

# **Treatment of PFOA using an innovative technology of UV-vis/ $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ /oxalic acid**

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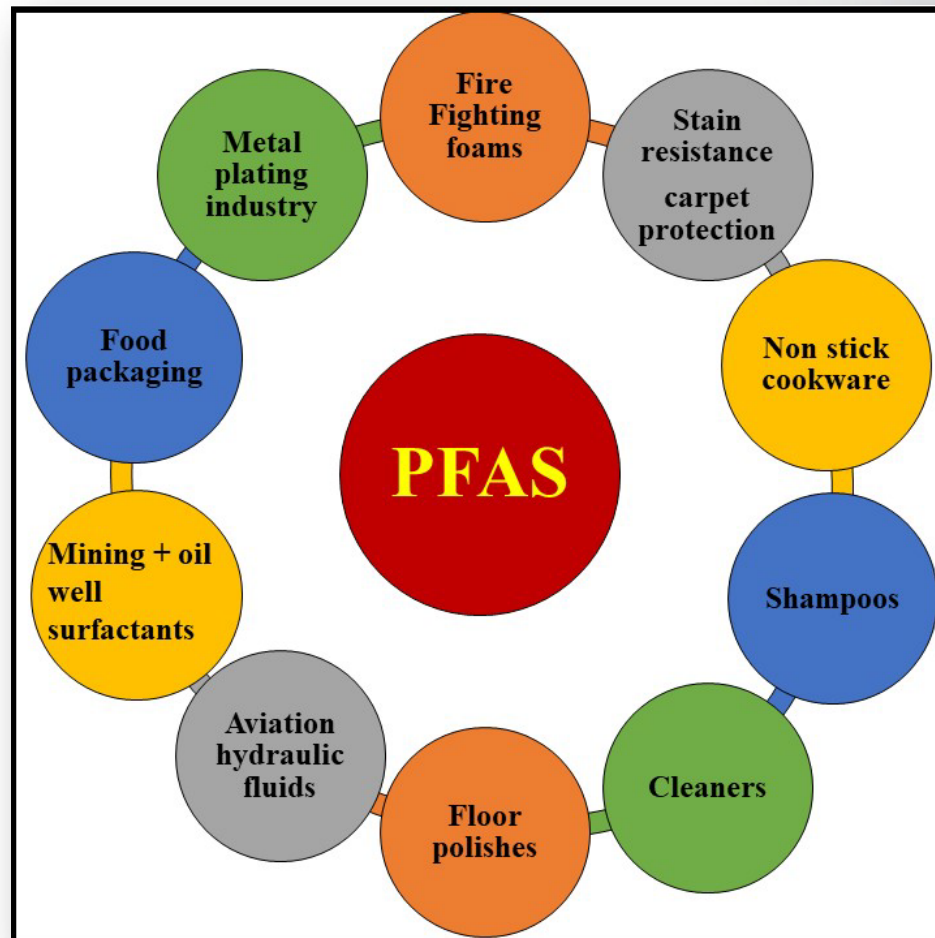
## Outline

- **PFAS Background**
- **PFAS Treatment Technologies**
  - **Ex-Situ**
  - **In- Situ**
- **Chemical/advanced photochemical oxidation processes**
- **Our approach: An innovative technology of UV-vis/  $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ /oxalic acid for PFOA treatment has been performed. The efficiency of the UV-radiation-induced degradation and defluorination of PFOA in aqueous solution has been explored.**
- **Results and Conclusions**



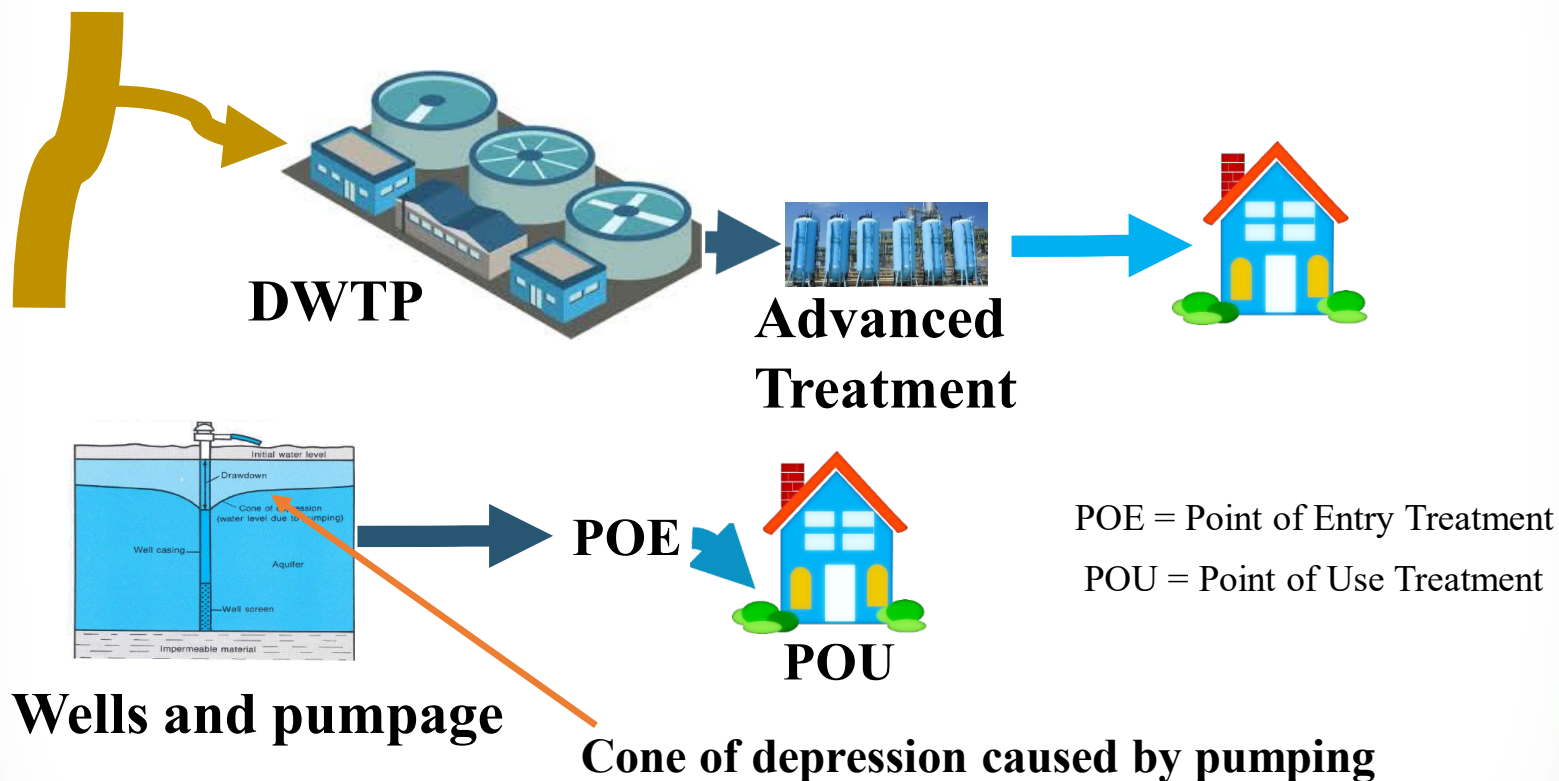
# PFAS Background

- PFAS are a group of human-made chemicals that are resistant to heat, water, and oil.
- Widely used since the 1950s in household and industrial products such as carpeting, waterproof clothing, upholstery, food paper wrappings, fire-fighting foams, and metal plating.
- U.S. EPA has issued a PFAS Action Plan to document steps that the agency is taking on PFAS



Ref: [https://www.epa.gov/sites/production/files/2020-01/documents/pfas\\_action\\_plan\\_feb2020.pdf](https://www.epa.gov/sites/production/files/2020-01/documents/pfas_action_plan_feb2020.pdf)

**Treat the drinking water to cut off the exposure route**



[Ref: https://pubs.usgs.gov/gip/gw\\_ruralhomeowner/](https://pubs.usgs.gov/gip/gw_ruralhomeowner/)

## Manage the sources



Primary and  
Secondary  
Manufacturing



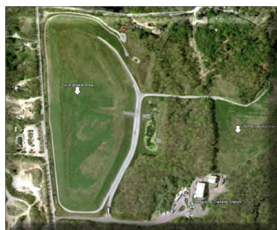
Consumer products  
use/disposal



Wastewater  
plants



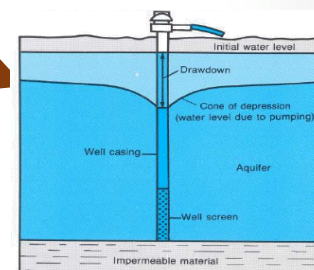
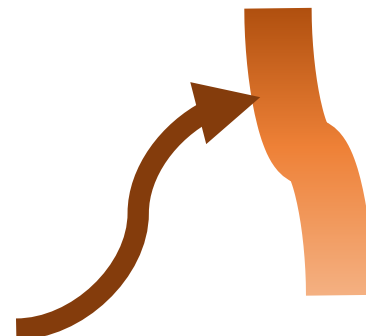
Industrial  
processes



