KINETIC STUDIES OF DEGRADATION OF P-AMINO BENZOIC ACID

BY THE UV/ H₂O₂/TiO₂ PROCESS

N. P. Mohabansi* , S. A. Mandavgane ᵃ, M. K. N. Yenkieᵇ, N. A. Barwatᶜ
*,ᶜ Assistant Prof**.,** Jankidevi Bajaj College of Science, Wardha (India)
ᵃAssistant Prof**.,** Sindhu Mahavidyalaya, Pachpavali, Nagpur (India)
ᵇ Pro-VC, R. T. M. Nagpur University, Nagpur (India)
E-mail : ***nitamohabansi@yahoo.com**

Abstract :-

Photo catalytic oxidation is a potential method for the treatment of organic contaminants and has received significant interest and research with tremendous potential in the near future. A model compound, p-amino benzoic acid was degraded by using hydrogen peroxide, photocatalyst (TiO₂) in presence of UV lamp. The experiments were carried out in a batch photo reactor using 8W low pressure mercury vapour lamp in lab-scale experiments. Substrate concentration was determined by UV-Visible spectrophotometer. Different [H₂O₂/p-ABA] molar ratios, photocatalyst doses and pH (plain water, 3, 5, 6, 7 and 9) were optimized in order to establish the most favorable experimental conditions for the photo catalytic process. The optimum [H₂O₂/p-ABA] molar ratio and pH were found to be 5 and 7 respectively. The rate of degradation was studied by varying the amount of catalyst doses from 10 to 90 mg. By applying the optimal experimental conditions, it was observed that 240 min irradiation of the wastewater in 50mg/l Degussa P25 with UV/H₂O₂/TiO₂ system was sufficient in order to degrade the organic substrate in the investigated wastewater. The studied photo catalytic processes were found to adhere to pseudo first-order kinetics with respect to the substrate concentration.

Key words:- Degradation, Photocatalyst, p- Amino benzoic acid, Photo reactor, Pseudo first- order kinetics.

Introducion:-

Photocatalytic oxidation is one of the advanced oxidation process for the treatment of organic contaminants and has received significant interest and research[1] Recently it has been demonstrated that semi-conductor materials mediated photo catalytic oxidation of organic compounds is a successful, convention alternative to conventional methods for the removal of organic pollutants from water. This process is

very promising for effluent treatment mainly due to their high efficiency and simplicity of operation. Photocatalysis process has been applied to solve various pollutant organic i.e. humic acid, dyes, pentachlorophenol, and alkylbenzene sulfonate [2-6]. In recent years semiconductors most frequently used are TiO_2, ZnO, CdS, and WO_3 etc. Titanium dioxide has the wide bandgap (3.0 eV) and is an n-type semiconductor with many attractive features and is capable to generate hydroxyl radicals [7-8]. These are very promising for effluent treatment mainly due to their high efficiency and simplicity of operation. TiO2 in the anatase form seems to possess the most interesting features, such as high stability, good performance and low cost. The photo catalytic degradation of nitrobenzene on TiO2 and ZnO, reporting that complete mineralization with TiO2 was achieved [9-10]. Mathew [11] also reported that more than 90% of nitrobenzene mineralization was achieved with TiO2 and sunlight. Phenolic compounds have been successfully degraded by photocatalytic process [12-16]. This research includes more advanced oxidation process, which can be powered by irradiation light with a wavelength longer than 300 nm, homogeneous and heterogeneous with photo catalysis using TiO_2, with and without addition of oxidants.

p- Amino benzoic acid is selected as the model compound for the present photo catalytic degradation study. The objective of the study is to degrade p-amino benzoic acid by AOP's like UV/ H_2O_2 and UV/TiO_2/ H_2O_2 and compare their degradation rates and to show that it follows a pseudo-first order kinetics.   .

