



## Heterogeneous photocatalytic degradation of pharmaceutical 5-HT receptor agonist rizatriptan benzoate using nanocrystalline TiO<sub>2</sub>

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Water pollution due to pharmaceuticals and personal care products (PPCPs) has been gaining attention of researchers all over the world. The heterogeneous photocatalytic degradation in the presence of semiconductor and UV radiation has been getting much more attention because it is an efficient, inexpensive, eco-friendly method and does not leave any waste material in water/wastewater. In the present study, photocatalytic degradation of rizatriptan benzoate (RTB) has been investigated using titanium dioxide (TiO<sub>2</sub>) photocatalyst. The photocatalytic degradation activity of the nanocatalyst has been evaluated on the basis of Langmuir kinetic model. The effects of pH, concentration of H<sub>2</sub>O<sub>2</sub> added, initial drug concentration and dosage of the catalyst have also been investigated. The best possible conditions for the degradation of the drug have been evaluated and found drug concentration 0.3 mg/mL, pH 11.5, and dose of catalyst 10 mg was optimum for this experiment. The effect of hydrogen peroxide on the degradation process was also done to study the effect of the electron acceptor and it was found that in the following process generation of hydroxyl radicals and retardation of electron-hole recombination both takes place. It was found by this study that photocatalytic degradation by titanium dioxide is a proficient, cost-effective and more rapidly form of degradation rizatriptan benzoate from aqueous solution.

Keywords: Rizatriptan benzoate (RTB), photocatalytic activity, titanium dioxide, kinetics, isotherm.

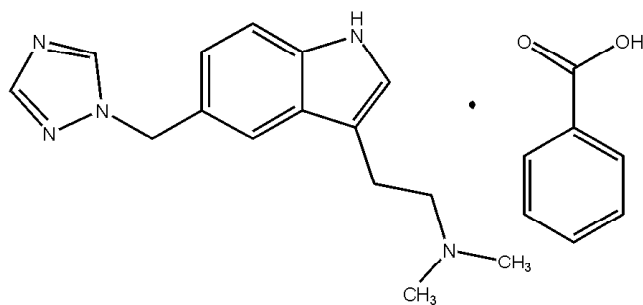
### Introduction

Pharmaceuticals get into the surroundings mostly by the different ways. Pharmaceuticals are excreted by the human beings and animals unbroken as well as metabolized via the urine passage or via sewage plants. Unused pharmaceuticals reach into the environment may be via household waste or by handling of urban solid garbage. Besides this another way is that the manufacturing plants which produce the active substances let loose the pharmaceuticals or their waste into the environment by chance. Pharmaceuticals are the most non-biodegradable chemical compounds in the environment<sup>1</sup>. Pharmaceuticals which are not able to soluble in water does not successfully washed away by rain. So, their residues stay in the environment and ultimately get collected in the bodies of terrestrial and aquatic organisms<sup>2</sup>. Several methods for the wastewater treatment and removal of these types of contaminants are at present carrying out. The predictable technologies that are at present used to de-

mean the colour of the organic impure stream containing primary method (adsorption, flocculation), secondary method which included biological methods and chemical processes like chlorination and ozonization. Still these technologies may produce some adverse effects because they shift the non biodegradable matter into sludge which requires additional treatment<sup>3-5</sup>. To solve these types of harms, another technique advanced oxidation processes (AOPs) have been well thought-out as a successful method in treating organic contaminants in water or wastewater because they do not necessitate large amount energy and chemicals unlike other treatment processes and they known for their ease use and effectiveness. This process does not leave any hazardous residues behind. AOPs are a cluster of procedures that are based on the generation of hydroxyl radicals (OH<sup>\*</sup>), which are highly reactive oxidants for the removal of wide variety of organic pollutants<sup>6</sup>. Heterogeneous catalysis is a type of advanced oxidation processes (AOP's) is a fast growing

method for treatment of water and to remove poisonous organic contaminants like pesticides, dyes and pharmaceuticals<sup>7–11</sup>. Several semiconductor materials were experimented as potential photocatalysts such as zinc oxide (ZnO)<sup>12</sup>, titanium dioxide (TiO<sub>2</sub>)<sup>13</sup>, tungsten trioxide (WO<sub>3</sub>)<sup>14</sup> etc. But the most extensively used semiconductor in photo induced procedure is titanium dioxide (TiO<sub>2</sub>). It is the most efficient and helpful photocatalyst because it have wide application in the different field like water or waste water treatment, air purification, hydrogen production through water splitting reaction, degradation of pollutants, removal of micro organisms etc.<sup>15–17</sup>. Photocatalysis using the titanium dioxide has been effectively used in the demineralization of different types of organic compounds such as pesticides, aromatics, azo dyes and herbicides<sup>18–20</sup>. Jain and Sikarwar 2006; Jain *et al.* 2007a; Jain *et al.* 2014; Mittal *et al.* 2010<sup>21–24</sup> have also used a variety of adsorbents for the elimination of pollutants from water or waste water. Our co-workers are also doing their research using adsorption, photocatalytic and electrochemical technique for the degradation of organic pollutants from aqueous solutions<sup>25–27</sup>.

