Remediation of water from per- and poly-fluoroalkyl substances (PFAS) with advanced oxidation processes: a comparative study of ozonation and photocatalysis

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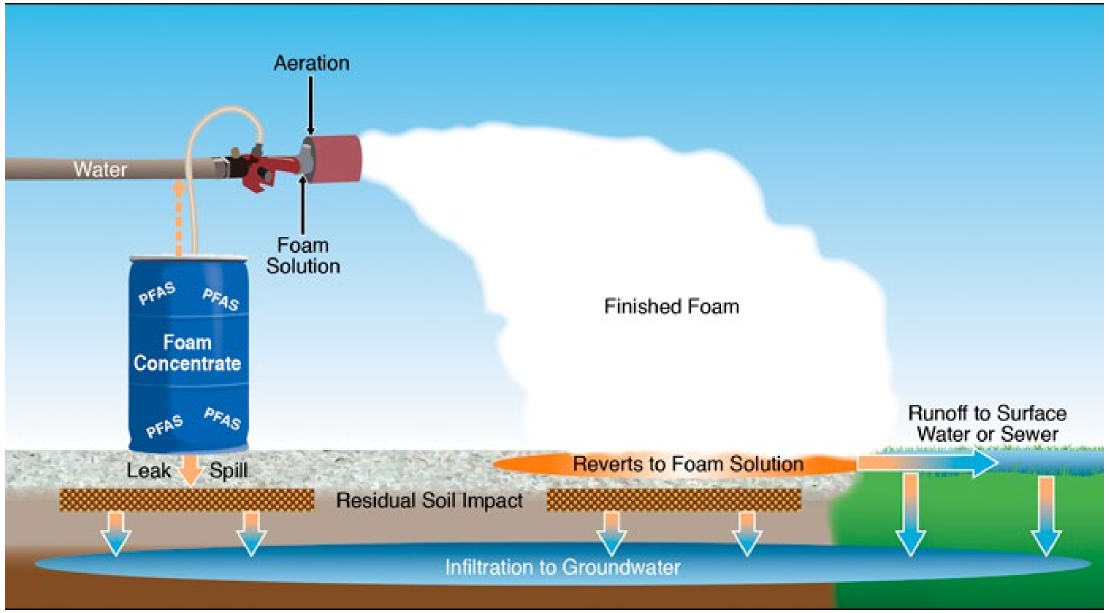
Water pollution by PFAS



- PFAS are persistent pollutants (AFFFs, coatings textiles etc.)
- Widespread pollution of vadose zone and groundwater by PFAS
- PFAS are surfactants and may generate foams and emulsions
- Intrusion in the food chain and human body with harmful health effects

- Fixed System Testing
- Mobile Firefighting Equipment Testing
- Training Exercises
- Emergency Firefighting Operations

Synthesis and immobilization of photocatalysts

- PFOA and three-distilled water were used to prepare stock solutions of desired concentration.
- ZnO photocatalytic nanoparticles were synthesized and immobilized on various non-porous beads by dip-coating in aqueous solutions of salts and thermal annealing.