Materials and Methods

2.1 Chemicals

Analytical grade p- amino benzoic acid was purchased from Merck, India; and was used as received without any further purification and stock solution of 0.01M of p- amino benzoic acid was prepared. Initial concentration of p- amino benzoic acid used during the experimental

runs was 0.15mM. Stock solution of H_2O_2 was prepared by diluting 30% w/v of hydrogen peroxide (Qualigens) with distilled water. All stock solutions were stored in amber colored light resistant. Pyrex glass bottles. TiO_2 (AR) (surface area $50m^2/g$) was obtained from s-d fine chemicals, India & was used as received. Sodium hydroxide (1N) and sulphuric acid (1N) were used for pH adjustments.

2.2. Experimental procedure

Batch experiments were conducted at room conditions to determine the effect of pH, H_2O_2 concentration and TiO_2 doses during degradation of p-amino benzoic acid. All experiments were conducted in a photo reactor (Fig.1) equipped with low pressure mercury lamp (8W, UV-C manufactured by Phillips, Holland) placed in its centre. During the reaction, the solution was stirred by magnetic pellet to ensure its homogeneity. Synthetic wastewater containing 0.15 mM solution of p-amino benzoic acid in double distilled water was used in this study. 750 ml. of this synthetic wastewater was taken in the photo reactor and irradiated with UV lamp of 8W. Various experiments were carried out using UV light with oxidant at various stoichiometric ratios of oxidant/pollutant.

The suspended TiO_2 solution was mixed very well using stirrer for 30 minutes so that adsorption equilibrium was reached. The time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment. Samples were taken at regular time interval from the reaction vessel and pipetted into test tubes. After photo catalysis a centrifugation process was applied to separate TiO_2 catalyst particles. The samples were immediately analyzed to avoid further

reaction. The overall degradation reaction was carried out for 240 min.

Fig.1. Photoreactor

2.3. Analysis

The initial pH of the solution was measured using Elico pH meter LI-120 equipped with a combined calomel-glass electrode. The UV-visible spectrophotometric method was used for measurement of p- amino benzoic acid and H_2O_2 concentration in aqueous solution. A UV- Visible spectrophotometer (Spectrascan UV 2600, Chemito, India) was used for this purpose. A calibration plot between absorbance and concentration of p- amino benzoic acid was plotted experimentally, which gave a high linear regression coefficient of 0.9969 at 266 nm (Fig.2).
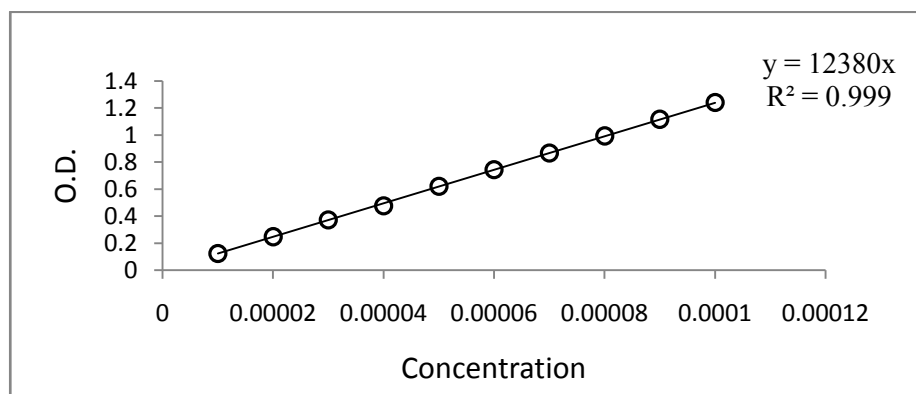

Fig 2. Calibration plot of p- amino benzoic acid

3. Results & Discussion

The results of the various studies in the present investigation are presented subsequently.

3.1. Effect of pH

pH is one of the most important parameters to be studied. The rate of degradation of p–amino benzoic acid at different pH was observed by carrying out the experiments at different pH conditions namely plain water, 3, 5, 6, 7 and 9. As depicted in the Fig. 3, in case of H_2O_2 /UV, the maximum degradation p- amino benzoic acid was achieved at pH 7 and shows decreasing trend of degradation at higher and lower pH.
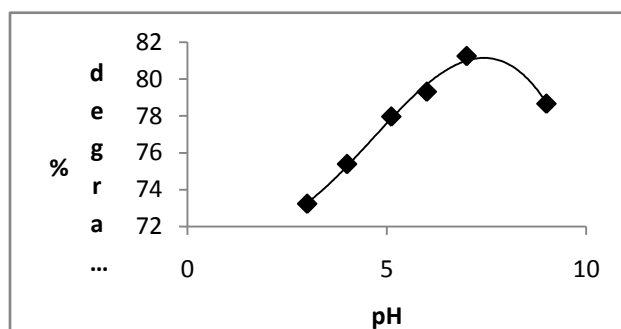

