DECOMPOSITION OF POLLUTANTS IN WATER BY PULSED-DISCHARGE PLASMA AND THE CLARIFICATION OF THE DECOMPOSITION PROCESS

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in O₂

\[ V_{chg} = -14.14kV, \ d = 4mm, \ 1 \ needle \]

Water bath

GC-MS

OES

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Outline

1. Introduction
   • background & objectives

2. Decomposition characteristics of methylene blue in an aqueous solution by pulsed plasma exposure
   • experimental apparatus & conditions
   • results
   • conclusions

   • experimental apparatus & conditions
   • results
   • conclusions
Introduction

Background

- Advanced oxidation processes (AOPs), such as ozone-UV oxidation, wet oxidation, photo-catalytic oxidation, pulsed discharge, etc. are known as effective methods for water purification.

- When a pulsed voltage is applied and a discharge plasma is generated above water, a mixture of effects causing water purification is expected, through high energy electrons, high-oxidation-potential species (OH, O₃, H₂O₂, etc.), UV radiation from excited species, etc.
Introduction

Background (cont’d)

- The production mechanism of the active species from ambient gas, and the influence of the active species on decomposition of pollutants, need to be clarified to control the discharge in order to achieve effective water purification.

- Clarifying decomposition process of pollutants is also essential for the proper control of the discharge plasma for better water purification.

- The safety verification based on detailed identification of by-products is important for practical application.

Objective

- To clarify the decomposition characteristics & decomposition process of pollutants in water, when a pulsed discharge is generated above the water. (The clarification of the decomposition process is followed by the identification of by-products.)
Introduction

Objectives (cont’d 1)

(1) For the clarification of decomposition characteristics

Methylene blue (C\textsubscript{16}H\textsubscript{18}ClN\textsubscript{3}S \cdot 3H\textsubscript{2}O) is used as a substitution of pollutants
   • easy to be decomposed
   • colourimetric determination for concentration measurement

Pulsed discharge plasma is generated above methylene blue aqueous solution with different background gas (N\textsubscript{2}, O\textsubscript{2}, Ar, N\textsubscript{2}-O\textsubscript{2}, Ar-O\textsubscript{2})

Decomposition rate & gaseous by-products are measured.

The effects of background gas composition on decomposition rate and reaction formulae, namely, the production & disappearance of active species, are examined, based on the results.
Objectives (cont’d 2)

(2) For by-product identification & decomposition process estimation

Phenol is used as a substitution of pollutants

• simple structure having benzene ring
• influence of plasma exposure on benzene ring cleavage can be simulated.
Pulsed discharge plasma is generated above phenol aqueous solution with different background gas (Ar, O₂, Ar-O₂).

By-products in a solution and a background gas are detected by GC-MS and IAS (FT-IR), respectively.
Decomposition process is examined, based on the result of the by-product identification.
Decomposition characteristics of methylene blue in an aqueous solution by pulsed plasma exposure

C$_{16}$H$_{18}$ClN$_3$S $\cdot$ 3H$_2$O
Experimental Apparatus

Gas feeding
- **flow rate**
  6 L/min atm. pressure

- **N₂-O₂ mixture**
  \[ \text{N}_2/\text{O}_2 = 100/0 \]
  \[ 90/10 \]
  \[ 80/20 \]
  \[ 60/40 \]
  \[ 40/60 \]
  \[ 20/80 \]
  \[ 10/90 \]
  \[ 5/95 \]
  \[ 0/100 \]

- **Ar-O₂ mixture**
  \[ \text{Ar}_2/\text{O}_2 = 100/0 \]
  \[ 90/10 \]
  \[ 80/20 \]
  \[ 60/40 \]
  \[ 40/60 \]
  \[ 20/80 \]
  \[ 10/90 \]
  \[ 5/95 \]
  \[ 0/100 \]

Electrode configuration
- single & multi needle (φ1.5 x 19mm)
- a water bath (φ119 x 12mm in depth, 0.13L capacity)

