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Effect of lateritic iron and hydrogen peroxide for degradation and mineralization of pyridine compound 2-aminopyridines

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ABSTRACT

Pyridine is an important raw material in the pharmaceutical industry. Aminopyridines are key intermediates for the synthesis of important pharmaceutical products. 2-Aminopyridine is used in the production of antibacterial and several antihistamines drugs. Pyridine compounds have harmful effects on the liver, kidneys, immune systems, and reproductive functions, and have potential carcinogenicity. It is very essential to degrade 2-aminopyridines from an aqueous environment on a priority basis. Large-scale application of Fenton/photo-Fenton processes employing ferrous salts Fe^{2+} may prove costlier for the complete treatment of contaminated water/wastewater containing such recalcitrant compounds. 100% degradation of 2-aminopyridine (10 mg·L^{-1}) by the Fenton process required 180 min out of which 58% degradation was achieved in the first 60 min of the reaction. The photo-Fenton oxidation process showed an improved rate of degradation. Parameters like pH, the dosage of hydrogen peroxide, and iron extracted from laterite soil are optimized for the effective degradation and mineralization of 2-aminopyridine in water. Kinetic studies were also conducted using the optimum conditions for 2-aminopyridine degradation and, the pseudo-first-order kinetic equation has been fit up to the reaction time of 30 min. High-performance liquid chromatography analysis was also carried out to confirm the cleavage of the pharmaceutical compound 2-aminopyridine.

Keywords: Chemical oxygen demand; Fenton oxidation; Lateritic iron; Photo-Fenton oxidation; Pharmaceutical compound

1. Introduction

Pyridine derivatives are value-added intermediates derived/prepared using pyridine. These are used for the manufacture of active ingredients in the pharmaceutical industry. Pyridine compounds were detected in drinking water samples taken around hazardous waste sites and industrial areas. Pyridine compounds were found in wells in an industrial area of Wyoming [1]. 2-Aminopyridines, if released into water, are not expected to adsorb to suspended solids and sediment in the water. 2-aminopyridine is also a major metabolite of 2-isopropyl amino pyrimidine, a drug that was implicated in several cases of hepatitis [2]. 2-Aminopyridine was also detected in the urine of male Sprague–Dawley rats treated with methapyrilene, a compound that induces liver tumors in rats [3]. Evidence of contamination of wastewater, surface water, and groundwater by different types of pharmaceutical compounds, suggests that indirect human exposure to these compounds

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via drinking water is a possible pathway. Substances synthesized in the pharmaceutical industry are structurally complex organic chemicals that are resistant to biological degradation. Biodegradation in water may slowly occur based on biodegradation studies [4]. Literature studies report that conventional methods like physical and biological methods are not so effective in treating pharmaceutical wastewater. Chemical pre-treatment like the advanced oxidation processes (AOPs) can be investigated because it can adequately increase biodegradability and remove toxicity of the wastewater prior to biological treatment. A chemical wastewater treatment using AOPs has been shown to produce the complete mineralization of pollutants, or at least their transformation into more innocuous products. Furthermore, the partial decomposition of non-biodegradable organic pollutants can lead to biodegradable intermediates which can be easily degraded by other conventional processes. Among AOPs, Fenton/photo-Fenton processes have shown a great ability for oxidizing and mineralizing many nonbiodegradable pharmaceuticals [5]. Extensive studies on the application of Fenton and Fenton-based systems are carried out for the treatment of various industrial wastewater containing recalcitrant compounds at laboratory or pilot plant scales. A great number of methods have been classified under the broad definition of AOPs. Most of them use a combination of strong oxidizing agents (e.g., hydrogen peroxide and or ozone) with catalysts (e.g., transition metal ions like ferrous salts) and irradiation (e.g., ultraviolet) [6]. It has been demonstrated that Fenton's reagent is able to destroy different phenols, nitrobenzene, and herbicides in water media as well as to reduce chemical oxygen demand (COD) in municipal wastewater. Choosing proper H_2O_2 doses is crucial to an effective AOP and also minimizes the scavenging contribution of H_2O_2. Completion of oxidation reactions, as well as oxidative destruction of compounds immune to unassisted H_2O_2 oxidation, can be achieved by supplementing the reaction with UV radiation. Thus, when exposed to UV irradiation, the complex compound is further subjected to decomposition. In the present study, both the Fenton and photo-Fenton oxidative experiments were studied using hydrogen peroxide with lateritic iron as a catalyst to achieve complete degradation of 2-aminopyridine from aqueous environments. Lateritic iron is eco-friendly when compared to ferrous (Fe^{2+}) and is naturally available. In India, laterite soil is spread, covering parts of Karnataka, Tamil Nadu, and Orissa. The laterite soil contains 16%–67% of ferric oxide (Fe^{3+}) and is easily available [7]. The evaluation of lateritic iron as an alternate catalyst in the Fenton reagent is a worthwhile effort attempted in this paper for the degradation of 2-aminopyridine. Several studies have shown that pyridine compounds are detected in drinking water samples taken around hazardous waste sites and industrial areas [8].

