Chemosphere 167 (2017) 396–405

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effective degradation of organic water pollutants by atmospheric non-thermal plasma torch and analysis of degradation process

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HIGHLIGHTS

- Use of single type of atmospheric cold plasma needle for degradation of pollutants.
- Spectroscopic and LCMS analysis of degradation process.
- Reduction in TOC and toxicity of the byproduct after degradation.
- Possible degradation pathway of MB has been proposed based on LCMS and FTIR data.

ARTICLE INFO

Article history:
Received 15 April 2016
Received in revised form
7 September 2016
Accepted 21 September 2016

Handling Editor: Jun Huang

Keywords:
Organic polluants
DBD plasma
Plasma catalyst
LCMS

ABSTRACT

The paper reports the use of atmospheric non-thermal plasma torch as a catalyst for degradation of various organic pollutants dissolved in water. A flow of He mixed with air was used to produce the dielectric barrier discharge (DBD), at the tip of the torch, using pulsed electric excitation at 12 kV. The torch, operated at a power of 750 mW/mm^2, was seen to completely degrade the aqueous solutions of the pollutants namely methylene blue (MB), methyl orange (MO) and rhodamine-B (RB), at around 10^{-4} M concentrations, the concentration of polluants is one order higher than of routinely used heterogeneous photocatalytic reactions, within 10 min of irradiation time at room temperature. UV Visible spectra of the organic dye molecules, monitored after different intervals of plasma-irradiation, ranging between 1 and 10 min, have been used as tools to quantify their sequential degradation. Further, instead of using He, only air was used to form plasma plume and used for degradation of organic dye which follow similar trend as that of He plasma. Further, Liquid Chromatography Mass Spectroscopy (LCMS) technique has been used to understand degradation pathway of methylene blue (MB) as a representative case. Total organic carbon (TOC) measurements indicates significant decrease in its content as a function of duration of plasma exposure onto methylene blue as a representative case. Toxicity studies were carried out onto Gram negative *Escherichia coli*. This indicated that methylene blue, without plasma treatment, shows growth inhibition, whereas with plasma treatment no inhibition was observed.

1. Introduction

Methods based on use of plasma as catalyst have been increasingly attractive in variety of applications including those requiring the environmental protection and treatment of waste water, natural plant fiber, textile material etc. (Bobkova et al., 2012; Kramar et al., 2014; Ribeiro et al., 2012; Zhang et al., 2015). This is possible because of its added advantages, such as ease of generation of reactive species, controlled temperature of treatment, dry and clean environment during the process, short processing time and single step product. It does not require additional solid catalyst and source of electromagnetic radiations, as required in case of photocatalysis. In addition there are large number of controlling parameters which assist in enhancing the efficiency of the degradation process. Recently non-equilibrium atmospheric pressure non thermal plasmas have emerged as efficient tools on account of their additional advantages. These include the capability of being used outside a vacuum and not producing excess heat. In

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http://dx.doi.org/10.1016/j.chemosphere.2016.09.089

such plasmas the energy of the charged species is sufficiently high (3–4 eV) and densities are negligibly smaller than those of neutral radicals in the remote plasma region.

The removal of organic dye from waste water happens to be an important issue in the environmental protection, since more than 10% of the world's total output of dye products is discharged into environment as waste water, which pollutes the ground water resources. The removal or degradation of organic dyes from the waste water, therefore, requires some efficient method. The purification techniques normally involve physical and biological treatments. There are many reports on the degradation of organic pollutants using heterogeneous catalysts involving photocatalytic materials. TiO_2 and ZnO based semiconductors are amongst the photocatalytic materials widely used for the degradation of organic pollutants (Alagarsamy Pandikumar, 2012; Dai and Chen, 2007; Kayaci et al., 2014; Matosa and Andreína Garcíaa, 2015; Raghavan et al., 2014; Xiong et al., 2011; Kuoa et al., 2011). Photocatalytic degradation using heterogeneous photocatalyst leads to i) difficulty in removal of the photocatalytic material after photocatalytic reaction. ii) reduction in the catalytic response after repeated use of photocatalyst, iii) need of UV/visible radiation source to activate the photocatalytic reaction iv) the process is slow due to number of rate determinant factors v) non-availability of a single catalyst which can be effective in degrading different organic pollutants. It is known that the single catalyst is not always equally effective in degrading all the pollutants. It is possible to overcome most of these limitations by using atmospheric plasma device.

Atmospheric non-thermal plasma processes, namely Dielectric Barrier Discharges (DBD) and plasma needles, are based on generating reactive oxygen species (ROS) which are fairly stable oxidizers and have capacity to degrade even the strong aromatic dyes as well as the microorganisms. They have been proved as efficient bio-technological devices for pedodontics and preventive dentistry. Moreover DBD based non-thermal plasmas have been proposed as prospective devices for removal of NO_x and solid carbon particulates in the automobile industries (Kim et al., 2002; Stamate et al., 2015).

