

# **Removal of Organic Pollutants from the Pharmaceutical Effluent by TiO<sub>2</sub> Based Photocatalysis**

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**ABSTRACT:** Photocatalytic technique, one of the advanced oxidation technique was studied for the removal of organic pollutants from pharmaceutical wastewater streams by using Titanium dioxide. Photocatalytic degradation significantly reduces the Chemical Oxygen Demand (COD) value in wastewater. A constant intensity of UV light was utilized in the experimental setup. The experimental setup consists of wooden box where UV light passes through mixture of TiO<sub>2</sub> powder and wastewater sample agitated with continuous stirring at room temperature. The photocatalytic removal of organics and its degradation efficiency was evaluated by determination of reduction in the COD values. The effects of initial effluent concentration, catalyst dosage, irradiation time, effect of temperature and effect of pH were studied. It was observed that effluent and TiO<sub>2</sub> mixed continuously in a flask followed by stirring for 1h, and the concentration of wastewater sample maintained at 10:6 ratio, the optimum values of the variables were the irradiation time 60 min, catalyst dosage 0.8 g/50ml, temperature 35°C and pH 12. The photocatalytic treatment was able to destruct organic pollutants of wastewater in 1h and induced a (COD) reduction of 93.06%.

**KEYWORDS:** Photo catalysis, Chemical oxygen demand, UV light source, TiO<sub>2</sub>.

## **I. INTRODUCTION**

Now a days, due to the presence of extremely refractory organic matter in the waste water stream, the use of conventional wastewater treatment methods are increasingly become challenged. So, now there is a clear need to test and setup the emerging alternative technologies that can deal with highly concentrated and toxic non biodegradable organic matter. With the in situ generation of electron-hole pairs upon irradiation with light, TiO<sub>2</sub> can mineralize a wide range of organic compounds into harmless end products such as carbon dioxide, water, and inorganic ions. So in this way advanced oxidation process (AOP's) has emerged in the last decade especially for the treatment of industrial wastewater. It has been frequently observed that pollutants not amenable to biological treatments may also be characterized by high chemical stability and/or by strong difficulty to be completely mineralized. In these cases, it is necessary to use reactive systems much more effective than those adopted in conventional purification processes. A lot of research work has been done in this direction in the last decades, pointing out the prominent role of a special class of oxidation techniques defined as Advanced Oxidation processes (AOPs). With this approach, harmful organics are broken down in the presence of a catalyst and ultraviolet (UV) irradiation without generating secondary harmful pollutants. In this regard, titanium dioxide (TiO<sub>2</sub>) semiconductors have demonstrated various advantages in heterogeneous photocatalysis. AOP application depends on the polluting load of wastes, normally expressed in chemical oxygen demand (COD). AOPs can be utilized in wastewater treatment for: overall organic content (COD) reduction, specific pollutant destruction, sludge treatment, increase of bioavailability of recalcitrant organics, and color and odor reduction (Tong Zhang, et al. [43] ).

Photo catalysis is basically the acceleration of a photoreaction by the presence of a catalyst. Catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct, depending upon the mechanism of the photoreaction. Catalysis implicates a catalytic entity that participates and

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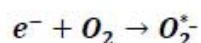
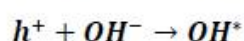
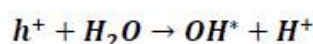
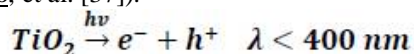
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accelerates the chemical transformation of a substrate, itself remaining unaltered at the end of each catalytic cycle. In photocatalysis, no energy is stored there is merely an acceleration of a slow event by a photon- assisted process (RM. Zakaria1, et al. [35]).