Methylene blue decom.
Experimental Apparatus

**Methylene blue decom.**

➢ Gas feeding
  • **flow rate**
    6 L/min atm. pressure
  • **N<sub>2</sub>-O<sub>2</sub> mixture**
    \[ \frac{N_2}{O_2} = \begin{array}{c|c}
    100 & 0 \\
    90 & 10 \\
    80 & 20 \\
    60 & 40 \\
    40 & 60 \\
    20 & 80 \\
    10 & 90 \\
    5 & 95 \\
    0 & 100 \\
  \end{array} \]
  • **Ar-O<sub>2</sub> mixture**
    \[ \frac{Ar}{O_2} = \begin{array}{c|c}
    100 & 0 \\
    90 & 10 \\
    80 & 20 \\
    60 & 40 \\
    40 & 60 \\
    20 & 80 \\
    10 & 90 \\
    0 & 100 \\
  \end{array} \]

➢ Electrode configuration
  - single & multi needle (φ1.5 x 19mm)
  - a water bath (φ119 x 12mm in depth, 0.13L capacity)

**Discharge chamber**
  - φ140 x 100 mm high
  - 1.5 L capacity

**Mixing chamber**

**Energy input**
\[ = 0.4 \text{ J/pulse} \]

**Current - Voltage**

- \( V_g \)
- \( I_g \)

**Current - Time**

- \( V_g = 5 \text{ kV} \)
- \( I_g = 1.5 \text{ µA} \)

**CH2**

**CH1**

**Digital Strage Osilloscope**

**GND**

**Energy input**
\[ = 0.4 \text{ J/pulse} \]
Photographs of discharges in O_2, N_2-O_2, & N_2

✓ Discharges are generated above water.
✓ Those discharges tend to shrink as the time proceeds.
Decomposition rate of methylene blue for different gas composition

- **O₂ atmosphere**
- **N₂ atmosphere**
- **N₂ – O₂ mixture**

**Graph:**
- **Y-axis:** decomposition rate [%]
- **X-axis:** operation energy density [J/(g • ppm)]
- **Legend:**
  - **N₂:O₂=100:0**
  - **N₂:O₂=90:10**
  - **N₂:O₂=80:20**
  - **N₂:O₂=60:40**
  - **N₂:O₂=40:60**
  - **N₂:O₂=20:80**
  - **N₂:O₂=10:90**
  - **N₂:O₂=60:40**
  - **N₂:O₂=5:95**
  - **N₂:O₂=0:100**

**Key:**
- 1 needle
  - d=4mm

**Note:**
- 15 min
Decomposition rate and concentrations of gaseous products in N$_2$-O$_2$

- Decomposition rate is the highest in O$_2$ atmosphere, decreases rapidly with N$_2$ additive, and slightly increase in N$_2$ atmosphere.
- O$_3$ concentration decreases rapidly when N$_2$ is added.
- NO and NO$_2$ are produced.
Decomposition rate and O$_3$ & NO$_x$ concentrations in N$_2$-O$_2$

Possible reactions in N$_2$-O$_2$ discharge above water$^{[1,2,3]}$.

1. $\text{H}_2\text{O} + \text{e} \rightarrow \text{OH} + \text{H}$
2. $\text{O}_2 + \text{e} \rightarrow 2\text{O} + \text{e}$
3. $\text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M}$
4. $\text{N}_2 + \text{e} \rightarrow \text{N} + \text{N} + \text{e}$
5. $\text{N}_2 + \text{e} \rightarrow \text{N}_2(\text{A}) + \text{e}$
6. $\text{N}_2(\text{A}) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{N}_2 + \text{H}$
7. $\text{N} + \text{O} + \text{M} \rightarrow \text{NO} + \text{M}$
8. $\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$
9. $\text{N}_2(\text{A}) + \text{O} \rightarrow \text{NO} + \text{N}$
10. $\text{NO} + \text{O} \rightarrow \text{NO}_2$
11. $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$

- Discharges spread over the water surface.
- OH radicals are produced by the reaction between electrons and H$_2$O vapour.
  
  \[ \text{H}_2\text{O} + \text{e}_{\text{fast}} \rightarrow \text{OH} + \text{H} + \text{e}_{\text{slow}} \]
- The emission from OH (308 nm) is observed in OES.

Decomposition characteristics at high oxygen mixture ratio

- **At high O₂ mixture ratio**, O₃ is produced by the reaction (3) with the high concentration, and higher decomposition rate is obtained.

  - O₃ is found to contribute to the methylene blue decomposition.

