Programa de Doctorado Electroquímica. Ciencia y Tecnología

Thorough assessment of reaction pathways involved in the electrochemical removal of persistent organic micropollutants from water

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Outline

- Introduction
- Main tasks
- Objectives
- Experimental setups and Analysis
- Work plan and Schedule
- References

◆ Emerging contaminants

Emerging contaminants (EC): a group of man-made and natural chemicals that have not been regulated or studied in depth, becoming dangerous for the environment and living beings

EC

- **Pharmaceuticals**
- **Pesticides**
- **Personal care products**
- **Industrial additives**
- **Food additives**
- **Flame retardants**
- **Surfactants**
- **Hormones and sterols**

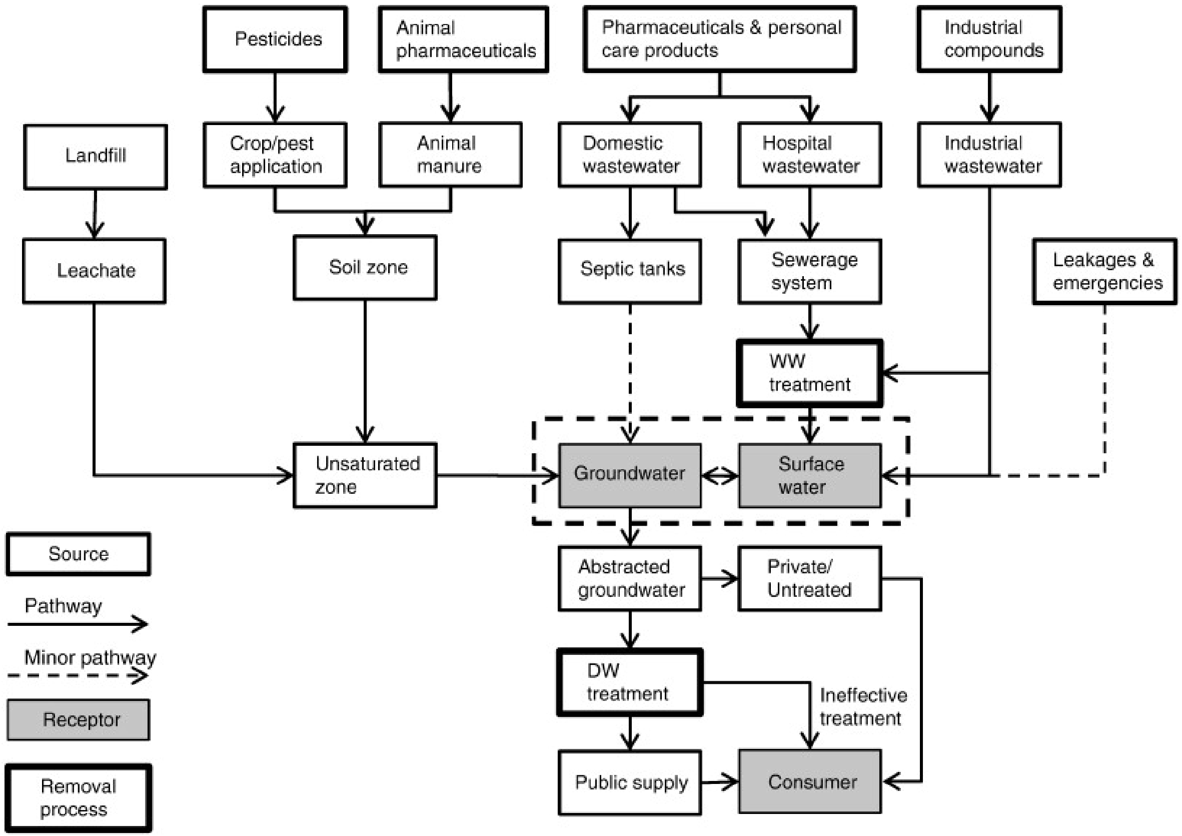
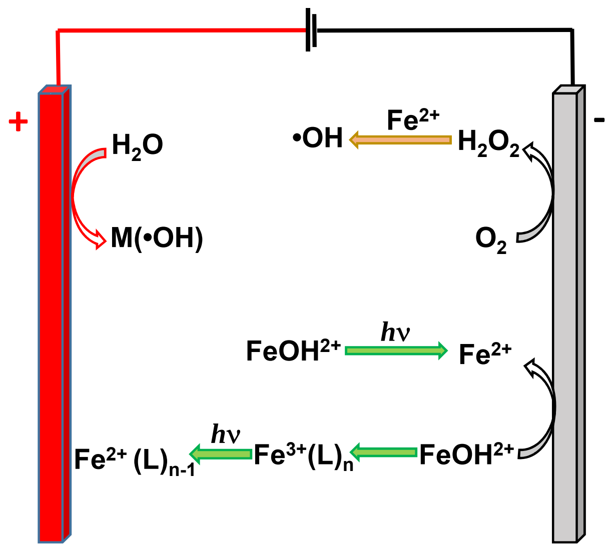


Fig.1. Sources (bold) and pathways for emerging contaminants to reach various receptors (grey)

