



DEGRADATION KINETICS OF P-AMINO BENZOIC ACID BY PEROXIDATION, PHOTO-PEROXIDATION AND PHOTOFENTON PROCESSES

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ABSTRACT:

In the present work p-amino benzoic acid in its aqueous solution was treated by peroxidation (H_2O_2), photo peroxidation (UV/H_2O_2) and photofenton ($UV/Fe^{2+}/H_2O_2$) processes. The experiments were taken out in a batch photoreactor using 8W low pressure mercury vapor lamp to examine the effects of different combinations and their degradation rates are compared. Substrate concentration was fixed by utilizing a UV-Visible spectrophotometer. The results indicated that the rate of degradation follows the following sequence; photofenton > photoperoxidation > peroxidation. The photo degradation processes were adhered to first order dynamics.

Keywords: *p-amino benzoic acid, peroxidation, photo-peroxidation, photofenton, first order dynamics.*

INTRODUCTION:

The pharmaceutical personal care products (PPCP's) are distinguished as a class of emerging contaminants of concern as very little is known about these contaminants' impact on the environment when released back into the ecosystem.

In recent years pharmaceutical, personal care products (PPCP's) production has risen exponentially. Lotions, pharmaceutical drugs, veterinary products and sunscreen products are included in PPCP's¹⁻⁴. These PPCP's should have an active element that can be organic or inorganic in nature. Because of the overconsumption PPCP's usually are found in wastewaters. Organic active ingredients have a chromophore responsible for the absorption of sun radiation; these include benzophenone-3, octocrylene and p-aminobenzoic acid (PABA). PABA was widely used in the 70's as a sun protection agent but in the 80's a group of researchers discovered that PABA was a disrupting agent against DNA cells.

With technology advances new remediation techniques have been explored and developed. Traditional remediation processes have demonstrated to be good with some organic pollutants but not enough with persistent organic pollutants such as those present in PPCP's. Some of the new developed technologies are the Advanced Oxidation Processes (AOP's)⁵⁻¹⁰. AOP's are carried out using a catalyst (semiconductor) with a wide band gap. $\cdot OH$ radicals are generated in the presence of radiation and an oxidation agent, mediated by electron-hole pairs. The hydroxyl radicals are very reactive species and helps in the decomposition organic substances. One of the AOP's widely studied is the photofenton process which has been demonstrated to be a successful technique in the degradation of phenol, benzoic acid, organic dyes and other emerging contaminants¹¹⁻¹⁴.

In this research we have used peroxidation, photoperoxidation and photofenton processes to

degrade the substrate. The present work demonstrates that p-aminobenzoic acid can be successfully degraded in short time periods with high degradation percentages.

MATERIAL & METHODS:

Isolation of thermophilic fungi:-

2.1 Chemicals

p- amino benzoic acid was purchased from Merck, India; and stock solutions of 0.01M were prepared. Initial concentration used during the experimental runs was 0.08mM. A stock solution of H₂O₂ was prepared by diluting 30% w/v of peroxide (Qualigens) with distilled water. For photo Fenton processes ferrous sulphate heptahydrate (FeSO₄.7H₂O) and hydrogen peroxide solution (30% w/w) were used are all of analytical grade obtained from Merck. Sodium hydroxide (1N) and sulphuric acid (1N) were used for pH adjustments. All stock solutions were stored in amber colored light resistant Pyrex glass bottles.

2.2. Experimental procedure

A photoreactor (Fig. 1) with a low pressure mercury lamp (8W, UV-C manufactured by Phillips, Holland) placed at its centre was used to carry out all the experiments. Synthetic wastewater containing 0.08mM solution of para-amino benzoic acid in double distilled water was used in this study and was irradiated with UV lamp of 8W. Several experiments were taken out using UV light with oxidant at various stoichiometric ratios of oxidant/pollutant. The overall degradation reaction was carried out for 90 minutes for fenton process and 180 minutes for peroxidation and photoperoxidation.

2.3. Analyses

The initial pH of the solution was measured using Elico pH meter LI-120 equipped with a combined calomel-glass electrode. The H₂O₂ concentration in the stock solution and in the samples was set by the standard iodometric titration method described in Jeffery et al. (1989).

