



# Enhanced methylene blue oxidative removal by copper electrode-based plasma irradiation with the addition of hydrogen peroxide



Guntae Son <sup>a,1</sup>, Do-hyung Kim <sup>b,1</sup>, Jung Seok Lee <sup>c</sup>, Hongshin Lee <sup>d,\*</sup>

<sup>a</sup> School of Civil and Environmental Engineering, Kumoh National Institute of Technology, 1 Yangho-dong, Gumi 730-701, Republic of Korea

<sup>b</sup> Soil Environment Center, Korea Environmental Industry & Technology Institute, 215 Jinheungno, Eunpyeonggu, Seoul, Republic of Korea

<sup>c</sup> Biomedical Engineering, Yale University, New Haven, CT 06511, United States

<sup>d</sup> Chemical and Environmental Engineering, Yale University, New Haven, CT 06511, United States

## HIGHLIGHTS

- The copper electrode based SPI/H<sub>2</sub>O<sub>2</sub> system oxidizes methylene blue in water.
- The copper electrode based SPI activate H<sub>2</sub>O<sub>2</sub> via Fenton-like reaction mechanisms.
- Hydroxyl radicals and cupryl ion are the dominant oxidants.

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## ABSTRACT

Submerged plasma irradiation (SPI)-based advanced oxidation processes have been studied for the oxidation of recalcitrant organic compounds because of their various physical and chemical properties. However, SPI technologies still have a few drawbacks such as relatively low efficiency for wastewater treatment and high energy consumption. In order to overcome these drawbacks, in this study, we proposed the combination of SPI and the Cu(II)-catalyzed Fenton-like system. The removal of methylene blue (MB) by the SPI system was significantly enhanced upon the addition of H<sub>2</sub>O<sub>2</sub>. The pseudo-first-order rate constants of MB removal increased with the increase of applied voltage. In addition, the optimum H<sub>2</sub>O<sub>2</sub> dose and initial solution pH were 100 mM and 9, respectively. The reactive oxidants responsible for MB removal in copper electrode-based SPI/H<sub>2</sub>O<sub>2</sub> systems are likely to be hydroxyl radicals ( $\cdot$ OH) or cupryl ion (Cu(III)), wherein Cu(III) is especially important. Furthermore, the copper electrode-based SPI/H<sub>2</sub>O<sub>2</sub> system is a novel advanced oxidation process capable of oxidizing water recalcitrant and toxic organic pollutants at neutral pH.

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## 1. Introduction

Advanced oxidation technologies (AOTs), for example, ozonation (O<sub>3</sub>), ultraviolet (UV)/H<sub>2</sub>O<sub>2</sub> treatment, the Fenton system, photocatalysis, supercritical water oxidation, and submerged plasma irradiation (SPI), use diverse reactive oxidants, such as  $\cdot$ OH and Fe(IV), to treat water recalcitrant and toxic organic pollutants in the environment, as they exceptionally react with the aforementioned reactive oxidants (Gloyna and Lee, 1991; Sun et al., 1999; Shanableh and Crain, 2000; Bianco Prevot et al., 2001; Kaneko

and Okura, 2002; Locke et al., 2006; Lucas and Peres, 2006; Haji et al., 2011). Recently, SPI has been widely considered as a potential technique for the degradation or mineralization of organic compounds because of their various physical and chemical properties, such as generation of various reactive oxidants ( $\cdot$ OH, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, etc.), shockwaves, and UV light as well as electrohydraulic cavitation (Joshi et al., 1995; Bogaerts et al., 2002; Locke and Thagard, 2012).

However, SPI technologies still have a few drawbacks, for example, high energy consumption, low efficiency, and unclear reaction mechanisms for environmental applications. In order to overcome these drawbacks, many researchers have suggested the use of SPI in combination with other AOPs, such as the Fenton system (Gao et al., 2003a, 2003b, 2006, 2008; Liu and Jiang, 2005),

\* Corresponding author.

E-mail addresses: [hongshin.lee@yale.edu](mailto:hongshin.lee@yale.edu), [ghdtsilee@gmail.com](mailto:ghdtsilee@gmail.com) (H. Lee).

<sup>1</sup> These authors contributed equally to this work.

TiO<sub>2</sub> system (Jin et al., 2012), activated carbon system (Grymonpre et al., 1999), and ozone system (Kato et al., 2014). Among these combination systems, the ability of the SPI/Fenton system to oxidize organic compounds in wastewater has been broadly investigated.

In general, the Fenton or Fenton-like systems involve catalytic reactions of iron with H<sub>2</sub>O<sub>2</sub>, which provide an effective approach for the removal of organic compounds in water, which is beneficial for wastewater treatment (Joshi et al., 1995; Pignatello et al., 2006). However, the advantages of the Fenton (i.e., iron (II)/H<sub>2</sub>O<sub>2</sub>) and Fenton-like systems (i.e., iron (III)/H<sub>2</sub>O<sub>2</sub>) are limited by low yields of reactive oxidants, high generation of iron sludge, and poor performance at near-neutral pH (De Laat and Gallard, 1999; Keenan and Sedlak, 2008a,b; Lee et al., 2008).

The use of copper catalysts in the Fenton reaction for this SPI-based combination system may help overcome the limitations of the traditional Fenton and Fenton-like systems, because copper ions (Cu(I), Cu(II)) are highly soluble at near-neutral pH (Pham et al., 2013; Lee et al., 2014). According to recent studies (Lee et al., 2013; Pham et al., 2013), the Cu(II)-catalyzed Fenton-like reaction may lead to the generation of different reactive oxidants (i.e., •OH and Cu(III)) depending on pH.