Duranit (80 % SiO_2-20% Al_2O_3) beads without and with ZnO particles

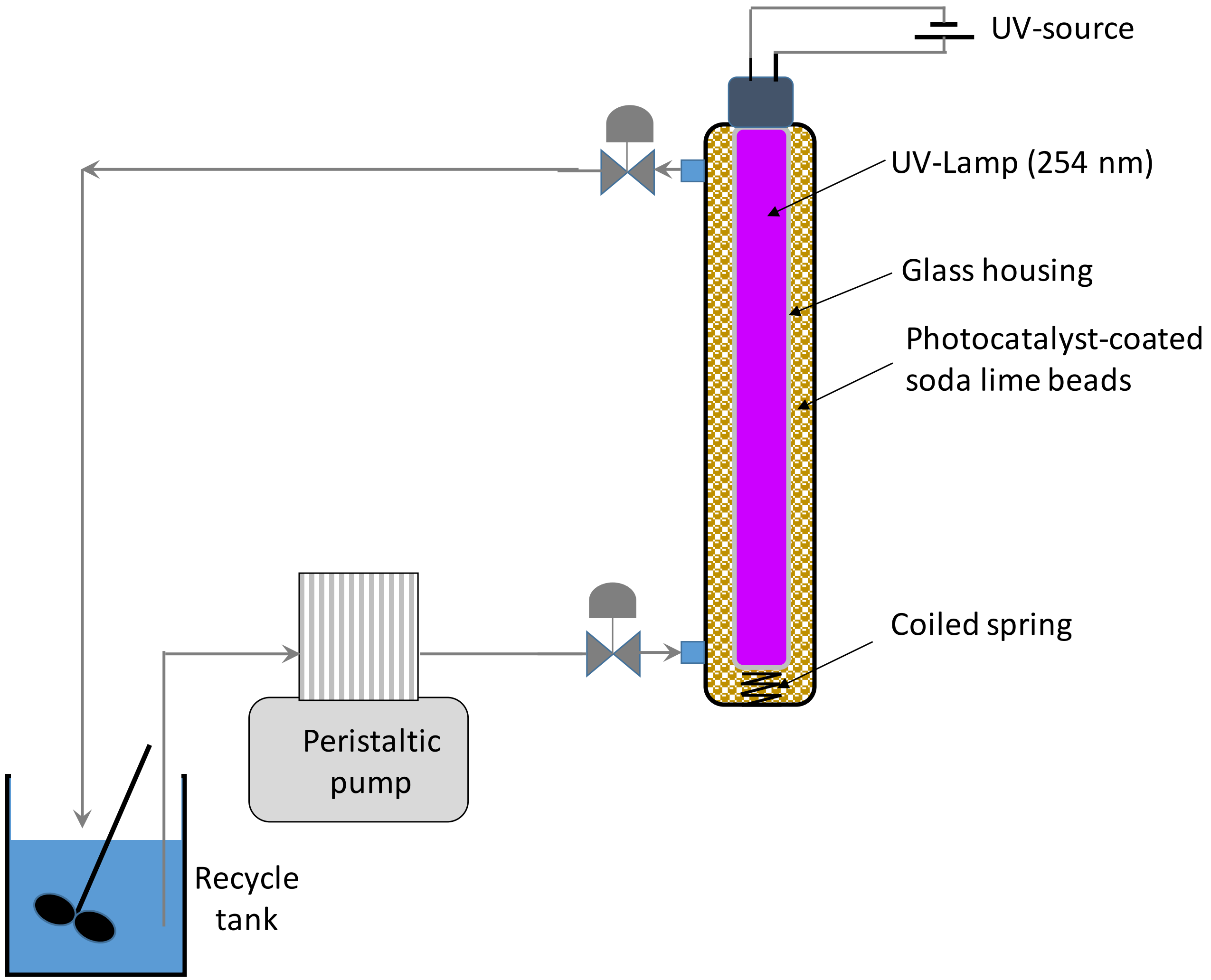
Soda-lime glass beads without and with Fe-doped ZnO particles

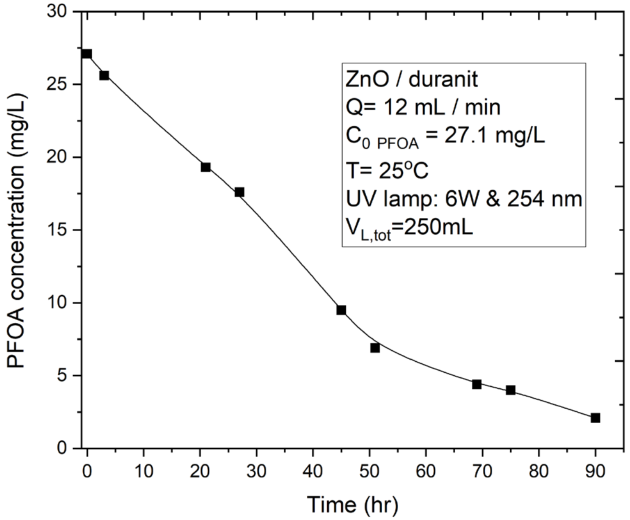
Karavasilis and Tsakiroglou, *Can. J. Chem. Eng.*,1-18 (2021). DOI: 10.1002/cjce.24199
Karavasilis et al., *Nanomaterials,* 12, 69 (2022). https://doi.org/10.3390/nano12010069
Karavasilis et al., *IOP Conf. Series: Earth and Environmental Science* 1123 (2022) 012082. DOI: 10.1088/1755-1315/1123/1/012082

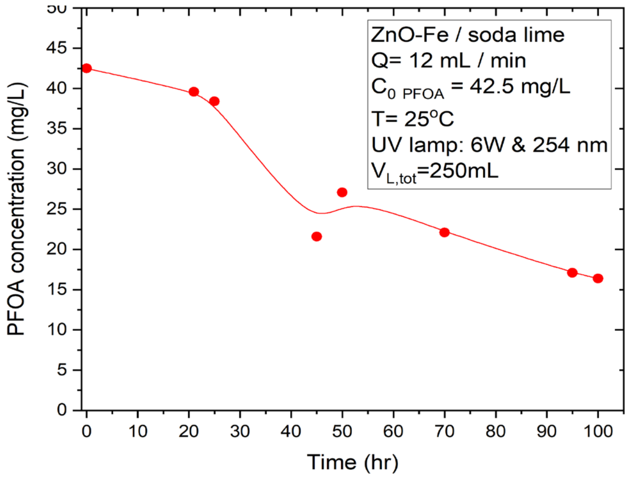
Spectophotometric (UV-Vis) determination of PFAS

- Collection of 4 mL PFOA aqueous solution
- Add 2mL Citrate buffer 0.01 M
- Add 2 mL Methylene Blue solution 0.001 M
- Add 20 mL of chloroform
- Mixing in funnel
- Moderate shaking for 15 min
- Centrifuging at 6000 rpm
- The aqueous layer was aspirated
- the absorbance of the chloroform layer was measured at the maximum absorbance(652 nm) with UV-VIS.

