

Applicability of pulsed power technique for the degradation of methylene blue



Raj Kamal Singh^a, Vigneshwar Babu^b, Ligy Philip^{a,*}, Sarathi Ramanujam^b

^a Department of Civil Engineering, Indian Institute of Technology Madras, 600036, India

^b Department of Electrical Engineering, Indian Institute of Technology Madras, 600036, India

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ABSTRACT

Present study evaluated the efficiency of pulsed power technique (PPT) for the degradation of methylene blue (MB) under different operating and environmental conditions. Various reactive oxygen species (ROS) such as hydroxyl radicals, hydrogen peroxide, ozone and superoxide radical were quantified. The maximum concentrations generated were found to be 63 mg/L, 28 mg/L, 1 mg/L and 18 mg/L for hydroxyl radicals, hydrogen peroxide, ozone and superoxide radical, respectively for 12 min of pulsed streamer discharge at 23 kV applied voltage and 25 Hz frequency. It was observed that magnitude of applied voltage, frequency (pulses/sec), pH, alkalinity and natural organic matter (NOM) present in the water had a significant effect on hydroxyl radical and hydrogen peroxide generation. MB degradation efficiency and ROS formation increased with applied voltage and frequency. An initial MB concentration of 50 mg/L was completely degraded within 10 min at 23 kV input voltage and 25 Hz frequency. Acidic pH favoured ROS formation whereas high alkalinity and NOM reduced the MB degradation efficiency and ROS formation. Treatment time for the 100% degradation of 10 mg/L of MB was increased from 6 min to 8 min in presence of 150 mg/L of alkalinity. The MB degradation efficiency was further decreased to 95.6% when alkalinity was increased to 300 mg/L for 10 min streamer discharge. Mineralization of dye during treatment was confirmed by total organic carbon and inorganic ions analyses and IR spectra. Energy efficiency of ROS formation in the reactor was also evaluated.

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1. Introduction

Voracious consumption and introduction of new dyes by textile industries are on rise, in an alarming rate. The ceaseless discharge of dyes into the water bodies are recognized as a worldwide threat to aquatic ecosystem. Over 700,000 tons of dyes per year are being used in the textile industries, 10–15% of which is being released directly through the wastewater [1]. Methylene blue (MB), an organic dye, is widely being used in textile industries for dyeing cotton, silk, wool and fibres. It is extensively used in the fields of biology and chemistry as an antiseptic, antioxidant, and as a robust staining agent. Though MB has diverse medical applications, many studies have showed the harmful effects of this dye in natural ecosystems. It is reported that many nitrifying bacteria and archaea are susceptible to MB toxicity within the range of 10 ppb–10 ppm concentrations [2]. Recently an *in vivo* and *in vitro* study was conducted with human cell lines, and was reported

that MB and its methylated derivatives are toxic within the range of 0.1–10 mM concentrations [3]. It was also reported that the low dose of MB (1 mg/kg) can cause acute serotonin toxicity in human [4]. In addition to MB, most of the dyes are highly carcinogenic, genotoxic, allergic and may even cause mental disorders [5]. Hence, it is essential to develop a simple, efficient and cost effective technique to mitigate the impact of the hazardous dyes. Several conventional methods such as coagulation/flocculation [6], adsorption [7], membrane separation [8], biological treatment [9], and different advanced oxidation processes (AOPs) like ozonation [10], Fenton oxidation [11], photo-Fenton [12], sonolysis [13] and photocatalytic degradation [14–17] have been implemented to treat the dye from industrial effluent. However, many of these techniques are having some limitations. Hence, researchers worldwide are still trying to find an optimized technique to reduce the impact of industrial discharges to the environment and ecosystem [18–22].

Pulsed power technology has been gaining importance as a clean and effective technology for the degradation of versatile pollutants. Pulsed power technique (PPT) is a process by which energy is accumulated over a relatively long time and then releases it rapidly, thereby increasing the instantaneous power. This technique is

* Corresponding author.

E-mail address: ligy@iitm.ac.in (L. Philip).

based on advanced oxidation process (AOP) works by creating *in-situ* strong oxidants. Rapid pulsed power electrical discharges in water (electro-hydraulic discharge) or in the gas phase (corona discharge) produce plasma, which comprises of many reactive oxygen species (ROS) like ozone, hydroxyl radical, nascent oxygen, hydrogen peroxide, superoxide and other radicals [23]. ROS generated by corona discharge has the ability to degrade organic pollutants [24] including dyes [1] [25–29]. ROS are also very efficient in killing the pathogens present in water [30]. Although plasma technologies are quite efficient in degradation of organic pollutants, presence of ubiquitous ROS scavengers such as alkalinity (HCO_3^- and CO_3^{2-} ions) and natural organic matters (humic acids and glucose) compete with organic pollutants and reduces the efficiency of treatment [31–33]. Application of plasma technology for water and wastewater treatment is still at infancy stage and more understanding of the process is required making it as a sort after technology for many practical problems.

In the present work, degradation of MB by PPT was studied and the amount of ROS generated by PPT was quantified. A systematic experimental study was carried out to understand the effects of different water quality parameters such as pH, alkalinity and natural organic compounds (humic acid and glucose) on dye degradation and ROS generation during the treatment process. Dye degradation mechanism has also been proposed by identifying the intermediate products using LC/MS and FTIR analyses. Mineralization of dye was confirmed by TOC analysis. 'G value' denotes the energy efficiency of a plasma reactor and it is defined as the amount of reactive species formed (or the amount of pollutant degradation) per unit energy consumption. The 'G value' for the comparison of different plasma reactor is recently mentioned in some literatures [24,34,35]. The 'G value', 'current efficiency' and 'degradation yield' were used to compare the performance of pulsed power technique with other technologies for dye degradation.

