

PRABIR GHOSH<sup>1</sup>, DAMODHAR GHIME<sup>1</sup>, DOLLY LUNIA<sup>1</sup>

## DEGRADATION OF *p*-AMINOPHENOL BY FENTON'S PROCESS. INFLUENCE OF OPERATIONAL PARAMETERS

Oxidative degradation of a model environmental pollutant, *p*-aminophenol (PAP), in aqueous solution has been investigated in an environmentally friendly advanced oxidation Fenton process. Effects of various operating parameters such as pH of solutions, dosage of hydrogen peroxide and ferrous ions, initial PAP concentration and temperature on the degradation of PAP have been studied using a batch stirred cell. Degradation kinetics for this pollutant was also investigated to determine the apparent rate constants ( $\text{min}^{-1}$ ). The optimum conditions for the degradation of PAP solution ( $200\text{--}500 \text{ mg/dm}^3$ ) were found to be  $\text{pH} = 3.0$ ,  $2400 \text{ mg H}_2\text{O}_2/\text{dm}^3$ ,  $300 \text{ mg Fe}^{2+}/\text{dm}^3$ ,  $30 \text{ }^\circ\text{C}$ . Under the optimum conditions, the degradation efficiency of PAP was 75% after 50 min of reaction. It was observed that process parameters play a major role in the overall degradation process.

### 1. INTRODUCTION

Environmental pollution, and especially water pollution is an emerging threat of great concern in today's context pertaining to its effect on the ecosystem. Industrial effluents often contain various toxic metals, harmful dissolved gases and several organic/inorganic compounds. These may accumulate in soil in excessive quantities in long-term use, ultimately it can cause some adverse effects on crop productivity. Therefore it is necessary to treat effluents containing harmful organic pollutants prior to their discharge to the receiving water stream and meet the stringent environmental regulations.

The main sources of phenolic effluents are oil refineries, petrochemical industries, phenol-based polymerization processes, pharmaceuticals, plastic, paints and varnish producing units and textile units making organic dyes. Phenol along with other compounds is one of the most common contaminants present in effluents from chemical

---

<sup>1</sup>Department of Chemical Engineering, NIT Raipur, India, corresponding author P. Ghosh, e-mail address: prabirg.che@nitrr.ac.in

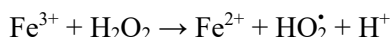
process industries. Even at lower concentrations, these phenolic compounds adversely affect aquatic as well as human life.

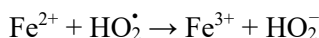
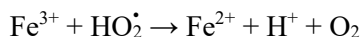
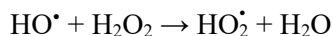
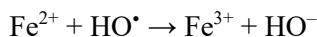
Degradation of these pollutants using conventional chemical and biological treatments is often very slow or ineffective [1, 2]. Although some standard treatment processes such as air stripping, steam stripping, carbon adsorption, conventional biological treatment methods are quite sufficient for treatment of wastewater carrying refractory, toxic and inhibitory organic compounds but they have certain limitations [3].

Advanced oxidation processes (AOPs) can effectively be used to remove dyes and phenol compounds from wastewaters. Among AOPs, Fenton oxidation, in which wastewater is treated with the Fenton reagent (ferrous salt and  $\text{H}_2\text{O}_2$ ) is an attractive oxidative process for wastewater treatment. Iron is a very abundant and non-toxic element, and hydrogen peroxide is easy to handle and environmentally safe. Other advantages of this techniques include absence of mass transfer limitation due its homogeneous catalytic nature and the simplicity of the technology and its capability for the elimination of recalcitrant compounds [4, 5].

Fenton's process has been proposed primarily as a pre-treatment to reduce the effluent toxicity to safe levels and to improve degradability for further treatment. One study investigated the effect of reaction conditions on the oxidation efficiency of non-biodegradable landfill leachate using Fenton's process [6]. In this work, authors mainly focused on the effect of pH,  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  on oxidation efficiency. In another study, the degradation of four nitrophenols (NPs) has been investigated, namely 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP) by the Fenton process and compared with solar and UV-assisted Fenton processes for their treatment efficiency [7]. Degradation of organic compound is not one step process, but may lead to number of steps. So there is a possibility of formation of various intermediates. A study has also been published explaining the role of intermediates in the degradation of phenolic compounds by Fenton-like process [8].

