



THE FORMATION OF REACTIVE OXYGEN SPECIES IN ADVANCED OXIDATION INDUCED BY COLD ATMOSPHERIC PLASMA TECHNOLOGY

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ABSTRACT

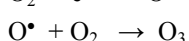
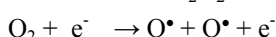
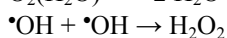
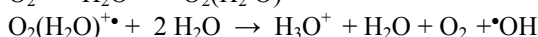
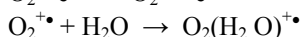
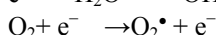
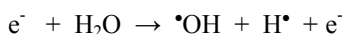
Advanced oxidation induced by cold plasma under the high voltage electrical barrier discharge exhibits a wide use in practice due to be able to produce very high concentrations of reactive oxygen species with short and long life. The reactive oxygen species generated include free radicals ($\cdot\text{OH}$) and other oxidative reagents like ozone, hydrogen peroxide. The quantification of these oxidative components is truly imperative to application in wastewater treatment to design plasma reactors. The concentrations of these species might be determined by many methods. The identification and analysis of these reactive oxygen species were successfully carried out by colorimetric method using the competition reaction of hydroxyl free radicals with ethanol (ETA) and trinitrophenol (TNP); using titanium (IV) as reagent for the quantification of H_2O_2 and HI 38054 test KIT for analyzing ozone and using iodometric method determining total reactive oxygen species. All experimental data were presented in this article.

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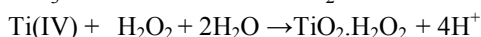
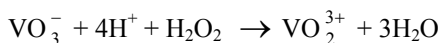
INTRODUCTION

Advanced oxidation induced by cold plasma under high – voltage electrical barrier discharge consists of a large amount of reactive oxygen species. Cold atmospheric plasma is an ionized gas produced by gas electrical discharges including high active species such as electrons, ions, radicals excited atoms and molecules (Locke, 2011; Alexander Fridman, 2008; Sieck, 2000). The formation of short lived hydroxyl radical ($\cdot\text{OH}$) and long-lived chemical species (H_2O_2 , O_3) in aqueous media in advanced oxidation cold atmospheric plasma was identified and quantified depending on plasma activated media (Sieck, 2000). In the presence of H_2O during electrical barrier discharge in the atmosphere the reactions to producing $\cdot\text{OH}$, H_2O_2 and ozone might be as following (Sieck, 2000 and Ketkar, 1991).



Based on these reactions the concentration of reactive oxygen species generated in cold atmospheric plasma based advanced oxidation would increase when oxygen introduces into the plasma reactor. The identification and quantification of these species in advanced oxidation cold atmospheric plasma exhibits an important significance for its application in practice in controlling degradation process of organic pollutants and designing plasma reactor. These oxidative species (reactive oxygen) that formed in advanced oxidation cold atmospheric plasma were determined by many methods, (Bruggeman Leys, 2009; Shih, Locke, 2010;

Locke, 2011; Clotilde Hoffmann, 2013 and Massima Mouele, 2018). Besides, many methods used for quantification of reactive oxygen species were presented in (Sieck, 2002). According these authors, H_2O_2 might be determined by colorimetric method using the following reactions:



In this article the reactive oxygen species such as $\cdot\text{OH}$, O_3 and H_2O_2 were analyzed using UV-Vis spectrophotometry, HI 38054 KIT. Here $\cdot\text{OH}$ was determined by indirect method based on the competition reaction between ETA and TNP in the same experimental conditions.

EXPERIMENTAL PROCEDURE

Chemicals: 2,4,6 – trinitrophenol, ethanol, KI, $\text{Na}_2\text{S}_2\text{O}_3$, Titanium sulfate, H_2SO_4 , H_2O_2 with the analytical purity grade bought from Merck Company are used. The all solutions were prepared prior carrying out experiments.

Apparatus

- Experimental system producing atmospheric cold plasma:
- The system used for this experiments was presented in our previous (Nguyen Van Hoang, 2018)
- The main parameters of experimental system used concluding electric current from 3.5 to 22 mA and electrode potential from 7 to 21 kV (HV). UV-Vis spectrophotometer, Agilent 8453 (USA).
- HPLC Model HP 1100, using diode-array detector. (DAD), Agilent (USA).
- The HI 38054 test KIT, HANNA Instruments.