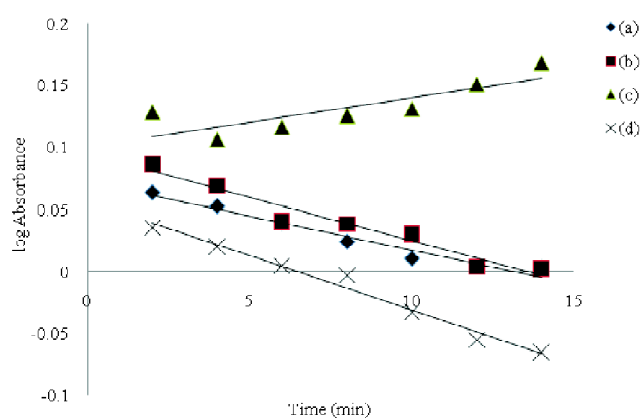
This study is intended to examine the photocatalytic activity on TiO<sub>2</sub> on the target compound. The targeted compound is rizatriptan benzoate (RTB) [A] which is a medicine of group of serotonin (or 5HT) agonists. It is an antimigraine, used to cure the migraines<sup>28</sup>. Subsequent experiments were conducted in aqueous suspensions of TiO<sub>2</sub> to investigate different parameters like the effect of dose of catalyst, concentration of the drug RTB, effect of H<sub>2</sub>O<sub>2</sub> concentration, effect of contact time, effect of irradiation time and pH. The Langmuir-Hinshelwood (L-H) kinetic model was used to study the kinetics of the photomineralization of RTB, and determination of different optimal conditions.



**Scheme [A].** Structure of rizatriptan benzoate.

## Results and discussion

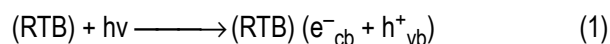
To study photodegradation of RTB the experiments were performed in the batch photoreactor using the following conditions i.e. (i) on keeping oxygen (O<sub>2</sub>) and titanium dioxide (TiO<sub>2</sub>) present but ultraviolet (UV) light absent, (ii) on keeping TiO<sub>2</sub> absent and O<sub>2</sub> and UV light present, (iii) on keeping UV light and TiO<sub>2</sub> present but O<sub>2</sub> absent and (iv) in last keeping all UV light, O<sub>2</sub> and TiO<sub>2</sub> present. The tested RTB were about totally soluble at a range of pHs. Better results were observed in the last condition keeping all UV light, O<sub>2</sub> and TiO<sub>2</sub> present (Fig. 1).



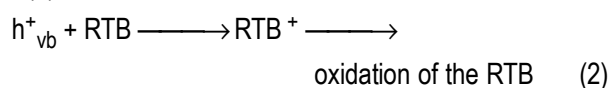
**Fig. 1.** Photocatalytic degradation of rizatriptan benzoate: (a) in presence of O<sub>2</sub> and TiO<sub>2</sub> but in absence of UV light, (b) in absence of TiO<sub>2</sub> but in presence of O<sub>2</sub> and UV light, (c) in presence UV light and TiO<sub>2</sub>, but in absence of O<sub>2</sub> and (d) in presence of UV light, O<sub>2</sub> and TiO<sub>2</sub>, at concentration 0.3 mg/mL, pH 11.5 and temperature 30±1°C.

### Degradation of RTB using photo catalyst TiO<sub>2</sub>:

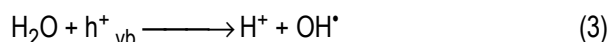
Experiments was performed using semi conductor TiO<sub>2</sub> (have valence band +3.2 and band gap 3.2 eV) as a photo catalyst. The photocatalytic detoxification of RTB in aqueous solution is irradiated by the photo excitation of the semiconductor, followed by the formation of electron-hole pair on the surface of catalyst shown in eq. (1).



The high oxidation potential of the hole (h<sup>+</sup><sub>vb</sub>) in the catalyst permit the direct oxidation of the RTB to reactive intermediates (2).



An additional hasty transitional which is accountable for the decaying is hydroxyl radical (OH<sup>•</sup>) which may be formed by the water decomposition (eq. (3)) or by the reaction with OH<sup>-</sup> (eq. (4)):



The hydroxyl radical is an very strong and non selective oxidant which can do mineralization of several organic chemicals partial or complete<sup>29</sup>.