Fig.3. Effect of initial pH on degradation efficiency for p- amino benzoic acid

(Conditions: [p ABA] = 0.15 mM, H_2O_2 /COD = 5)

3.2 Effect of dose of H_2O_2/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

H_2O_2/COD namely 2, 3, 4, 5, 6 &7); the optimum H_2O_2 stoichiometric ratio was found to be H_2O_2/COD=5 (Fig. 4). Further increase in H_2O_2 concentration lowered the degradation rate.

This is because of the excess H_2O_2 reacts with the hydroxyl radicals earlier formed and hence acts as an inhibiting agent of degradation by

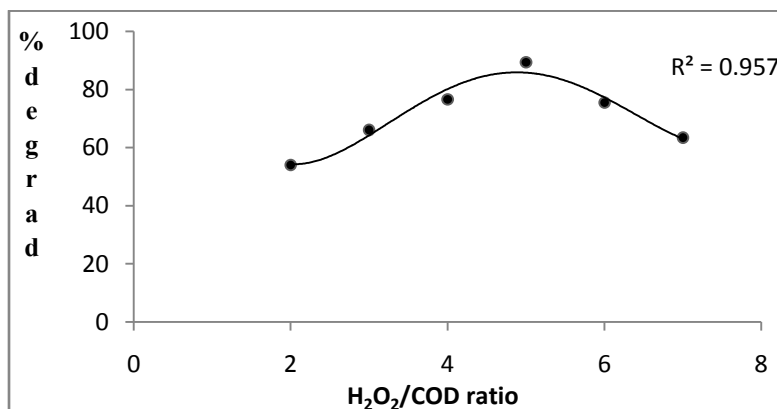consuming the hydroxyl radicals responsible for degrading the pollutant molecule [17].

Fig.4. Effect of initial H_2O_2/COD on degradation efficiency for p-amino benzoic acid (conditions: [p ABA] = 0.15 mM, pH = 7)

3.3 Effect of catalyst doses

The experiments were conducted to study the effect of varying catalyst doses from 10mg/lit to 90mg/lit on the degradation efficiency of p-amino benzoic acid. The application of oxidant along with photocatalyst enhances the degradation mechanism and hence gives much higher removal. Maximum degradation of 97.56% was observed with 50 mg of catalyst TiO_2 photocatalyst with rate constant k_1=0.0084 min^{-1}. Fig. 5 shows the oxidative degradation of p amino benzoic acid with various TiO_2 doses. It was observed that the increase in amount of catalyst loading increases the rate of degradation up to a certain catalyst amount. The increase in degradation rate may be explained by the fragmentation of catalyst which produces higher surface area. Thereafter with further increase in catalyst loading the degradation rate starts declining. This nature may due to the screening effect i.e., above a certain amount of catalyst loading, the turbidity of the solution increases and ultraviolet rays start getting scattered, hence reducing the optical path [18]. Aggregation of catalyst particles, which reduced the interfacial area

between the reaction solution & the photo catalyst, may be other reasons for the degradation rate.
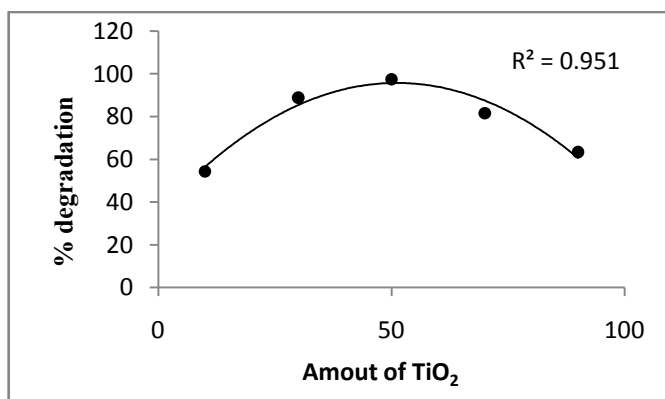

