Chapter 5: Photocatalytic removal of rifabutin

1.0 Introduction

Contamination of water resources due to industrial, agricultural, domestic and pharmaceuticals effluents is among the growing problems of human society. In recent years, there has been a growing interest in the presence of pharmaceutical substances in the aquatic environment [1–8]. In 2011, the World Health Organization (WHO) published a report on pharmaceuticals in drinking water which reviewed the risks to human health associated with exposure to trace concentration of pharmaceuticals in drinking water [9]. In general, wastewater from pharmaceuticals manufacturing, including hazardous pharmaceutical waste and chemicals, presents a potential hazard to the environment that must be dealt with before the wastewater can be discharged [10]. Due to the low pharmaceuticals removal efficiency of traditional wastewater treatment plants, worldwide concerns and calls are raised for efficient and eco-friendly technologies. Advanced oxidation processes attracted a growing interest over the last two decades, could achieve almost complete destruction of the pollutants studied. Photocatalytic oxidation processes have been known for its simplicity and efficiency [11, 12]. Experimental observations indicate that almost complete mineralization of organic compounds to carbon dioxide, water and inorganic anions have taken place by photocatalytic process. Semiconductors are the key materials and play a significant role in photocatalytic degradation process. Different semiconductors such as SnO₂, ZrO₂, CdS, ZnO and TiO₂ [13, 14] have been used as photocatalysts in the photocatalytic process. Among this titanium oxide (TiO₂) is a transition metal oxide photocatalyst. Using TiO₂ as the photocatalyst has been found effective for complete oxidation and mineralization of pharmaceuticals. Upon irradiation with suitable light energy the electron from the valence band of the titania catalysts promoted to its conduction band creating holes in valence
band. The electrons on the conduction band of the titania catalyst surface are scavenged by the molecular oxygen to produce reactive oxygen radicals, whereas the holes in the valence band become trapped by the surface bound hydroxyl radicals that are produced on oxidation of either the surface hydroxyl group and/or the surface bound water molecules. These hydroxyl radicals have very high oxidation potential, hence named advanced oxidation process (AOP), which results in the oxidation of the pollutants (15-18). The objective of this work is to determine the degradation route of rifabutin in the presence of TiO$_2$. Rifabutin is a bactericidal antibiotic used in treatment of tuberculosis. Rifabutin also have some serious side effects, as severe skin rash or itching, pale skin, weakness, easy bruising or bleeding, fever, chills, body aches, flu symptoms, or eye pain or redness, vision loss. In the present investigation some operational parameters such as effect of drug concentration, effect of catalyst, effect of pH and effect of hydrogen peroxide have been studied.

2.0 Experimental

2.1 Instrumentation

A cylindrical container made of quartz with a capacity of 150 mL, placed surroundings the UV lamp (6W) which works as sample holder. This setup was equipped with continues flowing oxygen system for proper mixing of the semiconductor to the drug solution. The source of irradiation is placed in the centre of the reactor to assure the maximum energy exchange between the source of irradiation and reaction mixture. For all the pH measurements the decibel DB 1011 digital pH meter was used and a spectrophotometer with a 1.0 cm light path quartz cells (systronic spectrophotometer 166
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India, over the wavelength range 325 – 900 nm) was used for all degradation analysis at λ max of 370 nm.

2.2 Reagents and solutions

The anatase form of titanium dioxide with a 325 mesh, 99+% was obtained from Sigma Aldrich and used as such without further treatment. Rifabutin (A), (4-deoxo-3, 4-[2-spiro-(N-iso-butyl - 4 - piperidyl) - 2, 5 - dihydro - 1H -imidazo] - rifamycin-S) was obtained from Lupin Pharmaceuticals Pvt Ltd. with the brand name Ributin. All laboratory chemicals used were of analytical grade, and purchased from S. D Fine Chem. Ltd, India.

![Chemical Structure of Rifabutin](A)

2.3 Photocatalytic degradation

To prepare a stock solution of rifabutin, 150 mg of drug was dissolved in 50 mL of methanol. The stock solution was used for further dilution to prepare working solution of 0.4 mg/mL concentration with distilled water. A 100 mL amount of the working solution was taken for the degradation process in a sample holder which was
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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 TiO₂ catalyst from the side of the reactor continuously. After a specific time interval a certain amount of drug is withdrawn and centrifuged so that the loss of compound due to photodegradation can be found out account spectrophotometrically at λ max 370 nm. 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 the following formula [eq. i]

\[
E (\%) = \frac{C_0 - C}{C_0} \times 100
\]

(i)

Where \(C_0\) represents the initial concentration of rifabutin and \(C\) is the concentration of rifabutin at time \(t\). \(E\) value indicates a higher efficiency of degradation of rifabutin onto the TiO₂.