(Stuart et al., 2012)

◆ Electrochemical advanced oxidation processes (EAOPs)

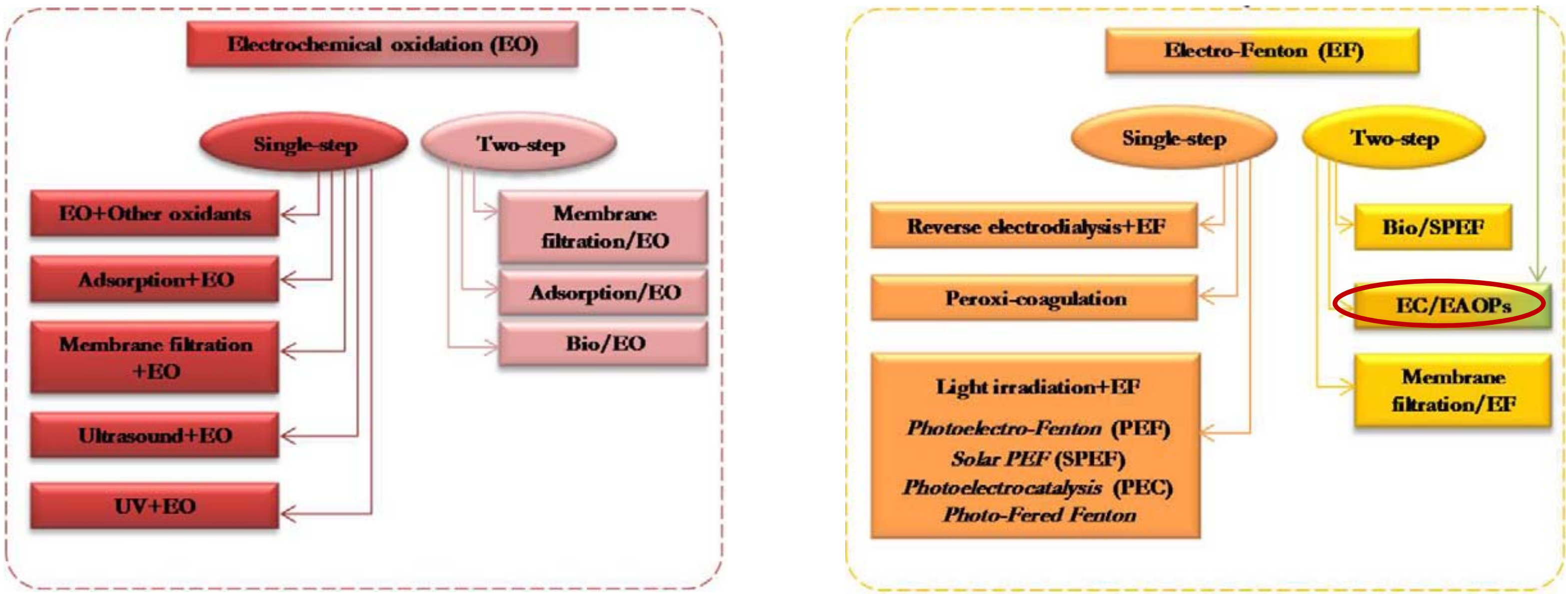
ANODIC OXIDATION (AO)	WATER OXIDATION AT THE ANODE SURFACE: $M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^-$
ANODIC OXIDATION WITH ELECTROGENERATED H_2O_2 ($AO\text{-}H_2O_2$)	REACTIONS OF AO + H_2O_2 ELECTROGENERATION AT THE CATHODE: $O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2$
ELECTRO-FENTON (EF)	REACTIONS OF AO, $AO\text{-}H_2O_2$ + FENTON'S REACTION: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$ Fe^{3+} REGENERATION TO Fe^{2+} AT THE CATHODE: $Fe^{3+} + e^- \rightarrow Fe^{2+}$
PHOTOELECTRO-FENTON (PEF) SOLAR PHOTOELECTRO-FENTON (SPEF)	REACTIONS OF AO, $AO\text{-}H_2O_2$, EF + PHOTOLYSIS OF $FeOH^{2+}$: $FeOH^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$ PHOTOLYSIS OF FERRICARBOXYLATE COMPLEXES: $Fe^{3+}(L)_n + h\nu \rightarrow Fe^{2+}(L)_{n-1} + L^{\bullet}_{ox}$



- Advanced treatment technology
- pH dependence
- In-situ H_2O_2 generation
- Refractory by-products

(Moreira et al., 2017)

