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## Fenton and Photo-Fenton Oxidation Processes for Degradation of 3-Aminopyridine from Water

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### Abstract

3-Aminopyridine (3AP), used in manufacture of anti-inflammatory drugs and also as a plant growth regulator is one of the emergent contaminant, because of its toxic and carcinogenic potential and hazardous effect on natural environment. The objective of present study was therefore to investigate chemical treatment like the advanced oxidation technologies employing the classic Fenton and Photo-Fenton oxidation wherein effect of operating conditions like pH, Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), Iron salts (both ferrous and iron extracted from laterite soil) and reaction time are optimized using synthetic 3-Aminopyridine solutions. In the present study, for 3AP conc. ranging from [10-80mg/L] under Fenton's oxidation at pH 3, optimum ratio of [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>] :: [24-40]/[1] showed upto [90-77%] removal efficiency. Studies on use of laterite iron replacing the traditional ferrous iron, also showed comparable removal efficiencies upto [82-65%] for [H<sub>2</sub>O<sub>2</sub>]/[laterite iron] :: [32-53]/[1]. Moreover Photo-Fenton oxidation studies showed 100% removal for conc. range (10-30mg/L) under both iron salts. For Fenton's oxidation, optimum reaction time of 5.0 hrs for 10-30mg/L to 7.0 hrs for 40-60mg/L and finally to 8.5 hrs for 70-80mg/L of 3AP was required. Whereas photo-Fenton reaction studies required much less reaction time equal to 1.5 hrs for 10-30mg/L to 2.0 hrs for 40-60mg/L and 4.0 hrs for 70-80mg/L. Also Chemical oxygen demand (COD) removal was increased in case of Photo-Fenton oxidation indicating improved mineralization. Fenton and photo-Fenton methods can be considered as an effective advanced oxidation methods at ambient conditions. Also iron extracted from laterite soil can be used effectively in Fenton's reagent instead of traditional ferrous salts to treat polluted water bodies containing 3-Aminopyridine.

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## 1. Introduction

Pharmaceutical and Personal Care Products (PPCPs) continues to grow worldwide on par with many agrochemicals. PPCPs are in part subjected to the metabolism of the user. The excreted metabolites plus some unaltered parent compounds get released into the sewage. Thus these chemicals enter the environment, where they are considered *pseudo-persistent* because the transformation/removal rate from the environment is compensated by the rate of replacement [1]. The detection of (PPCPs) in the aquatic environment has added a new dimension to water quality programs in developing regions of the world. PPCPs may cause infertility, birth defects, ovarian failure and growth retardation. Declined sex ratios in Canada and the United States have also been reported. Research and published data are increasingly showing evidence of deleterious impacts of PPCPs on the ecosystem. Feminizations of fishes and gulls and sexual abnormalities in alligators due to exposure of PPCPs have been reported [2]. Likewise Pseudo-persistency has been observed in nitrogen containing heteroaromatic pharmaceutical compounds like pyridine. These compounds have received immense attention recently, because of their presence in the environment and their toxic and carcinogenic potential and hazardous effect on natural environment [3]. Furthermore, some of the pyridine derivatives like aminopyridines can be toxic to certain life forms [4, 5]. Pyridines are rated as priority pollutants by United States Environmental Protection Agency (USEPA) [6]. Many pyridines of commercial interest find application in market areas where bioactivity is important. 3-Aminopyridine is also used as a plant growth regulator and also in azo dye in hair dyes and pharmaceutical drugs like Piroxicam, Tenoxicam, Ampiroxicam (anti-inflammatory drugs) [7]. Treatment of pharmaceutical wastewater containing 3AP has always been troublesome to reach the desired effluent standards. Also there is addition of similar substances due to municipal sewage discharges. Moreover it is resistant to biological degradation [5]. In such a case, chemical pre-treatment like the advanced oxidation technologies particularly Fenton and Photo-Fenton oxidation processes which rely on the generation of very reactive oxidizing agents, i.e. free radicals such as the hydroxyl radical ( $\bullet\text{OH}$ ) are found effective owing to their high oxidation potential (+2.80 eV) in aqueous solution. These processes can adequately increase the biodegradability and remove toxicity of the wastewater prior to biological treatment [8].

