Removal of Emerging Contaminants from aqueous solution by a novel Electro-Peroxone-ACF (EOA) process

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Outline

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2. Research contents
3. Result and discussion
4. Summary
Emerging Contaminants (ECs)

The pollution of water by “Emerging Contaminants" has become a major global environmental problem.

ECs such as perfluorochemical (PFOS), endocrine disruptors (EDCs), pharmaceuticals and personal care products (PPCPs), polycyclic aromatic hydrocarbons (PAHs) and brominated flame retardants (BFR) are constantly discharged into the water environment.

Risk of Emerging Contaminants

Toxicological studies show that ECs are of chronic toxicity to microorganisms, amphibians and fish even at trace levels of concentration.

Conventional water treatment can not effectively remove ECs.

Thus, it is urgent to develop novel water treatment technologies for removing ECs from water with high efficiency and low consumption.


Jeanne et al. found greatly reduced sperm viability caused by Tetracycline had passed from father to son in pseudoscorpions by inheritance. They suggest a similar effect could occur in humans and other species.

(Jeanne A. Zeh et al. Scientific Reports, 2012)

Currently, biological method, membrane filtration, and physicochemical methods are applied for ECs removal.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Removal Effect</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
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<tbody>
<tr>
<td>Biological method</td>
<td>unsatisfactory</td>
<td>Low cost</td>
<td>Poor stability</td>
</tr>
<tr>
<td>Membrane filtration (RO)</td>
<td>Fairly well</td>
<td>effective</td>
<td>Fouling and high cost</td>
</tr>
<tr>
<td>Physical adsorption</td>
<td>fair</td>
<td>Simple operation</td>
<td>Difficult to regenerate</td>
</tr>
<tr>
<td>Chemical oxidation</td>
<td>fair</td>
<td>Running steadily</td>
<td>High cost and low efficiency</td>
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Direct reaction:  
Organic pollutants + O₃ (E₀=2.08V) → product or intermediate products; low speed and selective oxidation

Indirect reaction:  
Organic pollutants + HO· → intermediate products or CO₂ + H₂O  
higher oxidation potential and react speed without selectivity for most of organic compounds; HO· (E₀=2.80V)
Indirect reaction: (homogeneous and heterogeneous catalysis of ozone)

$\text{O}_3/\text{Fe}^{2+}$, $\text{O}_3/\text{Cu}^{2+}$, $\text{O}_3/\text{UVA}$, $\text{O}_3/\text{Fe}^{2+}/\text{UVA}$, $\text{O}_3/\text{H}_2\text{O}_2$, $\text{O}_3/\text{AC}$, $\text{O}_3/\text{MnO}_2$, $\text{O}_3/\text{TiO}_2$, etc.
Advantages:

1) Rapid adsorption of trace organic pollutants

\[ ACF + \text{pollutant} \leftrightarrow ACF - \text{pollutant} \] (1)

2) Hydrogen peroxide is generated by the reaction of AC and O₃, which then acts with O₃ to generate hydroxyl radicals

\[ AC + H_2O + O_3 \rightarrow AC^+ + H_2O_2 + O_2^- \] (2)

\[ 2O_3 + H_2O_2 \rightarrow 2 \cdot OH + 3O_2 \] (3)

\[ ACF - \text{pollutant}^+ \cdot OH \rightarrow \text{byproducts} \] (4)

3) AC is a green “catalyst” without risk of heavy metal leaking

Disadvantages:

1) Relatively low efficiency.
2) AC served as an initiator/a promoter but not as a catalyst in AC-peroxone process.
3) AC-peroxone process alter the surface morphologies and surface functional groups of AC.

Theoretical hypothesis:

\[ AC + H_2O + O_3 \rightarrow AC^+ + H_2O_2 + O_2^- \]

\[ AC^+ + e^- \rightarrow AC \]

Inject electron onto ACF

\[ 2O_3 + H_2O_2 \rightarrow 2 \cdot OH + 3O_2 \]

Research contents

Target pollutant—nitrobenzene (NB)

✓ **Source**
   Industrial wastewater of printing, pharmacy, petrochemical engineering, etc.

✓ **Character and distribution**
   Stability of Structures, hydrophobic, refractory, and widespread.