Intensification of EAOPs

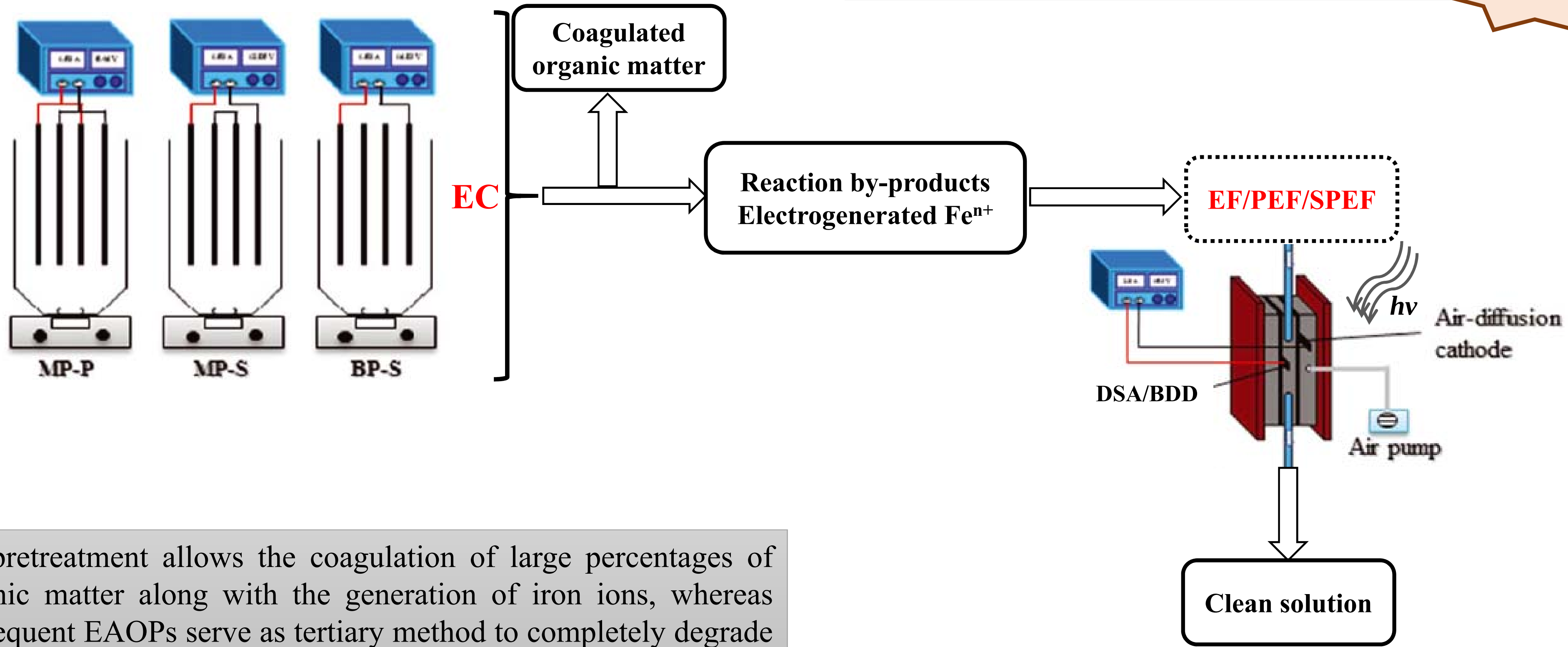


(Sirés and Brillas, 2017)

◆ Intensification of EAOPs

- ✓ alternating current (AC) and polarity reversal
- ✓ three-dimensional EC reactors
- ✓ operation in continuous mode

New



- EC pretreatment allows the coagulation of large percentages of organic matter along with the generation of iron ions, whereas subsequent EAOPs serve as tertiary method to completely degrade the refractory organics.

(Thiam et al., 2014)