Photocatalytic degradation of PFAS







Modeling the transport and reactive processes in photoreactor

$$\frac{\partial C_R}{\partial t} = D_L \frac{\partial^2 C_R}{\partial x^2} - u_0 \frac{\partial C_R}{\partial x} - r_{ph}$$ Mass balance in fixed-bed reactor

$$\frac{dC_T}{dt} = \frac{Q}{V_T}\left[C_R(t, z = L) - C_T\right]$$ Mass balance in recycling tank

$$r_{ph} = \frac{\rho_{sub}(1-\phi)}{\phi}\left(\frac{W_{cat}}{M_{sub}}\right) k' C_R^{\,n}$$ Local heterogeneous reaction rate

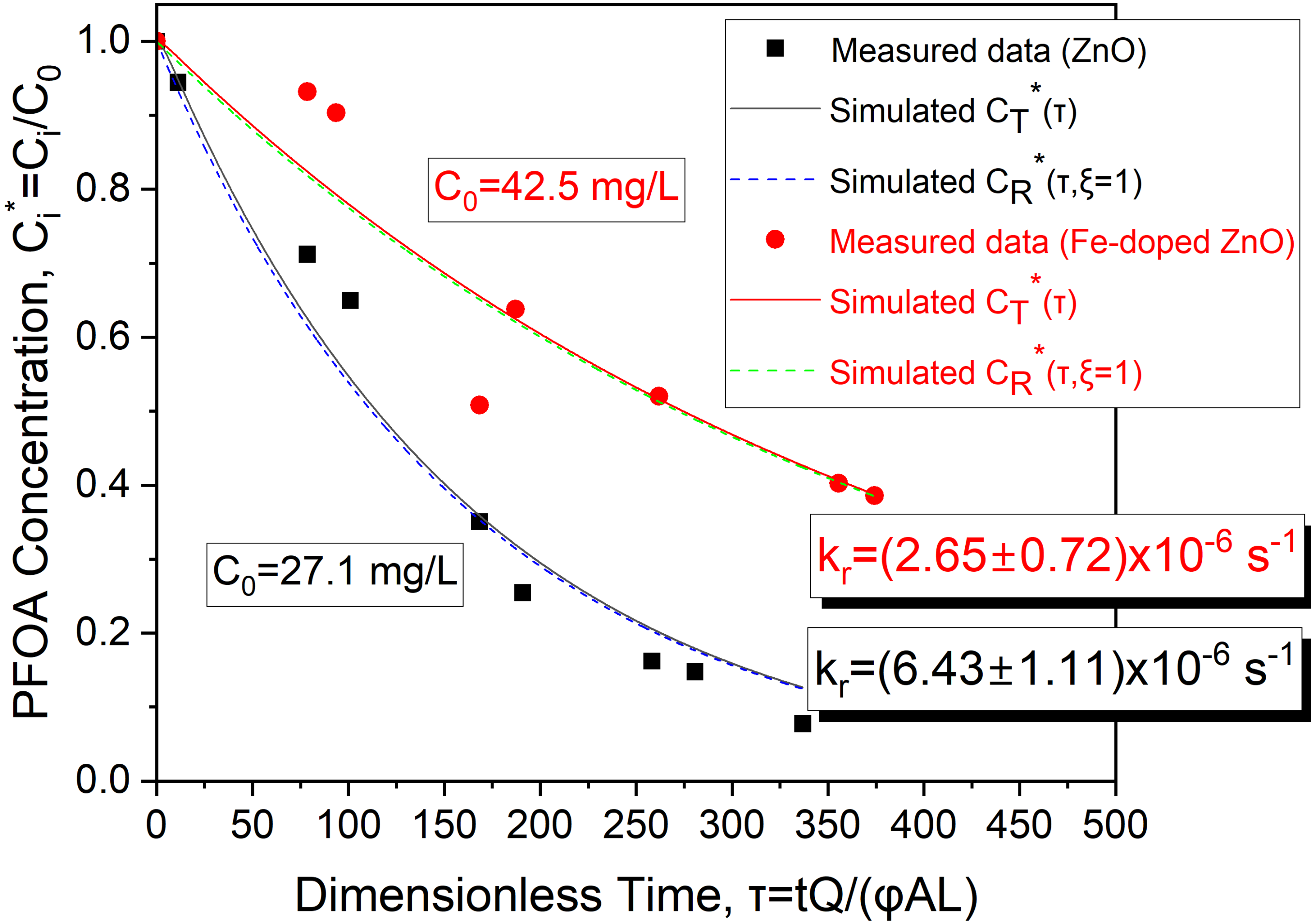
$$D_L = \frac{D_m}{F\phi} + a_L u_0 \qquad F = \phi^{-m}$$ Hydrodynamic dispersion coefficient in porous medium