✓ **Toxicity**
   Oxidation or complexation with hemoglobin, causes acute intoxication, accompanied with nausea, vomiting, headache and other symptoms.

 structural formula of NB

 NB contamination of Song hua river in 2005
Research contents

Reactor design

★ Reactor size:
  High: 15cm, Diameter: 7cm
★ Concentration and volume of NB:
  12mg/L, 500mL
★ Plate electrode size:
  3.5cm × 10cm
★ The way of sampling:
  Interval 4 min
★ Test method:
  HPLC

Xianke Zhang, Yu Zhou, Chun ZHAO*, et al., Electric field induced activated carbon fiber (ACF) cathode transition from an initiator/a promoter into an electrocatalyst in ozonation process[J], Chemical Engineering Journal, 2016,304: 129-133.
Result and discussion

Kinetic analyses of NB removal

1. All processes follow pseudo-first-order kinetics, the removal efficiency of EOA is much higher than the others.

2. NB can hardly be removed by ozone alone and electricity alone.

3. NB can be removed by E-ACF process with a high speed, which may be due to the high absorption ability of ACF.

4. There is a coupling effect between ozone, ACF, and electrolysis.

1. In EOA process, ACF can maintain the activity even after 100 times recycle. ($K_{app}$ decreased slowly from $14.90 \times 10^{-2}$ min$^{-1}$ to $12.18 \times 10^{-2}$ min$^{-1}$)

2. In OA process, ACF almost lost activity after 10 times recycle.

Result and discussion

Adsorption

1. ACF has a large adsorption capacity for NB, and the adsorption of NB decreases obviously with increasing the recycle times.

2. The cathode electric field has little influence on the adsorption of NB by ACF (Fig.(b)).

Effect of current density and ozone concentration

1. As shown in fig. (a), the optimum current intensity of NB degradation is 2.86 mA/cm$^2$. Massive generation of hydrogen peroxide (a kind of hydroxyl radical scavenger) could lead to the decrease of NB removal efficiency.

2. Excessive amount of hydrogen peroxide indicates that insufficient of ozone, so increasing the ozone concentration further increases the NB degradation efficiency (fig. (b)).

Result and discussion

Effect of initial pH

1. The initial pH of solution had great influence on O₃/ACF system (Fig.(a)). NB removal efficiency increased with the elevate of pH value due to hydroxide ion could promote the decompose of ozone.

2. Initial pH had little impact on removal rate of NB in EOA process.

Hydrogen peroxide concentration during reaction

The hydrogen peroxide which generates in the E-peroxone-ACF system is consumed by ozone, and generate hydroxyl radical which can react with NB.

Fig.(a) The concentration of hydrogen peroxide changes in E-ACF system

Fig.(b) The concentration of hydrogen peroxide changes in E-peroxone-ACF system

Result and discussion

Effect of radical scavenger

The removal rate decreased rapidly by added 1 mmol/L radical scavenger (methanol, ethanol or TBA) in E-peroxone-ACF system.

OH radical is the main oxidant!

Result and discussion

The effect of reaction to the surface of ACF

\[ ACF_{\text{Virgin}} \]

ACF react with \( O_3 \) for 100 times
\( (O_3/ACF) \)

ACF react with \( O_3 \) for 100 times under the protect of cathodic electric field
\( (E\text{-peroxone-ACF}) \)

Cathodic electric field can protect ACF to avoid the destruction of ACF surface in ozonation.

Result and discussion

Effects of reaction to the surface structure and functional groups of ACF

Table Comparison of the surface properties and three kinds of ACF

<table>
<thead>
<tr>
<th>ACF Sample</th>
<th>S\text{BET} (m²/g)</th>
<th>S\text{micropore} (m²/g)</th>
<th>V\text{micropore} (m³/g)</th>
<th>V\text{total} (m³/g)</th>
<th>Acidic functional groups (µmole/g)</th>
<th>Basic functional groups (µmole/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACF\text{vigin}</td>
<td>697.44</td>
<td>663.52</td>
<td>0.287</td>
<td>0.331</td>
<td>376</td>
<td>477</td>
</tr>
<tr>
<td>ACF\text{O3}</td>
<td>587.00</td>
<td>504.25</td>
<td>0.217</td>
<td>0.278</td>
<td>553</td>
<td>187</td>
</tr>
<tr>
<td>ACF\text{E-O3}</td>
<td>671.67</td>
<td>634.32</td>
<td>0.239</td>
<td>0.320</td>
<td>358</td>
<td>504</td>
</tr>
</tbody>
</table>

E-peroxone-ACF process does not alter the surface morphologies and the acidic/basic functional groups of ACF after long time service.

Result and discussion

Effects of reaction to the surface structure and functional groups of ACF

Fig. FTIR of $\text{ACF}_{\text{virgin}}$, $\text{ACF}_{\text{E-O}_3}$, and $\text{ACF}_{\text{O}_3}$ after 100 times recycle

Result and discussion

Reaction mechanism:

\[ ACF + NB \leftrightarrow ACF - NB \]
\[ ACF + O_3 \leftrightarrow ACF - O_3 \]
\[ ACF + O_2 \leftrightarrow ACF - O_2 \]
\[ ACF - NB + ACF - O_3 \rightarrow \text{byproducts} + H_2O_2 \]
\[ H_2O_2 + ACF - O_3 \rightarrow ACF^+ - O_2 + \bullet OH \]
\[ ACF^+ - O_2 + 2e^- + H_2O \rightarrow ACF + H_2O_2 \]
\[ ACF - O_2 + 2e^- + 2H_2O \rightarrow ACF + 2H_2O_2 \]
\[ ACF - NB + \bullet OH \rightarrow \text{byproducts} \]

ACF was induced from an initiator/a promoter into an electrocatalyst in ozonation by free electrons injection.

