

Photocatalytic degradation of carbamazepine using ozonation and photocatalytic ozonation with TiO₂ and WO₃

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Abstract

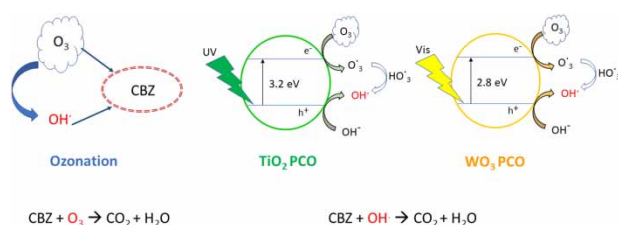
Ozonation, TiO₂ photocatalytic ozonation (PCO) and WO₃ PCO were used to demonstrate the removal of carbamazepine (CBZ), an antiepileptic drug commonly found in water bodies. The experiment was carried out in a lab-scale reactor (500 mL) at pH 7, CBZ concentration 1 mg/L and 0.25 g/L catalyst dose. The mixture was stirred in the dark for 30 minutes to achieve adsorption equilibrium. A UV and visible light source of 8 watt was used to photoactivate TiO₂ and WO₃. Ozonation alone using an ozone dose of 10 mg/hour was found to be very effective for CBZ removal. In all the processes investigated, CBZ was easily removed while the removal of by-products varied depending on the reaction pathway. The mineralization efficiencies (TOC removal) for complete by-products removal using ozonation, TiO₂ PCO and WO₃ PCO were 95, 73 and 62% respectively. TiO₂ PCO performed better than WO₃ PCO in achieving complete mineralization, but it would not be a sustainable solution considering the costs of UV lamps, harmful UV rays and toxicity of TiO₂. The removal efficiency of WO₃ PCO can be increased by increasing the ozone dose and duration of treatment.

Key words: carbamazepine, LC-MS, ozonation, photocatalytic ozonation

Highlights

- Degradation of carbamazepine, a commonly found contaminant in water body is studied.
- Comparison of different advanced oxidation processes.
- Ozonation, photocatalytic ozonation using TiO₂, WO₃ is carried out.
- This is the second study on WO₃ photocatalytic ozonation of CBZ.

Graphical Abstract



INTRODUCTION

Water quality is declining due to the presence of persistent organic pollutants (POPs). POPs are compounds such as pharmaceuticals, personal care products, contrast media, plasticizers, food additives, wood preservatives, laundry detergents, surfactants, disinfectants, flame retardants, pesticides, natural

and synthetic hormones, and some disinfection by-products (La Farré *et al.* 2008) from communities and industries. They escape treatment in conventional water and wastewater treatment plants and require advanced oxidation processes (AOP) for degradation due to their recalcitrant nature.

Heterogeneous photocatalysis, using semiconductor materials as photocatalysts, is very effective in advanced water treatment. TiO_2 is a versatile photocatalyst with unique physical and chemical properties (Wang *et al.* 2004). It is commonly used in photocatalysis due to its good performance, low cost and inert nature (Friedmann *et al.* 2010). The wavelength of light required to generate a photoexcited electron hole pair is inversely related to the band gap energy. TiO_2 has a high band gap of 3.2 eV, and light irradiation in the UV-A region or lower is required to generate electron hole pairs. Several studies have reported effective carbamazepine (CBZ) degradation using UV-A/ TiO_2 (Achilleos *et al.* 2010). The feasibility of AOP in large-scale water treatment is limited by the costs (sum of capital, operating, and maintenance costs). Photolytic degradation by UV irradiation is the most expensive AOP while ozonation is the least (Esplugas *et al.* 2002). Photocatalytic degradation using TiO_2 could reduce the total costs by one-third in comparison to other AOPs (Saritha *et al.* 2007).

Visible light induced photocatalysis is a promising technology that can achieve new levels of sustainability in water treatment (Surenjan *et al.* 2019). Tungsten trioxide (WO_3) is a photocatalyst with a low band gap energy of 2.8 eV. Visible light was used in this study to examine its effectiveness in photocatalytic ozonation. WO_3 has become an outstanding photocatalytic ozonation alternative to TiO_2 because of its low cost, lower toxicity, ready availability and visible light activity (Rey *et al.* 2014). CBZ, an antiepileptic, was used as a model pollutant in the study as India is the largest consumer of CBZ in Asia and second largest in the world after USA (Zhang & Geissen 2010). CBZ has been reported in Indian water bodies and across the globe (Tixier *et al.* 2003; Ramaswamy *et al.* 2011; Tran *et al.* 2014). In this study, the effectiveness of ozonation, TiO_2 photocatalytic ozonation (PCO) using UV light and WO_3 PCO using visible light irradiation for CBZ degradation was evaluated.

