Semiconductor Sensitized Photodegradation of Antibiotic Tetracycline in Water using Heterogeneous Nanoparticles

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Antibiotics have been considered emerging pollutants due to their continuous input and persistence in the aquatic ecosystem. The present paper addresses the degradation and removal processes applied to a specific class of micropollutants, the antibiotic tetracycline (TETRA). Photocatalytic degradation of tetracycline in aqueous suspensions of titanium dioxide in the presence of titanium dioxide (TiO$_2$) and ultraviolet (UV) illumination was performed in a vertical circulating photocatalytic reactor. The optimum catalyst concentration was about 0.1g/L. The disappearance of tetracycline follows a pseudo-first-order kinetics according to the Langmuir–Hinshelwood (L–H) model. The activated energy for the photocatalytic degradation of tetracycline is 24.17 kJ/mol.

Keywords: Photocatalytic degradation, titanium dioxide, tetracycline, and kinetic study.

Introduction

Pharmaceuticals, specifically antibiotics have been known for almost 40 years in the environment. In 1990, new analytical technologies were developed for determination of pharmaceuticals and became an interesting area of research. Pharmaceutical industry, intensive farming and human excretion residues are the principal sources of antibiotics and other drugs in the environment. Antibiotics may cause resistance in bacterial populations by making them ineffective in the treatment of several diseases. Antibiotics can directly influence the environment by disturbing ecosystem equilibrium. So there is need of a technique which could be successful for the removal of this type of contaminants. Several solutions are proposed in this regard, including adsorption, chemical oxidation, biological, and catalytic wet air oxidation (CWAO). Unfortunately, these techniques have some drawbacks such as, disposal of the spent contaminated activated sludges, the control of the appropriate reaction conditions, low efficiencies and reaction rates, and operation only within a narrow pH range. Advanced oxidation processes (AOPs) have been developed for rapid degradation of recalcitrant and non-biodegradable compounds in water. Fujishima and Honda first of all reported the photochemical splitting of the water using TiO$_2$ into hydrogen and oxygen. In this present investigation, TiO$_2$ photocatalysis has been used to degrade tetracycline [A] which has been chosen as a model compound for the investigation of the photocatalytic mineralization of low concentration of pollutants.

Principle of Photocatalytic Oxidation Process

In the mechanism of photocatalysis an electron from the valence band (VB) gets excited to the conduction band (CB) of the TiO$_2$ semi-conductor by creating an h$^+$ hole in the valence band. It is occurring due to UV irradiation of TiO$_2$ with energy equal or higher to the band gap (>3.2 eV):

\[
\text{TiO}_2 + h\nu \rightarrow e^- (\text{CB}) + h^+ (\text{VB}) \quad \ldots \ (1)
\]

Experimental

Chemical and Reagents

All reagents used in the present work were of analytical grade. Pharmaceutical grade Tetracycline hydrochloride purchased from Merck used as received (Table 1). The catalysts, Anatase titanium oxide, was obtained from Sigma Aldrich and used as such without further treatment (Table 2). Sodium carbonate was supplied by E. Merck, Darmstadt, Germany and chloramine-T trihydrate was obtained by J.T.Baker. Experiments were carried out at the basic pH corresponding to aqueous solutions of Tetracycline.

Instrumentation

All experiments of photocatalytic degradation were carried out in a photocatalytic reactor of 150 mL
capacity. Irradiation was carried out using a UV lamp of 6W which is placed inside the photo reactor. A Systronics model 166 digital spectrophotometer (India) in the wavelength range 325 to 990 nm was used to measure absorbance of solutions. Measurements of pH of the solutions were carried out on a digital pH meter (DB 1011 India).

**Preparation of Analytical Solution**

Stock solution of tetracycline (1mg/mL), standard solutions of sodium carbonate (1.4 M) and 2% chloramine-T trihydrate (w/v) were prepared in double distilled water. Working solution of tetracycline (0.6 mg ml⁻¹) was prepared with Na₂CO₃ (1.4 ml) and chloramine-T (5 ml) in a 100 mL volumetric flask. Solution was kept for 30 minutes at room temperature. Britton-Robinson Buffers in the pH range 6.5 to 12.0 were prepared by reported method¹². Double distilled water was used throughout the experiment.