## 1.1. Photo-catalytic Process with Titanium Dioxide (TiO<sub>2</sub>/UV):

A wide range of organic contaminants can be oxidized by light with a band gap energy of  $\lambda < 400$  nm in the presence of TiO<sub>2</sub> catalyst. The reaction mechanism occurs in several steps, and is described in Reaction. As light strikes the TiO<sub>2</sub> surface, valence band electrons (e<sup>-</sup>) are excited to the conduction band, creating holes behind (h<sup>+</sup>). The holes react with water molecules to produce OH\* radicals. Aeration is often used to prevent electron-hole recombination. The excited electron will then react with O<sub>2</sub> (electron acceptor) to form the O<sub>2</sub><sup>\*-</sup> ion which will act as an additional oxidant (S.Murgolo, et al. [37]).



The nature of the TiO<sub>2</sub> catalyst (surface area with active sites) plays an important role in the overall rates of degradation of pollutants. A larger surface area with increased number of active sites will result in a more rapid and extended reaction. TiO<sub>2</sub> has band gap energy of 3.02 eV, which means that the optimal wavelength of irradiation is around 400 nm.

## II. MATERIALS AND METHODS

### 2.1 Reagents and chemicals used:

COD of industrial effluent and treated sample was determined by using potassium dichromate solution (containing Mercury Sulphate, Silver Sulphate and concentrated Sulphuric Acid), COD reagent, ferrous ammonium sulphate (0.1N) and Ferroin indicator. For the experiments de-ionized water is used. Magnetic stirrer was used during experimentation to solve the problem of mixing and TiO<sub>2</sub> remains in suspension.

#### 2.1.2 Photo Reactor:

Photocatalytic treatment of effluent was performed in batch experiments. For Photocatalytic treatment UV reactor was used which is in rectangular shape and having dimension of 4.5 feet length, 3.5 feet width and made of wooden. UV light source fitted inside the rectangular box (400w). Photocatalytic reaction is carried out inside of the Photo Reactor.

### 2.2 Experimental parameters:

#### 2.2.1 Effect of effluent concentration:

Optimum effluent concentration was determined by taking 45ml of de-ionized water and 5ml (10:1 ratio) of effluent adding 0.1 g of catalyst in a conical flask provided with magnetic stirrer of constant speed and kept under UV lamp at constant room temperature. After 1hr, filtrate the solution and then analyzed COD degradation of the sample. Then the same procedure is repeated with different initial effluent concentrations like 40ml, 35ml, 30ml, 25ml, 20ml, 15ml, and 10ml, keeping the remaining conditions constant, like stirring speed, irradiation time, catalyst load, and pH. This gives an opportunity for determination of optimum effluent concentration.

#### 2.2.2 Effect of catalyst dosage:

To study the effect of catalyst dosage, 20ml of de-ionized water 30 ml effluent solution with a known amount of catalyst dosage 0.1g is taken in a conical flask provided with magnetic stirrer of constant speed and kept under UV lamp at constant room temperature. After 1hr filtered the solution and then analyzed COD degradation of the sample. This is repeated for different dosages ranges from 0.2g to 0.8g. The COD removal of each individual sample is determined by cod digester.

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## 2.2.3 Effect of irradiation time:

The required duration for the complete photocatalytic treatment of organic pollutants in the wastewater was studied based on the duration of catalyst irradiation to the light source. By adding optimum catalyst dosage 0.8gm in 20ml of de-ionized water 30ml concentration of effluent solution with a pH of 12 in a beaker. Magnetic stirring was provided for different time intervals like 20 min, 30 min, etc. up to 120 min, at constant agitation speed, under the UV light source.

## 2.2.4 Effect of temperature:

Higher temperatures will generally increase the reaction rate. To study the effect of temperature, taken optimum concentration (30ml) effluent solution with an optimum catalyst dosage 0.8g is taken in a conical flask provided with magnetic stirrer of constant speed and kept under UV lamp varying temperatures from 20°C to 45°C. After 1hr filtered the solution and then analyzed COD degradation of the sample.

## 2.2.5 Effect of pH:

The various pH of (3 to 12) effluent solutions were used to estimate the effect of pH on COD reduction. pH changes of 3-12 in the system resulted in minimal impact on COD and removal efficiencies. The OH\* radical formation was however dominant at high pH ( $\geq 10$ ) which is why a pH interval in between is preferred to obtain an oxidation that is relatively fast. The effect of pH was determined by addition of 0.8 g of catalyst and 30 ml of sample solution 20 ml of de-ionized water in a flask, at different pH values of the solution ranging from 3 to 12 by adding 0.1 N HCl or 0.1 N NaOH. UV light passes through the sample at optimum contact time 1h at constant agitation speed and at 35°C temperature. The cod of sample is determined for each pH.