MATERIALS AND METHODS

Materials

Laboratory grade CBZ (Extra Pure) was procured from Alpha Chemika, Mumbai, TiO_2 from Merck, and WO_3 from Sajan Overseas Pvt Ltd, Ahmedabad. Other materials used include deionized water, acetonitrile, formic acid, methanol, potassium iodide and starch. The light source was an 8 W UV lamp in the TiO_2 PCO and an 8 W visible light lamp for the WO_3 PCO.

Methods

The experimental setup consisted of a glass batch annular photoreactor with an effective volume of 500 mL, gas inlet and sample outlet. The ozone – gas flow rate was 5 L/min and ozone dose was 10 mg/hour as determined by oxidation of potassium iodide followed by titration against sodium thio-sulphate using starch as the indicator. A UV-A lamp operating at 365 nm and intensity 22.15 mW/cm² in a quartz tube was positioned axially in the reactor. The reactor was wrapped in a black cloth and aluminum foil to prevent UV exposure. A similar, visible light lamp was used for the WO_3 PCO.

The photocatalytic degradation experiment was carried out using 1 mg/L CBZ in deionized water at pH 7 and catalyst doses of 0.25, 0.5, 1.0 and 1.5 g/L for 30 minutes. The chemical oxygen demand (COD) of each sample was determined and the sample with the highest COD removal was considered to be the most efficient catalyst dose among 0.25, 0.5, 1.0 and 1.5 g/L. The reactor contents were stirred using a magnetic stirrer for 30 minutes to distribute the catalyst uniformly through the sample and for adsorption of CBZ onto the catalyst surface. 1 mg/L CBZ at pH 7 with the most efficient catalyst

dose was irradiated with the light source and sub-samples collected at stipulated time intervals for 120 minutes. It was then centrifuged at 2,500 rpm for 10 minutes and filtered through 0.45 μm filters. The most efficient process was determined by comparing reduction in CBZ concentration, and degradation (COD removal) and mineralization efficiency (TOC removal). Calibration of the ozonator to obtain the ozone dose (mg/min) was determined by passing into (KI) traps and titrating against sodium thiosulfate solution using starch as the indicator (Equation (1)).

$$\text{Ozone dose mg/min} = \frac{(A + B) * N * 24}{T} \quad (1)$$

where

A and B = titre value for 2 KI traps, mL

N = normality of sodium thiosulphate, N

T = ozonation time, min

The CBZ concentrations were analyzed using Agilent Technologies 6,120 Quadrupole Liquid Chromatography – Mass Spectroscopy (LC-MS) System. Aliquots (20 μL) of calibration standards and samples were prepared with prior filtration using 0.22 μm filters. The mobile phase used comprised methanol and 0.1% formic acid in acetonitrile (80:20). The Liquid Chromatography-Mass Spectrometry (LC-MS) was run in selected ion monitoring mode and positive electrospray ionization. All LC-MS analysis was carried out at 0.5 mL/min flow rate and 10 minutes' retention time. The absorbance spectrum of the sample before (untreated) and after (treated) irradiation was determined using UV-Vis spectrophotometry (SPEKOL 1,200, Analytik Jena, Jena, Germany) by scanning in the wavelength range 200 to 900 nm. The crystalline phases of the photocatalysts (TiO_2 and WO_3) were evaluated from X-ray diffraction (XRD) patterns recorded using PANalytical X'Pert PRO, Philips, Almelo, The Netherlands. The angle between the incident and reflected x-rays was 2θ (10° to 80°), and data were collected by continuous scanning with 0.02° step size.

RESULTS AND DISCUSSION

Characterization of catalysts

The absorbance spectra of untreated and treated CBZ (5 mg/L) were obtained using a UV-Vis spectrophotometer by scanning in wavelengths 200 to 900 nm. The characteristic λ_{max} was found at 284 nm, as shown in Figure 1. Other studies have also reported similar $\lambda_{\text{max}} = 284$ nm for CBZ (Borse & Mulgund 2015; Zadbuke *et al.* 2016).

