Enhanced degradation of methylene blue by a solution plasma process catalyzed by incidentally co-generated copper nanoparticles
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ABSTRACT
This study presents a catalytic organic pollution treatment using the solution plasma process (SPP) with incidentally co-generated copper (Cu) nanoparticles via Cu electrode erosion. Methylene blue (MB) was used as a model organic contaminant. The treatment time was from 0 to 60 minutes at the plasma frequencies of 15 and 30 kHz. The treatment efficacy using the Cu electrode was compared with that of the tungsten (W) electrode. The high erosion-resistant W electrode provided no W nanoparticles, while the low erosion-resistant Cu electrode yielded incidental nanoparticles (10–20 nm), hypothesized to catalyze the MB degradation during the SPP. The percentage of MB degradation and the hydrogen peroxide (H2O2) generation were determined by an ultraviolet-visible spectrophotometer. The results showed that, after the SPP by the Cu electrode for 60 minutes, the MB was degraded up to 96%. Using the Cu electrode at a high plasma frequency strongly accelerated the Cu nanoparticle generation and MB treatment, although the amount of H2O2 generated during the SPP using the Cu electrode was less than that of the W electrode. The Cu nanoparticles were hypothesized to enhance MB degradation via both homogeneous (release of dissolved Cu ions) and heterogeneous (on the surface of the particles) catalytic processes.

Key words | catalytic degradation, copper nanoparticles, methylene blue, solution plasma

INTRODUCTION
With a constant increase in population, water demand for domestic, industrial, and agricultural applications is also increasing. Due to the excessive usage of chemicals in industry, wastewater from various industries contains harmful compounds. For example, the wastewater from the paper and textile industries is highly contaminated by dyes and hazardous compounds (Ong et al. 2011; Manoj REDDY & SUBRAHMANYAM 2012; Manoj REDDY et al. 2013a). To treat contaminants from these industries, various decontamination methods, including biological treatment, membrane filtration, ion exchange (Thamaraivelan & Noel 2013), and adsorption (Bharathi & Ramesh 2013), have been extensively examined. However, some of these decontamination techniques may just transfer...
contaminants from one phase to another instead of desirably mineralizing them.

Advanced oxidation processes (AOPs) are a promising contaminant mineralization alternative via the generation and reaction of hydroxyl radicals. These radicals could oxidize organic pollutants present in the wastewater and contaminated groundwater (Crimi & Taylor 2007; Siegrist et al. 2011; Manoj Kumar Reddy et al. 2015b; Sacco et al. 2015; Shen et al. 2016; Pankaj et al. 2017; Sarangapani et al. 2017). The oxidation potential of hydroxyl radicals (E0 = 2.8 V) is relatively high in comparison to that of conventional oxidants, such as ozone (E0 = 2.0 V) and hydrogen peroxide (E0 = 1.7 V), making the hydroxyl radical capable of promptly mineralizing various pollutants, including dyes and hazardous volatile and semi-volatile organic compounds. Various AOP techniques, such as photocatalysis, photo-Fenton, and O3/ultraviolet (UV), have been extensively studied and utilized (Wang & Xu 2012; Bokare & Choi 2014). Nevertheless, the limitation of these techniques is the insufficient quantity of the oxidants, especially hydroxyl radical, to sustain and speed up contaminant degradation. To overcome this problem, a catalytic AOP is preferable (Khan et al. 2016; Thao et al. 2017).

Electrical discharge in the liquid phase, also known as the solution plasma process (SPP), has been widely utilized for nanomaterial synthesis, surface modification, water treatment, sterilization, and decomposition of organic contaminants and molecules (Locke et al. 2006; Takai 2008; Manoj Kumar Reddy & Subrahmanyam 2012; Prasertsung et al. 2012; Pootawang et al. 2013; Prasertsung et al. 2013). This process produces highly active species, such as hydroxyl radicals (OH•), hydroperoxyl radicals (HO2•), free electrons (e−), superoxide anions (O2•−), and atomic oxygen anions (O•−) (Yuan et al. 2010; Wong & Mongkolnavin 2016). Since the molecular density of the liquid phase is much higher than that of the gas phase, it is reasonable to expect a higher reaction rate of active species generated by the SPP in comparison to that of other gas phase generations (Pocostales et al. 2010; Tichonovas et al. 2015; Pankaj et al. 2017; Sarangapani et al. 2017).