The UV-visible spectrophotometric method was applied for measurement of benzoic acid, and H₂O₂ concentration in aqueous solution. A UV-visible spectrophotometer (Spectrascan UV 2600, Chemito, India) was employed for this determination. A calibration plot between absorbance and concentration were plotted experimentally, which made a high linear regression coefficient of 0.9942 at 268.2 nm for p- amino benzoic acid (Fig. 2).

RESULTS & DISCUSSION:

3.1 Effect of peroxidation (H₂O₂) on degradation of p-amino benzoic acid

The aqueous solutions of the organic compounds were subjected to the process of oxidation by H₂O₂. Para amino-benzoic acid, when subjected to peroxidation showed 10.5% reduction in concentration.

3.2 Effect of dose of H₂O₂/COD ratio on degradation of p-amino benzoic acid

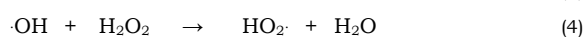
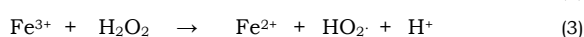
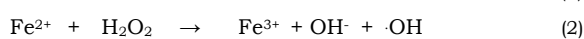
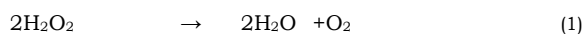
By carrying out a series of experiments of p-amino benzoic acid (with different ratio of H₂O₂/COD namely 2, 3, 4, 5, 6); the optimum H₂O₂ stoichiometric ratio was found to be H₂O₂ /COD=4 and maximum removal efficiency at neutral pH. (Fig. 4).

3.3 Fenton process

3.3.1 Effect of initial H₂O₂ concentration on degradation of p-amino benzoic acid

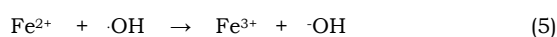
Hydrogen peroxide acts as an oxidant in the Fenton process. The effect of change in H₂O₂ concentration on degradation efficiency for p-amino benzoic acid is depicted in Fig. 5. The concentration of H₂O₂ was varied from 1 to 2 mM at room conditions while keeping the Fe²⁺ ion concentration at 9.3μM and pH at 3.0 ± 0.2. The degradation efficiency increases with increasing H₂O₂ concentration, due to incremental ·OH radical produced by UV enhanced H₂O₂. Maximum degradation efficiency was attained at 1.7 mM. Further addition of H₂O₂, did not

improve the degradation efficiency may be due to self-decomposition of H_2O_2 to oxygen and water as in eq. (1). Moreover, the excess H_2O_2 react with ferric ions (Fe^{3+}) to form weaker hydroperoxyl radical ($\text{HO}_2\cdot$) as presented in eq.(3) and eq.(4), which is not as active as $\cdot\text{OH}$ radical towards p-amino benzoic acid degradation.



3.3.2. Effect of Fe^{2+} ion concentration on degradation of p-amino benzoic acid

To elucidate the role of Fe^{2+} ion on degradation of p-amino benzoic acid, a series of experiment were performed at room conditions by varying the concentration of Fe^{2+} ion from $3.2 \mu\text{M}$ to $12 \mu\text{M}$ for fixed H_2O_2 concentration of 1.7 mM and at $\text{pH } 3.0 \pm 0.2$. The degradation efficiency for p-amino benzoic acid at different Fe^{2+} ion concentration is illustrated in Fig 6. The degradation efficiency increased progressively with increase in Fe^{2+} ion concentration due to higher amount of $\cdot\text{OH}$ radical generated as depicted in eq. (1). Maximum degradation efficiency was achieved at $9.3 \mu\text{M}$. Further increase in Fe^{2+} ion concentration did not correspondingly increase its reactivity probably due to direct reaction of $\cdot\text{OH}$ radical with metal ion (Joseph et al., 2000) as follows:



4. Comparison of various AOPs studied and the kinetic studies

A comparative work was held out for p-aminobenzoic acid by peroxidation, photo-peroxidation and photofenton processes in terms of percentage degradation and rate constant as illustrated in Fig 7 and table 1. And was found that the pace of degradation is highest in photofenton process.

The semilogarithmic graph of the concentration of p-aminobenzoic acid with time yield a straight line indicating the reaction is of pseudo-first order (eq. A)

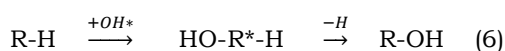
$$-d/dt[c(X)] = kc(X) \quad \dots\dots\dots (A)$$

Where $c(X)$ is the concentration of substrate and $k(\text{min}^{-1})$ is reaction rate constant.

