Ultraviolet Light Induced Photocatalytic Degradation of Phthalic Anhydride Using Aeroxide P-25 and Kronos

Anand Kulkarni¹, Dhananjay Bhatkhande*¹
¹Chemical Engineering Department, Vishwakarma Institute of Technology, Pune 411037, Maharashtra, India

Abstract: In this work, photocatalytic degradation of phthalic anhydride using Aeroxide P-25 and kronos 7050 was performed under external UV light source. The photocatalytic activity for both of the catalysts was investigated under external UV light source. The effect of various parameters such as catalyst loading, initial concentration and initial pH of PAN on degradation was studied. The results showed that phthalic anhydride was degraded to 71% in 4h using Aeroxide P-25 at pH 3.5 while 55% degradation was achieved by kronos 7050 at same conditions. It was observed that 51% degradation of PAN was achieved by photochemical route. Under UV+Visible light illumination, 83% of degradation of PAN was achieved using (C-doped TiO₂) Kronos 7000 which proved to be the best among three catalysts. In this work the kinetic model (r = 0.005 C² 0.825 t) was developed that satisfactorily described the photocatalytic degradation of phthalic anhydride across the different sets of experimental conditions and it was observed that the experimental data for different concentration of phthalic anhydride fit this equation.

Keywords: Aeroxide P-25, Kronos, phthalic anhydride, Photocatalyst, UV radiations.

1. Introduction

Today the living style and pattern has improved to a great extent owing to large-scale industrialization and urbanization. However this has occurred at the cost of environmental degradation. The resources are simultaneously getting depleted and polluted. Despite various treatment schemes by industries to combat pollution, the desired decrease in levels with respect to specific pollutants has not been achieved. Frequent upsets in the effluent stream limits have an impact on the effluent treatment plant which adds to the constraint of an efficient central treatment facility.

Ironically, water which is essential to sustain life, acts as a carrier of deadly diseases due to discharge from untreated industrial effluents. There is an urgent need to address this alarming increase in contamination of surface and ground water. [1] We can achieve this by acquiring expertise in pollution control strategies beyond the conventional methods and implementation of novel techniques for the treatment of industrial wastewater. [2-4] Water pollution caused by organic compounds has received worldwide attention due to their potentially toxic effects on environment.

Several important studies on photochemical degradation are reported for degradation of organic compounds. [5-7] H₂O₂/UV process can not use the solar light as a source of UV radiation due to the fact that the required UV energy for the photolysis of the oxidizer is not adequate in solar spectrum. [8] It was previously demonstrated that degradation of various organic pollutants such as halogenated hydrocarbons, phenols, dyes, phthalates, organochloric pesticides was achieved using photocatalytic oxidation using TiO₂, as photocatalyst in artificial UV source. [9-18]

TiO₂ has been most widely used photocatalyst due its non-toxicity, high stability and cost-effectiveness and it exhibits high photocatalytic activity in UV-light source. [19-20]

In this work, photocatalytic degradation of phthalic anhydride (PAN) was studied using Kronos 7050 and Aeroxide P-25 under UV light illumination and using Kronos 7000 under visible light illumination. The results of degradation by photocatalytic and photochemical route are also compared. Herein, PAN was selected as model pollutant for degradation study. It has wide applications in the production of phthalate plasticizers, unsaturated polymer resins and alkyd resins. Several industrial plants produce large amount of wastewater containing high concentration of phthalates causing the threat to the environment and health. Those compounds are endocrine disruptors and have carcinogenic and mutagenic effects on human health. [21-24] It also has toxic effects on human fertility and hormone prone cancers. [25] Several studies reported that phthalate esters (PAEs) are poorly degraded by conventional treatments. [26] Because of its large production and toxicity, there is strong need to develop the efficient process for the treatment of such contaminated water. Trabelsi et al. (2010) studied the degradation of phthalic anhydride using plasma chemical oxidation in presence of Fe (II), Fe (III) and TiO₂ photocatalyst and investigated that upto 65% of degradation was achieved.
by this method. Bajt et al. (1993) studied the oxidation of phthalic anhydride using photo-Fenton process and reported 97% of degradation of PAN. Very few references are available on the degradation of PAN using AOPs. This work includes photocatalytic degradation of PAN using Kronos and Aeroxide P-25 which was performed for the first time. In this work the effect of catalyst loading, initial concentration and pH on degradation of PAN was investigated. In addition to the experimental work, kinetic model was employed to predict the photocatalytic degradation of PAN and validated for the experimental data.