## 2. Experimental Details

All the chemicals required for carrying out the aforesaid study with selected pyridine derivative viz; 3-Aminopyridine (3AP), extra pure (98% assay) were purchased from Merck. (India). The experiments were conducted at ambient temperature ( $27\pm 3^{\circ}\text{C}$ ) in batch reactors. A 1000 mL solution of required 3AP concentration was prepared from the stock 3AP solution and was taken in a 2 litre reactor. Appropriate amount of  $\text{Fe}^{2+}$  concentration from the 1000 mg/L stock solution, freshly prepared from  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , was added to the reactor bath and stirred with magnetic stirrer. Also stock solution of iron extracted from laterite soil of NITK campus, India was prepared as per standard procedure. The iron from laterite soil was extracted using procedure given by Olanipekun [9]. Required amount of  $\text{H}_2\text{O}_2$  was added to the reactor bath to initiate the reaction. For the experiments, pH (digital pH meter, Model EQ-610-Equiptronics) was adjusted after adding appropriate iron and  $\text{H}_2\text{O}_2$  solution, stirred with magnetic stirrer (Model EQ-772-Equiptronics). pH of the solution was adjusted using  $0.1\text{NH}_2\text{SO}_4$  and  $0.1\text{NNaOH}$ . The mixture of 3AP solution and Fenton's reagent ( $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ ) 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 in the lab. The 3AP solution samples were taken out for analysis at pre-defined time intervals and filtered through 0.45  $\mu\text{m}$  Millipore filter membrane for Chemical Oxygen Demand (COD) analysis using COD Digester (Lovibond ET 125) by Closed Reflux Titrimetric method as per the procedure outlined in the Standard Methods [1] and for determination of 3AP concentration by using UV-VIS Double Beam Spectrophotometer (Systronics-2201).

### 3. Results and Discussion

#### 3.1. Effect of pH on removal of 3AP from synthetic water sample.

To determine optimal pH, experiments were conducted at different pH values varying from 2 to 5.5 with initial trial concentration of 10 mg/L of 3-Aminopyridine,  $[\text{H}_2\text{O}_2] = 30 \text{ mg/L}$ , and  $[\text{Fe}^{2+}] = 1 \text{ mg/L}$ . In the present study max.3-AP removal is obtained corresponding to pH 3 under both oxidation processes using either ferrous or laterite iron. Therefore subsequent experiments of Fenton and Photo-Fenton oxidation were set for pH=3. The drug removal efficiency was found to get reduced at other pH values. This may be because at higher pH (above 4), ferrous ions get easily converted to ferric ions, which have a tendency to produce ferric-hydroxo complexes with  $\text{H}_2\text{O}_2$ . The low degradation at pH 2 and 2.5 may be due to the hydroxyl radical scavenging by  $\text{H}^+$  ions and also there may be inhibition for the radical forming activity of iron [11,13,17].

#### 3.2. Effect of $\text{H}_2\text{O}_2$ and iron concentration during Fenton and Photo-Fenton Oxidation of 3AP.

The investigation for optimization of hydrogen peroxide concentration was carried out by varying  $\text{H}_2\text{O}_2$  concentration from 10 to 50 mg/L, keeping the iron concentrations (0-2mg/L) constant for each varied set of  $\text{H}_2\text{O}_2$  conc.

**Fenton oxidation** using ferrous sulphate heptahydrate along with hydrogen peroxide was carried out to check percent drug and COD removal corresponding to optimum pH 3.0 for all sets. The max 3AP and COD removal of 90% and 84% (data not shown) respectively were measured at optimum pH = 3.0 corresponding to optimum  $\text{H}_2\text{O}_2$  conc. of 30mg/l and optimum  $\text{Fe}^{2+}$  conc. of 1.25 mg/L as shown in Fig.1 (a). Similar study was carried out to check effect of Fenton oxidation using iron extracted from laterite soil of NITK campus.