3.0 Results and discussion

3.1 Preliminary Investigation

A certain concentration of drug solution (0.4 mg/mL) was kept in the photocatalytic reactor for preliminary analysis at a fix pH 10.5. Catalyst dose was fixed at 0.06 g/L. In order to define the system completely experimental conditions were fixed as photo degradation of the drug (a) In presence of all parameter viz. UV light, O₂ and TiO₂. (b) in presence of O₂ and TiO₂ but in absence of UV light. (c) in absence of TiO₂ but in presence of O₂ and UV light (d) in presence UV light and TiO₂, but in absence of O₂. Fig. 1 shows that in the absence of UV light TiO₂ 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$_2$ surface. Similarly in the absence of O$_2$, when solutions were irradiated by UV light no change in the absorbance was recorded. However, when a small amount of TiO$_2$ 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 measured in the presence of all components (UV light, O$_2$ and TiO$_2$).

![Graph](image)

**Fig.1.** Photocatalytic degradation of rifabutin (a) in presence of all parameter viz. UV light, O$_2$ and TiO$_2$, (b) in presence of O$_2$ and TiO$_2$ but in absence of UV light and (c) in absence of TiO$_2$ but in presence of O$_2$ and UV light (d) in presence UV light and TiO$_2$, but in absence of O$_2$. Photo degradation of the drug at concentration 0.4 mg/mL at pH 10.5 and 30±1°C

### 3.2 Reaction kinetics: Langmuir-Hinshelwood model

Langmuir–Hinshelwood (L-H) model represents the mechanism required for the contaminant adsorbs on the catalyst surface as a prerequisite for efficient oxidation.
The adsorption–desorption process is characterized by the transfer of the reactants in the aqueous phase to the surface; adsorption of the reactants; reaction in the adsorbed phase; desorption of the products; and removal [19-20]. L-H model equation is represented by the equation [eq. ii].

\[
dC/dt = -k_1KC/(1+KC)
\]  

(ii)

Where C is the bulk concentration of contaminant in the solution, k is the reaction rate constant and K represents the equilibrium adsorption constant for a particular contaminant to the photocatalyst [21]. At low bulk concentration values, the Langmuir–Hinshelwood equation becomes equivalent to a first order reaction equation.

3.3 Effect of catalyst concentration

Photodegradation of rifabutin takes place on active surface of the catalyst particles and in bulk solution by means of photocatalytically generated active oxidant species. Therefore the photocatalyst dosage plays an important role in photo degradation processes. The effect of the catalyst doses has been examined in the range of 0.02 to 0.08 g/L of TiO\(_2\). The initial concentration of the rifabutin solution was 0.4 mg/mL, and upon illumination, measurements of the efficiency of the catalyst were carried out in 80 min. The plots of residual concentration of rifabutin vs. various doses of catalysts have been given in Fig. 2. (a). It shows that minimum amount of catalyst also gives a noticeable removal of drug; since more catalyst lead to more effective photons, the photo degradation efficiency increases with the dosage of catalyst. It is seen by Fig.2 (b) as the amount of catalyst increased, the rate of degradation of rifabutin is gradually increased. Due to a sudden increase in the rate of degradation of rifabutin at TiO\(_2\) concentration
(0.06 g/L) the optimum amount of TiO$_2$ is taken 0.06 g/L for the degradation of rifabutin at pH 10.5.

**Fig.2. (a)** Effect of catalyst concentration on photocatalytic degradation of rifabutin at concentration 0.4 mg/mL at pH 10.5, 30±1°C.

**Fig.2. (b)** Variation of rate constant with different concentration of TiO$_2$ at concentration 0.4 mg/mL at pH 10.5 and 30±1°C.
3.4 Effect of drug concentrations

In order to study influence of the drug concentration on the degradation process, the drug concentrations for the tests were varied from 0.1 mg/mL to 0.5 mg/mL at the optimum catalyst concentration 0.06 g/L. Results obtained of degradation of rifabutin are shown in Fig.3 (a). It can be seen that the photodegradation efficiency of rifabutin is directly proportional to its concentration, which means, the higher of the drug concentration, the higher efficiency of the drug photodegradation. From Fig. 3 (b) it is seen, that on increasing the initial drug concentration from 0.10 mg/mL to 0.40 mg/mL the degradation rate of rifabutin increases (from 40 to 89 %). On the further increase in drug concentration degradation rate became constant.

