ROS/RNS generation by various discharge plasma

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Background & Objective

Plasma treated water

- Plasma treated water is produced by dissolution of some active species in plasma into water.
- Reactive oxygen species (ROS) and reactive nitrogen species (RNS) are produced in the plasma treated water.
- ROS/RNS play important roles in the fields of medicine[1] and agriculture[2].

To use the plasma treated water effectively and efficiently, it is important to control the ROS/RNS concentration.

Objective

- To investigate and control the kinds and quantities of ROS/RNS in plasma treated water.

- We used a plasma jet, a corona discharge, a pulsed discharge, and a packed-bed dielectric barrier discharge (PB-DBD) to produce plasma treated water.

- We investigated ROS/RNS concentration in the water.

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Experimental apparatus & conditions – plasma jet

**Power supply**
- Applied voltage: AC 13 kV\textsubscript{p-p}
- Frequency: 17 kHz
- Input power: 4 W

**Photograph**
- w/o plasma
- w/ plasma

**Diagram**
- Ar (10 L/min)
- Copper tube (\(\phi 3 \times 2\) mm)
- Aluminium sheet
- Glass tube (\(\phi 6 \times 3\) mm)
- Deionised water (200 mL)
- \(\text{N}_2/\text{O}_2\) mixture ratio: 100/0, 80/20, 60/40, 40/60, 20/80, 0/100
- Autosampler
- Vial
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Experimental apparatus & conditions – corona discharge

- Applied voltage: +15 kV
- Discharge current: 0.4 mA
- Input power: 6 W

Background Gas
- Ar/O₂ = 80/20, 60/40, 40/60 %
- N₂/O₂ = 60/40, 40/60 %
- Flow rate: 2.0 L/min
Experimental apparatus & conditions – pulsed discharge

- **Charged voltage:** 14.14 kV
- **Pulse repetition rate:** 20 pps

**Background gas**

Ar, O₂, N₂

Ar/O₂ = 80/20, 60/40, 40/60, 20/80 %

N₂/O₂ = 80/20, 60/40, 40/60, 20/80 %

N₂/Ar = 80/20, 60/40, 40/60, 20/80 %

**Flow rate:** 5.0 L/min
Experimental apparatus & conditions – PB-DBD

- Glass ball (φ 3.0 mm)
- Rod (φ 2 mm)
- Glass tube
- Mesh
- Gas-Mixing Chamber: Ar, N₂, O₂
- Applied voltage: AC 8 - 26 kV
- Frequency: 12 kHz
- Input power: 6 - 15 W
- Background gas: Ar, O₂, N₂
  - Ar/O₂ = 80/20, 60/40, 40/60, 20/80 %
  - N₂/O₂ = 80/20, 60/40, 40/60, 20/80 %
  - N₂/Ar = 80/20, 60/40, 40/60, 20/80 %
- Flow rate: 2.0 L/min

High Performance Liquid Chromatograph

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**Comparison of H$_2$O$_2$ concentration**

- **Plasma jet**
  - Ar
  - Ar + N$_2$
  - Ar + N$_2$/O$_2$ (80/20)
  - Ar + N$_2$/O$_2$ (60/40)
  - Ar + N$_2$/O$_2$ (40/60)
  - Ar + N$_2$/O$_2$ (20/80)
  - Ar + O$_2$

- **Corona**
  - Ar:O$_2$ = 80:20
  - Ar:O$_2$ = 60:40
  - Ar:O$_2$ = 40:60
  - Ar:O$_2$ = 20:80
  - O$_2$:N$_2$ = 80:20
  - O$_2$:N$_2$ = 60:40
  - O$_2$:N$_2$ = 40:60
  - O$_2$:N$_2$ = 20:80

