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Synthesis, characterization and performance of visible light active C-TiO_2 for pharmaceutical photodegradation

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ABSTRACT

The present paper deals with photocatalytic degradation of carbamazepine and diclofenac by using a modified catalyst with band gap excitations in visible light. The C-doped TiO_2 was synthesized using a microwave digestion method from titanium oxyacetylacetate with glucose as the carbon source. The synthesized catalyst was then characterized using Scanning Electron microscopy (SEM), X-ray Diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and UV-VIS-NIR spectrophotometer. The TiO_2 present was in anatase phase and showed significant absorption in visible region. The catalyst was tested for the degradation of carbamazepine and diclofenac under visible light, where complete removal was achieved and the reaction followed first order kinetics. System parameters like catalyst and pollutant concentration, light intensity and time of reaction, were optimized using response surface methodology. In optimum conditions (catalyst concentration of 244 mg/L and light intensity of 7715 lx) 99% removal was achieved.

1. Introduction

Occurrence of pharmaceutically active compounds (PhACs) in aquatic systems and drinking water has emerged as one of the major issues of water and wastewater treatment plants [1]. The main factors contributing to this problem are the substantial increase in the consumption of drugs over the past years and prevalence of improper disposal procedures [2]. The present water and wastewater treatment plants are not equipped with proper facilities to handle PhACs [3]. Two main reasons are attributed to this reduced removal efficiency. Firstly, as the PhACs are present in enzyme sub-saturating concentrations, they require oligotrophic microbes which cannot grow at the high carbon fluxes present in the wastewater treatment plants [4]. Secondly, PhACs tend to remain in the aqueous phase than in the biological sludge due to the acidity and a very low solid liquid partition coefficient, K_d (less than 2.7) limiting their availability to the microorganisms [5]. The exposure to these PhACs has caused a serious problem for aquatic life in streams around the world [3]. This study focuses on the removal of carbamazepine (CBZ), which is an anti-epileptic drug and diclofenac (DCF) a non-steroidal anti-inflammatory drug, both are known to have acute and chronic toxicity in aquatic organisms. Carbamazepine has an extremely low removal rate in sewage treatment plants (STPs) (7%) and it has been detected in aquatic systems around the world at concentrations up to 595 ng/L [5]. Among the nonsteroidal anti-inflammatory drugs (NSAIDs), diclofenac showed the most acute toxic nature with effects being observed at concentrations below 100 mg/L [6].

To tackle this problem, several research efforts have been made in the past decade to study the removal of PhACs using various conventional and advanced treatment technologies [7]. As most PhACs are resistant to biological degradation, conventional treatment processes have failed to achieve complete removal [8]. Advanced oxidation processes (AOPs) including fenton, photo-fenton, UV-H_2O_2, ozonation, photocatalysis and sonication have shown promising results [9]. Of all the AOPs, semiconductor photocatalysis has been reported to yield better results because of the key advantages arising from its operation at ambient conditions and the fact that the catalyst itself is inexpensive, commercially available in various crystalline forms and with different particle characteristics, non-toxic and photochemically stable [10].

The catalyst mainly used in most of the studies is TiO_2, which has some disadvantages including poor absorbance in the visible

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region that constitutes more than 90% of the solar radiation and fast electron-hole pair recombination [11]. Since the band gap of the material falls in the ultraviolet region, it makes it unsuitable for visible light applications. Hence, various mechanisms have been reported to improve the efficiency of TiO_2 in the visible region by doping with metals and non-metals and photosensitization [12]. The process of doping with non-metals such as carbon and nitrogen in TiO_2 has attracted significant attention of many researchers due to the reduced number of possible traps compared to metal doping [13,14]. Carbon can greatly shift the band gap of TiO_2 into the visible region, thereby making it a key material for photocatalytic applications [15]. The process of band gap tuning is mainly dependent on synthesis routes. Studies have been carried out to explore the enhancement of photocatalytic activity of carbon-doped TiO_2 (C-TiO_2) and they have reported three to ten times increase in degradation rate of the pollutant [16,17]. In one of the latest studies N-doped TiO_2 was used to study the removal CBZ and reported a complete removal with major influence of system parameters like pollutant concentration, light intensity etc. [18].

There have been no studies which have explored the key parameters that affect the photocatalytic removal efficiency of C-TiO_2 such as morphology, band gap, light intensity, pollutant concentration and catalyst concentration. Also these studies did not concentrate on optimizing the efficiency in the visible region for removal of CBZ and DCF. The main objectives of this study are i) the synthesis of C-TiO_2 that has photocatalytic activity in the visible region, and ii) to optimize the key parameters affecting photocatalytic removal of CBZ and DCF.