2. Materials and methods

2.1. Reagents

Methylene blue as a commonly used dye was used in the present study (Fig. 1d). MB (99% purity) was procured from Paxmy chemicals, India and Milli-Q water was used for preparing different concentrations of dye solution. Sodium bicarbonate (Rankem, India) was used to vary the alkalinity. Glucose (Himedia, India) was used as easily biodegradable organic matter while humic acid (Himedia, India) was used as natural organic matter. NaOH (Rankem, India) and HCl (Merck, India) were used to adjust the pH of dye solution.

2.2. Experimental set up and reactor configuration

The experimental set up used for dye degradation using pulsed power technique is shown in Fig. 1. The set-up had two parts (a) high voltage source (Fig. 1a) and reactor cell (Fig. 1b). The discharge free test transformer (100 kV, 5 kVA) was used for generation of high AC voltage. The generated AC voltage was converted to DC voltage by using high voltage diode (140 kV, 20 mA, 100 k Ω) and DC voltage was measured using a resistor divider subsequently. The constant DC voltage was converted to square pulse with the help of rotating spark gap (RSG). The duration of the pulse was controlled by varying the speed of the RSG. The shape and magnitude of generated square wave pulse were recorded using high voltage probe connected to the oscilloscope (HP 54645A, 100 MHz). The rise time of the pulse was measured to be 0.8 μs and duration of the pulse was 18 ms, 15 ms and 12 ms for frequencies of 20 Hz, 25 Hz and

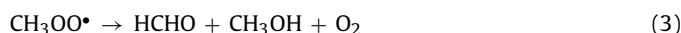
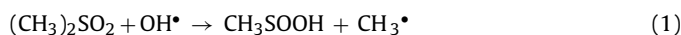
30 Hz, respectively. A typical generated voltage wave is shown in Fig. 1c.

In the present study, streamer discharge was obtained using needle plate configuration. Multiple needles, made up of tungsten, were attached to a circular plate, which was then connected to the high voltage terminal. The bottom of the set-up was a circular plane electrode, connected to the ground terminal. The high voltage and ground electrode were fixed in a cylindrical container which was filled with water for treatment. The tip of the tungsten electrode needle had a radius of curvature of about 50 μm . The gap between needle tip and water surface in container could be adjusted from 3 mm to 8 mm, which aids optimum ROS formation. Two ports were provided in the top electrode: one for injecting sample and the other for extracting the sample for characterization. The applied voltage magnitude was fixed in such a way that the streamer propagation could be observed during the test. Water jacket was provided to avoid temperature rise. Thermal vision camera (Fluke Ti20, USA) was fixed to monitor the temperature change during the test.

2.3. Analytical methods

2.3.1. Reactive oxygen species (ROS) quantification

2.3.1.1. Estimation of hydroxyl radical (OH^\bullet). Quantification of hydroxyl radical was carried out by derivatization technique as per the literature [36,37]. For the study, 28.2 mM concentration of dimethyl sulfoxide (DMSO) was dissolved in Milli-Q water and streamer discharge treatment was provided to DMSO solution subsequently. DMSO is highly water soluble and able to trap most of the generated OH^\bullet radicals and form methyl radicals and methane sulfinic acid as primary intermediates products (Eq. (1)). The methyl radicals react further with oxygen molecules to form formaldehyde (Eqs. (2) and (3)). The formaldehyde thus formed was quantified using derivatization technique.



For the derivatization process, 5 mL of the aqueous solution from reactor was taken out at 0 min, 2 min, 4 min, 6 min, 8 min and 10 min intervals and mixed with 5 mL of pH 4 buffer ($\text{NaH}_2\text{PO}_4 + \text{H}_3\text{PO}_4$), and 1 mL of saturated solution of dinitro phenyl hydrazine (DNPH). All the reaction mixtures were kept in an oven at 40 °C for 1 h to ensure complete reaction to occur to form hydrazone. Reaction mixtures were then equilibrated to room temperature and then analysed by the HPLC–UV/Vis at 360 nm. Analysis was carried out using a reverse phase HPLC unit with a LC-18 column (Dionex ultimate 3000, USA) using 70:30 ratio of acetonitrile and water with 0.5% acetic acid solution. Reaction stoichiometry indicate that 2 mol of hydroxyl radicals yield 1 mol of formaldehyde as per Eqs. (1)–(3).

2.3.1.2. Estimation of hydrogen peroxide (H_2O_2). Colorimetric determination of hydrogen peroxide concentration was performed by mixing 3 mL of aqueous solution from reactor and 1.5 mL of titanium (IV) oxysulfate-sulfuric acid solution and analysing the concentration of resulting perititanic acid complex at 410 nm in spectrophotometer [36,38].

2.3.1.3. Estimation of ozone (O_3). Ozone is very unstable in water. Hence, ozone test kit (Prerana laboratories, Pune, India) was used for colorimetric determination of dissolved ozone in water by DPD (N, N-diethyl-p-phenylenediamine) method [39].

2.3.1.4. Estimation of super oxide radicals ($\text{O}_2^{\bullet-}$). Analytical method described by Goto [40] was used to estimate the super oxide ion

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