Since Fenton and photo-Fenton are catalyzed by lateritic iron by considering that these are hydrolyzed to form insoluble hydroxides, the pH of the medium has an important role in the reactions, thus affecting the rate of degradation of organic compounds. The influence of pH was also evaluated in the present study. The extent of mineralization is monitored from the COD values. The residual concentration of the drug was measured using a UV-Vis double-beam spectrophotometer. This study focuses on the catalytic use of lateritic iron, extracted from locally available soil, as a replacement for conventional ferrous salts. Fenton/photo-Fenton experiments were conducted on different initial concentrations of 2-aminopydine. 2-Aminopyridine concentration varying from 10 to 80 $mg{\cdot}L^{-1}$ contained in separate batch reactors is dosed with lateritic iron, and hydrogen peroxide to check the effect on its degradation and mineralization.

2. Material

The pharmaceutical compound used in the present paper was 2-aminopyridine. The simulated pyridine compound aqueous stock of each 1,000 $mg{\cdot}L^{-1}$ concentration was prepared weekly with deionized water (electrical conductivity ≤ 10 $\mu S{\cdot}cm^{-1}$) and stored in the dark at 4°C in an air-tight amber glass bottle. All the chemicals used in the experimentation are AR grade or high-performance liquid chromatography (HPLC) grade. All experiments are performed in deionized water. All the reagents required are prepared with the same deionized water. The instruments used for experimentation and analysis in the present study are UV-VIS double beam spectrometer, 2201, and AU 2701 (Systronics, India) for the measurement of absorbance, characteristic wavelength, and concentration of 2-aminopyridine. HPLC system (Shimadzu LC Solutions, Japan and Agilent 1600 series, Germany) was also used for experimental analysis of 2-aminopyridine degradation studies. COD digester – ET 125 (Lovibond, Germany) was used for COD determination. Photo-Fenton oxidative experiments were performed using a UV-C lamp (diameter – 10 mm, length – 330 mm, power – 8 W, light intensity – 30 $mWs{\cdot}cm^{-2}$).

3. Methodology

This deals with the determination of pH, 2-aminopyridine concentrations, COD, H_2O_2 concentration, and iron concentrations measured in every experiment and HPLC analysis. To achieve the most accurate and reliable results possible, extreme care is taken to ensure all lab and sampling equipment are as clean as possible. This is achieved by adhering to the methods and procedures described in Standard Methods for the Examination of Water and Wastewater (APHA 2005). All glassware used is thoroughly washed immediately after use. To remove the organic matter (e.g., COD vials) chromic acid is used to clean the glassware. The glassware is rinsed with reagent water before use.

3.1. Spectral characterization and concentration of 2-aminopyridine using UV-Vis spectrophotometer

UV-Vis spectrum is recorded using a UV-Vis double-beam spectrophotometer. The characteristic wavelength (λ_{max}) of 2-aminopyridine at maximum light absorbance is observed to be at wavelength 290 nm. For the range of 2-aminopyridine concentrations, a linear relationship (calibration curve) between absorbance and concentration is established.

3.2. Determination of hydrogen peroxide (H_2O_2)

In the present study, 50% hydrogen peroxide solution is used to prepare to work H_2O_2 solutions of different

concentrations. H_2O_2 concentration in the sample is determined by Iodometric Titration Method. The method is less susceptible to interference by organics and is more suitable for measuring mg·L^{-1} levels of H_2O_2. Typically, 25 mL of sample is taken in the conical flask. 10 mL H_2SO_4 (20%) and 10–15 mL KI (1% wv^{-1}) solution and then 2 drops of ammonium molybdate are added to the sample. Upon addition of iodide solution in the presence of an oxidant, the solution becomes dark yellow. The solution is left standing for 20–30 min at room temperature in a closed bottle protected from light. The sample mixture is titrated with 0.1 N sodium thiosulphate till colour changes to straw yellow colour. Then, 2–5 drops of starch solution are added as an indicator. The solution becomes dark blue upon the addition of the starch solution. Subsequently, titration is continued with 0.1 N $Na_2S_2O_3$ solutions. The hydrogen peroxide concentration can be calculated assuming that all oxidation of iodide to triiodide ion is due to its presence [9]. The sodium thiosulphate is standardized periodically to evaluate its strength and then used in the experiments.

3.3. High-performance liquid chromatography (HPLC analysis)

The chromatographic system employed in this study is Shimadzu LC-Solutions HPLC. The system consists of a solvent delivery pump (sub-master/A pump and vice/B pump), Autosampler, 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 mm × 250 mm). The whole system control and the data evaluation are conducted via PC interface LC solution software. An appropriate volume of sample is drawn and filtered through 0.45 μm pore size Millipore syringe-driven filters. 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 mobile phase includes Solvent A: acetonitrile (HPLC Grade) and Solvent B: Water with a Solvent Ratio of 50:50 of acetonitrile and water.

The chromatograms are then recorded using the developed HPLC chromatographic conditions and the response for major peaks at retention time is monitored.

3.4. Extraction of lateritic iron from laterite soil

The dried laterite soil was crushed to powder and was passed through a 150 μm sieve. 0.5 g of this sieved soil is taken in a glass beaker and 20 mL of 1:1 HCl is added. This solution is mixed and grinded till the entire sample is dissolved. Then this beaker with the sample is kept for heating on a sand bath for maximum evaporation till a residue is formed at the bottom of the beaker. The residue left is baked in an oven for 1 h. Again, to this baked residue, 20 mL of 1:1 HCl is added and it is heated for 1 min after heating 20 mL of hot distilled water is added. This solution is filtered through a Whatman-42 filter paper and the filtrate obtained is transferred to a Nessler's cylinder and is diluted up to 100 mL The resulting solution obtained after dilution is the iron extract from the laterite soil. The iron extraction from laterite is schematically represented. Though this method gives maximum extraction efficiency using HCL, the chances of scavenging of hydroxyl radicals generated during Fenton and photo-Fenton oxidation, by chloride ions cannot be ignored [10,11]. Scavenging of hydroxyl radicals by sulfate ions is very less compared to chloride ions and therefore in the present paper, H_2SO_4 was used as a medium in the extraction of iron from laterite soil instead of HCL. The extracted sample was analyzed for the determination of iron.