Possible reactions in N₂-O₂ discharge above water:

1. \( H_2O + e \rightarrow OH + H \)
2. \( O_2 + e \rightarrow 2O + e \)
3. \( O_2 + O + M \rightarrow O_3 + M \)
4. \( N_2 + e \rightarrow N + N + e \)
5. \( N_2 + e \rightarrow N_2(A) + e \)
6. \( N_2(A) + H_2O \rightarrow OH + N_2 + H \)
7. \( N + O + M \rightarrow NO + M \)
8. \( N + O_3 \rightarrow NO + O_2 \)
9. \( N_2(A) + O \rightarrow NO + N \)
10. \( NO + O \rightarrow NO_2 \)
11. \( NO + O_3 \rightarrow NO_2 + O_2 \)
**Decomposition characteristics in N\(_2\) atmosphere**

In **N\(_2\)** atmosphere, O\(_3\) is not produced in the plasma, but the decomposition rate slightly increases.

It is probably due to the contribution of **OH radicals**, produced by the reaction between **N\(_2\) molecules excited in metastable state** (N\(_2\)(A\(^3\)Σ\(_u^+\))) and H\(_2\)O vapour, as shown in (6).

The possible reactions in N\(_2\)-O\(_2\) discharge above water are:

1. \(\text{H}_2\text{O} + e \rightarrow \text{OH} + \text{H} \)
2. \(\text{O}_2 + e \rightarrow 2\text{O} + e\)
3. \(\text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M}\)
4. \(\text{N}_2 + e \rightarrow \text{N} + \text{N} + e\)
5. \(\text{N}_2 + e \rightarrow \text{N}_2(A) + e\)
6. \(\text{N}_2(A) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{N}_2 + \text{H}\)
7. \(\text{N} + \text{O} + \text{M} \rightarrow \text{NO} + \text{M}\)
8. \(\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2\)
9. \(\text{N}_2(A) + \text{O} \rightarrow \text{NO} + \text{N}\)
10. \(\text{NO} + \text{O} \rightarrow \text{NO}_2\)
11. \(\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2\)
The decomposition rate of methylene blue stays low values, and at the same time, NO\textsubscript{x} concentration increases. Also, in this region, O\textsubscript{3} concentration remains at low values.

Namely, \(\text{O}_3\) is probably used to produce N and NO, respectively, as shown in (8) and (11), not to be used for methylene blue decomposition.

\(\text{O}_3\) generation is inhibited since O atoms are consumed by NO\textsubscript{x} production in (7), (9) and (10).
Decomposition characteristics in N$_2$-O$_2$ mixture

- Since discharges spread over the water surface, OH radicals are produced, and OH radicals contribute to methylene blue decomposition.

  \[ \text{H}_2\text{O} + e_{\text{fast}} \rightarrow \text{OH} + \text{H} + e_{\text{slow}} \]

  This can be the basis of methylene-blue decomposition.

- At high oxygen concentration, O$_3$ contribute to the decomposition of methylene blue.

- At high nitrogen concentration, OH radicals, produced by the reaction between N$_2$ excited in metastable state (N$_2$(A$^3\Sigma_u^+$)) and H$_2$O vapour, contribute to the methylene blue decomposition.

  \[ \text{N}_2(A^3\Sigma_u^+) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} + \text{N}_2 \]
Decomposition characteristics in Ar-O₂

- **In Ar**, filamentary discharges spread more widely over the water surface.

- Many OH radicals can be produced by the reactions between electrons in the plasma and H₂O (vapour).
- The OH radicals probably contribute to the decomposition of methylene blue.

• In Ar, filamentary discharges spread more widely over the water surface.

Further

- OH radicals may be produced by the reaction between H₂O vapour and ³P₂ and ³P₀.

  \[
  \text{H}_2\text{O} + \text{Ar}_m^* \rightarrow \text{OH} + \text{H} + \text{Ar}
  \]
Conclusions for the decomposition characteristics of methylene blue

Decomposition characteristics of methylene blue in an aqueous solution by the exposure of pulsed-discharge plasma are investigated for different background-gas composition.

✓ OH radicals, produced by the reaction between electrons and H₂O vapour, contribute to methylene blue decomposition.

\[ \text{H}_2\text{O} + e_{\text{fast}} \rightarrow \text{OH} + \text{H} + e_{\text{slow}} \]

This can be the basis of methylene-blue decomposition, and this contribution is significant in Ar atmosphere.

✓ O₃ contributes to the decomposition of methylene blue at high oxygen concentration.