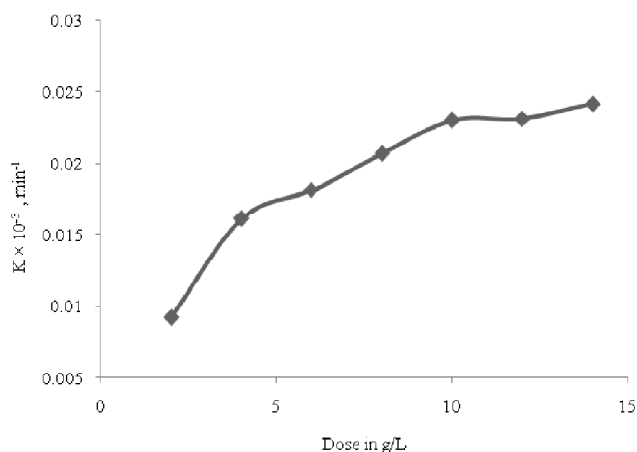
*Effect of photocatalyst dosage:*

The effect of different catalyst doses on the photomineralization of water or wastewater has been broadly explored<sup>30-32</sup>. Several authors studied this parameter in their research<sup>33,34</sup>. The effect of different amounts of TiO<sub>2</sub> on the degradation of rizatriptan benzoate has been examined in this study. Experiments were performed by varying the dose of TiO<sub>2</sub> amount from the range 0.02 g/L to 0.14 g/L at 650 nm and result has been shown in Fig. 2. It is clear from the plateau that the photocatalytic degradation rate increases along with increase in TiO<sub>2</sub> dosages but the reaction was retarded at higher dosages. The optimum TiO<sub>2</sub> concentration for degradation of RTB in aqueous solution is 0.1 g/L was find out on the basis of these experiments. It can be due to this, that when we initially increase the catalyst dose, it increases the number of active sites of TiO<sub>2</sub> that consequently increases the number of OH<sup>•</sup> and O<sub>2</sub><sup>•-</sup> radicals<sup>35</sup> and rate of degradation. After a convinced point when the saturation

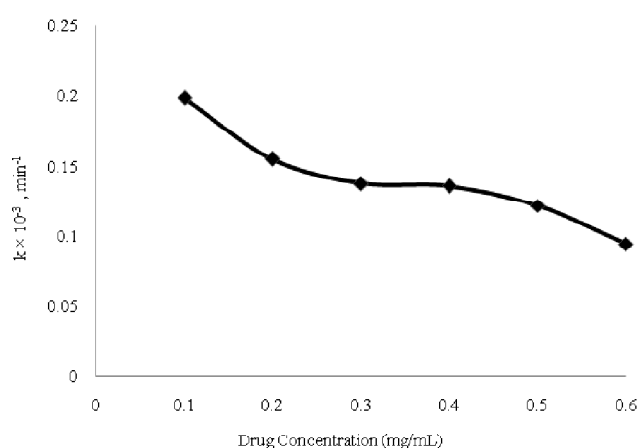
occurs, the quantity of RTB molecules is not enough to seal the active sites of TiO<sub>2</sub>. Hence it get started to turbid the solution and reduces the transmission of the light through the solution which additional does not enhance the rate of degradation and it get constant<sup>36,37</sup>. The degradation rate of RTB get a maximum removal 94.3% with catalyst dosage of 0.1 g/L, therefore it was taken as optimum dose for further degradation of RTB.

*Effect of RTB concentration:*

Concentration of the RTB is a extraordinarily significant parameter in the photocatalysis. The main reason behind this may be due to this reason that the rate of degradation reaction found in both TiO<sub>2</sub> particles and the solution. The reaction occurs between the OH radical and a RTB molecule on the photocatalyst. The OH radical generated at the active OH<sup>-</sup> sites and RTB molecule generated from the solution surface. Accordingly, when the initial RTB concentration is high, the number of these available active sites is decreased by RTB molecules due to their competitive adsorption on TiO<sub>2</sub> particles and rate of transfer of RTB from the solution does not affect the degradation rate. But transfer rate plays an important role if the initial RTB concentration is low. This parameter effect of initial RTB concentration was studied within the range of concentration 0.1 to 0.6 mg/mL and the results are exposed in Fig. 3. The results show that the rate constants of degradation of RTB obtained in this study are inversely proportional to the initial RTB concentration. It was find out that rate constant *k* of the degradation decreases rapidly by increasing the RTB concentrations, from 0.1 to



**Fig. 2.** Different concentrations of TiO<sub>2</sub> versus rate constant graph at concentration 0.3 mg/mL at pH 11.5 and temperature 30±1°C.



**Fig. 3.** Variation of rate constant with substrate concentrations at pH 11.5 and temperature 30±1°C.

0.3 mg/mL and then it becomes almost constant. After increasing the concentration degradation rate constant again began to decrease upto 0.6 mg/mL. Therefore 0.3 mg/mL is taken as optimum RTB concentration. This result confirms that the kinetics of RTB degradation is pseudo-first order not simple first order.