3.5. Determination of Iron concentration

The iron concentration was measured using a spectro colorimeter (PC Spectroll-Lovibond) by Thiocyanate-Colorimetric Method. A series of iron standards ranging from 0.5 to 2.5 mg·L^{-1} is prepared using ferrous ammonium sulphate. Each iron standard is mixed with 4 mL of 4N HCl, 5 mL 5% KSCN, and made to 100 mL with deionized water in a Nessler's tube. The spectrometer is calibrated using these standards by setting the wavelength at 510 nm and the method is stored in it. The sample is taken in the Nessler's tube and to this, 4 mL of 4 N HCl, 5 mL 5% KSCN is added and the entire solution volume is made to 100 mL with the same sample. The mixture is thoroughly mixed and kept for 15 min to develop a stable red colour. The ferric iron combines with thiocyanate ions to form a red-coloured ferric thiocyanate complex which can be measured calorimetrically at 510 nm. The sample is taken in a 10 mm path length cuvette and iron concentration in the sample is measured using the calibrated method stored in the spectrophotometer. The sample was found to be rich in iron content (soil containing 25%–30% of Fe^{3+}). The extracted iron from the locally available laterite soil was in ferric form (Fe^{3+}).

3.6. Experimental procedure adopted for Fenton and photo-Fenton oxidation

The experiments were conducted at ambient temperature (27°C ± 3°C) in batch reactors. A 1,000 mL solution of the required drug concentration was prepared from the stock solution and was taken in a 2 L reactor. The suitable quantity of ferrous ion concentration from the 1,000 mg·L^{-1} standard solution, freshly prepared from $FeSO_4{\cdot}7H_2O$, was added to the reactor bath and stirred with a magnetic stirrer. For all the experiments, pH was adjusted after adding an appropriate iron solution. A required amount of hydrogen peroxide was added to the reactor bath to initiate the reaction.

The mixture of pyridine drug solution and Fenton reagent was stirred with a magnetic stirrer during treatment. The experiment of photo-Fenton oxidation is similar except stirring was carried out in presence of UV-C light (253.7 nm) with the help of an 8 W low-pressure mercury vapor lamp (Philips lamp) covered with a quartz jacket, connected to AC power and located in the center of the photo-reactor in specially designed UV reactor chamber in the lab. The low-pressure lamp did not warm up and hence no cooling device was required during the photo-chemical experimental runs. The solution samples were taken out for analysis at pre-defined time intervals and filtered through 0.45 μm Millipore filter membrane for COD analysis, for determination of p and it would pyridine drug concentration by using UV-Vis double beam spectrophotometer and also by high-performance liquid chromatogram (HPLC).

The key features of Fenton, and photo-Fenton oxidation are its reagent conditions, that is, the concentration of iron, the concentration of hydrogen peroxide and the reaction characteristics, that is, pH, the quantity and chemical structure of the drug to be oxidized. Hence, the optimization of pH, $[H_2O_2]_0$, $[Fe(L)]_0$, is carried out at ambient temperature with an objective to achieve maximum degradation and mineralization of 2-Aminpyridine containing aqueous solution.

3.7. Reaction time

Initially, all the samples were analyzed after a reaction time of 24 h. However as per literature the oxidation runs are rapid during the initial stages of the reaction and later slows down. Therefore, an investigation on the effect of reaction time was found to be vital to observe the degradation pattern during the reaction period. Aliquots were withdrawn at predetermined time intervals from the reactor during both Fenton and photo-Fenton oxidation experiments. These were then analyzed for percent drug removal using UV-VIS spectrophotometer corresponding to the time intervals. The samples are quenched by adding 1–2 mL of sodium thiosulfate so as to take care of any residual H_2O_2 remaining in the sample.

3.8. Kinetic studies on 2-aminopyridine

The kinetic models illustrated in literature are comparatively complex involving a large number of reactions to illustrate the interactions among the chemical species involved in the oxidation process. Therefore, in the present study the pseudo-first-order kinetic model is adopted. The reaction time upto which the degradation is fast is observed and aliquots are taken at suitable time intervals based on the degradation pattern for Fenton's and photo-Fenton's oxidation runs at optimized experimental conditions established.

4. Result and discussion

A detailed study using Fenton's and photo-Fenton's oxidation is carried out in order to optimize the reaction conditions like pH, dosage of hydrogen peroxide (H_2O_2), dosage of lateritic iron [Fe(L)] for the maximum drug degradation and maximum mineralization (represented in terms of COD removal). The effect of initial drug concentration on the degradation and mineralization is also evaluated.

4.1. Effect of pH

2-Aminopyridine reactors loaded with trial doses of lateritic iron and hydrogen peroxide were stirred continuously under different pH conditions varying from 2 to 5 at ambient temperature. It was observed that maximum degradation takes place at initial pH of 3.0.