II. Experimental

2.1 Materials

Aeroxide P-25 TiO$_2$ with average particle size of 20 nm and BET surface area 60 m$^2$ g$^{-1}$ was used as photocatalyst. Aeroxide P-25 was supplied from GEM Corporation, Mumbai (INDIA). Kronos with 250 m$^2$ g$^{-1}$ BET surface area was provided by Kronos International Inc., Germany. Phthalic anhydride was procured from E Merc India Ltd, Mumbai (India). Hydrogen peroxide (30%) was supplied by Loba chemie (P) Ltd, Mumbai.

2.2 Method

2.2.1 Characterization

The UV-Vis absorption spectra was obtained for Kronos 7000, using a UV-Vis spectrophotometer (Shimadzu 2501 PC) mounted with an integrating sphere accessory (ISR1200) using BaSO$_4$ as reference standard.

2.2.2 Photocatalytic degradation of PAN in external artificial UV-light source

Photocatalytic experiments were carried in the quartz reactor of 800 cm$^3$ capacity, with centrally mounted air sparger, so as to ensure photocatalyst in suspension during experimentation, surrounded by cooling coil. The temperature of the reaction was maintained at room temperature by circulating chilled water through the coil to avoid any loss of solution evaporation. 500 cm$^3$ PAN solution was taken for the experimentation with known weight of the photocatalyst. Intensity meter (Sun meter, Sun associates, India) was used to measure the average intensity of external visible light source and was found to be 80 W/m$^2$. In case of photocatalytic degradation using UV, UV lamp of 125 watt was placed at the bottom of the reactor so as to ensure uniform illumination.

The catalyst optimization for Kronos 7050 and Aeroxide P-25 was performed by varying the catalyst loading from 0.1 to 0.4 g L$^{-1}$ in each case. The effect of initial concentrations of PAN was studied on PAN degradation. The effect of initial pH of the solution on degradation was studied at different pH conditions (1.2, 2.5, 3.2 and 8.5). The samples were withdrawn at regular time interval of 60 minutes using syringe and analyzed with High Pressure Liquid Chromatograph [Shimadzu] using C8-column. The mobile phase composition was 0.1% formic acid in water and acetonitrile with a flow rate of 1.0 ml/min.

III. Results and discussion

3.1 Photocatalytic degradation of PAN in external artificial UV light source

3.1.1 Catalyst optimization

The effect of catalyst loading on degradation of PAN was evaluated using both the photocatalysts namely Aeroxide P-25 and Kronus-7050. Fig. 1 and 2 illustrates the optimization of catalyst loading for Aeroxide P-25 and Kronos 7050 respectively. The results showed that initially photocatalytic degradation increases with increase in catalyst loading till it reaches the optimal loading (0.3 g L$^{-1}$ Aeroxide P-25 and 0.25 g L$^{-1}$ Kronos 7050) and further increase in catalyst loading reduces degradation due to shielding effect hindering the light transmission through the solution causing the less generation of electrons and positive holes and thus reducing the photocatalytic activity. [10, 29-31]

3.1.2 Effect of initial concentration of PAN

The effect of initial concentration of PAN on photocatalytic degradation at different initial concentrations (100, 200, 250, 300 ppm) was evaluated and from Fig. 3 it was investigated that with the increase in initial concentration for PAN, the rate of degradation decreases, as Aeroxide P-25 loading, rate of generation of *OH radicals, illumination intensity and time are constant during photodegradation.
3.1.3 Effect of initial pH of PAN solution

