Micro-organic pollutant removal by VUV/UV process: Bench- and pilot-scale studies

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Photochemical processes play an important role in water processes. Direct photolysis and photon(UV)-AOP will be very important in micropollutant control.
Both bench- and pilot-scales studies were important for micro-pollutant removal evaluation by AOPs.

Mini-fluidic photoreaction system provide a powerful tool to study the photochemical process in water.

- Install various lightsources: low-pressure lamp, med-pressure lamp, VUV/UV lamp, UV-LED, excimer lamp, etc.
- Accurate fluence determination.
- Online measurement of the sample absorbance.
- Fast kinetic determination.
- VUV/UV and sole UV outputs with identical UV fluence.
Water supply in rural area in East China

**Rural area in East China: rich-region**

- **Flat-land region**
- **Mountain regions and islands**

The urban and people in rural should have the same water quality in East China, so the water supply apparatus should be upgraded.
Vacuum UV technology – AOP

VUV can be strongly absorbed by water to form •OH. Because the VUV process does not need any additional chemical reagents, it can be an effective and convenient AOP for the degradation of organic contaminants in water.

$$\text{H}_2\text{O} + h\nu(\text{VUV}) \rightarrow \cdot\text{OH} + \text{H}$$

$$\text{H}_2\text{O} + h\nu(\text{VUV}) \rightarrow \cdot\text{OH} + \text{H}^+ + \text{e}^-$$
VUV light source

Low-pressure mercury lamp (254 nm and 185 nm i.e. VUV/UV)

- Monochromaticity (185 nm 254 nm)
- High efficiency (30–40%)
- High power (1–1000 W)
- Long life (16000 hours)

Synthetic quartz was used

Excilamps (172 nm)

Cited from http://www.hcei.tsc.ru

LED

Cited from http://www.hcei.tsc.ru
VUV/UV problems

Low VUV power output from the LP lamp (8% of 254 nm photons)

Low transmittance in air and water

It is necessary to develop a high efficiency VUV technology for water treatment.

How to determine and monitor the VUV output?

It is a challenge to develop a high accurate bench-scale VUV experimental device. The conventional used quasi-collimated beam apparatus can not work for VUV study.

Cited from Wang et al. Photochem. Photobiol. 2010
Objectives

This study aim to investigate the micro-pollutant removal by VUV/UV process in rural area.

1. By using the bench-scale MVPS, degradation kinetics, impact factors (pH, inorganic anions, and NOM) and toxicity variation of five typical pesticides by VUV/UV were discussed.

2. The pilot-scale tests were performed to evaluate the technical and economic feasibility of the VUV/UV process for pesticide removal in small-scale water treatment.

3. A green and simple method to evaluate the VUV efficiency was developed.
2 Mini-fluidic VUV photoreaction system

- VUV/UV and sole UV outputs with identical UV fluence.
- Accurate fluence determination.
- Online measurement of the sample absorbance.
- Fast kinetic determination.

- aldicarb (ALD)
- alachlor (ALA)
- chloroneb (CHL)
- methiocarb (MET)
- atrazine (ATR)
The UV and VUV fluence rates output by MVPS were determined to be $8.88 \times 10^{-4}$ and $4.93 \times 10^{-5}$ einstein m$^{-2}$, respectively.
3 Pilot reactor

Schematic diagram of the pilot reaction system consisting of three series-connected VUV/UV reactors.
4 Results and discussion

4.1 UV and VUV/UV exposure

Pesticide degradation by VUV/UV and UV alone followed well pseudo-first-order reaction kinetics ($r^2 > 0.99$)

VUV/UV process was much more efficient and energy-saving than the UV process for pesticide removal. This is mainly due to the highly oxidative HO• produced by VUV photolysis of water. Direct VUV photolysis of pesticides could be neglected.

All Pesticides were degraded by >90% after VUV/UV irradiation for VUV fluence = 12 mJ cm$^{-2}$, UV fluence = 156 mJ cm$^{-2}$.
4.2 Effect of pH and inorganic ions value

In the VUV/UV process, Cl$^-$ and NO$_3^-$ could compete for HO• against a target pesticide. As SO$_4^{2-}$ reacted slowly with HO•, its competition for HO• was insignificant. Moreover, the formation of HO• via SO$_4$$^{2-}$ produced under VUV/UV irradiation may also promote pesticide degradation to some extent.
4.3 Effect of HCO$^{3-}$ and NOM

As typical HO• scavengers, HCO$_3^-$ and NOM inhibited pesticide degradation by VUV/UV.

\[ \text{HO}^• + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{•^-} \]

\[ \text{HO}^• + \text{NOM} \rightarrow \]

\[ k_{21} = 8.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1} \]

\[ k_{24} = 2.5 \times 10^4 \text{ (mg/L)}^{-1}\text{s}^{-1} \]
4.4 Degradation, mineralization and solution toxicity change ($C_0 = 5$ mg L$^{-1}$).

