2018 UK-China Workshop on Water-wise cities and smart water systems

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

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Outline

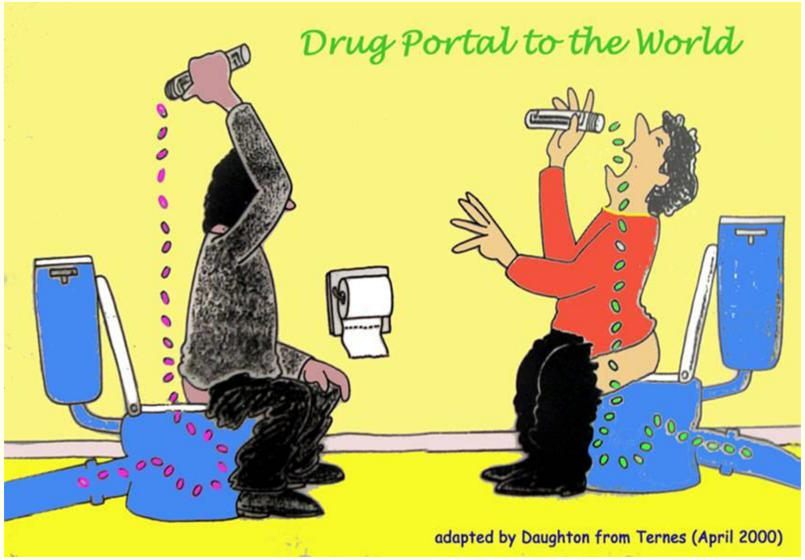
1. Back ground

2. Research contents

3. Result and discusstion

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.

Madden, J.C., et al. oxicology Letters, 2018. 185(2): p. 85. Sarmah, A.K., et al. Chemosphere, 2017. 65(5): p. 725.

Risk of Emerging Contaminants

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

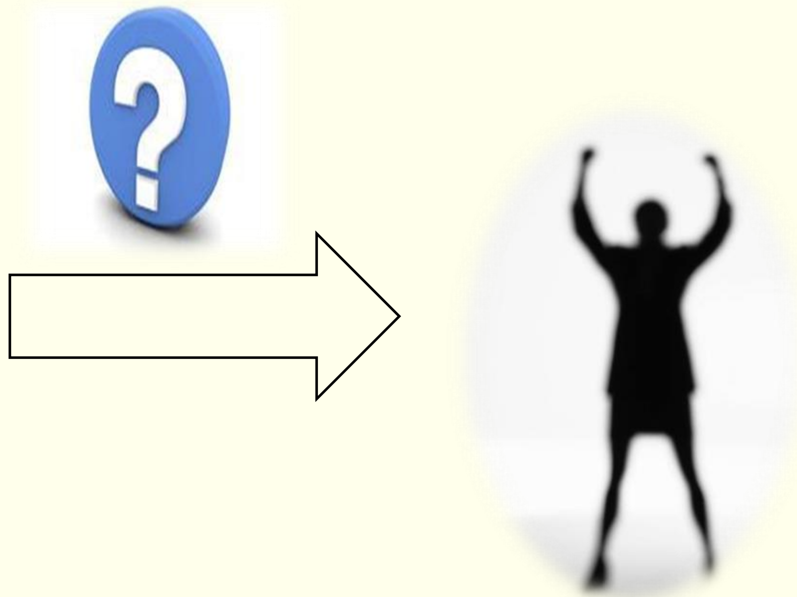
Conventional water treatment can not effectively remove ECs.

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

Daughton, C.G., et al. International Encyclopedia of Public Health. 2017: Academic Press. 66. C.S.G.

Ferreira, et al., Ecotoxicol. Environ. Saf. 67 (2018), pp. 452.

The potential harm for human



http://www.nsf.gov/news/news_summ.jsp?cntn_id=123689&WT.mc_id=USNSF_51&WT.mc_ev=click

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)

Research Progress on Removing ECs from Water

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

Methods	Removal Effect	Advantage	Disadvantage
Biological method	unsatisfactory	Low cost	Poor stability
Membrane filtration (RO)	Fairly well	effective	Fouling and high cost
Physical adsorption	fair	Simple operation	Difficult to regenerate
Chemical oxidation	fair	Running steadily	High cost and low efficiency

[1] Yang X, Flowers R C, Weinberg H S, et al. Water Research. 2015, 45(16): 5218-5228.
[2] Liu Z, Ogejo J A, Pruden A, et al.. Science of The Total Environment. 2016, 409(24): 5149-5161.
[3] Chen H, Li X J, Zhu S C. Environmental Science and Pollution Research. 2017, 19(6): 2381-2389.
[4] Esplugas S, Bila D M, Krause L G T, et al. Journal of Hazardous Materials. 2017, 149(3): 631-642.

Research Progress on Ozonation

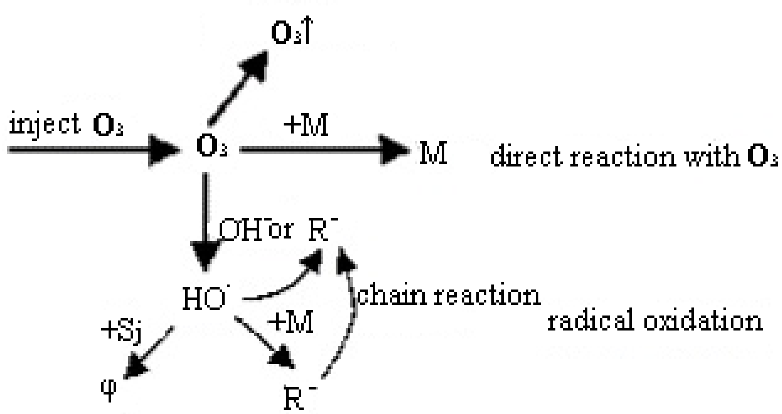
Direct reaction:

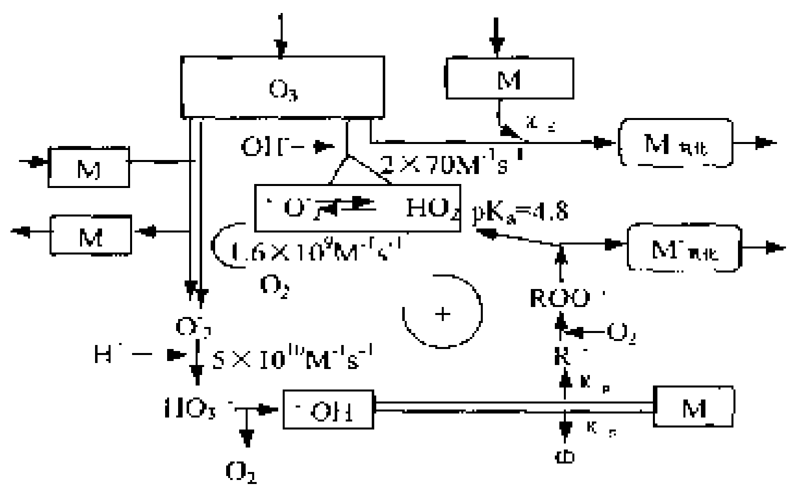
Organic pollutants+ O_3 (E_0=2.08V) → product or intermediate products; low speed and selective oxidation

Indirect reaction:

Organic pollutants + HO·→ intermediate products or CO_2+H_2O

higher oxidation potential and react speed without selectivity for most of organic compounds; HO·(E_0=2.80V)



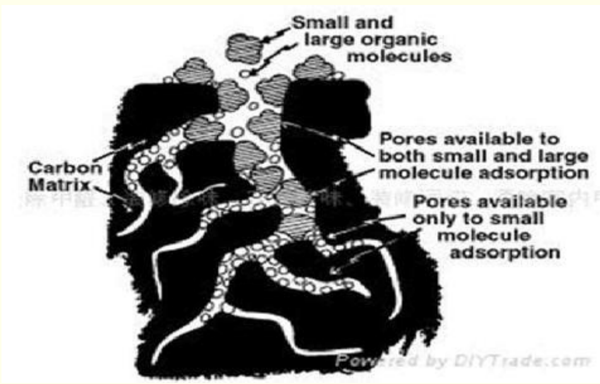


J. Hoigné, et.al. Water Res. 17 (1983) 173-183.
J. Nawrocki, et. al. Appl Catal B-Environ. 99 (2010) 27-42.

Research Progress on Ozonation

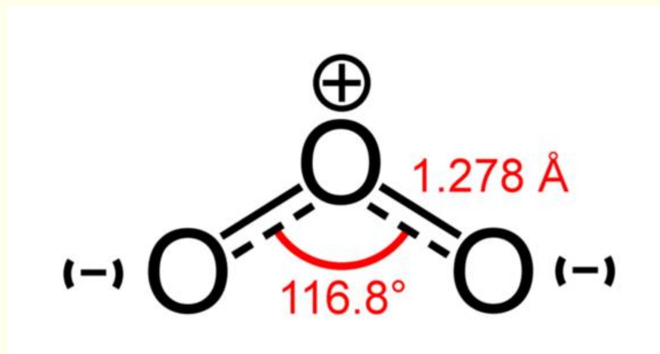
Indirect reaction: (homogeneous and heterogeneous catalysis of ozone)

O_3/Fe^{2+}, O_3/Cu^{2+}, O_3/UVA, O_3/Fe^{2+}/UVA , O_3/H_2O_2, O_3/AC, O_3/MnO_2, O_3/TiO_2, etc.



AC

+



ozone

M. Sánchez-Polo, U. von Gunten, J. Rivera-Utrilla, Water Res. 39 (2005) 3189-3198.

P.M. Alvárez, J.F. García-Araya, F.J. Beltrán, I. Giráldez, J. Jaramillo, V. Gómez-Serrano, Carbon. 44 (2006) 3102-3112.