## 2.3 Analysis of the sample

### 2.3.1 Collection and storage of waste water sample:

Sample was collected from homogenous tank of effluent treatment plant of pharmaceutical industry. Sampling vessel was cleaned and rinsed carefully with distilled water and then washed with sample and stored and maintained at 4°C.

Waste water sample was analyzed for the COD, pH and Photo catalytic treatment was carried out under UV lamp using TiO<sub>2</sub> as a catalyst and observed the following parameters:

- Concentration
- Catalyst dose
- Contact time
- Temperature
- pH

### 2.3.2 Photocatalytic Treatment:

Photocatalytic treatment was done for pharmaceutical effluent sample. The effluents of pharmaceutical industry were treated and the various parameters like pH, catalyst dose, contact time, temperature, and concentration of effluent are optimized.

### 2.3.3 Degradation of Pharmaceutical Effluent:

Initially the collected effluent sample from homogenous tank of effluent treatment plant of pharmaceutical industry sample COD & pH is found 18000ppm and 10 respectively and varied all parameters to optimize pH, catalyst dose, contact time, temperature, and concentration of effluent. De-ionized water was used for all the dilutions.

First the known amount of waste water sample was taken in a vessel and TiO<sub>2</sub> (0.1g/50ml) was added. Then the solution was stirred continuously with the help of magnetic stirrer for 1hr under the UV lamp radiation. After 1hr the sample was filtered to separate TiO<sub>2</sub> and COD value of filtrate was checked. The same procedure was followed to determine COD by varying concentration as 10:1 10:2 10:3 10:4 10:5 10:6 10:7 10:8. By using above procedure the dose of TiO<sub>2</sub> as 0.1g/50ml 0.2g/50ml, 0.3g/50ml, 0.4g/50ml 0.5g/50ml 0.6g/50ml 0.7g/50ml 0.8mg/50ml the rate of degradation was calculated from the different photo catalyst doses. Rate of photo catalytic degradation was also studied from 10min to 1hr under optimum catalyst dose (0.8g/50ml). Under the same set of condition effect of optimum temperature on photo catalytic degradation was determined. Under irradiation time of 1hr with optimum catalyst dose and continuous stirring, the effect of pH was studied. COD value of each sample obtained under various parameters was determined by following standard procedure given in APHA.

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## III. RESULTS AND DISCUSSION

### 3.1. Effect of concentration:

The rate of photocatalytic degradation of certain pollutant depends on its concentration and other existing compounds in water matrix. High concentration of pollutants in water saturates the  $\text{TiO}_2$  surface and hence reduces the photonic efficiency and deactivation of the photocatalyst. To study the effect of initial dye concentration, 0.1 g of catalyst is taken in a beaker and of synthetic solution of initial dye concentration of 20 mg/L is mixed with it and it is kept for shaking for optimum time. Then the same procedure is repeated with 30 ml of stock solution, but with different initial concentrations like 40mg/L, 60mg/L, etc., keeping the remaining conditions like agitation speed and room temperature constant. Maximum removal takes place at optimum concentration of 10:6 ratio and COD removal 86.13% was observed.

