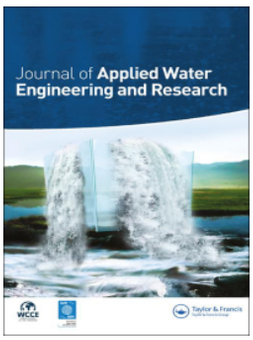

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Effect of hydrogen peroxide and ferrous ion on the degradation of 2-Aminopyridine

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Pharmaceutical compounds 2-Aminopyridine were detected in drinking water, surface water, and groundwater. 2-Aminopyridine is a colourless solid used for manufacturing drugs, sulphapyridine which is extremely poisonous and carcinogenic. Its appearance in drinking water needs prior treatment to dispose of safely. Fenton, Photo-Fenton oxidation processes were carried out to degrade 2-Aminopyridine. Parameters like pH, the dosage of Hydrogen peroxide, and Iron are optimized for the effective degradation of a 2-Aminopyridine compound in water. The effect of the initial concentration (10-80) mg/L of a 2-Aminopyridine pharmaceutical compound on degradation was studied. Drug at initial concentration of 10 mg/L, 40 mg/L and 80 mg/L is 100% degraded in 30 mins,45 mins and 120 mins respectively. Similarly, COD removals of 94.6%, 88.6% and 81% were detected at 10 mg/L, 40 mg/L and 80 mg/L of initial drug dosage. The degradation was enhanced by photo-Fenton oxidation. Both the drug degradation and COD reduction were improved by UV-C-assisted photo-Fenton oxidation processes.

Keywords: 2-Aminopyridine; chemical oxygen demand; degradation; Fenton oxidation; photo-Fenton oxidation; pharmaceutical compound

1. Introduction

Sparkling, clean water is the basic need for all living creatures and human beings. But its availability is a major problem nowadays. This problem is increasing due to global industrialization and population growth. Normal water is polluted by domestic, industrial, and agricultural wastes. Hence, it is very important to remove the pollutants and pathogens from the wastewater to make it reusabl for irrigation, industrial and domestic purposes. Pharmaceutical compounds are detected in surface water, groundwater, sewage effluents (Adukia 2014), and drinking water (Babuponnusami and Muthukumar 2011). Advances in systematic treatment technology have been helpful in their augmented detection. Many surveys and studies have detected pharmaceuticals in municipal wastewater and effluents, which are as a major source in drinking water (Bai et al. 2009; Bidhan et al. 2009; Bach et al. 2010; Bernabeu et al. 2012; Bokhove et al. 2012; Bai 2013 and 2013). The results indicated the adverse health impacts on humans from exposure to the trace concentrations of pharmaceuticals found in drinking water (Sun et al. 2007; Grebel et al. 2010; Chaubey and Pandey 2011; Cuevas 2011; Damodhar and Reddy 2013; Jihyun et al. 2014). The up-to-date approach to the management of wastewatersresults from quantity minimization and in-situ pollution prevention. Despite the use of the best available technologies, the generation of wastewaters in industrial processes is sometimes unavoidable. Also, the discharges of pyridine compounds exhibit toxic characteristics with high carcinogenic and mutagenic activity (Lataye et al. 2008; Jiquan et al. 2012; Jihyun et al. 2014). Also, pharmaceutical agents, such as isoniazid, cetyl pyridinium bromide, analgesic dermal, and cephalexin, are manufactured using pyridine as a catalyst (Lindqvista et al. 2005; Li et al. 2009; Lin et al. 2010). Therefore, a large amount of pyridine-containing wastewater as effluents is released by various industries. Numerous pyridine compounds are dangerous and prevalent for a longer time in the environment, as they are poor substrates to indigenous microorganisms. The removal of pyridine from the water stream is, therefore, of great importance (Malhotra et al. 2005; Malesic et al. 2006; Luis et al. 2009; Loures et al. 2013). To remove most of the organic load, biological processes are usually used, because they are more economical than the physical and chemical ones. Most physical methods like adsorption are very sensitive to the pH of the wastewater. Other methods, such as Thermal incineration and Ultrafiltration, are not economical. Biological methods are environment-friendly, using optimized natural pathways to eradicate pollution and transform it into another form (Niu

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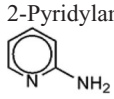
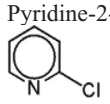
and Brain 2002; Mohan et al. 2003; Neyens and Baeyens 2003; Mohan et al. 2004; Padoley et al. 2008; Ortega et al. 2012 Oliveira et al. 2014). In some cases, however, due to high organic load, toxicity, or persistent compounds like pyridine, biological treatment is not feasible. Substances synthesized in the pharmaceutical industry are structurally complex organic chemicals resistant to biological treatment (Rodriguez et al. 2011; Shamba et al. 2013). In such a case, chemical pre-treatment, like the advanced oxidation technologies, can be investigated,because it can adequately increase the biodegradability and remove toxicity of the wastewater before biological treatment (Padoley et al. 2011). When wastewater's biological treatment is unachievable, a cost- and resource-efficient substitute to direct chemical treatment includes a biological treatment with a chemical pre-treatment to convert the hazardous pollutants into more biodegradable compounds (Yao et al. 2011). AOPs are processes that rely on the generation of very reactive oxidizing agents, i.e. free radicals, such as the hydroxyl radical (OH∗). Hydroxyl radicals can initiate oxidative degradation reactions of refractory synthetic and natural organic compounds and mineralize them ultimately to carbon dioxide and water due to their high oxidation potential ($+2.80$ V) in aqueous solution (Stapleton et al. 2010). Many methods have been classified under the AOPs. Many researchers use a combination of strong oxidizing agents (e.g. hydrogen peroxide and or ozone), catalysts (e.g. transition metal ions like ferrous salts) and irradiation (e.g. ultraviolet). Among AOPs, Fenton and photo-Fenton oxidation processes are the most promising ones for the effective degradation of organic non-biodegradable pollutants (Wu et al. 2010). Several studies have indicated that Fenton oxidation is very effective in removing many hazardous organic pollutants from water and wastewaters. The Fenton oxidation process is cost-effective, clean, easy to operate; it can degrade and mineralize most organic compounds; it has more pharmaceutical removal efficiencies. In photo-Fenton process oxidation degradates organics quickly. The efficacy of the Fenton and photo-Fenton process may also depend upon the type of catalyst used in the Fenton reagent. The catalyst like ferrous iron has been extensively used in Fenton reagent for several years. Therefore, in this paper, the Fenton and photo-Fenton oxidation treatment technology wase adopted to degrade a 2-Aminopyridine pharmaceutical compound derived from pyridine.