AOPs have been recognized promising processes, capable of destroying wide range of similar organic pollutants in water and wastewater as reported by several researchers [9–13]. The main mechanism of AOPs follows in the generation of highly reactive free radicals. Hydroxyl radicals are effective in destroying aqueous organic pollutants as they are reactive electrophiles (electron preferring), thus reacting quickly and non selectively with almost all electron-rich organic compounds. Initially target molecules are attacked by  $\text{OH}^\cdot$  radicals and subsequently their breakdown to fragments, i.e., the reaction of these oxidants with organic contaminants in water led to ultimate mineralization. The following main Fenton's reactions are summarized below:





Various oxidation processes such as hydrogen peroxide photolysis, the Fenton treatment, photo-Fenton treatment and ozonation combined with hydrogen peroxide and UV radiation were compared for the destruction of 2,4-dinitrophenol [14]. Among all the processes studied, the Fenton oxidation was found to be the most effective in the degradation of 2, 4-dinitrophenol. It was concluded that advanced oxidation led to complete its detoxification.

Sureyya et al. [15] studied the degradation of Reactive Black 5 from synthetic wastewater using Fenton's oxidation (FO) process. They determined the optimum values of  $\text{FeSO}_4$  (100 mg/dm<sup>3</sup>) and  $\text{H}_2\text{O}_2$  (400 mg/dm<sup>3</sup>) concentrations, pH (3) and temperature (40 °C).

A comparative study on the degradation of various chlorophenols by the electro-Fenton method was made by some researchers [16]. It was found that under optimal conditions, various chlorophenols may be treated, including PCP, 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and their mixture aqueous solutions. Serious disadvantage of this process is that it requires DC power supply as well as using electrodes. The Fenton process can also be coupled with aerobic biological treatment [17], to achieve decolorization and to enhance mineralization of azo dyes such as Reactive Black 5, Reactive Blue 13, and Acid Orange 7, etc.

Photocatalytic degradation processes were successfully used for decontamination of PAP. CuO supported clinoptilolite zeolite was used as a photocatalyst to degrade PAP aqueous solution [18]. Photocatalytically-assisted electrochemical degradation processes were also used for degradation of aqueous PAP solution [19, 20]. In this process, boron-doped diamond anodes and a TiO<sub>2</sub>-supported zeolite catalyst under UV irradiation were applied for the degradation and mineralization of aqueous solution of PAP.

The inefficiency and limitations of conventional water treatments in destroying many toxic and biorecalcitrant and persistent organic pollutants before its final disposal, has promoted the search for simple, safe, effective, and economical technologies.

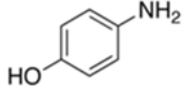
In this work, the influence of most relevant process parameters (initial pH,  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  dosage, temperature, initial concentration) were studied. The purpose of this research was to find the applicability of a treatment system which can effectively reduce the concentration of pollutants.

## 2. MATERIALS AND METHODS

*Materials.* All chemicals employed in this study were of analytical grade. All solutions were prepared with distilled water, PAP as procured from Loba Chemie Pvt., Ltd., India. Hydrogen peroxide (30 wt. %) and ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) (Merck), sulfuric acid and sodium hydroxide were procured from M/s Merck, India. Solutions of 4 M NaOH and 1.5 M  $\text{H}_2\text{SO}_4$  were used for pH adjustments. Table 1 shows the properties of PAP.

Table 1

Properties of *p*-aminophenol

Chemical formula	Structure	Density [g/cm <sup>3</sup> ]	Other names	Melting point [°C]	Boiling point [°C]	Solubility
C <sub>6</sub> H <sub>7</sub> NO		1.21	<i>p</i> -hydroxyaniline paranol, Azol	180–190	284	complete in hot dilute acids and in water

*Experimental procedures.* For all degradation experiments 500 cm<sup>3</sup> glass beakers were used with 300 cm<sup>3</sup> of PAP solution (200–500 mg/dm<sup>3</sup>) equipped with magnetic stirrers (310 rpm). pH of each solution was adjusted to the desired value by using  $\text{H}_2\text{SO}_4$  or NaOH solution and measured using a pH meter. pH was varied from 2 to 5. The reactions were initiated by adding required amounts of  $\text{H}_2\text{O}_2$  and ferrous sulfate to the reactor. Concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  were varied from 1500 to 4500 mg/dm<sup>3</sup> and from 200 to 600 mg/dm<sup>3</sup>, respectively. Samples were taken out from the reactor periodically using a pipette. To remove residual oxidant in the samples, they were mixed with NaOH solution to stop the reaction by raising the pH above 7 before measuring the concentration. A Shimadzu UV spectrophotometer (UV-1800) was used to measure the concentration of PAP at various time intervals. For this purpose, a calibration curve was made by using known standard concentration to measure unknown concentration at 297 nm. Each experiment was performed twice under identical conditions. The reproducibility of the measurement was within  $\pm 3\%$ .