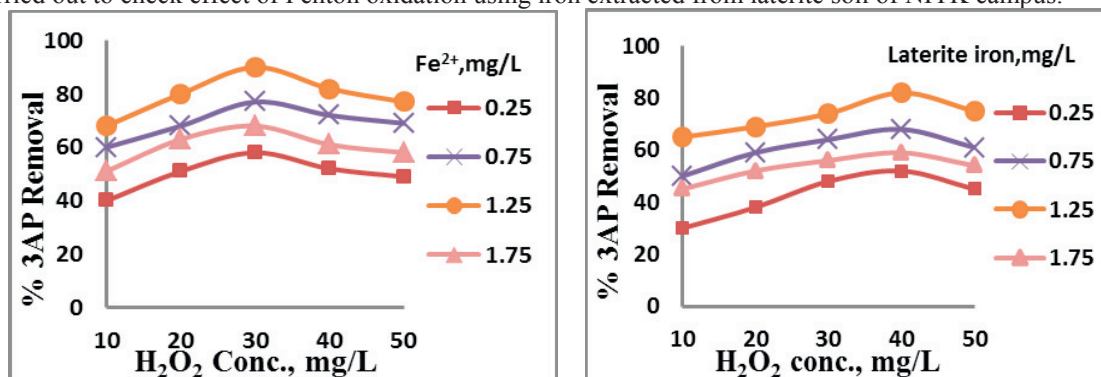


Fig. 1. (a). Effect of Fenton oxidation using ferrous iron on % 3AP removal; (b) Effect of laterite iron; Operating cond;  $[\text{3AP}]_0 = 10 \text{ mg/L}$ , pH=3.0; Ferrous  $[\text{H}_2\text{O}_2]_{\text{opt}} = 30 \text{ mg/L}$ ; laterite  $[\text{H}_2\text{O}_2]_{\text{opt}} = 40 \text{ mg/L}$   $[\text{Fe}^{2+}]_{\text{opt}} = [\text{laterite iron}]_{\text{opt}} = 1.25 \text{ mg/L}$ .

It has also been observed that at higher  $\text{Fe}^{2+}$  concentrations, the drug and COD removals (data not shown) were reduced. This may be due to the ferrous ion inhibition that occurs when high concentration of  $\text{Fe}^{2+}$  is

present in the system and  $\text{Fe}^{2+}$  itself can react with OH radicals resulting the scavenging of OH radical. Fig.1. (b) shows the effect of laterite iron on 3AP. The reaction of hydrogen peroxide with laterite iron (ferric ions) is referred to as a Fenton-like reaction. It is seen that use of laterite iron in Fenton's oxidation results in more hydrogen peroxide consumption than that using ferrous iron. This may be because; initially some  $\text{H}_2\text{O}_2$  is used to convert  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . Reaction of  $\text{Fe}^{3+}$  with  $\text{H}_2\text{O}_2$  leads to regeneration of  $\text{Fe}^{2+}$  ions and formation of hydroperoxyl radicals ( $\text{HO}_2\bullet$ ) which have less oxidation potential than hydroxyl radicals [30]. Additional  $\text{HO}_2\bullet$  can participate in propagating radical chain reactions by reducing ferric to ferrous ion and can result in larger consumption of hydrogen peroxide [30]. In the present study iron extracted from laterite iron showed max 3AP removal of 82% which is less as compared, when ferrous is used. Moreover this was also true for the degree of mineralization wherein COD removal of 75% was achieved (fig. not shown).

Fig.2.(a) and (b) shows 100% 3AP removal for **Photo-Fenton oxidation studies**. Also doses of ferrous and hydrogen peroxide required are less as compared to those in Fenton's oxidation since UV light serves as an additional pathway for generation of hydroxyl radicals which contribute to the overall removal thus eliminating excess reagent doses which otherwise have proved to scavenge the generated radicals.