Research Progress on Ozonation

✓ Advantages:

1) Rapid adsorption of trace organic pollutants

$$ACF + pollutant \leftrightarrow ACF - pollutant \quad (1)$$

2) Hydrogen peroxide is generated by the reaction of AC and O_3, which then acts with O_3 to generate hydroxyl radicals

$$AC + H_2O + O_3 \rightarrow AC^+ + H_2O_2 + O_2^- \quad (2)$$

$$2O_3 + H_2O_2 \rightarrow 2 \bullet OH + 3O_2 \quad (3)$$

$$ACF - pollutant + \bullet OH \rightarrow byproducts \quad (4)$$

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

M. Sánchez-Polo, U. von Gunten, J. Rivera-Utrilla, Water Res. 39 (2005) 3189-3198.

P.M. Alvárez, J.F. García-Araya, F.J. Beltrán, I. Giráldez, J. Jaramillo, V. Gómez-Serrano, Carbon. 44 (2006) 3102-3112.

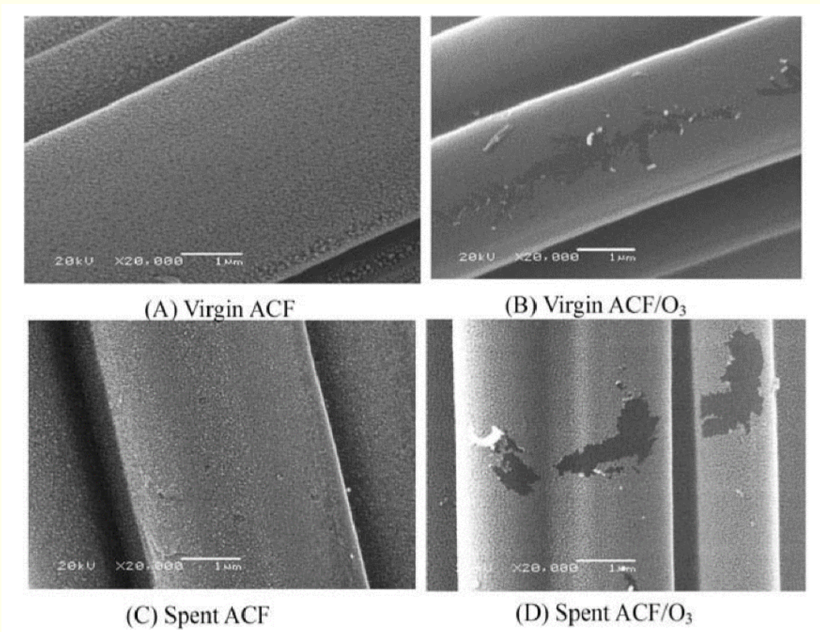
Research Progress on Ozonation

× 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.



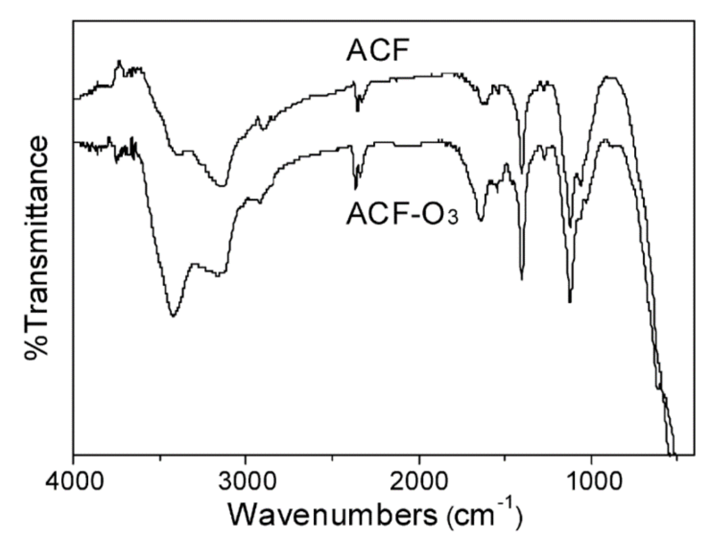


Fig. 6. FTIR spectra of virgin ACF and ACF exhausted after ozonation.

K. Shang, J. Li, N. Lu, Q. Sun, Y. Wu, Y. Yang, Ozone-Sci Eng. 37 (2015) 178-185.

Research contents

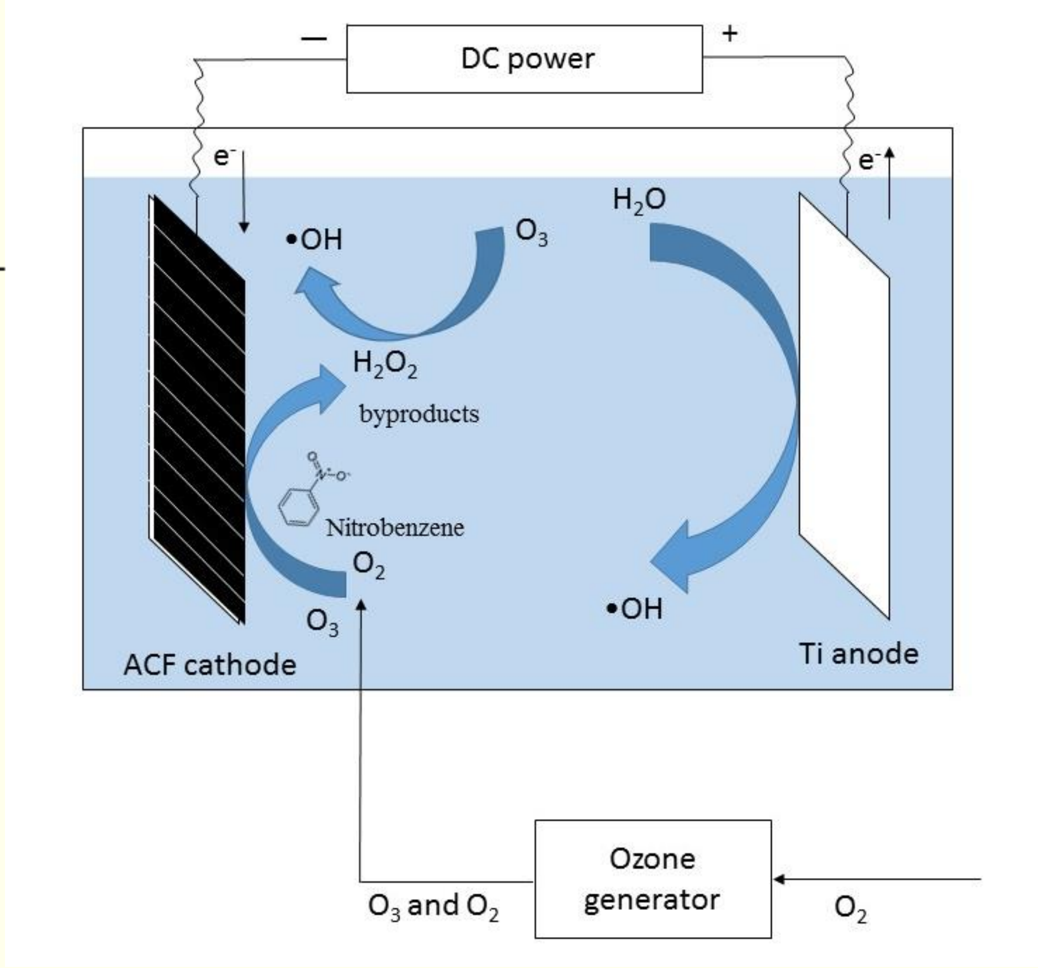
Theoretical hypothesis:

$$AC + H_2O + O_3 \rightarrow AC^+ + H_2O_2 + O_2^-$$

$$AC^+ + e^- \rightarrow AC$$

Inject electron onto ACF

$$2O_3 + H_2O_2 \rightarrow 2 \bullet OH + 3O_2$$



Xianke Zhang, Yu Zhou, Chun ZHAO*, et al.,, Chemical Engineering Journal, 2016,304: 129-133.

Research contents

Target pollutant—nitrobenzene (NB)

- ✓ **Source**

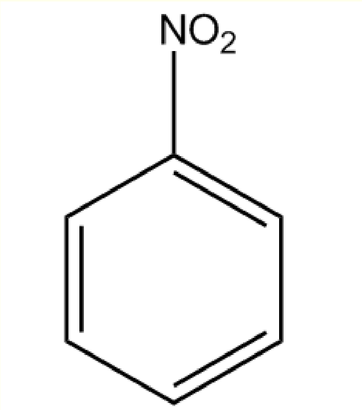
  Industrial wastewater of printing , pharmacy, petrochemical engineering, etc.

- ✓ **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.