EOA process can enhance the removal efficiency of refractory organic contaminations.

Cathodic electric field can protect ACF to avoid ozone oxidation to destroy the surface of ACF.

ACF can be regenerated in situ in the EOA process.

The cathodic ACF combined with ozone can provide effective and sustainable approach to water treatment.
Extended research based on persulfate

E-persulfate-ACF

**Direct reaction:**
pollutants+ $S_2O_8^{2-}$ ($E_0=2.01V$) $\rightarrow$ product or intermediate products; only for few organic compounds: such as BTEX.

**Indirect reaction:**
pollutants+ $SO_4^{2-}$ $\cdot$ $\rightarrow$ product or intermediate products; for unsaturated hydrocarbon and organic compounds containing benzene ; $SO_4^{2-}$ ($E_0=2.60V$), high react speed, high potential; low cost

**Activated carbon activation:**

Yang, B. et. al.. Water Res. 2016, 100, 413-420.
Free electron injection on carbon based cathode:

$$\text{ACF} + S_2O_8^{2-} \rightarrow \text{ACF}^+ + \text{SO}_4^{-}$$

$$\text{ACF} \leftarrow \text{ACF}^+ + e^-$$

**Electro-persulfate-ACF (E-PS-ACF) process**
E-PS-ACF applied for Carbamapine (CBZ) degradation

1. All processes follow first-order kinetics. The removal efficiency of E-PS-ACF is much higher than the others.

2. CBZ can hardly be removed by PS alone and electricity alone.

3. There is a coupling effect between persulfate, ACF, and electrolysis.

Fig. Reaction kinetics of CBZ removal
Extended research based on persulfate

E-PS-ACF

Fig. (a) Degradation of CBZ by PS-ACF process with ACF recycled for 50 times

Fig. (b) Degradation of CBZ by E-PS-ACF process with ACF recycled for 100 times

1. With the increase of ACF recycle times, the removal efficiency of CBZ decreases gradually in PS-ACF system.

2. With the increase of ACF recycle times, the removal efficiency of CBZ almost unchanged in E-PS-ACF system.

Zhen Liu, Chun ZHAO*, et al, Chemical Engineering Journal, 2018, 343: 28-36..
Cathodic electric field can protect ACF to avoid persulfate oxidation or destroy the surface of the ACF.

## E-PS-ACF

Table Comparison of the pore texture properties and surface groups of ACF

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m²·g⁻¹)</th>
<th>$S_{\text{micropore}}$ (m²·g⁻¹)</th>
<th>$V_{\text{micropore}}$ (cm³·g⁻¹)</th>
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<th>Acidic functional groups (μmol·g⁻¹)</th>
<th>Basic functional groups (μmol·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACF&lt;sub&gt;virgin&lt;/sub&gt;</td>
<td>624.46</td>
<td>557.71</td>
<td>0.259</td>
<td>0.291</td>
<td>408</td>
<td>505</td>
</tr>
<tr>
<td>ACF&lt;sub&gt;E-PS100&lt;/sub&gt;</td>
<td>589.38</td>
<td>525.66</td>
<td>0.243</td>
<td>0.276</td>
<td>389</td>
<td>534</td>
</tr>
<tr>
<td>ACF&lt;sub&gt;PS50&lt;/sub&gt;</td>
<td>376.48</td>
<td>330.42</td>
<td>0.154</td>
<td>0.180</td>
<td>595</td>
<td>355</td>
</tr>
</tbody>
</table>

ACF<sub>E-PS100</sub> was the ACF reacting in E-PS-ACF system for 100 times.
ACF<sub>PS50</sub> was the ACF reacting in PS-ACF system for 50 times.

E-PS-ACF process does not alter the surface morphologies, BET, and acidic-basic functional group of ACF after long times recycle.

Extended research based on persulfate

E-PS-ACF

Fig. FTIR of ACF_virgin, ACF reacted with persulfate (PS-ACF), ACF reacted in E-persulfate (E-PS-ACF).

A spiral electrochemical reactor

The reactor consists of a cylindrical shell, an inlet/port, an outlet/port, and a winding electrode assembly inside the shell.

When the reactor is electrified with oxidants, such as ozone and/or persulfate, it can produce hydroxyl radical and sulfate radical. Most organic pollutants are filtrated, adsorbed, and degraded by the cathodic membrane from the raw water.
Acknowledgement

- National natural science foundation (No.51308563)
- Central university basic research fund (No.106112013CDJZR210006)
- The Frontier Interdisciplinary Training Project of Fundamental Research Funds for the Central Universities of China (No. 2018CDQYCH0053)
Thanks for your attention!