



Decoloration of methylene blue hydrate by submerged plasma irradiation process

Guntae Son^a, Hongshin Lee^b, Joung-Eun Gu^b, Seunghwan Lee^{c,*}

^aDepartment of Environmental Engineering, Kumoh National Institute of Technology, Gumi, Korea, Tel. +82 54 478 7645; Fax: +82 54 478 7859; email: so20110@hanmail.net (G. Son)

^bSchool of Urban & Environmental Engineering, Ulsan Institute of Science and Technology, Ulsan, Korea, Tel. +82 52 217 2872; Fax: +82 52 217 2809; email: ghdtlsl@unist.ac.kr (H. Lee), Tel. +82 2 958 5359; email: novelje@unist.ac.kr (J.-E. Gu)

^cDepartment of Civil and Environmental Engineering, Kumoh National Institute of Technology, Gumi, Korea, Tel. +82 54 478 7632; Fax: +82 54 478 7859; email: dlee@kumoh.ac.kr (S. Lee)

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ABSTRACT

In this study, a submerged plasma irradiation (SPI) process was attempted for the decoloration of methylene blue hydrate (MBH) in synthetic dye wastewater from aqueous solution. Several series of experiments were conducted to study the effects of electrode materials, oxidants, applied voltage, pH, and type of buffer solution by monitoring MBH removal efficiency in 50 mL of batch reactor. More than 80% of removal efficiency was achieved within 2 min of plasma irradiation at 800 V, with a pH of 7. Electrode materials in SPI process were found to affect the MBH removal efficiency. Tungsten electrode produced a higher decoloration rate constant (0.38 s^{-1}) than those of iron (0.28 s^{-1}) and aluminum (0.33 s^{-1}) ones. Electrode length in plasma irradiation system also affected the MBH removal. Decolorization reaction of MBH was found to follow the pseudo-first-order laws. The rate constant (k) of MBH as a decoloration index increased with the increase in applied voltage, pH, DO, and conductivity.

Keywords: Submerged plasma irradiation; Methylene blue hydrate; Decolorization; Electrode

1. Introduction

With the development of textile printing and dyeing productions, the amount of wastewater generated by the textile industry has increased, containing considerable amounts of synthetic organic dyes. Dyes are widely used in various textile industries to color final products and 10–15% of the world's total output of

dye products is released directly into the environment as wastewater [1]. Most of dyes are toxic and, biologically, are rather resistant and apt to cause genetic mutations, which cannot be recognized by the natural environment. Dyes are also not easily degraded [2,3]. The removal of these dyes from effluents has become a major environmental concern for the textile industry.

Advanced oxidation technology, which has received extensive attention, effectively promotes the

*Corresponding author.

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degradation or mineralization of organic pollutants in water. Advanced oxidation processes, including non-thermal plasma technology [4,5], photo catalysis [6–8], supercritical water oxidation [9,10], Fenton processes [11], and UV/H₂O₂ [12], have been studied with respect to their application to wastewater treatment. Although these technologies are promising in terms of cost and performance, they still require further research and need broader validation. High-voltage pulsed discharge plasma technology is based on *in situ* generation of strong oxygen-based oxidizers: hydroxyl radicals, ozone, atomic oxygen, hydrogen peroxide, and perhydroxyl radicals, which promote the destruction of the target pollutant until mineralization [13]. High-voltage pulsed discharge plasma enhances the degradation rate of organic pollutants, produces no secondary pollution, operates under normal condition of temperature and pressure, and has low power consumption. This technology leads to various physical and chemical effects, such as pyrolysis, UV photolysis, and electrohydraulic cavitation, as well as formation of oxidizing species [1]. This study presents the experimental data on the oxidative decolorization of dye in water using high-voltage pulsed plasma discharge. Selected factors influencing dye removal were studied including voltage, initial dye concentration, and reaction time. The effects of initial pH, oxidants, and electrode materials on decoloration efficiency were also investigated.