$C_R(t,z)$: PFOA concentration in aqueous phase (kg/m^3)
D_L: longitudinal dispersion coefficient ($m^2 s^{-1}$)
F: porous medium electrical formation factor
$u_0 = Q/(\varphi A)$: average pore velocity ($m\ s^{-1}$)
ϕ : bed porosity
ρ: solid substrate density ($kg\ m^{-3}$)
Q: volumetric rate ($m^3\ s^{-1}$)

r_{ph}: PFOA photocatalytic reaction rate ($kg\ m^3\ s^{-1}$)
k': heterogeneous reaction kinetics ($m^3\ kg^{-1}\ s^{-1}$)
$C_T(t)$: MB concentration in recycle tank
V_T: volume of recycle tank
$C_R(t,z=L)$: PFOA concentration in the effluent
W_{cat}: catalyst mass
M_{sub} : substrate mass

Karavasilis et al., *Nanomaterials,* 12, 69 (2022).
https://doi.org/10.3390/nano12010069
Karavasilis et al., *Chem. Eng. Res. & Des.* 195 (2023) 490–507.
https://doi.org/10.1016/j.cherd.2023.06.014

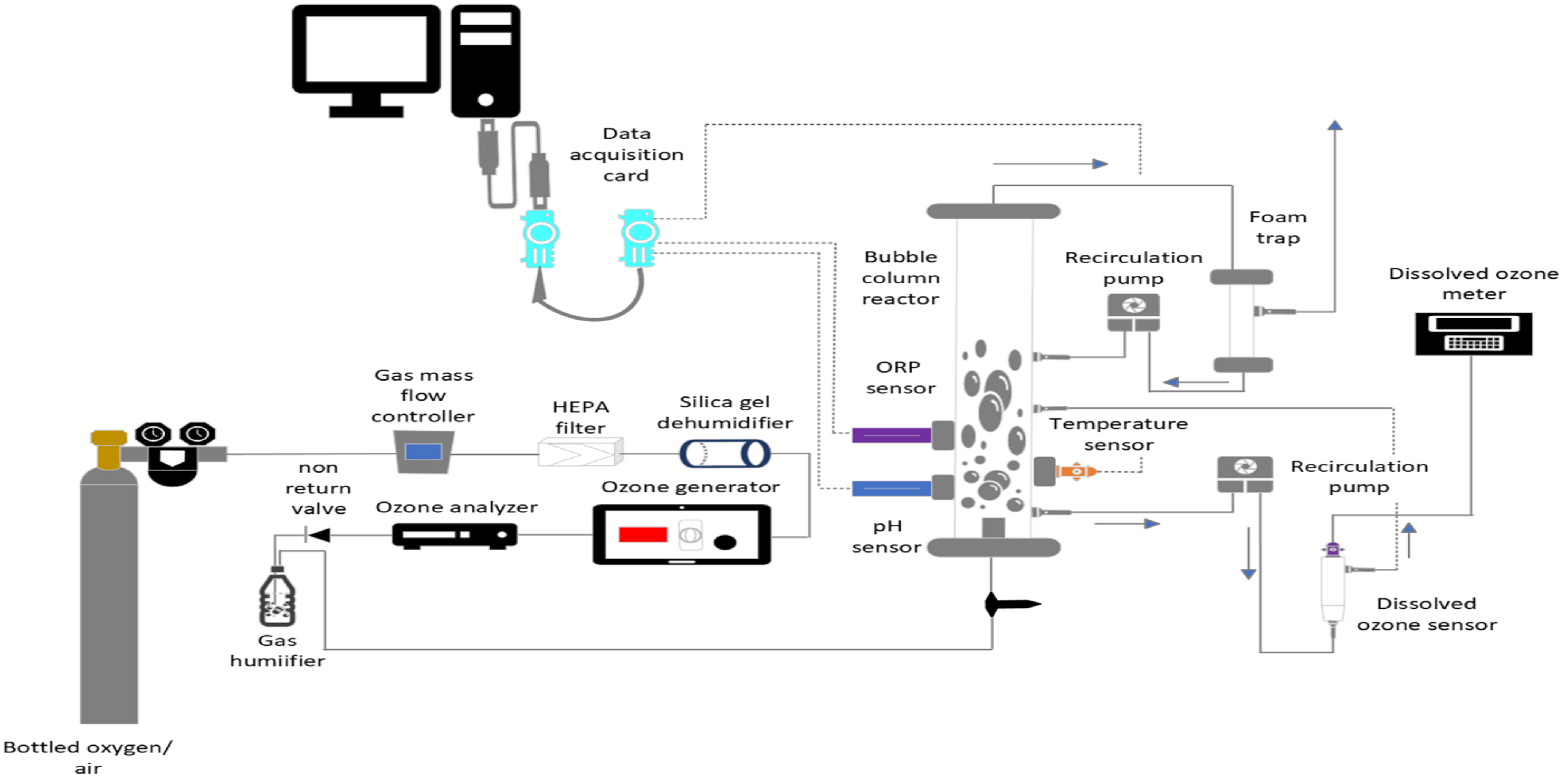
Inverse modeling and parameter estimation