To evaluate the effect of pH on degradation, photocatalytic degradation of PAN was carried out at different pH conditions (1.2, 2.5, 3.5, 8.5). The pH was adjusted by perchloric acid for acidic solutions and 0.1 NaOH for basic solutions. From fig. 4 it was observed that 52.5% and 45.9% degradation of PAN was achieved in 4 h at pH 2.5 and pH 8.5 respectively. At pH 3.5 maximum degradation of PAN (71%) was achieved. The zero point charge of TiO\(_2\) is at pH 6 and TiO\(_2\) is of amphoteric in nature. Due to this, in both acidic and alkaline range photocatalytic degradation decreases. This is in agreement with results of Mangrulkar et al. (2011) who have used N-doped TiO\(_2\).

3.2 Photocatalytic activity of Aeroxide P-25 and Kronos (7050 and 7000)

The photocatalytic degradation experiments were carried out at identical conditions using Aeroxide P-25 and Kronos 7050 under external UV light source. It was observed that 71% and 55% degradation was achieved in case of Aeroxide P-25 and Kronos 7050 in 4 h respectively. Though Kronos 7050 has more surface area (250 \(\text{m}^2 \text{g}^{-1}\)) than Aeroxide P-25 (60 \(\text{m}^2 \text{g}^{-1}\)), it exhibited less degradation. From XRD patterns of Kronos 7050, only anatase crystal phase was identified by its major (101) peak at (2 \(\theta\)=25.5º) whereas from literature it was observed that Aeroxide P-25 exhibited major peak of anatase (101) at 25.5º and rutile phase (110) at 27.3º. Anatase is more active crystalline form of TiO\(_2\) however the presence of rutile (30%) in Aeroxide P-25 decreases the recombination of generated *OH radicals which is responsible for greater photocatalytic activity. The presence of rutile form (30%) in Aeroxide P-25 prevented the recombination of holes and electrons thus improving the performance of photocatalytic degradation. This justification is in agreement with Bhatakhande et al. (2004).

Photocatalytic degradation of PAN under visible light illumination was carried using Kronos 7000 (C-doped TiO\(_2\)). The UV-vis absorption spectra obtained for Kronos 7000 was shown in Fig. 6. It was observed that 83% of the degradation of PAN was achieved in 4 h and it proved to be more effective than Aeroxide P-25. Compared to non doped photocatalyst (Aeroxide P-25), in case of C-doped TiO\(_2\) (Kronos 7000), there is intense absorption of visible light resulting in more photogenerated electrons and holes thereby increased photocatalytic activity. Also due to increased surface area there was more adsorption resulting in more absorption of energy enhancing the photocatalytic activity.

Using HPLC analysis it was investigated that intermediates like salicylic acid, catechol, and benzoquinine were formed during degradation in very small quantities which are further oxidized.

3.3 Comparison of photocatalytic and photochemical degradation of PAN under external UV source

Photochemical degradation of PAN under external UV source was studied using stoichiometric amount of hydrogen peroxide (30%) and 200ppm of PAN concentration. Fig. 7 shows that photochemical degradation is much lower as compared to photocatalytic degradation. By photochemical route 51% degradation of PAN was achieved in 4 h at same operating conditions and pH 3.5.

Stasinakis et al. (2008) investigated that lower pH values ranging from 2.5-3.5 are usually preferred for the photochemical degradation however at very low pH, hydrogen peroxide is stable and it forms oxonium ion (H\(_3\)O\(^+\)) which enables H\(_2\)O\(_2\) electrophile to enhance its stability, decreasing the formation of hydroxyl radicals and thereby reducing the degradation rate. Anamtoniou et al. (2010) have reported that since the UV lamps in the study emit light at a range of wavelengths (300< <400 nm) the activation of oxidants is believed to be caused by the emission spectra and not \(\lambda_{\text{max}}\)=365nm. The applied wavelength in the experiment was 365-435 nm at which H\(_2\)O\(_2\) has low absorption resulting in less degradation of model compound. In case of photochemical degradation, better results would have been obtained using UV source with shorter wavelength (180-200 nm). [3]