The main objective of this paper is to evaluate the efficacy of Fenton and Photo-Fenton oxidation processes for possible degradation and mineralization of 2-Aminopyridine.

2. Materials

The pharmaceutical compound, 2-Aminopyridine, is selected on the basis of comprehensive application, production in large quantities, subsequent occurrence in aquatic systems, and their toxic and carcinogenic effects on the environment. Table 1 highlights the physicochemical properties such as the structure, molecular weight, water solubility, stability, melting point/boiling point, and applications of 2-Aminopyridine.

Table 1. Physicochemical characteristics of the 2-Aminopyridine.

Properties	2-Aminopyridine
Synonym	2-Pyridylamine, pyridine-2-amine
Structure	
Formula	$C_5H_6N_2$
Mol. wt (g)	94.12
Water solubility at 20°C in g/100 mL	$>$ 100
Stability	Stable at ambient temp.
M.*P* / B.*P*, °C	58/211
pK_a	6.9
Use	Anti-histamines and piroxicam (anti-inflammatory drug). ciclopiroxolamine, diphenpyramide, methaqualone, propiram fumarate, pyrilamine.
Properties	**2-Chloropyridine**
Synonym	Pyridine-2-chloro
Structure	
Formula	C_5H_4NCl
Mol. Wt (g)	113.55
Water Solubility at 20°C in g/100mL	2.5
Stability	Stable at ambient temp.
M.*P* / B.*P*, °C	$-$ 46.5/169

3. Experimental methodologies

This section deals with the determination of pH, drug concentrations, Chemical oxygen demand (COD), Hydrogen peroxide (H_2O_2) concentration, iron concentrations measured in the experiment, and also the HPLC analysis was performed for the experiments. To achieve the most accurate and reliable results, extreme care was taken to ensure that all the laboratory and sampling equipment are as clean as possible. This was achieved following the methods and procedures described in the Standard Methods for the Examination of Water and Wastewater. All glassware was thoroughly washed immediately after use. To remove the organic matter (e.g. COD vials) chromic acid was used to clean the glassware. The glassware was rinsed with reagent water before use. UV-Vis spectrum was recorded using a UV-Vis double beam spectrophotometer, and the characteristic wavelength (λmax) of the drug at maximum light absorbance was observed at wavelength 290 nm. For the range of concentrations depending upon each drug, a linear relationship (calibration curves) between absorbance and

Table 2. Chromatographic condition.

Condition	2-Aminopyridine
Column (stationary phase).	100 × 4.6 mm, 3.5-micron Eclipse plus C_{18} column
Column temp.	25°C
Autosampler temp.	NA
Detection wavelength	290 nm
Flow rate	0.8 mL/min
Injection volume	20 µL
Mobile phase	Solvent A: Acetonitrile (HPLC Grade) Solvent B: Water (Solvent Ratio: 50: 50 of A: B)

concentration was established. These calibration curves were used to measure the drug concentration in the sample.

HPLC chromatographic system: The chromatographic system used in this study is Shimadzu LC-Solutions HPLC. The system consists of a solvent delivery pump (sub-master/A pump and vice/B pump), an Autosampler, a UV–Vis detector, a desktop computer and other components. The chromatographic column used for separation was a C18 reversed-phase column (5-micron inertsil, 4.6 × 250 mm). The whole system control and the data evaluation are conducted by PC interface LC solution software. An appropriate volume of the sample is drawn and filtered through 0.45 µm pore size Millipore syringe-driven filters. An autosampler is fitted with vials containing 20 µL sample for analysis. A suitable chromatographic method is fixed after taking trials involving solvents in proper proportion to suit the analysis of drugs. The chromatograms are recorded using the developed HPLC chromatographic conditions, and the response for major peaks at retention time is monitored. Table 2 illustrates the chromatographic condition used for analysis.

4. Results and discussions

A detailed study using the Fenton and photo-Fenton oxidation was done to optimize the reaction conditions such as initial pH of the solution matrix, the dosage of hydrogen peroxide (H_2O_2), the dosage of ferrous (Fe^{2+}) for the maximum drug degradation and COD removal. The effect of initial drug concentration on the degradation and COD removal was also evaluated. The kinetic studies on drug degradation were conducted, and the corresponding chemical reaction kinetic rate constants (k) were calculated.

4.1. Fenton and photo-Fenton oxidation of 2-Aminopyridine in water

The peak of maximum absorbance for 2-Aminopyridine was detected at wavelength 290 nm using a UV–Vis spectrophotometer. Therefore, a calibration curve was established between sample absorbance and concentration for this wavelength. The 2-Aminopyridine sample concentration, before and after treatment, was measured using a developed calibration curve (Figure 1).

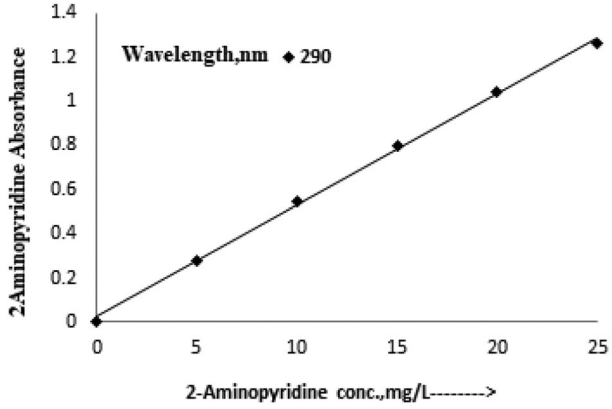


Figure 1. Calibration curves of 2-Aminopyridine pharmaceutical compounds.

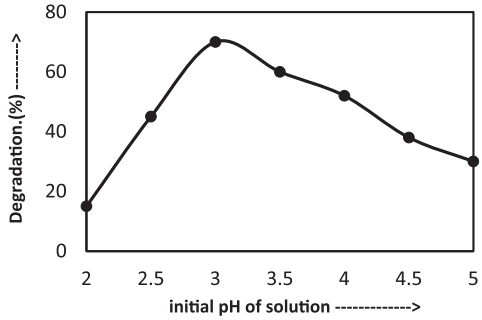


Figure 2. Effect of initial pH of solution on 2-Aminopyridine degradation. Expt. conditions: $[2\text{-Aminopyridine}]_0 = 10$ mg/L; $[H_2O_2]_0 = 50$ mg/L; $[Fe^{2+}]_0 = 1.5$ mg/L.