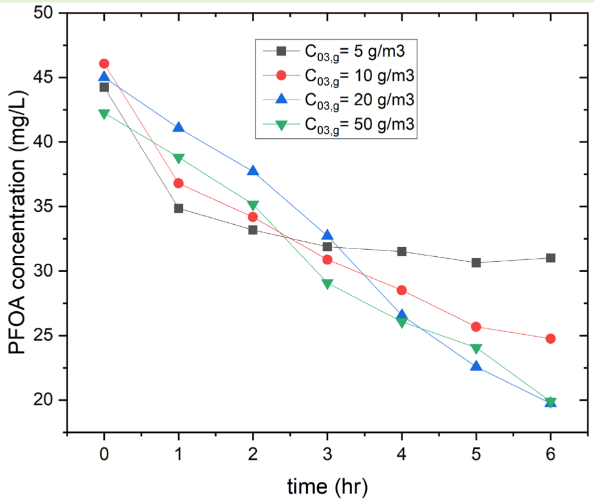
Catalyst: ZnO nanoparticles immobilized on Duranit beads

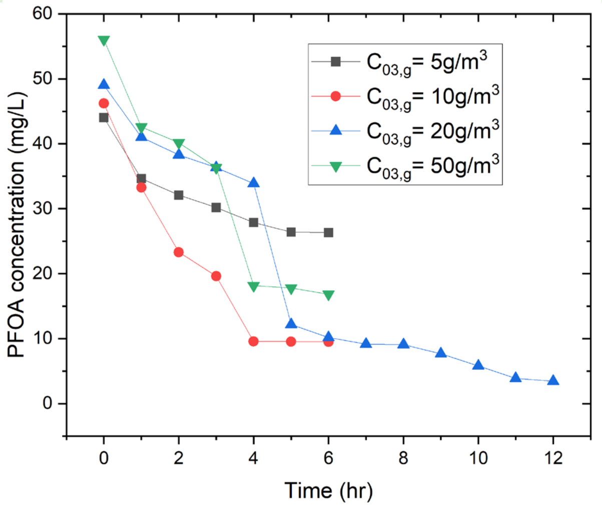
Catalyst: Fe-doped ZnO nanoparticles immobilized on soda lime beads