Landfills



Firefighters



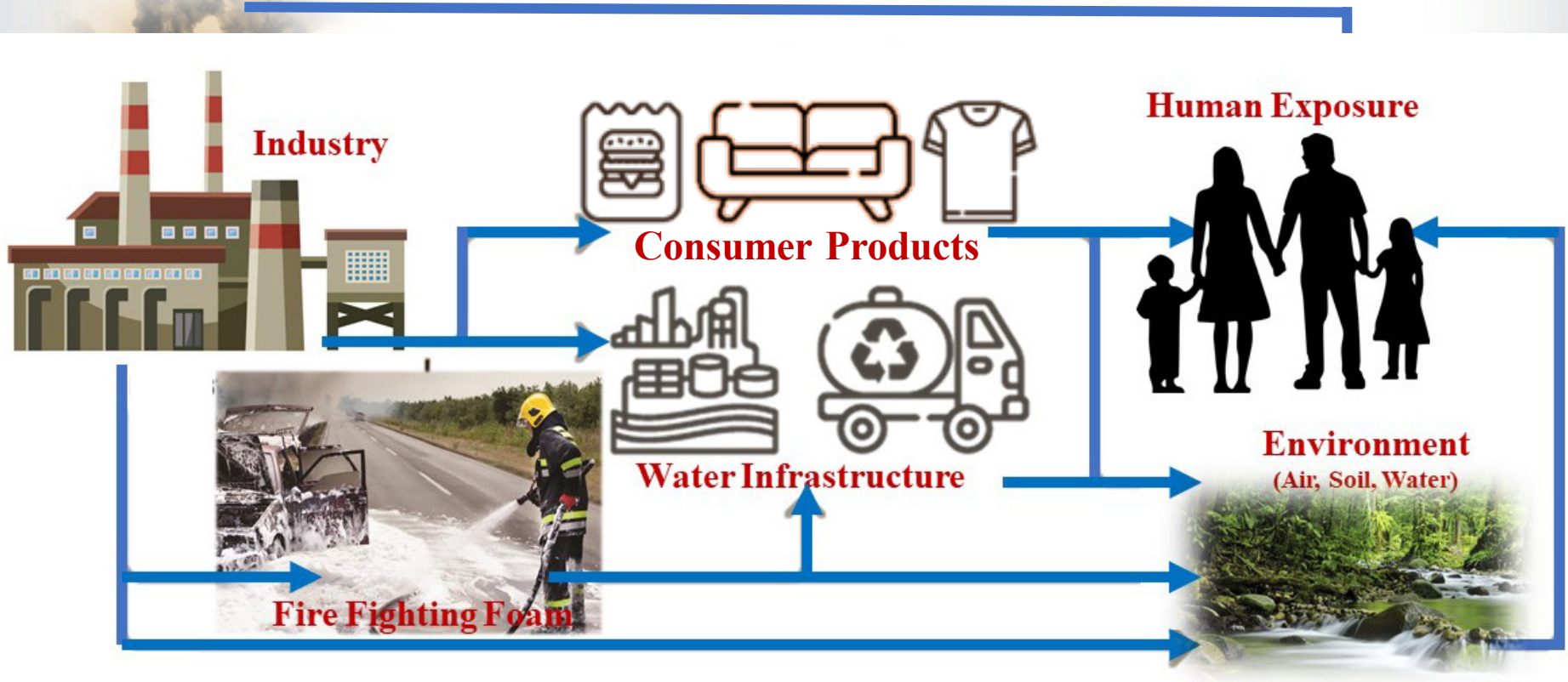
Ref: [https://pubs.usgs.gov/gip/gw\\_ruralhomeowner/](https://pubs.usgs.gov/gip/gw_ruralhomeowner/)





# Fate and Transport Considerations: Overview of PFAS Exposure Pathways

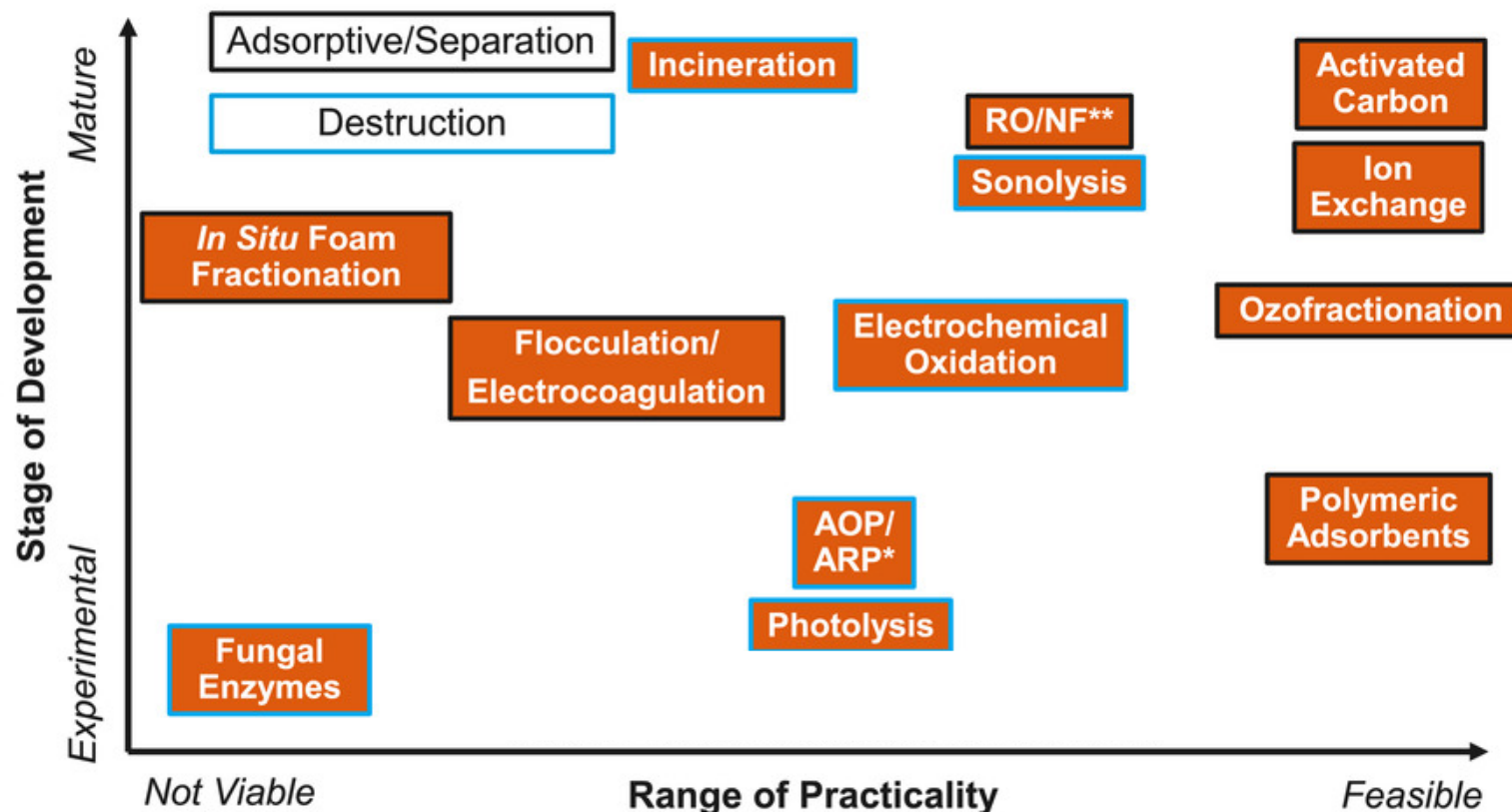
## Stack Emissions



Ref: 1. H.-M. Shin *et al.* Environmental science & technology, 2011, 45, 1435-1442  
2. E. M. Sunderland *et al.* Journal of exposure science & environmental epidemiology 2019, 29, 131-147



# PFAS Treatment Technologies



\*AOP/ARP: Advanced oxidation processes/advanced reduction processes

\*\*RO/NF: reverse osmosis/nanofiltration

Ref: I. Ross et al. Remediation 2018, 28, 101-126



# Drinking Water Treatment for PFAS

## Ineffective Treatments

Conventional Treatment  
Low Pressure Membranes  
Biological Treatment (including slow sand filtration)  
Disinfection  
Oxidation  
Advanced oxidation

### PAC Dose to Achieve

50% Removal 16 mg/l

90% Removal **>50**

**mg/L**

*Dudley et al., 2015*

## Effective Treatments

Anion Exchange Resin (IEX)  
High Pressure Membranes  
Powdered Activated Carbon (PAC)  
Granular Activated Carbon (GAC)

### Percent Removal

90 to 99

93 to 99

10 to 97

0 to 26

> 89 to > 98

- **Effective**

- **Effective**

- **Effective for only select applications**

- **Ineffective**

- **Effective**

Extended Run Time

Designed for PFAS Removal





# Ex-Situ PFAS Water Treatment Technologies

Compound	M.W. (g/mol)	Aeration	Coagulation Dissolved Air Floatation	Coagulation Flocculation Sedimentation Filtration	Conventional Oxidation (MnO <sub>4</sub> , O <sub>3</sub> , ClO <sub>2</sub> , CLM, UV-AOP)	Anion Exchange	Granular Activated Carbon	Nano Filtration	Reverse Osmosis
PFBA	214	assumed	assumed						
PFPeA	264								
PFHxA	314								
PFHpA	364								
<b>PFOA</b>	<b>414</b>								
PFNA	464					assumed	assumed		
PFDA	514					assumed	assumed		
PFBS	300								
PFHxS	400								
<b>PFOS</b>	<b>500</b>								
FOSA	499						assumed		assumed
N-MeFOSAA	571	assumed				assumed	assumed	assumed	
N-EtFOSAA	585					assumed	assumed	assumed	

■ < 10% removal    ■ > 90% removal  
■ unknown    ■ > 10%, < 90% removal

Source: Dickenson and Higgins, 2016.