4.2. Fenton oxidation of 2-Aminopyridine using ferrous ion (Fe^{2+})

Oxidation experiments were conducted following the method described earlier using ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) as the source for ferrous ion as the iron catalyst. Parameters, such as the effect of initial pH, doses of iron, and hydrogen peroxide, were suitably optimized for every initial concentration of 2-Aminopyridine varying from 10 to 80 mg/L.

4.3. Effect of initial pH

To determine the optimum pH, experiments were conducted at pH values from 2 to 5. Figure 2 shows the degradation (%) of 2-Aminopyridine with the initial concentration of 10 mg/L. Trial doses of $[H_2O_2]0 = 50$ mg/L and $[Fe^{2+}]0 = 1.5$ mg/L were selected to get considerable degradation of 2-Aminopyridine. All the treated samples were analyzed after 24 h of reaction time.

Figure 2 shows that as pH increases from 2 to 3, degradation of 2-Aminopyridine also increases. A maximum degradation of 77% was achieved at an initial pH value of 3. The removal efficiencies were less for the other values of pH. When pH $>$ 3, oxidation efficiency was rapidly decreased. This may be due to the auto-decomposition of hydrogen peroxide affecting the production of hydroxyl radicals and deactivation of the ferrous catalysts with the formation of ferric hydroxide precipitates [Fe $(OH)_3$]. Ferrous iron oxidizes to ferric iron, and ferric hydroxide forms a yellowish-orange solid (commonly called yellow boy), precipitating at pH $>$3. With the increase in pH, hydrolysis occurs by forming hydroxylating species, whose proportion depends on pH (Luis et al. 2009; Loures et al. 2013). When pH $<$3, the degradation was lowered. This is because at pH $<$3, the reaction of hydrogen peroxide with ferrous ion is seriously affected to reduce hydroxyl radical production. Water is formed by the reaction of hydroxyl radicals with H+ ions, as reported by Lucas and Peres 2006.

4.4. *Effect of hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) concentration on degradation and COD reduction of 2-Aminopyridine using Fenton oxidation process*

Hydrogen peroxide (H_2O_2) was the basis for the radical generation in Fenton Oxidation. The hydroxyl radicals oxidize the pollutants and other intermediates. Hence, an investigation of hydrogen peroxide consumption and optimization of Fenton and photo-Fenton oxidation was vital. The investigation for optimization of hydrogen peroxide concentration was carried out by varying hydrogen peroxide concentration, but keeping the iron concentration constant. The amount of hydrogen peroxide (H_2O_2) required, based on stoichiometric calculation (Equation 1), is 6.5 mg per mg of 2-Aminopyridine.

$$C_5H_6N_2 + 18H_2O_2 + Fe^{2+} \rightarrow 5CO_2 + 20H_2O + 2HNO_3 + Fe^{2+} \quad (1)$$

Fenton oxidation trials were conducted with doses of hydrogen peroxide starting from 10 mg/L. Initially, the trials were carried out without using ferrous ions, and the effect of adding only the oxidant (H_2O_2) was observed. The reaction proceeds very slowly and the maximum degradation was only 17% with the corresponding COD reduction of 10% (3.28 mgO_2/L). Ferrous ion of 0.25 mg/L with hydrogen peroxide has improved the degradation pattern compared with the trials using only hydrogen peroxide. Figure 3 shows that degradation of 2-Aminopyridine is achieved with COD reduction of 90% (29.52 mg O_2/L). The corresponding doses of hydrogen peroxide and ferrous ion required are 30 mg/L and 1.25 mg/L, respectively. Several researcher observed that an increase in the concentration of ferrous ions and hydrogen peroxide results in the increased production of the hydroxyl radicals, and hence the degradation is improved (Zhang et al. 2009). At higher ferrous ion concentration, the drug and COD removals were reduced.

This may be due to the ferrous ion inhibition when a high concentration of ferrous ion is present in the system, and the ferrous ion itself can react with hydroxyl radicals to scavenge them. This is also true for hydroxyl radical scavenging at a high concentration of hydrogen peroxide. When the initial concentration of hydrogen peroxide was less than 30 mg/L, the degradation was less, which may be due to low production of hydroxyl radicals. When the initial concentration of hydrogen peroxide was greater than 30 mg/L, the degradation and COD reduction were also less because of the scavenging effect of hydroxyl radicals with the increase in the hydrogen peroxide concentration, as reported by several research workers. This can be explained by that the very reactive hydroxyl radicals are consumed by the increased concentration of hydrogen peroxide that generates less reactive hydroperoxyl radical (HO_2*) (Equation 2). The hydroxyl radical is scavenged according toEquations 3 and 4. Hydrogen peroxide decomposes catalytically by Fe^{3+} and generates again Fe^{2+} and hydroperoxyl radicals (HO_2*), as shown in (Equations 5 and 6), which has low oxidation potential than hydroxyl radicals

$$H_2O_2 + OH^* \rightarrow H_2O + HO_2{}^* \quad (2)$$

$$HO_2{}^* + OH^* \rightarrow H_2O + O_2 \quad (3)$$

$$OH^* + OH^* \rightarrow H_2O_2 \quad (4)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH_2+ \rightarrow HO_2{}^* + Fe^{2+} \quad (5)$$

$$HO_2{}^* + H_2O_2 \rightarrow OH^* + H_2O + O_2 \quad (6)$$

The drug sample, treated by Fenton oxidation, using the optimum dosage of ferrous ion and hydrogen peroxide, was scanned throughout the UV–Vis spectrum range from 200 to 400 nm wavelength. Figure 4 shows the UV–Vis profiles of the 2-Aminopyridine drug (10 mg/L initial concentration) at before and after treatment conditions. The absorbance peak of 2-Aminopyridine at 290 nm was absent after treatment. It was, therefore, concluded that 2-Aminopyridne was completely degraded.