Lakshmi vandanapu et al., [38] obtained the maximum COD removal at 10:6 concentration

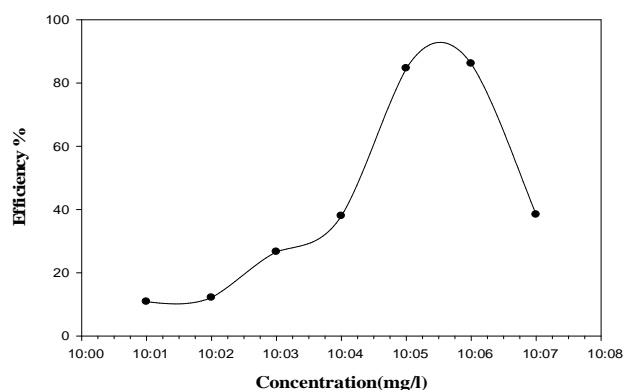


Fig1: Effect of concentration on photocatalytic degradation efficiency of organic pollutants

### 3.2. Effect of dosage:

For economic removal of pollutants from the pharmaceutical wastewater, it is necessary to find the optimum amount of catalyst load for efficient Photocatalytic degradation. The effect of catalyst load on the Photocatalytic degradation efficiency of industrial wastewater was studied by using  $\text{TiO}_2$ . The Photocatalytic degradation experiments were carried out under the UV light by varying the amount of Photocatalyst load from 10 mg to 100 mg and the illumination time was fixed for 1 h. Fig. shows the effect of Photocatalyst load on the Photocatalytic degradation efficiency. When the amount of Photocatalyst load was increased in the wastewater, Photocatalytic degradation efficiency was significantly increased and degradation rate constant was found at 80 mg of Photocatalyst load and removal efficiency 90.08% was obtained.

Gaya U.I, Chong M.N[22] reported the maximum COD removal at 0.8g catalyst  $\text{TiO}_2$  dosage.

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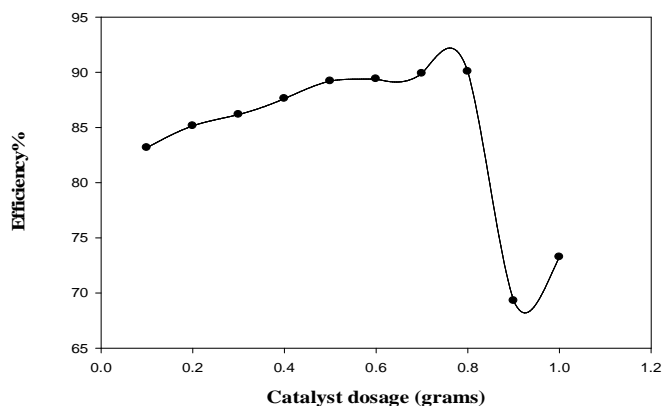


Fig2: Effect of dosage on photocatalytic degradation efficiency of organic pollutants

### 3.3. Effect of time:

The effect of irradiation time on the organic pollutants percentage removal is shown in Figure 3. The Figure illustrates a typical experimental curve where the percentage removal increases as the irradiation time increases. This can be attributed to the reduction of organic waste molecules on the activated surface of TiO<sub>2</sub> particles. The percentage removal shows a sharp increase with the stirring time up to approximately 60 min. The percentage removal value ranged from 25% to approximately 91.08%. The time required to achieve the concentration, the irradiation time was considered the time necessary to reach the equilibrium for the adsorption reaction and based on the results obtained 60 min time was adopted in the remaining experiments.

Bhavanth et al, [5] obtained maximum COD removal at 1h irradiation time.

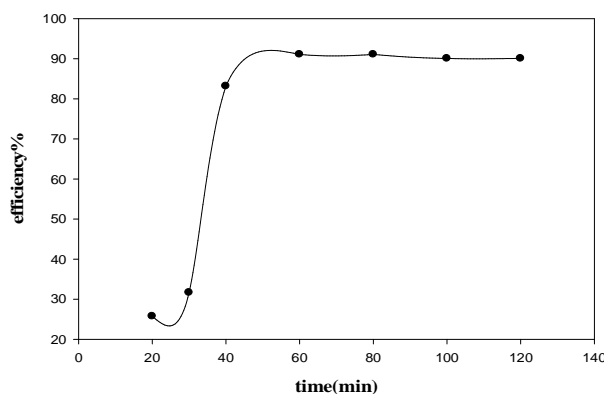


Fig3: Effect of irradiation time on the photocatalytic degradation efficiency of organic pollutants

### 3.4. Effect of temperature:

An increase in reaction temperature generally results in increased photocatalytic activity. To study the effect of temperature, taken optimum concentration (30ml) effluent solution with an optimum catalyst dosage 0.8g is taken in a conical flask provided with magnetic stirrer of constant speed and kept under UV lamp varying temperatures from

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20°C to 45°C. After 1hr filtered the solution and then analyzed COD degradation of the sample. At 35°C COD removal efficiency 92.07% obtained.

