



DEGRADATION OF WASTEWATER CONTAINING O-HYDROXY BENZOIC ACID BY USING PHOTOCATALYSTS TiO₂ AND ZnO

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ABSTRACT

This study compares the treatment of photocatalytic advanced oxidation processes (AOPs) of an aqueous solution containing O-Hydroxy benzoic acid and TiO₂ with ZnO photo catalytic processes. The various advanced oxidation processes (AOPs) such as the UV/H₂O₂, UV/H₂O₂/TiO₂ and UV/H₂O₂/ZnO were investigated for the degradation of substrate in lab-scale experiments. The experiments were carried out in a batch photo reactor using 8W low pressure mercury vapour lamp. Substrate concentration was determined by UV-Visible Spectrophotometer. The semi-log plot of substrate concentration versus time suggests first order kinetics. The effects of parameters viz. pH, photo catalyst doses and hydrogen peroxide were also examined.

Keywords: Advanced Oxidation Processes, O-hydroxy benzoic acid, Photo reactor, Degradation, Photo catalytic, First order kinetics

1. Introduction

New developments in the variety of fields have also led to the presence of new compounds in the effluent streams of processing plants, which are not readily degraded by the conventional effluent treatment methods [1-3]. Oxidation of organic pollutants present in water is an attractive method of treatment because, if carried to completion, it results in the conversion of carbon dioxide and water. Unfortunately, the direct oxidation of organic compounds by molecular oxygen at ambient conditions is, in most cases, too slow to be of kinetics and mechanism of the degradation

processes any potential use. On the other hand, Advanced Oxidation Processes (AOPs) offers the most effective way of oxidizing organic contaminants to less harmful compounds [4-6]. Typically AOPs are ambient temperature and pressure process that involve in situ generation of highly reactive species such as hydroxyl radical ($\bullet\text{OH}$). The $\bullet\text{OH}$ radicals are powerful oxidizing reagents with an oxidation potential of 2.80 V and exhibits faster rates of oxidation reactions as compared to that using conventional oxidants like hydrogen peroxide or KMnO₄[4]. Among AOPs, photocatalytic oxidation (PCO) has proved to be of real interest as efficient tool for degrading aquatic organic contaminants. PCO involves the acceleration of photoreaction in presence of semiconductor photocatalyst. One of the major applications of PCO is heterogeneous photocatalysis to effect total mineralization of liquid phase organic contaminants. The term "photocatalytic degradation" usually refers to complete photocatalytic oxidation or photo mineralization, essentially to CO₂ H₂O, NO₃, PO₄ and halide ions [5,6]. Metallic oxides and sulfides are among the most used semiconductor materials available for photocatalytic purposes. Nowadays, titanium dioxide (TiO₂) is the most frequently used semiconductors for heterogeneous photocatalytic processes anytime it has demonstrated to be the most active[7,8]. Table 1 depicts some of the semiconductor materials used in photocatalytic reactions along with their band gap energy required for catalyst activation and the maximal wavelength required for activation. Degradation of organic pollutants by heterogeneous photocatalytic is among the most successful applications.

Table 1-Band gap energy and activation wavelength for some semiconductors[9]

Material	Bandgap energy (eV)	Activation wavelength (nm)
BaTiO ₃	3.3	
CdO	2.1	375
CdS	2.5	590
CdSe	1.7	497
Fe ₂ O ₃		730
GaAs	2.2	565
SnO ₂	2.3	540
SrTiO ₃	3.9	318
TiO ₂	3.4	365
WO ₃	3.2	390
ZnO	2.8	443
	3.2	

Dhanshvar et al reported [10] that ZnO is better alternative for the degradation of dyes as its photodegradation mechanism similar to that of TiO₂. Lizama et al. [11] reported higher photocatalytic efficiency of ZnO in the colour removal of Reactive Blue 19. The biggest advantage of ZnO is that it can absorb over a larger fraction of UV spectrum[12]. Keeping this in view we focussed our work to compare the photocatalytic efficiency of TiO₂ and ZnO. This may lead to cost effective treatment technology for most of the organic pollutants. Salicylic acid is chosen as modern pollutant for the present study. Salicylic acid is very toxic and it is widely present in pharmaceutical industrial effluents[13]. It can stimulate skin and mucous membrane and react with protein. In addition, it can bring about tinnitus, qualm, naupathia and electrolytical turbulence. Hence this compound is selected for the present study.