## 3. RESULTS AND DISCUSSION

The operating variables ( $\text{H}_2\text{O}_2$  dose,  $\text{Fe}^{2+}$  concentration, initial pH, reaction time, initial substrate concentration and temperature) were optimized for maximizing reduction of PAP concentration. These parameters affect the Fenton oxidation reaction and reaction rate significantly.

## 3.1. EFFECT OF INITIAL pH

pH of solutions is an important parameter for Fenton's reactions which determines the production rate of OH<sup>•</sup> radicals and concentration of ferrous ion. At high pH (pH 5), the degree of degradation was reduced to 55% from 75% at pH 3 (Fig. 1). At higher pH, generation of OH<sup>•</sup> radicals decreases because of the formation of ferric ions and deactivation of ferrous ion catalyst due to the formation of ferrous/ferric hydroxide complexes [21, 22]. In addition, the decreasing oxidation potential of OH<sup>•</sup> radicals at higher pH was another reason for diminishing the degradation efficiency of PAP.

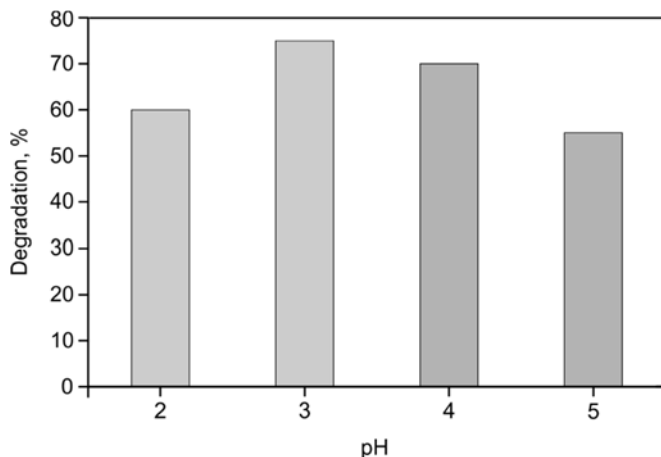


Fig. 1. Effect of pH on degradation of PAP;

$[PAP]_0 = 300 \text{ mg/dm}^3$ ,  $[Fe^{2+}]/[H_2O_2] = 1:8$ ,  $[Fe^{2+}] = 300 \text{ mg/dm}^3$ , 50 min, 30 °C

On the other hand, when pH of solution was decreased from 3.0 to 2.0, the degradation efficiency of PAP also decreased from 75% to 60%. At lower pH, H<sub>2</sub>O<sub>2</sub> molecule becomes stable with a solvated proton and forms an oxonium ion, which severely reduces its reactivity with ferrous ion. Some complex species such as  $[Fe(H_2O)_6]^{2+}$  and  $[Fe(H_2O)_6]^{3+}$  are also formed which leads to slowing the Fenton reactions [23]. Additionally, the scavenging effect of the OH<sup>•</sup> radicals by H<sup>+</sup> is enhanced in this pH range. These result in reducing the generation of OH<sup>•</sup> radicals and consequently diminishing the degradation efficiency of PAP.

3.2. EFFECT OF H<sub>2</sub>O<sub>2</sub> CONCENTRATION

Concentration of H<sub>2</sub>O<sub>2</sub> is one of the operating parameters that significantly influence the final mineralization of the solution. Initially, upon increasing H<sub>2</sub>O<sub>2</sub> concentra-

tion, degradation efficiency increases to a certain level. This is expected due to additional hydroxyl radicals being available at higher dosage of  $\text{H}_2\text{O}_2$ . Maximum degree of degradation was 75% at  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  ratio of 1:8. Upon further increasing  $\text{H}_2\text{O}_2$  contents to 1:15 ratio, the degradation efficiency decreases to 50% (Fig. 2) due to the scavenging nature of  $\text{H}_2\text{O}_2$  towards  $\text{OH}^\bullet$  radicals [24].

