



## Degradation, mineralization of bromoxynil pesticide by heterogeneous photocatalytic ozonation



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### ABSTRACT

The photocatalysts of Cs doped bare TiO<sub>2</sub>, 0.50 and 1.0 wt% were prepared by wet-impregnation method and characterized by XRD, SEM-EDX, TEM, BET, ICP, FTIR, and UV-DRS analyses. The degradation of bromoxynil was investigated under visible irradiation with ozone to compare the efficiency of these photoinduced advanced oxidation techniques. Photocatalysis with 1% Cs/TiO<sub>2</sub> was yielded 100% degradation and mineralization of bromoxynil in 2 h at basic pH. The extent of degradation was confirmed by GC–MS. The oxidation products were identified by <sup>1</sup>H NMR and GC–MS spectral analyses. The catalyst is fully recoverable and reusable multiple times with no loss of activity.

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### Introduction

The widespread application of pesticides has raised concerns about their persistence in the environment and their potential toxic effects on non-target organisms. Pesticides are used globally in agriculture and urban environments to prevent or destroy pests, including weeds, insects, and fungus. As a result of their ubiquitous application, pesticides are commonly found in surface and ground waters [1]. Pesticides are biodegradable, toxic by design and have been linked to adverse health effects in living organisms. Recently, crop safety issues such as contamination with agricultural pesticides have become a major concern for both producers and consumers. As a result, there has been a significant interest in developing methods to remove the pesticides from agricultural products before selling them in markets.

Bromoxynil is a phenolic benzonitrile-based pesticide used for the control of broadleaved weeds in grain crops [2]. Bromoxynil is categorized as the class II–moderately toxic pesticide. Workers chronically exposed to bromoxynil over a year-long span showed symptoms of weight loss, fever, vomiting, headache and urinary problems [3]. Bromoxynil can be present in air, food and soil as well as in surface water and contaminated ground waters by runoff and leaching. Bromoxynil in water is likely to pose health hazards

to non-target aquatic organisms. Researchers have earlier reported the acute pesticide poisoning of bromoxynil [4,5]. Moreover, bromoxynil has been found extensively to contaminate the soil [6]. In view of this, it is prudent to improve the technologies that could promote easy degradation of these organic pesticides.

Heterogeneous photocatalysis has proved to be of existence interest as efficient tool for degrading both aquatic and atmospheric organic contaminants. One of the major applications of heterogeneous catalysis is photocatalytic oxidation to effect partial or total mineralization of contaminants to benign substances [7]. Photocatalytic degradation comprises the use of certain semiconductors as catalysts for the production of highly reactive radicals under light irradiation [8,9]. TiO<sub>2</sub>, as a semiconductor, known to have high surface area, excellent stability, large band gap, can be regarded as non-toxic, and has a highly porous (2–50 nm in diameter) framework characteristics [10,11]. Therefore, it is regarded as an ideal photocatalytic material [11]. The TiO<sub>2</sub> structure has some fascinating physical–chemical implications, such as ease in transfer of electrons within the material, and aids in the recovery of catalyst [12]. The photocatalytic activity of TiO<sub>2</sub> is generally governed on the basis of electromagnetic radiation having equal or higher photon energy than its band gap energy (3.2 eV). In general, the photocatalytic mechanism is established around the excitation of electrons from the valence band (VB) to the conduction band (CB) of TiO<sub>2</sub>, leaving holes in the valence band. It is the electrons (e<sup>-</sup>) and holes (h<sup>+</sup>) that initiates redox reactions with molecular species adsorbed on the catalyst surface (TiO<sub>2</sub>)

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[13,14]. However, its wide band gap energy and high electron–hole recombination rate limits its application under visible light conditions.

Doping or surface modification by alkali metals is considered as one of the most efficient methods in reducing electron–hole recombination [15]. The metal on the surface of the photocatalyst can act as a trap-site for the photo-generated electrons, which can prevent electron–hole recombination, and thereby improve photocatalytic activity.

Photocatalysed oxidation as an auspicious chemical process to degrades organic pollutants [16]. The photocatalytic oxidation based systems have been developed in order to develop the  $\cdot\text{OH}$  radical production [17]. Ozonation can react with organic matter using two ways: direct molecular ozone reactions or indirect pathway leading to ozone decomposition and the generation of  $\cdot\text{OH}$  [18,19]. Carbonyl compounds and carboxylic acids are formed during the degradation of organics by ozone, both of which react with ozone only at slowly reactive rate. In addition, oxidation reaction is not satisfactorily fast, thus radical processes have to be executed. Reaction of radical with pollutants is fast. In contrast to ozonation alone, photocatalytic oxidation using a catalyst allows for the effective formation of hydroxyl radicals [20]. The decomposition of ozone can take place on different types of active centers. Therefore, basicity and acidity of surface plays an important role in the process [20,21].