2. Materials and methods

2.1. Materials

Distilled water was used throughout the entire experiments for solution preparation and cleaning. Methylene blue hydrate (MBH, C₁₆H₁₈N₃SCl·xH₂O, 309 gmol⁻¹) was used as an organic dye pollutant and without any further purification. Methylene blue is one of the most commonly used dyes for industrial application and main classes of commercial dyes. It has a very short life in an excited state, and is stable in the visible and near UV ranges of light [14]. MBH is not regarded as acutely toxic, but it can have various harmful effects. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis. A large amount creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturition, and methemoglobinemia-like syndromes [15]. Chemical structure of MBH is shown in Fig. 1. Perchloric acid and sodium hydroxide were used for pH adjustment. Sodium dihydrogen

phosphate (NaH₂PO₄) and disodium phosphate (Na₂HPO₄) were used for phosphate buffer. Carbonic acid (H₂CO₃) and sodium bicarbonate (NaHCO₃) were used as a carbonate buffer. Methanol (CH₃OH, 32.04 gmol⁻¹), t-butyl alcohol (C₄H₁₀O, 74.12 gmol⁻¹), and DMSO (dimethyl sulfoxide, (CH₃)₂SO, 78.12 gmol⁻¹) were used to the radical scavengers.

2.2. Methods

Schematic diagram of experimental apparatus is shown in Fig. 2. The experimental apparatus included a power supply and reactor. The supplied voltage was maximum 1,900 V (1.9 kV) and square pulse was used for discharge.

High-voltage pulsed plasma discharge was generated in the electrode system of the cylindrical reactor. The reactor volume was of 50 mL and the reactor had four electrodes with one of these earthed. Electrode was made of tungsten, iron, and aluminum (2.0 mm diameter). The electrode protruded 1–1.5 mm from the ceramic insulator and was placed. The reactor had four different positions to accommodate needle electrodes. The ground electrode was at the outside end of the bottom of the reactor. One opening of the reactor was connected to the inlet tank through the flow meter, while the next one was the outlet for the treated water. The needle electrode was connected to high-voltage power supply. MBH degradation experiments were performed in 50 mL cylindrical reactor. All the experiments were conducted in a batch mode. Typically, 50 mL of the dye solution was discharged into the reactor during each run. And then, the sample was discharged into the reactor at 2 min. All the experiments were duplicated under each experimental condition with resulting errors of less than 5% and demonstrated high reproducibility.

Finally, the sample was measured by UV spectrophotometer at 664 nm with deionized water as blank. The UV spectrophotometer used was a Humas HS3300 UV-vis one in the wavelength range of 200–900 nm. Matched quartz cuvettes with path length 1 cm were used. The MBH removal was calculated using the following Eq. (1).

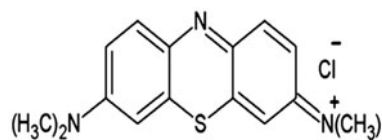


Fig. 1. Chemical structure of MBH.

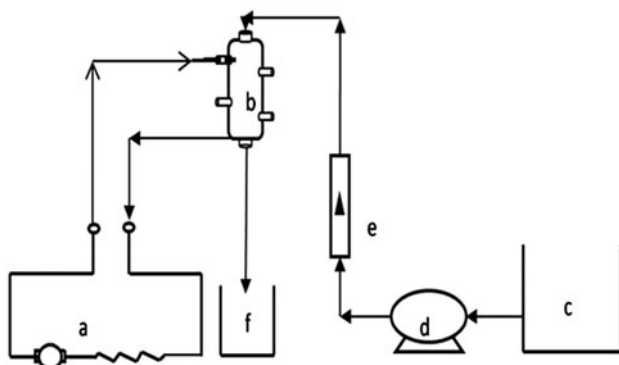


Fig. 2. Schematic diagram of submerged plasma irradiation: (a) generator, (b) reactor, (c) inlet tank, (d) pump, (e) flow meter, and (f) outlet.

$$\text{MBH removal (\%)} = \frac{\text{MBH}_0 - \text{MBH}}{\text{MBH}_0} \times 100 \quad (1)$$

where MBH_0 (mgL^{-1}) is the initial concentration of MBH and MBH (mgL^{-1}) is the concentration of MBH at reaction time. MBH removal rates could be described by pseudo-first-order kinetics with good correlation coefficient values (>0.95) as shown in Eq. (2).

$$\text{Ln}\left(\frac{\text{MBH}}{\text{MBH}_0}\right) = -kt \quad (2)$$

3. Results and discussion

3.1. Effect of initial concentration on MBH decoloration

Decoloration rate constants as a function of initial MBH concentration is presented in Fig. 3. As can be noted, decoloration rate constants decreased with an increase in initial MBH concentration. Decoloration rate constants for 1, 5, 10, and 20 mgL^{-1} of MBH solution treatment, when introduced voltage was 800 V, and phosphate buffer were changed from 0.3560 to 0.0101 s^{-1} . Under steady conditions, the active species produced in pulse discharge were maintained at specific concentration levels leading to a maximum degradation capability [3].