4.2. Effect of hydrogen peroxide (H_2O_2) and lateritic iron [Fe(L)] concentration on degradation and mineralization of 2-aminopyridine (2-APy)

Experiments were conducted at different dose combinations of the oxidant and the laterite catalyst. An increase in lateritic iron and hydrogen peroxide dosage to 1.25 and 40 mg·L^{-1}, respectively caused 100% drug degradation with 85% mineralization. For the trials with catalyst dosage of 0.25 mg·L^{-1} and hydrogen peroxide of 40 mg·L^{-1}, maximum degradation and mineralization achieved were only 52% and 46%, respectively. This can be attributed to the fact that initially hydrogen peroxide is required to generate ferrous ion (Fe^{2+}) from the lateritic iron (where iron is in ferric form (Fe^{3+})) as seen from Eq. (1). The generated Fe^{2+} further requires hydrogen peroxide to produce hydroxyl radicals. Further, the hydroperoxyl radicals (HO^*_2) which are generated as a result of the reaction between ferric ions and hydrogen peroxide also affect the oxidation process by consuming hydrogen peroxide and generating hydroxyl radicals as seen from Eq. (2). The oxidation potential of hydroperoxyl radicals is less than that of hydroxyl radicals [12]. The reaction of Fe^{3+} with H_2O_2 is very slow and takes a long time to achieve a desired degradation. Iron salts act as a catalyst for hydrogen peroxide decomposition.

$$Fe^{3+} + H_2O_2 \rightarrow Fe - OOH^{2+} \rightarrow HO_2^* + Fe^{2+} \quad (1)$$

$$HO_2^* + H_2O_2 \rightarrow OH^* + H_2O + O_2 \quad (2)$$

4.3. Effect of initial concentration of 2-aminopyridine by Fenton oxidation using lateritic iron [Fe(L)]

The degradation and COD removals for different concentrations of 2-aminopyridine are shown in Table 1. 2-Aminopyridine concentrations varying from 10 to 80 mg·L^{-1} contained in separate batch reactors were dosed with optimized lateritic iron and hydrogen peroxide. The dosage of lateritic iron and hydrogen peroxide was optimized by conducting Fenton experimental trials for each set of 2-aminopyridine concentrations. The optimized dosage is also shown in Table 1. It is seen that complete degradation of 2-aminopyridine (10 mg·L^{-1} initial conc.) takes place when 1.25 mg·L^{-1} of lateritic iron was dosed along with 40 mg·L^{-1} of hydrogen peroxide. The use of lateritic iron is found effective in 2-aminopyridine degradation. More than 90% drug degradation was achieved for the selected range of initial drug concentrations. Further the extent of mineralization as monitored from the COD values depicts the lower mineralization degree with increase in initial 2-aminopyridine concentration. The decrease in extent of mineralization is attributed due to increase in intermediate compound's concentration upon degradation of parent compound. The generated intermediates can scavenge the hydroxyl radicals and also contributes to the COD value.

4.4. Effect of reaction time

For complete degradation of 10 mg·L^{-1} of 2-aminopyridine by Fenton oxidation using lateritic iron, 180 min of reaction time was required. Moreover, 58% degradation was achieved in the first 60 min of the reaction. The lateritic Fenton trials, so-called the Fenton-like oxidation processes are slow because of the slower rate of reaction of Fe^{3+} (the oxidized state of the iron present in laterite soil containing Fe_2O_3 with hydrogen peroxide. Though these

Table 1
Effect of initial concentration of 2-aminopyridine on the degradation and chemical oxygen demand removal by Fenton oxidation using lateritic iron

Initial concentration (mg·L^{-1})	Fe(L) (mg·L^{-1})	H_2O_2 (mg·L^{-1})	2-Aminopyridine degradation (%)	COD removal (%)
10	1.25	40	100	85
20	2.5	80	98	83.2
30	3.75	120	97	81.6
40	4.75	160	96.5	77.5
50	5.75	200	96	76.8
60	6.5	230	92	73.3
70	7.25	260	91	70.2
80	8	290	88	67

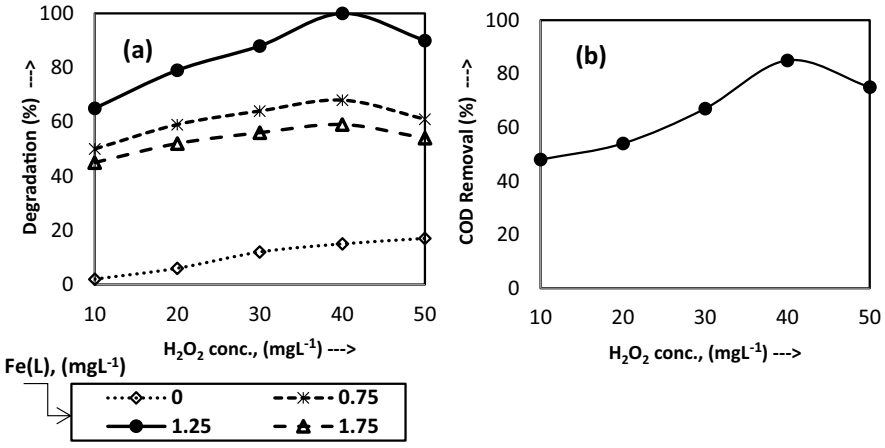

Fig. 1. Effect of hydrogen peroxide and laterite ion concentration on (a) degradation and (b) chemical oxygen demand removal of 2-aminopyridine by Fenton oxidation using lateritic iron.

