

CATALYTIC USE OF LATERITE IRON FOR DEGRADATION OF 2-AMINOPYRIDINE USING ADVANCED OXIDATION PROCESSES

Rahul Karale, Basavaraju Manu and S.Shrihari

Abstract— Pyridine derivatives like 2-aminopyridine (2-AP) can be toxic to certain life forms and are rated as priority pollutants by United States Environmental Protection Agency (USEPA). In the present study, degradation of 2-AP is carried out by Advanced oxidation employing Fenton and Photo-Fenton processes using iron extracted from laterite soil. Effect of pH, Hydrogen peroxide (H₂O₂) concentration and Lateritic iron concentration (Fe³⁺) was investigated under different doses of synthetic 2-AP solutions varying from 10-80mg/L. At [H₂O₂] : [Laterite iron] :: [40-65] : 1 for Fenton process and [40-47]:1 for Photo-Fenton process, maximum 2-AP removal was obtained. 2-AP removal of 88% and 100% respectively for Fenton and Photo-Fenton was obtained at pH= 3 corresponding to 10 mg/L initial concentration. Studies showed that Advanced oxidation processes undergoing Fenton and Photo-Fenton treatments using low cost iron, extracted from laterite soil, can be a suitable alternative to the traditional ferrous salts. Catalytic use of laterite iron with H₂O₂ is effective and can be used to treat polluted water bodies containing 2-Aminopyridine.

Index Terms— 2-Aminopyridine, Degradation, Fenton, Photo-Fenton, Hydroxyl radical, Laterite iron, Reaction time.

1 INTRODUCTION

NITROGEN containing heteroaromatic pharmaceutical compounds like pyridine have received immense attention recently, because of their presence in the environment and their toxic and carcinogenic potential and hazardous effect on natural environment. Pyridine derivatives like 2-aminopyridines can be toxic to certain life forms. [1]. These are rated as priority pollutants by (USEPA) United States Environmental Protection Agency [2]. Of the three monoaminopyridines, 2-Aminopyridine appears to have the highest production [3]. 2-Aminopyridine has various uses, but is primarily a starting material in the production of various drugs. The primary use of 2-Aminopyridine is as an intermediate in the manufacturing of pharmaceuticals, particularly antihistamines and piroxicam.

2-Aminopyridine is not expected to be readily biodegradable in aerobic and anaerobic conditions [3]. If released into water, 2-Aminopyridine is not expected to adsorb to suspended solids and sediments in water. Biodegradation in water may slowly occur. Because of its high water solubility, a large fraction of vapour phase pyridine released to the atmosphere would also tend to dissolve in

water vapour. In one study, 2-Aminopyridine was found to completely degrade in greater than 96 days under both aerobic and anaerobic conditions. [3]. Industrial wastewater containing 2-Aminopyridine must be treated, before discharging into the environment. Methods like thermal incineration and Ultrafiltration are not economical. Biological methods are environmentally friendly, using optimised natural pathways to actually destroy pollution and transform it into another form [4]. However due to the high organic load, toxicity and persistent nature of 2-Aminopyridine, biological treatment is not feasible. 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 prior to biological treatment [5].

AOPs which rely on the generation of very reactive oxidizing agents, i.e. free radicals such as the hydroxyl radical (•OH). •OH can initiate oxidative degradation reactions of refractory synthetic and natural organic compounds and is capable of mineralizing them ultimately to carbon dioxide and water owing to their high oxidation potential (+2.80 eV) in aqueous solution. 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].

One such advanced oxidation method called the Fenton and Photo-Fenton oxidation using iron extracted from laterite soil is therefore studied here for such type of waste containing the 2-Amino derivatives of pyridine.

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2 MATERIALS AND METHODS

2.1 Chemicals: 2-Aminopyridine Extra pure (98% assay) was purchased from SD Fine Chem. Ltd. (India).

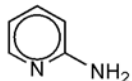


Fig.1 Chemical Structure of 2-Aminopyridine

Hydrogen Peroxide (H_2O_2) (50% w/w) and Ferrous Sulfate Heptahydrate ($FeSO_4 \cdot 7H_2O$) was purchased from Merck (India). The chemicals were used as received in the Oxidation Process. Hydrochloric acid (HCl, Merck, India, 35% purity), Sulfuric acid (H_2SO_4 , Merck, India, 98% purity), Sodium hydroxide (NaOH, Merck, India, 98% purity), were also used in the experiments. The 2-Aminopyridine aqueous stock solution of 1000mg/L concentration was prepared with Millipore Elix-3 deionized water every week and stored in the dark at $4^\circ C$.