→ Low molecular weight PFAS are more challenging for treatment

Ref: Dickenson, E. and C. Higgins. 2016. Treatment Mitigation Strategies for Poly- and Perfluorinated Chemicals. Project 4322. Denver, Colo.: Water Research Foundation



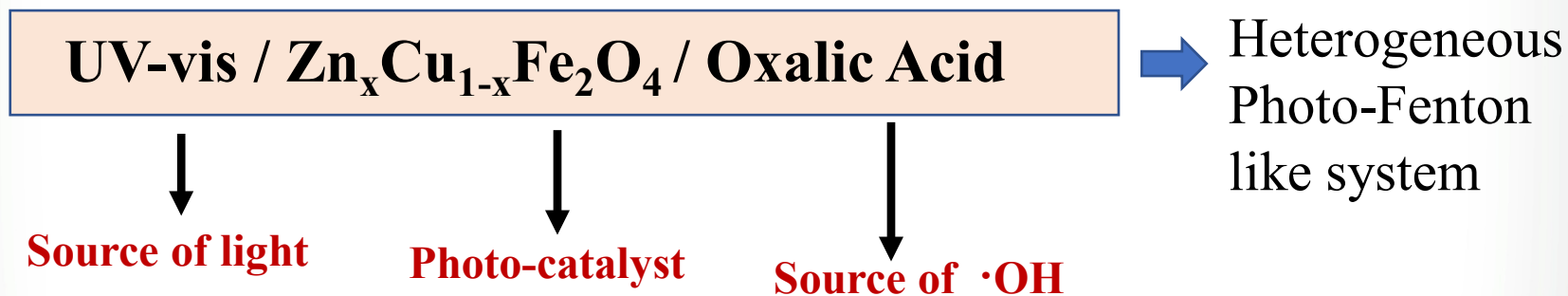
## Our Approach

- ❑ Magnetically separable heterogenous photocatalyst  $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$  ( $x = 0.2, 0.4, 0.5, 0.6$  and  $0.8$ ) has been synthesized.
- ❑ Electrochemical reduction of PFOA has been performed.
- ❑ An innovative technology of UV-vis/  $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ /oxalic acid has been performed for PFOA treatment. Additionally, the efficiency of the UV-radiation-induced degradation and defluorination of PFOA in aqueous solution has been explored.
- ❑ The degradation of by-products has been measured to assess the removal and transformation of PFOA.
- ❑ Based on LC-TOF analysis, the plausible photo-mineralization mechanism of PFOA has been proposed.



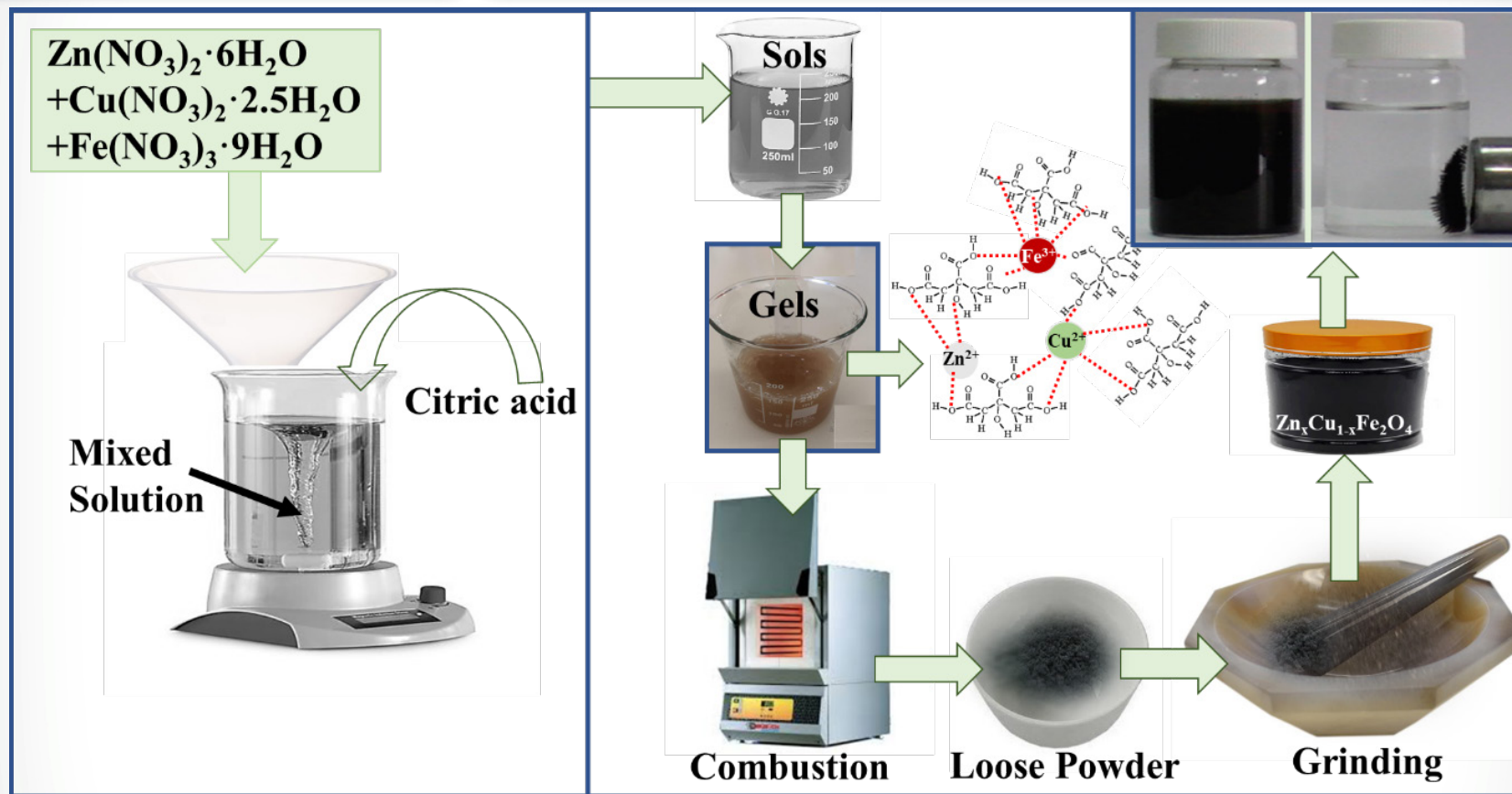
## New Catalytic Approach: UV-vis / $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ / Oxalic Acid

- ❑ Oxidation can transform PFOA and PFOS to less toxic products, mainly fluoride ions, carbon dioxide and shorter chain perfluorocarboxylic acids (PFCAs).
- ❑ Chemical oxidation has the potential to destroy PFOS and PFOA *in situ* rather than transferring contamination to another waste stream or area.



The combination of  $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$  and oxalic acid behaves as a heterogeneous photo-Fenton like system generating of  $\text{OH}^\bullet$  radicals without an addition of  $\text{H}_2\text{O}_2$  under UV light irradiation.

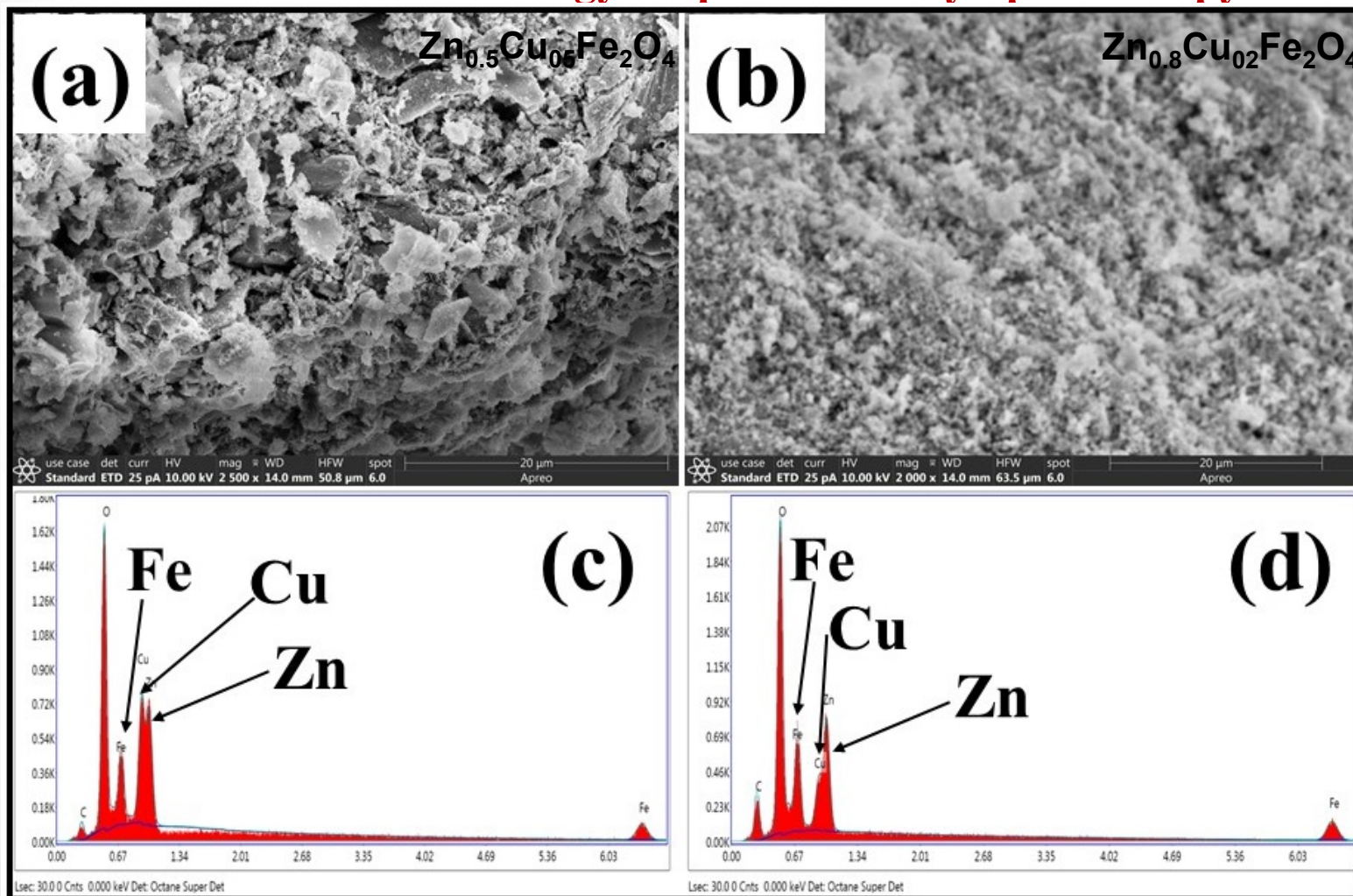
# Synthesis of $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ catalyst