The experimental procedure

Indirect determination of $\cdot\text{OH}$ free radical in cold atmospheric plasma: The determination of value of $\cdot\text{OH}$ in cold atmospheric plasma, during electric discharge, was carried out based on the competition reaction between TNP and ETA present in the same sample with free radical $\cdot\text{OH}$. The selected two samples were introduced into the reactors. The first sample consisted of 500 mL with TNP and ETA, in which the ratio TNP/ETA = 1/1000 by mol. The second one only consisted of the TNP, without ETA. After a certain time interval the TNP concentration remained in two samples was determined by HPLC method (Clotilde Hoffmann, 2013 and Massima Mouele, 2018).

Determination of ozone generated in cold atmospheric plasma: The HI 38054 is a chemical test KIT that lets determine the ozone concentration in samples within the 0.0 to 2.23 mg/L (Nguyen Van Hoang, 2018).

Determination of H_2O_2 generated in cold atmospheric plasma: The H_2O_2 concentration in the samples was determined by colorimetric method using titanium (IV) sulfate as a reagent, based on the work (Dhingra Gaurav, 2007). An intensive yellow color that develops as a result of the formation of a titanium(IV) peroxy complex was used for determination of H_2O_2 in samples by colorimetric method at the wave length of 400 nm. The titanium (IV) sulfate was prepared by dissolving TiO_2 (1.0 g) in 100 mL H_2SO_4 concentrated ($d = 1.84 \text{ mg/mL}$), then diluted with distilled water and filtered before used. Before used, the H_2O_2 concentration in the stock solution was determined by volumetric titration method using KMnO_4 solution 0.05N (Sun, 2000). The calibration curve of H_2O_2 with the concentrations varying from 2.28 to 36.0 mg/L with titanium (IV) sulfate in the ratio of $\text{Ti(IV)}/\text{H}_2\text{O}_2 = 1/9$ by mol represented in Fig.1.

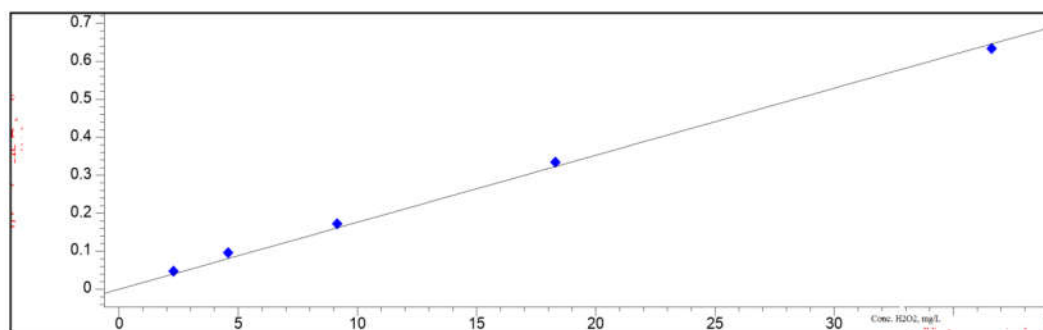


Fig. 1. The calibration curve of H_2O_2

This plot corresponding the equation $Y = 0.0168 \times C_{\text{H}_2\text{O}_2} + 0.0151$ with $R^2 = 0.999$ was used to determination of H_2O_2 concentration in samples from cold atmospheric plasma.

Determination of total oxidative species concentration from cold atmospheric plasma: The total oxidative species concentration from advanced oxidation cold atmospheric plasma was determined based on the reaction with KI solution. The oxidative species

might oxidize KI to produce iodine (I₂). The iodine resulting in then was determined by titration with standard solution Na₂S₂O₃[13]. The total oxidative species activated oxygen equivalent (O^{*}) by the following expression:

$$C_{oxid} = \frac{C_{Na_2S_2O_3} \times V_{Na_2S_2O_3}}{V_{Sample}} \times 16 \times 1000, \text{ mg/L}$$

Here C_{Na₂S₂O₃} (conc), V_{Na₂S₂O₃} (volume) tetrated of Na₂S₂O₃

Pipette 10ml of sample solution from plasma reactor into a 100mL triangular flask. Add 10ml of KI 0.01N solution, cover, shake for 1 minute and let in a dark chamber for 2-5 minutes. Take 1-3 drops of starch indicator into the flask and by using standard solution Na₂S₂O₃(0.01N) to titrate iodine produced (I₂). Determine the equivalence point when the solution turns from blue to colorless.