Fig. 5: Degradation of p- amino benzoic acid with photo catalyst TiO_2

4. Comparison of various AOPs studied and the kinetic studies

A comparative study was carried out for degradation of p- amino benzoic acid at optimum conditions for different AOPs studied like UV, H_2O_2, UV/H_2O_2, $UV/TiO_2/ H_2O_2$, it was found that the rate of degradation is highest when the combination- $UV/TiO_2/H_2O_2$ was used.
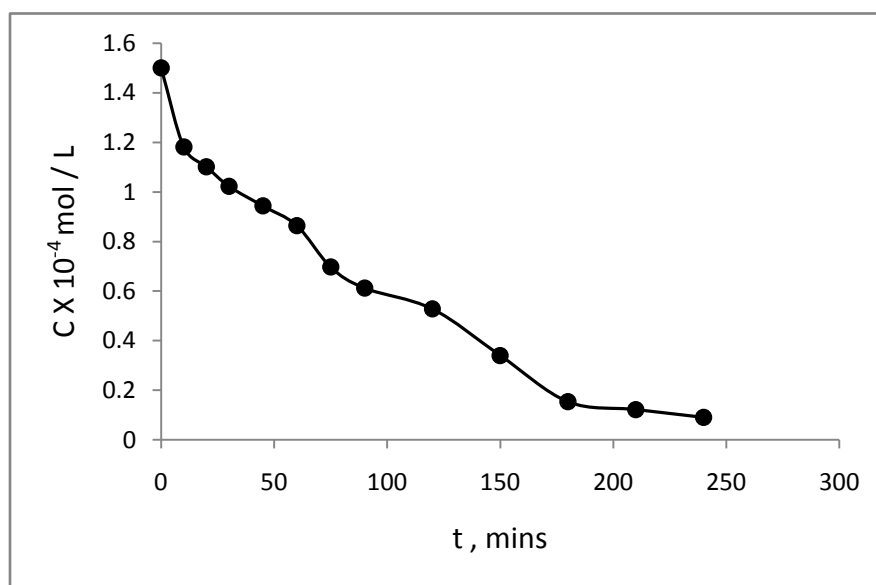

Fig.6 Photo-oxidative decay of p-ABA with respect to time

5. Degradation Rate Kinetics

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

$\ln (C_t / C_0) = - k t$ (A)

where C_0 and C_t are the concentration of pollutant at irradiation times 0 and t,

k is a first-order rate constant (min $^{-1}$) and t is the irradiation time (min).

$-d/dt [C(X)] = k. C(X)$ (B)

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

For p- amino benzoic acid, first order reaction was found to have maximum value of R^2 as compared to the second order. Hence kinetic constant based on p- amino benzoic acid degradation found to follow first order kinetics. Table 2 gives the first order rate constant for $UV/H_2O_2/TiO_2$ system.

TABLE 2: Rate Constant data for $UV/H_2O_2/TiO_2$ process for the degradation of p- amino benzoic acid

Substrate	Amount of photocatalyst (mg)	Rate constant, (min^{-1})
	10	0.0038
	30	0.0047
p-Amino benzoic acid	50	0.0113
	70	0.0062
	90	0.0050

6. CONCLUSION

This study showed the potentialities of photo catalytic degradation in water purification. Out of different processes employed, a significant enhancement of the photo catalytic activity was observed in the system using combination of oxidant and photo catalyst irradiated under UV

light. Concentration of both oxidant and photocatalyst greatly influences the degradation rate.

Also the process was observed to be strongly pH dependent. The degradation follows pseudo first- order kinetics. Photo degradation can be a recommended approach for the treatment of wastewater containing p- amino benzoic acid. Keeping in view all the factors, it can be easily said that $UV/H_2O_2/TiO_2$ system is an efficient process. The best reaction dose of TiO_2 was found to be 50 mg/lit.

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