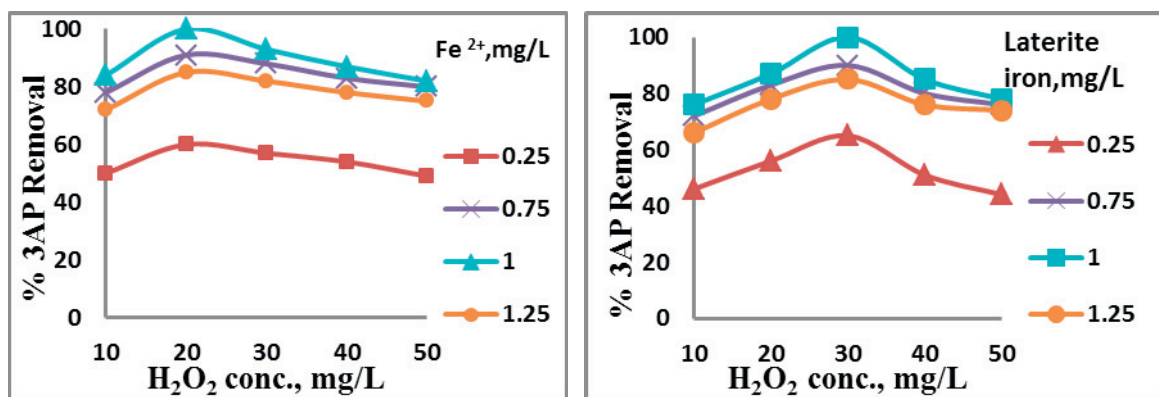


Fig. 2. (a) Effect of Photo-Fenton oxidation using Ferrous iron on % 3AP removal; (b) Effect of laterite iron. Operating conditions:  $[\text{3AP}]_0 = 10\text{mg/L}$ ; at  $\text{pH} = 3.0$ ;  $[\text{H}_2\text{O}_2]_{\text{opt}}$  with ferrous =  $20\text{mg/L}$ ;  $[\text{H}_2\text{O}_2]_{\text{opt}}$  with laterite =  $30\text{mg/L}$   $[\text{Fe}^{2+}] = [\text{laterite iron}]_{\text{opt}} = 1.0\text{mg/L}$ .

### 3.3. Effect of initial concentration of 3AP

For initial 3AP concentrations from 10 to 80mg/L using Fenton oxidation employing ferrous ions, the optimum ratio of  $[\text{3AP}] : [\text{H}_2\text{O}_2] :: [1] : [3.0]$  was observed, which increased to 1: 4 in case of laterite iron indicating more consumption of  $\text{H}_2\text{O}_2$  by ferric ions present in laterite iron. In Fenton oxidation using ferrous iron, as initial conc. of 3AP was increased from 10 to 80mg/L the percent removals reduced from 90% to 77%. For Fenton's oxidation, optimum reaction time of 5.0 hrs for 10-30mg/L to 7.0 hrs for 40-60mg/L and finally to 8.5 hrs for 70-80mg/L of 3AP was required. Fenton oxidation using laterite iron shows a slow reaction requiring more reaction time to degrade the target drug. This may be due to generation of hydroperoxyl radicals as explained earlier. Whereas photo-Fenton reaction studies required much less reaction time equal to 1.5 hrs for 10-30mg/L to 2.0 hrs for 40-60mg/L and 4.0 hrs for 70-80mg/L. Photo-Fenton oxidation process showed 100% removal of 3AP for increase in conc. upto 30mg/L under both ferrous and laterite iron. Thereafter percent removals were reduced to 91.7% as conc. increased to 80mg/L.

Finally the treated samples after Fenton and Photo-Fenton oxidation were scanned using UV-VIS double beam spectrophotometer from 200 to 400nm wavelength to check for degree of treatment and to confirm the

presence or absence of any formed intermediates which can be predicted from the absorbance peaks. Absence of peak (scan data not shown) indicated that, 3AP of initial conc is degraded and no intermediates are present in the treated sample of water.

