

## Photocatalytic Degradation of Antibiotic Rifabutin in the Presence of TiO<sub>2</sub> Nanocatalyst Assisted UV Radiation

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In the present investigation photocatalytic degradation of an antibiotic rifabutin in aqueous solution with TiO<sub>2</sub> as photocatalyst has been investigated under UV irradiation. The efficiency of degradation was quantified by several parameters such as effect of initial concentration, catalyst loading, pH and addition of H<sub>2</sub>O<sub>2</sub> as a co-oxidant. The effect of operational parameters on the decolourisation and degradation under UV irradiation in TiO<sub>2</sub> suspension has been investigated to find out the optimum conditions. The optimum conditions for the degradation of the rifabutin have been found as 0.4 mg/mL drug concentration, pH 10.5, and 0.06 g/L catalyst dose. The decolourisation and degradation kinetics followed first-order kinetics.

**Keywords:** Photocatalytic Degradation, UV, TiO<sub>2</sub>, Rifabutin, Kinetic Study

### Introduction

Photocatalytic oxidation processes have been known for their simplicity and efficiency<sup>1,5</sup>. Experimental observations indicate that almost complete mineralization of organic compounds to carbon dioxide, water and inorganic anions is possible by photocatalytic process<sup>6-11</sup>. It has been reported that the heterogeneous photocatalysis in the presence of semiconductor act as a promising tool and a fast-growing field of basic and applied research for water treatment with effective degradation of major pharmaceuticals waste water which is emitted by pharmaceutical industry without formation of harmful intermediates<sup>12,14</sup>. Several investigators have reported<sup>15,18</sup> photocatalytic degradation of different types of organic and inorganic pollutants onto various semiconductors such as SnO<sub>2</sub>, ZrO<sub>2</sub>, CdS, ZnO, CNT, MWCNT, CuO, WO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub><sup>19,28</sup> either alone or in combination as photocatalysts in photocatalytic processes. Among them titanium oxide (TiO<sub>2</sub>) as the photocatalyst has been found effective for complete oxidation and mineralization of pharmaceuticals.

### Experimental

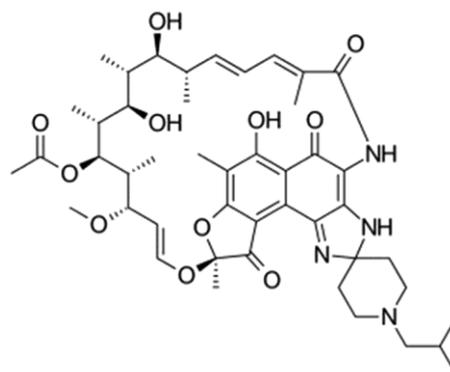
#### Instrumentation

All experiments were performed in a photocatalytic reactor of 150 mL capacity having 6W UV lamp for

irradiation. To prevent UV radiation leakage the reactor set up was covered with wooden box of black colour. The lamp emits predominantly UV radiation of 10 mW/cm<sup>2</sup> at 254 nm. For pH measurements decibel DB 1011 digital pH meter was used. The reaction kinetics was studied at Systronic spectrophotometer 166 at 370 nm.

#### Reagents and chemicals

The anatase form of titanium dioxide (99+%) of 325 mesh was obtained from Sigma Aldrich and used as such without further treatment. Rifabutin Scheme 1, was procured from Lupin Pharmaceuticals Pvt Ltd. with the brand name Rifabutin. All laboratory chemicals used were of analytical grade. To prepare a stock solution of rifabutin, 150 mg of drug was dissolved in 50 mL of methanol. The stock solution



Scheme 1: Structure of Rifabutin

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was used for further dilution to prepare working solution of 0.4 mg/mL with double distilled water. Britton-Robinson Buffers in the pH range 6.5 to 12.0 were prepared by reported method<sup>29</sup>. Double distilled water was used throughout the experiment.

#### Photocatalytic degradation

A 100 mL of the working solution was taken for the degradation process in a sample holder which was equipped with a UV lamp. Whole assembly was placed in a dark chamber for the photocatalytic reaction. Oxygen was bubbled at a fix flow rate in to the reactor to ensure thorough mixing of the TiO<sub>2</sub> catalyst from the side of the reactor continuously.

After a specific time interval a certain amount of the solution is withdrawn and centrifuged so that the loss of compound due to photodegradation can be found out spectrophotometrically. The rate of decrease of colour with time was continuously monitored.

All the experiments were carried out at room temperature (30±0.1°C). The efficiency of degradation of rifabutin can be calculated using:

$$E (\%) = C_0 - C / C_0 \times 100 \quad \dots (1)$$

Where C<sub>0</sub> represents the initial concentration of rifabutin and C is the concentration of rifabutin at time t. E is a higher efficiency of degradation of rifabutin onto the TiO<sub>2</sub>.