✓ OH radicals, produced by the reaction between molecules (atoms) in metastable state and H₂O vapour, make contribution to methylene blue decomposition.

\[ \text{H}_2\text{O} + \text{N}_2(A^3\Sigma_u^+) \rightarrow \text{OH} + \text{H} + \text{N}_2 \]

\[ \text{H}_2\text{O} + \text{Ar} (3P_2 & 3P_0) \rightarrow \text{OH} + \text{H} + \text{Ar} \]

✓ In N₂-O₂ mixture, NOₓ probably decomposes O₃, and inhibits O₃ generation. (namely, O atoms are consumed by NOₓ production.)
By-product identification from phenol in an aqueous solution by pulsed plasma exposure, and the estimation of phenol decomposition process

\[ \text{C}_6\text{H}_5\text{OH} \]
Experimental apparatus & Conditions

Blumlein HV pulse generator

1M Ω

Transmission lines (100 pF/m, 50m)

Max-Electronics LS40-10R1

400k Ω

Chg. voltage -14kV

rotary switch (20pps)

DC POWER SUPPLY

Gas feeding
Ar-O₂ mixture
Ar/O₂ = 0 /100
5 / 95
10 / 90
50 / 50
100 / 0
flow rate: 6L/m atm. pressure

Discharge chamber
φ140x100 mm high
1.5 L capacity

Phenol
3000 ppm
70g

Purity
Ar: 99.99%
O₂: 99.5%

Electrode configuration
a needle (φ1.5 x 19mm) &
a water bath (φ119 x 12mm in depth, 0.13L capacity)
Experimental apparatus & Conditions

Analysis of liquid sample

- Gas Chromatograph Mass Spectrometer
  - Shimadzu GCMS-QP2010 Plus with column: DB-17 ms

By-products analysis in liquid sample

- LC-MS: useful, but no library.
- GC-MS: only evaporated molecules are detected, but libraries for molecules are provided.
Pulsed discharge for different gas composition

When oxygen concentration in Ar-O<sub>2</sub> mixture increases, the number of discharge decrease but each of the discharge tends to thicken.
Decomposition rate of phenol in aqueous solution

(Initial phenol concentration: 3000 ppm)

- Ar/O2 = 100 / 0
- Ar/O2 = 90 / 10
- Ar/O2 = 50 / 50
- Ar/O2 = 0 / 100

- (1506 ppm)
- (1650 ppm)
- (1904 ppm)
- (2177 ppm)

(Exposed time [min])

- O2 atmosphere

- Ar atmosphere
Identification of products in liquid (Ar atmosphere)

Chromatogram of sampled liquid after 120 min of plasma exposure

after discharge (120 min)
Ar / O₂ = 100 / 0

Catechol
Identification of products in liquid (Ar atmosphere)

Chromatogram of sampled liquid

Concentration variation of products

- phenol
- 4-hydroxy-2-cyclohexene-1-one
- catechol
- hydroquinone
- pyrogallol
- hydroxyhydroquinone

✓ The products have benzene ring → no cleavage reaction
✓ No active species is detected in the off-gas. → OH radical
Identification of products in liquid (O₂ atmosphere)

Chromatogram of sampled liquid after 120 min of plasma exposure

after discharge (120 min)
Ar / O₂ = 0 / 100

- Formic acid
- Maleic anhydride
- Phenol
- Succinic anhydride
- Catechol
- Hydroquinone

5-(2-hydroxyethylidene)-2(5H)-furanone

Retention time [min]
Identification of products in liquid (O₂ atmosphere)

Chromatogram of sampled liquid after 120 min of plasma exposure

- Formic acid
- Phenol
- Maleic anhydride
- Succinic anhydride
- Catechol
- Hydroquinone

Chromatogram after discharge (120 min)
Ar / O₂ = 0 / 100

Retention time [min]

Intensity [a.u.]

Intensity [%]

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Detected products by GCMS & those in liquid

By-products detected by GCMS

- Formic acid (HCOOH)
- Maleic anhydride (C₄H₄O₃)
- Succinic anhydride (C₄H₄O₃)
- 5-(2-hydroxyethylidene)-2(5H)-furanone (C₆H₆O₃)

The flow of GCMS analysis

- Liquid sample from the water bath electrode
- Injector 150 °C
- Column (oven) ~ 230 °C
- MS

✓ Dehydration reaction takes place in GC.