**Photoreaction Operation and Analysis**

To run the experiment, 100 ml solution of the drug of desired concentration and with the appropriate amount of added catalyst, was transferred to the reactor. After adjustment of temperature and pH, the UV irradiation was begun. Then the solution was irradiated and oxygen is bubbled to ensure mixing of the TiO₂ catalyst from the side of the reactor continuously throughout the reaction. An appropriate aliquot of the drug was withdrawn after a precise time interval and after centrifugation the loss of compound due to adsorption was evaluated at λₘₐₓ 535 nm 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 degradation efficiency of tetracycline can be calculated by using the following expression³:

\[
E(\%) = \frac{C_0 - C}{C_0} \times 100 \quad \ldots (2)
\]

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

**Results and Discussion**

**Optimization of Catalyst Dosage on Photocatalytic Process**

In order to examine the effect of photocatalyst dose on the efficiency of tetracycline degradation, experiments were set up with varying the dose (0.02g/l to 0.14 g/l) of TiO₂ by keeping constant initial drug conc. and pH of the solution. Photodegradation of tetracycline increases rapidly with increasing the amount of TiO₂. The increase in the amount of catalyst increases the number of active sites on the TiO₂ surface which in turn increases the number of OH⁻ and O₂. It was observed that 0.1 g/l of TiO₂ is the optimum dose for efficient degradation of tetracycline. The comparative study of optimum dosage of TiO₂ used by various authors either alone or in combination with other catalysts is given in Table 3 which shows that minimum dose of TiO₂ is required in the present study¹⁴–²².

**Effect of Initial Tetracycline Concentration**

The dependence of the degradation rate constants on the initial concentrations of the tetracycline was also investigated over the range of 0.02mg/ml to
0.14mg/ml. It was observed that the rate of photodegradation decreases from 0.02mg/ml to 0.08mg/ml and then it becomes almost constant up to 0.14mg/ml. Due to this, 0.08mg/mL has been taken as optimum drug concentration.

Effect of pH
The influence of pH on catalytic efficiency of TiO₂ nanoparticles was examined by adjusting the pH of the reaction mixture at values from 6.5 to 12. The results show that the maximum degradation was obtained at pH 10.5 under UV light, where the available hydroxyl ions can react with holes (h⁺) to form hydroxyl radicals (OH•), which have high oxidation capability, subsequently enhancing the photodegradation rate of tetracycline. At low pH values (pH=6.5) the photodegradation of tetracycline was retarded under UV light by the high concentration of protons, which hold high affinity for the hydroxyl anion, preventing the formation of hydroxyl radicals.

Effect of Electron Acceptor
To investigate the effect of catalysis on the photocatalysis of drug, the experiment was carried out in the range of H₂O₂ from 0.002mM to 0.012mM as shown in Fig. 1. It was observed that the percent degradation was very high in the presence of hydrogen peroxide in comparison to in the absence of H₂O₂. The degradation of the drug increased rapidly up to H₂O₂ concentration 0.008 mM. Further increase of H₂O₂ concentration from 0.008mM to 0.012mM does not affect the degradation of drug due to quenching of OH• by H₂O₂. 0.008mM concentration of H₂O₂ was selected as optimum concentration. Photocatalytic degradation studies of tetracycline with H₂O₂ were carried out in three different conditions, viz. in presence of H₂O₂ and TiO₂ but absence of air, in presence of H₂O₂, TiO₂ and air, and in presence of H₂O₂ only. The better results are obtained in presence of all parameters in comparison to other experimental conditions.

Effect of Temperature
The results concerning the dependence of the rate constant k of the photocatalytic degradation of tetracycline from the reaction temperature was investigated in the range of in the range 303–323 K. By increasing the temperature, an increase of the apparent reaction rate constant k is achieved for photocatalytic systems until 45°C. The activation energy (Ea) was obtained from a plot of ln k versus 1/T, gives a straight line whose slope is equal to –Ea/R. From the data obtained, the apparent activation energy is 24.17 kJ mol⁻¹.

Langmuir Isotherm
An adsorption isotherm describes the fraction of sorbate molecules that are divided between liquid and solid phases at equilibrium. This model assumes that there is no interaction between molecules adsorbed on neighbouring sites. Based upon these assumptions, Langmuir represented the following equation:

\[
\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0C_e} \quad \ldots (3)
\]

Where Cₑ is the equilibrium concentration of the adsorbate (mol/L), qₑ is the amount adsorbed (mol/g), and Q₀ and b is Langmuir constants related to maximum adsorption capacity and energy of adsorption relatively. When 1/qₑ is plotted a gainst 1/Cₑ, L shape graph is obtained (Fig. 2) which shows that there is no strong competition between the solvent and the drug to occupy the TiO₂ surface sites.

![Structure of Tetracycline](image_url)
Conclusions

The result of this study clearly indicates that TiO$_2$ can efficiently catalyses the photodegradation and photomineralization of the Tetracycline in the presence of UV light and oxygen. Tetracycline degraded in an aqueous TiO$_2$ suspension by following a pseudo-first-order kinetic behaviour. The maximum degradation efficiency 94.56% of drug was achieved with the combination of UV + H$_2$O$_2$ + TiO$_2$. Photocatalytic decomposition of organics assisted by heterogeneous catalysts based on titania minimizes the use of high cost hazardous chemicals and promotes the green chemistry concept.

References