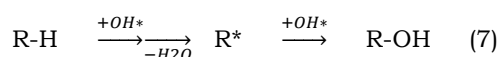
5. Reaction products

There are two possible mechanisms to explain hydroxylation (Omura & Matsuura, 1968):

The hydroxyl radical attacks the phenolic ring R forming a cyclohexadienyl radical (intermediate), which is converted by further abstraction of a hydrogen atom to the hydroxylated product as in eq. (6).



The hydroxyl radical abstracts a hydrogen atom from the phenolic compound R yielding a phenolic radical (intermediate). This in turn adds a hydroxyl radical giving the hydroxylated phenolic product as in eq (7).



CONCLUSION

Treatment of simulated wastewater containing p-aminobenzoic acid by peroxidation, photo-peroxidation and photofenton processes has been submitted into consideration in the present work. On the base of the results obtained the following conclusions have been reached:

As peroxide in all the cases are in excess concentration to the substrate, all the AOPs studied were modelled into pseudo-first-order kinetics.

In all the AOPs studied the combination UV/ Fe^{2+} / H_2O_2 was found to be the fastest among them. It took only 1.5 hours to degrade 98.98% of p-amino benzoic acid whereas the degradation by peroxidation and photo-peroxidation was 5% and 44.45% respectively.

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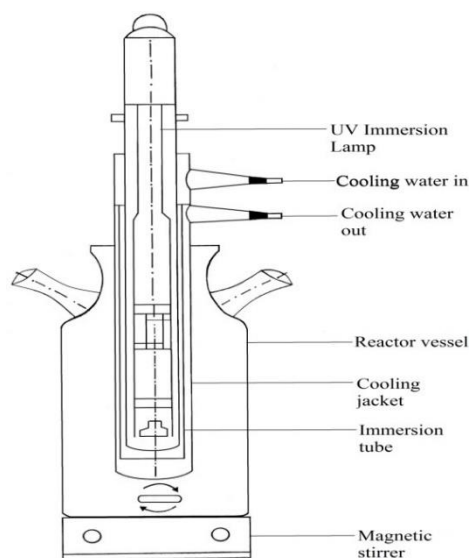


