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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[1]. Pharmaceutical industry, intensive farming and human excretion residues[2] 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[3]. Antibiotics can directly influence the environment by disturbing ecosystem equilibrium[4]. 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[5], chemical oxidation[6], biological[7], and catalytic wet air oxidation (CWAO)[8]. 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[9]. Advanced oxidation processes (AOPs) have been developed for rapid degradation of recalcitrant and non-biodegradable compounds in water[10]. Fujishima and Honda first of all reported the photochemical splitting of the water using TiO_2 into hydrogen and oxygen[11]. 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) get excited to the conduction band (CB) of the TiO_2 semi-conductor by creating an h^+ hole in the valence band[11]. It is occurring due to UV irradiation of TiO_2 with energy equal or higher to the band gap (>3.2 eV):

$$TiO_2 + h\nu \rightarrow e^- (CB) + h^+ (VB) \quad \ldots (1)$$

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

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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 Na_2CO_3 (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 method[12]. 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 TiO_2 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 λ_{max} 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 expression[13]:

$$E\ (\%) = C_0 - C / C_0 \times 100 \quad \ldots (2)$$

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 TiO_2.

Table 1—Main properties of the pharmaceutical used

Property	Tetracycline
Therapeutic group	Antibiotic
Molecular formula	$C_{16}H_{18}N_3SC$
Molecular weight (g)	319.85
Solubility in water (g L^{-1})	50 (20°C)
Bioavailability	75%
Melting Point	170-173°C (with decomposition)

Table 2—Main properties of the applied catalyst (manufacturer data)

Chemical formula	TiO_2
Mesh size	325
Molar mass (g/ mol)	79.866
Bulk density (g/cm^3)	3.78
Crystalline phase	Tetragonal

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 TiO_2 by keeping constant initial drug conc. and pH of the solution. Photodegradation of tetracycline increases rapidly with increasing the amount of TiO_2. The increase in the amount of catalyst increases the number of active sites on the TiO_2 surface which in turn increases the number of $OH^{\bullet}$ and O_2. It was observed that 0.1 g/l of TiO_2 is the optimum dose for efficient degradation of tetracycline. The comparative study of optimum dosage of TiO_2 used by various authors either alone or in combination with other catalysts is given in Table 3 which shows that minimum dose of TiO_2 is required in the present study[14-22].

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

Table 3—Comparison of optimum dosage of various photocatalyst for the degradation of organic compounds

S. No.	Photocatalyst	Substrate Compound	Catalyst Concentration (g/L)	References
1	TiO_2	Trichlorfon	8	[14]
2	Ag- TiO_2	Direct red 23	3	[15]
3	TiO_2	Imazapyr	2.5	[16]
4	Pt-TiO_2	Aniline	2.5	[17]
5	TiO_2	Triclopyr	2	[18]
55125				
6	Pr- TiO_2	Phenol	1	[19]
7	Re- TiO_2	Methaodiphos	1	[20]
8	TiO_2	Phorate	0.5	[21]
9	TiO_2	Turbophos	0.5	[22]
10	TiO_2	Tetracycline	0.1	Present study

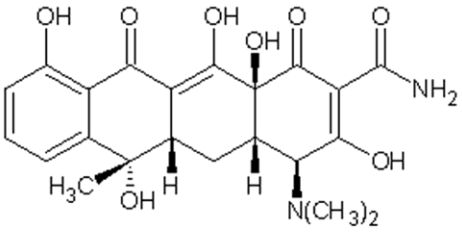
0.14mg/ml. It was observed that the rate of photodegradation decreases from 0.02mg/ml to 0.08mg/ml and then it becomes almost constant up to 0.14mg/ml. Due to this 0.08mg/mL has been taken as optimum drug concentration.

Effect of pH

The influence of pH on catalytic efficiency of TiO_2 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 H_2O_2 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 H_2O_2. The degradation of the drug increased rapidly up to H_2O_2 concentration 0.008 mM. Further increase of H_2O_2 concentration from 0.008mM to 0.012mM does not affect the degradation of drug due to quenching of $OH^•$ by H_2O_2. 0.008mM concentration of H_2O_2 was selected as optimum concentration. Photocatalytic degradation studies of tetracycline with H_2O_2 were carried out in three different conditions, viz. in presence of H_2O_2 and TiO_2 but absence of air, in presence of H_2O_2, TiO_2 and air, and in presence of H_2O_2 only. The better results are obtained in presence of all parameters in comparison to other experimental conditions.



[A] Structure of Tetracycline

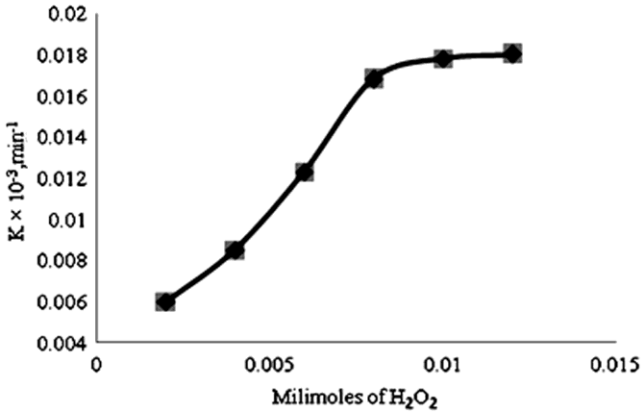


Fig. 1—Different concentrations of H_2O_2 versus Rate Constant graph at conc. 0.08mg/ml and temperature 30 ± 0.1°C.

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 45^0C. 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[23]. Based upon these assumptions, Langmuir represented the following equation:

$$1/qe = 1/Q^0 + 1/bQ^0 C_e \quad \ldots (3)$$

Where C_e is the equilibrium concentration of the adsorbate (mol/L), q_e is the amount adsorbed (mol/g), and Q^o and b is Langmuir constants related to maximum adsorption capacity and energy of adsorption relatively. When 1/qe is plotted a gainst $1/C_e$, L shape graph is obtained (Fig. 2) which shows that there is no strong competition between the solvent and the drug to occupy the TiO_2 surface sites.

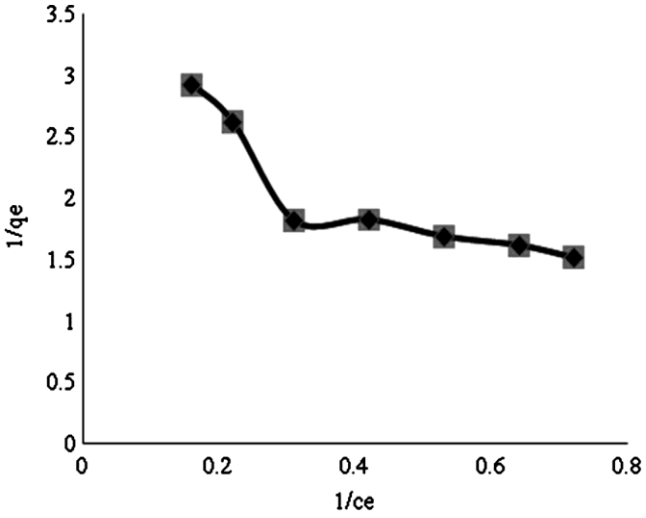


Fig. 2—Teracycline isotherm on TiO_2 at conc. 0.08mg/ml and temperature 30 ± 0.1°C.

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_2O_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.

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