◆ Intensification of EAOPs

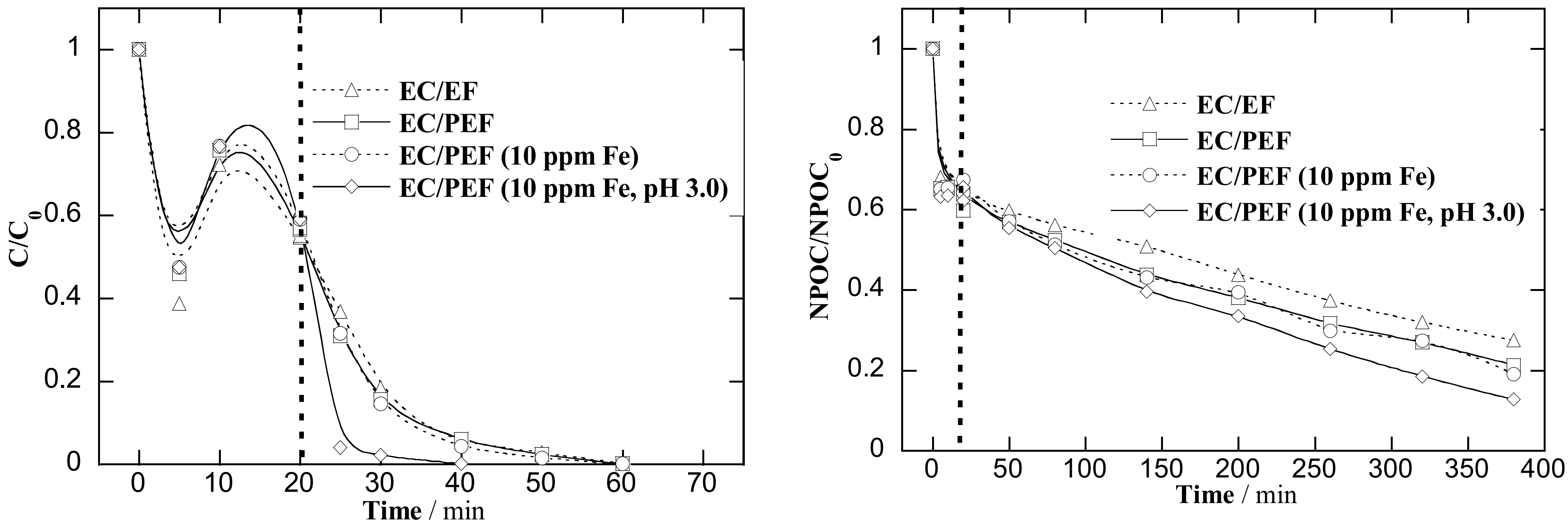


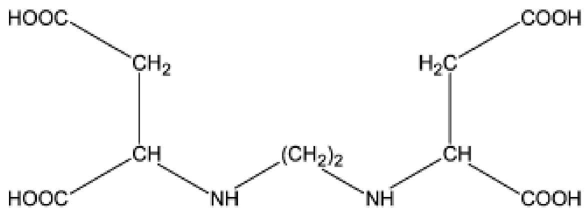
Fig. 2 The application of coupling electrocoagulation with electrochemical advanced oxidation processes for the degradation of benzophenone-3.

(EC: 150 mL, 35 ºC, BP-3 4 ppm C, Fe-Fe, 150 mA; EF/PEF: 100 mL, BDD anode, 35 ºC, 100 mA)

Paper in preparation……

◆ Fe(III)-EDDS assisted EAOPs

EDDS



Distribution of different iron species

$$Fe^{3+}_{(aq)} + L^{4-} \underset{}{\overset{K_0^{exp}}{\rightleftharpoons}} FeL^-$$

$$FeL^-_{(aq)} + HO^- \overset{K_1^{th}}{\rightleftharpoons} FeOHL^{2-}_{(aq)}$$

$$FeOHL^{2-}_{(aq)} + HO^- \overset{K_2^{th}}{\rightleftharpoons} Fe(OH)_2L^{3-}_{(aq)}$$

$$Fe(OH)_2L^{3-}_{(aq)} + HO^- \overset{K_3}{\rightleftharpoons} Fe(OH)_{3\,(aq)} + L^{4-}$$

$$Fe(OH)_{3\,(aq)} + HO^- \overset{K_4}{\rightleftharpoons} Fe(OH)_4^-{}_{(aq)}$$

Regeneration of iron

$$[Fe^{3+}L]^- + h\nu \rightarrow [Fe^{3+}L]^{-*} \rightarrow Fe^{2+} + \bullet L^{2-}$$