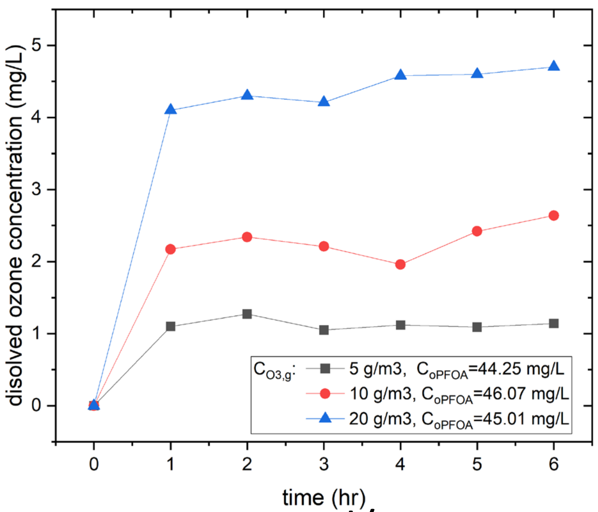
PFAS ozonation - experimental setup



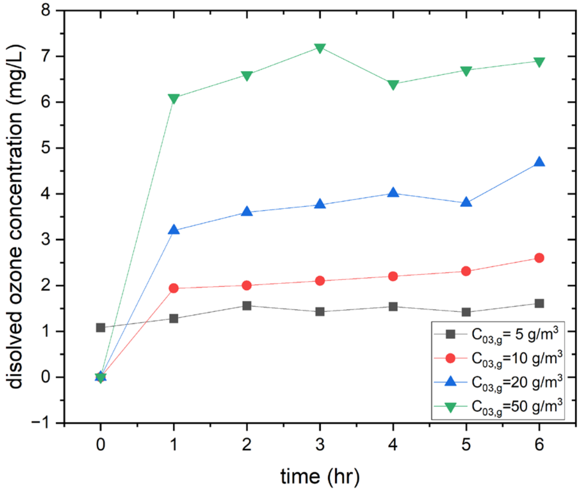
PFOA ozonation - results





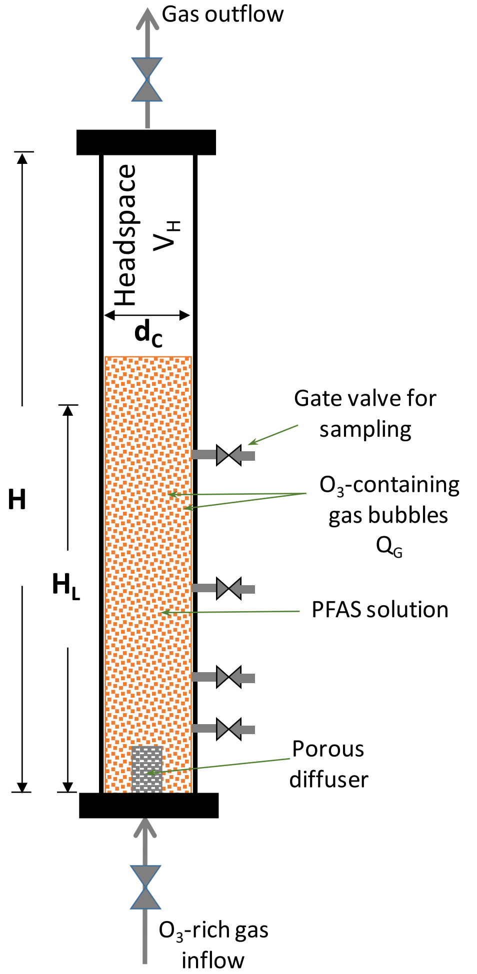


Q=0,1ml/min

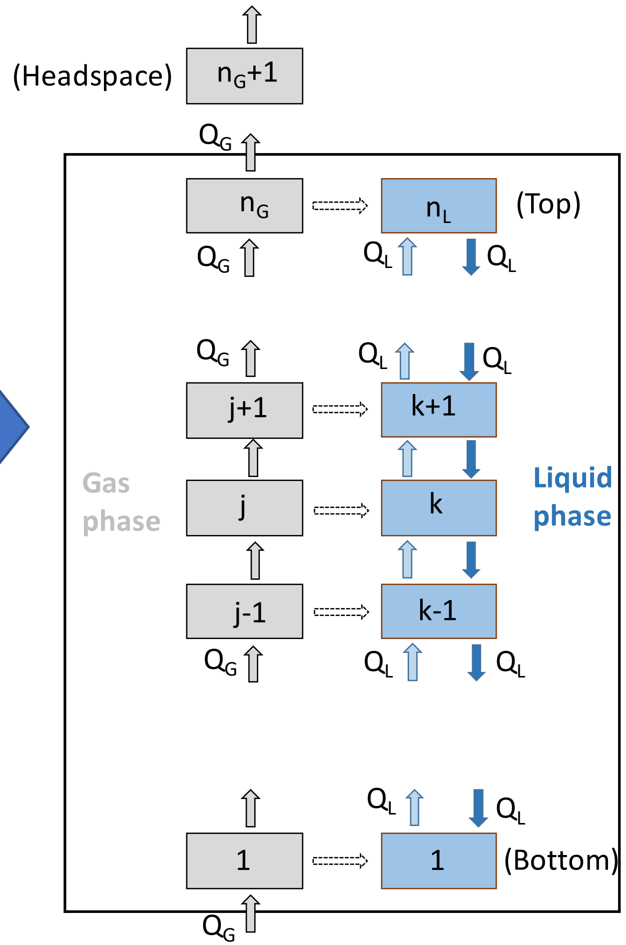


Q=0,2ml/min

Modeling the PFAS ozonation in bubble flow reactor



Tank-in-series model



- The aqueous phase is represented by a number of n_L well-stirred tanks with the up-flow rate being equal to the backflow rate, Q_L
- The gas phase is approximated by a number of n_G separate tanks of constant flow rate, Q_G, where $n_G > n_L$ since the mixing of aqueous phase is more efficient than that of the gas phase.
- Depending on the conditions, the ozone dissolves in the liquid phase and a fraction of dissolved ozone is decomposed.
- The dissolved ozone and other strong oxidants generated from it (hydroxyl roots, hydrogen peroxide) contribute to the mineralization of PFAS

Kalari et al., *Chem. Eng. J.*, 471 (2023) 144433.
https://doi.org/10.1016/j.cej.2023.144433

Parameters to estimate with inverse modeling

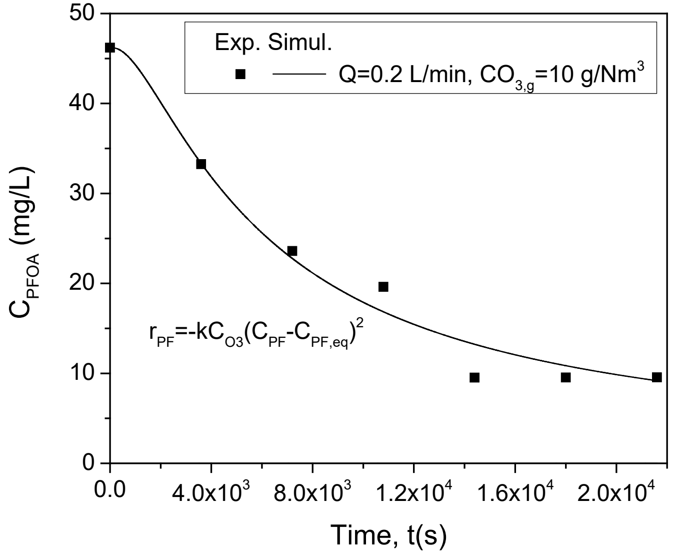
$$\frac{dC^l_{O3,i}}{dt} = K_L a_L\left(C^{l,*}_{O3,i} - C^l_{O3,i}\right) + r_{O3,i} + \boldsymbol{\alpha_{O3/PF}} r_{PF,i} + \frac{Q_L}{(V_L/n_L)}\left(C^l_{O3,i-1} - C^l_{O3,i}\right) + \frac{Q_L}{(V_L/n_L)}\left(C^l_{O3,i+1} - C^l_{O3,i}\right)$$