2. Experimental

2.1 Chemicals

Analytical grade O-Hydroxybenzoic acid was purchased from Merck, India; and was used as received without any further purification and stock solution of 0.01M of O-Hydroxybenzoic acid was prepared. Initial concentration of O-Hydroxybenzoic acid used during the experimental runs was 0.15mM. Stock solution

of H₂O₂ was prepared by diluting 30% w/v of hydrogen peroxide (Qualigens) with distilled water. All stock solutions were stored in amber coloured light resistant Pyrex glass bottles. TiO₂ (AR) (surface area 50m²/g) and ZnO were obtained from s-d fine chemicals, India & were 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, H₂O₂ concentration, TiO₂ doses & ZnO doses during degradation of O-Hydroxybenzoic 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 O-Hydroxybenzoic 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 TiO₂ 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 pipette out into test tubes. Then a

centrifugation process was applied to separate TiO_2/ZnO catalyst particles after photocatalysis. The Samples were immediately analyzed to avoid further reaction. The overall degradation reaction was carried out for 240 min.

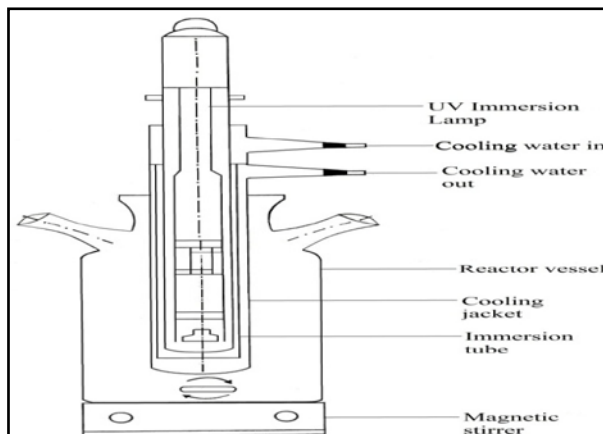


Fig. 1 - Photoreactor

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 O-Hydroxybenzoic 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 O-Hydroxybenzoic acid was plotted experimentally, which gave a high linear regression coefficient of 0.996 at 229.5 nm (Fig.2).

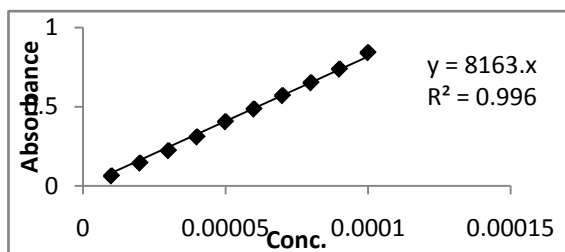


Fig. 2- Calibration Curve of O-Hydroxy benzoic acid

3. Results & Discussion

3.1. Effect of pH

pH is one of the most important parameters to be studied. The rate of degradation of O-Hydroxybenzoic acid was observed by carrying out the experiments at different pH conditions

namely 2, 3, 4, 5, 6, 7 and 9. In case of $\text{H}_2\text{O}_2/\text{UV}$, the maximum degradation O-Hydroxybenzoic acid was achieved at pH 7 and shows decreasing trend of degradation at higher and lower pH

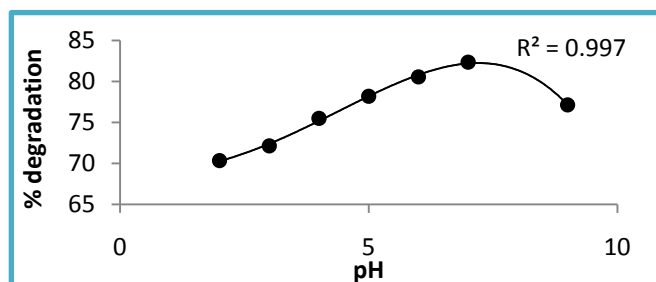


Fig. 3- Effect of pH on degradation efficiency for O-Hydroxy benzoic acid (Conditions: [O-HBA] = 0.15 mM, H_2O_2 /COD = 5)

3.2 Effect of dose of H₂O₂/COD ratio on degradation of O-Hydroxy benzoic acid

By carrying out a series of experiments of O-Hydroxybenzoic acid (with different ratio of H₂O₂/COD namely 2, 3, 4, 5, 6 & 7); the optimum H₂O₂ stoichiometric ratio was found to be H₂O₂ /COD=5 (Fig. 4). Further increase

in H₂O₂ concentration lowered the degradation rate. This is because of the excess H₂O₂ 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 pollutants [14].