$$[Fe^{3+}L]^- + e^- \rightarrow [Fe^{2+}L]^{2-}$$

$$[Fe^{2+}L]^{2-} + H_2O_2 \rightarrow [Fe^{3+}L]^- + \bullet OH + OH^-$$

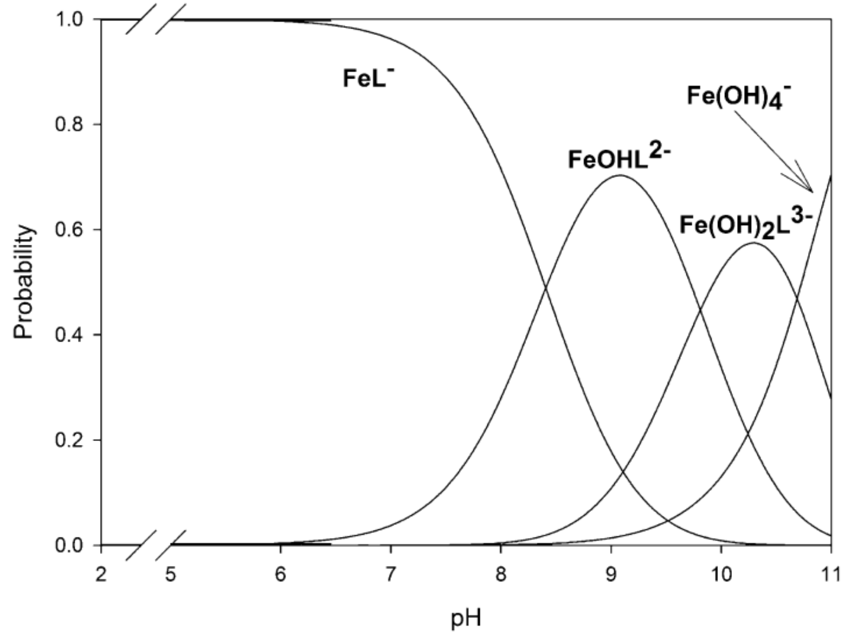


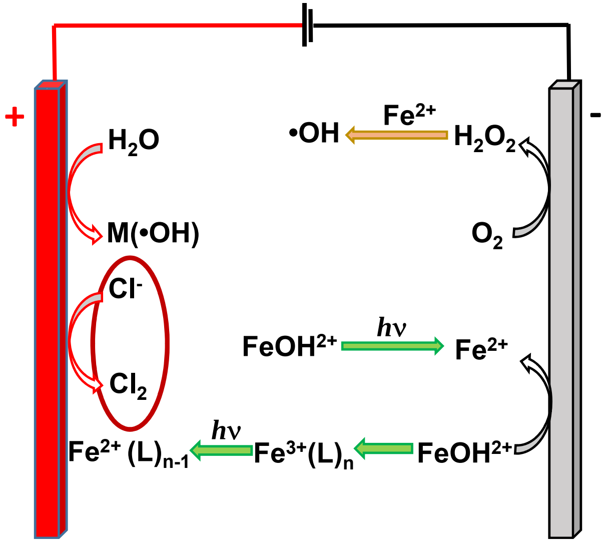
Figure 3. Proposed theoretical model distribution of the predominant species for the Fe(III)-[S,S]-EDDS complexation reaction as a function of pH.

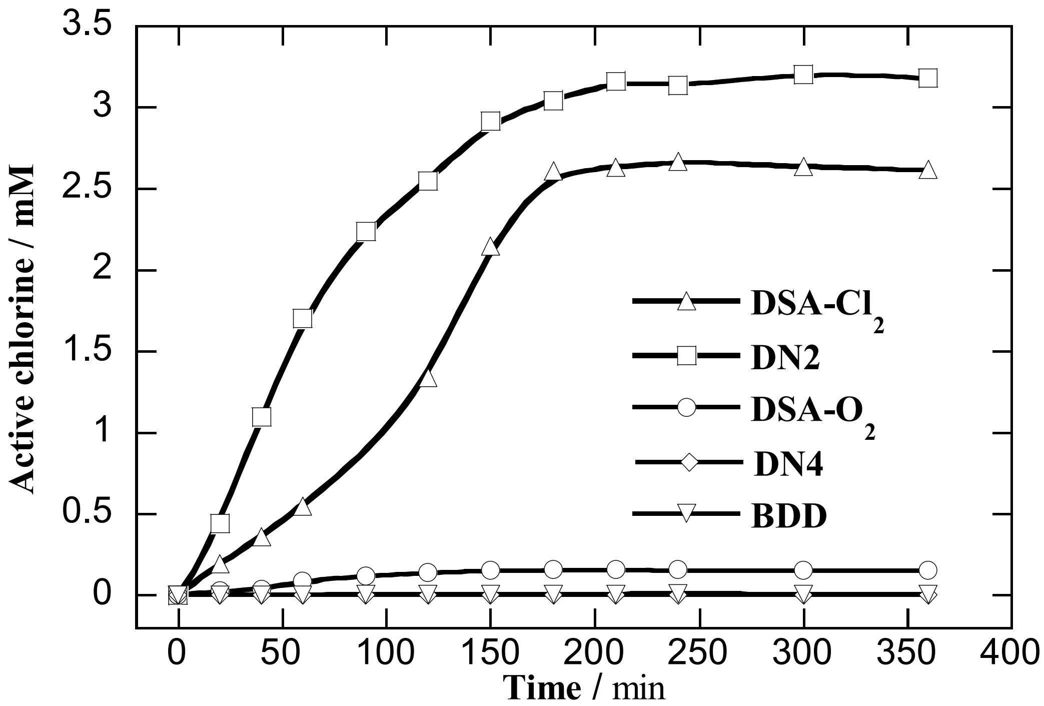
The resulting iron complexes maintain great solubility at a wide pH range, which allowing EAOPs running at neutral pH especially at plant scale.

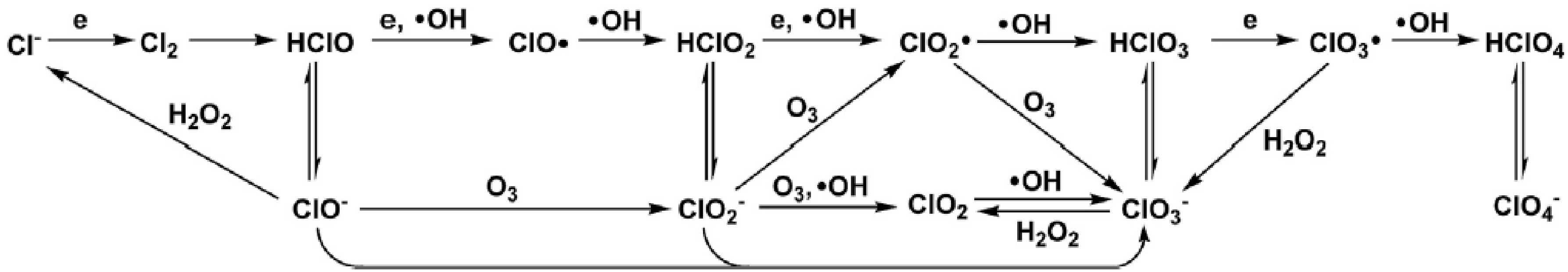
(Wu et al., 2013)

◆ Control of perchlorate generation

- The health risk related to ClO^{-}_{4} is the disruption of the iodine uptake by thyroid gland, which is very critical to synthesize the thyroid hormone