The HPLC analysis of the drug samples was also performed using the optimized experimental conditions. Figure 5 shows the HPLC chromatogram of the 2-Aminopyridine drug. HPLC chromatogram of the sample at 290 nm wavelength, containing 10 mg/L of 2-Aminopyridine, shows a prominent peak at a retention time of 1.531 min. The area under the 2-Aminopyridine peak was 693 mAU∗s. The absence of a peak in the treated sample corresponding to this retention time indicated that no residual 2-Aminopyridine was present in the treated sample. Therefore, it was concluded that complete degradation of the drug was achieved. Samples treated by the

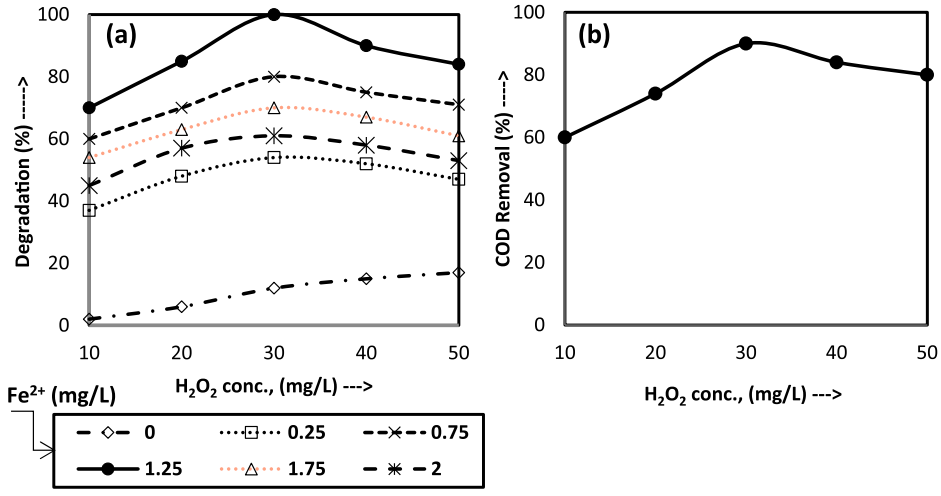


Figure 3. Effect of Hydrogen peroxide and Ferrous ion on (a) Degradation and (b) COD removal of 2-Aminopyridine by Fenton oxidation. Expt. conditions: $[\text{2-Aminopyridine}]_0 = 10$ mg/L; $[\text{COD}]_0 = 32.8$ mg/L.

oxidation processes show very marginal peaks at other retention times, which were below the detection limit of the instrument. These may be the complex intermediate compounds generated due to 2-Aminopyridine degradation. These complex intermediates and other organic acids generated that are recalcitrant to oxidative treatments, contribute to the COD value measured.

4.5. *Photo-Fenton oxidation of 2-Aminopyridine using Fe^{2+} as iron catalyst*

Oxidation experiments were conducted in UV-C light (253.7 nm) using a 8W low-pressure mercury lamp. The low-pressure lamp did not warm up, and hence no cooling device was required during the photo-chemical experimental runs. Parameters, such as the effect of initial pH, doses of iron and hydrogen peroxide, are suitably optimized for every initial concentration of 2-Aminopyridine from 10 mg/L to 80 mg/L. All the experimental runs were conducted at optimum pH = 3.0. Figure 6 indicates the effect of photo Fenton and Fe^{2+} concentration on degradation and % COD removal. It is seen that 100% degradation of 2-Aminopyridine is achieved corresponding to 1 mg/L and 20 mg/L of Fe^{2+} and H_2O_2, respectively. The dose of oxidant required in photo-Fenton runs using Fe^{2+} is less than Fenton runs. This is mainly because hydrogen peroxide exposure to UV-C light creates an additional pathway to the generation of hydroxyl radicals in addition to the Fenton reaction taking place in the reactor between the catalyst Fe^{2+} and H_2O_2. The COD reduction ,is also improved to 94% (30.83 mgO_2/L) from 90% (29.52 mgO_2/L), as achieved by Fenton runs. Experimental runs without the catalyst but with the oxidant (H_2O_2) alone could achieve only 24% of 2-Aminopyridine degradation at 20 mg/L of H_2O_2. The increase in the oxidant dose to 30, 40 and 50 mg/L has increased the degradation to 30%, 35% and 38%, respectively. The addition of Fe^{2+} dosage of 0.25 mg/L had doubled the percent degradation. The degradation increased to 60% at 20 mg/L of the oxidant dosage with 1 mg/L of Fe^{2+}. For all the other dose combinations of Fe^{2+} and H_2O_2, the percent degradation of 2-Aminopyridine was less. This was also observed by several researchrs, who pointed out the scavenging effect of H_2O_2 and Fe^{2+} at high-dose combinations, as shown on the generated radicals, thereby affecting the degradation and COD reduction.

4.6. *Effect of initial concentration of 2-Aminopyridine by Fenton oxidation using ferrous ion.*

The effect of the initial concentration of 2-Aminopyridine was studied by conducting Fenton oxidation in separate reactors, each containing 20 to 80 mg/L of 2-Aminopyridine, respectively. The doses of ferrous ion and hydrogen peroxide were optimized, as shown in Table 3. Table 3 shows that the degradation and COD removal get lowered with an increase in the initial concentration of 2-Aminopyridine. An increase in doses of Fenton reagent parameters beyond the optimum values, shown in Table 3, affected the degradation process. This may be due to their scavenging action on generated hydroxyl radicals. This action limits the maximum initial dose concentration that can be added to the reactor. As shown in Table 3, complete degradation of 2-Aminopyridine was achieved for 10 and 20 mg/L initial concentrations.

For 2-Aminopyridine with 80 mg/L of initial concentration, the maximum degradation achieved was 90%. At the same time, 74% (194.176 mgO_2/L) COD removal was achieved in the present study.

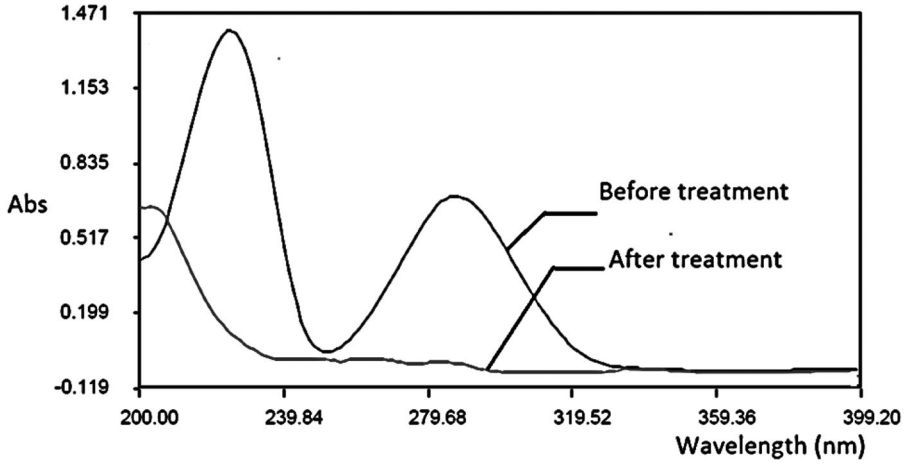


Figure 4. UV–Vis profiles of 2-Aminopyridine for before and after treatment by Fenton oxidation using ferrous ion.