RESULTS AND DISCUSSION

Identification of the presence of free radical •OH: The identification of •OH produced in advanced oxidation cold atmospheric plasma has been carried out based on the competition reaction between •OH with ethanol and TNP present in the same sample. Comparing the degradation of TNP by cold atmospheric plasma for the reaction time in the presence of ethanol (ETA) or without ETA represented in the Fig. 2.

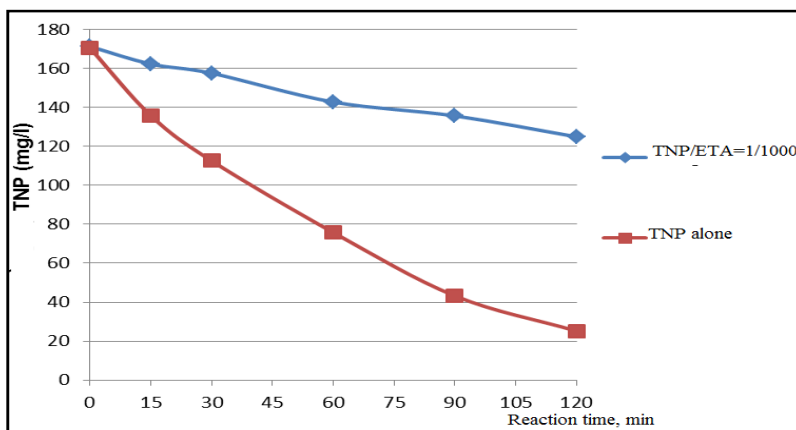


Fig. 2. The degradation of tnp in presence of eta and without eta

The Fig. 2 showed that the in the presence of ETA the degradation of TNP reduced significantly. This is due to the radical •OH prefers reacting with ETA with high reaction constant (1.8 × 10⁹ M⁻¹.s⁻¹) than the TNP. For 120 min in the cold atmospheric plasma, without ETA, TNP could reduce from 170 mg/L to 25 mg/L, while with ETA present in sample, TNP concentration only reduced to 124 mg/L. This demonstrated that free radical •OH generated in advanced oxidation cold plasma in aqueous media as suggested above.

Determination of ozone generated in advanced oxidation cold atmospheric plasma: The result of concentrations of ozone generated during electrical discharge was determined by using HI 38054 KIT represented in Fig.3.

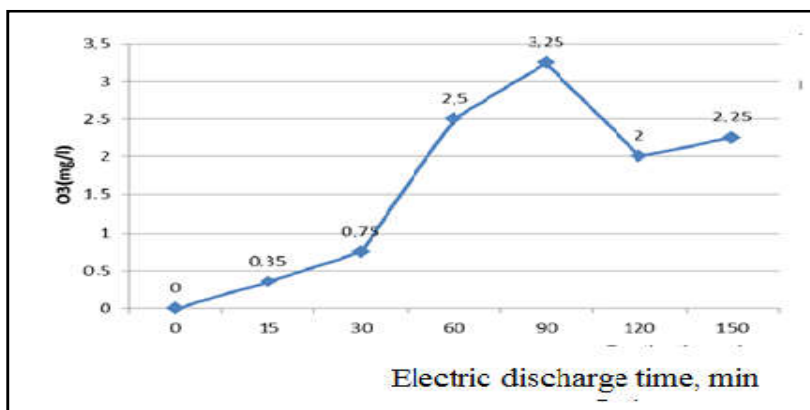


Fig. 3. Formation of O₃ concentration in coldatmospheric plasma

The experimental data from Fig.2 indicated that the maximum value of O₃ reach 3.25 mg/L for 90 min, then decrease. The decrease of O₃ after 90 min might be explained by the increasing temperature of in the reactor that caused a decrease of O₃ in the

water sample. In fact that, the temperature of water sample in the reactor was determined presented in Table 1, for the 90 min the temperature increased from 30.2 to 58.4 °C. This is the reason causing decrease of O₃. This phenomenon is fitted into the result of the paper (Hanna Instrument, 2007).

Table 1. The variation of temperature of water sample in reactor

Electric Discharge time, min	0	15	30	60	90	120	180
Temperature (°C)	30.2	44.4	53.2	56.2	58.4	58.4	58.3

Determination of H₂O₂ generated in advanced oxidation cold atmospheric plasma: The generation of H₂O₂ in the water sample during electrical discharge was analyzed, represented in Fig. 4.