Ref: Nadagouda *et al.* "Treatment and Removal of PFOA Using an Innovative Technology of UV-vis/ $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ /Oxalic Acid: A Sustainable Approach to Effectuate  $\cdot\text{OH}$ " ES&T preparation

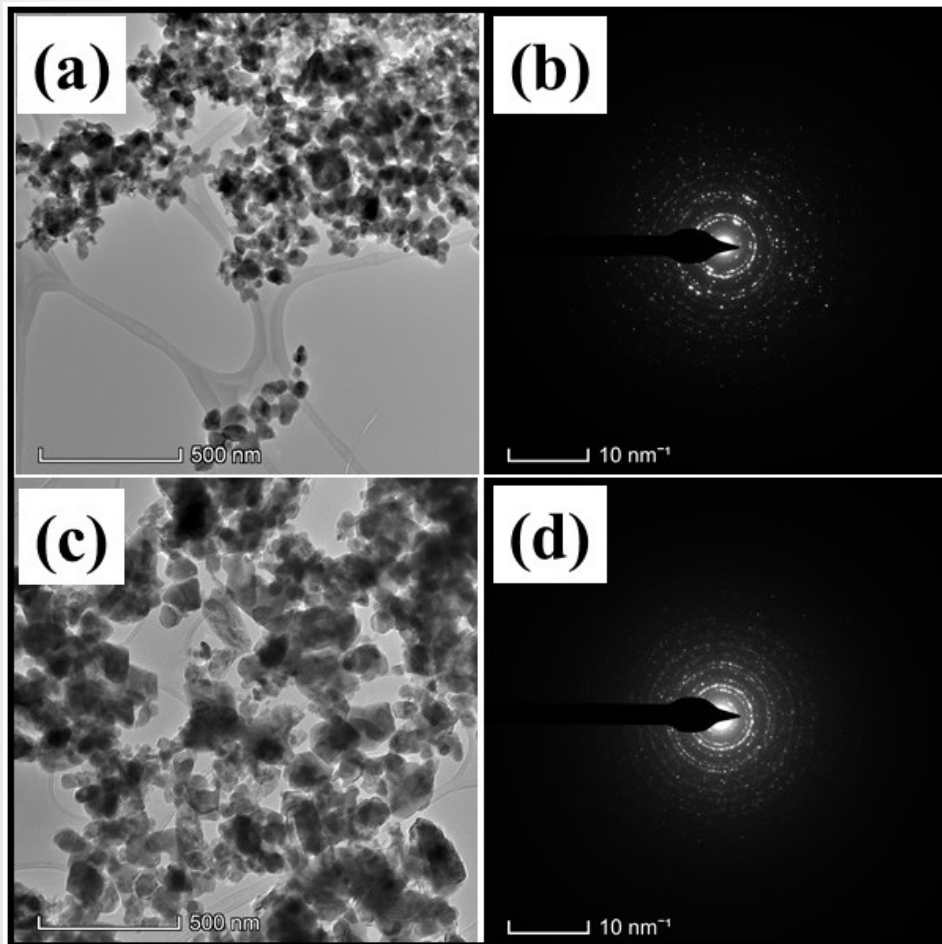
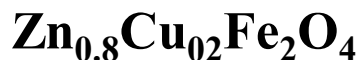
# Characterization of $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$

## SEM and Energy Dispersive X-ray Spectroscopy





# High resolution transition electron micrograph

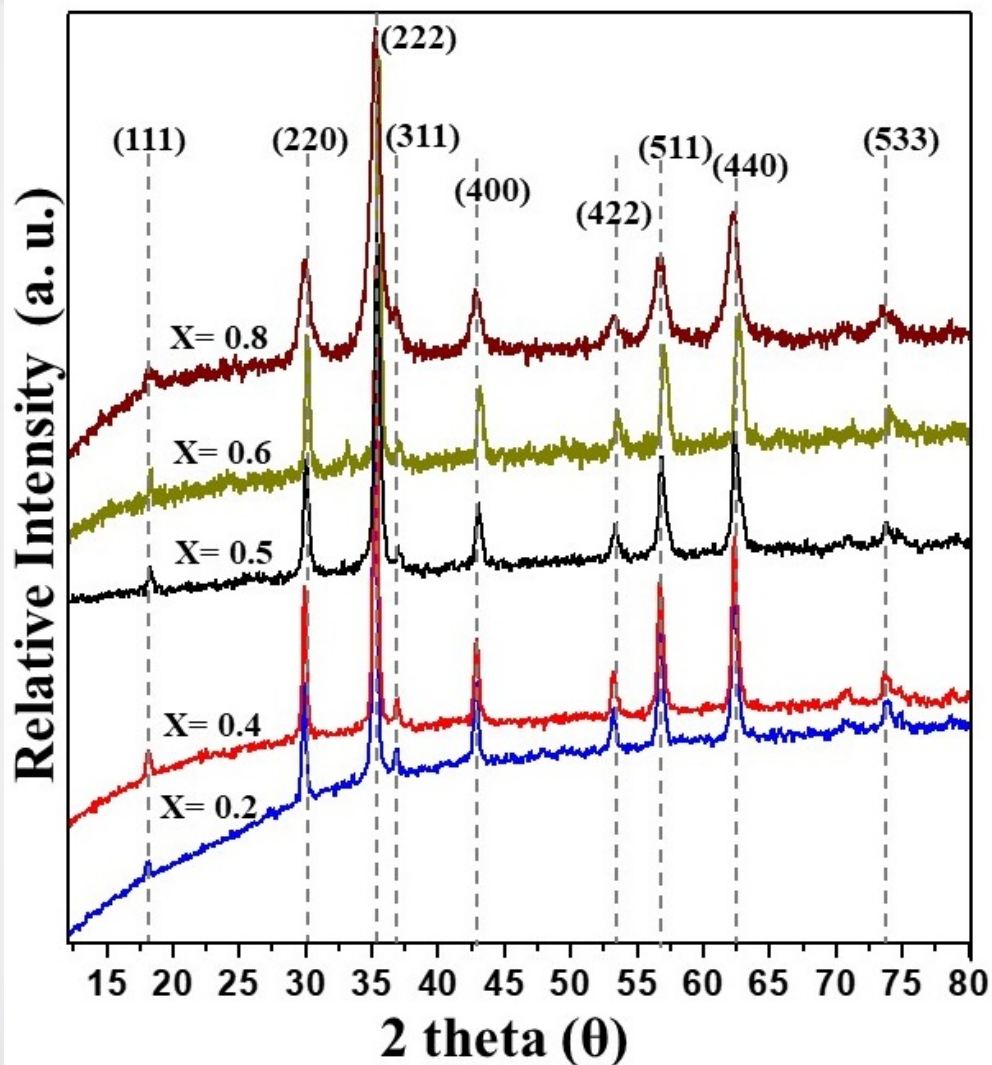


Particle size ~20 nm.  
Selected area diffraction (SAED) images (b) and (d) confirm the crystallinity of the materials.



# X-Ray Diffraction

## Phase identification and crystallinity

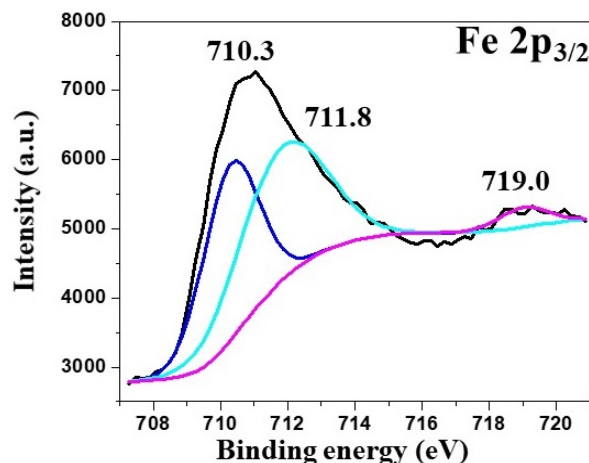
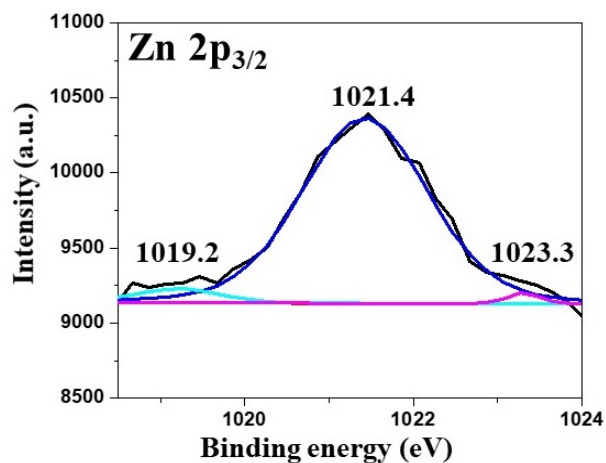
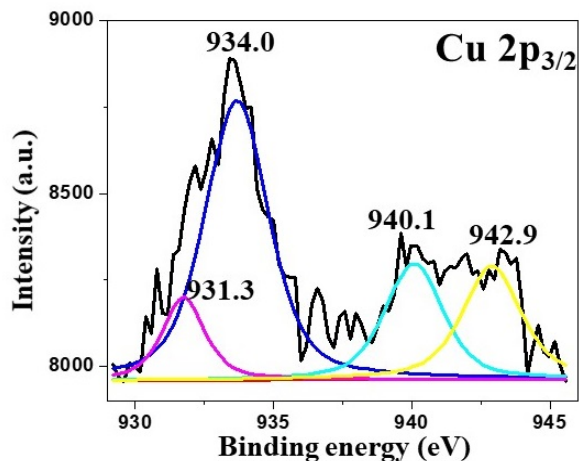
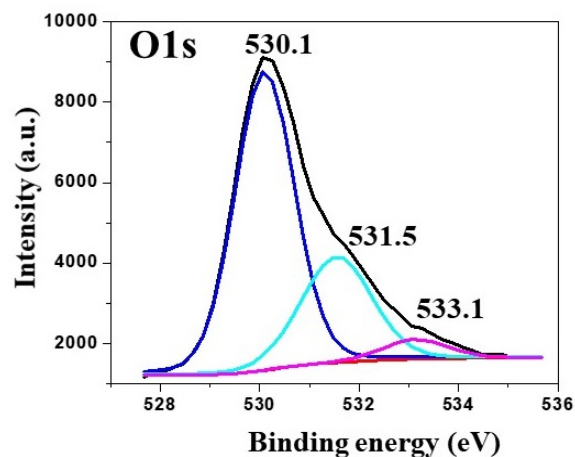


The observed peaks at  $18.34^\circ$ ,  $30.20^\circ$ ,  $35.53^\circ$ ,  $36.93^\circ$ ,  $43.05^\circ$ ,  $53.53^\circ$ ,  $56.90^\circ$ ,  $62.23^\circ$ , and  $73.89^\circ$  are, respectively, representing the (111), (220), (222), (311), (400), (422), (511), (440), and (533) Bragg reflection as compared with the spinel copper zinc ferrite ( $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ , JCPDS#01-077-0012).



