



# Catalytic non-thermal plasma reactor for mineralization of endosulfan in aqueous medium: A green approach for the treatment of pesticide contaminated water



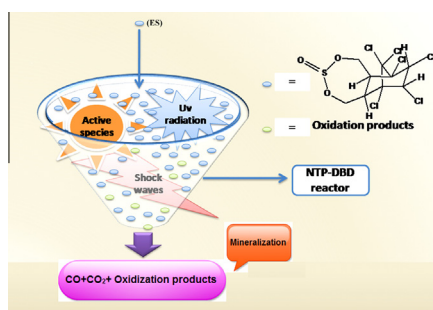
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## HIGHLIGHTS

- NTP-DBD reactor for in situ generation of oxidizing species.
- Confirmation of mineralization by TOC and infrared gas analyzers.
- Synergy effect on addition of catalyst.
- Confirmation of first order kinetics for the pollutant degradation.

## GRAPHICAL ABSTRACT



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## ABSTRACT

An advanced oxidation process for the mineralization of a model pesticide endosulfan from aqueous medium has been developed by non-thermal plasma combined with cerium oxide catalysts. Plasma was generated in a dielectric barrier discharge reactor, whereas ceria was prepared by combustion synthesis and characterized by various physico-chemical techniques. Typical results indicated the synergy between plasma excitation of endosulfan followed by the catalytic action of cerium oxide, which not only improved the conversion, but also increased the mineralization efficiency, which was confirmed by a total organic carbon content analyzer and an infrared CO<sub>x</sub> analyzer. Catalytic plasma approach showed a threefold increase in mineralization. Degradation followed first-order kinetics and rate of degradation is proportional to power input and reciprocal to initial endosulfan concentrations.

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## 1. Introduction

A fundamental contributor to the green revolution is the development and usage of pesticides for controlling a wide variety of insectivorous and herbaceous pests that would otherwise affect the quantity of agro products [1–3]. Even though pesticides are expected only to reach the target organisms, they may also affect non-target organisms such as humans and wildlife and may cause loss of biodiversity, deaths of wildlife and animals [1]. Hence, pesticides may pose threat to the ecosystems [2,3]. Endosulfan (ES)

metabolic compounds may cause adverse effects on humans and wildlife via interactions with the endocrine system [4]. ES may be contaminated in air, surface water, groundwater, soil, and sediment [5]. The World Health Organization (WHO) puts it in Class II “moderately hazardous”, (WHO, 2005), whereas, the US Environmental Protection Agency (USEPA) classifies it as a category 1b (highly hazardous). Because of growing concerns of the ES on the ecosystem, it has been banned in many countries, including India [6]. Hence, removal of ES is a contemporary research topic and needs immediate attention [7].

Various physico-chemical techniques like adsorption [8], membranes [9], biobed [10] and advanced oxidation processes (AOPs) like photocatalysis [11], UV/ozone [12], ultrasonication [13] have

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been tested for the removal of water bound pollutants, including ES. However, the scope of many of these processes is limited to transfer the contaminant from one phase to another; however a complete oxidation is desired. In this context, application of non-thermal plasma (NTP) for the removal of aqueous pollutants may offer specific advantages like one pot generation of short-lived oxidants like OH<sup>•</sup>, H<sup>•</sup>, O<sup>•</sup>, HO<sub>2</sub><sup>•</sup>, O<sub>2</sub><sup>•</sup>, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, UV irradiation and shock waves that can mineralize the pollutant molecules [14–23]. As NTP reactors produce ozone, various catalysts were combined with plasma for effective utilization of ozone as an oxidant [20–28].

The objective of the present study is to design and test the feasibility of NTP dielectric barrier discharge (NTP-DBD) reactor during the mineralization of the ES in aqueous medium. At a later stage, NTP is combined with a catalyst, as some of the oxidants like ozone, etc. may decompose to secondary oxidants like atomic oxygen that are capable of promoting complete oxidation. Various parameters like applied voltage, concentration and the addition of a catalyst were studied.

## 2. Experimental section

### 2.1. Materials and methods

High purity (>99.5%) endosulfan was obtained from Sigma–Aldrich, 15 mg of endosulfan dissolved in 30 ml of acetonitrile then make it up to 1 liter with water. It is a mixture of two biologically-active isomers, the alpha and beta isomers ( $\alpha$  and  $\beta$ ), in the proportions  $\alpha/\beta = 70/30$ . Nano sized CeO<sub>2</sub> was prepared by combustion synthesis as reported earlier [29]. In a typical synthesis method, 2.52 g of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 1.01 g of citric acid (CA) to maintain oxidant/fuel ratio = 1. Minimum amount of distilled water was added and the resulting solution was sonicated for 15 min and transferred into alumina crucible. Then the mixture was placed in a preheated furnace maintained at 573 K for 5 min to complete combustion. Then the catalyst was dried and calcined at 873 K for 60 min.