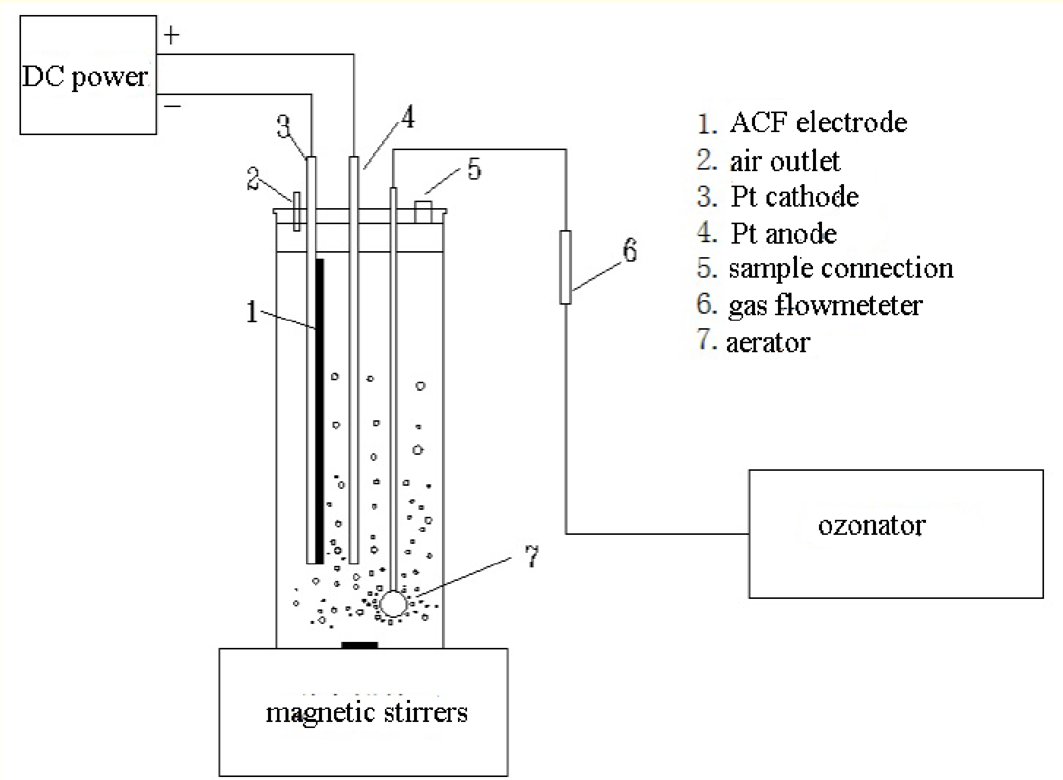


structural formula of NB

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

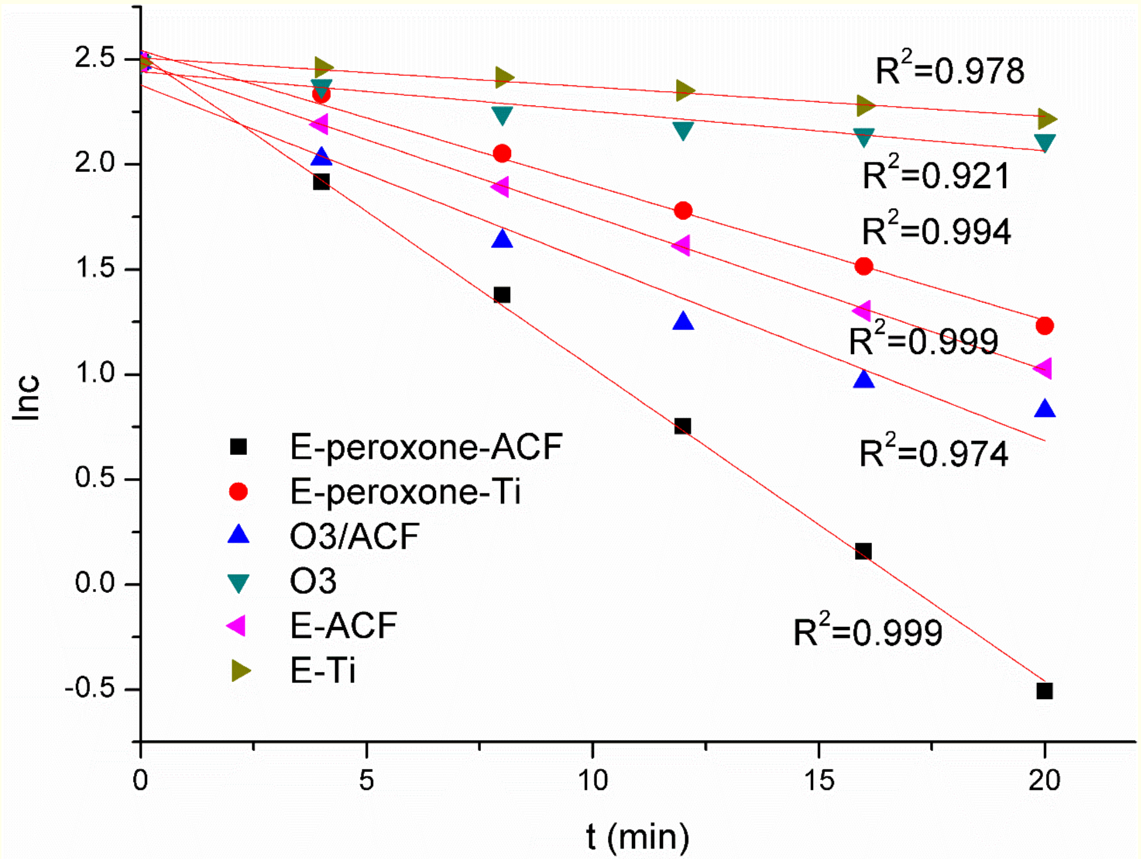
★ **Test method :**

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 follows pseudo-first-order kinetics, the removal efficiency of EOA is much higher than the others.