# X-ray photoelectron spectroscopy

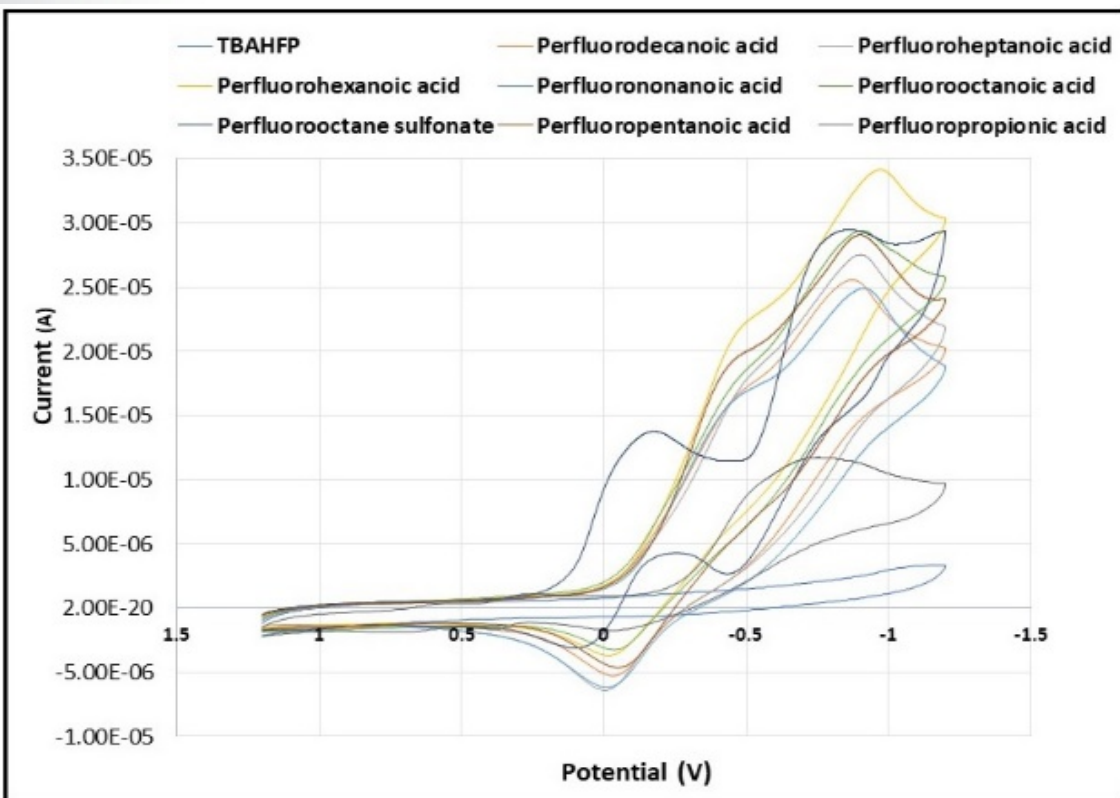
## $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ Catalyst



Elemental composition  
of catalyst surfaces and  
the chemical state of  
surface atoms



# Electrochemical Reduction

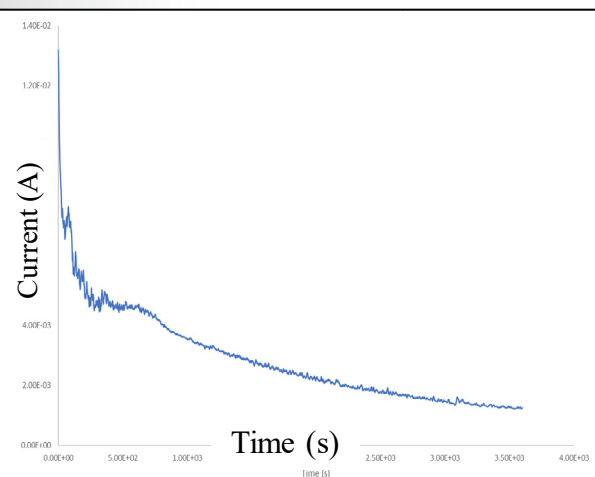


- ❑ Cyclic voltammetry (CV) studies of seven (PFAS) show that the compounds are reducible.
- ❑ This suggests electrochemical reduction method for the decomposition of PFAS in water is possible.

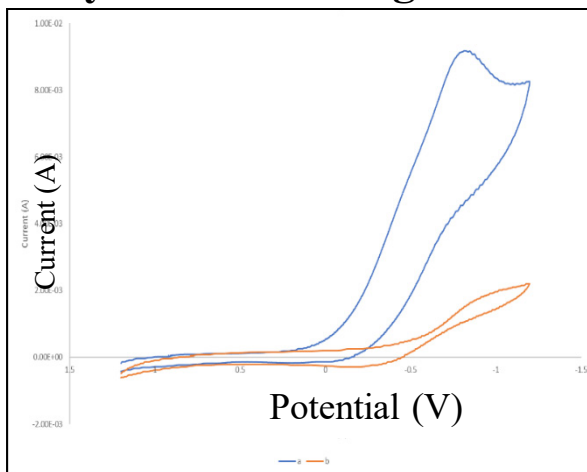


# Exhaustive electrolysis study of PFOA

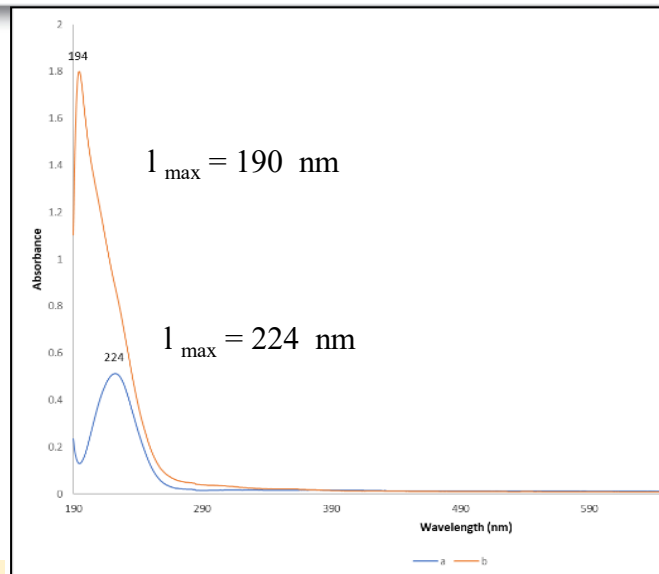
## Cyclic voltammograms



**Chronoamperometric response for 25 mL of the 5.0 mM PFOA in 0.1 M TBAHFP-CH<sub>3</sub>CN using a platinum gauze electrode. Potential applied vs. Ag/AgCl, KCl(satd.).**



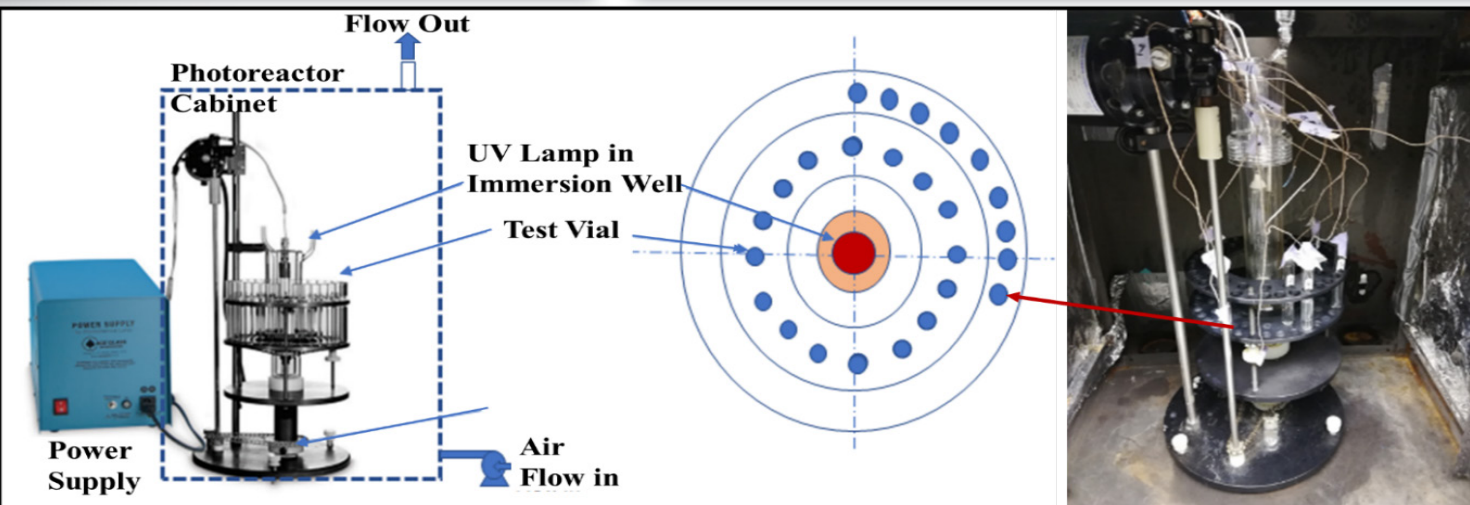
**CV of 5.0 mM perfluorooctanoic acid at a platinum electrode in 0.1M TBAHFP-CH<sub>3</sub>CN 100 mV/s scan rate (a) before exhaustive electrolysis and (b) after exhaustive electrolysis.**