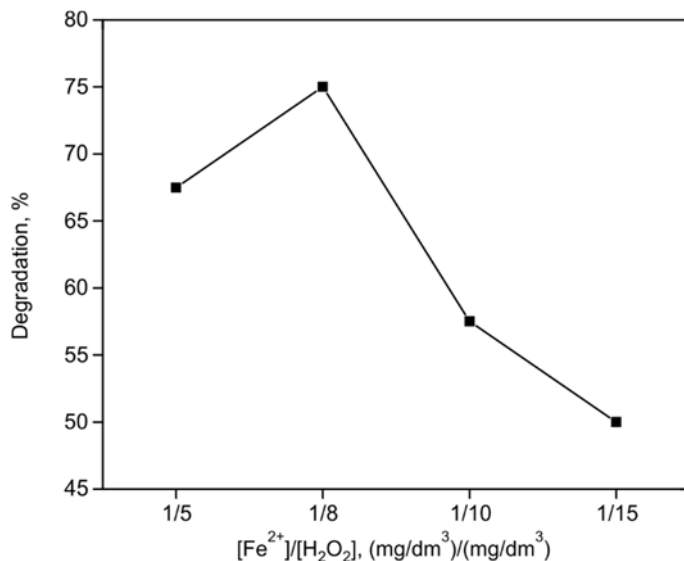
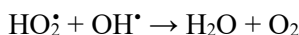
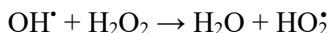


Fig. 2. Effect of  $\text{H}_2\text{O}_2$  dosage on degradation of PAP by Fenton process;  $[\text{PAP}]_0 = 300 \text{ mg}/\text{dm}^3$ ,  $\text{pH}_0 = 3$ ,  $[\text{Fe}^{2+}] = 300 \text{ mg}/\text{dm}^3$ , 50 min, 30 °C

At high dosages of  $\text{H}_2\text{O}_2$ , the decrease in degradation rate is possible due to the recombination of hydroxyl radicals and to hydroxyl radical scavenging effect of  $\text{H}_2\text{O}_2$ . The reactions are as follows.



### 3.3. EFFECT OF INITIAL $\text{Fe}^{2+}$ CONCENTRATION

$\text{Fe}^{2+}$  ions catalyze decomposition of  $\text{H}_2\text{O}_2$  resulting in  $\text{OH}^\bullet$  radical production and consequently the degradation of organic molecules. Upon increasing ferrous salt concentration, the degradation rate of organic compound also increases to a certain level where further addition of iron becomes inefficient. The effect of  $\text{Fe}^{2+}$  concentration on

degradation efficiency was examined (Fig. 3) by changing the  $\text{Fe}^{2+}$  concentration between 200 and 600  $\text{mg Fe}^{2+}/\text{dm}^3$  while keeping other parameters constant. As  $\text{Fe}^{2+}$  doses increased from 200 to 300  $\text{mg Fe}^{2+}/\text{dm}^3$ , the degradation rate increased from 65% to 75% at 50 min. Higher ferrous doses lead to the generation of more  $\text{OH}^\bullet$  radicals. At higher  $\text{Fe}^{2+}$  doses (400–600  $\text{mg}/\text{dm}^3$ ), the efficiency decreases indicating that  $\text{H}_2\text{O}_2$  becomes the limiting factor for further  $\text{OH}^\bullet$  generation and also the decrease in degradation efficiency is due to the scavenging action of excess  $\text{Fe}^{2+}$  ions [25]. Higher  $\text{Fe}^{2+}$  concentration favors the scavenging reaction:

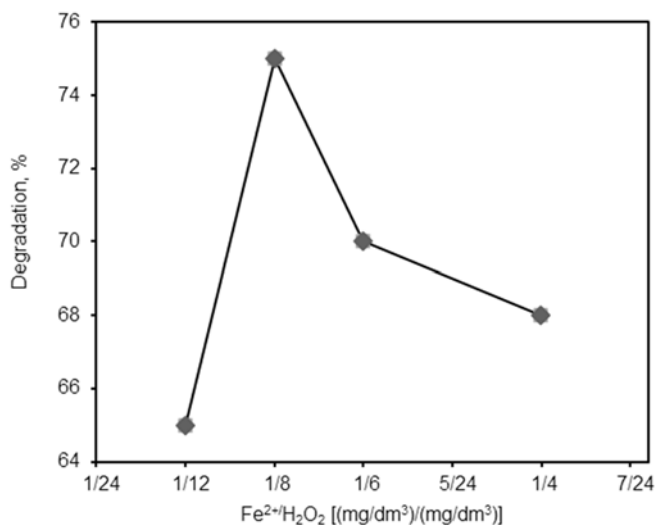
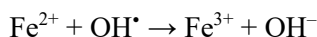