In the present investigation, Cs doped titania was prepared by the impregnation method with metal loadings of bare titania, 0.50, and 1.0 wt% and characterized using Powdered XRD, TEM, SEM-EDX, BET, ICP, FT-IR and UV-DRS analyses. We carry out a series of investigations on the effect of Cs dopant level on  $\text{TiO}_2$  support, which in turn is directly related to its performance in the photocatalytic ozonated degradation of bromoxynil. The study is also anticipated to give a picture of the influence of catalyst loading, dose of Cs on photocatalytic oxidation of bromoxynil. We paid attention to improve activities in the visible range linking with Cs/doped catalysts.

## Materials and methods

### Preparation of catalysts

The wet impregnation method was used in the preparation of metal oxide supported catalysts [21,22]. The catalysts were prepared by dissolving appropriate amount of cesium nitrate in distilled water (40.0 mL) and adding it to 1 g of Titania ( $\text{TiO}_2$ , Aldrich) stirring for 3 h using a magnetic stirrer at room temperature and again at room temperature for overnight [22]. Catalysts are further dried in an oven at 140–150 °C for 12 h. Then the catalysts are calcined in the presence of air, at 550 °C for 3 h to obtain the bare  $\text{TiO}_2$ , 0.50% and 1% Cs/ $\text{TiO}_2$  (w/w) catalysts [23].

### Instrumentation

#### Textural properties

The Brunauer–Emmett–Teller (BET) surface area, total pore volume and average pore size were measured using a Micromeritics Tristar II surface area and porosity analyzer. Prior to the analysis, the powdered samples (~0.180 g) were degassed under  $\text{N}_2$  for 12 h at 200 °C using a Micromeritics FlowPrep 060 instrument. Textural properties of catalyst samples were measured by  $\text{N}_2$  adsorption–desorption isotherms obtained at -196 °C.

#### Inductively coupled plasma–optical emission spectroscopy (ICP–OES)

The actual metal loading was determined by using Perkin Elmer inductively coupled plasma optical emission spectrometer

(ICP–OES) Optima 5300 DV. Samples were solubilized in aqua regia and homogenized by a microwave digestion process, prior to ICP analysis.

#### Scanning electron microscopy (SEM)

The SEM measurements were carried out using a JEOL JSM-6100 microscope equipped with an energy-dispersive X-ray analyzer (EDX). The images were taken with an emission current = 100  $\mu\text{A}$  by a Tungsten (W) filament and an accelerator voltage = 12 kV. The catalysts were secured onto brass stubs with carbon conductive tape, sputter coated with gold and viewed in JEOL JSM-6100 microscope. The pre-treatment of the samples consisted of coating with an evaporated Au film in a Polaron SC 500 Sputter Coater metallizator to increase the catalyst electric conductivity.

#### Transmission electron microscopy (TEM)

The TEM images were viewed on a Jeol JEM-1010 electron microscope. The images were captured and analyzed by using iTEM software. The particle sizes obtained were the average particle size of 40–60 particles and the standard deviation is done in order to determine the range of the particle sizes. High resolution TEM images were recorded by using Jeol JEM 2100 Electron Microscope.

#### Power X-ray diffraction analysis (XRD)

Different metal oxide phases in the catalysts were observed using powder X-ray diffraction (XRD) performed on a Bruker D8 Advance instrument, equipped with an Anton Paar XRD 900 reaction chamber, a TCU 750 temperature control unit and a  $\text{Cu K}\alpha$  radiation source with a wavelength of 1.5406 nm at 40 kV and 40 mA. Diffractograms were recorded over the range 15–90° with a step size of 0.5 per second.

#### GC–MS analysis

In all the experiments the organic layer was extracted by using  $3 \times 5.0$  mL diethyl ether in a separating funnel and excess water was removed by the addition of anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ). The product was filtered and the solvent was allowed to evaporate. The product was characterized by GC–MS. The amount of TCP consumed in the reaction is expressed as a percentage of original amounts and it refers to reaction conversion. Selectivity refers to the amount of product formed divided by the reactant consumed.

#### $^1\text{H}$ NMR

$^1\text{H}$  NMR (400 MHz) spectra were recorded on a Bruker AMX 400 MHz NMR spectrometer in  $\text{CDCl}_3/\text{DMSO}-d_6$  solution using TMS as an internal standard. All chemical shifts are reported in  $\delta$  (ppm) using TMS as an internal standard.

#### FT-IR analysis

FT-IR spectra of various catalyst samples were recorded on a Nicolet Impact 400 equipment and Nicolet Impact Model-420 spectrometer with a  $4\text{ cm}^{-1}$  resolution and 128 scans in the mid IR ( $400\text{--}4000\text{ cm}^{-1}$ ) region using the KBr pellet technique. About 100.0 mg of dry KBr was mixed with a little amount (10.0 mg) of the sample and was ground for homogenization. During the mixing an IR lamp was used for drying. The mixture was then pressed into a transparent, thin pellet at  $10\text{ t/cm}^2$ . These pellets were used for the IR spectral measurements.

#### UV–visible diffuse reflectance spectra (UV-DRS)

UV–visible diffuse reflectance spectra were recorded with an Ocean Optics high resolution spectrometer (HR2000+) equipped with an integrating sphere accessory, using  $\text{BaSO}_4$  as a reference.

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