3.2. Effect of peak-to-peak voltage

Fig. 4 presents the MBH decoloration rate constants as a function of voltage. As can be seen in Fig. 4, MBH decoloration constants increases with an increase in applied voltage. The higher the applied voltage, the larger was the quantity of generated

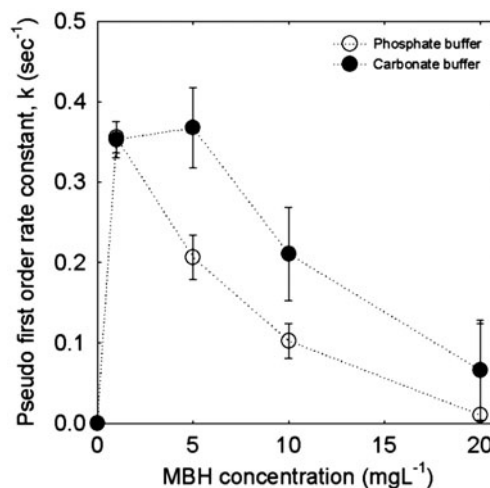


Fig. 3. Pseudo-first-order rate constants for the decoloration of MBH as a function of initial MBH concentrations ($[\text{MBH}]_0 = 1, 5, 10,$ and 20 mgL^{-1} ; $[\text{Phosphate buffer}]_0 = [\text{Carbonate buffer}]_0 = 50 \text{ mM}$; $[\text{Electrode}] = \text{Tungsten}$; $[\text{Applied voltage}] = 800 \text{ V}$; and $[\text{Electrode depth}] = 1.0 \text{ mm}$).

radicals. Nevertheless, it should be noted that the quantity of radicals fixed in the absorbent liquid arrives to a saturation level at very high-voltage [16]. In plasma process, the plasma originating from the high-voltage electrode directly attacks MBH molecules and decomposes water molecules into hydroxyl radicals which then destroy organic bonds [3].

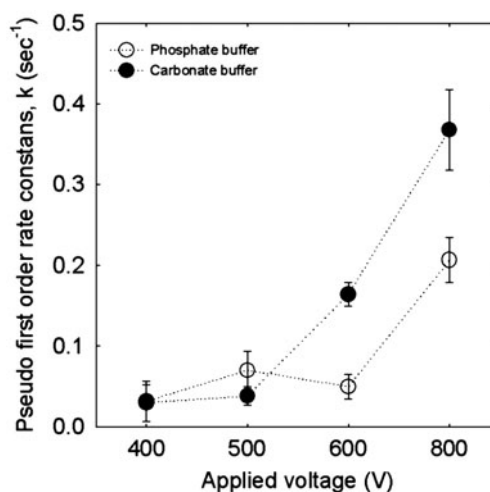


Fig. 4. Pseudo-first-order rate constants for decoloration of MBH as a function of applied voltages ($[\text{MBH}]_0 = 5 \text{ mgL}^{-1}$; $[\text{Carbonate buffer}]_0 = 50 \text{ mM}$; $[\text{Electrode}] = \text{Tungsten}$; $[\text{Applied voltage}] = 400, 500, 600,$ and 800 V ; and $[\text{Electrode depth}] = 1.0 \text{ mm}$).

3.3. Effect of buffer types

Electrons are transferred through the circuit to the cathode, where they combine with protons and oxygen to form water. Charged ions must be transported between the electrodes to maintain a charge balance

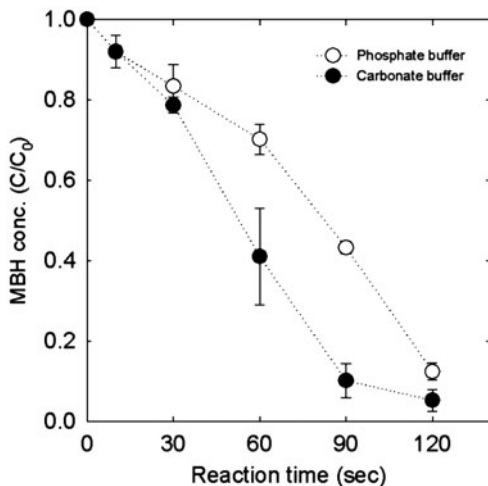


Fig. 5. Removal efficiency for decoloration of MBH as a function of buffer type ([MBH]₀ = 5 mgL⁻¹; [Phosphate buffer]₀ = [Carbonate buffer]₀ = 50 mM; [Electrode] = Tungsten; [Applied voltage] = 800 V; and [Electrode depth] = 1.0 mm).