Fig. 3. Effect of  $\text{Fe}^{2+}$  dosage on the degradation of PAP;  $[\text{PAP}]_0 = 300 \text{ mg}/\text{dm}^3$ ,  $\text{pH}_0 = 3$ ,  $[\text{H}_2\text{O}_2] = 2400 \text{ mg}/\text{dm}^3$ , 50 min, 30 °C

### 3.4. EFFECT OF TEMPERATURE ON DEGRADATION OF PAP

The effect of temperature on the degradation of PAP in water by Fenton's process was studied and the results are shown in Fig. 4. It can be seen that temperature has a significant effect on the degradation of PAP. The degradation efficiency decreased from 75% to 60% when the temperature increased from 30 to 40 °C. Figure 4 shows that at 30 °C, the highest degradation rate was obtained. Higher temperature is detrimental to Fenton oxidation process as at higher temperature  $\text{H}_2\text{O}_2$  loses its oxidation capability and it decomposes to  $\text{H}_2$  and  $\text{O}_2$  [26–28].

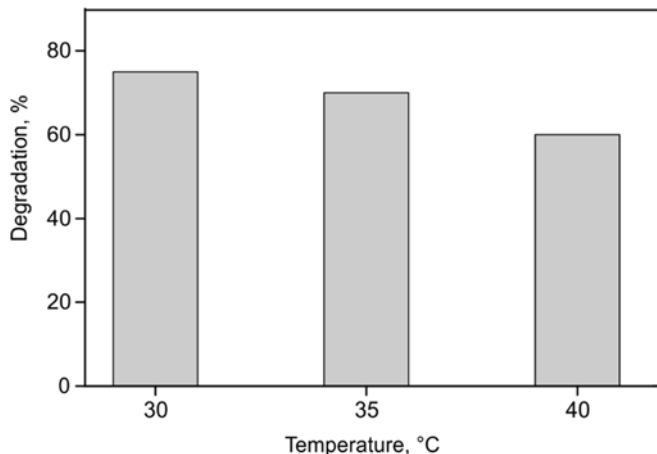


Fig. 4. Effect of temperature on the degradation PAP;  $[\text{PAP}]_0 = 300 \text{ mg/dm}^3$ ,  $\text{pH}_0 = 3$ ,  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2] = 1:8$ ,  $[\text{Fe}^{2+}] = 300 \text{ mg/dm}^3$ , 50 min

### 3.5. EFFECT OF INITIAL PAP CONCENTRATION

The effect of initial PAP concentration (Fig. 5) was studied for the concentration range of 200–500  $\text{mg/dm}^3$ . The other process parameters were kept constant. It can be seen that the degradation efficiency decreases upon increasing initial PAP concentration. This is expected due to the oxidizing agent being the limiting reactant. Since the concentrations of other chemicals do not change, the generation of  $\text{OH}^\bullet$  radicals remains constant.

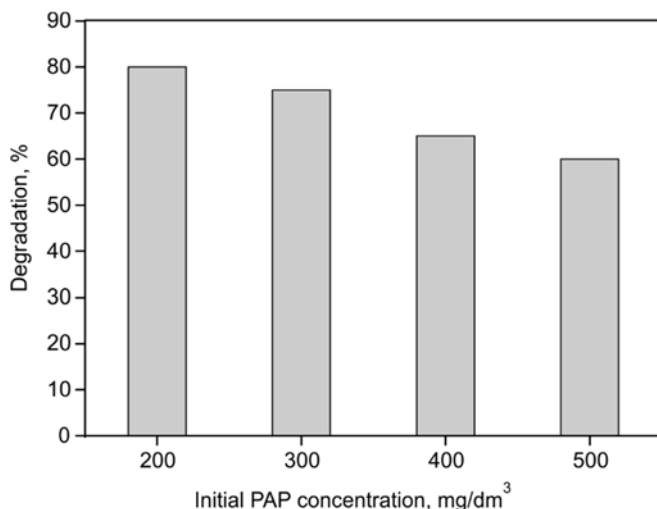
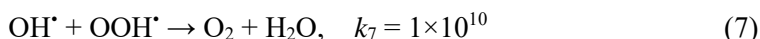
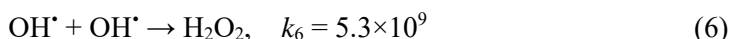
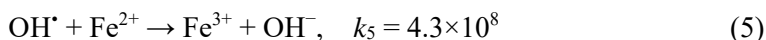
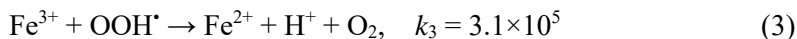
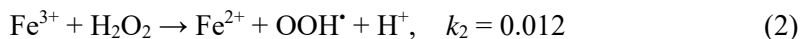


