are observed in 120 min reaction time. HPLC analysis has demonstrated complete degradation of paracetamol for the photo-Fenton process in 120 min and for the Fenton process in 240 min. As compared to the works in literature, the present study is most effective in degradation and mineralization of paracetamol. The UV-Fenton process is observed

Table 1 | Comparison of the literature results with the present study

Reference	Method	Results Degradation	Mineralization	Reaction time
Andreozzi *et al.* (2003)	Ozonation		30%	120 min
	H_2O_2/UV		40%	120 min
Sires *et al.* (2006)	Electrochemical		98%	360 min
Skoumal *et al.* (2006)			83%	240 min
Garrido *et al.* (2007)			96%	240 min
Dalmazio *et al.* (2008)	TiO_2/UV	90%		160 min
Yang *et al.* (2008)		95%		80 min
Isariebel *et al.* (2009)	Sonolysis	100%	39%	480 min
Present study	H_2O_2/Fe^{2+}	100%	73%	240 min
	H_2O_2/Fe^{2+}/UV-C	100%	82%	120 min

to be an effective treatment method over the Fenton process for the removal of paracetamol in aqueous solutions and can be effectively applied to treat paracetamol industrial wastewater. Fenton's oxidation process can also be applied *in-situ* for the treatment of paracetamol in surface water, ground water and lateritic soils in addition to industrial application.

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