Maleic anhydride

Maleic acid

+ H₂O

by-product in liquid detected by-product
GCMS analysis of maleic acid aqueous solution

For confirmation, maleic acid aqueous solution is analysed by GCMS

maleic acid aqueous solution → Injector 150 °C → GC Column (oven) ~ 230 °C → MS

Chromatogram of maleic acid aqueous solution

- No spectrum for maleic acid is detected, and only the spectrum of maleic anhydride is detected.
- Maleic acid in the sample is detected as maleic anhydride (acid anhydride) by dehydration reaction in GC.
Products detected by GCMS & those in liquid

**By-products detected by GCMS**

- **Formic acid**
  - \( \text{HCOOH} \)
  - \( (\text{HCOOH}) \)
- **Maleic anhydride**
  - \( \text{C}_4\text{H}_2\text{O}_3 \)
  - \( (\text{C}_4\text{H}_2\text{O}_3) \)
- **Succinic anhydride**
  - \( \text{C}_4\text{H}_4\text{O}_3 \)
- **5-(2-hydroxyethylidene)-2(5H)-furanone**
  - \( \text{C}_6\text{H}_8\text{O}_3 \)

**Dehydration reaction in GC**

- Maleic anhydride → Maleic acid + \( \text{H}_2\text{O} \)
- Succinic anhydride → Succinic acid + \( \text{H}_2\text{O} \)
- 4,6-dihydroxy-2,4-hexadienoic acid → 5-(2-hydroxyethylidene)-2(5H)-furanone + \( \text{H}_2\text{O} \)

**By-products in the phenol aqueous solution**

- **Formic acid**
  - \( \text{HCOOH} \)
  - \( (\text{HCOOH}) \)
- **Maleic acid**
  - \( \text{C}_4\text{H}_2\text{O}_3 \)
  - \( (\text{C}_4\text{H}_2\text{O}_3) \)
- **Succinic acid**
  - \( \text{C}_4\text{H}_4\text{O}_3 \)
  - \( (\text{C}_4\text{H}_4\text{O}_3) \)
- **4,6-dihydroxy-2,4-hexadienoic acid**
  - \( \text{C}_6\text{H}_8\text{O}_3 \)
  - \( (\text{C}_6\text{H}_8\text{O}_3) \)
Identification of by-products in off-gas (O\textsubscript{2} atmosphere)

Infrared absorbance spectra of off-gas from the discharge chamber

- CO\textsubscript{2} and CO are produced from phenol.
- O\textsubscript{3} is produced from the background gas.
① Phenol is decomposed by 1,3-dipolar addition reaction with O₃, and 4,6-dihydroxy-2,4-hexadienoic acid is produced.

② 4,6-dihydroxy-2,4-hexadienoic acid is decomposed into two fragments by 1,3-dipolar addition reaction.
   - Fragments contain four carbon atoms: maleic acid or succinic acid
   - Fragment contains two carbon atoms: oxalic acid (not detected)

③ Formic acid (HCOOH), CO₂ and CO are produced from oxalic acid (HOOC-COOH)
   \[
   \text{HOOC-COOH} \rightarrow \text{HCOOH} + \text{CO}_2 \\
   \text{HOOC-COOH} \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O} \quad \text{(T. Kakimoto et al.: J. Phys. Chem. 91, 2366 (1987))}
   \]
The concentrations of \textit{by-products} produced by the cleavage of an \textbf{aromatic ring} increase with the increase of O$_2$ mixture ratio.

The concentration of O$_3$ increase with the increase of O$_2$ mixture ratio.

O$_3$ cleaves an aromatic ring of phenol.
Products with an aromatic ring decrease rapidly by the mixture of O₂ into Ar.

4-hydroxy-2-cyclohexene-1-one is produced only in Ar atmosphere.
Conclusions

In Ar atmosphere

- **OH** etc.
- 4-hydroxy-2-cyclohexene-1-one
- Catechol
- Hydroquinone
- Oxalic acid
- Formic acid
- CO

No open ring reaction

In O₂ atmosphere

- **O₃**
- 1,3-dipoler addition
- 4,6-dihydroxy-2,4-hexadienoic acid
- Maleic acid
- Succinic acid
- CO₂
- Formic acid

In Ar-O₂ mixture

| Increase proportionally with the mixture ratio of O₂. |
| decrease by O₂ mixture. |

- Oxalic acid

OH

Phenol