2.2. Experimental Procedure

The experiments were conducted at ambient temperature ($27 \pm 3^\circ C$) in batch reactors. A 1000 mL solution of required 2-Aminopyridine concentration was prepared from the stock 2-Aminopyridine solution and was taken in a 2 litre reactor. Initial pH of the solution was maintained using 0.1 N H_2SO_4 and 0.1N NaOH. Appropriate amount of Fe^{2+} concentration from the 1000 mg/L stock solution, freshly prepared from $FeSO_4 \cdot 7H_2O$, was added to the reactor bath and stirred with magnetic stirrer. Required amount of H_2O_2 was added to the reactor bath to initiate the reaction. For the experiments, pH was adjusted after adding appropriate iron and H_2O_2 solution, stirred with magnetic stirrer. The mixture of 2-Aminopyridine solution and Fenton's reagent was stirred with magnetic stirrer during treatment. The experiment of Photo-Fenton oxidation is similar except stirring is carried out in presence of UV light (253.7nm) in specially designed UV reactors. The 2-Aminopyridine solution samples were taken out for analysis at pre-defined time intervals and filtered through a 0.45 μm Millipore Syringe filter for determination of residual 2-Aminopyridine concentration by using UV-VIS Spectrophotometer.

2.3. Analytical Methods

2-Aminopyridine solutions of concentration 10, 20, 30, 40, 50, 60, 70 and 80mg/L were prepared and UV-VIS spectra were recorded from 190 to 400 nm using UV-VIS double beam spectrophotometer (Systronics-2201). The absorbance peaks of 2-Aminopyridine for all the considered concentrations were at wavelength 290 nm. A standard absorbance versus 2-Aminopyridine concentration calibration curve was prepared by single wavelength mode using 2-Aminopyridine standards. This curve was used to determine the 2-Aminopyridine concentrations in aqueous solutions during the subsequent experiments. The concentration of 2-Aminopyridine in the aqueous solution at wavelength 290 nm was measured immediately after removal of samples from the reactor using the standard curve, which has already been calibrated with UV-VIS Double beam Spectrophotometer. The pH was measured with a digital pH meter (Lovibond - pH 100). The Iron concentration was measured using Spectrocolorimeter (PC Spectroll, Lovibond) by Thiocyanate-colorimetric Method. The H_2O_2 concentration was determined by Iodometric titration method.

3 RESULTS AND DISCUSSION

3.1 Effect of pH on % 2-AP removal under Fenton's Oxidation.

To determine optimal pH, experiments were conducted at different pH values varying from 2 to 5.5 with initial trial 2-Aminopyridine (2-AP) concentration of 10 mg/L, $[H_2O_2] = 30$ mg/L and [Laterite iron] = 1 mg/L.

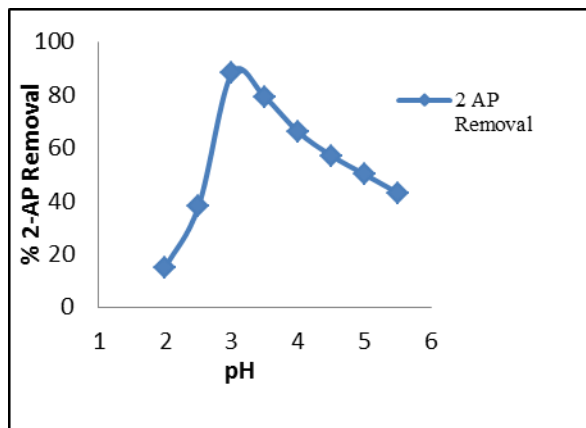


Fig.2 Effect of pH on % 2AP removal by Fenton Oxidation, $[2AP]_0 = 10$ mg/L; $[H_2O_2] = 30$ mg/L; [laterite iron]=1.0mg/L.

Optimum pH 3 was obtained in the present study on Fenton's oxidation of 2AP solutions and was set for subsequent experiments. The 2-AP removal efficiency was reduced for the other pH values. At higher pH (above 4), ferrous ions get easily converted to ferric ions, which have a tendency to produce ferric-hydroxo complexes with H_2O_2 . The low degradation at pH 2 and 2.5 is due to the hydroxyl radical scavenging by H^+ ions and also there was an inhibition for the radical forming activity of iron.

3.2 Effect of H_2O_2 and Laterite iron concentration

The investigation for optimization of hydrogen peroxide concentration was carried out by varying H_2O_2 concentration from 10 to 50 mg/L, keeping the Laterite iron concentrations (0-2mg/L) constant for each varied set of H_2O_2 conc.

