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Photocatalytic degradation of lignocaine in aqueous suspension of TiO_2 nanoparticles: Mechanism of degradation and mineralization

Manoj P. Rayaroth[a], Usha K. Aravind[b], Charuvila T. Aravindakumar[a,c,*]

[a] School of Environmental Sciences, Mahatma Gandhi University, Kottayam 686560, Kerala, India
[b] Advanced Centre of Environmental Studies and Sustainable Development, Mahatma Gandhi University, Kottayam 686560, Kerala, India
[c] Inter University Instrumentation Centre, Mahatma Gandhi University, Kottayam 686560, Kerala, India

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ABSTRACT

A detailed investigation on the photocatalytic degradation and mineralization of lignocaine, a local anesthetic, under UV irradiation has been carried out in this study. The dose of TiO_2 was optimized initially and was found as 250 mg L^{-1} for the degradation of 2 mg L^{-1} concentration of lignocaine. The scavenging experiment using isopropanol and methanol revealed that the degradation is mainly controlled by hydroxyl radical. A fast disappearance of the parent compound (within 1 h) and nearly 75% of mineralization (after 6hr) were observed using this method. The relatively low mineralization efficiency is due to the evolution of various transformation products during the degradation as identified by high-resolution mass spectrometry (LC-Q-TOF-MS). Ten well-separated product peaks were observed in the total ion chromatogram (TIC) for 30 min irradiated sample of lignocaine. Based on the formation of these products, a degradation mechanism is proposed involving mainly hydroxylation, N-de-ethylation, and hydrogen abstraction. As part of mineralization study, the evolution of various inorganic ions was analyzed and the ammonium ion is found as the major inorganic species. A detailed mechanism is proposed for the inorganic ion release as well.

1. Introduction

Personal and pharmaceutical care products are important category of emerging contaminants, and their presence in various water matrices such as wastewater, surface water, groundwater, estuarine water, and drinking water is an increasing concern throughout the world [1–3]. The major parts of this type of compounds are coming from prescription and over-the-counter therapeutic drugs, veterinary drugs, and many others. The possibility of finding these compounds in surface and groundwater is related to the sales amount, the pharmacokinetic behavior (half-life, urinary and fecal excretion, metabolism, etc.), and the rate of degradation of the compounds in the sewage system and in wastewater treatment plants (WWTPs). Since most of these compounds cannot be removed from the WWTPs they can be present in surface and groundwater [4]. Nearly nanogram per liter to low microgram per liter levels of the pharmaceuticals in surface and even in drinking water has been reported worldwide. The selected compound lidocaine (lignocaine) (LGN) is a non-extensively investigated pharmaceutical commercialized by ASTRA AB as Xylocaine®, widely used as a local anaesthetic and antiarrhythmic agent. Various parameters such as high solubility, low Henry coefficients, and the low *n*-octanol/water partition coefficient value indicates that there is a great chance of finding this type of compound in the aqueous environment [5]. Consequently, this compound has been detected and reported in effluents from WWTPs and in some rivers and lakes in Europe and North America [5]. All these factors show the necessity of finding a suitable route for the removal of this kind of pollutants from water.

Advanced oxidation processes (AOPs) are promising and well-known oxidation techniques for the degradation of various organic contaminants in the context of complete mineralization [6–8]. The various oxidation techniques experimented for the removal of recalcitrant organic contaminants from the aqueous medium are UV/H_2O_2 photolysis [6], electrochemical methods [9], sonolysis [10], photocatalysis [11,12], etc., The wide spectrum application of semiconductor photocatalysis has been established with the discovery of photolysis of water using TiO_2 electrode by K. Honda and A. Fujishima in 1972 [13,14]. Among the various semiconductors, TiO_2 is preferred for the photocatalytic processes due to its high photosensitivity, non-toxic nature, and large band gap (3.2 eV) [14]. The absorption properties of TiO_2 NPs had been extended to the visible region with various surface modifications on the NPs [15–17]. More recently, the application of the nano-sized semiconductor photocatalyst themselves or their

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* Corresponding author at: School of Environmental Sciences, Mahatma Gandhi University, Kottayam 686560, Kerala, India.
E-mail address: cta@mgu.ac.in (C.T. Aravindakumar).

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surface-modified form is extended for the detoxification of soil and air in addition to water [14]. The major reactions involved by the absorption of light by the TiO_2 catalysts are given in equations 1–4

$$TiO_2 + hv \rightarrow h^+_{VB} + e^-_{CB} \quad (1)$$

$$h^+_{VB} + (OH^-)_{ads} \rightarrow \cdot OH_{ads} \quad (2)$$

$$h^+_{VB} + (H_2O)_{ads} \rightarrow \cdot OH_{ads} + H^+ \quad (3)$$

$$e^-_{CB} + O_2 \rightarrow O_2 \cdot^- \quad (4)$$

However, one of the disadvantages of this oxidation technique relies on the formation of intermediate products, with more toxic behavior than the parent compound [18,19]. In order to assess the toxicity of the transformed products, the identification of the unknown degradation compound is required. Moreover, due to the difference in the polarity and the difficulty in the separation of the transformed products, the conventional analytical techniques fail to identify these products. Liquid chromatography coupled with mass spectrometry is the most commonly used technique for the identification of intermediates in this type of oxidation methods [20–23]. Thus the main objectives of the present study are the identification of the transformation products of LGN using LC-Q-TOF-MS and to interpret a possible degradation pathway. Another aim is to study the mineralization efficiency which includes a detailed analysis of TOC removal and the estimation of the inorganic ions and depict a suitable mechanism for their release.