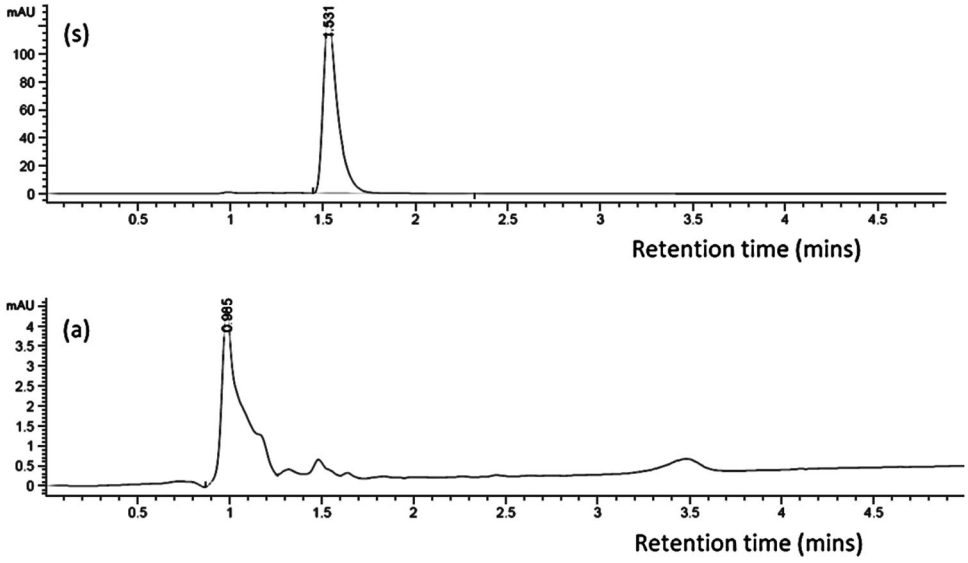


Figure 5. HPLC chromatogram of 2-Aminopyridine; (s) 10 mg/L concentration after treatment by Fenton oxidation using Ferrous ion.

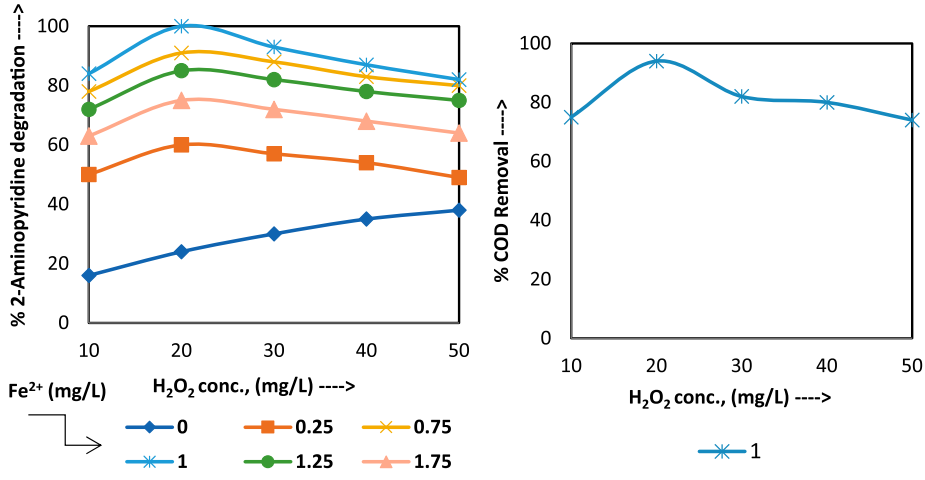


Figure 6. Effect of H_2O_2 and Fe^{2+} concentration on degradation and % COD removal of 2-Aminopyridine by photo-Fenton's oxidation using ferrous iron. Experiment conditions: $[\text{2-Aminopyridine}]_0 = 10$ mg/L; $[\text{COD}]_0 = 32.8$ mg/L.

Table 3. Effect of initial concentration of 2-Aminopyridine on the degradation and COD removal by Fenton oxidation using ferrous ion.

Initial concentration (mg/L)	Fe^{2+} (mg/L)	H_2O_2 (mg/L)	2-Aminopyridine degradation (%)	COD removal (%)	COD removal (mgO_2/L)	COD remaining (mgO_2/L)
10	1.25	30	100	90	29.52	3.28
20	2.5	60	100	88.2	57.86	7.74
30	3.75	90	98	86.5	85.11	13.29
40	4.75	120	97.6	84	110.2	21
50	5.75	150	97.1	82.6	135.46	28.54
60	6.5	180	93	80.4	158.23	38.57
70	7.25	210	92	77.7	178.4	51.2
80	8	240	90	74	194.17	68.23

4.7. *Effect of initial concentration of 2-Aminopyridine by photo-Fenton oxidation using ferrous ion*

To study the effect of the initial concentration of 2-Aminopyridine on its degradation, UV-C light-induced photo-Fenton processes were carried out in lab-scale reactors each containing doses of 2-Aminopyridine varying from 10 to 80 mg/L. The optimum doses of Fe^{2+} and H_2O_2 for each set of initial 2-Aminopyridine concentration are determined experimentally, as shown in Table 4. Due to the scavenging action of Fenton's reagent parameters (Fe^{2+} and H_2O_2), there is a limit on their maximum dose combination. For 30 mg/L the initial concentration of the drug and the corresponding dosage of Fe^{2+} and H_2O_2 were 3 and 60 mg/L, respectively. If the initial concentration is 40 mg/L, the dosage of Fe^{2+} and H_2O_2 is 3.75 mg/L and 80, mg/L respectively.