#### Results and Discussion

Initially drug solution (0.4 mg/mL) of rifabutin was kept in the photocatalytic reactor for preliminary analysis at pH 10.5. Catalyst dose was fixed at 0.06 g/L. In order to define the system completely following experimental conditions were set for the photo degradation of the rifabutin (a) In presence of UV light, O<sub>2</sub> and TiO<sub>2</sub>. (b) in presence of O<sub>2</sub> and TiO<sub>2</sub> but in absence of UV light. (c) in absence of TiO<sub>2</sub> but in presence of O<sub>2</sub> and UV light (d) in presence UV light and TiO<sub>2</sub>, but in absence of O<sub>2</sub>. It is evident that in the absence of UV light TiO<sub>2</sub> did not catalyze the degradation process. However, a slight decrease in absorbance was observed, which may be due to the initial adsorption of the drug on to the TiO<sub>2</sub> surface. Similarly in the absence of O<sub>2</sub>, when solutions were irradiated by UV light no change in the absorbance was recorded. However, when a small amount of TiO<sub>2</sub> was added to the solution in the presence of oxygen and UV light an exponential increase in the

absorbance was observed. The maximum degradation (85%) of rifabutin was observed in the presence of UV light, O<sub>2</sub> and TiO<sub>2</sub>.

#### Effect of catalyst concentration

The effect of the catalyst doses has been examined in the range of 0.02 to 0.08 g/L of TiO<sub>2</sub>. Variation of rate constant with different concentrations of TiO<sub>2</sub> was evaluated by the plot of log absorbance vs time. It is evident from figure that as the amount of catalyst increases, the rate of degradation of rifabutin is gradually increased due to sudden increase in the rate of degradation of rifabutin at 0.06 g/L TiO<sub>2</sub> concentration. The optimum amount of TiO<sub>2</sub> is taken as 0.06 g/L for the degradation of rifabutin at pH 10.5. The comparative study of optimum dosage of different types of semiconductor (either alone or in combination) onto different organic compounds has been studied and results are given in Table 1 which shows that minimum dose of TiO<sub>2</sub> is required in the present study<sup>30-38</sup>.

#### Effect of rifabutin concentrations

In order to study influence of the drug concentration on the degradation process, the rifabutin concentrations were varied from 0.1 mg/mL to 0.5 mg/mL catalyst concentration 0.06 g/L. It can be seen that the photodegradation efficiency of rifabutin is directly proportional to its concentration. As on increasing the initial drug concentration from 0.1 mg/mL to 0.4 mg/mL, the degradation rate of rifabutin increases from 40 to 85 %. On further increase in drug concentration, degradation rate becomes constant.

Table 1 — Comparison of optimum dosage of various photocatalyst for the degradation of organic compounds

S. No.	Substrate Compound	Photocatalyst	Catalyst Concentration (g/L)	References
1m	Direct red 23	Ag- TiO <sub>2</sub>	3	30
2	<i>p</i> -cresol	ZnO	2.5	31
3	Phenol	Pr- TiO <sub>2</sub>	1	32
4	Methaodiphos	Re- TiO <sub>2</sub>	1	33
5	Methylene Blue	CdS	1	34
55125				
6	Malachite Green	TiO <sub>2</sub> -WO <sub>3</sub>	1	35
7	Phenol	TiO <sub>2</sub> - ZrO <sub>2</sub>	0.35	36
8	Phenylephrine hydrochloride	SnO <sub>2</sub> -ZnO	0.28	37
9	Balsalazide	TiSiO <sub>4</sub>	0.1	38
10	Rifabutin	TiO <sub>2</sub>	0.06	Present study

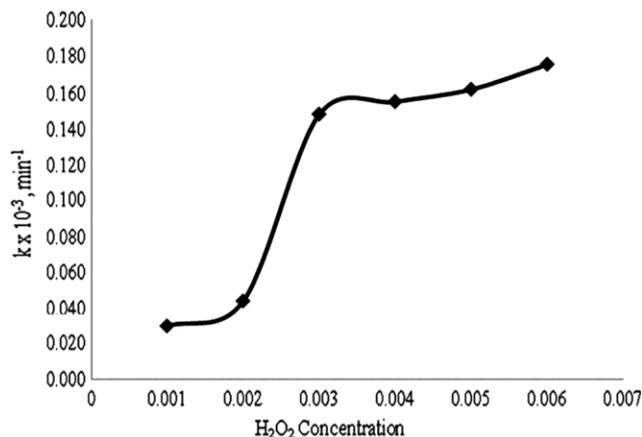


Fig. 1 — Variation of rate constant with different concentrations of H<sub>2</sub>O<sub>2</sub> at conc. 0.4 mg/mL and temp. 30±1°C

#### Effect of pH

Effect of pH on the adsorption percentage of aqueous rifabutin solution on TiO<sub>2</sub> as a photocatalyst was investigated in the pH range 6.5 to 12.0. Degradation rate is increased with pH in the range 6.5 to 9.7. With increase in pH a sudden increase in the degradation rate is observed upto pH 10.5 and after that it becomes almost constant at pH 12.0.

#### Effect of H<sub>2</sub>O<sub>2</sub> concentration

Photocatalytic degradation of rifabutin experiments with H<sub>2</sub>O<sub>2</sub> were carried out in three different experimental conditions viz. in presence of H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub> but absence of O<sub>2</sub>, in presence of H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub>, and O<sub>2</sub>, and in presence of H<sub>2</sub>O<sub>2</sub> only. Maximum photodegradation could be achieved in presence of H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub> in comparison to other experimental conditions Figure 1.

#### Langmuir isotherm

From Langmuir isotherm<sup>39</sup> it is concluded that there is no strong competition between the solvent and the rifabutin to occupy the TiO<sub>2</sub> surface sites.

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