Akira fujishima et al [4] studied the maximum COD removal obtained at 35°C temperature.

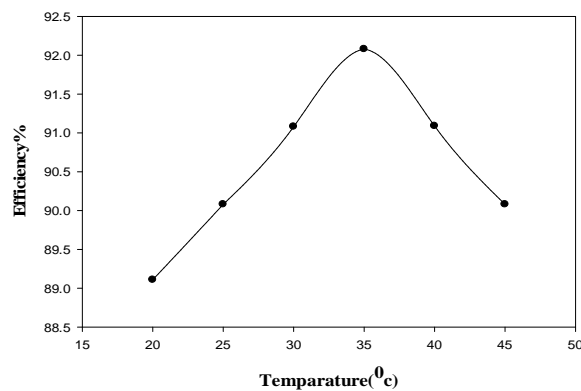


Fig4: Effect of temperature on photocatalytic degradation efficiency of organic pollutants

### 3.5. Effect of pH:

The negative effect of radical scavengers is minimized at neutral pH, because anions and cat-ions that might be present in the wastewater will compete for the active sites on the TiO<sub>2</sub> surface. At low pH, the TiO<sub>2</sub> particles will be surrounded by positive charges, which cause an adsorption of anions to the surface. At high pH the opposite effect will occur; cat-ions will be attracted to the surface. The various pH of effluent solutions were used to estimate the effect of pH on COD reduction. pH changes of 3-12 in the system resulted in minimal impact on COD and removal efficiencies. The effect of pH was determined by addition of 0.8 g of catalyst and 30 ml of sample solution 20 ml of de-ionized water in a flask, and temperature of 35°C at different pH values of the solution ranging from 3 to 12. At pH of 9 maximum COD reduction takes place from 30% to 93.06% obtained.

Meng nan chong et al.[21] obtained maximum COD removal at pH 9.

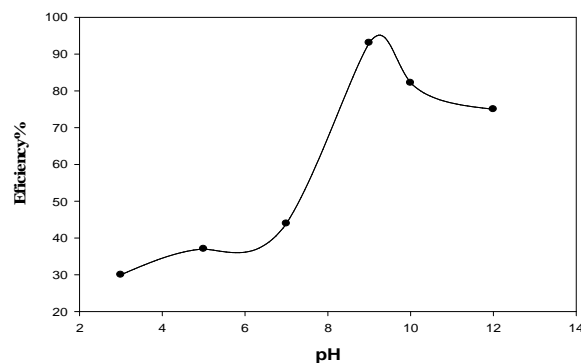


Fig5: Effect of pH on photocatalytic degradation efficiency of organic pollutants

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## IV. CONCLUSION

Photocatalysis has large capability for the water treatment. It can be utilized for the decomposition of organic and inorganic compounds. Photocatalytic degradation of organic pollutants is promising technology due to its advantage of degradation on pollutants instead of their transformation under ambient conditions. The process is capable of removing a wide range of organic pollutants such as pesticides, herbicides, and micro pollutants. Although significant amount of research has been conducted on TiO<sub>2</sub> Photocatalysis at laboratory scale, photocatalytic degradation of pharmaceutical wastewater using the catalyst as TiO<sub>2</sub> was investigated. The results achieved can be used to optimize the process parameters. Photo catalyst, TiO<sub>2</sub> gives higher degradation efficiency. Photocatalytic degradation efficiency was observed as 93.06% using TiO<sub>2</sub> as a photocatalyst with optimum catalyst dose of 80mg/50ml for irradiation time of 1hr under continuous stirring with maximum intensity, pH of 9 and temperature of 35°C.

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