4.8. *Effect of reaction time on degradation and COD reduction by Fenton's process*

The reactors were dosed with their corresponding initial optimum concentrations of hydrogen peroxide and ferrous ion, as shown in Table 4. Aliquots were withdrawn at predetermined time intervals and analyzed for 2-Aminopyridine degradation and COD measurement. Figure 7 shows the variation in residual 2-Aminopyridine and COD removal with the increase in the initial concentration of 2-Aminopyridine from 10 to 80 mg/L. The reaction of hydrogen peroxide and ferrous ion degrades the target compound very fast. In the first 15 min of reaction 57% of 2-Aminopyridine (10 mg/L) was degraded n. After 30 min the degradation improved to 76%. However, for complete degradation of 10 and 20 mg/L of the initial concentration of 2-Aminopyridine, 75 min were required. The reaction is fast only up to the first 30 min and slows down. This was observed by several researchrs on different compounds treated with Fenton oxidation. The overall Fenton reaction is governed by the oxidation state of iron used in the reaction. The reaction of ferrous ion is very fast with hydrogen peroxide, which gives rise to the generation of hydroxyl radicals and oxidized iron in the form of ferric ion (Fe^{3+}). Fe^{3+} reacts very slowly with hydrogen peroxide, generating hydroperoxyl radicals (HO_2*). The oxidation potential of this radical is less than that of hydroxyl radical. Owing to this condition the reaction slows down. Thus, the overall reaction can be composed of two stages. The rapid first stage and the slow second stage of Fe^{3+} are called the Fenton-like oxidation stages. With the increase in the initial concentration of 2-Aminopyridine, the percent degradation was lowered. 68% and 48% degradation were observed after 30 min reaction time with 40 and 80 mg/L of 2-Aminopyridine concentration, respectively. The corresponding COD reduction also got lowered to 41% and 28%, respectively, for the above concentration values. There was an increase in the reaction time with an increase in 2-Aminopyridine concentration. Maximum degradation of 97.6% and 90% was seen after 105 and 150 min, with COD removals of 84% and 77.7%, respectively. The decrease in degradation with the increase in 2-Aminopyridine concentration can be due to an increase in the recalcitrant nature of the sample with the increase in concentration. The degradation leads to the formation of intermediate compounds which consume the generated radicals and further affect the degradation process.

4.9. *Effect of Reaction time on degradation and COD reduction by the photo-Fenton process*

Complete degradation of 2-Aminopyridine was achieved at all the initial concentrations. The degradation time increased with the initial concentration of the drug. From Figures 8(a,b), it is seen that drugs at initial concentrations of 10, 40 and 80 mg/L are 100% degraded in 30, 45 and 120 min, respectively. COD reduction was not complete, due to the increased concentration of intermediates at higher drug concentration. COD removals of 94.6%, 88.6% and 81% were witnessed at 10, 40 and 80 mg/L of initial drug dosage, respectively. The drug degradation and COD reduction were improved by UV-C-assisted photo-Fenton oxidation processes compared with Fenton's process.

Table 4. Optimum doses of Fe^{2+} and H_2O_2 for different initial concentrations of 2-Aminopyridine, $[2\text{-AP}]_0$, by photo-Fenton's oxidation using Fe^{2+}.

Initial concentration (mg/L)	Fe^{2+} (mg/L)	H_2O_2 (mg/L)	% 2-AP removal	% COD removal	COD removal (mgO2/L)	COD remaining (mgO2/L)
10	1	20	100	94.6	31	1.8
20	2	40	100	92.3	60.55	5
30	3	60	100	90.5	89	9.4
40	3.75	80	100	88.6	116.24	15
50	4.5	100	100	86.3	141.53	22.5
60	5.25	120	100	84.1	165.5	31.3
70	6	140	98	83.2	191	38.6
80	6.75	160	95	81	212.54	49.86

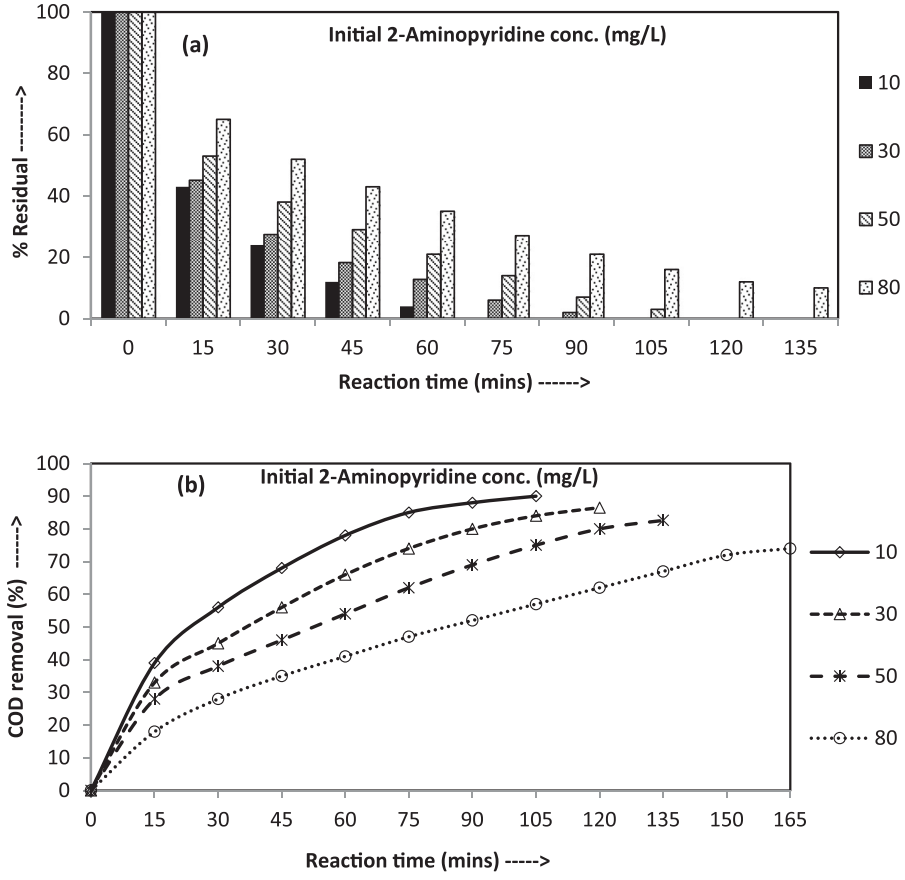


Figure 7. Variation in (a) residual 2-Aminopyridine and (b) COD removal with reaction time by Fenton oxidation using ferrous ion. Expt. condition: Fenton oxidation at optimum conditions using Ferrous ion.

4.10. Kinetic studies of 2-Aminopyridine (2-APy) degradation by the Fenton oxidation using ferrous ion (Fe^{2+})

The kinetic studies were conducted using the optimum conditions for 2-Aminopyridine degradation. The oxidation reactions of organic species may be described with a pseudo-first-order kinetic model (Equations 7 and 8) for the first few minutes of the oxidation reaction (Zwiener 2007; Babuponnusami and Muthukumar 2011). The degradation was fast in the beginning for reaction time up to 30 min, and the pseudo-first-order kinetic equation has been matched the reaction time of 30 min. Figure 9 shows the trend of a pseudo-first-order reaction kinetic model for the initial 2-Aminopyridine concentration from 10 to 80 mg/L at optimum conditions in the first 30 min.

$$\frac{d}{dt}[\mathrm{C}] = -\mathrm{K}\,[\mathrm{C}] \tag{7}$$

where C = concentration of pyridine compound, $[C]_0$ at time $t = 0$ and $[C]t$ at time "t", K = reaction rate constant.