**UV-Vis spectrum of PFOA (a) before exhaustive electrolysis, and (b) After exhaustive electrolysis**  
**Shift in  $\lambda_{\text{max}}$  Indicates the formation of a new product**



# Photodegradation of PFOA

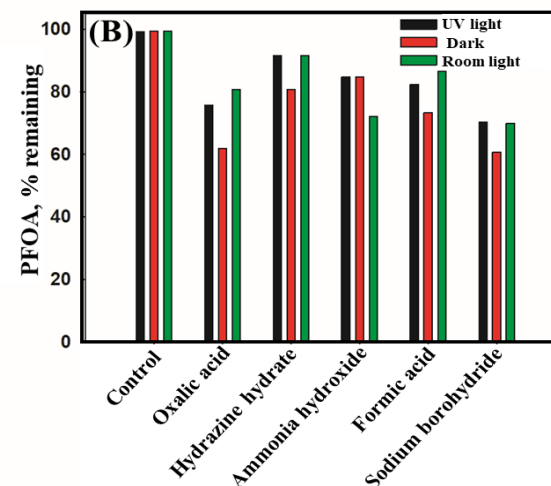
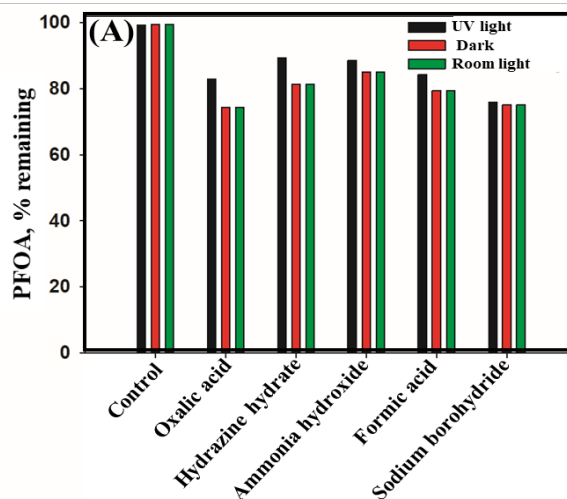


## Effects of

A) lower and,

B) higher

concentrations of various additives on the degradation of PFOA ( $C_0=100$  ppb)



# Photo-Catalytic degradation PFOA

**$\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$  catalyst (50 mg) + PFOA (6 mL) and oxalic acid (0.1 M, 1 mL)**



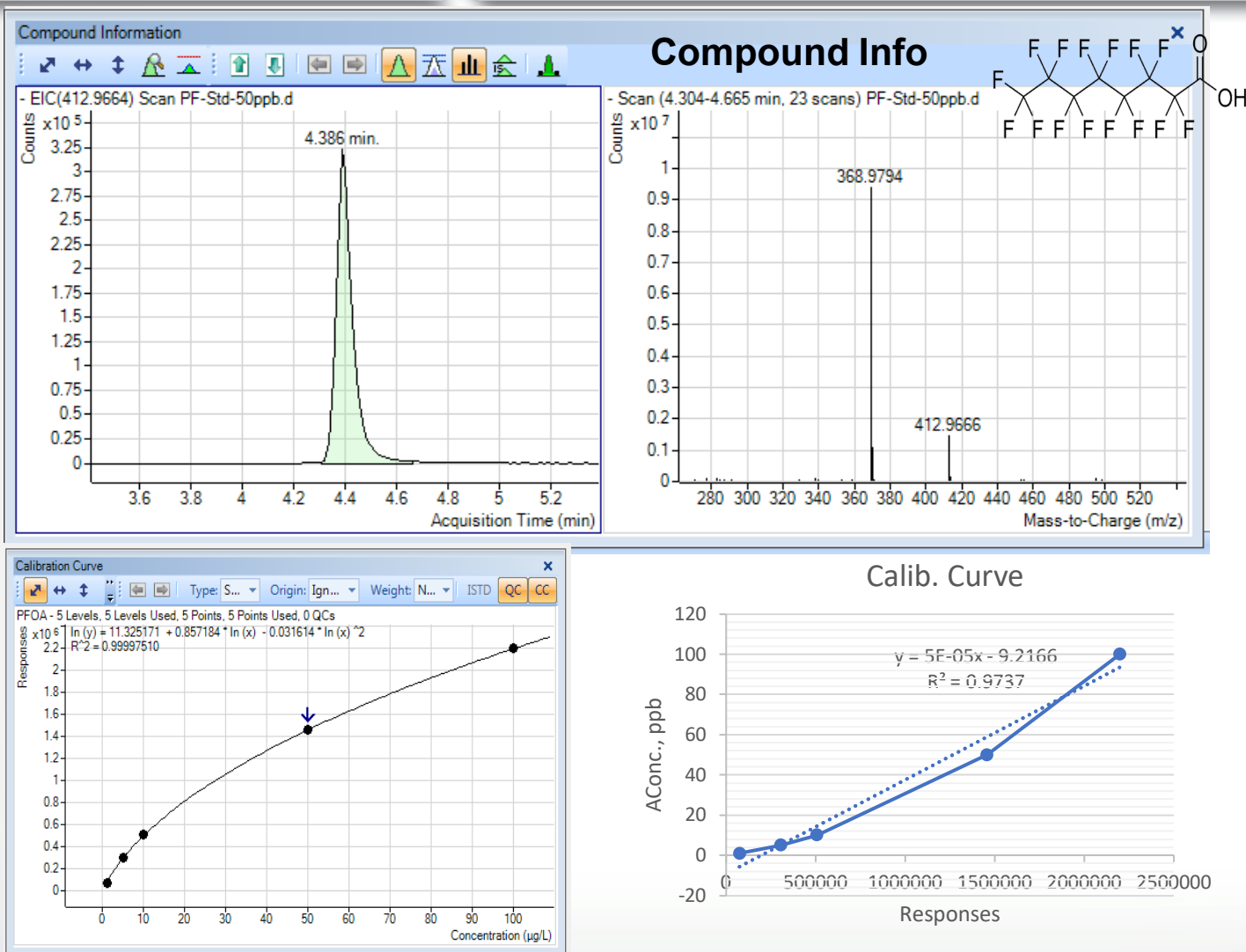
Water cooled UV reactor

Rotating platform @ 15 RPM

- PFOA concentration: 100 ppm, 10 ppm and 100 ppb
- Mixtures were shaken for 10 min before placed in the reactor.
- Sample tubes were taken at given time intervals of 2, 4 and 6 hours and filtered through 0.45  $\mu\text{m}$  Polyvinylidene difluoride (PVDF) filter with polypropylene syringe housing
- All experiments were conducted in triplicate at room temperature.
- All samples are analyzed by LC-Q-TOF (Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS)