Solution plasma conditions, such as electrode materials, appear to influence the degradation of organic molecules and the synthesis of nanomaterials. For example, recent research found that among three metals (tungsten (W), copper (Cu), and iron (Fe)), at high pulse frequency, the Fe electrodes strongly promoted the degradation of chitosan, making chitosan more water soluble (Tantiplapol et al. 2015). Similarly, Fe and Cu electrodes could grow carbon nanotubes from propane via AC arc and dielectric barrier discharge plasma, while the W electrode could not (Sun et al. 2016). Nevertheless, to our knowledge, only a few studies investigated the effects of electrode materials on the degradation rate of organic contaminants using the SPP. A recent study reported that, in comparison to the titanium dioxide (TiO2) electrode, using W as a high-voltage electrode in pulse corona discharge with needle-plate electrode geometry caused the erosion of W and released dissolved WO42− ions, which are involved in the catalytic degradation of dimethyl sulfoxide using hydrogen peroxide (H2O2) (Lukes et al. 2011). For instance, platinum-tungsten alloy as a high-voltage electrode decreased the yield of H2O2 produced by a pulsed corona discharge in water. At the same time, when used as high-voltage electrodes, these materials increased the efficiency of the plasma chemical removal of organic compounds from water due to their catalytic effects. When the electrode is coated with a thin ceramic layer, the electric field strength on the electrode surface may be enhanced by the concentration of the pre-discharge current in small open pores. As a result of the inhomogeneous nature of the ceramic layer, the electric field may be higher, and it may be easier than expected to initiate streamers from some spots. Such a system can be promoted with its catalytic activity or be designed as a support for a suitable catalyst of the plasma chemical reactions (Lukes et al. 2011).

In the current study, we hypothesized that low erosion-resistant electrode materials, such as Cu, could be sputtered during plasma treatment, yielding Cu nanoparticles, which are involved in pollution abatement. The Cu nanoparticles were intentionally engineered for use as a solid catalyst to enhance the degradation rate of organic contaminants. Nevertheless, to our knowledge, only a few researchers have investigated the role of incidental nanoparticles on pollution abatement (Glover et al. 2011; Srivastava et al. 2013), and none have investigated the SPP treatment with incidentally co-generated Cu nanoparticles. For this purpose, methylene blue (MB) was used as a model of organic contaminants to evaluate the catalytic treatment in a plasma reactor with different types of electrodes and applied pulse frequencies. Two types of electrodes, one with high erosion resistance (W) and one with low erosion resistance (Cu), were used. The sputtered solid metal particles were characterized in terms of the concentration, shape, and size. The MB degradation extent and rate as well as the formation of H2O2 in the electrical discharge in the solution were also quantified.
EXPERIMENTAL SECTION

Solution plasma setup

The setup of the SPP, modified from our previous study (Tantiplapol et al. 2015), is shown in Figure 1. The needle electrodes, which are 1 mm in diameter and covered by a ceramic tube, were fixed by silicone in a glass reactor and used to generate a pulsed electric discharge. The high-frequency bipolar pulsed DC power supply was connected to the needle electrodes. The frequencies, voltages, and pulse widths used in the experiment are described next.

Solution plasma treatment of methylene blue

The MB powder was dissolved in distilled water to obtain 125 mg/L of the MB solution, which was placed in the glass reactor. The plasma in the solution was produced at the fixed voltage of 1.6 kV and pulse width of 3 μs. Two types of electrodes, which were different in erosion resistance – 0.5% thoriated W and Cu, were used. The frequencies of power supply varied in the range of 15–30 kHz, and the treatment time of the plasma varied at 0–60 minutes. To enhance the uniformity of the MB solution to contact the plasma, the solution was continuously stirred by a magnetic stirrer. To characterize the species in plasma-treated MB solutions, optical emission spectroscopy (OES) was used to monitor the light emitted from the plasma in the wavelength range of 200–1100 nm. The emission was detected at the plasma treatment time of 1 minute, through the quartz glass window, with an optical fiber placed 1 mm in front of the glass chamber. Data were acquired with Avantes software.

The degradation of MB was monitored for every 10-minute interval of plasma treatment using a double beam UV spectrophotometer (Shimadzu) at the wavelength of 668 nm. The degradation percentage was calculated using Equation (1).

\[
\text{% degradation} = \frac{C_0 - C_t}{C_0} \times 100
\]

(1)

where \(C_0\) and \(C_t\) are the initial concentration and the concentration of the MB solution at time \(t\), respectively. All experiments were conducted in duplicate.

H₂O₂ quantification

In SPP treatment, the H₂O₂ can be produced by recombination reaction of OH· radicals. Therefore, the H₂O₂ generated in the solution was determined colorimetrically using the reaction of H₂O₂ with titanyl ions (Ti⁴⁺), giving the yellow-color complex of pertitanic acid (TiO₂H₂O₂) (Chandana et al. 2015).

\[
\text{Ti}^{4+} + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2\text{H}_2\text{O}_2 + 4\text{H}^+
\]

(2)

In brief, 1.00 mL of the solution and 2.0 mL of titanium sulfate (12 g/L in 40% sulfuric acid) were mixed together and diluted to 10.00 mL with distilled water in a volumetric flask. The absorbance of the mixture was measured at 410 nm with a 5-mm colorimetric cuvette. The standard curve was obtained using the standard H₂O₂ solution and is shown in Figure 2.