[17,18]. Buffers are considered as an important component of chemical- and photo-degradation systems to achieve optimum stability of a compound, or to perform a reaction under controlled conditions of pH, buffer concentration, and ionic strength [19]. In

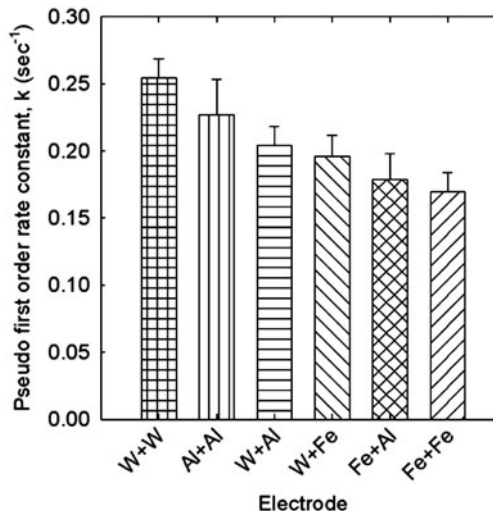


Fig. 7. MBH decoloration rate constant as a function of numbers of electrode ([MBH]₀ = 5 mgL⁻¹; [Carbonate buffer]₀ = 50 mM; [Electrode] = Tungsten, Iron, Aluminum; [Applied voltage] = 800 V; and [Electrode depth] = 1.0 mm).

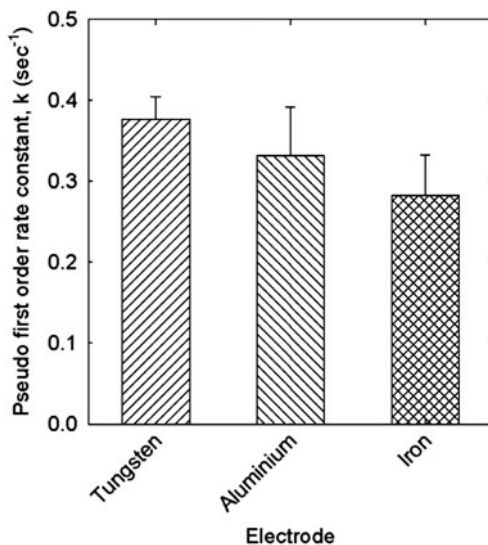


Fig. 6. Pseudo-first-order rate constants for decoloration of MBH as a function of electrode materials ([MBH]₀ = 5 mgL⁻¹; [Carbonate buffer]₀ = 50 mM; [Electrode] = Tungsten, Iron, Aluminum; [Applied voltage] = 800 V; and [Electrode depth] = 1.0 mm).

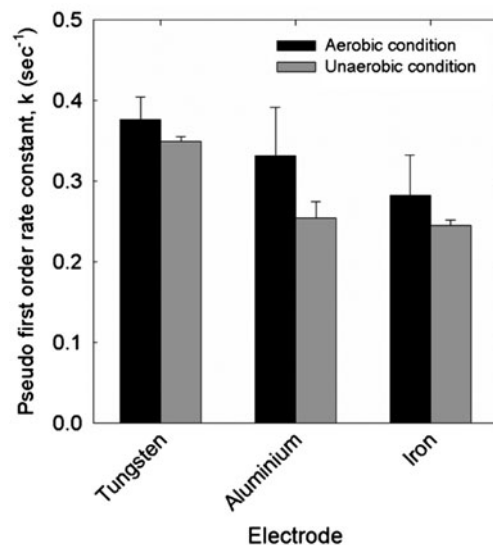


Fig. 8. Pseudo-first-order rate constants of decoloration of MBH as a function of oxygen concentration ([MBH]₀ = 5 mgL⁻¹; [Carbonate buffer]₀ = 50 mM; [Electrode] = Tungsten, Iron, Aluminum; [Applied voltage] = 800 V; [Electrode depth] = 1.0 mm; [DO concentration] = 8, 0 mgL⁻¹; and [Nitrogen gas purging]).