Fig. 5. Effect of initial PAP concentration on degradation  $\text{pH}_0 = 3$ ,  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2] = 1:8$ ,  $[\text{Fe}^{2+}] = 300 \text{ mg/dm}^3$ , 30 °C, 50 min



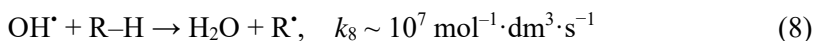
## 3.6. KINETIC STUDIES

In classic Fenton's chemistry, the reactions between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  ions in acidic aqueous medium involves the following steps:

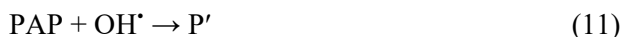


The rate constants are reported in  $\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$  for a second order reaction rate.

Although the degradation of an organic compound by Fenton's reagent is complex, several researchers have offered evidence of the formation of the  $\text{OH}^\bullet$  radicals as a principle active oxidant in the Fenton system.  $\text{OH}^\bullet$  radical can attack and initiate the oxidation of organic pollutants molecule (R) by several degradation mechanisms:0



Therefore, the following simplified mechanism may explain the degradation of PAP by Fenton's oxidation process:



Where  $\text{S}_i$  is a scavenger species such as intermediates, excess of  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$ ,  $\text{OH}^\bullet$  radical,  $\text{OOH}^\bullet$  radical, etc.,  $k_i$  is the global rate constant of the following kinetic equation:

$$\frac{d[\text{PAP}]}{dt} = -k_i[\text{PAP}][\text{OH}^\bullet] \quad (13)$$

The steady state assumption was used with respect to the concentrations of reactive radicals in the kinetics studies. Based on the pseudo steady state assumption, at a certain time, the concentration of reactive OH<sup>•</sup> radical will be constant, i.e.,

$$\frac{d[\text{OH}^{\bullet}]}{dt} = 0 \quad (14)$$

If the concentration of PAP is high, i.e., the concentration of OH<sup>•</sup> radicals is insufficient because of insufficient concentration of H<sub>2</sub>O<sub>2</sub>, the reaction can be simplified to a zero order with respect to PAP

$$\frac{d[\text{PAP}]}{dt} = -k_1 [\text{H}_2\text{O}_2][\text{Fe}^{2+}] \quad (15)$$

Equation (13) can be written as

$$\ln \frac{[\text{PAP}]_0}{[\text{PAP}]} = k_{ap} t \quad (16)$$

The effect of pH on the rate constant  $k_{ap}$  for PAP degradation in the range of 2–5 was studied for  $[\text{PAP}]_0 = 300 \text{ mg/dm}^3$ ,  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2] = 1:8$  and  $T = 30 \text{ }^\circ\text{C}$ . Time dependences of  $\ln([\text{PAP}]_0/[\text{PAP}])$  for various pHs were plotted to calculate the apparent rate constants. It seems that PAP degradation fits the pseudo-first order kinetic model. The results showed that the  $k_{ap}$  of PAP degradation was significantly influenced by pH of the solution.

Table 2

Apparent rate constants  $k_{ap}$  at various pH

pH	$k_{ap} [\text{min}^{-1}]$
2	0.003
3	0.007
4	0.006
5	0.002

The value of  $k_{ap}$  ( $\text{min}^{-1}$ ) sharply increases from 0.003 to 0.007 when pH increases from 2 to 3 and suddenly decreases from 0.007 to 0.002 when pH increases from 3 to 5 (Table 2). The poor degradation of PAP at a pH > 4.0 was attributed to the formation of ferrous and ferric hydroxide complexes with much lower catalytic capability than ferric ions.