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

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

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

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

Result and discussion

Recycle experiments

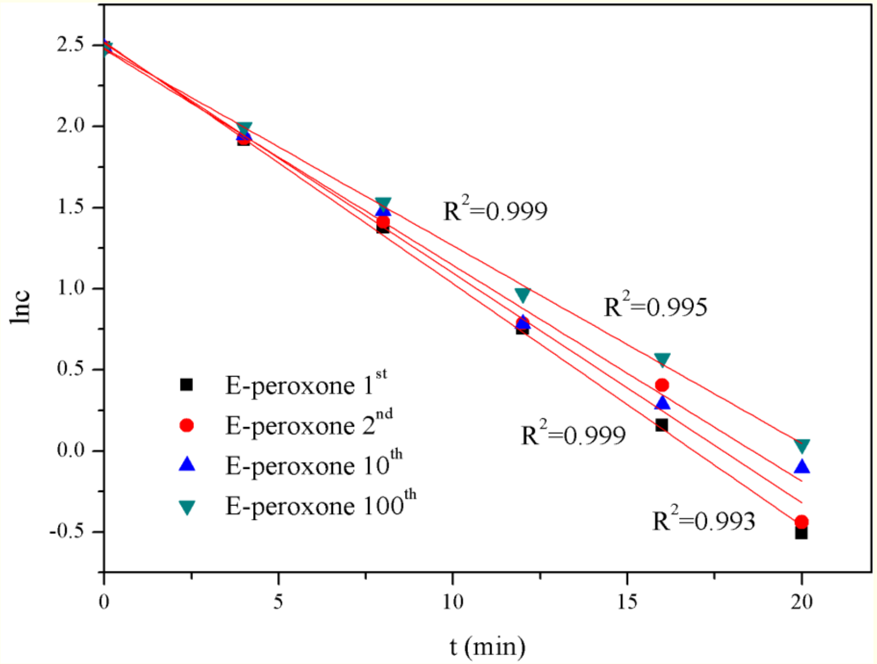


Fig. (a) ACF recycle in E-peroxone-ACF process

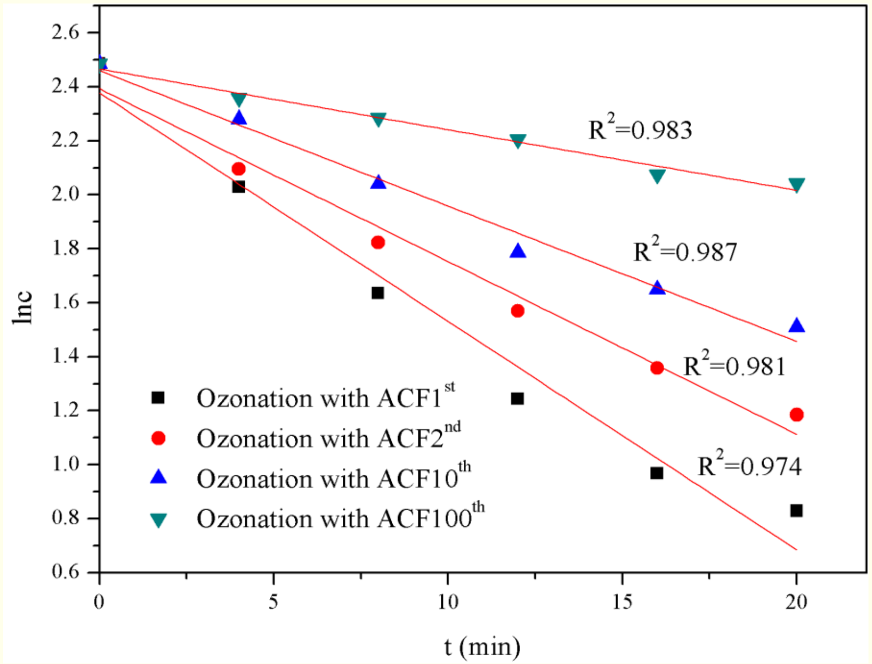


Fig. (b) ACF recycle ACF/O_3 process

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

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

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

Result and discussion

Adsorption

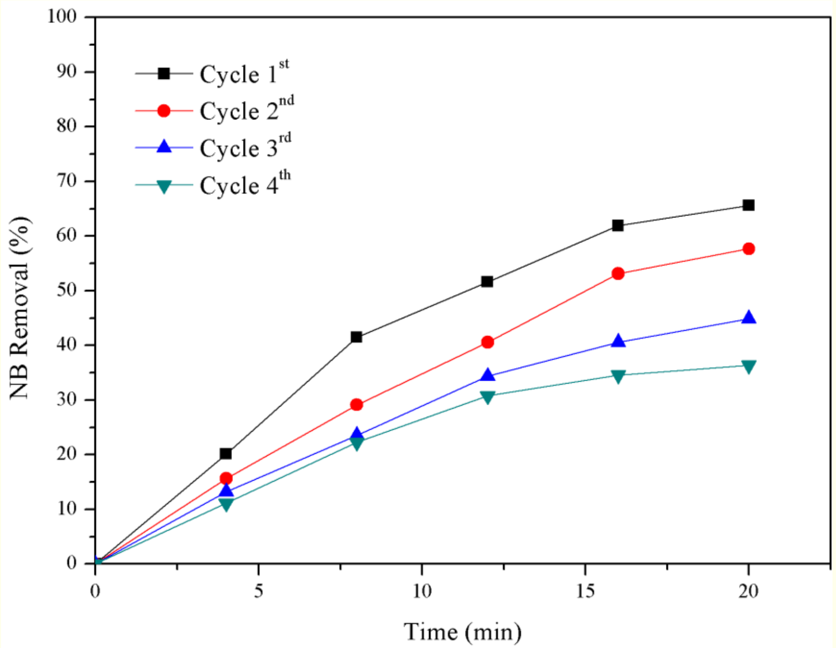


Fig. (a) Removal of NB by ACF for 4 times recycle

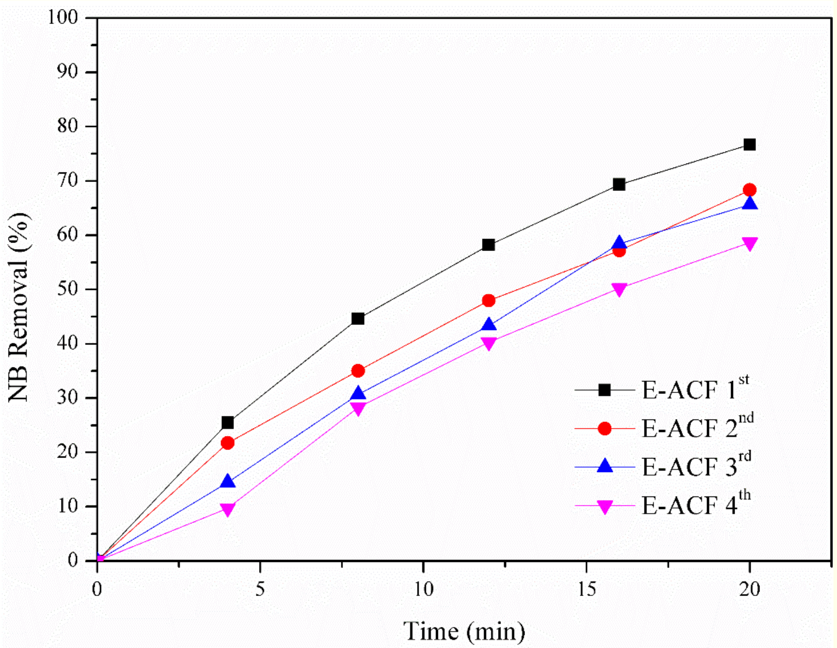


Fig. (b)) Removal of NB by E-ACF for 4 times recycle

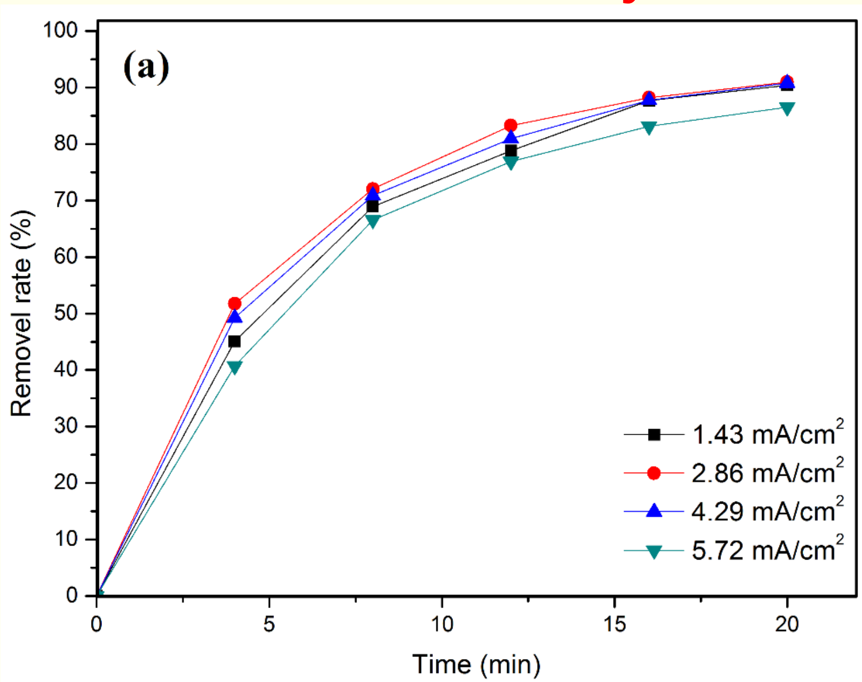
1.ACF has a large adsorption capacity for NB, and the adsorption of NB decreases obviously with increasing the recycle times.

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

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

Result and discussion

Effect of current density and ozone concentration



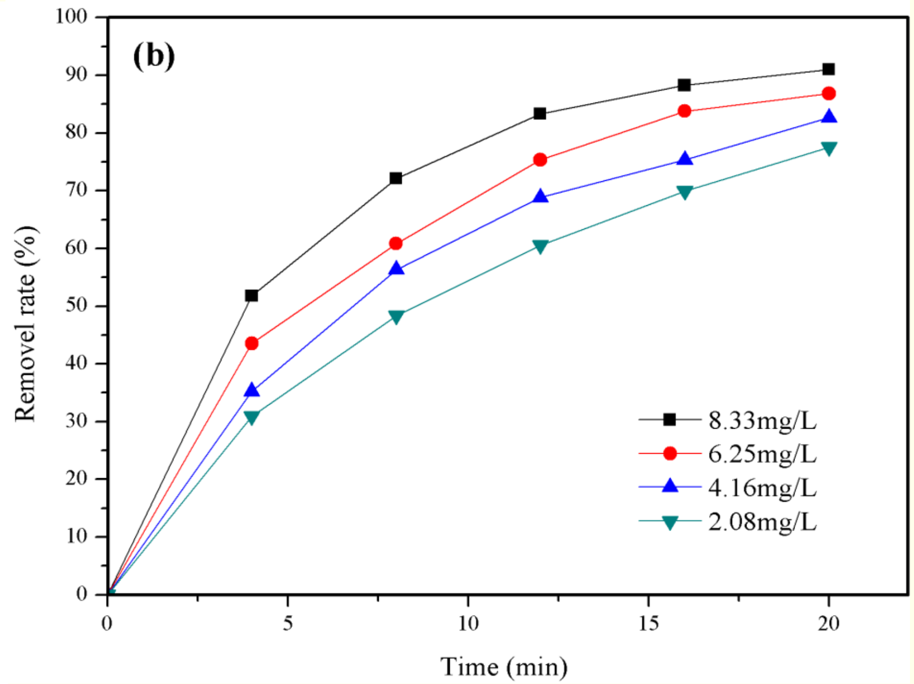


Fig. (a) Effect of current density on E-peroxone-ACF process   Fig. (b) Effect of O_3 concentration on E-peroxone-ACF process

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)).