Microscopic characterization of electrodes and incidentally co-generated Cu nanoparticles

The morphology of the Cu electrode surface was examined by scanning electron microscopy (SEM; JEOL, JSM-6400). To identify the shape and size of the sputtered solid particles obtained from the plasma treatment of MB using a Cu electrode, a transmission electron microscope (TEM; Philips, EM208) was employed. After plasma treatment for 60 minutes, 50 μL of the solution was collected and dispersed in 2 mL of ethanol. A small drop of solution was placed onto a grid prior to evaporation at room temperature overnight. The TEM microscope was operated at an accelerating voltage of 120 kV.
RESULTS AND DISCUSSION

Species in the emission spectra of plasma-treated MB solution

The emission spectra of the plasma-treated MB solution using the two different types of electrodes, W (high erosion-resistant) and Cu (low erosion-resistant), which were observed at a treatment time of 1 minute, are presented in Figure 3. The OES spectra of the plasma-treated MB solution using the W electrode exhibited strong peaks at the wavelengths of 486.0, 656.5, 777.3, and 844.0 nm, corresponding to Hα, Hα, O/ C0 radical, and O/ C0 radical, respectively (Baroch et al. 2008). This was possibly due to the ionic current generated in the MB solution during the solution plasma treatment. As a result, the reactive species could be produced by the decomposition of water molecules (Watthanaphanit et al. 2014). On the other hand, for the Cu electrode, the additional spectrum peaks were observed at the wavelengths of 309.0 and 521.8 nm, corresponding to OH radicals and Cu I, respectively (Tepe et al. 1997). The Cu I species could be generated from the erosion of electrode material during plasma treatment, resulting in Cu particles or ions. This was because the erosion resistance of the Cu electrodes is lower than that of W. The volumetric erosion rate of Cu and W was measured to be 13.4 × 10⁻⁸ and 6.4 × 10⁻⁸ cm³/s, respectively (Holzer & Locke 2008). Therefore, the Cu particle, which was generated by the electrode release of material, was easily formed by electrolysis (Potocký et al. 2009). This hypothesis will be verified later in this study.

Kinetics of MB degradation

Figure 4(a) shows the percentage of MB degradation as a function of treatment time for the two types of electrodes at 15 kHz. The results showed that, after plasma treatment using the W electrode for 10 minutes, the percentage of MB degradation rapidly increased to 40%. After that, a slight increase in the percentage of MB degradation was noticed until the treatment time reached 60 minutes. The maximum percentage of MB degradation treated by plasma using the W electrode was 79%. The degradation of MB was predominantly caused by free radicals, such as hydroxyl that is generated during plasma treatment. The mechanism of MB degradation by hydroxyl radicals has been discussed in detail elsewhere (Manoj Kumar Reddy et al. 2013a; Chandana et al. 2015).

On the other hand, for the plasma treatment using the Cu electrode at 15 kHz, the MB degradation reaction was dramatically enhanced. The percentage of MB degradation by plasma using the Cu electrode was much higher than that of W. The maximum percentage of MB degradation by plasma using the Cu electrode was 92%. A stronger degradation effect from the use of the Cu electrode could be attributed to copper particles or ions, which were generated by the erosion of the Cu electrode via electrolysis during plasma treatment.

Furthermore, the applied pulse frequency played a substantial role in the percentage of MB degradation, as shown in Figure 4(b). Noticeably, the degradation rate of MB was increased with the increase in applied pulse frequency from 15 to 30 kHz. The greater improvement on the degradation rate of MB at a high pulse frequency could be attributed to the energy input increase when the
pulse frequency increased, as previously reported (Kang et al. 2015). The increase of energy input could enhance the number of hydroxyl radicals during plasma treatment and thus promote the MB degradation process (Chandana et al. 2015). In addition, an increase of energy could strongly affect the concentration of Cu nanoparticles. This could be described by an accelerated erosion of Cu electrodes during the plasma treatment, which provided a high number of solid particles. As the result, the MB degradation process could be catalytically enhanced, resulting in a high degradation rate.