the previous research, many different types of buffers have been used to maintain suitable pH conditions and increase the solution conductivity including phosphate and carbonate [20,21]. Carbonate and phosphate are the most commonly used buffer solutions with optimal performance. Previous studies indicate that increasing buffer concentration can improve power within certain concentration ranges. For example, increasing the phosphate buffer concentration from 50 to 100 mM increased the maximum power density by 45%, but a further increase to 200 mM increased power by only 11% [20]. The use of high concentrations of phosphate is not feasible in practice due to its high cost and the need to avoid phosphate releases into the environment [22]. Effect of buffer types on the MBH decoloration efficiency using the plasma treated was investigated as shown in Fig. 5.

Decoloration efficiency of MBH with carbonate buffer is faster and higher than that of using phosphate buffer.

3.4. Decolorization under different electrode materials

Figs. 6 and 7 show observed decoloration rates for different types/numbers of electrodes. Fig. 6 shows the decoloration rate of MBH using different electrode materials. MBH decoloration is strongly dependent on electrode materials. As shown in Fig. 7, tungsten electrode has demonstrated higher decoloration rate constants due to the decomposition processes of H_2O_2 by catalytic reactions caused by tungsten particles or tungsten ions from the electrode. This phenomenon is more obvious for the bridged discharge mode of operation as the corresponding erosion rate is high [23].