reactions cause regeneration of ferrous ion (Fe^{2+}) from ferric ion (Fe^{3+}), there is the consumption of the oxidant, hydrogen peroxide. The regenerated ferrous ion (Fe^{2+}) requires hydrogen peroxide to remain in the system to produce the high potential hydroxyl radicals so as to degrade the target compound. As it can be seen that the amount of hydrogen peroxide required, increased with the increase in the initial 2-aminopyridine concentration. Hydrogen peroxide required was 160 and 290 mg·L^{-1} for initial 2-aminopyridine concentration of 40 and 80 mg·L^{-1}, respectively. Further, the extent of mineralization as monitored from the COD values depicts the lower mineralization degree with the increase in initial 2-aminopyridine concentration. The COD removals corresponding to 40 and 80 mg·L^{-1} were 77.5% and 66.7%, respectively for lateritic Fenton trials. The decrease in the extent of mineralization is attributed due to an increase in the intermediate compound's concentration as discussed earlier.

4.5. Kinetic studies of 2-aminopyridine (2-APy) degradation by Fenton oxidation using lateritic iron [Fe(L)]

Kinetic studies were conducted using the optimum conditions for 2-aminopyridine degradation using lateritic iron for reaction time up to 30 min and the pseudo-first-order kinetic equation has been fit up to the reaction time up to 30 min. Fig. 3 shows the trend of a pseudo first-order reaction kinetic model for initial 2-aminopyridine concentrations from 10 to 80 mg·L^{-1} at optimum conditions in the first 30 min.

The molar relationships were established as shown in Table 2. $[H_2O_2]_0$:$[Fe(L)]_0$ = [53–60]:[1] (molar); $[2\text{-APy}]_0$:$[H_2O_2]_0$:$[Fe(L)]_0$ = [1]:[11–10]:[0.2–0.17] (molar). For every mole of the drug to be degraded by Fenton oxidation using lateritic iron, 0.2–0.17 moles of lateritic iron and 11–10 moles of hydrogen peroxide was required. Also, 53–60 moles of the oxidant were required per mole of lateritic iron to react depending upon the initial range of concentrations of the drug under study.

4.6. Photo-Fenton oxidation of 2-aminopyridine using lateritic iron

Oxidation experiments were conducted in presence of UV-C light (253.7 nm) using an 8 W low-pressure mercury lamp. Parameters like the effect of initial pH, doses of iron, and hydrogen peroxide were optimized for every initial concentration of 2-aminopyridine varying from 10 to 80 mg·L^{-1}. All the experimental trials were conducted at optimum pH = 3.0.

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Fig. 4a and b show 2-aminopyridine degradation and COD removal achieved with varying doses of hydrogen peroxide. it is seen that complete degradation of 2-aminopyridine is achieved by using a dose combination of 1 mg·L^{-1} of lateritic iron. Along with 30 mg·L^{-1} of hydrogen peroxide. The corresponding degree of mineralization achieved (measured in terms of percent COD removal) is 91%. The dose of hydrogen peroxide required in photo-Fenton trials using ferrous ion was found less as compared to Fenton trials. 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 ferrous ion and hydrogen peroxide. In acidic solution, lateritic iron, Fe^{3+} may be present as $Fe(OH)^{2+}$. The most important species is $Fe(OH)^{2+}$ due to a combination of its relatively high absorption coefficient and concentration relative to other Fe^{3+} When exposed to UV irradiation, the complex is further subjected to decomposition and will produce OH* and Fe^{2+} ions. The classical Haber–Weiss view of the process reads as follows. It is apparent that the photo-Fenton type reaction relies heavily on the UV irradiation to initiate the generation of OH*.

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^{*} \quad (3)$$

4.7. Effect of initial concentration of 2-aminopyridine

To study the effect of the initial concentration of 2-aminopyridine on its degradation and mineralization, UV-C light-induced photo-Fenton oxidation trials were carried out in lab-scale reactors each containing doses of 2-aminopyridine varying from 10 to 80 mg·L^{-1}. The optimum doses of lateritic iron and hydrogen peroxide for each set of initial 2-aminopyridine concentration were determined experimentally and are as shown in Table 3. From the experimental

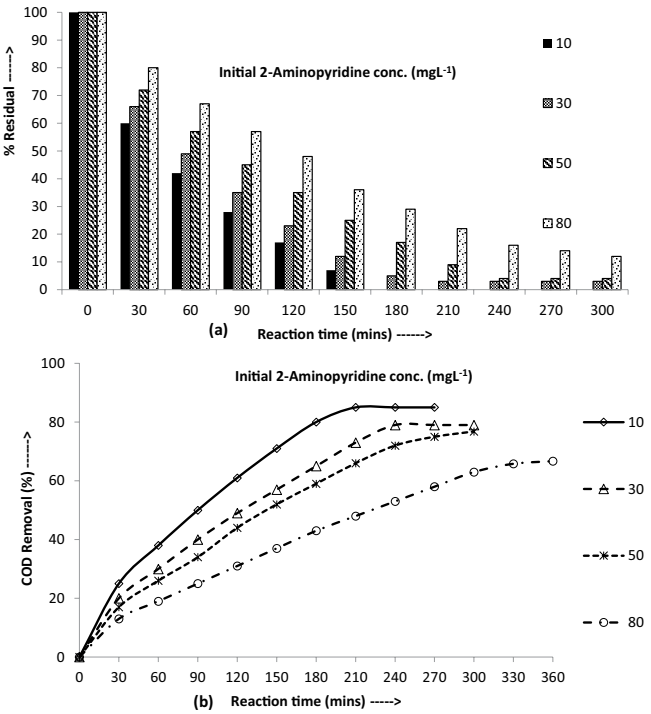

Fig. 2. Variation in (a) residual 2-aminopyridine and (b) chemical oxygen demand removal with reaction time by Fenton oxidation using lateritic iron.