#### 4. Conclusion

- Use of Iron ( $\text{Fe}^{3+}$ ) extracted from laterite soil showed a slight synergy in the degradation of 3AP when compared with traditional ferrous iron ( $\text{Fe}^{2+}$ ) in both Fenton's and Photo-Fenton processes. Thus iron extracted from laterite soil can be a cost effective option to treat polluted water bodies containing 3AP.
- Degradation of 3AP using Photo-Fenton oxidation was found to be an additive effect requiring less degradation time than that using Fenton oxidation. For highly polluted water bodies containing 3AP, Photo-Fenton oxidation can be a suitable alternative as it can degrade the target compound at higher reaction rates.

#### 5. References

- [1] Kreisberg,J, Green Pharmacy: Preventing Pharmaceutical Pollution, *The Journal of Ecologically Sustainable Medicine* Spring/Summer, 2007. (www.teleosis.org).
- [2] Westerhoff.P ,Yoon.Y,Snyder.S. and Mert.E. Fate of Endocrine-Disruptor, Pharmaceutical and Personal Care Product Chemicals during Simulation Drinking Water Treatment Processes. *Environ. Sci. Technol.*; 2005; 39(17);6649-6663.
- [3] Walling.C, Goosen.A, Mechanism of the ferric ion catalysed decomposition of hydrogen peroxide: effects of organic substrate, *J. Am. Chem. Soc.*;1973; 95 (9) ; 2987–2991.
- [4] Padoley.K.S, Mudliar, Banerjee.S, Deshmukh.S and Pandey.R, Fenton oxidation: A pretreatment option for improved biological treatment of pyridine and 3-cyanopyridine plant wastewater, *Chemical Engg Jr.*,2011; 166; 1–9.
- [5] Padoley.K.S, Mudliar and Pandey.R, Heterocyclic nitrogenous pollutants in the environment and their treatment options –An overview, *Bioresource Technology*, 2008; 99; 4029–4043.
- [6] EPA,EPA-540/-002 Registration Standard: Products Containing 4-Aminopyridine, *AVITROL (Trade Name)*, Office of Pesticide Programs, U.S, Environmental Protection Agency, 1980, 202.
- [7] Nora.L ,Aminopyridine data sheet, NCI, Technical Resources International, Inc., 6500 Rock Spring Drive Suite 650, Bethesda, MD, 20817, U.S. 2006.
- [8] APHA, AWWA, WEF, Standard methods for the Examination of Water and Wastewater, 21st ed., Washington, DC. USA 2005.
- [9] Olanipekun.E, Kinetics of leaching laterite, *Int. J. Miner. Process.*, 2000;60, 9-14
- [10] Dunnick.J, NTP Research Concept:Aminopyridines, Federal Register,Vol.72, 14817, 2008. (<http://ntp.niehs.nih.gov/go/9741>).
- [11] Daughton.C and Ternes.T, Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? *Environ. Health Perspective*.1999;107(6);906-942.
- [12] Neyens.E and Baeyens. J, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater*,2003; 98; 33-50.
- [13] Rogers.J, R. Rily, Li.S, O'Melley and Thomas.B, Microbial transformation of alkyl pyridine in ground water, *Water Air Soil Pollution*;1985;24; 443–454.
- [14] Stapleton.D, Mantzavinos.D and Papadaki.M. Photolytic (UVC) and photocatalytic (UVC/TiO<sub>2</sub>) decomposition of pyridines. *J. Hazard. Mater* ; 2007; 146; 640–645.
- [15] Tekin.H, Bilkay.O, Ataberk.S, Balta.T, Ceribasi.I, Sanin.F. Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater.*J. Hazard. Mater.*; 2006;136, 258-265.
- [16] Timothy.E , Director,Handbook on Advanced Photochemical and Nonphotochemical Oxidation Processes, Center for Environmental Research Information, National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268 , 1998