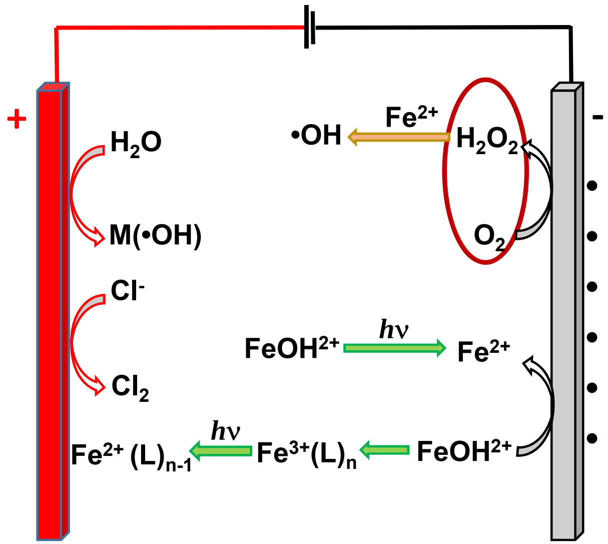






(Lin et al., 2016)

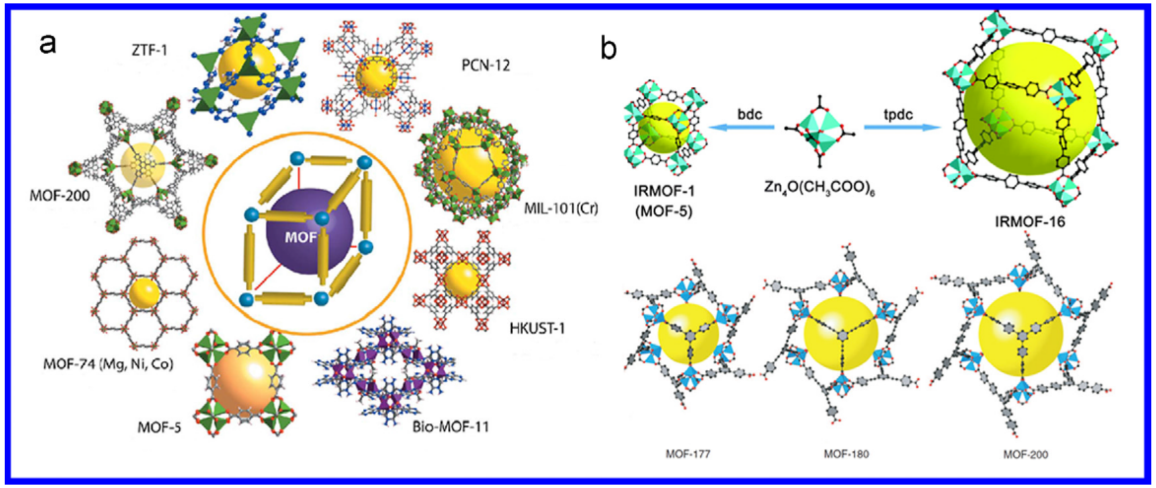
◆ Enhancement of H_2O_2 generation



- activated carbon fiber
- gas diffusion electrode (GDE)
- carbon/graphite felt
- carbon sponges
- reticulated vitreous carbon
- carbon aerogel (CA)

MOFs, coordination polymers formed by connecting metal ions with polytope organic linkers, is a new family of porous materials which own many advantages including:

✓ High surface areas
✓ Good electrical conductivity
✓ High adsorption properties
✓ Crystalline porous materials
✓ High degree of crystallinity
✓ Stable up to temperatures above 200 ° C



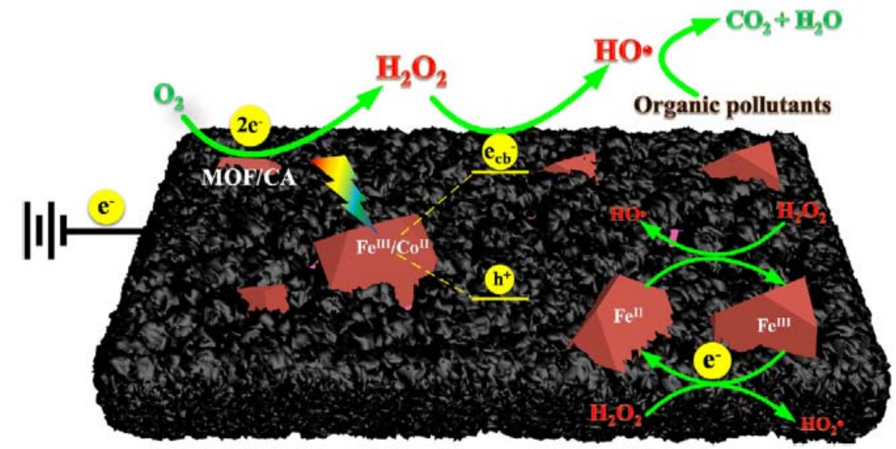


Fig. 15. Schematic illustration of solar–photo–electro–Fenton oxidation mechanism with MOF(2Fe/Co)/CA cathode in acidic condition.