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

Result and discussion

Effect of initial pH

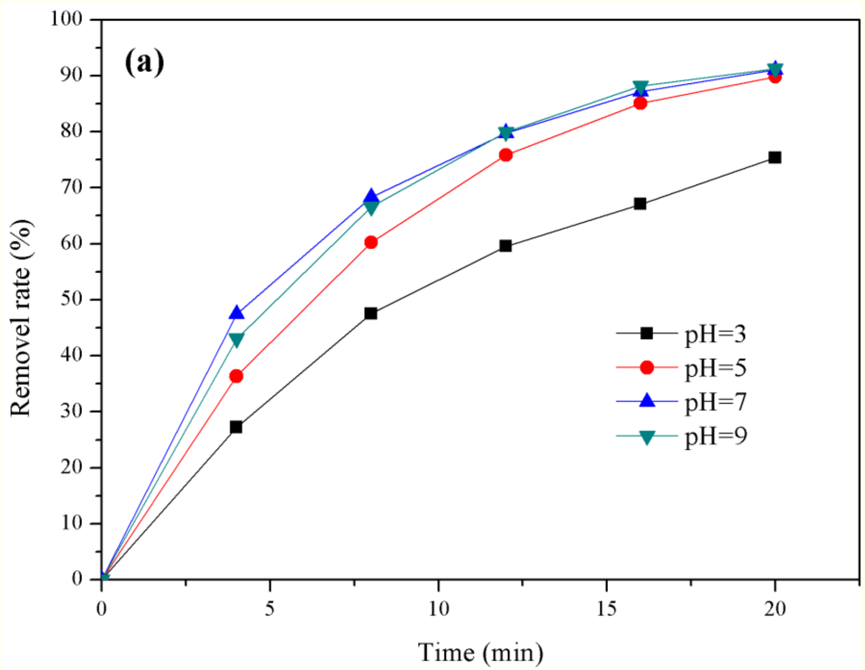


Fig. (a) Effect of pH on ACF/O_3 process

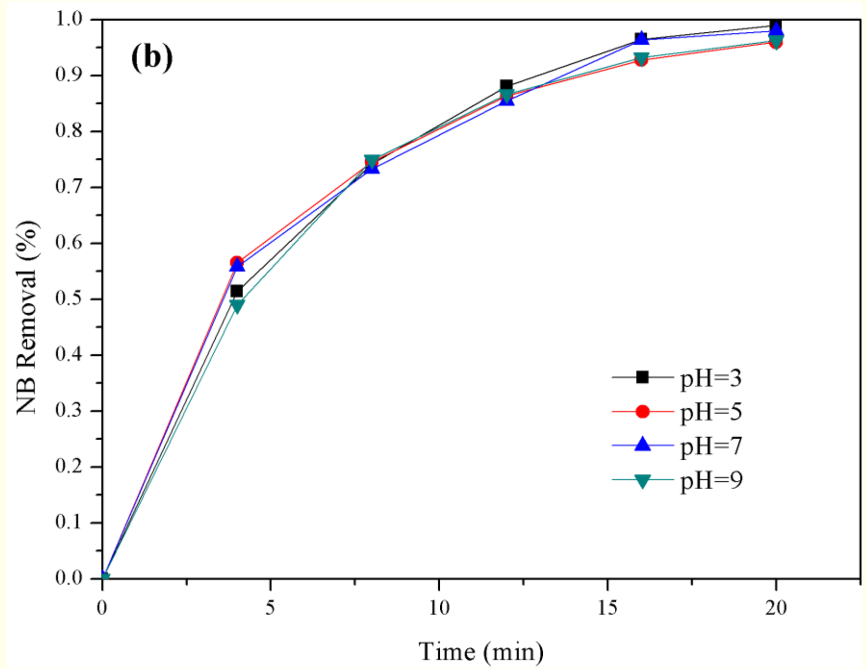


Fig. (a) Effect of pH on E-peroxone-ACF process

1. The initial pH of solution had great influence on O_3/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.

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

Result and discussion

Hydrogen peroxide concentration during reaction

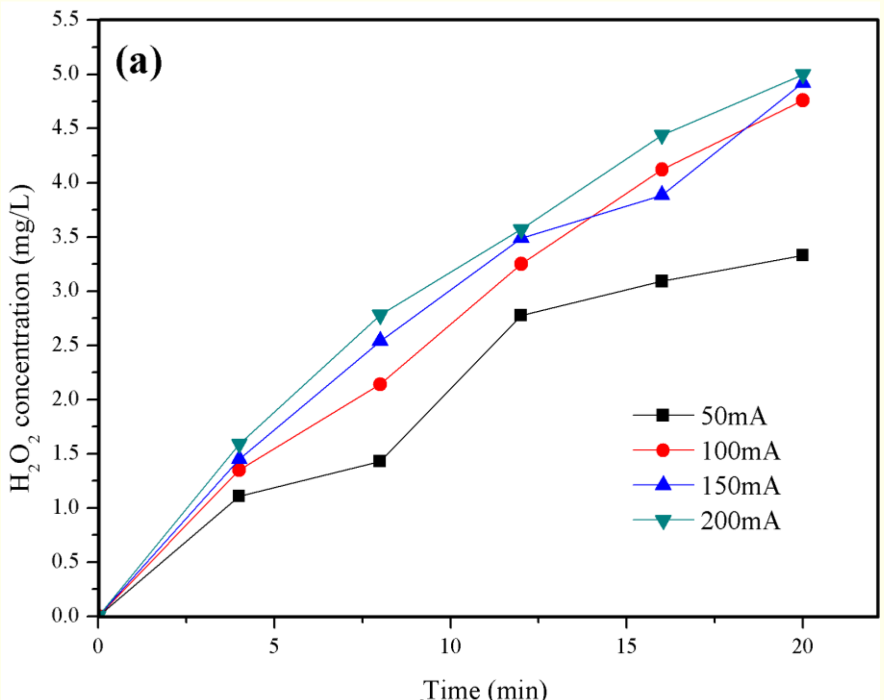


Fig.(a) The concentration of hydrogen peroxide changes in E-ACF system

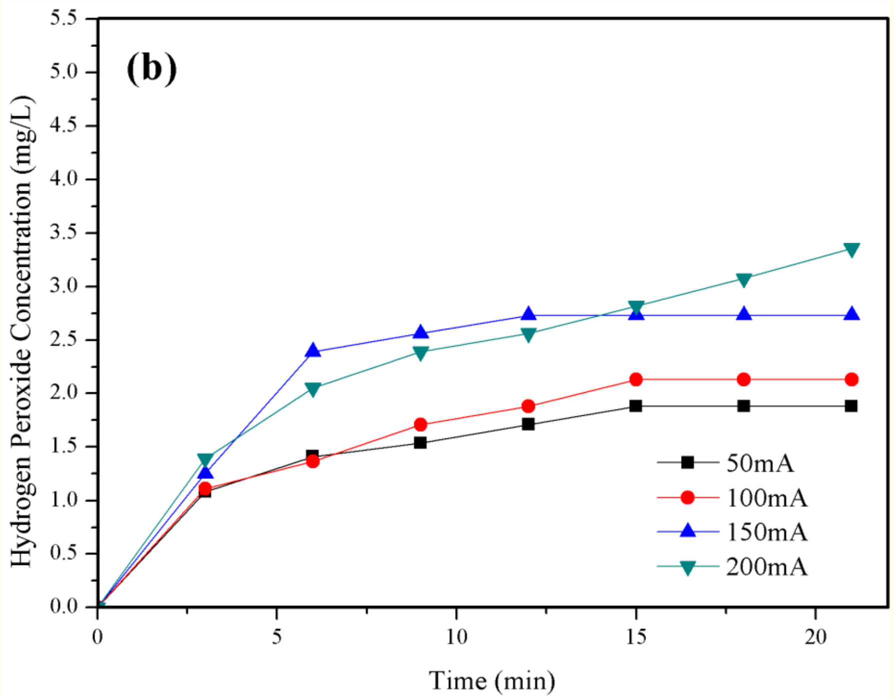


Fig.(b) The concentration of hydrogen peroxide changes in E-peroxone-ACF system

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

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

Result and discussion

Effect of radical scavenger

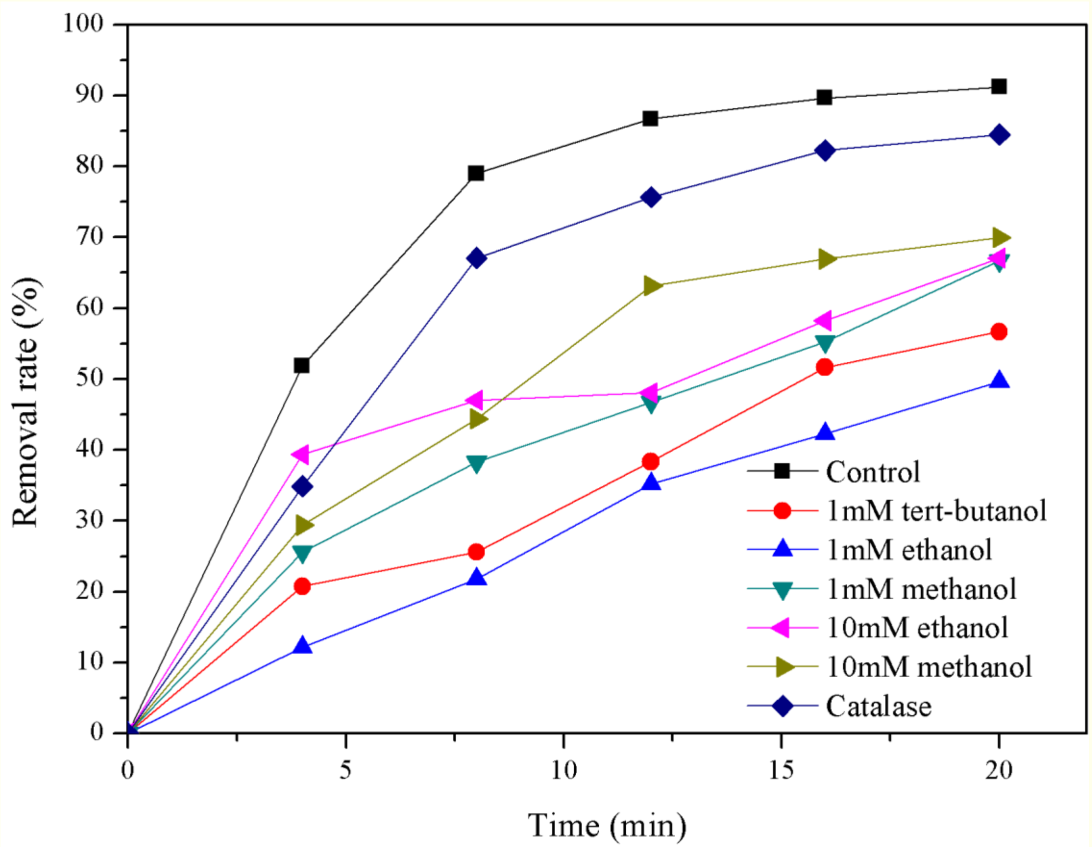


Fig. Effect of radical scavenger on E-peroxone-ACF system

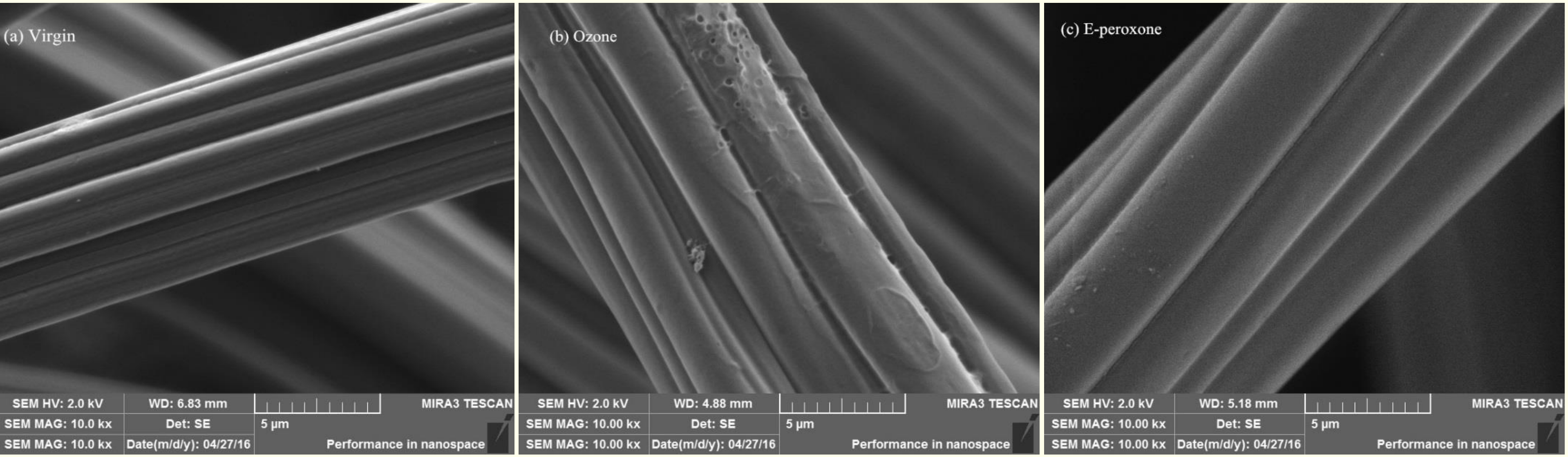
The removal rate decreased rapidly by added 1 mmol/L radical scavenger (methanol, ethanol or TBA) in E-peroxone-ACF system.

OH radical is the main oxidant!