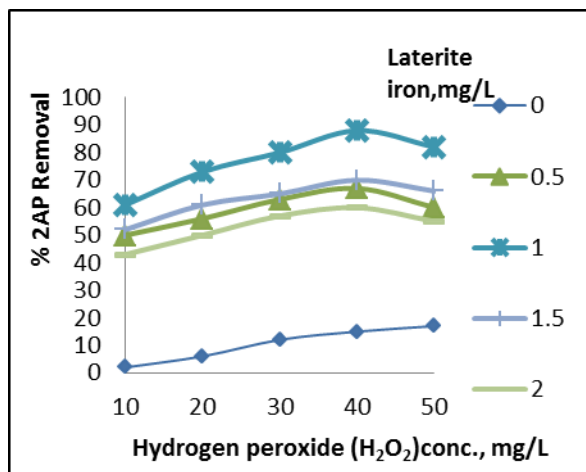


Fig.3. Fenton studies on Degradation of 2-AP; $[2AP]_0 = 10$ mg/L at pH 3.0; $[H_2O_2]_{opt} = 40$ mg/L; [Laterite iron]_{opt} = 1.0mg/L

As seen from Fig.3, the max degradation of 88 % at optimum pH = 3.0 was obtained corresponding to optimum H₂O₂ conc. of 40mg/l under Fenton's oxidation and 100% degradation of 2-AP corresponding to H₂O₂ conc. of 30mg/l in case of Photo-Fenton treatment. This is due to the fact that Photo-Fenton results in additional pathway for the generation of hydroxyl radicals which in turn helps in further degradation of compound so as to completely eliminate it from the system as shown in Fig.4

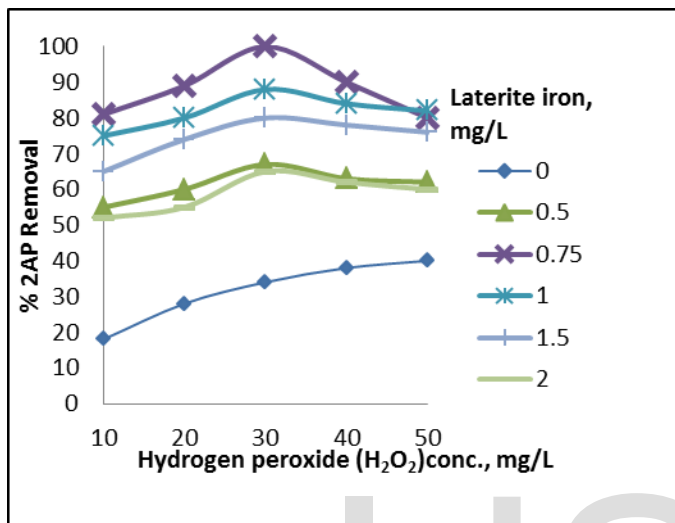


Fig.4 Photo-Fenton studies on Degradation of 2-AP; [2AP]₀ = 10mg/L at pH = 3.0; [H₂O₂]_{opt} = 30mg/L; [Laterite iron]_{opt} = 0.75mg/L.

It has also been observed that at higher laterite iron concentrations the 2-AP removals were reduced. This may be due to the inhibition that occurs when high concentration of laterite iron was present in the system as it can react with OH radicals resulting in the scavenging of OH radicals.

3.3. Effect of initial concentration of 2-Aminopyridine (2-AP)

Experiments were conducted to study the effect of initial 2-AP concentrations (10, 20, 30, 40, 50, 60, 70 and 80 mg/L) using both Fenton's and Photo-Fenton oxidation process as shown in Fig.5 and 6.

For initial 2-AP concentrations from 10 to 80mg/L using Photo-Fenton oxidation, the optimum ratio of [2AP]/ [H₂O₂] was observed to be 1:[2.5] (w/w) and the optimum ratio of [H₂O₂]/[Laterite iron] was [40-47]:1 (w/w) at pH 3. Fenton runs showed higher ratios [2AP]/[H₂O₂]:[1]/[3.5] and [H₂O₂]/ [Laterite iron]:[40-65]/[1].

At optimum conditions of Fenton oxidation ,as conc. of 2-AP was increased from 20 to 80mg/L, the percent 2- AP removals reduced from 86.3 to 70.4 %.This is mainly because of built up of recalcitrant intermediates as initial conc. increases. It is also seen from the present study that increase in conc. of 2-AP from 10-80mg/L, also increases the reaction time from 6.5 to 11 hrs. Photo-Fenton oxidation process showed 100% removal of 2-AP for conc. upto 40mg/L in 1.5 hrs of irradiation and thereafter percent removals were reduced to 86.5 as conc. increased to 80mg/L, thus requiring 4hrs for effective removal. Almost complete mineralisation can be achieved by extending the UV irradiation time.