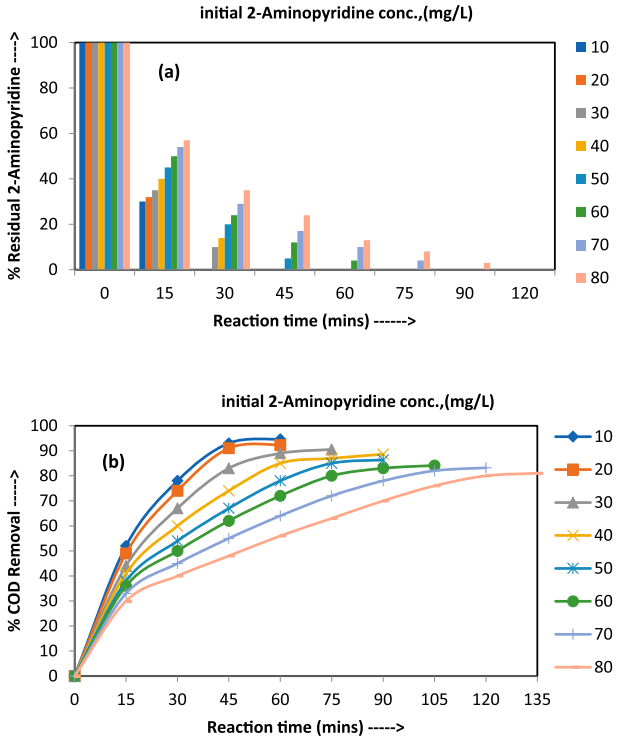


Figure 8. (a) Variation in percent 2-Aminopyridine degradation and (b) COD removals at different initial concentrations of 2-Aminopyridine. Experiment condition: photo-Fenton's oxidation at optimum conditions using Fe^{2+}.

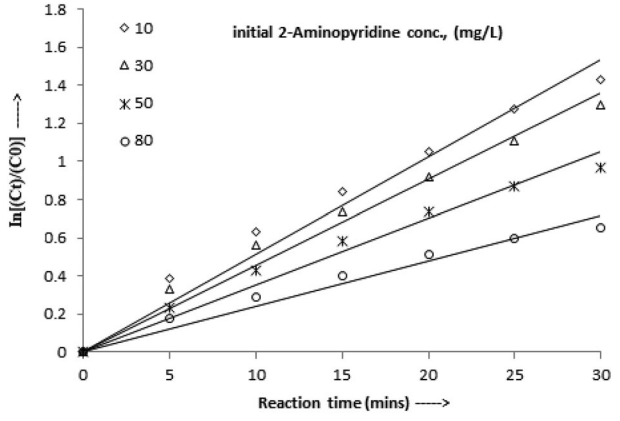


Figure 9. Trend of pseudo-first-order kinetics for the degradation of 2-Aminopyridine by Fenton oxidation using Ferrous ion. Expt. conditions: Fenton oxidation; pH 3; $[2\text{-APy}]_0$ = 10 mg/L (0.106 mM) to 80 mg/L (0.848 mM).

The integration of this equation gives the following equation:

$$\text{In } [C]t/[C]_0 = -K\,t \tag{8}$$

where "t" is the reaction time. The relationship between In $[C]t/[C]_0$ versus time (t) is plotted, and a straight trendline line was established so that the degradation follows pseudo-first-order kinetics. The slope of the straight line gives the value of the rate constant (k) (Figures 10 and 11).

Table 5. Pseudo-first-order kinetic rate constants for degradation of 2-Aminopyridine (2-APy) by Fenton oxidation using ferrous ion.

Optimum conditions			Pseudo-first-order kinetic constants	
$[2\text{-APy}]_0$, mM	$[Fe^{2+}]_0$, mM	$[H_2O_2]_0$, mM	min^{-1}	R^2
0.106	0.022	0.882	0.051	0.967
0.212	0.044	1.765	0.049	0.975
0.318	0.067	2.65	0.045	0.975
0.424	0.085	3.53	0.040	0.975
0.53	0.103	4.41	0.035	0.970
0.636	0.116	5.294	0.030	0.988
0.742	0.13	6.176	0.026	0.976
0.848	0.143	7.06	0.024	0.964

The molar relations were established, as shown in Table 5.

$[H_2O_2]_0$: $[Fe^{2+}]_0$ = [41-49]: [1] (molar); $[2\text{-APy}]_0$: $[H_2O_2]_0$: $[Fe^{2+}]_0$ = [1]: [8.32]: [0.2-0.17] (molar). It was seen that 41–49 moles of hydrogen peroxide were required per mole of ferrous ion, whereas for one mole of the drug to be degraded 0.2–0.17 moles of ferrous ion, and 8.32 moles of hydrogen peroxide were required depending upon the initial concentration range of the drug selected in the present study.

4.11. Kinetic studies on 2-Aminopyridine degradation by the photo-Fenton oxidation using Fe^{2+} catalyst.

The molar ratios of Fenton's parameters and the drug are established.

$[H_2O_2]_0$: $[Fe^{2+}]_0$ = [33-39]: [1] (molar); $[2\text{-AP}]_0$: $[H_2O_2]_0$: $[Fe^{2+}]_0$ = [1]: [5.5]: [0.17-0.15] (molar). 33–39 moles of H_2O_2 are required to react with one mole of ferrous ion under photo-Fenton's oxidation of drug at different initial concentrations. Also, for one mole of the drug to be degraded by photo-Fenton's oxidation, 5.5 moles of H_2O_2 and 0.17–0.15 moles of ferrous ion are required.

The reaction rate constants observed in the case of photo–Fenton runs are comparatively more than the rate constants of ferrous Fenton runs, as shown in Tables 5 and 6. The reaction rate is 1.83–1.4 times faster than that for ferrous Fenton runs, as indicated by the ratio $[K_{pff}]$: $[K_{ff}]$ = [1.83–1.4]: [1].