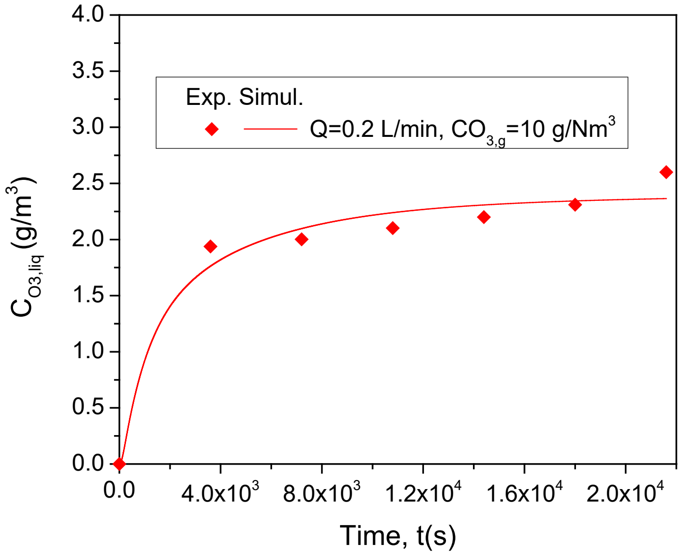
$$r_{O3,i} = -\boldsymbol{f_{dis}} k_{O3,1} e^{-4964/T} C^l_{O3,i} - \boldsymbol{f_{dis}} k_{O3,2} e^{-10130/T} {C^l_{O3,i}}^{3/2} {[OH^-]_i}^{1/2}$$

$$r_{PF,i} = -\boldsymbol{k_{PF}} C^l_{O3,i}\left(C_{PF,i} - \boldsymbol{C_{PF,eq}}\right)^2$$

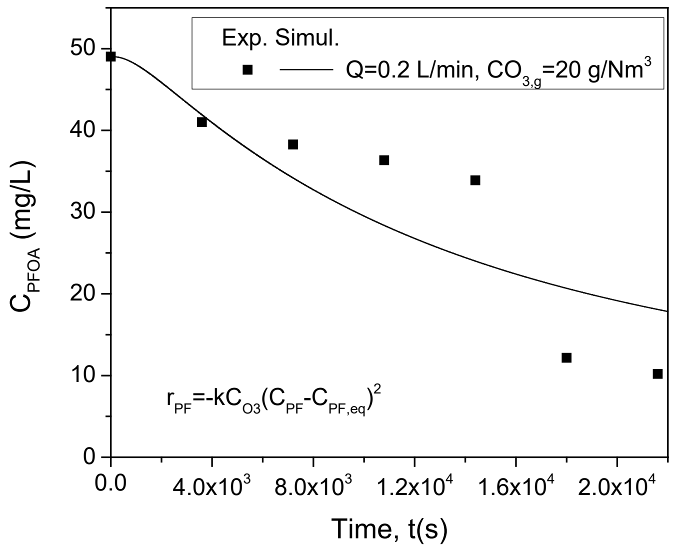
$\boldsymbol{k_{PF}}$	Kinetic constant of PFOA degradation rate
$\boldsymbol{C_{PF,eq}}$	Lower limit of PFOA concentration
$\boldsymbol{\alpha_{O3/PF}}$	Ratio of O3 mass consumed per unit mass of PFOA
$\boldsymbol{f_{dis}}$	Fraction of O3 decomposition rate

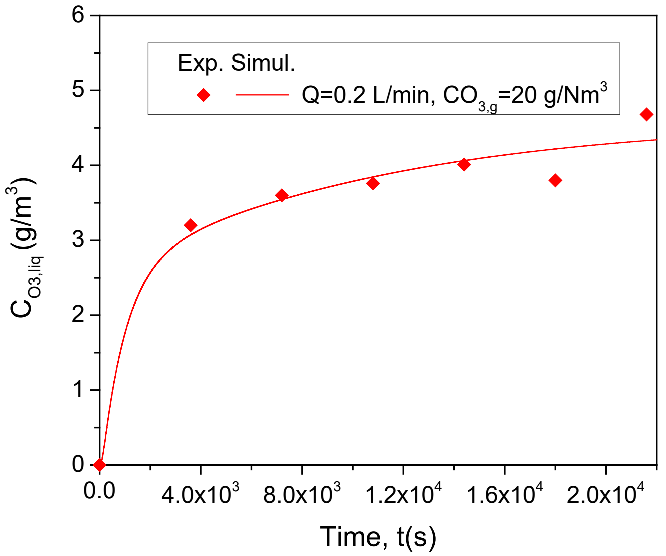
Numerical predictions vs experimental results