The XRD pattern for TiO_2 showed stronger peaks at 2θ values of 25.31° and 48.03° besides 38° , 54° (Figure 2). The absence of spurious diffractions indicates the crystallographic purity of the material (Varshney *et al.* 2010) and the strong peaks at 25° and 48° indicate that the TiO_2 is in the anatase phase (Thamaphat *et al.* 2008; Ba-Abbad *et al.* 2012). The XRD analysis of WO_3 reported sharp peaks at 16.47° and 25.65° (Figure 2), which are attributable to the orthorhombic phase of tungstite, although a small shoulder around 24.2° could indicate a low contribution from the cubic WO_3 phase (Rey *et al.* 2014).

Ozonation

CBZ degradation by ozonation was carried out using 1 mg/L CBZ at pH 7. Ozone reacts with organic compounds either directly, via a molecular ozone pathway, or indirectly via a radical pathway (Hoigne 1998). At alkaline pH, ozone molecules react with hydroxyl ions to produced hydroxyl

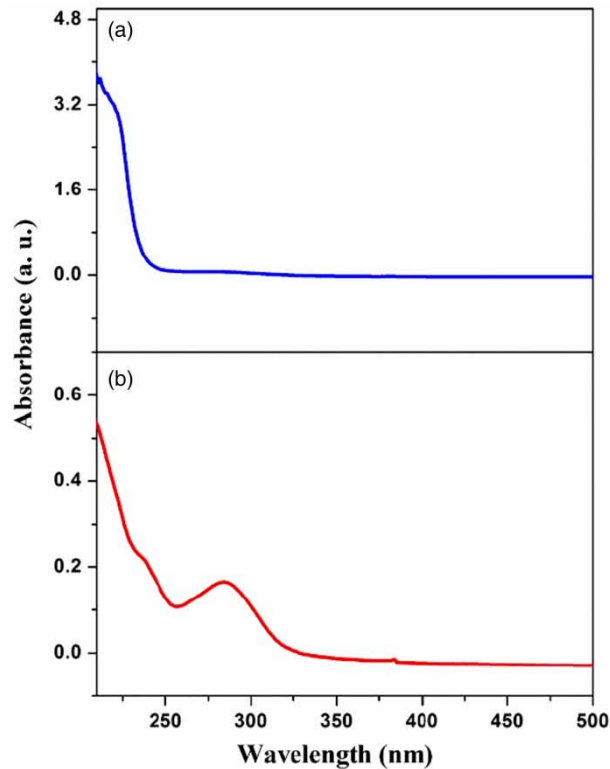


Figure 1 | UV absorbance spectra of treated and untreated CBZ.

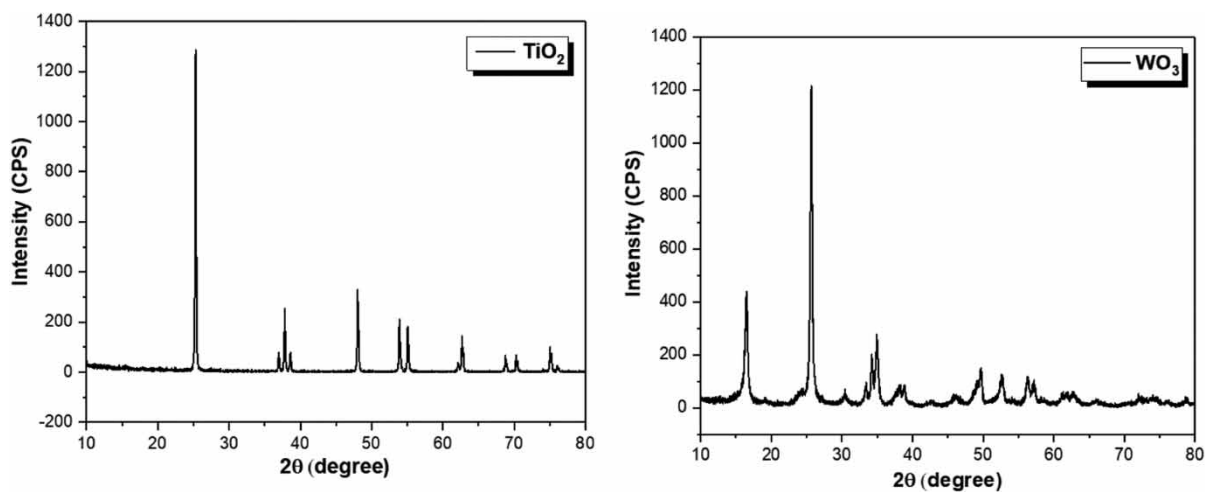


Figure 2 | XRD patterns of TiO_2 and WO_3 .