HPLC chromatography of the sample at 290 nm wavelength containing 10 mg/L of 2-Aminopyridine shows a prominent peak at the retention time of 1.531 min. The area under the 2-Aminopyridine peak is 693mAU∗s. Samples treated by the oxidation processes show very marginal peaks (less than 3mAU∗s), and some peaks are below the detection limit of the instrument. Thus more than 99.5% degree of treatment efficiency is achieved by the present study. Small peaks observed at other retention

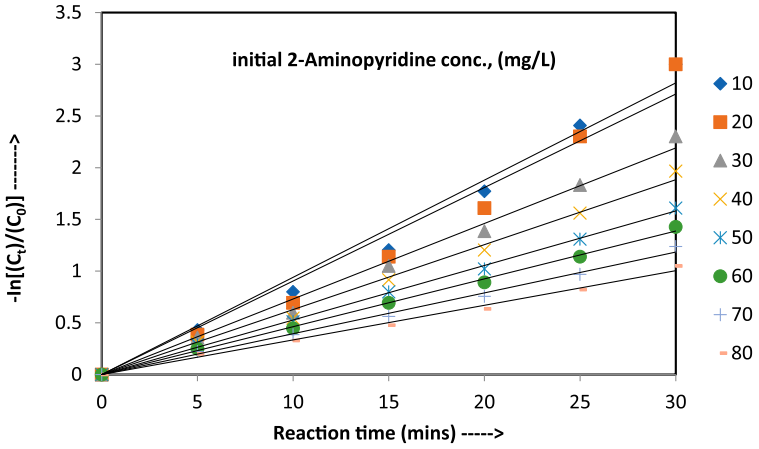


Figure 10. Trend of pseudo-first-order reaction kinetics for the degradation of 2-AP in 30 min. Expt. conditions; photo-Fenton oxidation; pH 3; $[2\text{-AP}]_0 = 0.106\_0.848$ mM.

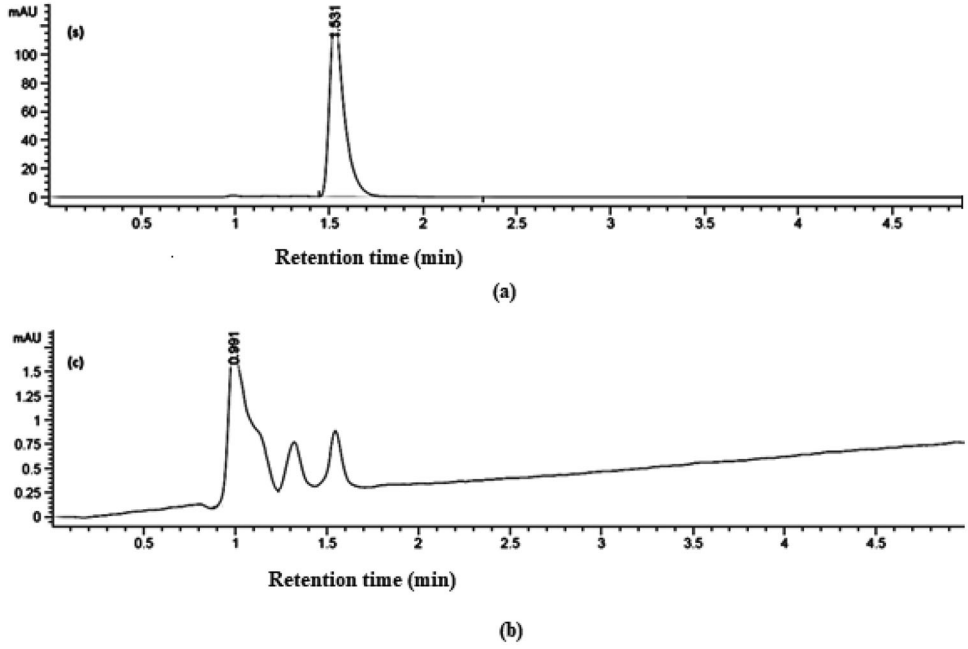


Figure 11. HPLC chromatograph of 2-Aminopyridine before and after treatment by the photo-Fenton's Oxidation process: (a) chromatograph of 2-Aminopyridine at 10 mg/L initial concentration and (b) chromatograph of 2-Aminopyridine sample treated by the photo-Fenton's oxidation process using Fe^{2+}.

times are complex intermediate compounds generated due to 2-Aminopyridine degradation. These complex intermediates and other organic acids generated that are recalcitrant to oxidative treatments, contribute to the COD value measured.

5. Conclusion

As the pH increases from 2 to 3 the degradation of 2-Aminopyridine also increases. Maximum degradation of 77% was achieved at an initial pH value of 3. The maximum degradation of 2-Aminopyridine was achieved for the entire concentration range [(10–80) mg/L]. Complete degradation of 2-Aminopyridine is achieved with 90% ($29.52 mgO_2/L$) COD reduction. The optimum doses of iron and hydrogen peroxide, required to achieve maximum degradation of the drugs, increased with an increase in the initial concentration of the drug. (90–100)% degradation of 2-Aminopyridine drugs was achieved with a single-stage feeding of hydrogen peroxide. UV–Vis profiles of the 2-Aminopyridine drug (10 mg/L initial concentration) at before and after treatment conditions have shown the absence of the drug. HPLC chromatogram illustrated the absence of a peak in the treated sample corresponding to the retention time. Hence no residual of 2-Aminopyridine was present in the treated sample. It was, therefore, concluded that 2-Aminopyridine was completely degraded. Small peaks were observed at other retention times, which

Table 6. Pseudo-first-order kinetic rate constants for degradation of 2-Aminopyridine (2-AP) by photo-Fenton oxidation using Fe^{2+} as iron catalyst.

Optimum conditions			Pseudo-first-order kinetic constants	
$[2\text{-AP}]_0$, mM	$[Fe^{2+}]_0$, mM	$[H_2O_2]_0$, mM	min^{-1} [Kpff]	R^2
0.106	0.017905	0.588235	0.094	0.984
0.212	0.03581	1.176471	0.09	0.962
0.318	0.053715	1.764706	0.073	0.968
0.424	0.067144	2.352941	0.0628	0.973
0.53	0.080573	2.941176	0.0527	0.993
0.636	0.094002	3.529412	0.0463	0.976
0.742	0.107431	4.117647	0.0395	0.98
0.848	0.120859	4.705882	0.0335	0.983

are due to complex intermediate compounds generated due to 2-Aminopyridine degradation. These complex intermediates and other organic acids generated that are recalcitrant to oxidative treatments, contribute to the COD value measured.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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