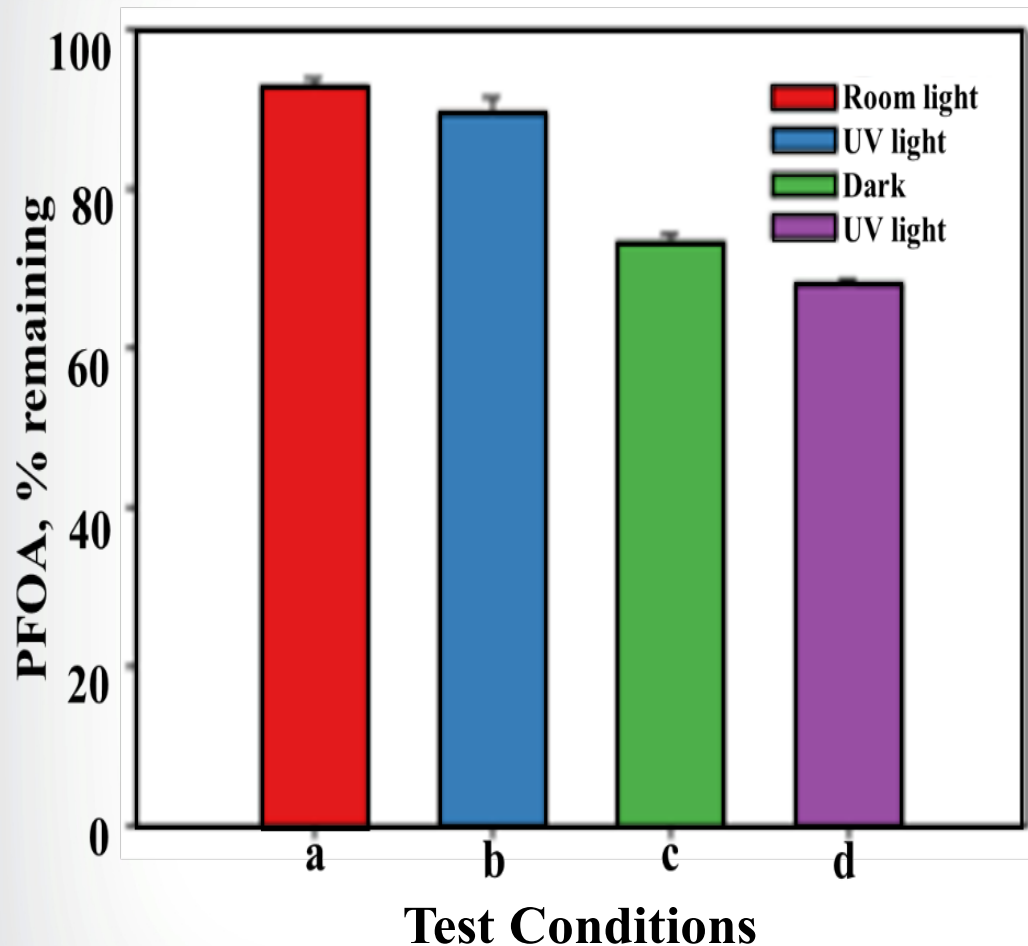


# LC-QTOF analysis of PFOA





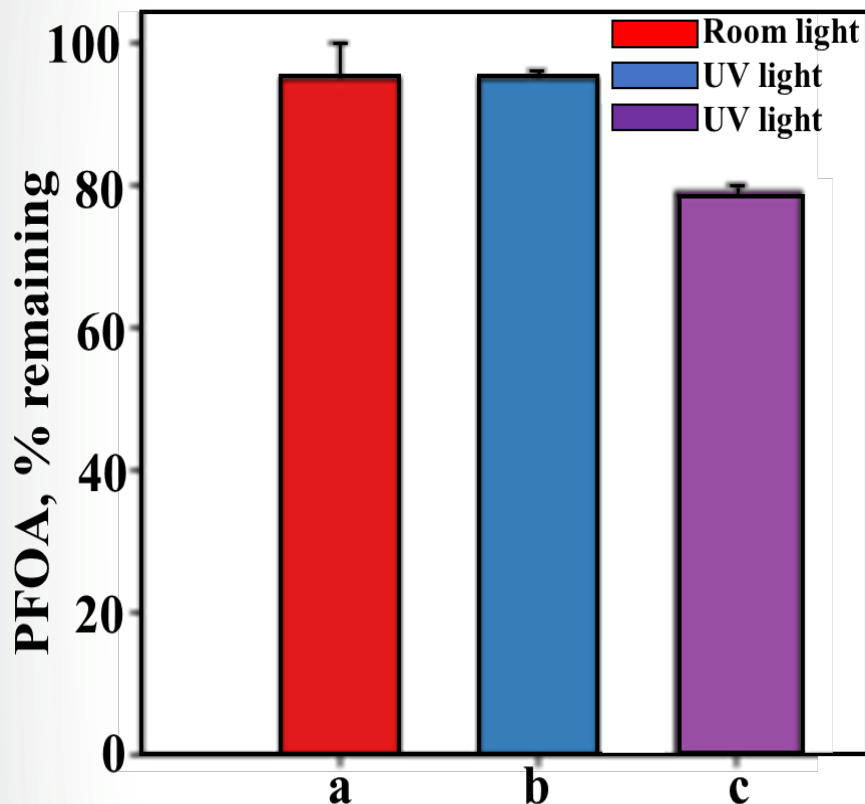
# Photodegradation of PFOA ( $C_o=100\text{ppm}$ , 6 ml, $\text{pH}=2.03$ )



- a) Without catalyst: 6.0 ml PFOA ( $C_o=100\text{ ppm}$ ) in room light;
- b) Without catalyst: 6.0 ml PFOA ( $C_o=100\text{ ppm}$ ) in UV light;
- c) With catalyst: 6.0 ml PFOA ( $C_o=100\text{ ppm}$ ) +  $8.3\text{ g L}^{-1}\text{ Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$  + 0.1 M Oxalic acid (1 ml) in dark;
- d) With catalyst: 6.0 ml PFOA ( $C_o=100\text{ ppm}$ ) +  $8.3\text{ g L}^{-1}\text{ Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$  + 0.1 M Oxalic acid (1 ml) in UV light



# Photodegradation of PFOA at different test conditions



$C_o = 10$  ppm

$V = 6$  ml,

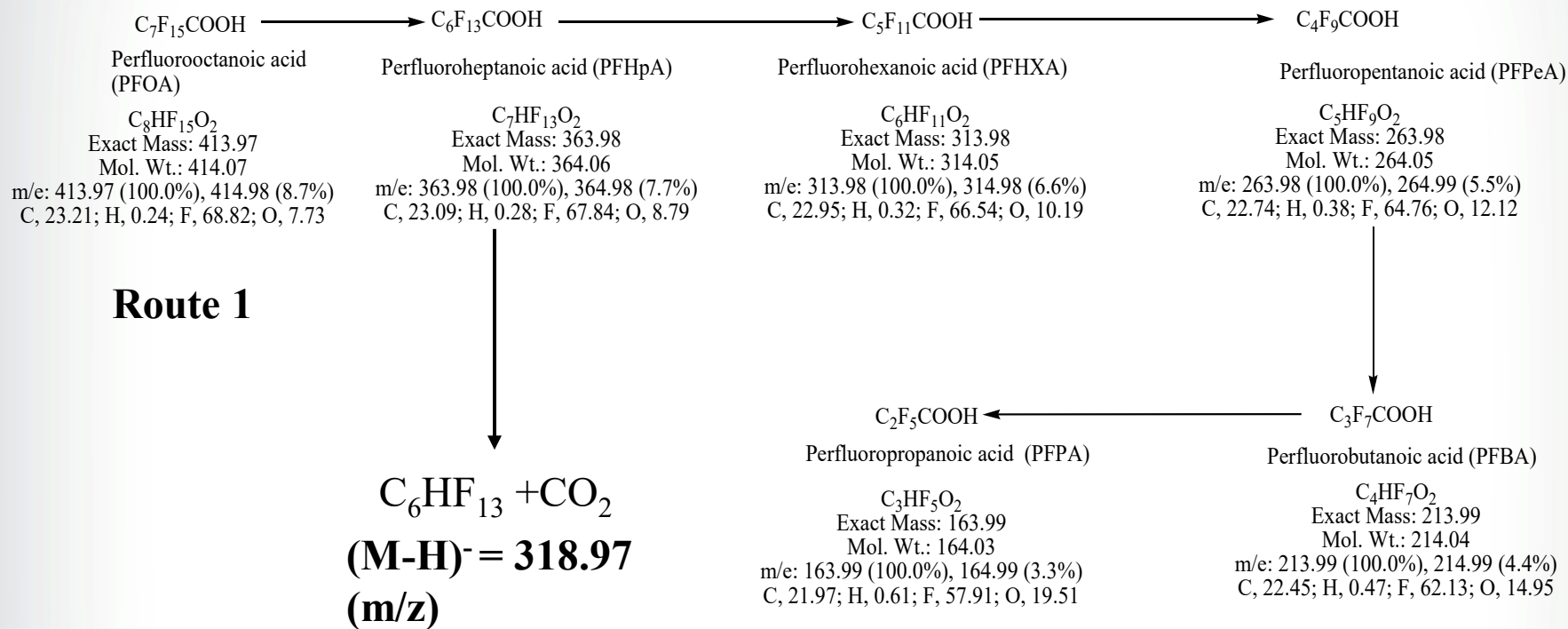
pH = 2.03

- a) Without catalyst: 6.0 ml PFOA ( $C_o=10$  ppm) in room light;
- b) Without catalyst: 6.0 ml PFOA ( $C_o=10$  ppm) in UV light
- c) With catalyst: 6.0 ml PFOA ( $C_o=10$  ppm) +  $8.3 \text{ g L}^{-1} \text{ Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$  + 0.1 M Oxalic acid (1 ml) in UV light





# Possible intermediate products for the mineralization of PFOA



We observed one by-product  $C_6HF_{13}$  ( $(M-H)^- = 318.97$  (m/z)) during Q-TOF analysis.

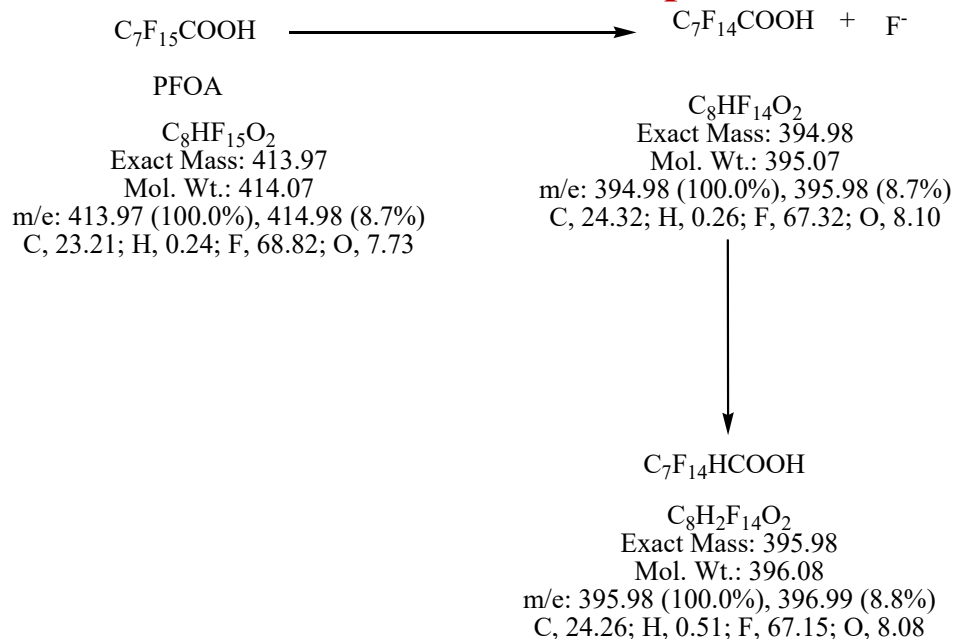
Ref: 1. Scientific Reports volume 4, Article number: 7418 (2014)