Finally the treated samples were scanned for UV-VIS range using spectrophotometer which proved the absence of 2-AP peak after both Fenton and Photo-Fenton oxidation treatments as shown in

Fig 7.

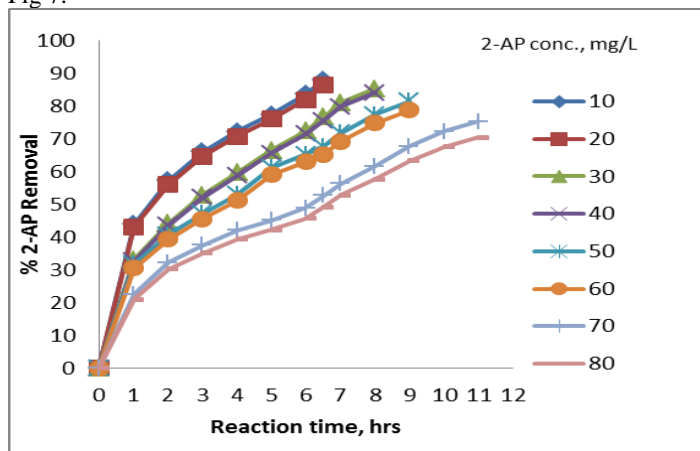


Fig.5 Effect of Initial conc. of 2-AP on reaction time under Fenton's oxidation at optimum conditions at pH=3.

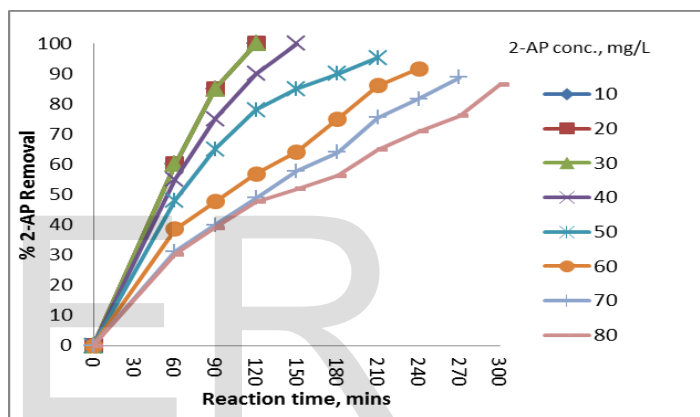


Fig.6 Effect of Initial conc. of 2-AP on reaction time under Photo-Fenton's oxidation at optimum conditions at pH=3

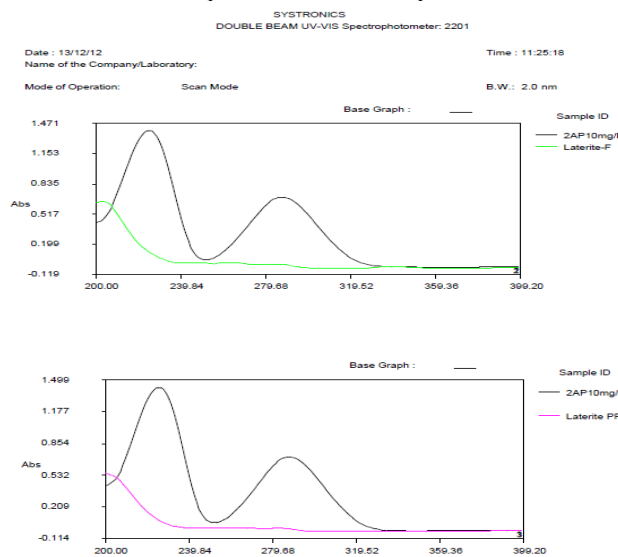


Fig.7 UV-VIS scan showing pre and post treatment curves indicating absence of 2-AP peak after Fenton (F) Oxidation (shown by green curve) and Photo-Fenton (PF) Oxidation (shown by pink curve) using iron extracted from laterite iron.

4 CONCLUSION

2-AP degradation of 100% was observed in Photo-Fenton oxidation for 10-40mg/L of 2-AP. Higher conc. requires more irradiation time to completely degrade the compound. Removal efficiency upto 90% can be achieved at lower conc. of 2-AP in case of Fenton oxidation using laterite iron. At higher conc. of 2-AP, there are increased chances of scavenging by laterite iron. Photo-Fenton oxidation of 2-AP is very effective as compared to Fenton process.

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