The effect of initial  $\text{H}_2\text{O}_2$  concentration on the kinetic rate constant  $k_{ap}$  for PAP degradation was examined by varying the  $[\text{H}_2\text{O}_2]_0$  from 1500 to 4500  $\text{mg}/\text{dm}^3$  and for  $[\text{PAP}]_0 = 300 \text{ mg}/\text{dm}^3$ ,  $[\text{Fe}^{2+}]_0 = 300 \text{ mg}/\text{dm}^3$ , pH 3.0 and  $T = 30 \text{ }^\circ\text{C}$ . During the experiment,  $k_{ap}$  ( $\text{min}^{-1}$ ) increased from 0.005 to 0.007 upon increasing  $[\text{H}_2\text{O}_2]_0$  in the range of 1500–2400  $\text{mg}/\text{dm}^3$  and decreased to 0.003 for higher  $[\text{H}_2\text{O}_2]_0$  (Table 3).

Table 3

Apparent rate constants  $k_{ap}$   
at various initial  $\text{H}_2\text{O}_2$  concentrations

$\text{H}_2\text{O}_2$ concentration [ $\text{mg}/\text{dm}^3$ ]	$k_{ap}$ [ $\text{min}^{-1}$ ]
1500	0.005
2400	0.007
3000	0.004
4500	0.003

Such behavior could be explained in terms of the critical concentration. Below the critical concentration of  $\text{H}_2\text{O}_2$ , the degradation rate of PAP increased upon increasing  $[\text{H}_2\text{O}_2]_0$  due to increase of concentration of  $\text{OH}^\bullet$  radicals produced through the decomposition of  $\text{H}_2\text{O}_2$ . After exceeding the critical concentration of  $\text{H}_2\text{O}_2$ , the degradation rate of PAP decreased due to scavenging of  $\text{OH}^\bullet$  radicals by  $[\text{H}_2\text{O}_2]$  and incremental generation of  $\text{OOH}^\bullet$  also consuming  $\text{OH}^\bullet$ .

#### 4. CONCLUSIONS

The degradation of PAP by Fenton's process was significantly influenced by pH of the solutions, hydrogen peroxide and ferrous ion dosage, initial PAP concentration and the reaction temperature. The optimum conditions for the degradation of PAP (200–500  $\text{mg}/\text{dm}^3$ ) in waste water were found to be: pH at 3.0,  $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}] = 8:1$  ( $\text{mg}/\text{dm}^3$ )/( $\text{mg}/\text{dm}^3$ ) and temperature 30  $^\circ\text{C}$ . Under the optimum conditions, the degradation efficiency of PAP was higher than 75% within 50 min reaction. The results showed that in Fenton's process, PAP can effectively be degraded. The degradation model fits well to the pseudo-first order reaction and apparent rate constants were determined.

#### ACKNOWLEDGEMENTS

This work was supported by the Department of Science and Technology, Science and Engineering Research Board (File No. YSS/2014/000996), India.