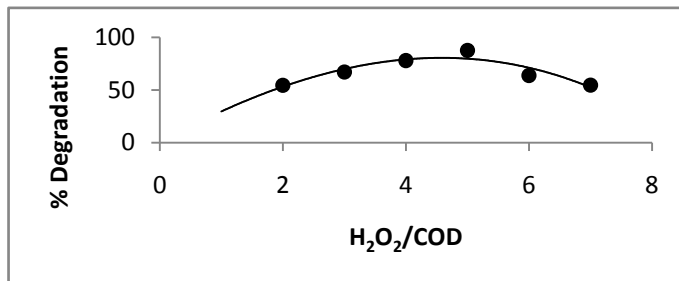


Fig.4- Effect of initial H₂O₂/COD on degradation efficiency for O-Hydroxy benzoic acid (conditions: [O-HBA] = 0.15 mM, pH = 7)

3.3 Effect of catalyst doses

The experiments were conducted to study the effect of varying catalyst doses from 10mg/lit to 90mg/lit for the degradation efficiency of O-Hydroxybenzoic acid. Application of both oxidant and photocatalyst enhances the degradation mechanism and hence gives much higher removal. Maximum degradation of 93.14% was observed with 70 mg of catalyst TiO₂ & 89.62% with 70 mg ZnO photocatalyst. Bar diagram (Fig. 5) shows comparison of efficiency of the oxidative degradation photocatalytic processes using photocatalysts TiO₂ & ZnO. 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 is 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 [15]. Aggregation of catalyst particles, which reduced the interfacial area between the reaction solution & the photo catalyst, may be other reasons for the degradation rate.

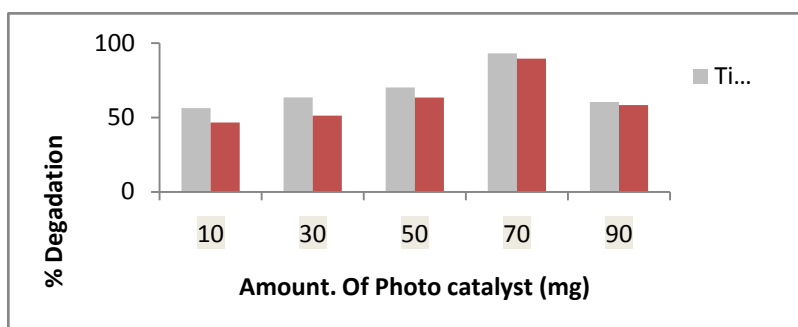


Fig. 5- Bar diagram showing rate of degradation of O-Hydroxy benzoic acid with photo catalyst TiO₂ and ZnO

4. Comparison of various AOPs studied and the kinetic studies

A comparison study was carried out for degradation of O-Hydroxy benzoic acid at optimum conditions for different AOPs studied viz. UV/H₂O₂, UV/TiO₂/H₂O₂ and UV/H₂O₂/ZnO. It was found that the rate of

degradation is highest when the combination-UV/TiO₂/H₂O₂ was used.

5. Degradation Rate Kinetics

The semi logarithmic graph of the concentration of O-Hydroxybenzoic acid with time yield a straight line indicating the reaction is of pseudo

first order (eq. 1)

$$\ln(C_t/C_0) = -K \cdot t \quad (1)$$

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).

$$-d/dt[C(X)] = k \cdot C(X) \quad (2)$$

Where C(X) is the concentration of substrate

and K (min^{-1}) is reaction rate constant.

For O-Hydroxy 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 O-Hydroxybenzoic acid degradation found to follow first order kinetics. Table 2 gives the first order rate constant for UV/ H_2O_2 /TiO₂ system.