radicals, which have higher oxidation potential than ozone, so maintaining the pH near neutral or alkaline conditions is effective. COD was used as an indicator of CBZ degradation because it denotes the amount of oxygen required to oxidize the residual parent CBZ and its transformation by-products. The COD of the sample after 120 minute ozonation can be attributed to residual parent CBZ, and ozonation by-products such as 1-(2-benzaldehyde)-4-hydro(1H,3H)-quinazoline-2-one, 1-(2-benzaldehyde)-(1H,3H)-quinazoline-2,4-dione and 1-(2-benzoic acid)-(1H,3H)-quinazoline-2,4-dione (McDowell *et al.* 2005). Lower COD removal indicates persistent CBZ and by-products, thus that the degradation efficiency is lower. The mineralization efficiency (TOC removal) after 120 minutes was 95%; that is, ozonation removes CBZ very effectively. LC-MS analysis of ozonated 1 mg/L CBZ at

pH 7 reported a sharp drop in CBZ concentration within 5 minutes and it was below the limit of detection after 20 minutes (Figure 3). CBZ was easily degraded by ozonation (Hua *et al.* 2006; Vieno *et al.* 2007; Rey *et al.* 2015).

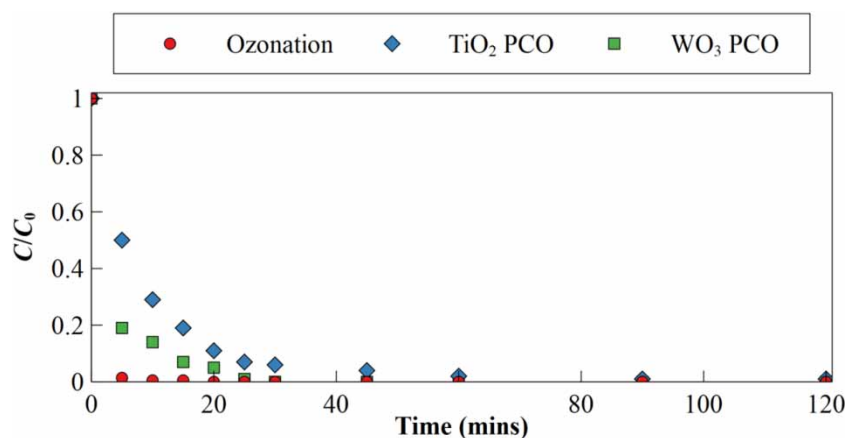


Figure 3 | Normalized CBZ concentration during ozonation, TiO₂ PCO and WO₃ PCO.

TiO₂ photocatalytic ozonation

TiO₂ PCO was tested for degradation of 1 mg/L and 5 mg/L CBZ sample solutions at pH 7. The point of zero charge (pzc) of TiO₂ is 6.25 (Son *et al.* 2004). At pzc, the catalyst has no net surface charge and hence it does not have an electrostatic repulsion. The TiO₂ surface has negative charge as the pH exceeds the pzc. The negative logarithm of acid dissociation constant (pKa) of CBZ is 13.9 (Scheytt *et al.* 2005) thus CBZ is protonated as pKa > pH. This results in increased adsorption of protonated CBZ on negatively charged TiO₂ due to electrostatic attraction. Since the diffusion length of reactive oxygen species (ROS) is very small, in the order of 10 nm, adsorption of the pollutant onto catalyst surfaces is crucial for effective degradation. The appropriate TiO₂ dosage was determined by varying the catalyst dose (0.25, 0.5, 1.0 and 1.5 g/L) at the higher initial concentration of 5 mg/L CBZ. The most efficient of the various doses used was 0.25 g/L, which achieved the highest COD removal of 66.71% after 30 minutes of TiO₂ PCO. It is essential try to minimize the photocatalyst dose, within reason, as higher doses may cause UV light scattering, while lower doses may result in low ROS generation and inhibit treatment efficiency.

The COD removal for both 1 and 5 mg/L CBZ of TiO₂ PCO was evaluated at different time intervals for 120 minutes at 0.25 g/L TiO₂ dose and pH 7. The COD removal for one set of sample run found the highest COD removal of 83% for 1 mg/L CBZ sample, while 5 mg/L CBZ achieved 68% COD removal after 120 minutes of TiO₂ PCO (Figure 4). Chong & Jin (2012) obtained 40% COD removal using photocatalytic oxidation of 5 mg/L CBZ after 4 hours – that is, photocatalytic ozonation appears to be more effective in degrading CBZ than photocatalytic oxidation. The LC-MS analysis showed 99% removal of 1 mg/L CBZ after 120 minutes of TiO₂ PCO (Figure 3). The chromatogram results showed significant reduction in the parent CBZ peak, while a new peak appeared indicating formation of a new degradation by-product. Im *et al.* (2012) proposed a plausible degradation pathway for TiO₂ PCO of CBZ, the major product being acridine. TOC removal after 120 minutes was 73%, further confirming incomplete mineralization and the presence of by-products.