Most of the organic dyes consist of aromatic rings of carbon and various functional group attached to carbon. Methylene blue, for example, consists of C–N=C, C–S–C, C–N–CH_3 functional groups. Whereas, methyl orange consists of N=N joining two aromatic carbon rings, N–CH_3 and C–S=O type of functional groups. The functional groups with Rodamine B are, N–CH_3, C–O–C in addition to aromatic ring of carbon. Even other organic dye molecules consist of similar structures. In the present paper we have, therefore, explored the use of cold plasma needle for degradation of organic dye mixed in water. A few important dye materials like methylene blue (MB), methyl orange (MO) and rhodamine-B (RB) were tested. One amongst these, namely, methylene blue was analyzed in detail. The same approach can be extended for the degradation of other organic pollutants. The indigenously developed plasma needle, in the present work, is small in size (about 10 cm long) and operates at low power (less than 30 mW). Experiments have been carried out to assess the degradation of aqueous solution of dye by recording photo-absorption spectra in the visible region of electromagnetic spectrum. The degradation is evaluated by reduction in the intensity of absorption peak as a function of time of plasma-irradiation. Fourier Transform Infrared Spectroscopic (FTIR) has been used to understand the degradation mechanism. Insitu Optical Emission Spectroscopy (OES) was used to record and identify different species present in the plasma. Further the degradation of organic dye molecule using air based plasma needle torch, has been analyzed using Liquid chromatography-mass spectrometry (LCMS). FTIR and LCMS data is used to understand the degradation pathway of MB.

2. Materials and method

The non-thermal atmospheric plasma was generated by a 'Needle Torch' shown in schematic diagram in Fig. 1. The plasma was excited using a pulsed DC gas ignition transformer (BRAHMA TC2SVCS) having pulse DC voltage of 12 kV, 20 Hz pulse frequency and 50% duty cycle. The size of the ignition transformer is 48 mm × 40 mm x 10 mm and weight is 500 g. The power delivered to the torch was measured by recording the current waveform across a series resistance during the operation of the plasma. The plasma current was varied from 1 to 10 mA as a function of distance between the tip of the torch and anode in the range of 1–3 cm. Variation in the resulting power at different separations of cathode and anode is shown in Fig. 2. All the degradation experiments were carried out by keeping the distance of 2.1 cm, where the power delivered was 750 mW/mm^2. Helium was made to flow from one end of the torch with a flow rate of 0.2 L/min. There are several advantages of using He as a plasma forming gas like, it helps in achieving the breakdown at relatively low voltage and that the gas flow propels radicals and metastables towards the surface to be treated. Also the flow gets mixed with the atmosphere and interacts with the medium which consists of H_2O, N_2, and O_2 at the downstream from the nozzle. This has led to the formation of plasma plume having diameter of 1–2 mm and length of 2–3 cm. The plume was then directed towards the aqueous dye solution in a beaker placed on the anode plate. The plasma plume was seen to penetrate up to a depth of about 5–6 mm inside the solution. The species generated during the plasma irradiation were studied using the optical emission spectroscopy. The light collection was facilitated with an optical fiber which was directed towards the interface between the plasma plume and the upper meniscus of the dye solution. Ocean Optics spectrophotometer (model HR-4000) was employed to record emission spectra. The aqueous solution of organic pollutant was exposed to plasma plume for different intervals of time viz. 1–10 min. The solution was constantly stirred by magnetic needle during the irradiation process.

Aqueous solutions, with 1×10^{-4} M concentration of each dye, were exposed to plasma radiations. To prepare aqueous solution of the dye, de-ionized water was used. Optical absorption spectra of the solution under investigation were recorded as a function of

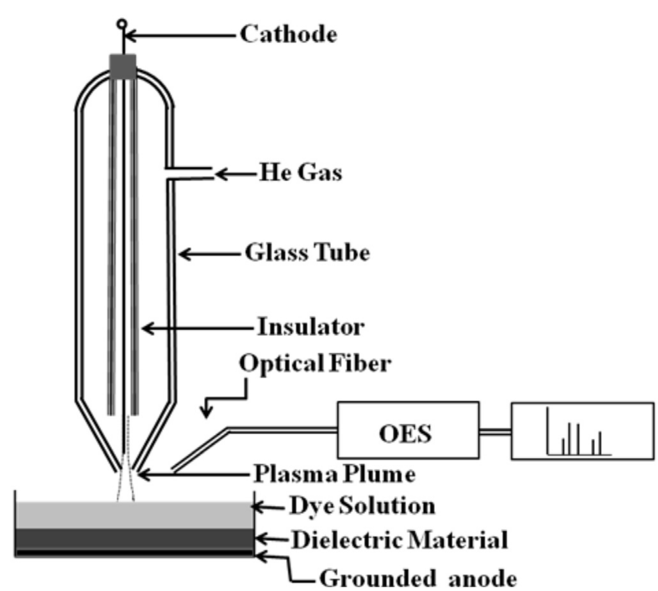

Fig. 1. : Schematic diagram of Dielectric Barrier Discharge (DBD) type needle torch.