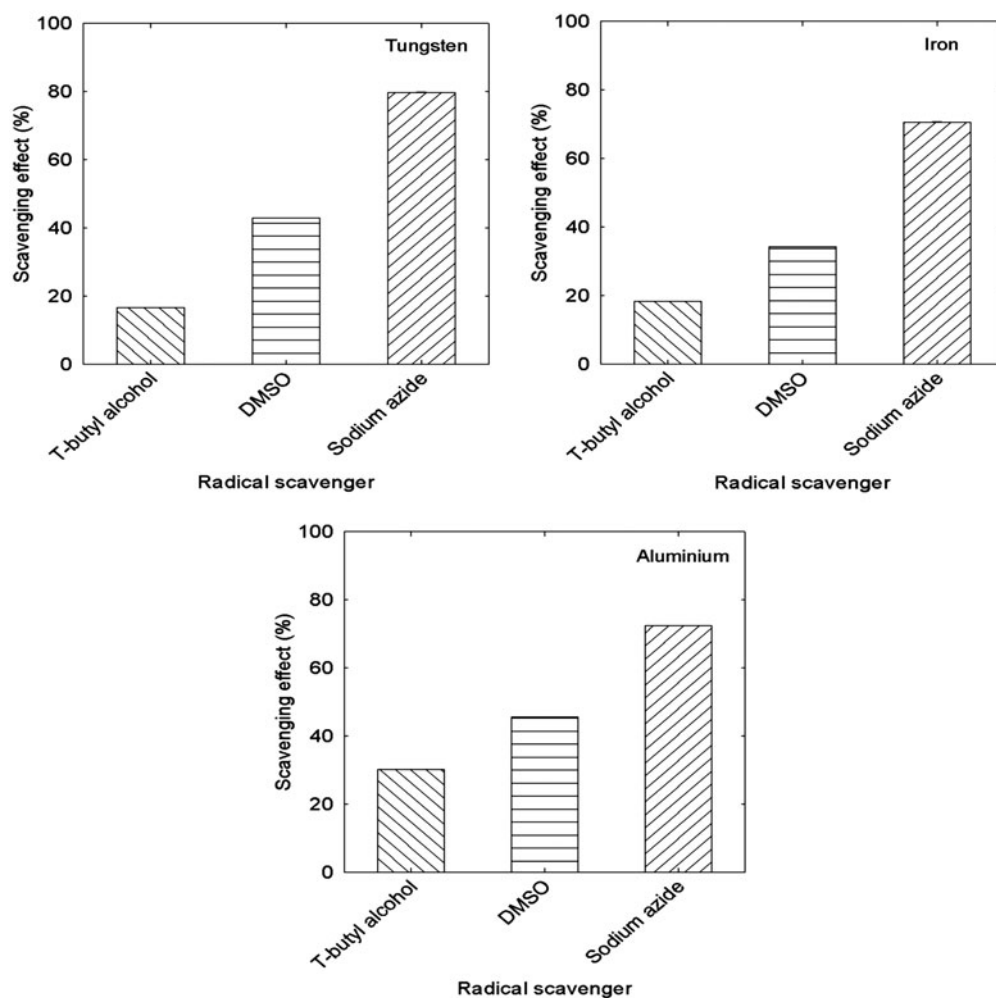


Fig. 9. Scavenging effect of MBH decoloration as a function of radical scavenger ($[MBH]_0 = 5 \text{ mgL}^{-1}$; $[Carbonate \text{ buffer}]_0 = 50 \text{ mM}$; $[Electrode] = Tungsten, Iron, Aluminium$; $[Applied \text{ voltage}] = 800 \text{ V}$; $[Electrode \text{ depth}] = 1.0 \text{ mm}$; and $[Methanol]_0 = [t\text{-butyl alcohol}]_0 = [DMSO]_0 = [Sodium \text{ azide}]_0 = 100 \text{ mM}$).

Fig. 7 shows the degradation of dyes upon electrode addition under the same condition as previous. It is clear that the degradation of dyes increases with an increase in electrode numbers. Discharge intensity increased with an increase in plasma power injected into more electrodes, potentially increasing the amount of active species [24].

3.5. Effect of dissolved oxygen

Fig. 8 presents the effect of dissolved oxygen concentration on decoloration rate constants of MBH. Results indicate that the decoloration of MBH was affected by DO concentration. Decoloration rate constants of MBH increased under aerobic condition. As shown in Fig. 8, oxygen concentration may play an important role in plasma treatment because DO is fundamental to the production of reactive components such as O , OH^- , O_3 , and H_2O_2 . In addition, variation in DO concentration influences pulse properties such as peak current, pulse width, and voltage rising time as DO has large electron attachment process coefficient [25]. Since the electron attachment process reduces the number of electrons, the pulse current decreases with DO concentration. The decrease in current surely decreases the energy delivered to the reactor [26].

3.6. Effect of radical scavengers

A series of experiments was conducted to analyze the relationship between concentrations of radical species and the decoloration of MBH. Effluent streams from the dyeing process are typically heavily colored with high loading of inorganic components of great environmental importance. The presence of high concentrated inorganic component will decrease the activity of oxidation reactions such as methanol, DMSO (dimethylsulfoxide), and sodium azide. These latter chemicals are types of free radical scavenger. Experiments were carried out by adding different radical scavengers (methanol, tert-Butyl alcohol, DMSO, and sodium azide) to the MBH solution during plasma treatment. MBH decoloration was significantly inhibited by the presence of radical scavengers as shown in Fig. 9. During the plasma treatment of MBH, radicals are formed as a component of oxidants, and these may play an important role in the treatment process. The reaction between radicals and radical scavenger occurs more easily than others, and the reaction rate is also faster than the reaction between radicals and MBH. Most of the radicals react with the radical scavenger instead of MBH molecules. The collision

probability between OH radicals and MBH molecules is therefore reduced, leading to a decrease in the decoloration rates with decreasing oxidants concentration [27].

4. Conclusions

Decoloration of MBH using plasma treatment was investigated in this study. Decoloration of MBH was found to depend upon initial concentration of MBH, peak voltage, electrode characteristics, DO concentration, and radical scavengers. Based on the results, the following conclusions were derived:

- (1) Plasma is an efficient technology for the removal of MBH, especially at 5 mgL^{-1} MBH concentration. The decoloration of MBH with carbonate buffer is faster and greater than that of using phosphate buffer.
- (2) When higher-voltage and two electrodes were applied, the decoloration rate of MBH increased. This is due to an increase in plasma power injected into reactor, potentially increasing the amount of active species.
- (3) DO concentration plays an important role in the decoloration of MBH as DO produces more active species. DO has influenced the intensity of plasma such as peak current, pulse width, and voltage rising time.
- (4) Radical scavengers, such as methanol, t-Butyl alcohol, DMSO, and sodium azide, reduce the decoloration efficiency of MBH. Radical scavengers react with active species (OH radicals) instead of with MBH molecules. Decoloration rate is therefore decreased with the concentration increase in radical scavengers.

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