Fig. 1. Photoreactor

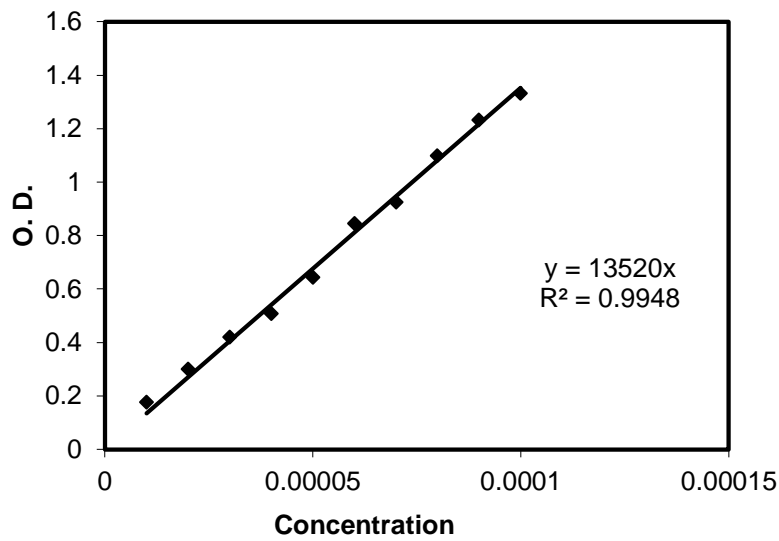


Fig. 2. Calibration plot of p-amino benzoic acid

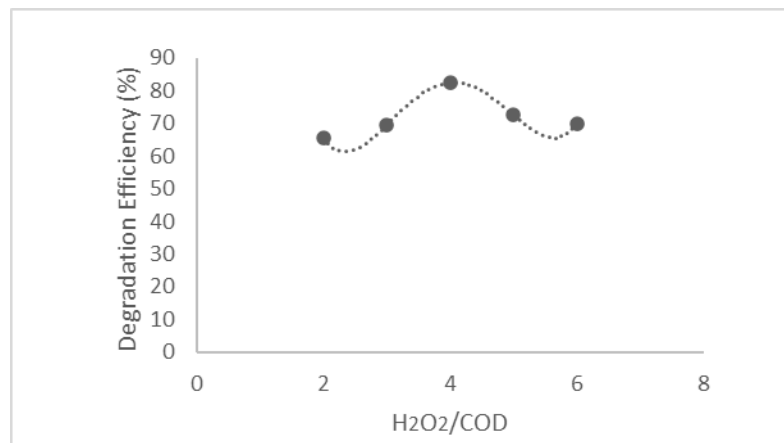


Fig. 3. Effect of initial H₂O₂/COD on degradation efficiency for p-amino benzoic acid (conditions: [PABA] = 0.08 mM, pH = 7)

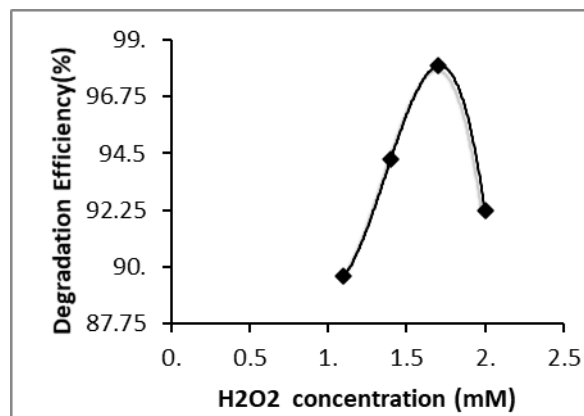


Fig. 5. Effect of initial H₂O₂ concentration on degradation of p-amino benzoic acid (conditions: [2TA] = 0.08mM, pH = 3.0 ± 0.2, [Fe²⁺] = 9.3μM).

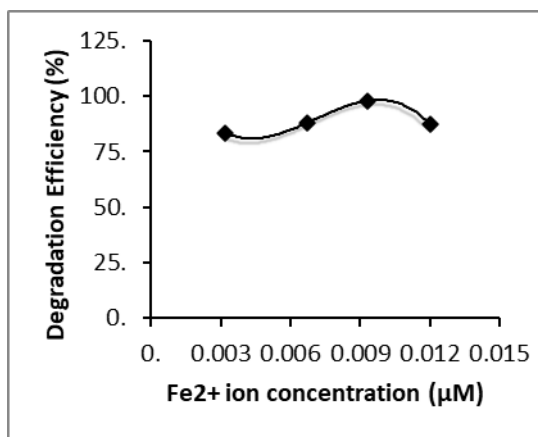


Fig. 6. Effect of initial Fe²⁺ concentration on degradation of p-amino benzoic acid (conditions: [PABA] = 0.08 mM, pH = 3.0 ± 0.2, H₂O₂ = 1.7mM).

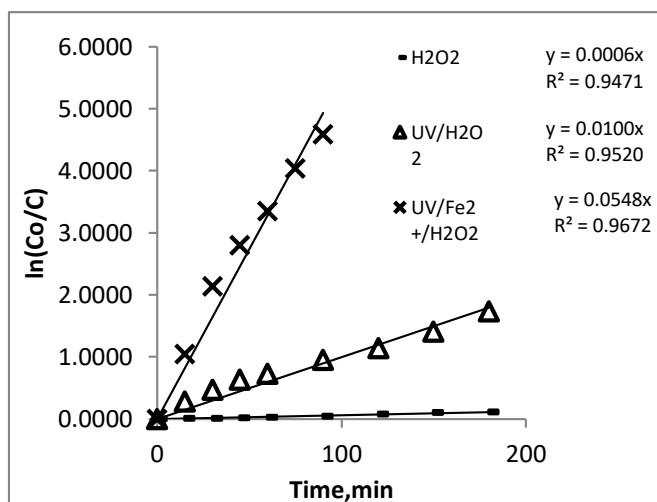


Fig. 6. Comparison of different AOPs on degradation of p-amino benzoic acid Table1. Summary of different AOP's studied

S. No.	Process	Percentage degradation For 1.5 hour of process	k/(min ⁻¹)
1	H ₂ O ₂	5	0.0006
2	UV/H ₂ O ₂	44.45	0.01
3	UV/Fe ²⁺ /H ₂ O ₂	98.98	0.0548