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

Result and discussion

The effect of reaction to the surface of ACF



ACF_{Vrigin}

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-peroxone-ACF）

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

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

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

ACF Sample	S_{BET} (m^2/g)	$S_{micropore}$ (m^2/g)	$V_{micropore}$ (m^3/g)	V_{total} (m^3/g)	Acidic functional groups (μmole/g)	Basic functional groups (μmole/g)
ACF_{vigin}	697.44	663.52	0.287	0.331	376	477
ACF_{O3}	587.00	504.25	0.217	0.278	553	187
ACF_{E-O3}	671.67	634.32	0.239	0.320	358	504

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

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

Result and discussion

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

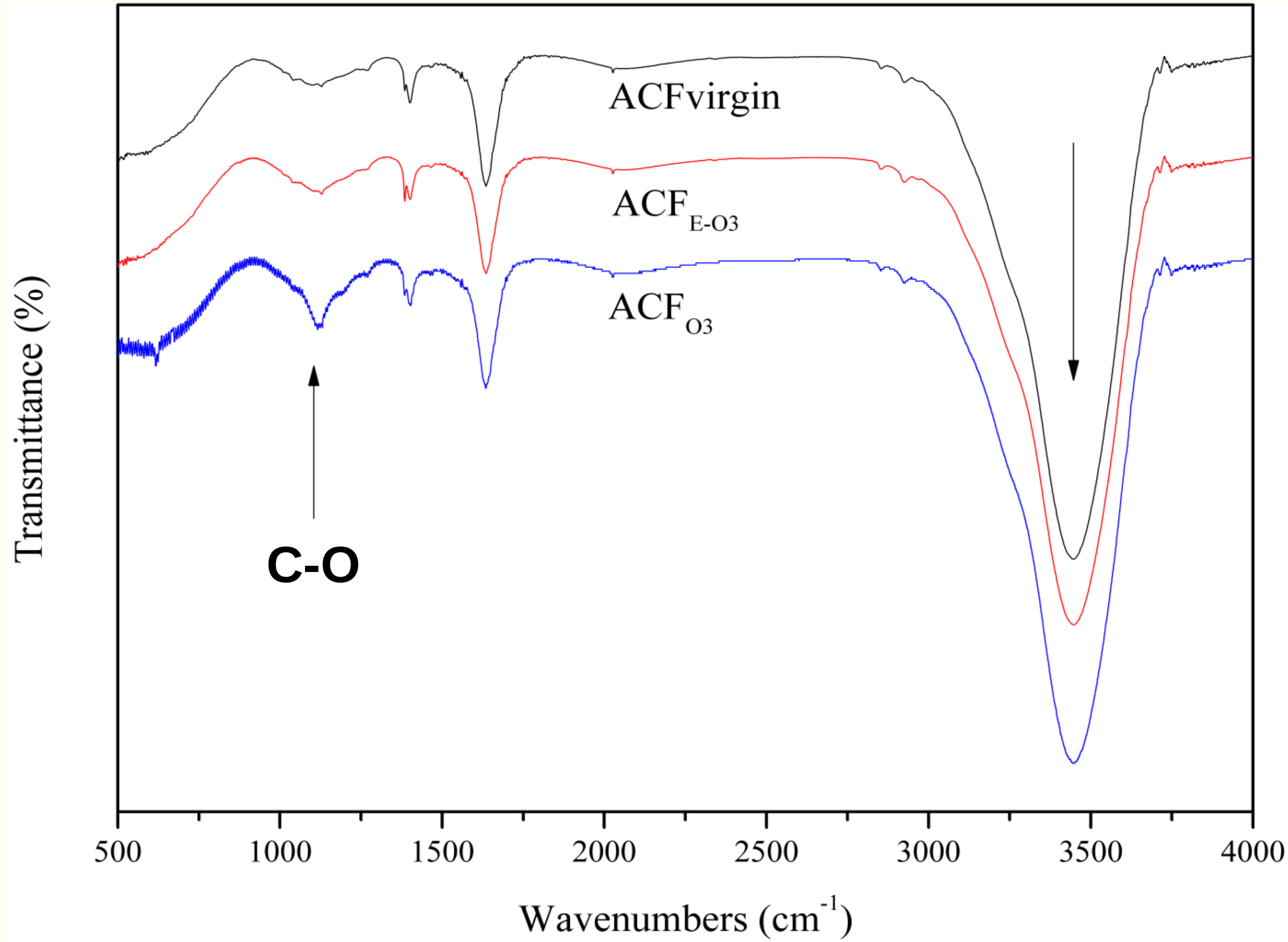


Fig. FTIR of ACF_{virgin}, ACF reacted with O_3, ACF reacted in E-O_3 after 100 times recycle

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

Result and discussion

Reaction mechanism:

$$ACF + NB \leftrightarrow ACF - NB$$

$$ACF + O_3 \leftrightarrow ACF - O_3$$

$$ACF + O_2 \leftrightarrow ACF - O_2$$

$$ACF - NB + ACF - O_3 \rightarrow byproducts + H_2O_2$$

$$H_2O_2 + ACF - O_3 \rightarrow ACF^+ - O_2 + \bullet OH$$

$$ACF^+ - O_2 + 2e^- + H_2O \rightarrow ACF + H_2O_2$$

$$ACF - O_2 + 2e^- + 2H_2O \rightarrow ACF + 2H_2O_2$$

$$ACF - NB + \bullet OH \rightarrow byproducts$$

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

Xianke Zhang，Yu Zhou, Chun ZHAO*, et al, Chemical Engineering Journal, 2016,304: 129-133.

Summary

- 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

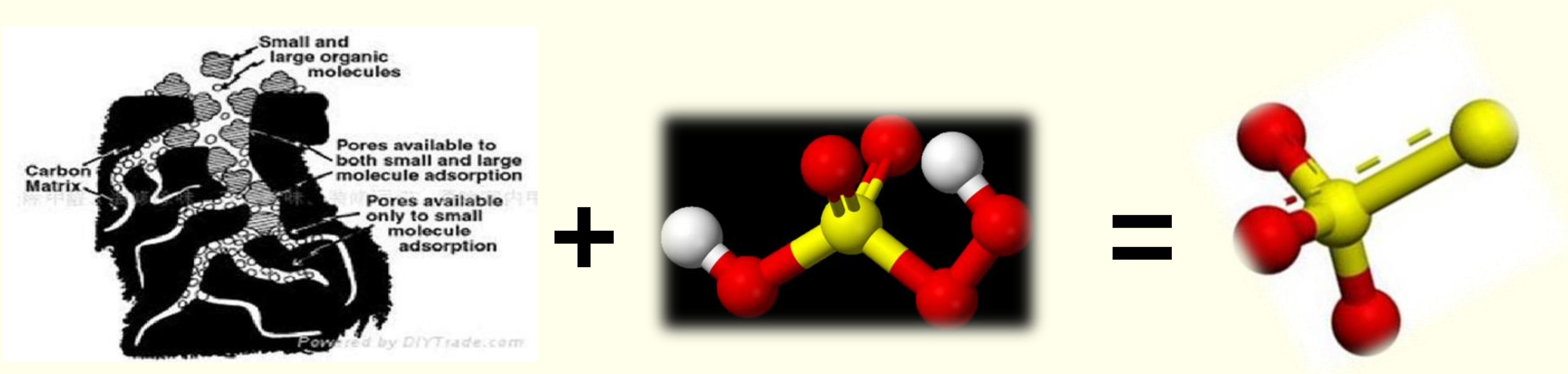
Direct reaction:

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

Indirect reaction:

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

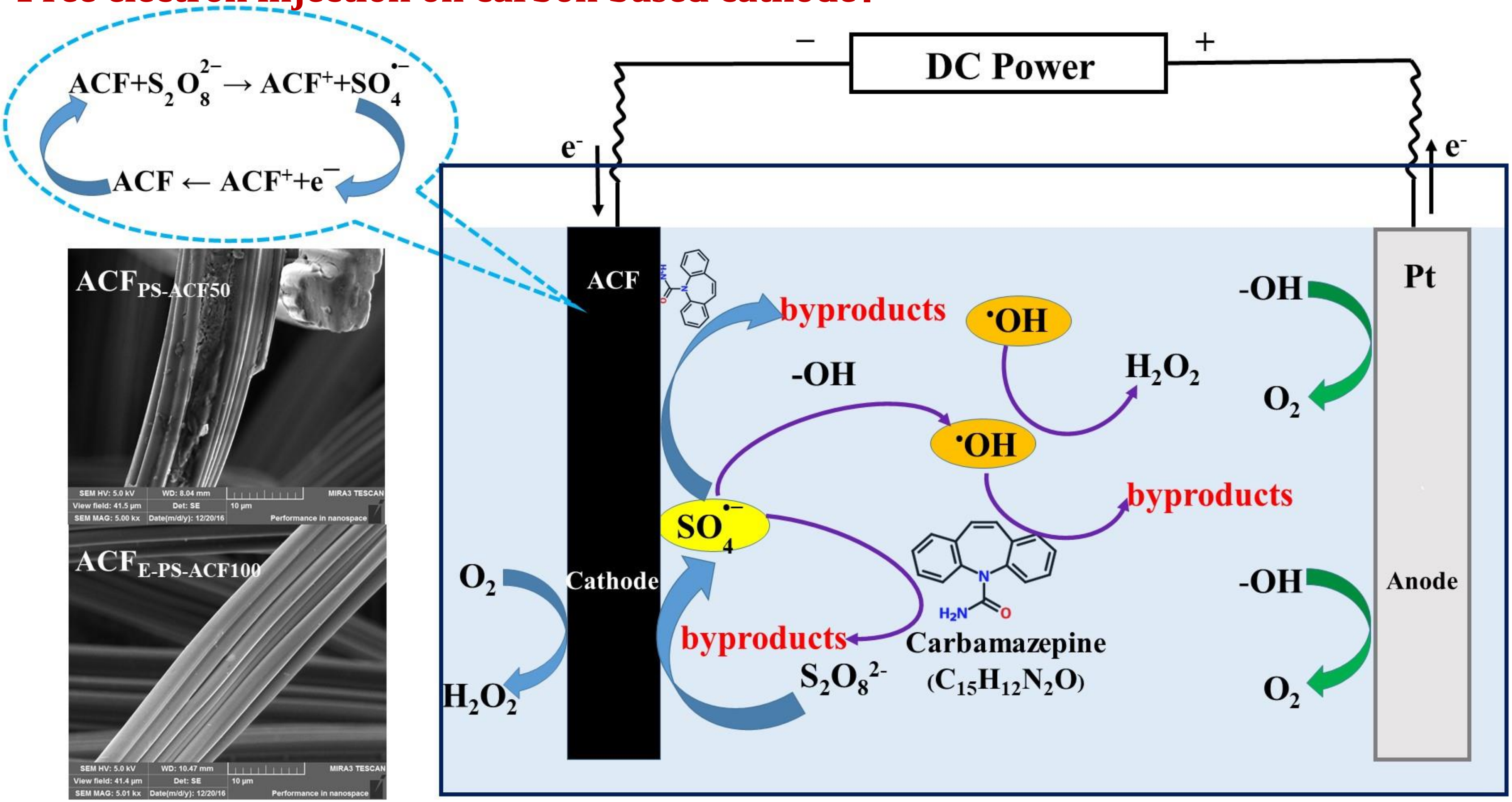
Activated carbon activation:



Block, P. A.et. al. Chemosphere. 2005, 61 (4), 551-560.
Yang, B. et. al.. Water Res. 2016, 100, 413-420.

Extended research based on persulfate

Free electron injection on carbon based cathode：



Electro-persulfate-ACF (E-PS-ACF) process

Zhen Liu，Chun ZHAO*, et al. Chemical Engineering Journal, 2018, 343: 28-36..

Extended research based on persulfate

E-PS-ACF applied for Carbamapine (CBZ) degradation

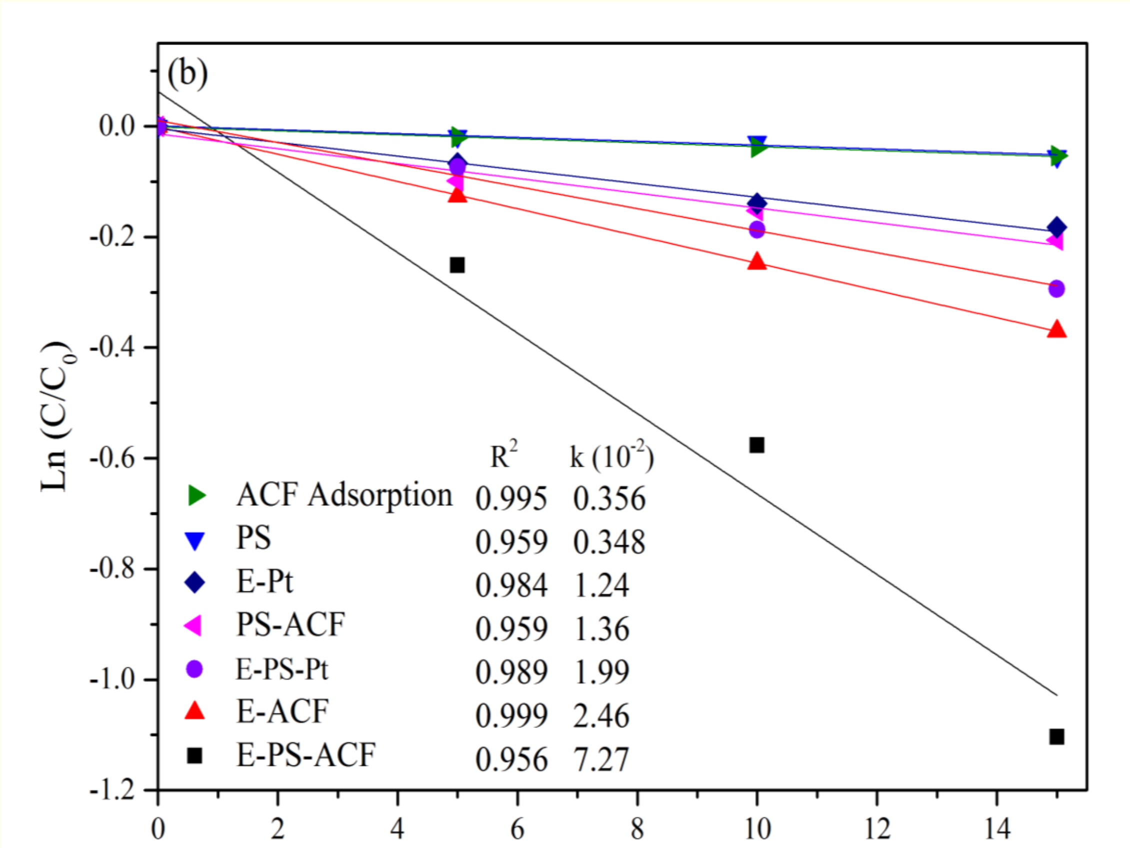


Fig. Reaction kinetics of CBZ removal

1.All processes follows 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.**

Zhen Liu, Chun ZHAO*, et al, Chemical Engineering Journal, 2018, 343: 28-36..

Extended research based on persulfate

E-PS-ACF

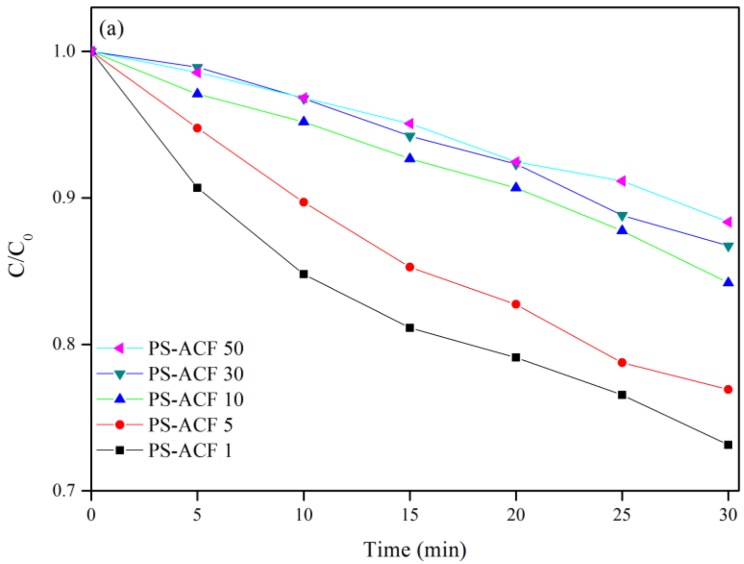


Fig. (a) Degradation of CBZ by PS-ACF process with ACF recycled for 50 times

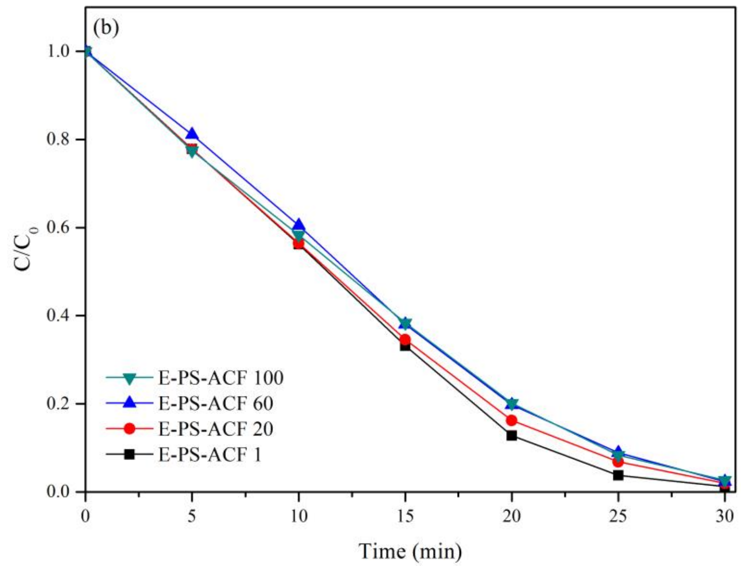


Fig. (b) Degradation of CBZ by E-PS-ACF process with ACF recycled for 100 times

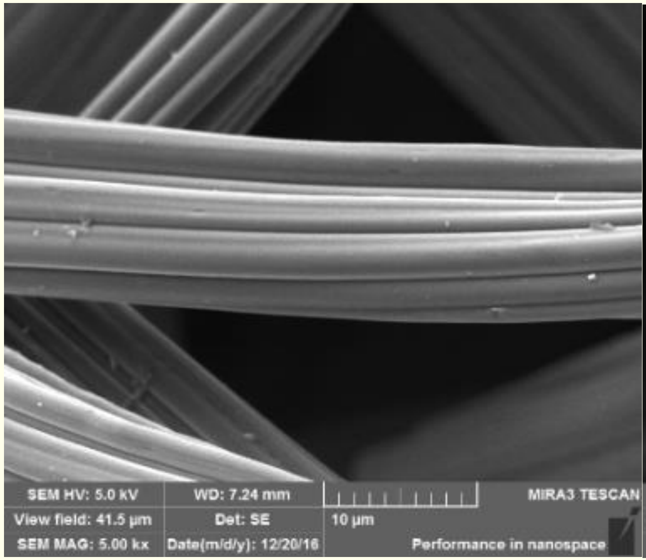
1. With the increase of ACF recycle times, the removal efficiency of CBZ decreases gradually in PS-ACF system.