5 mg L$^{-1}$ was purposely used for each pesticide.

The toxicity change of pesticide solutions during the VUV/UV process was assessed with luminescent bacteria. The I values were reduced by 74.8%, 61.0%, 68.8%, 49.8% and 33.7% for ALD, ALA, CHL, MET and ATR solutions, respectively, after 30 min irradiation.
4.5 Pilot study

Pilot-scale tests were conducted with a once-through VUV/UV reaction system. The effects of pH, inorganic anions (Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻) and NOM on pesticide removal were also examined and the results were similar to those obtained in the bench-scale study.
$E_{EO}$ value evaluation

### Table 1

$E_{EO}$ values\(^a\) for removal of mixed pesticides in sand-filtered water by the pilot reaction system.

<table>
<thead>
<tr>
<th>$Q$ (m(^3) h(^{-1}))</th>
<th>$E_{EO}$ (kWh m(^{-3}) Order(^{-1}))</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ALD</td>
<td>ALA</td>
</tr>
<tr>
<td>0.6</td>
<td>$-$</td>
<td>0.59</td>
</tr>
<tr>
<td>1.2</td>
<td>0.28</td>
<td>0.56</td>
</tr>
<tr>
<td>1.8</td>
<td>0.27</td>
<td>0.59</td>
</tr>
<tr>
<td>2.4</td>
<td>0.29</td>
<td>0.60</td>
</tr>
</tbody>
</table>

\(^a\)Pump energy consumption is included.

\(^b\) $E_{EO}$ cannot be calculated because of a rapid and complete removal of ALD.
4.6 Long term running

Continuous operation performance of the pilot reaction system for removal of mixed pesticides in sand-filtered water ($C_0 = 10 \, \mu g \, L^{-1}$ each, $Q = 0.6 \, m^3 \, h^{-1}$).
4.6 VUV fluence determination method

\( \text{H}_2\text{O}_2 \) was formed in DI water during VUV irradiation.

\[
\begin{align*}
\text{H}_2\text{O} \xrightarrow{\text{VUV}} & \text{HO}^\cdot + \text{H}^\cdot \\
\text{HO}^\cdot + \text{HO}^\cdot & \rightarrow \text{H}_2\text{O}_2 \\
\text{HO}^\cdot + \text{H}^\cdot & \rightarrow \text{H}_2 \\
\text{H}^\cdot + \text{H}^\cdot & \rightarrow \text{H}_2 \\
\text{H}_2\text{O}_2 \xrightarrow{\text{UV}} & \text{HO}^\cdot + \text{HO}^\cdot \\
\text{H}_2\text{O}_2 + \text{HO}^\cdot & \rightarrow \text{HO}_2^\cdot + \text{H}_2\text{O} \\
\Phi_{185\ nm} & = 0.33 \\
k & = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \\
k & = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \\
k & = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \\
\Phi_{\text{H}_2\text{O}_2} & = 0.555 \\
k & = 3.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}
\end{align*}
\]

\[
q = \frac{r_{\text{H}_2\text{O}_2} V}{\Phi} = 0.024
\]

Getoff and Schenck (18) reported a quantum yield of 0.022
H₂O₂ generation as a function of irradiation time, pH value and dissolve oxygen.

H₂O₂ formation as a function of irradiation time

\[ y = 0.80 \times \]
\[ R^2 = 0.9992 \]
In summary, the micro-pollutant removal by VUV/UV process was discussed for the water supply in rural area:

- The bench-scale test on MFPS investigated the effects of pH values, water matrix components (e.g., inorganic anions and NOM). The pesticide mineralization rates were lower than their degradation rates, but the toxicity of pesticide solutions was obviously reduced after the VUV/UV treatment.

- The pilot results shows that the economically acceptable $E_{EO}$ values (0.27 - 1.52 kWh m$^{-3}$ Order$^{-1}$) and the stable performance of the pilot reaction system suggested a good application potential of the VUV/UV process for pesticide removal in small-scale water treatment.

- A new green method for VUV output determination and monitoring was proposed.
Thanks for your attention!