2. Experimental section

2.1. Reagents

Carbamazepine and diclofenac used in the present study was procured from Sigma Aldrich. Titanium oxyacetylacetate (purity over 98%), ammonium fluoride, glucose, H_2O_2, and ethyl alcohol purchased from Ranbaxy India, were used for the preparation of C-TiO_2. All solutions were prepared using ultra-pure millipore water.

2.2. Analytical methods

Powder XRD measurements were done by Bruker Discover D8 with default background correction. Raman spectra were recorded using WiTec GmbH, CRM αS300 instrument with 532 nm Nd: YAG laser line as an excitation source. High resolution transmission electron microcopy (HRTEM) images of the catalysts before and after photocatalytic reaction were analyzed in JEOL 3010 HRTEM instrument by dispersing the samples in ethanol. Solid state UV–vis measurements were performed by using a Cary 5E UV-VIS-NIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were done using an Omicron ESCA Probe spectrometer with polychromatic MgKα X-rays ($h\upsilon$ = 1253.6 eV). The microwave digestion was carried out using the CEM Mars 5 microwave digester. HRSEM measurements were performed using FEI Quanta FEG 200.

2.3. Catalyst preparation

The catalyst synthesis procedure adopted for the present work followed the published procedure elsewhere [19]. In a typical synthesis, equal concentrations of titanium oxyacetylacetate (10 mM, TOAA) and ammonium fluoride (10 mM, NH_4F) were dissolved in 50 ml of millipore water with constant stirring. To the above solution, 20 mg of glucose and 10 ml of H_2O_2 were added. The resultant solution was subjected to microwave digestion, heating at 150 °C with 400 W microwave power for 30 min duration. The turbid solution was centrifuged and the precipitate was washed with ethanol and water several times. Finally, the sample was dried at 80 °C for 3 h. In order to remove the excess carbon source, the sample was annealed at 350 °C for 3 h.

2.4. Photo reactor

Photocatalytic batch experiments were conducted in a cylindrical photochemical reactor of 400 ml volume, with water circulation arrangement for maintaining the temperature between 25 °C and 30 °C. A 150 W high pressure tungsten visible lamp (λ > 400 nm) was used for irradiation. Stirring at 150 rpm was done using a magnetic stirrer and an oxygen flow rate of 300 ml/min was maintained throughout the experiment [20]. Stock solution of the pollutant was prepared using ultra-pure millipore water. Samples were collected at regular intervals of time and analyzed using HPLC.

2.5. Batch studies

Batch degradation studies were carried out on stirred aqueous solutions contained in the photo reactor as mentioned above under continuous scavenging by O_2. 200 ml of aqueous solutions with varying different initial concentrations of pollutants (50–250 μg/L) and catalysts (50–350 mg/L) were performed. Also studies were done to understand the influence of different system parameters like pH, light intensity, and presence of external carbon source like glucose. Before the start of each run, the aqueous solutions were kept in dark for 1 h under constant stirring to reach adsorption equilibria. The temperature (25–30 °C) of the apparatus was maintained by water recirculation around the quartz tube. Samples were collected at the sampling port through a syringe with 0.45 mm polymer membrane filters and were further analyzed by HPLC.

2.6. Kinetic studies

The kinetic study using suspended form of catalyst was carried out with different concentration of diclofenac and carbamazepine. For all the studies, the reaction solution volume of 400 ml was maintained, with constant oxygen sparging and continuous stirring throughout the experiment. Pseudo-first order kinetic expression was used to analyze the photocatalytic reaction rate. The kinetic expression is given by Eq. (1)

$$\ln (C_0/C) = kt \quad (1)$$

Where, C and C_0 are concentration of pollutants at time t and t = 0, respectively and k is pseudo-first-order rate constant.

2.7. Mineralization and intermediates studies

Samples from batch studies were analyzed for intermediates and degree of complete mineralization observed using ESI–MS and total organic carbon (TOC) was measured on filtered suspensions using a Shimadzu TOC-5000 analyzer. The change in pH during the degradation of pharmaceutical was monitored with Digital pH meter supplied by Digisun Electronics, model: DI-707

2.8. Optimization studies

To optimize the photocatalytic degradation of CBZ in visible light, a central composite design (CCD) was used. Four parameters (i.e. k = 4) were considered i.e. catalyst concentration (50–250 mg/L), light intensity (4000 to 10000 lx) and pollutant concentration (50–250 μg/L).