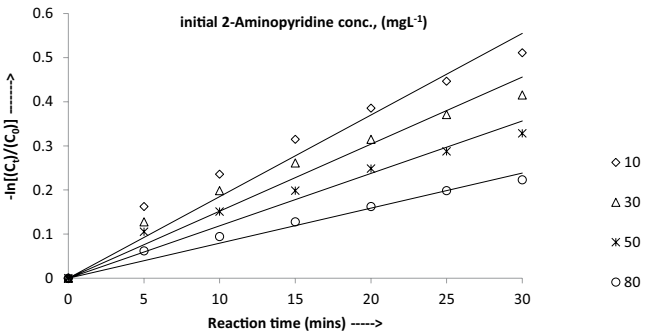

Fig. 3. Trend of pseudo-first-order kinetics for degradation of 2-aminopyridine by Fenton oxidation using lateritic iron.

Table 2
Pseudo-first-order kinetic rate constants for degradation of 2-aminopyridine (2-APy) by Fenton oxidation using lateritic iron [Fe(L)]

Optimum conditions			Pseudo-first-order kinetic constants	
$[2\text{-APy}]_0$, mM	$[Fe(L)]_0$, mM	$[H_2O_2]_0$, mM		R^2
0.106	0.022	1.176	0.0185	0.936
0.212	0.044	2.353	0.0165	0.913
0.318	0.067	3.53	0.015	0.938
0.424	0.085	4.706	0.013	0.943
0.53	0.103	5.882	0.012	0.941
0.636	0.116	6.765	0.01	0.936
0.742	0.13	7.65	0.009	0.938
0.848	0.143	8.53	0.008	0.972

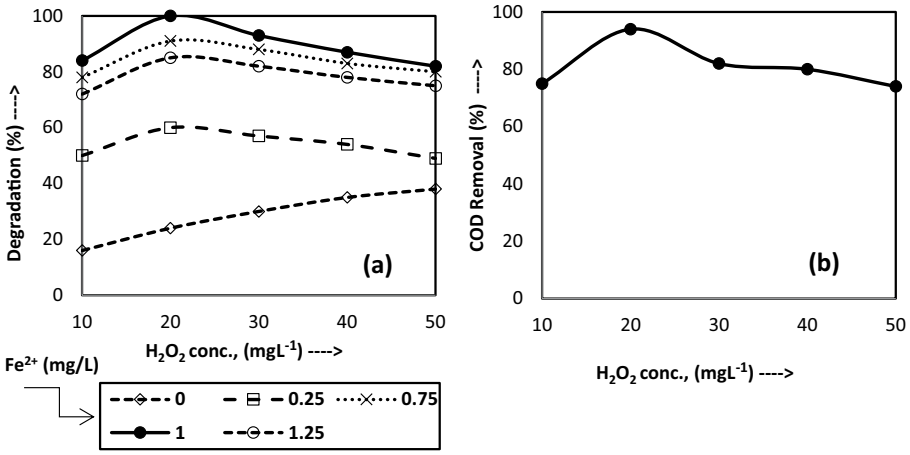

Fig. 4. Effect of hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}) on (a) degradation and (b) chemical oxygen demand removal of 2-aminopyridine by photo-Fenton oxidation.

Table 3
Effect of initial concentration of 2-aminopyridine on the degradation and chemical oxygen demand removal by photo-Fenton oxidation using lateritic iron

Initial concentration (mg·L^{-1})	Fe(L) (mg·L^{-1})	H_2O_2 (mg·L^{-1})	2-Aminopyridine removal (%)	COD removal (%)
10	1	30	100	93
20	2	60	100	91.2
30	3	90	100	90.5
40	3.75	120	100	88.8
50	4.5	150	100	86.4
60	5.25	170	98	84.2
70	6	190	96	81.7
80	6.75	210	94	79

trials at different initial concentrations of 2-aminopyridine, it was seen that there is a decrease in degradation of the drug with every increase in 2-aminopyridine concentration. Also due to the scavenging action of Fenton reagent parameters (Fe^{3+} and H_2O_2), there is a limit on their maximum dose combination as seen from Table 3. Complete degradation of 2-aminopyridine was achieved for initial concentration of 10–50 mg·L^{-1}. Thereafter the degradation was slightly less for the dose combination established experimentally. However complete degradation was also achieved for initial concentration beyond 50 mg·L^{-1} by suitably feeding the reactor with an additional dosage of hydrogen peroxide at an intermediate time interval in addition to the first oxidant feed.