(Zhao et al., 2017)

◆ Thorough assessment of degradation by-products

Two drawbacks:

- Detecting transformation products (TPs) accumulated in the liquid phase without pay attention to gas-phase intermediates
- Using offline GC-MS or LC-MS but failing to detect short-lived and unstable TPs

Two solutions:

- ✓ In gas phase, an online and multidimensional GC-MS technology will be employed for volatile organic compounds (VOCs) analysis
- ✓ In liquid phase, an online electrochemistry coupled to mass spectrometry (EC-MS) will be applied for TPs detection

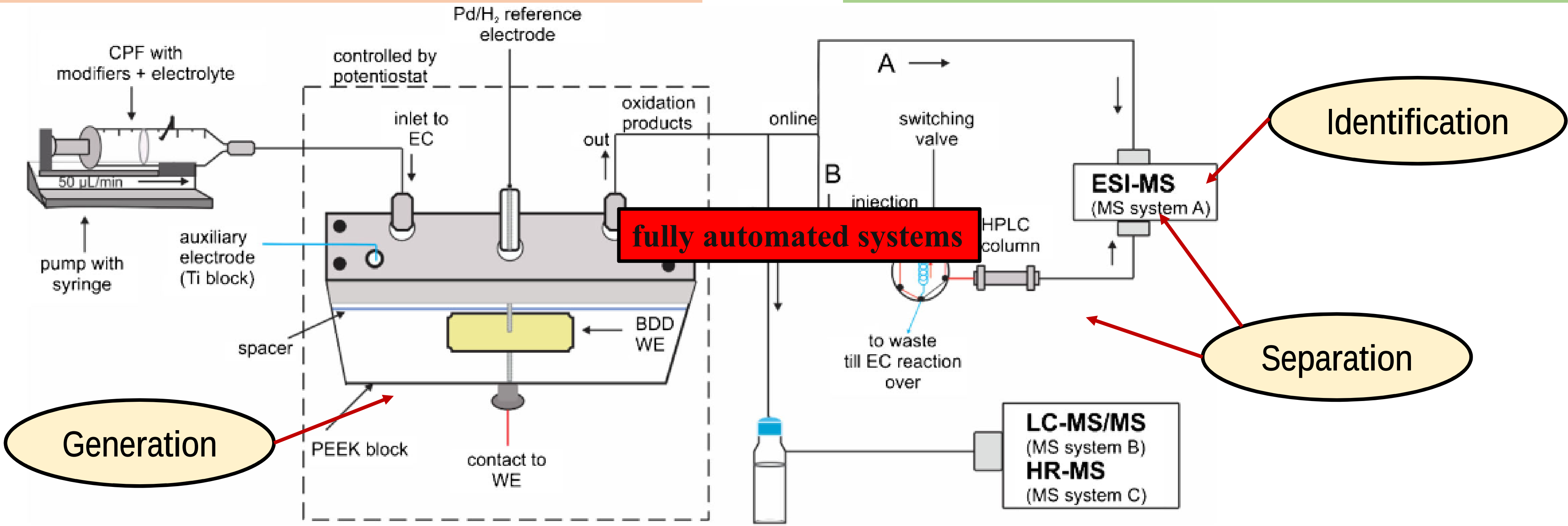


Fig. 1 Set-ups of online EC-ESI-MS (*flow path A*), EC-LC-MS (*flow path B*), and EC offline LC-MS/MS or HRMS (*flow path C*) used for CPF oxidation TPs analysis

(Mekonnen et al., 2017)

Objectives

The main objective of this PhD is to achieve total mineralization of different emerging contaminants in both, simulated and real wastewater, at lab- and pilot-scale.

In detail:

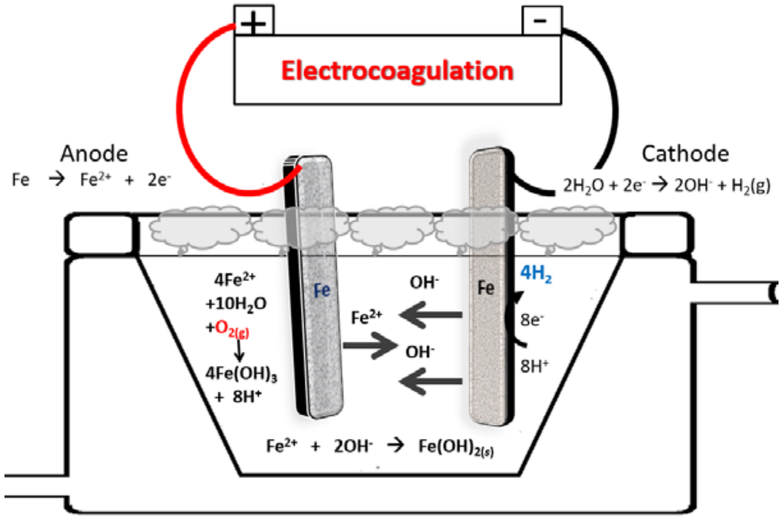
a) Introduce an energy saving and efficient two-step process, EC/EAOPs, to treat emerging contaminants in aqueous media.