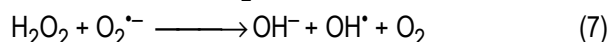
*Effect of electron acceptor:*

Hydrogen peroxide shows different effects on degradation of organic contaminants depending on its concentration and nature of reductants<sup>38,39</sup>. At most favorable concentration, H<sub>2</sub>O<sub>2</sub> increase the rate of degradation by formation rate of hydroxyl radical in following ways:

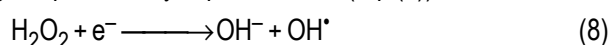
(i) By direct photolysis of H<sub>2</sub>O<sub>2</sub><sup>40</sup>



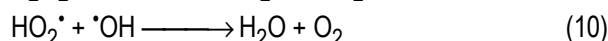
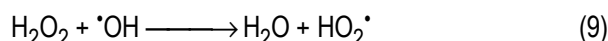
(ii) By reaction with O<sub>2</sub><sup>41</sup>



(iii) In addition this H<sub>2</sub>O<sub>2</sub> can detain a single electron from the conduction band and construct the hydroxyl radical and hinder the electron-hole recombination process by increasing the photocatalytic process rate (eq. (8))<sup>42</sup>.



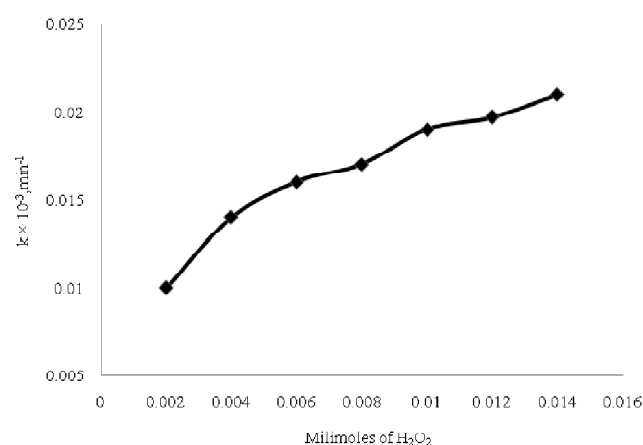
(iv) Now the H<sub>2</sub>O<sub>2</sub> and the OH<sup>•</sup> radical react with each other and form the hydroperoxyl radical (HO<sub>2</sub><sup>•</sup>). In addition to this the neutral species formed between the two radicals, HO<sub>2</sub><sup>•</sup> and OH<sup>•</sup> which form H<sub>2</sub>O and O<sub>2</sub> those will contribute in degradation rate<sup>43</sup>.



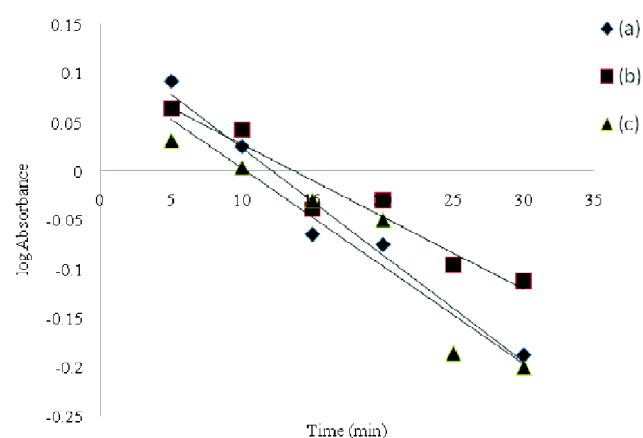
Aiming at having a deeper insight into the effective reactivity of OH<sup>•</sup> radicals and avoiding the detrimental light scattering effect due to the presence of semiconductor particles such as TiO<sub>2</sub> in this study, RTB was investigated in aqueous solution initially containing different amounts of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>/UV) ranging from 0.002 to 0.014 mM. Results are shown in Fig. 4a. When irradiation was applied only in the presence of H<sub>2</sub>O<sub>2</sub>, the RTB did not degrade satisfactorily, whereas in the presence of the semiconductor the rate increased significantly. The plot of degradation shows that the reaction rate increases along with increasing H<sub>2</sub>O<sub>2</sub> dosages. At maximum, rate increment was achieved at the optimal concentration of 0.010 mM compared to that of sole photocatalysis without H<sub>2</sub>O<sub>2</sub>. Above this optimal concentration, the

RTB photocatalytic rates get almost constant. Accordingly, 0.010 mM concentration is taken as optimal H<sub>2</sub>O<sub>2</sub> concentration. Alike behaviour was obtained for other organic molecules such as organic phosphorus pesticides and 4-chlorobenzoic acid<sup>44,45</sup>.

Photocatalytic degradation of rizatriptan benzoate experiments with H<sub>2</sub>O<sub>2</sub> were carried out in three different conditions, viz. in presence of H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub> but absence of air, in presence of H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub> and air, and in presence of H<sub>2</sub>O<sub>2</sub> only. The better results are obtained in presence of H<sub>2</sub>O<sub>2</sub> in comparison to other experimental conditions which are shown in Fig. 4b.



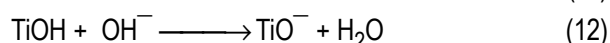
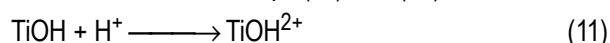
**Fig. 4a.** Different concentrations of H<sub>2</sub>O<sub>2</sub> vs rate constant at concentration 0.3 mg/mL and temperature 30 ± 0.1°C.