4.8. Effect of reaction time

Oxidation experiments were conducted at the optimized conditions established as shown in Table 3. Aliquots were withdrawn at predetermined time intervals and the samples were analyzed for percent drug degradation and percent COD removals. A plot was obtained for the percent residual 2-aminopyridine and percent COD removals with reaction time as shown in Fig. 5. Complete degradation of 2-aminopyridine was achieved at all the initial concentration range. However, the degradation time increased with the initial concentration of the drug. From Fig. 6, it was seen that complete degradation of 2-aminopyridine is achieved after 45, 60 and 90 min, respectively at initial drug dosage of 10, 30 and 50 mg·L^{-1}. For higher initial doses of 2-aminopyridine beyond 50 mg·L^{-1}, the percent degradation is less.

As far as mineralization is concerned, it was not complete, owing to the increased concentration of intermediates at higher drug concentrations. However, both the drug degradation and mineralization improved by UV-C assisted photo-Fenton oxidation processes when compared with the earlier experiments on the Fenton process.

4.9. Kinetic studies on 2-aminopyridine degradation by photo-Fenton oxidation using laterite ion

Kinetic studies were conducted only up to the first 30 min of reaction time using the optimized conditions as established by conducting batch experiments. The reactors containing different initial concentrations of 2-aminopyridine were dosed with optimum doses of lateritic iron and hydrogen peroxide. Aliquots were withdrawn at every 5 min time interval and were analyzed for percent 2-aminopyridine degradation and percent COD removals. Fig. 7 shows a straight trend line plot depicting a

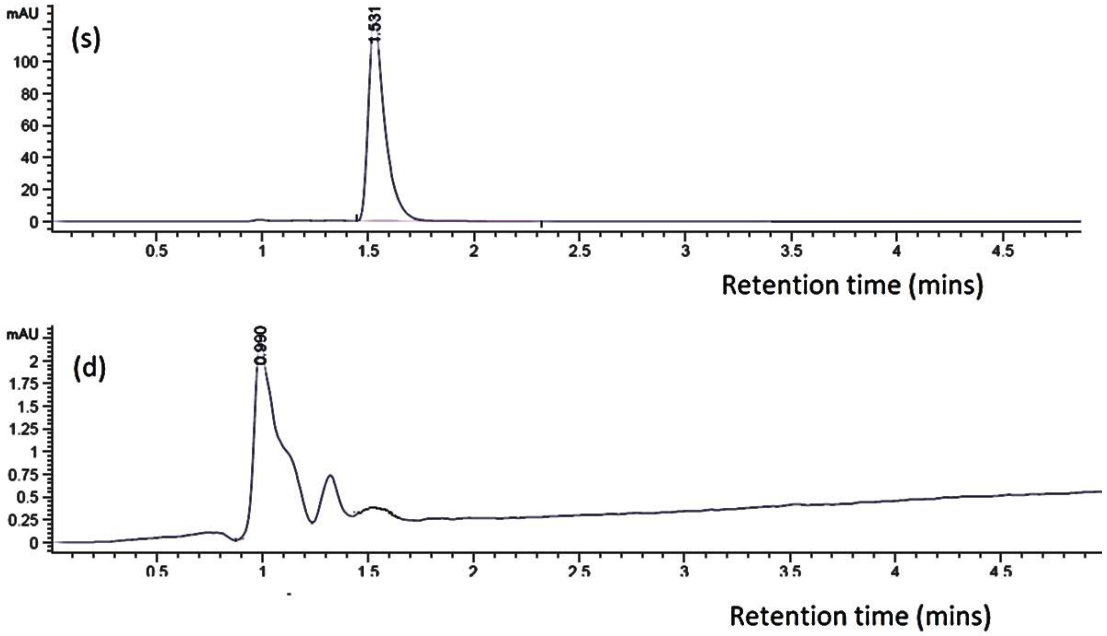

Fig. 5. High-performance liquid chromatography chromatogram of 2-aminopyridine (s) 10 mg·L^{-1} concentration (b) sample after treatment by photo-Fenton oxidation using lateritic iron.

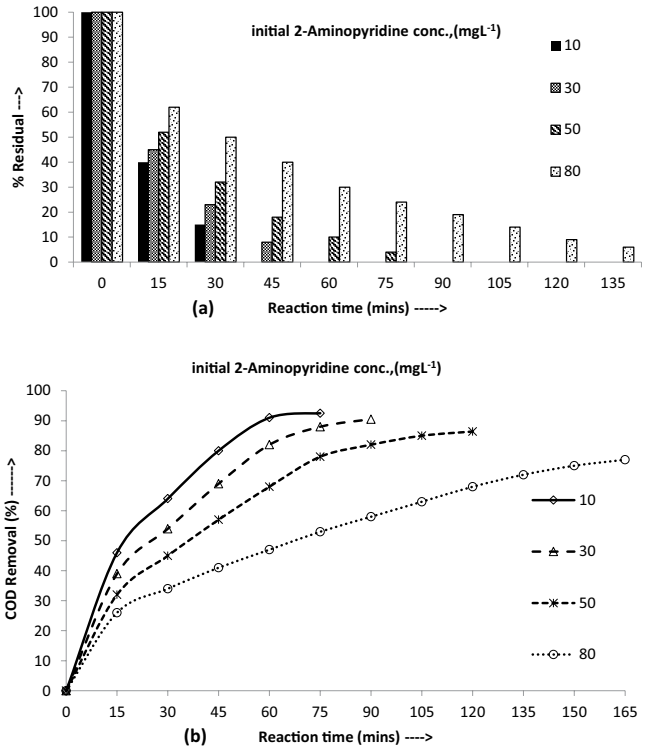

Fig. 6. Variation in (a) residual 2-aminopyridine and (b) chemical oxygen demand removal with reaction time by photo-Fenton oxidation using lateritic iron.