2. Journal of Hazardous Materials 2018, 344, 950-957



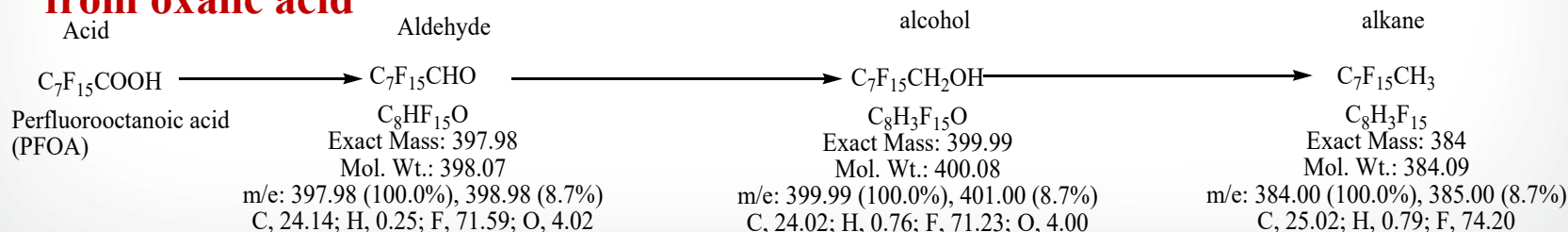
# Possible intermediate products for the mineralization of PFOA

## Route 2 Reductive defluorination of perfluorooctanoic acid

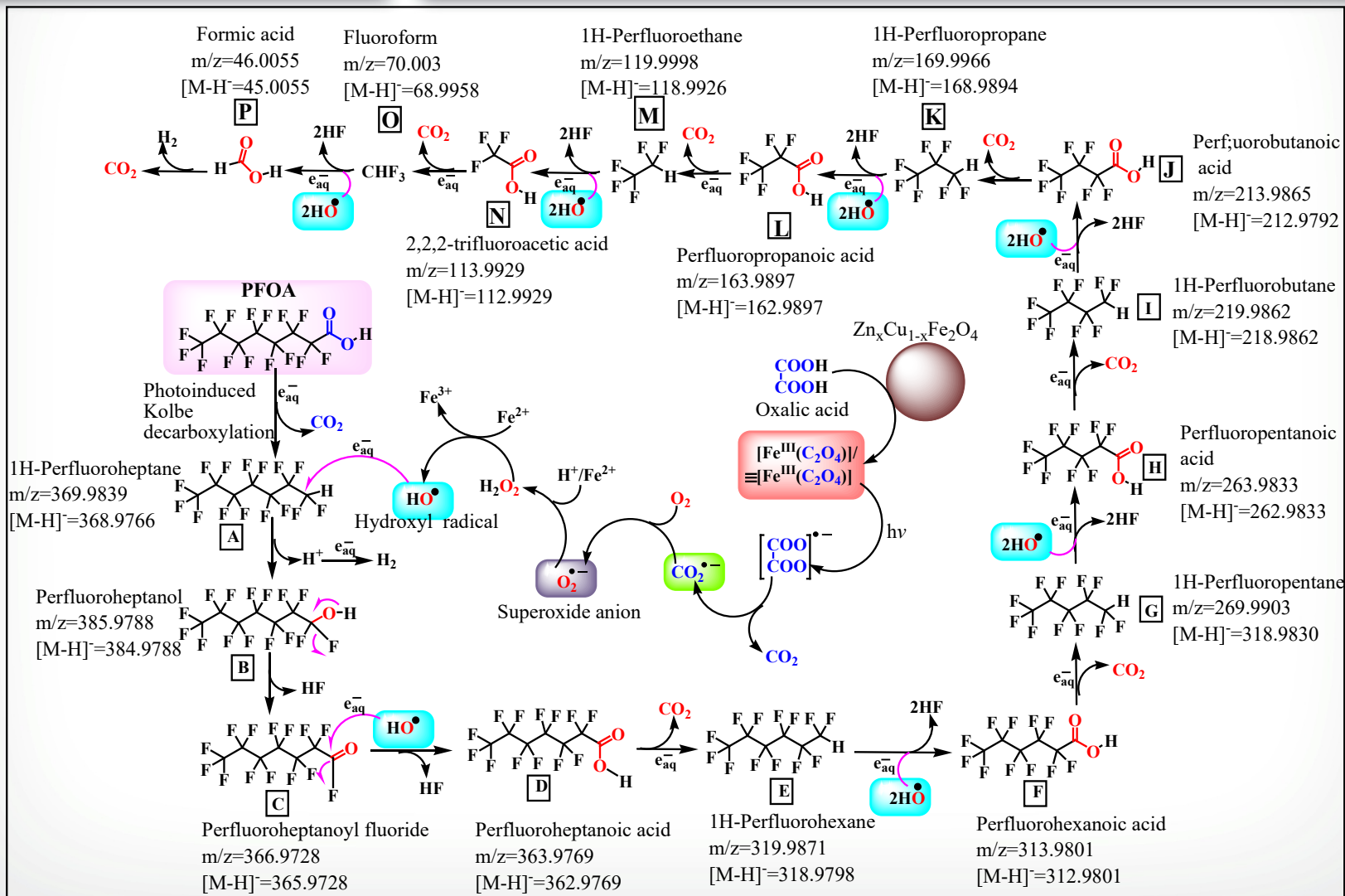


Ref: Journal of Hazardous Materials 2017, 340, 336-343

## Route 3 Other Plausible intermediate products: Reduction of -COOH group by $\text{H}_2$ from oxalic acid

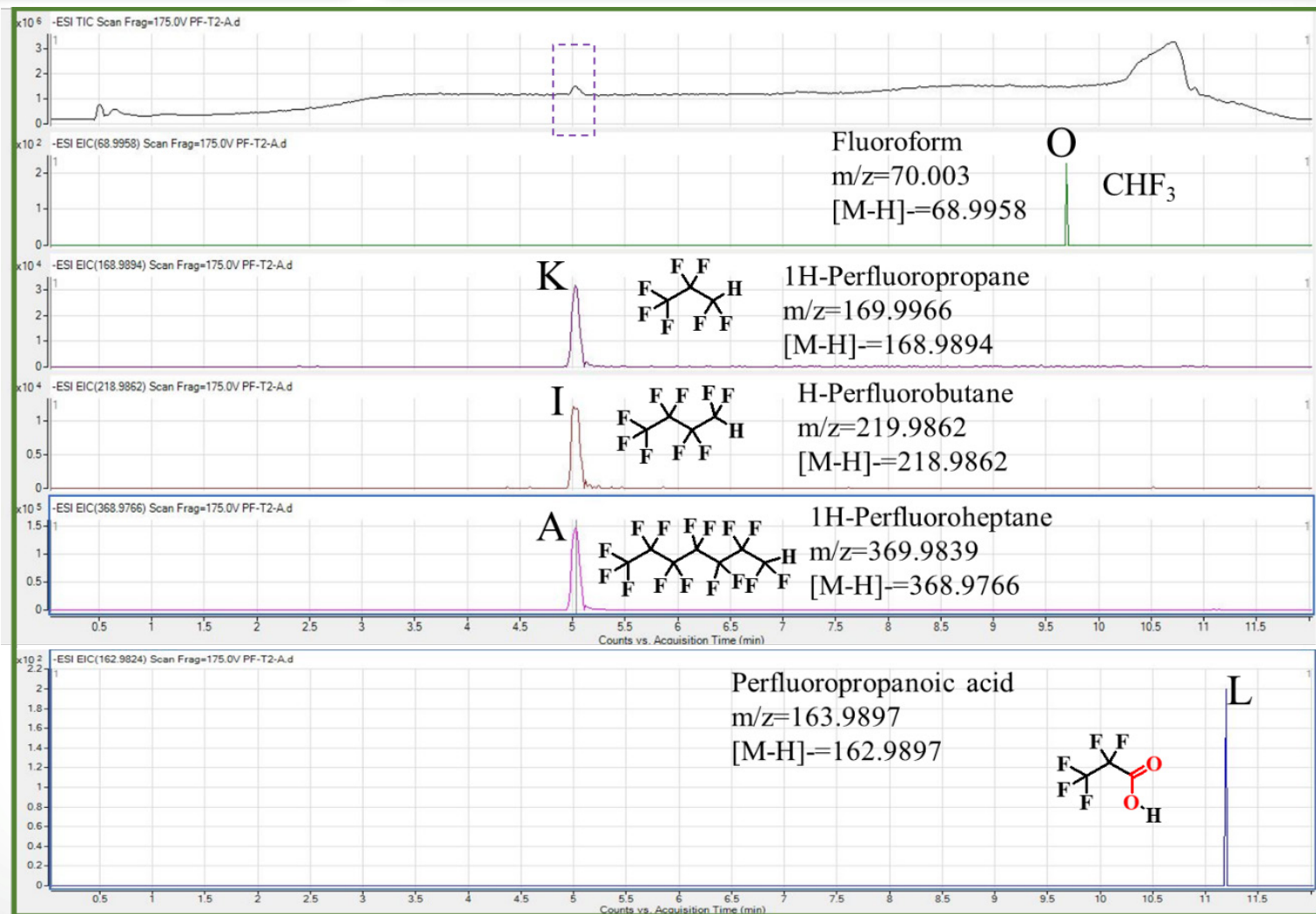


# Plausible pathway for oxidative decomposition and defluorination of PFOA





# Analysis of PFAS by-products using LC-QTOF analysis (Extracted ion chromatogram)





## Conclusions

- ❖ UV-light with  $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$  and oxalic acid have shown to reduce PFOA significantly.
- ❖ Preliminary tests of cyclic voltammetry (CV) show electrochemical reduction of PFOA. This will be utilized to create an electrochemical method for the decomposition of PFAS in water.
- ❖ Additional analysis is necessary to evaluate performance in the presence of multiple PFAS, as well as that a combination of approaches may be necessary

## Future research/next step

The ultimate goal is to develop an innovative technology for the complete mineralization of PFAS at a reduced cost.





## Disclaimer

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**Thank you**