**Fig. 4b.** Photocatalytic degradation of rizatriptan benzoate: (a) in presence of H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub>, (b) in presence of H<sub>2</sub>O<sub>2</sub> only and (c) in presence of H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub> and O<sub>2</sub>.

*pH effect:*

pH value is one of the important factor influence the degradation rate of organic compounds in the photocatalytic processes<sup>46,47</sup>. The pH dose not affects the TiO<sub>2</sub> surface properties as well as RTB degradation rate and the hydroxyl radical's formation. According to the zero point of charge of TiO<sub>2</sub> it can be stated that its surface is most probably positively charged in acidic solution and negatively charged in basic solution<sup>48,18</sup> as shown in eqs. (11) and (12).



The pharmaceutical industries wastewater generally has a broad series of pH values. Three possible reaction mechanisms<sup>49</sup> can contribute in photodegradation of RTB viz.,

(i) Direct oxidation by the positive hole



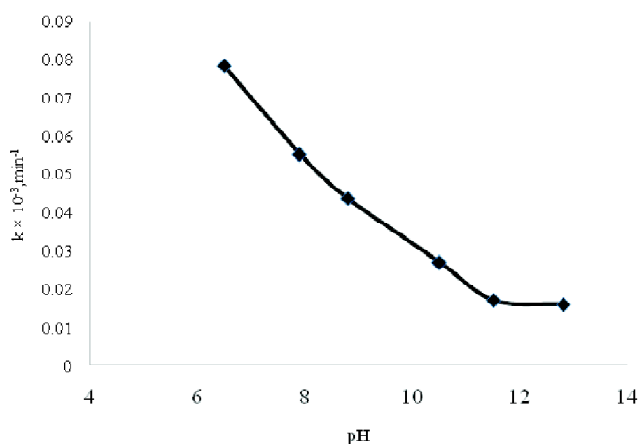
(ii) Hydroxyl radical attack and



(iii) Direct reduction by the electron in the conducting band



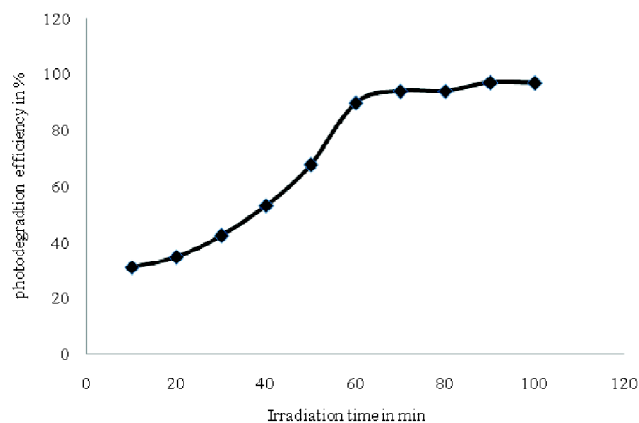
The degradation rate of RTB in aqueous suspension of TiO<sub>2</sub> has been calculated by changing the range of pH from 6.5 to 12.8 at a fixed concentration of TiO<sub>2</sub> (0.1 g/L) and RTB concentration (0.3 mg/mL). Fig. 5 demonstrates the photodegradation of RTB at different pH, which obviously exhibits that the most excellent results are found in alkaline solution (pH = 11.5, X = 94.3%).



**Fig. 5.** Variation of rate constant with different pH at concentration 0.3 mg/mL and temperature 30 ± 0.1°C.

*Irradiation time:*

It is also an important parameter for the total photocatalysis of RTB. In the present investigation the irradiation time period was varied from 10 min to 90 min under the UV light source in 100 mL of RTB solution. To understand the result a graph was plotted between photodegradation effectiveness versus irradiation time which is presented in Fig. 6 which clearly shows that on increasing the irradiation time, the rate of degradation increases. The degradation procedure proceeds after 20 min irradiation time with a slow kinetics. This show that intermediates and its competitiveness are formed in the following process. The slow kinetics of degradation after certain time limit is due to the difficulty in converting of present atom ions or slow reaction of OH\* radicals. Similar results have been reported by this study<sup>49</sup>. After increasing the time photodegradation efficiency of RTB also increases. Highest degradation efficiency occurred when the irradiation of photocatalyst was continued till 90 min under UV light source and the removal efficiency of RTB reached upto 94.3% for 100 min irradiation time. This occurred due to the formation of hydroxyl radicals. The OH\* radicals are strong enough to break the different bonds in the RTB molecules adsorbed on the surface of the catalyst which lead to the formation of CO<sub>2</sub> and inorganic ions.