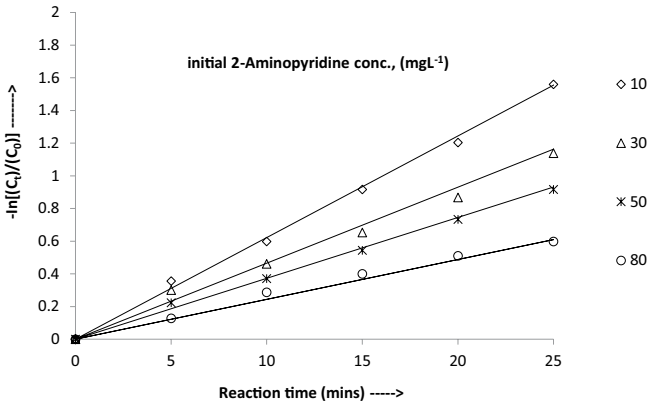

Fig. 7. Trend of pseudo-first-order kinetics for degradation of 2-aminopyridine by photo-Fenton oxidation using lateritic iron.

pseudo-first-order pattern. The reaction rate constants in the case of photo-Fenton oxidation using lateritic iron were seen to improved when compared to those obtained by Fenton oxidation using lateritic iron. The molar relationships between the drug and Fenton parameters were established. $[H_2O_2]_0$:$[Fe(L)]_0$ = [50–52]:[1] (molar); $[2\text{-APy}]_0$:$[H_2O_2]_0$:$[Fe(L)]_0$ = [1]:[8.3–7.3]:[0.17–0.14] (molar). It was seen that 50–52 moles of hydrogen peroxide were required to react with every mole of lateritic iron in photo-Fenton oxidation of the selected drug. Whereas to degrade one mole of the same drug 8.3–7.3 moles of hydrogen peroxide along with 0.17 to 0.14 moles of lateritic iron was required depending upon the initial drug concentration. The lateritic iron and hydrogen peroxide required per mole of the drug were seen decreasing relatively with increasing initial drug concentration on a molar basis. This is because of the scavenging effect of both the Fenton reagent parameters when present at higher concentrations. From the kinetic studies, it can be stated that the degradation rate of 10 mg·L^{-1} initial concentration of

Table 4
Pseudo-first-order kinetic rate constants for degradation of 2-aminopyridine (2-APy) by photo-Fenton oxidation using lateritic iron

Optimum conditions			Pseudo-first-order kinetic constants	
$[2\text{-APy}]_{0'}$ mM	$[Fe(L)]_{0'}$ mM	$[H_2O_2]_{0'}$ mM		R^2
0.106	0.0180	0.882	0.062	0.998
0.212	0.036	1.765	0.053	0.997
0.318	0.054	2.647	0.046	0.989
0.424	0.067	3.53	0.044	0.993
0.53	0.080	4.411	0.042	0.997
0.636	0.094	5	0.04	0.99
0.742	0.107	5.588	0.037	0.99
0.848	0.120	6.176	0.035	0.986

2-aminopyridine was 3 times more than that observed for 80 mg·L^{-1} initial concentration of 2-aminopyridine. From Table 4 it is observed that the rate constant for 10 mg·L^{-1} drug degradation was 0.0622 while that for 80 mg·L^{-1} L drug it is 0.035 up to the first 30 min as studied.

5. Conclusion

Use of lateritic iron in combination with hydrogen peroxide has proved effective in complete degradation and mineralization of 2-aminopyridne. The degradation was fast in the first 30 min of the reaction. The use of iron, extracted from locally available laterite soil, instead of the traditional ferrous ion, has achieved complete degradation of compounds (10–30 mg·L^{-1} initial conc.) by photo-Fenton oxidation. The degradation rate by photo-Fenton oxidation using lateritic iron is 2.5 to 3 times more than that by Fenton oxidation. The time required to achieve maximum degradation of compounds using lateritic iron. Was more compared to that required using ferrous ion. The iron extracted from laterite soil as a catalyst in the Fenton reagent has demonstrated satisfactory degradation and mineralization of 2-aminopyridine compounds and hence may be used as an alternate catalyst in the Fenton reagent.

The increased efficiency of Fenton/Fenton-like reagents with UV irradiation is attributed to irradiation of ferric ion (and/or ferric hydroxide) which will produce ferrous ion. The ferrous ion produced reacts with hydrogen peroxide generating a second hydroxyl radical and ferric ion, and the cycle continues.

In addition to conventional Fenton's reagent, which is catalyzed by ferrous iron (Fe^{2+}), modified Fenton's reagent relying on iron, extracted from locally available laterite soil as the catalysts can be widely investigated for their abilities to degrade the hazardous pyridine derivatives in aqueous solutions. The area of pre-treatment using Fenton reagent of complex wastewater containing pyridine and its derivatives is less studied and needs more focus and attention for the treatment of such wastewaters which contain a wide spectrum of heterocyclic nitrogenous bases which are difficult to remove completely. Fenton oxidation studies can work efficiently at near ambient conditions and are economical as the reagents are cheaply available.

Author contributions

All authors contributed to the work presented in the manuscript.

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