Table -2 Rate Constant data for UV/ H_2O_2 /TiO₂ process for the degradation of O-Hydroxy benzoic acid

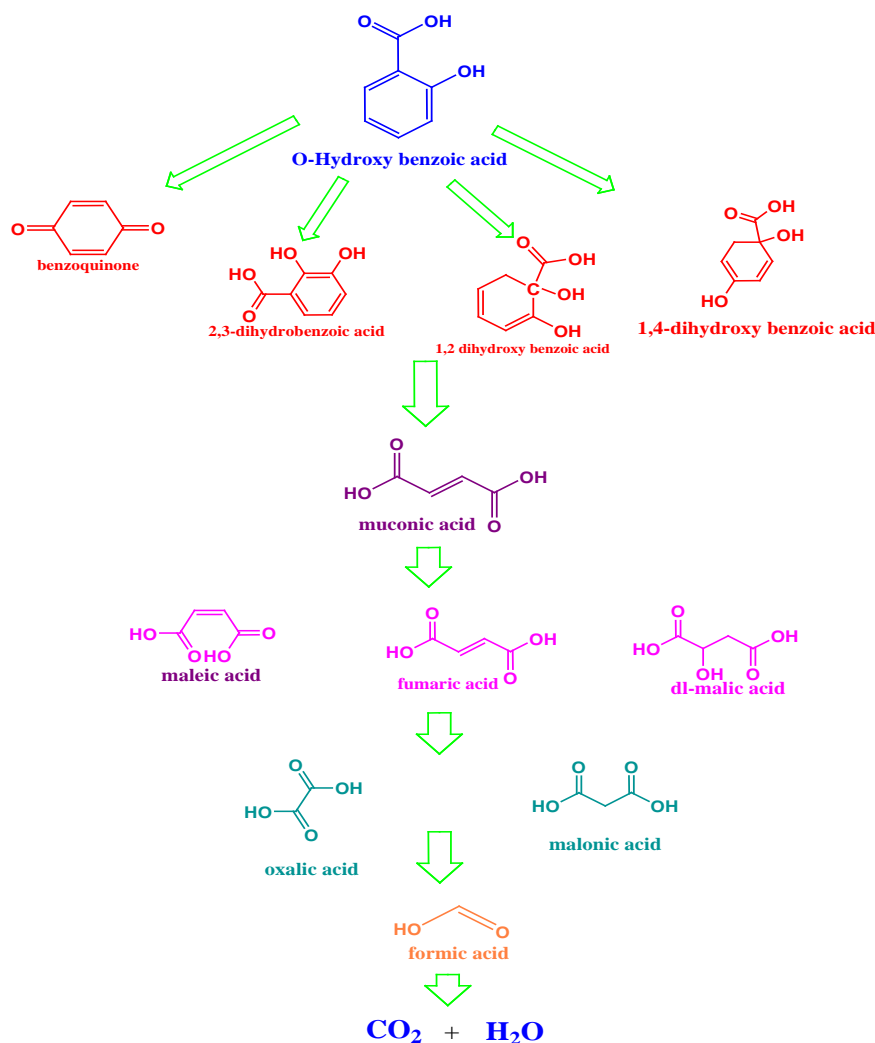
Amount of TiO ₂ (mg/L)	k_1 (min^{-1})	R^2
10	0.0046	0.9481
30	0.0047	0.9713
50	0.0056	0.9595
70	0.0105	0.9771
90	0.0046	0.9453

Table -3: Summary of data for various advanced oxidation processes (AOP) for the degradation of O- Hydroxy benzoic acid

AOP Processes	Rate constant (min^{-1})	R^2
UV/ H_2O_2	0.0072	0.9423
UV/ H_2O_2 /TiO ₂	0.0105	0.9771
UV/ H_2O_2 /ZnO	0.0098	0.9595

On the basis of the results obtained, the following reaction scheme is proposed as the most probable reaction mechanism for the photodegradation of O-hydroxybenzoic acid.

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6. Conclusion

This study showed the potentialities of photocatalytic degradation in water purification. Out of different processes employed, a significant enhancement of the photocatalytic activity was observed in the system using combination of oxidant and photocatalyst 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. Photodegradation can be a recommended approach for the treatment of wastewater containing O-Hydroxybenzoic acid. Keeping in view all the factors, it can be easily said that UV/H₂O₂/TiO₂ system is an efficient one amongst all other processes studied. The best reaction dose of TiO₂ was found to be 70 mg/lit. Hence TiO₂ was found to be more

efficient than the photocatalyst ZnO in the degradation of the selected pollutant substrate.

Conflict of interests:

The authors declare that there is no conflict of interest regarding the publication of this paper.

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