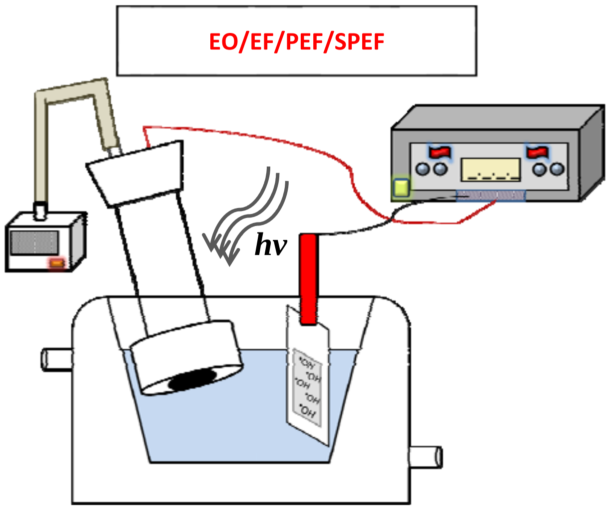
b) Successfully apply EAOPs to treat emerging contaminants under neutral pH by introducing iron-chelating agents.

c) Develop novel DSA anode to minimize perchlorate generation and novel MOF-based GDE cathodes to promote H_2O_2 generation.

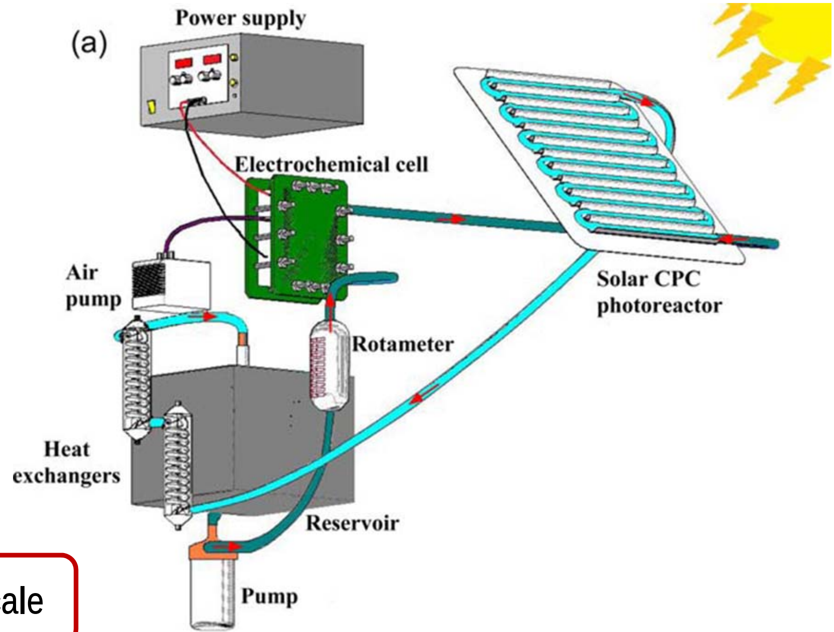
d) Exhaustive study of the degradation pathway for different micropollutants.

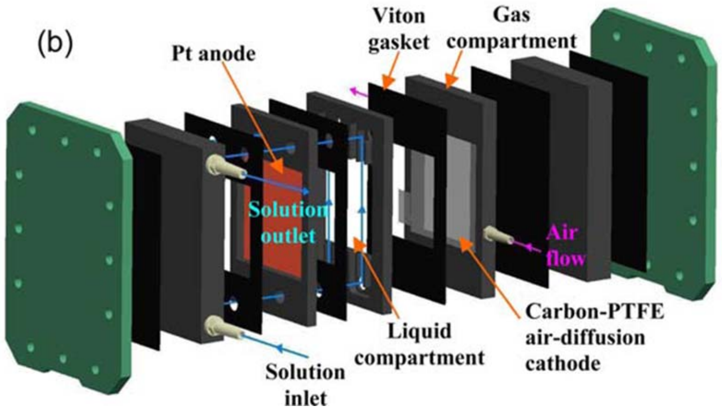
◆ Experimental setups and analysis





Lab-scale ⇒ Pilot-scale





Experimental setups and analysis

UV-Vis Spectrophotometer

Total Organic Carbon Analyzer

LC-MS

Ion Chromatograph

HPLC

SEM

BET

XRD

Up to now......

Work plan and Schedule

Assignment/Trimester	1	2	3	4	5	6	7	8	9	10	11	12
1. Get familiar with lab general learning	X											
2. Investigation of electrocoagulation performance	X	X	X	X			X	X				
3. Evaluation of different EAOPs	X	X	X	X	X	X	X	X	X	X		
4. Application of Fe(III)- in EAOPs				X				X				
5. Fabrication and of new electrodes				X	X	X	X	X				
6. Learning in an abroad							X					
7. Thorough analysis of reaction pathways		X	X	X		X	X	X		X		
8. Attending to conferences		X	X			X	X			X	X	
9. Writing and defense of thesis											X	X

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