According to the result of the MB degradation, the initial rate constants were calculated by fitting the data to the first order rate equation:

\[ -\ln(C_t/C_0) = kt \]  

where \(C_t\) is the concentration of the MB solution at reaction time \((t)\), \(C_0\) is the initial concentration of the MB solution, \(k\) (min\(^{-1}\)) is the degradation rate constant, and \(t\) is the reaction time. A linear relationship between \(-\ln(C_t/C_0)\) and the reaction time for the degradation of MB by plasma (reaction time from 0 to 30 min) is shown in Figure 4(c). The \(k\) value of the degradation of MB by plasma using the W electrode was \(4.2 \times 10^{-2}\) min\(^{-1}\) at 15 kHz. Interestingly, the \(k\) values of degradation of the MB were enhanced and measured as \(6.1 \times 10^{-2}\) min\(^{-1}\) at 15 kHz when the Cu electrode was introduced. The obtained \(k\) value for the plasma treatment using Cu was higher than that of the W electrode.

The pulse frequency clearly affected the MB degradation rate. Obviously, the MB degradation was increased with the increasing pulse frequency. The \(k\) value of the MB degradation treated by plasma at the pulse frequency of 30 kHz was \(8.4 \times 10^{-2}\) min\(^{-1}\). According to the calculation of \(k\), the degradation reaction of MB by plasma was evaluated to be in the following order: Cu at 30 kHz (8.4 \(\times\) 10\(^{-2}\) min\(^{-1}\)) > Cu at 15 kHz (6.1 \(\times\) 10\(^{-2}\) min\(^{-1}\)) > W at 15 kHz (4.2 \(\times\) 10\(^{-2}\) min\(^{-1}\)). Therefore, the finding in this study proved that the SPP treatment using the Cu electrode with high applied pulse frequency (30 kHz) is effective for MB degradation.

**Microscopic change of Cu electrodes and incidentally co-generated Cu nanoparticles**

Figure 5 shows a SEM micrograph of Cu electrodes (a) before and (b) after plasma treatment. The results showed a smooth surface of the Cu electrode before the plasma was applied. However, the electrode surface became rough when the plasma was applied for 60 minutes. This ensured that the erosion of the Cu electrode via material sputtering existed during plasma treatment. Figure 6 shows a TEM micrograph of Cu solid particles generated during plasma treatment of the MB solution by electrode material sputtering. Noticeably, the Cu nanoparticles are nearly spherical with a random orientation. The sizes of the nanoparticles are in the range of 5-10 nm.
Mechanisms of enhanced MB degradation by Cu nanoparticles

The MB degradation is predominantly affected by H$_2$O$_2$, which is generated during plasma treatment by the recombination reaction of hydroxyl radicals as follows (Tantiplapol et al. 2018).

$$\text{OH}^\cdot + \text{OH}^\cdot \rightarrow \text{H}_2\text{O}_2 \quad (4)$$

A couple of possible mechanisms of enhanced MB degradation by Cu nanoparticles formed during the SPP can be described as follows. First, Cu nanoparticles could act as a solid catalyst in MB degradation, as previously described in a recent study (Ndolomingo & Meijboom 2015). These authors proposed the MB degradation mechanism shown in Equation (5).

The peroxide can react on the surface of the Cu nanoparticles leading to the absorption of the reactive species, especially hydroxyl radicals. The MB reacts with hydroxyl radicals, resulting in the decomposition of MB on the surface of the nanoparticles followed by the desorption of by-products from the nanoparticle surface.

Second, these nanoparticles could be transformed into Cu ions through oxidation reaction at the electrode during plasma treatment (Sarahney et al. 2012). As reported in a recent study (Friedrich et al. 2012), Cu ions can also act as a catalyst, which could enhance the Fenton reaction (cupro-Fenton reaction). Therefore, the decomposition of the H$_2$O$_2$, which is generated in the system during plasma treatment by the recombination reaction of hydroxyl radicals, could occur and provide a high number of hydroxyl radicals (as noted in Figure 3) as follows (Friedrich et al. 2012).

$$\text{H}_2\text{O}_2 + \text{Cu}^+ + \text{H}^+ \rightarrow \text{OH}^\cdot + \text{Cu}^{2+} + \text{H}_2\text{O} \quad (6)$$

This result corresponds with the generation of H$_2$O$_2$ during plasma treatment as illustrated in Figure 7. Notably, the amount of H$_2$O$_2$ produced during plasma treatment using the W electrode was dramatically increased with the
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REFERENCES


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In this study, solution plasma was introduced to treat the MB solution. The percentage of plasma-treated MB solution was increased with the increasing plasma treatment time, compared to that of an untreated sample. The degradation rate was greatly affected by the types of electrodes and the applied pulse frequency. The plasma treatment of the MB solution using the Cu electrode and a high pulse frequency strongly promoted the degradation rate of MB. We identified the incidentally co-generated Cu nanoparticles via the Cu electrode erosion during the solution plasma treatment. We also found that these nanoparticles strongly promoted the degradation of the MB solution during the SPP by heterogeneous and/or homogeneous catalytic degradation.