k_{PF}= 1.97x10^{-6}
$C_{PF,eq}$= 0.0
$\alpha_{O3/PF}$= 0.0631
f_{dis}= 0.307





k_{PF}= 4.49x10^{-7}
$C_{PF,eq}$= 0.0
$\alpha_{O3/PF}$= 0.343
f_{dis}= 0.343

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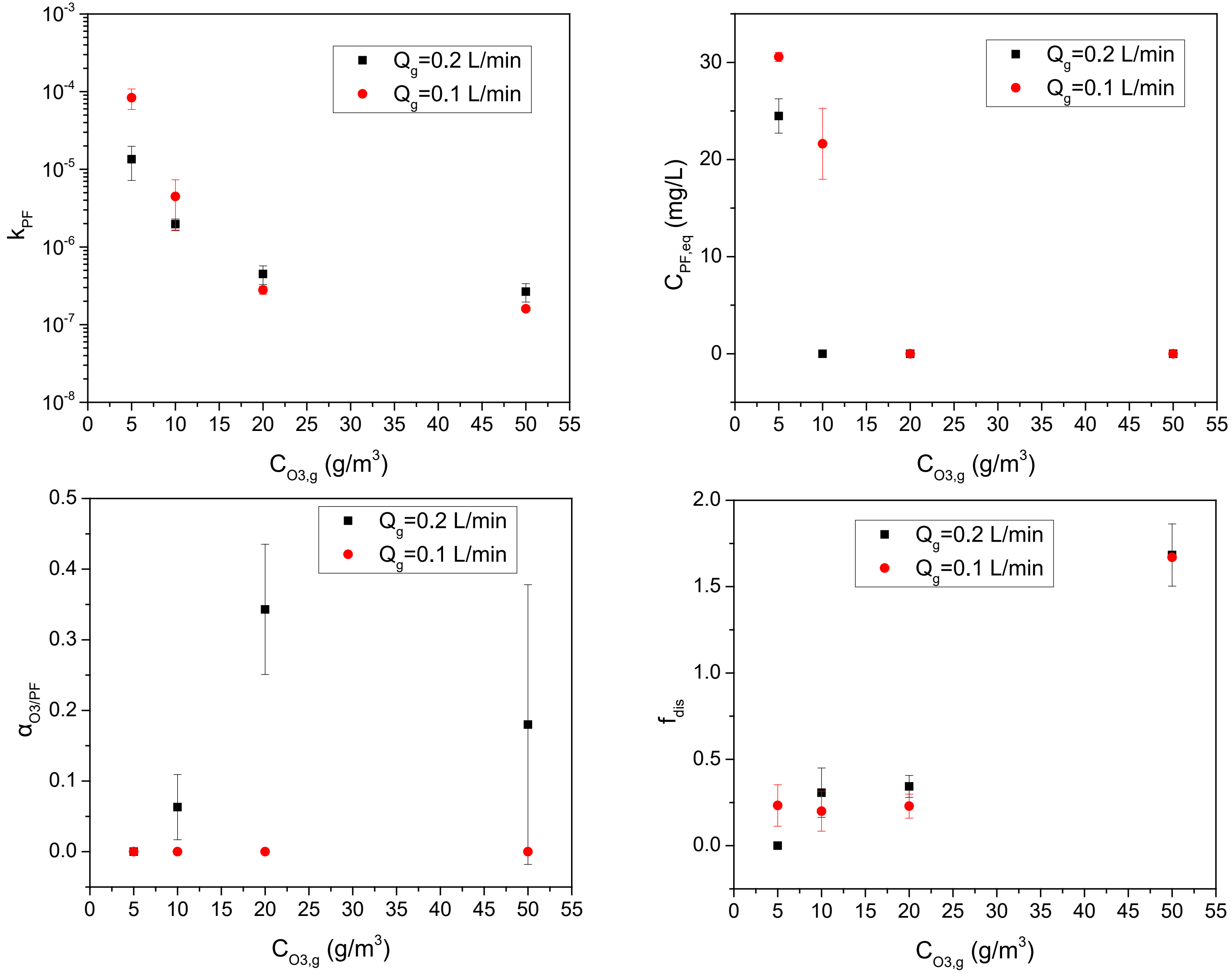
Variation of estimated parameters



Conclusions

- PFOA can be degraded by immobilized ZnO based photocatalyst.
- PFOA photocatalysis is a slow but cost efficient process.
- PFOA photocatalysis by ZnO is faster than photocatalysis with iron dopped ZnO.
- Ozonation is a fast PFOA remediation method, depending on the O_3 concentration of injected gas.
- Moderate O_3 concentration are more effective than low and high O_3 concentration.
- Inverse modeling of PFOA ozonation experiments indicates that:
    1. Low O_3 concentration and low flow rates are unable to decrease respectably the PFOA concentration.
    2. The higher the O_3 concentration, the higher the O_3 decomposition rate.
    3. The kinetic constant is inversely proportional to O_3 concentration.
    4. The direct PFOA oxidation is favored by high O_3 concentration.

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Thank you for your attention

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