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

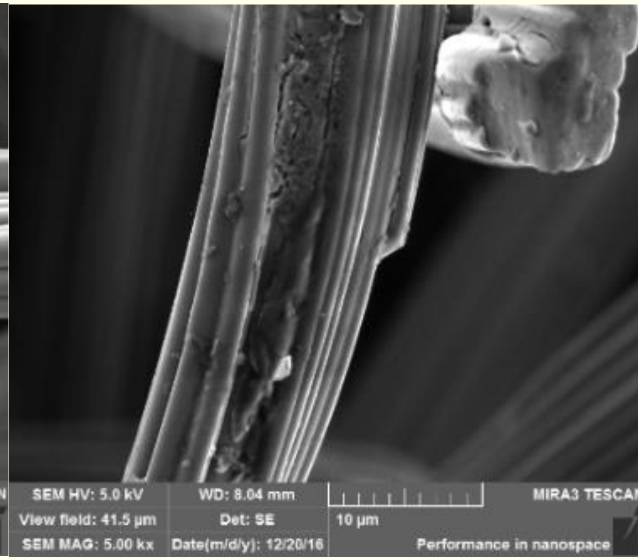
Zhen Liu，Chun ZHAO*, et al, Chemical Engineering Journal, 2018, 343: 28-36..

Extended research based on persulfate

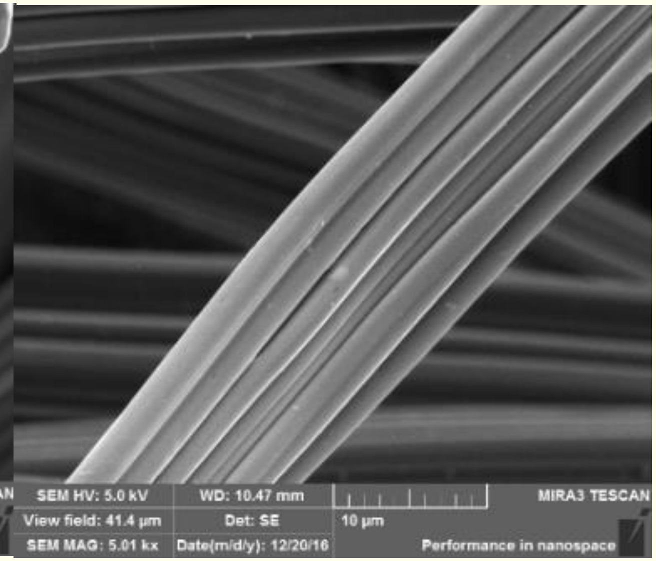
E-PS-ACF



$\mathrm{ACF}_{\mathrm{vrigin}}$



$\mathrm{ACF}_{\mathrm{PS\text{-}ACF50}}$



$\mathrm{ACF}_{\mathrm{E\text{-}PS\text{-}ACF100}}$

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

Zhen Liu，Chun ZHAO*, et al, Chemical Engineering Journal, 2018, 343: 28-36..

Extended research based on persulfate

E-PS-ACF

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

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	$S_{micropore}$ ($m^2 \cdot g^{-1}$)	$V_{micropore}$ ($cm^3 \cdot g^{-1}$)	V_{total} ($cm^3 \cdot g^{-1}$)	acidic functional groups ($\mu mol \cdot g^{-1}$)	Basic functional groups ($\mu mol \cdot g^{-1}$)
ACF_{vrigin}	624.46	557.71	0.259	0.291	408	505
$ACF_{E\text{-}PS100}$	589.38	525.66	0.243	0.276	389	534
ACF_{PS50}	376.48	330.42	0.154	0.180	595	355

ACFE-PS100 was the ACF reacting in E-PS-ACF system for 100 times.
ACFPS50 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

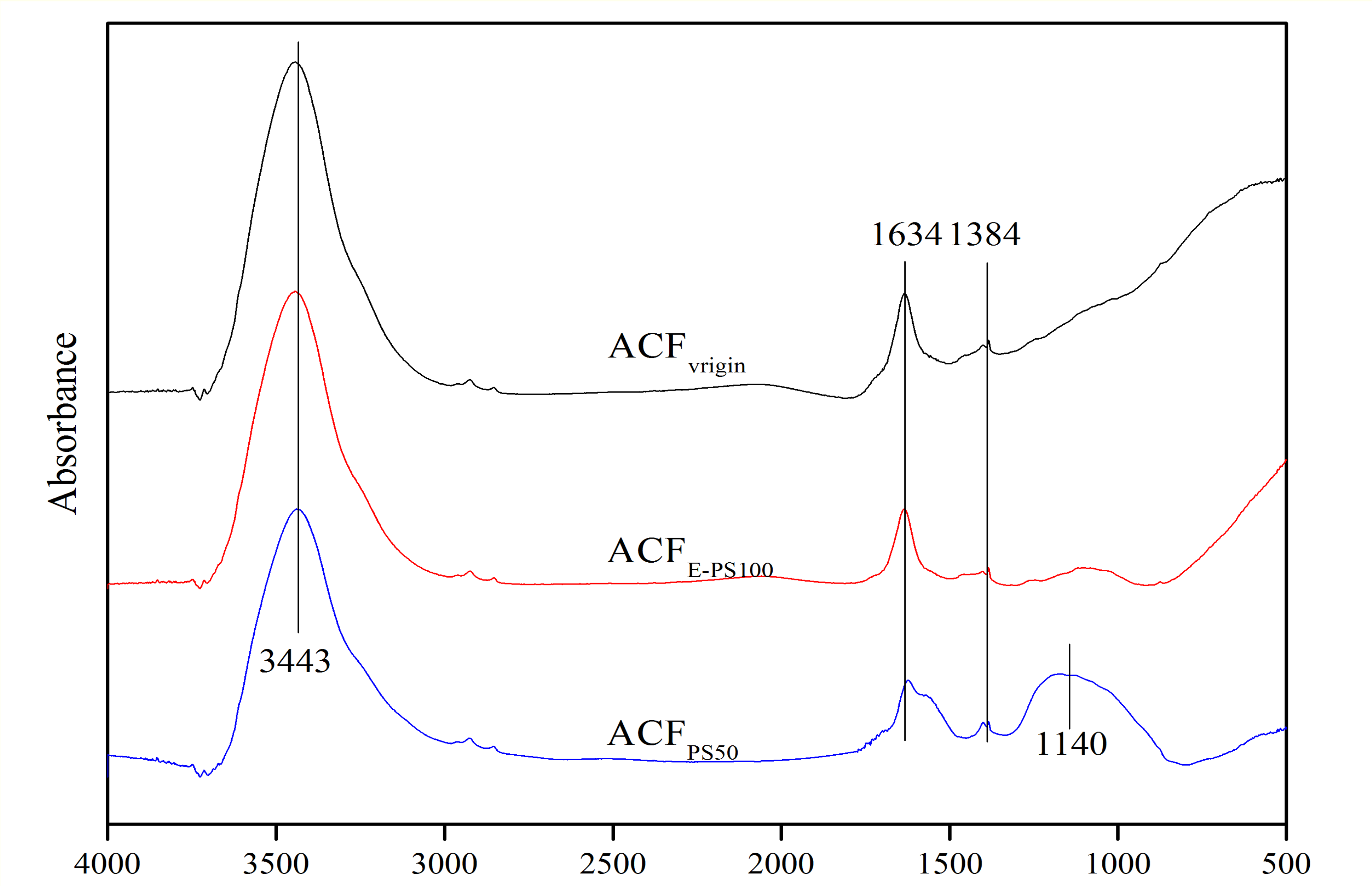


Fig. FTIR of ACFvirgin, ACF reacted with persulfate (PS-ACF), ACF reacted in E-persulfate (E-PS-ACF).

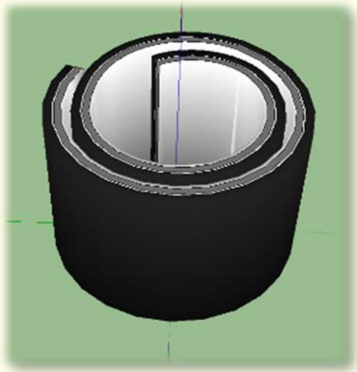
Zhen Liu，Chun ZHAO*, et al, Chemical Engineering Journal, 2018, 343: 28-36..

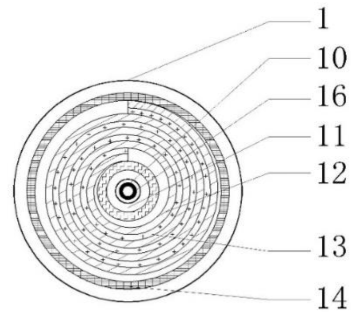
Reactor Development

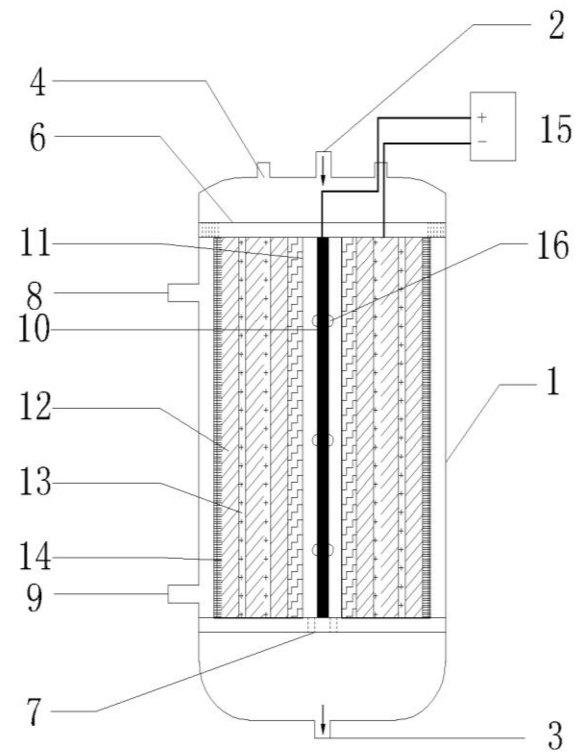
A spiral electrochemical reactor

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.







Top View

Perspective Drawing

注：装置壳体（1），进水口（2），出水口（3），出气口（4），接线口（5），布水板（6），过水孔（7），进液口（8），进气口（9），阳极电极层（10），阴阳电极隔绝层（11），阴极电极层（膜过滤层）（12），膜支撑层（13），紧固层（14），直流电源（15），紧固丝（16）

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Thanks for your attention!