3.4 Kinetic model development

It was observed that photocatalytic degradation of PAN using Aeroxide P-25 and Kronos 7050 exhibited pseudo first order reaction. Several recent reports claim that the photocatalytic degradation follows Langamuir-Hinshewood model (L-H model) of kinetics. [29] However it is still a subject of debate that the validity of L-H model in photocatalytic degradation could be misconception without proper experimental evidences. In this work the
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objective was to establish a model that satisfactorily describes the photocatalytic degradation across a variety of experimental conditions which will useful for scale-up.

Considering first order reaction, the rate equation can be expressed as:

\[ -r_A = \frac{dC_A}{dt} = k C_A^a I^b \]  

(1)

Where \( -r_A \): rate of reaction; \( k \): rate constant; \( C_A \): Concentration; \( I \): intensity of light

\[
\ln \left( -r_A \right) = \ln K + a \ln C_A + b \ln I \]  

(2)

\[
\ln \left( -r_A^1 \right) = \ln K + a \ln C_A + b \ln I_1 \]  

(3)

\[
\ln \left( -r_A^2 \right) = \ln K + a \ln C_A + b \ln I_2 \]  

(4)

During the experimentation considering, intensity of light source kept constant throughout he experiment, the modified form of equation becomes

\[
\ln \left[ \frac{-r_A^1}{-r_A^2} \right] = a \ln \left[ \frac{C_A^1}{C_A^2} \right] \]  

(5)

\[
a = \ln \left[ \frac{-r_A^1}{-r_A^2} \right] / \ln \left[ \frac{C_A^1}{C_A^2} \right] \]  

(6)

Solving the above equations, model equation for photocatalytic degradation of PAN was derived as \( -r_A = 0.005 C_A^{0.825} \).

The experimental data for another set with different concentrations of PAN (100 ppm, 250 ppm) was tested for the above model equation (refer Fig. 8) and it was observed that the experimental data is fitted successfully for the developed model equation.

IV. Conclusion

In this work, the comparative study was done for photocatalytic degradation of PAN using Kronos (7050 and 7000) and Aeroxide P-25 and by photochemical route. It was observed that catalyst loading and initial pH has significant effect on photocatalytic degradation. The presence of rutile form (30 %) in Aeroxide P-25 prevented the recombination of holes and electrons and showed higher photocatalytic activity than Kronos 7050 inspite of less surface area. It was observed that 71 % and 55 % of degradation was achieved in case of Aeroxide P-25 and Kronos 7050 in 4 h respectively under external UV light illumination. The applied wavelength in the experiment was 365-435 nm at which H_2O has low absorption which may have caused the less degradation (51%) of model compound by photochemical route whereas using Kronos 7000 under visible light illumination 83% of degradation was achieved.

The kinetic model for photocatalytic degradation of PAN was predicted successfully with the model equation \( -r_A = 0.005 C_A^{0.825} \) and the results confirmed that this model could be effectively predict the photocatalytic degradation of PAN and can be use for the scale up. UV light accounts only 4-8% in solar radiation and is not sufficient for activation of photocatalysts. There is need to develop the visible light induced photocatalysts such as Kronos 7000, so as to promote the photocatalytic treatment for full scale application in industries.

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Figure Captions: 

Figure 1. Effect of Catalyst loading for Aerosoxide P-25 

Figure 2. Effect of catalyst loading for Kronos 7050 

Figure 3. Effect of initial concentration on degradation for Aerosoxide P-25 

Figure 4. Effect of pH on degradation for Aerosoxide P-25 

Figure 5. ln (C/Co) vs. Time for Aerosoxide P-25 and Kronos 7050 

Figure 6. UV-vis absorbance of Kronos 7000 

Figure 7. Photocatalytic and Photochemical Degradation of PAN 

Figure 8. Test of a rate equation for different concentrations of PAN
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Figure 1

Figure 2

Figure 3
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Figure 7

Figure 8