Crystal structure was confirmed with XRD patterns recorded on X'Pert Pro, PAN analytical diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The X-ray tube was operated at 40 kV and 30 mA. Nitrogen adsorption–desorption isotherms at 77 K were carried out using a Quantachrome Nova 2200. The samples were degassed at 300 °C for 3 h. The Raman spectrum was recorded with Bruker optics SENTERRA multi-laser dispersive Raman microscope at room temperature. Catalyst characterization results are given in Supporting information S1–S3.

### 2.2. Discharge reactor

The details of the NTP discharge reactor (Fig. 1) were given elsewhere [30]. Briefly, plasma is generated by applying a high voltage (using by a Jayanthi transformer range 1–40 kV) between ground and the inner electrodes that were separated by a 3.5 mm discharge gap. The inner electrode is a stainless steel rod placed at the center of a quartz tube coated with silver paste that also acts as the ground electrode. The applied voltage was measured with a high-voltage probe (Agilent 34136A HV 1/1000). Charge and voltage are recorded with a 100 MHz bandwidth (maximum 1 GS/s) oscilloscope (Tektronix TDS 2014B). The flow rate of the bubbling air (200 ml/min) was adjusted by using a mass flow controller from AALBORG flow instruments (GFC 17).

Endosulfan concentration in aqueous medium was monitored as a function of time and quantified by using High Performance Liquid Chromatography (HPLC–Waters Corporation 515 model) with a photodiode array detector with a mobile phase consisted

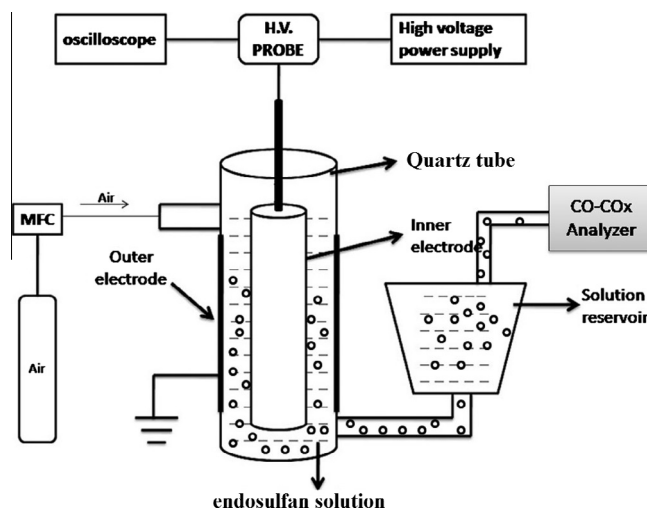


Fig. 1. Experimental setup.

of acetonitrile: water solution (70:30). The degradation percentage was calculated by using:

$$\text{Degradation percentage (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

$C_o$  and  $C_t$  are the initial and the final concentrations of ES, respectively. The energy yield of the degradation was calculated from the following equation [30,31]:

$$Y \text{ (g/kWh)} = \frac{C \text{ (g/l)} \times V \text{ (L)} \times \frac{1}{100} \times \text{Conv (\%)}}{P \text{ (kW)} \times t \text{ (h)}} \quad (2)$$

where  $C$  is initial ES concentration,  $V$  is the volume of the solution,  $P$  is power and  $t$  is time [30,31]. It has been observed that increasing applied voltage decreases the energy yield.

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) produced in water by the discharge was quantified by following a reported procedure, which involves the spectrophotometric quantification of the pertitanic acid formed when Titaniumsulphate reacts with H<sub>2</sub>O<sub>2</sub> at 418 nm [32]. Titaniumsulphate was prepared by dissolving 1 g of anhydrous titanium powder with 100 ml of hot sulfuric acid. The resulted solution was kept at 150 °C for 20 h, cooled to room temperature, filtered and kept in reagent bottle. The degradation experiments were conducted in a semi continuous mode using a fixed volume of water containing ES 5–15 mg/L. Each reaction was carried

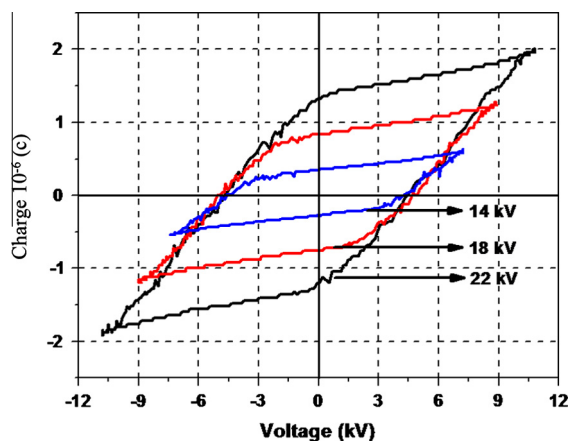


Fig. 2. V–Q diagram (Lissajous figure) at different applied voltages.

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