Similarly, the combination of SPI and the Cu(II)-catalyzed Fenton-like system may accelerate the formation of reactive oxidants. This new combination system is yet to be investigated.

Therefore, this study assesses the synergistic enhancement of the degradation of methylene blue (MB) when H<sub>2</sub>O<sub>2</sub> was added to a copper electrode-based SPI system. The oxidative degradation kinetics and mechanisms in the copper electrode-based SPI/H<sub>2</sub>O<sub>2</sub> system are examined by varying the reaction parameters (e.g., H<sub>2</sub>O<sub>2</sub> dose, initial pH of the solution, and applied voltage). In order to understand the nature of the reactive oxidants, a series of experiments were conducted with an excess of probe compounds (i.e., 200 mM *tert*-butanol and 200 mM methanol).

## 2. Materials and methods

### 2.1. Materials

All chemicals used were of high-purity reagent grade. Deionized water (18 MΩ cm Milli-Q water from a Millipore system) was used to prepare all solutions. MB (C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl·xH<sub>2</sub>O, 95%), reactive black 5 (Na<sub>4</sub>C<sub>26</sub>H<sub>21</sub>N<sub>5</sub>O<sub>19</sub>S<sub>6</sub>), reactive black 4 (NaC<sub>15</sub>H<sub>14</sub>N<sub>3</sub>O<sub>3</sub>S),

indigo carmine (Na<sub>2</sub>C<sub>16</sub>H<sub>8</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>), methyl orange (NaC<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O<sub>3</sub>S), chromotrope FB (Na<sub>2</sub>C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>O<sub>7</sub>S<sub>2</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), sodium phosphate (Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>), methanol (CH<sub>3</sub>OH), *tert*-butyl alcohol (*t*-BuOH, C<sub>4</sub>H<sub>10</sub>O), and ethylenediaminetetraacetic acid (EDTA, Na<sub>2</sub>C<sub>10</sub>H<sub>14</sub>O<sub>8</sub>N<sub>2</sub>) were purchased from Sigma-Aldrich Co., USA.

### 2.2. Experimental setup and procedure

All plasma irradiation tests were performed in a batch system using a 50-mL acrylic SPI reactor equipped with a high-voltage (0–1900 V) alternating current (AC) power supply system. The electrode used in the SPI system was 2.0 mm in diameter and 150 mm in length, and it was made of Cu. The electrode was placed in the reactor using a 1.0–1.5 mm ceramic insulator. The experimental setup of the SPI system is shown in Fig. 1.

The initial pH of the reaction solutions was adjusted by adding NaOH or HClO<sub>4</sub> without the use of a buffer solution. In general, the target compound and oxidant were added to MB (5 mg L<sup>-1</sup>) and hydrogen peroxide (50 mM), respectively. Hydrogen peroxide was added to the MB solution within the reactor, and the reaction was initiated by plasma irradiation. In order to determine the nature of the receptive oxidants, an excess amount of test compounds (i.e., 200 mM methanol and 200 mM *tert*-butyl alcohol) was added as the reactive oxidant scavengers. At least duplicate or triplicate runs for each experiment were carried out, the mean values and standard deviations of which are presented.

### 2.3. Analytical methods

The concentrations of MB and H<sub>2</sub>O<sub>2</sub> were determined using a UV–Vis spectrophotometer (Humas, HS-3300) with UV absorbance detection at 664 and 405 nm (titanium sulfate method), respectively. The total copper dissolution concentration was analyzed using inductively coupled plasma atomic emission spectroscopy (Varian, ICP-OES720). The MB removal efficiency was calculated as

$$\% \text{ Color removal} = ((A_0 - A)/A_0) \times 100, \quad (1)$$

where A<sub>0</sub> (mg L<sup>-1</sup>) is the initial concentration of MB (mg L<sup>-1</sup>) and A is the concentration of MB (mg L<sup>-1</sup>) after a designated reaction time. The rate of MB removal was calculated using pseudo-first-order kinetics, which showed good correlation coefficient values as shown in Eq. (2) as follows:

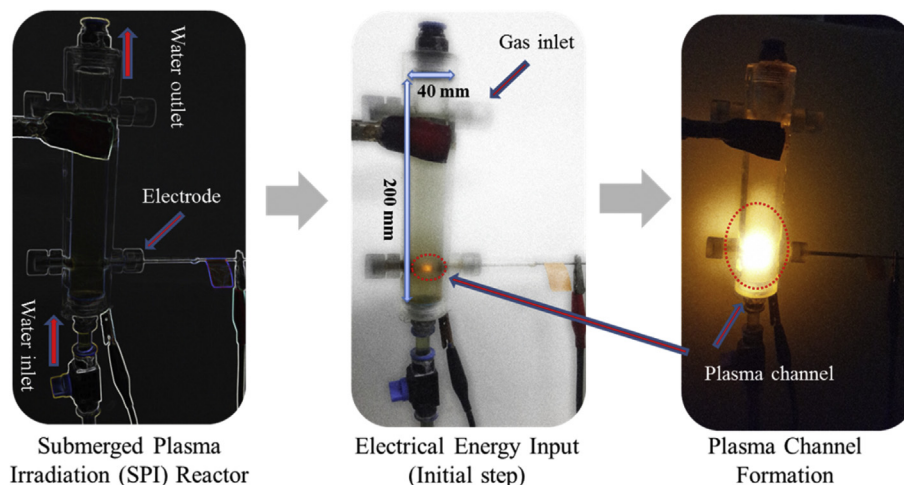


Fig. 1. Images of SPI reactor.

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