## REFERENCES

- [1] ESPLUGAS S., GIMENEZ J., CONTRERAS S., PASCUAL S., RODRIGUEZ M., *Comparison of different advanced oxidation processes for phenol degradation*, *Water Res.*, 2002, 36 (4), 1034.
- [2] CHATTERJEE D., DASGUPTA S., *Visible light induced photocatalytic degradation of organic pollutants*, *J. Photochem. Photobiol. C*, 2005, 6 (2–3), 186.
- [3] JARDIM W.F., MARAES S.G., TOKIYAMO M.M.K., *Photocatalytic degradation of aromatic chlorinated compounds using TiO<sub>2</sub>: Toxicity of intermediates*, *Water Res.*, 1997, 31 (7), 1728.
- [4] APLIN R., WAITE T., *Comparison of three advanced oxidation processes for degradation of textile dyes*, *Water Sci. Technol.*, 2000, 42 (5–6), 345.
- [5] KAVITHA V., PALANIVELU K., *The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol*, *Chemosphere*, 2004, 55 (9), 1235.
- [6] KANG Y.W., HWANG K.Y., *Effects of reaction conditions on the oxidation efficiency in the Fenton process*, *Water Res.*, 2000, 34 (10), 2786.
- [7] KAVITHA V., PALANIVELU K., *Degradation of nitrophenols by Fenton and photo-Fenton processes*, *J. Photochem. Photobiol. A*, 2005, 170 (1), 83.
- [8] YINGXUN D., MINGHUA Z., LECHENG L., *Role of the intermediates in the degradation of phenolic compounds by Fenton-like process*, *J. Hazard. Mater.*, 2006, 136 (3), 859.
- [9] LEGRINI O., OLIVEROS E., BRAUN A.M., *Photochemical processes for water treatment*, *Chem. Rev.*, 1993, 93 (2), 671.
- [10] MALATO S., BLANCO J., VIDAL A., RICHTER C., *Photocatalysis with solar energy at a pilot-plant scale. An overview*, *Appl. Catal. B*, 2002, 37 (1), 1.
- [11] NEYENS R., BAEYENS J., *A review of classic Fenton's peroxidation as an advanced oxidation technique*, *J. Hazard. Mater.*, 2003, 98 (1–3), 33.
- [12] GRIGOROPOULOU H., PHILIPPOPOULOS C., *Homogeneous oxidation of phenols in aqueous solution with hydrogen peroxide and ferric ions*, *Water Sci. Technol.*, 1997, 36 (2–3), 151.
- [13] MA Y.S., HUANG S.T., LIN J.G., *Degradation of 4-nitrophenol using the Fenton process*, *Water Sci. Technol.*, 2000, 42 (3–4), 155.
- [14] GOI A., TRAPIDO M., *Hydrogen peroxide photolysis, Fenton reagent and photo-Fenton for the degradation of nitrophenols. A comparative study*, *Chemosphere*, 2002, 46 (6), 913.
- [15] METRIC S., KAPTAN, D., OLMEZ, T., *Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process*, *Chemosphere*, 2004, 54 (3), 435.
- [16] YUAN S., LU X., *Comparison treatment of various chlorophenols by electro-Fenton method: relationship between chlorine content and degradation*, *J. Hazard. Mater. B*, 2005, 118 (1–3), 85.
- [17] TANTAK N.P., CHAUDHARI S., *Degradation of azo dyes by sequential Fenton's oxidation and aerobic biological treatment*, *J. Hazard. Mater. B*, 2006, 136 (3), 698.
- [18] NEZAMZADEH-EJHIEH A., AMIRI M., *CuO supported Clinoptilolite towards solar photocatalytic degradation of p-aminophenol*, *Powder Technol.*, 2013, 235, 279.
- [19] RATIU C., MANEA F., LAZAU C., GROZESCU I., RADOVAN C., SCHOONMAN J., *Electrochemical oxidation of p-aminophenol from water with boron-doped diamond anodes and assisted photocatalytically by TiO<sub>2</sub>-supported zeolite*, *Desalination*, 2010, 260 (1–3), 51.
- [20] RATIU C., FLORICA M., LAZAU C., ORHA C., BURTICA G., GROZESCU I., SCHOONMAN J., *Photocatalytically-assisted electrochemical degradation of p-aminophenol in aqueous solutions using zeolite-supported TiO<sub>2</sub> catalyst*, *Chem. Pap.*, 2011, 65 (3), 289.
- [21] BADAWY M.I., GHALY M.Y., GAD-ALLAH T.A., *Advanced oxidation processes for the removal of organophosphorus pesticides from wastewaters*, *Desalination*, 2006, 194 (1–3), 166.
- [22] KWON B.G., LEE D.S., KANG N., YOON J., *Characteristics of p-chlorophenol oxidation by Fenton's reagent*, *Water Res.*, 1999, 33 (9), 2110.

- 
- [23] LUCAS M.S., PERES J.A., *Decolorization of the azo dye reactive black 5 by Fenton and photo-Fenton oxidation*, Dye Pigm., 2006, 71 (3), 236.
- [24] GHALY M.Y., HARTEL G., MAYER R., HASENERK R., *Photochemical oxidation of p-chlorophenol by UV/H<sub>2</sub>O<sub>2</sub> and photo-Fenton process. A comparative study*, Waste Manage., 2001, 21 (1), 41.
- [25] YANG M., HU J., ITO K., *Characteristics of Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV oxidation process*, Environ. Technol., 1998, 19 (2), 183.
- [26] DUTTA K., MUKHOPADHYAY S., BHATTACHARJEE S., CHAUDHURI B., *Chemical oxidation of methylene blue using a Fenton-like reaction*, J. Hazard. Mater., 2001, 84 (1), 57.
- [27] GUEDES A.M.F.M., MADERIA L.M.P., BOAVENTURA R.A.R., COSTA C.A.V., *Fenton oxidation of cork cooking wastewater – overall kinetic analysis*, Water Res., 2003, 37 (13), 3061.
- [28] CATRINESCU C., TEODOSIU C., MACOVEANU M., MIEHE-BRENDLE J., DRED R.L., *Catalytic wet peroxide oxidation of phenol over Fe-exchanged pillared beidellite*, Water Res., 2003, 37 (5), 1154.