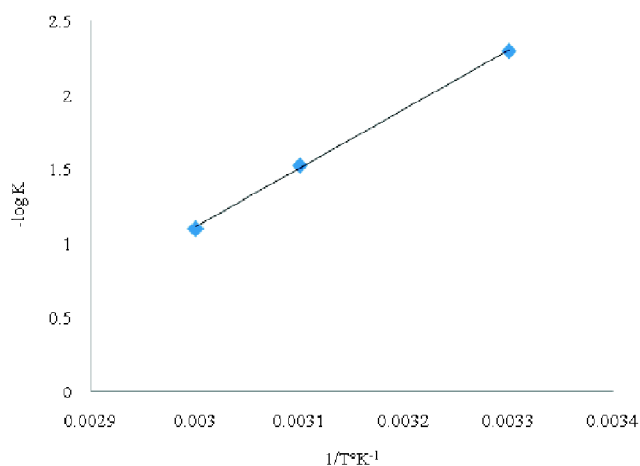


**Fig. 6.** Effect of irradiation time on the photocatalytic degradation efficiency of rizatriptan benzoate at concentration 0.3 mg/mL.

*Effect of temperature :*

The temperature always plays an important role in a chemical reaction. The dependency of the RTB degradation rate constants on temperature was experimented by varying

the range of temperature from 293–323 K and the results are confirmed in Fig. 7. The results show that an increment of reaction rate constant  $k$  is achieved for photocatalytic degradation until 45°C as we increase the temperature. Abass and Hussen 2010, Saïen and Nejati 2007<sup>50,51</sup> also studied that degradation of real textile industrial wastewater with same effect as shown for RTB. Their results prove that higher temperature is considerably helpful to putrefy the organic contaminants in water or wastewater. Higher TiO<sub>2</sub> electron transfers takes in valance bond to higher energy levels in the presence of higher temperature which facilitating the electron-hole production that could be utilized in initiating oxidation and reduction reactions, respectively<sup>51</sup>. The species photon-generated holes ( $h^+_{vb}$ ), and electrons ( $e^-_{cb}$ ), and hydroxyl radicals (OH<sup>\*</sup>) can therefore disgrace organic pollutant to intermediates, and after that the intermediates are further degraded to CO<sub>2</sub> and H<sub>2</sub>O. The activated energy of photocatalytic reaction is somewhat affected by the temperature, but successive redox response may be mostly affected by temperature which affects collision frequency of molecules as well as adsorption equilibria<sup>52</sup>. Therefore the overall effect on the photocatalytic performance will depend on the relative importance of these phenomena.



**Fig. 7.** Effect of temperature on the photocatalytic degradation of rizatriptan benzoate at concentration 0.3 mg/ml, dosage 0.10 g/L and pH 11.5.

The activation energy ( $E_a$ ) determined according to Arrhenius equation:

$$\ln K = \ln A - E_a/RT \quad (16)$$

Here  $k$  represents the rate constant,  $T$  is temperature (K),  $A$

is a constant,  $E_a$  is the activation energy and  $R$  is the universal gas constant. The activation energy ( $E_a$ ) was find out from the plot of  $\ln k$  versus  $1/T$ , gives a straight line whose slope is equal to  $-E_a/R$ . From the data obtained, the apparent activation energy is 23.19 kJ mol<sup>-1</sup>.

## Experimental

### Materials and reagents/chemicals:

Pharmaceutical grade rizatriptan benzoate (RTB) (*N,N*-dimethyl-5-(1*H*-1,2,4-triazol-1-ylmethyl)-1*H*-indole-3-ethanamine monobenzoate) was obtained as a gift from Alkem laboratories (Mumbai, India) which is reported to be 99.65% pure. Commercial tablet dosage forms of rizatriptan benzoate (Table 1), Rizact (Cipla Pharmaceuticals Limited, Hyderabad, India), were purchased from a local pharmacy store. Titanium oxide (Anatase) was procured from Sigma-Aldrich and used as such without any further treatment (Table 2). All the reagents used in the experiment were of analytical grade. Double distilled water was used during the experiment.

**Table 1.** Physical and chemical properties of the rizatriptan benzoate

Main properties of the pharmaceutical used	
Property	Rizatriptan benzoate
Therapeutic group	Antimigraine
Molecular formula	C <sub>15</sub> H <sub>19</sub> N <sub>5</sub>
Molecular weight (g)	269.345
Solubility in water (mg mL <sup>-1</sup> )	42
Bioavailability	45%
Melting point	178–180°C

**Table 2.** Physical and chemical properties of the titanium dioxide TiO<sub>2</sub> (manufacturer data)

Main properties of the applied catalyst (manufacturer data)	
Property	TiO <sub>2</sub>
Chemical formula	TiO <sub>2</sub>
Mesh size	325
Molar mass (g/mol)	79.866
Bulk density (g/cm <sup>3</sup> )	3.78
Crystalline phase	Tetragonal

### Apparatus:

All experiments were done in a photocatalytic reactor of 150 mL capacity having 6W UV lamp for irradiation. The reactor set up was covered with wooden box of black colour so

that UV radiation leakage can be prevented. The UV lamp emits mostly UV radiation of 10 mW/cm<sup>2</sup> at wavelength of 254 nm. The kinetics of reaction was calculated by systronics spectrophotometer (166) over the wavelength range of 340 to 990 nm with matched 1-cm quartz cells. A Decibel DB 1011 digital pH meter having a glass electrode was used for pH metric measurements.