- **Pulse**
  - Ar
  - Ar:O$_2$ = 80:20
  - Ar:O$_2$ = 60:40
  - Ar:O$_2$ = 40:60
  - Ar:O$_2$ = 20:80
  - O$_2$
  - O$_2$:N$_2$ = 80:20
  - O$_2$:N$_2$ = 60:40
  - O$_2$:N$_2$ = 40:60
  - O$_2$:N$_2$ = 20:80
  - N$_2$
  - N$_2$:Ar = 80:20
  - N$_2$:Ar = 60:40
  - N$_2$:Ar = 40:60
  - N$_2$:Ar = 20:80

- **PB-DBD**
  - Ar
  - Ar:O$_2$ = 80:20
  - Ar:O$_2$ = 60:40
  - Ar:O$_2$ = 40:60
  - Ar:O$_2$ = 20:80
  - O$_2$
  - O$_2$:N$_2$ = 80:20
  - O$_2$:N$_2$ = 60:40
  - O$_2$:N$_2$ = 40:60
  - O$_2$:N$_2$ = 20:80
  - N$_2$
  - N$_2$:Ar = 80:20
  - N$_2$:Ar = 60:40
  - N$_2$:Ar = 40:60
  - N$_2$:Ar = 20:80

- **3800 µg/Wh**

- **w/o N$_2$**

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- **No H$_2$O$_2$ is detected in the case of PB-DBD, but O$_3$ is detected in the off-gas of the PB-DBD.**
  - \( \text{O}_3 \) does not contribute to produce H$_2$O$_2$, though \( \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \) is reported.

- **H$_2$O$_2$ is mainly produced from the reaction:**
  - \( \text{H}_2\text{O} + \text{e}_{(\text{fast})} \rightarrow \text{OH} + \text{H} + \text{e}_{(\text{slow})} \),
  - \( \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \).

- **Pulsed discharge without N$_2$ gas can effectively produce H$_2$O$_2$.**
Comparison of NO$_2^-$ concentration

No NO$_2^-$ is produced in the case of PB-DBD.

To produce NO$_2^-$ is required for generation plasma in the vicinity of water.

NO$_2^-$ is effectively produced in pulsed discharge with N$_2$ gas.

NO$_2^-$ production may prohibit H$_2$O$_2$ production.
Comparison of NO$_3^-$ concentration

PB-DBD

- PB-DBD off-gas sparging can produce only NO$_3^-$.
- Pulsed discharge with N$_2$ gas and PB-DBD off-gas sparging with N$_2$-O$_2$ mixture can effectively produce NO$_3^-$.
- NO$_3^-$ production may also prohibit H$_2$O$_2$ production.
Conclusions

- We generated an Ar plasma jet, a positive DC corona discharge and a positive pulsed discharge above water, sparged PB-DBD off-gas into water, and then investigated ROS/RNS in the water using HPLC.

  - \( \text{H}_2\text{O}_2 \) can be produced from the following reaction:
    \[
    \text{H}_2\text{O} + e_{(\text{fast})} \rightarrow \text{OH} + \text{H} + e_{(\text{slow})}, \quad \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2.
    \]
  - \( \text{O}_3 \) does not contribute to produce \( \text{H}_2\text{O}_2 \).
  - Generating plasma in the vicinity of water is necessary to produce \( \text{H}_2\text{O}_2 \) and \( \text{NO}_2^- \) into water.
  - \( \text{NO}_x^- \) production may prohibit \( \text{H}_2\text{O}_2 \) production.
  - Pulsed discharge plasma is effective to produce \( \text{H}_2\text{O}_2 \) (3800 \( \mu \text{g/Wh} \)) and \( \text{NO}_2^- \) (400 \( \mu \text{g/Wh} \)).
  - PB-DBD off-gas sparging can only and effectively produce \( \text{NO}_3^- \) (2500 \( \mu \text{g/Wh} \)).

Detailed presentation
  Corona: “Generation of ROS in water by DC corona discharge exposure”, 11p-A28-13 (finished)
  Pulse : “Production of ROS/RNS in water by pulsed discharge exposure”, 13p-P11-3
Thank you for your attention.