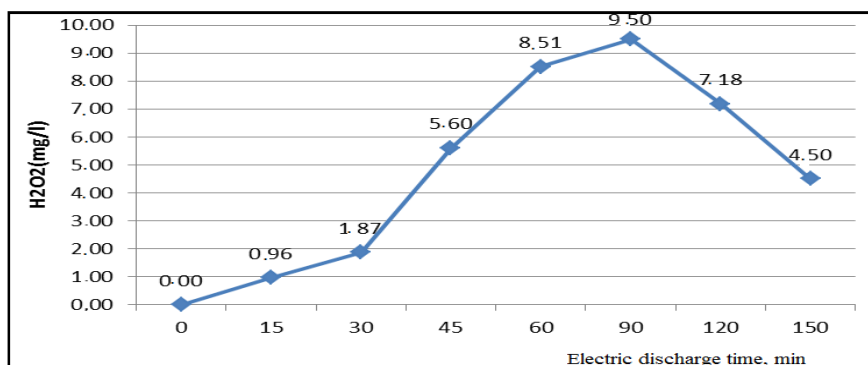


Fig. 4. The generation of H₂O₂ during electrical discharge

The experimental data from Fig.4 indicated that the concentration of H₂O₂ increased from beginning time to 90 min of reaction time, reached maximum value of 9.50 mg/L (for 90 min), then decreased. The decrease of H₂O₂ concentration is also due to the increasing temperature in reactor. It is similar to the case of O₃ suggested above.

Determination of total oxidative species concentration in advanced oxidation cold atmospheric plasma: The result of analysis of total oxidative species concentration in advanced oxidation cold plasma was represented in Fig.5. The obtained result in Fig.5 has shown that the total oxidative species concentration during electrical discharge increased with the reaction time increasing. In the both cases (line 1, 2) using air flow from atmosphere and adding oxygen into the air flow, the total oxidative species concentration has rapidly increased from beginning reaction time then slowly and reach approximately constant value at the constant experimental parameters like electric current and temperature used. But there is a strange thing when adding a certain amount of H₂O₂ to the reactor, the initial concentration of the oxidant (line 3) decreases, then increase faster and then slower. The decrease of oxidant species might be explained by the consuming them with H₂O₂. The fresh reactive oxygen species generated in advanced oxidation cold atmospheric plasma consisting of main free radical •OH might directly react with H₂O₂.

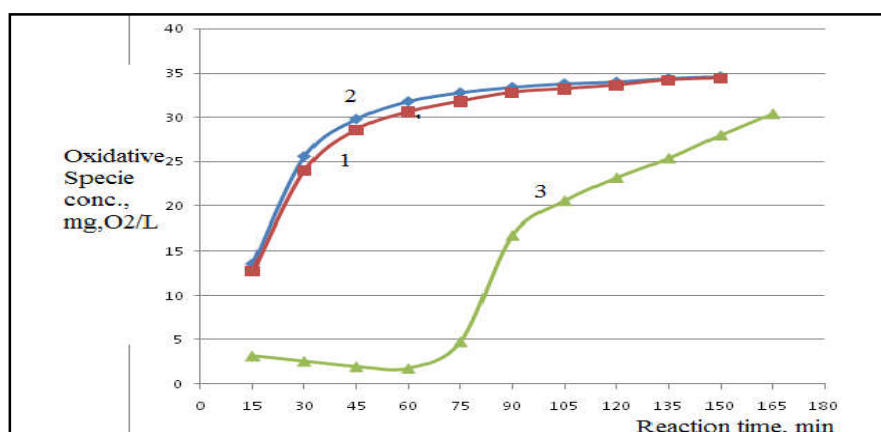


Fig. 5. The formation of oxidative species in cold atmospheric plasma

- Using air flow from atmosphere.
- Adding oxygen into air flow.
- Using air flow and adding H₂O₂ into reactor

Conclusion

There are many reactive oxygen species of advanced oxidation cold atmospheric plasma such as free radicals hydroxyl, hydrogen peroxide, ozone. These reactive components of plasma were determined by UV-Vis absorption, HPLC methods and using HI 38054 KIT ozone. The obtained experimental data have exhibited that during electrical discharge at high voltage producing cold

plasma consisting of reactive oxygen components with high concentrations. That is why the advanced oxidation cold plasma has been widely used in practice.

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