**Fig. 3.** (a) Effect of substrate concentrations on photocatalytic degradation of rifabutin at pH 10.5, and 30 ± 1°C.
3.5 Effect of pH

Effect of pH on the adsorption percentage of aqueous rifabutin solution on TiO$_2$ as a photocatalyst was investigated in the pH range of 6.5 to 12.0. Controlling the pH of the solution during the operations normally affects the photocatalytic oxidation efficiency of TiO$_2$ catalyst. The pH effect found in this study proves that the rate of oxidation of rifabutin drug is faster at higher pH using TiO$_2$ catalyst [Fig. 4. (a)]. Negative charges at the photocatalyst surface cause more drug adsorption or migration of drug near to the catalyst surface due to electrostatic interaction between rifabutin (under basic medium) and catalyst surface. Therefore, the target drug is more susceptible to photodegradation [22, 23]. Fig. 4 (b) shows that the pH of drug solution directly affects the degradation rate of the drug. The degradation rate is slightly increased in pH range 6.5 to 9.7. Further increase in pH shows a sudden increment in the degradation rate upto pH 10.5 and became almost constant at pH 12.0.

Fig. 3. (b) Variation of rate constant with substrate concentrations at pH 10.5, (30 ±1°C).
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Fig. 4. (a) Influence of pH on photocatalytic degradation of rifabutin at concentration 0.4 mg/mL, and 30 ± 1°C.

Fig. 4. (b) Variation of rate constant with different pH at conc. 0.4 mg/mL, and 30 ± 1°C.
3.6 Effect of H$_2$O$_2$ concentration

In the photo assisted reaction, the molar concentration of H$_2$O$_2$ has direct influence on OH$^-$ radicals. The addition of H$_2$O$_2$ as oxidant together with the UV light was more effective for drug removal. This is attributed to the adsorption of the drug molecules on the surface of the catalyst, where water molecules adsorbed on the surface of the catalyst generate OH radicals efficiently. In the presence of H$_2$O$_2$, the UV light induces the formation of OH radicals from H$_2$O$_2$. The degradation rate of rifabutin increases as the H$_2$O$_2$ concentration increases until a critical H$_2$O$_2$ concentration is achieved. The reaction to generate the reactive species may be written as follows [24].

\[
H_2O_2 + e^- \rightarrow OH^* + OH^- \quad (iii)
\]

\[
H_2O_2 + OH^* \rightarrow H_2O + HO_2^* \quad (iv)
\]

\[
HO_2^* + OH^* \rightarrow H_2O + O_2 \quad (v)
\]

**Fig.5.** (a) Photocatalytic degradation of rifabutin with different molar concentrations of H$_2$O$_2$ in presence of TiO$_2$ at pH 10.5 and 30±1°C
Fig. 5 (b) Variation of rate constant with different concentrations of H₂O₂ at conc. 0.4 mg/mL and 30±1°C

Photocatalytic degradation of rifabutin experiments with H₂O₂ were carried out in three different conditions viz. in presence of H₂O₂ and TiO₂ but absence of O₂, in presence of H₂O₂, TiO₂, and O₂ and in presence of H₂O₂ only. Better results are obtained in presence of H₂O₂ in comparison to other experimental conditions which are shown in Fig. 6.
Fig. 6 Photocatalytic degradation of rifabutin (a) in presence of H$_2$O$_2$ only (b) in presence of H$_2$O$_2$ and TiO$_2$ and O$_2$ (c) in presence of H$_2$O$_2$ and TiO$_2$.

6.0 Conclusion

Results showed that photodegradation is an effective technique for the removal of rifabutin from wastewaters. Titanium dioxide photocatalyst is very active in rifabutin degradation. The efficiency of the process depends strongly on the experimental conditions. The amount of catalyst, effect of drug concentration, pH and hydrogen peroxide are important parameters in the degradation process. Rifabutin degradation was more effective under basic conditions than acidic because the values obtained in basic pH are higher than those calculated for acidic pH media. The rate constants for the different parameters were evaluated and the results show that rifabutin degradation in aqueous suspension of TiO$_2$ follows the first order kinetic behaviour. The photodegradation of rifabutin by TiO$_2$ photocatalyst can be used as a practical technique for the removal of environmental pollutants.
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7.0 Reference


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