*Experiment design:*

On the basis of literature, process factors namely, pH, concentration of catalyst, RTB concentration, H<sub>2</sub>O<sub>2</sub> concentration, temperature, and reaction time were studied to study the photocatalytic degradation of RTB using TiO<sub>2</sub> nanoparticles and RTB removal efficiency was calculated as the process response<sup>52</sup>. It was observed that four factors viz. concentration of RTB, pH, temperature and time have the most significant effect on RTB photocatalysis rate.

*Preparation of analytical solutions:*

Standard stock solution of RTB (1 mg/mL) was prepared in double distilled water. Working solution of RTB was prepared with sodium hydroxide and FC reagent. Aliquot (3 ml) was mixed with 2.5 mL of NaOH and 1.5 mL of F-C reagent in a 10 mL volumetric flask. After that the solution was kept for 10 min at room temperature and after that make up the volume with water. Britton-Robinson buffers were prepared by reported method<sup>53</sup> in the pH range 6.5 to 12.8.

*Simple colorimetric method for RTB :*

This method is based on the development of colour. Working solution of RTB is prepared with the sodium hydroxide (NaOH) and F-C reagent. A chromogen of blue black coloured was formed. A blank solution was also prepared in the similar method except the addition of RTB and was measured against water. Maximum absorbance of coloured chromogen was observed at 650 nm and fixed as analytical wavelength.

*Photocatalytic activity evaluations:*

All adsorption activities were carried out at 11.5 pH and the reaction temperature 30±0.1°C by batch adsorption technique. In each experiment, 100 mL of the operational solution of RTB of preferred concentration was taken into the photoreactor and necessary quantity of photocatalyst was mixed. After that solution was irradiated and oxygen is bubbled, to make certain mixing of the TiO<sub>2</sub> catalyst, from

the wall of the reactor continuously throughout the reaction. An appropriate aliquot of the RTB was taken out after a specific time interval and the absorbance was recorded spectrophotometrically at λ<sub>max</sub> 650 nm after centrifugation.

The amount of RTB adsorbed, q<sub>e</sub> (mg/g), was calculated by a mass balance relationship eq. (17).

$$q_e = \frac{(C_o - C) \times W}{V} \quad (17)$$

where C<sub>o</sub> is the initial concentrations of RTB whereas C is the equilibrium liquid-phase concentrations of RTB in (mg/L), V and W are the volume of the solution (L) and the weight of TiO<sub>2</sub> used (g) respectively.

The photodegradation efficiency (P.D.E.) (X) of RTB was calculated from the expression which is used before<sup>54,55</sup>:

$$X (\%) = C_o - C / C_o \times 100 \quad (18)$$

The comparative study of optimum dosage of TiO<sub>2</sub> and degradation efficiency on other organic and inorganic compounds has been done and the results are given in Table 3 which shows that highest photodegradation efficiency is occurred onto minimum dose of TiO<sub>2</sub> in the present study<sup>56-63</sup>.

*Quality assurance/quality control:*

All batch tests were repeated thrice, and experimental blanks were run in parallel to set up the accurateness, consistency, and reproducibility of the collected data. All glasswares used in the study were kept in 5% HNO<sub>3</sub> for a period of 3 days then triply rinsed with distilled deionized water and dried in an oven. The accuracy of the procedures expressed as the relative standard deviation (RSD) was found to be ±1.87%. All observations were recorded in triplicate, and average values of the three measurements are reported.

*Heterogeneous mechanism:*

Two major challenges are involve in this process one is to select the most capable types of semiconductor which have higher efficiency and another is clearly identification of a photocatalytic mechanism(s), in particular the interactions occurring at the semiconductor interface. The nature of the reaction depends upon several parameters related to the semiconductor, to the solution pH and the chemistry of the targeted compound. Heterogeneous photocatalysis is a multifaceted series of the reactions. It's mechanism involves five steps<sup>64, 65</sup>, which are as following:

**Table 3.** Comparison of optimum dosage and photodegradation efficiency of various photocatalyst for the degradation of organic compounds

Sr. No.	Target compound	Photocatalyst	Concentration (g/L)	Photodegradation efficiency (%)	References
1.	Trichlorofon	TiO <sub>2</sub>	8	83	56
2.	Floumeturon	TiO <sub>2</sub>	3	90	57
3.	Glyphosate	TiO <sub>2</sub>	3	92	58
4.	Triclopyr	TiO <sub>2</sub>	2	95	59
5.	Picloram	TiO <sub>2</sub>	2	73	57
6.	Phorate	TiO <sub>2</sub>	0.5	99	60
7.	Turbophos	TiO <sub>2</sub>	0.5	69.2	61
8.	Carbendazim	TiO <sub>2</sub>	0.5	90	62
9.	Erioglucine	TiO <sub>2</sub>	0.3	82	63
10.	Rizatriptan benzoate	TiO <sub>2</sub>	0.1	95	Present study

Comparison of optimum dosage and photodegradation efficiency of various compounds on TiO<sub>2</sub> for the degradation of organic compounds.