WO₃ photocatalytic ozonation

WO₃ dose of 0.25 g/L was used to evaluate the effect of contact time on 1 mg/L CBZ degradation at pH 7. The visible light-mediated photocatalytic ozonation achieved COD removals of 52% and 68%

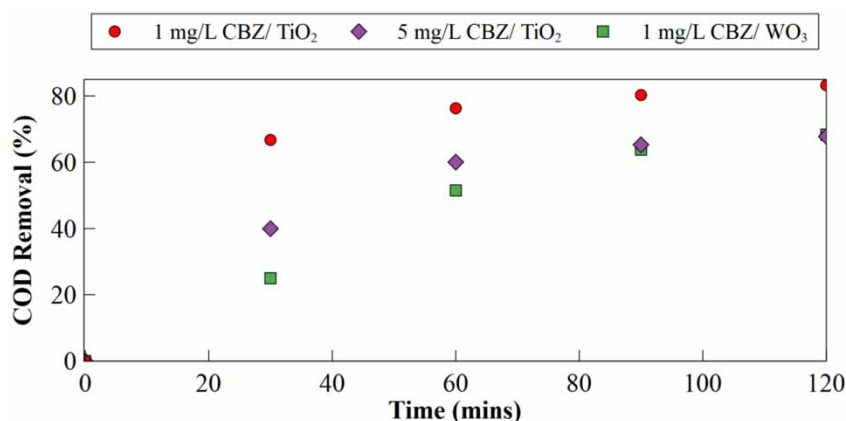


Figure 4 | COD removal by photocatalytic ozonation using 0.25 g/L TiO₂ and WO₃.

after 60 and 120 minutes, respectively. It was found that WO₃ PCO had similar COD removal to 5 mg/L TiO₂ PCO at higher reaction time (Figure 4). Although this is low compared to TiO₂ PCO (76%) for 60 minutes, WO₃ is cheaper than TiO₂, and visible light is less harmful and more cost effective than UV. LC-MS analysis of parent CBZ showed complete elimination of CBZ in 30 minutes (Figure 3). Although the WO₃ PCO removed CBZ parent compound better than TiO₂ PCO, its mineralization efficiency was lower, which could be attributed to the differences in the degradation pathway involved resulting in the formation of more recalcitrant by-products in WO₃ PCO. Rey *et al.* (2015) studied removal of 0.5 mg/L CBZ using 0.25 g/L WO₃ PCO, which achieved complete CBZ elimination in 20 minutes but no information on degradation by-products was provided. LC-MS chromatogram results showed that the CBZ peak had been removed completely after 30 minutes but two new peaks had appeared, indicating the formation of intermediates during degradation. WO₃ PCO achieved TOC removal of 62%, which was low compared to the other methods, after 120 minutes.

CONCLUDING REMARKS

The CBZ treatability studies using ozonation, TiO₂ PCO and WO₃ PCO were carried out in a lab-scale reactor. The experiment was conducted at pH 7, using 0.25 g/L catalyst dose and 1 mg/L CBZ concentration. The catalyst dose was based on COD removal over 30 minutes. The light source was an 8 W UV lamp in the TiO₂ PCO and an 8 W visible light lamp for the WO₃ PCO. The ozone dose was 10 mg/hour and ozonation alone achieved complete removal of CBZ in 20 minutes. CBZ is easily removed in all processes, but intermediate removal varied depending on the degradation pathway. The mineralization efficiency for complete by-product removal was ascertained by determining the TOC removal, which was 95, 73 and 62%, using ozonation, TiO₂ PCO and WO₃ PCO respectively. The by-products formed during ozonation were easily mineralized compared to other processes, leading to higher – more efficient – TOC removal.

WO₃ PCO removed CBZ faster than TiO₂ PCO, but mineralization was slower. The cost of UV lamps, the harmful nature of UV rays and toxicity of TiO₂ might take the edge off its better performance. The removal efficiency of WO₃ PCO could be increased by increasing both the ozone dose and the treatment time, which in turn would increase treatment costs. WO₃ PCO could be a future choice of visible light active photocatalyst as it is less toxic and less expensive than TiO₂, and an effective photocatalyst. WO₃ PCO could be scaled up for water treatment plants to remove persistent organic pollutants but the presence of organic matter could reduce photocatalytic efficiency due to ROS scavenging.

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