2. Materials and methods

2.1. Chemicals

Lignocaine (lidocaine) and the catalyst TiO_2, (TiO_2, anatase nanopowder < 25 nm) were purchased from Sigma-Aldrich. Other reagents such as HPLC grade methanol and isopropanol were purchased from Merck India. The aqueous solution was made from water collected from Cascada™ Lab water systems (18.2 MΩ cm).

2.2. Characterization of nanoparticles (NPs)

The surface morphology of the TiO_2 NPs was obtained from scanning electron microscopy images (JEOL, JSM 6390). The crystallinity of the nanoparticles was characterized by X-ray diffractometer, XPERT-PRO system employing Cu Kα radiation. Raman spectrum was recorded on a WITec Alpha 300RA confocal Raman spectrometer with AFM (excitation laser 15 mW 633 nm He-Ne laser).

2.3. Photoreactor

The degradation experiments were carried out in a cylindrical flask of length 310 mm and diameter 70 mm. The light source used was a 125 W medium pressure mercury lamp (~254 nm) kept on a double-walled immersion well of dimension 265 × 38 mm supplied by Scientific Aids & Instruments Corporation (SAIC, Chennai, India). A water circulator was used to control the temperature. The radiant flux of the reactor was estimated by potassium ferrioxalate actinometry and it is found as 101.5 mW cm^{-2}. The light intensity measured by Lux meter (TES 1332A digital Lux meter) was 250×10^2 lx. About 250 ml of the sample was taken in a reaction flask and the required amount of the catalyst was added to it and stirred. The quartz cell containing light source was dipped in it and the samples were taken out from the vessel for analysis at a time interval of 15 min.

2.4. Analyses

2.4.1. High-performance liquid chromatography (HPLC) analyses

High-performance liquid chromatography analysis was carried out on a Shimadzu Prominence UFLC, equipped with a quaternary pump (LC 20 AD) and a diode array detector (SPD-M20 A). The column used for the separation of the individual component was Enable C18G 250 mm × 4.6 mm × 5 μm and the eluent as 20% acetonitrile in water.

2.4.2. LC-Q-TOF-MS analyses

LC-Q-TOF-MS (waters xevo G2 Q-TOF) with an electrospray ionization (ESI) technique was performed to identify the intermediate products formed during the degradation process. Acidified water (0.1% formic acid) as eluant A and acetonitrile as eluant B and a gradient elution were used for the separation of each component. The capillary and cone voltages of the Q-TOF instrument were set at 3 kV and 30 V in the case of positive mode and 2.5 kV and 30 V for negative ionization mode, respectively, with a desolvation temperature of 135 °C. The m/z was scanned from 50 to 500. Nitrogen gas was used as both the desolvation and nebulizing gas at a flow rate of 50 and 900 l/hr, respectively and Argon gas was used as the collision gas in MS/MS analysis.

2.4.3. TOC analyses and estimation of inorganic ions

TOC reduction during the degradation process was analyzed by a TOC analyzer (HiPer TOC programmed by ThEuS software) worked based on the UV-persulfate method. The release of the inorganic ions during the degradation processes was also monitored by ion chromatography (Dionex ICS1100). The nitrate ions were eluted by a mixture of sodium carbonate (2.7×10^{-3} M) and sodium bicarbonate (3×10^{-4} M) in water. 20×10^{-3} M methanesulfonic acid was used for ammonium ions. The anion-specific column was Ion Pac AS12A (4 mm × 200 mm) and that of cation was Ion Pac CS12A (4 mm × 200 mm). The eluted ions were detected by conductivity detection.

3. Results and discussions

3.1. Characterization of NPs

The morphologies of TiO_2 NPs were determined using SEM and is given in Fig. 1A. It is found that the TiO_2 particles have an irregular and aggregated structure. The crystalline nature of the NPs was obtained from XRD data and Raman spectra, as given in Fig. 1B and C, respectively. The observed XRD pattern could be indexed as tetragonal titania anatase. As can be seen from Fig. 1B, TiO_2 NPs showed diffraction peaks at $2\theta = 25.4°$, 38°, 48.1°, 53.9°, 55.1°, 62.9°, 69.1°, 70.3°, and 75.1°. The strong diffraction peak at 25.4°, 38°, and 48.1° corresponds to the reflection planes with indices (101), (004), and (200) and other peaks could be indexed to (105), (211), (204), (116), (220), and (215) crystal planes. These results show that the NPs are purely in anatase form [24]. This is further confirmed by recording the Raman spectra and is given in Fig. 1C. It showed Raman bands at 142 cm^{-1} (Eg), 194.6 cm^{-1} (E_g), 397 cm^{-1} (B_{1g}), 513.5 cm^{-1} (A_{1g}), and 637.9 cm^{-1} (E_g). These Raman shifts were already reported for the anatase form of TiO_2 [25].

3.2. Optimization of TiO_2 loading

The most important parameter in a semiconductor photocatalysis is the catalyst dosage. In order to optimize the TiO_2 concentration for further study, we have carried out experiments with different dosages such as 125 mg L^{-1}, 250 mg L^{-1}, 500 mg L^{-1}, and 1000 mg L^{-1} of TiO_2. The TiO_2 dosage-dependent degradation of LGN is presented in Fig. 2. As can be seen from the figure, maximum degradation was observed at a TiO_2 dosage of 250 mg L^{-1}. With the increase of TiO_2 concentration, the degradation is reduced. This is the typical behavior of heterogeneous photocatalysis [26,27]. The observed inverse relationship between the TiO_2 dose and the degradation is attributed to the light scattering due to the aggregation of NPs that reduces photonic flux within the irradiated solution. The optimum concentration is thus found to be 250 mg L^{-1}. This concentration is used for further experiments.