(i) First of all in the liquid phase to the catalyst surface mass transfer of the organic contaminant take place.

(ii) Then adsorption of the organic contaminant occurs on the surface of photon activated catalyst.

(iii) After that photocatalysis reaction take place on the catalyst surface.

(iv) Now desorption occurs of the intermediate from the catalyst surface.

(v) Finally mass transfer of the intermediate was found from the interface region to the bulk fluid.

**Kinetic analysis:**

Pseudo-first order kinetics describe the degradation rate of rizatriptan benzoate so the rate of photocatalysis of drug could be expressed by the following equation:

$$C = C_0 e^{-kt} \tag{19}$$

where  $C$  is the concentration of RTB at irradiation time  $t$ ,  $C_0$  is the initial concentration,  $t$  irradiation exposure time and  $k$  is the evident reaction rate constant of the pseudo-first order kinetics.

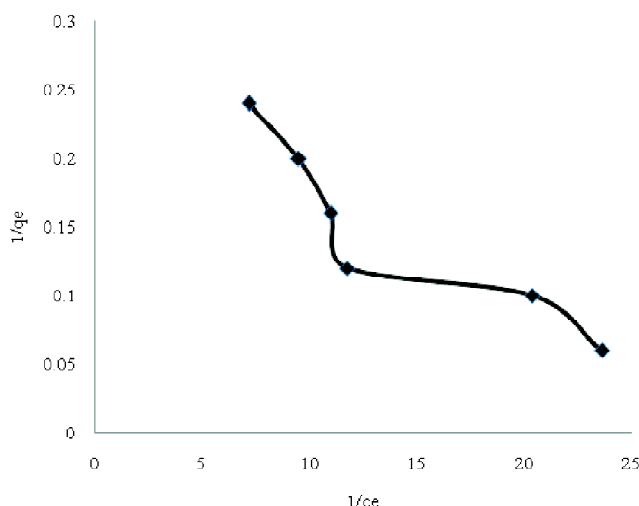
$$C/C_0 = e^{-kt} \tag{20}$$

$$\ln C/C_0 = -kt \tag{21}$$

or

$$\ln C/C_t = kt \tag{22}$$

The optimum conditions for the exclusion of the RTB are conc. 0.3 mg/mL, pH 11.5 and temp. 30±0.1°C. Following expression was used to determine the rate of reaction ( $k$ ):



**Fig. 8.** Langmuir isotherm at concentration 0.3 mg/mL and temperature 30±0.1°C.

$$\text{Rate } (k) = 2.303 \times \text{slope} \tag{23}$$

**Langmuir Isotherm:**

The experimental data for degradation of RTB degradation were processed using the Langmuir adsorption isotherm model and graph is plotted between the  $1/C_e$  and  $1/q_e$  (Fig. 8). The Langmuir sorption isotherm is one of the initial theoretical treatments of sorption of contaminants from a liquid solution and suggests that the sorption takes place on a homogenous surface inside the adsorbent by monolayer sorption. This sorption isotherm, which is based on three assumptions:



(i) adsorption cannot progress beyond the monolayer coverage means once an adsorbate molecule occupies a particular site, saturation value is reached beyond and no additional adsorption can take place at that site;

(ii) there is no change occurs in surface coverage at equilibrium condition;

(iii) and the capacity of a molecule to adsorb at a specified site is independent. The molecule can occupy the nearby sites.

The linear form of isotherm equation can be represented as<sup>66</sup>:

$$1/q_e = 1/Q^0 + 1/bQ^0 C_e \quad (24)$$

where  $q_e$  is the amount adsorbed ( $\text{mol g}^{-1}$ ), and  $C_e$  is the equilibrium concentration of the adsorbate ( $\text{mol L}^{-1}$ ),  $Q^0$  is langmuir constants related to maximum adsorption capacity and  $b$  is energy of adsorption relatively.

## Conclusion

In the present investigation a detailed feasibility study has been carried out on photocatalytic degradation of rizatriptan benzoate in aqueous suspension using  $\text{TiO}_2$  powder as a photocatalyst under UV radiation at  $30^\circ\text{C}$ . This procedure proved to be a very proficient system for the removal of rizatriptan benzoate. A number of experimental parameters those were studied appear that the dose of catalyst, pH of solution, concentration of hydrogen peroxide and concentration of drug mainly controls the rate of degradation. At the most favorable conditions, approximately 95% of RTB was degraded in almost 1 h. Mainly under basic conditions the total removal of the substrate is affected by the catalyst dose. The maximum degradation efficiency of drug was achieved with the combination of UV +  $\text{H}_2\text{O}_2$  +  $\text{TiO}_2$ . The kinetics of photocatalysis of RTB followed Langmuir model along with first-order kinetics. This confirms that degradation of rizatriptan benzoate is a promising technology.

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