Remediation of oil-drilling cuttings with ozonation in bubble flow reactors, and process simulation with a machine-learning approach

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Challenges – Remediation of Oil-drilling cuttings

Oil drilling cuttings (ODC)

- Main wastes generated during oil reservoir drilling.
- Fully water-saturated, high percentage of TOC, TPH
- Treatment is needed before their disposal on the ground

ODC Composition (Data from POLYECO S.A.

Parameter	Units	Minimum value	Maximum value	Average	Number of analyses
TOC	% w/w (dry basis)	2.45	27.1	7.21	79
SiO_2	% w/w db	5.4	37.42	22.68	37
AlO_3	% w/w db	1.5	6.89	4.59	37
CaO	% w/w db	3.87	19.8	10.63	37
Fe_2O_3	% w/w db	0.94	4.87	2.51	37
Na_2O	% w/w db	1.6	11.9	5.26	78
As+Ni+Co+Se+Te+ Cr+Pb+Sb+Sn+V	mg / kg db	311.42	3646.33	630.82	37
Cl	mg / kg db	0.84	18	5.98	81
Ash	% w/w	36.6	90.1	78.31	79

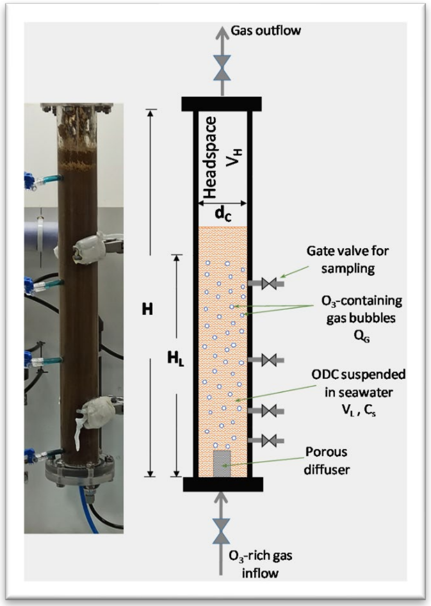
Main remediation technologies

- Solidification / Stabilization
- Thermal desorption, microwave heating, bioremediation

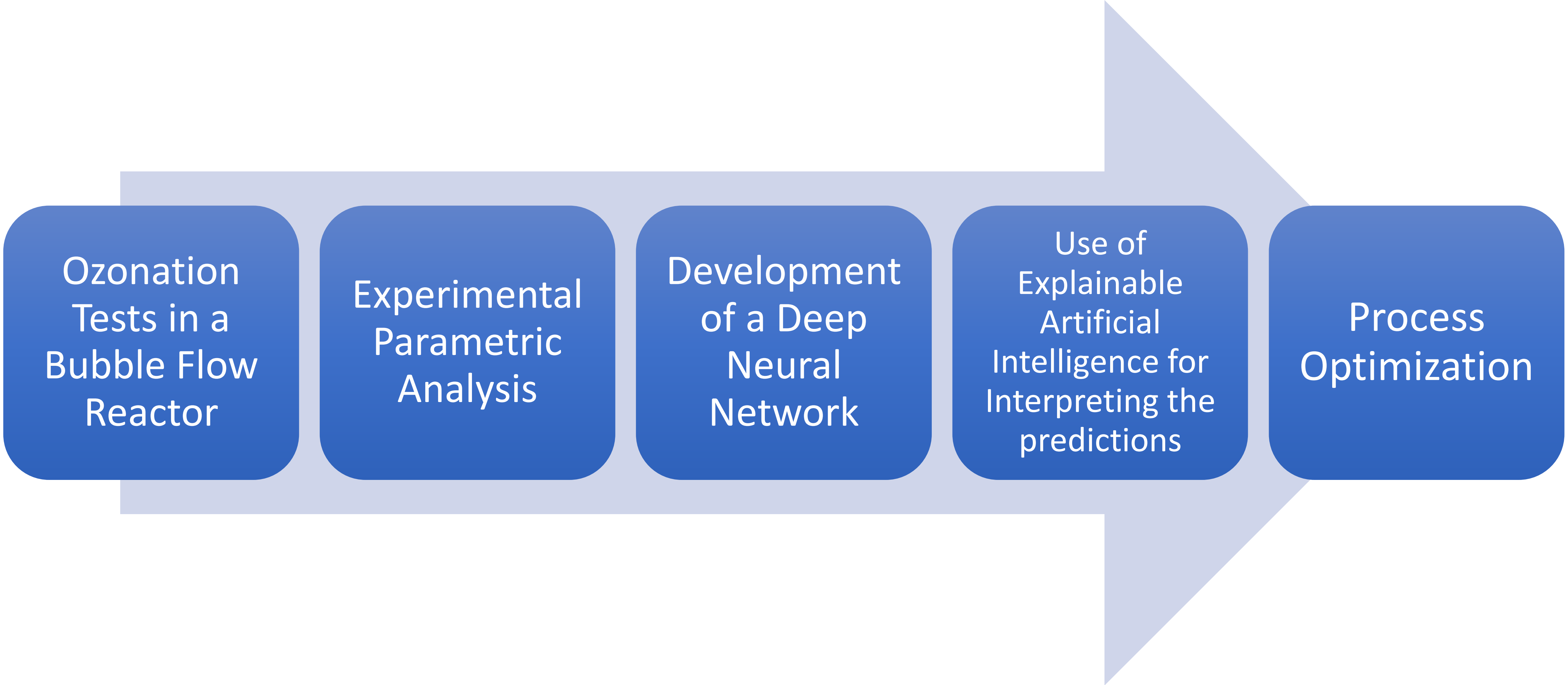
Exploratory Treatment Approach:

OZONATION in a multiphase reactor

- To what extent can ozonation effectively remediate ODC?
- What are the optimal conditions for achieving efficient remediation?
- How can machine – deep learning techniques contribute to the modeling and optimization of a such system?



Objectives

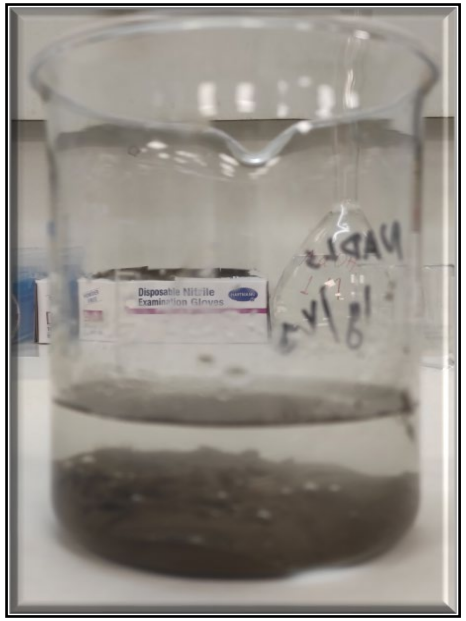


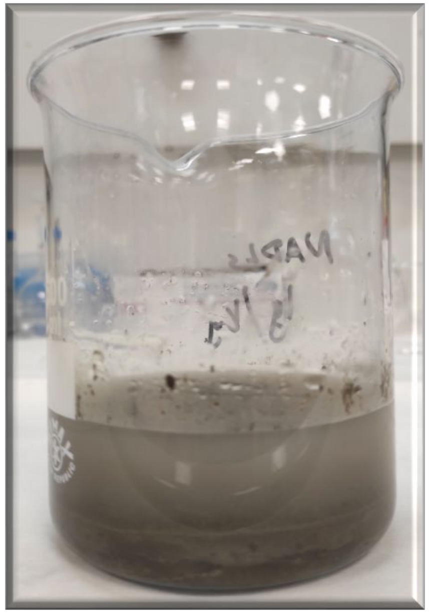
Ozonation Tests in a Bubble Flow Reactor
Experimental Parametric Analysis
Development of a Deep Neural Network
Use of Explainable Artificial Intelligence for Interpreting the predictions
Process Optimization

Ozonation of ODC

Experimental Setup

① Pre-treatment of oil drilling cuttings:
- Enhancement of hydrocarbon solubilization in liquid phase.
- Seawater mixtures with surfactant (SDS) in various concentrations and ratio.
- Ultrasonic bath (30 min in 30 ^oC).





Measured Parameters (step 1):

Dilution Ratio
Concentration of SDS
Initial Concentration of TOC
Initial Concentration of TOC in solid phase
Initial Concentration of TOC in liquid phase
Initial Concentration of TPH

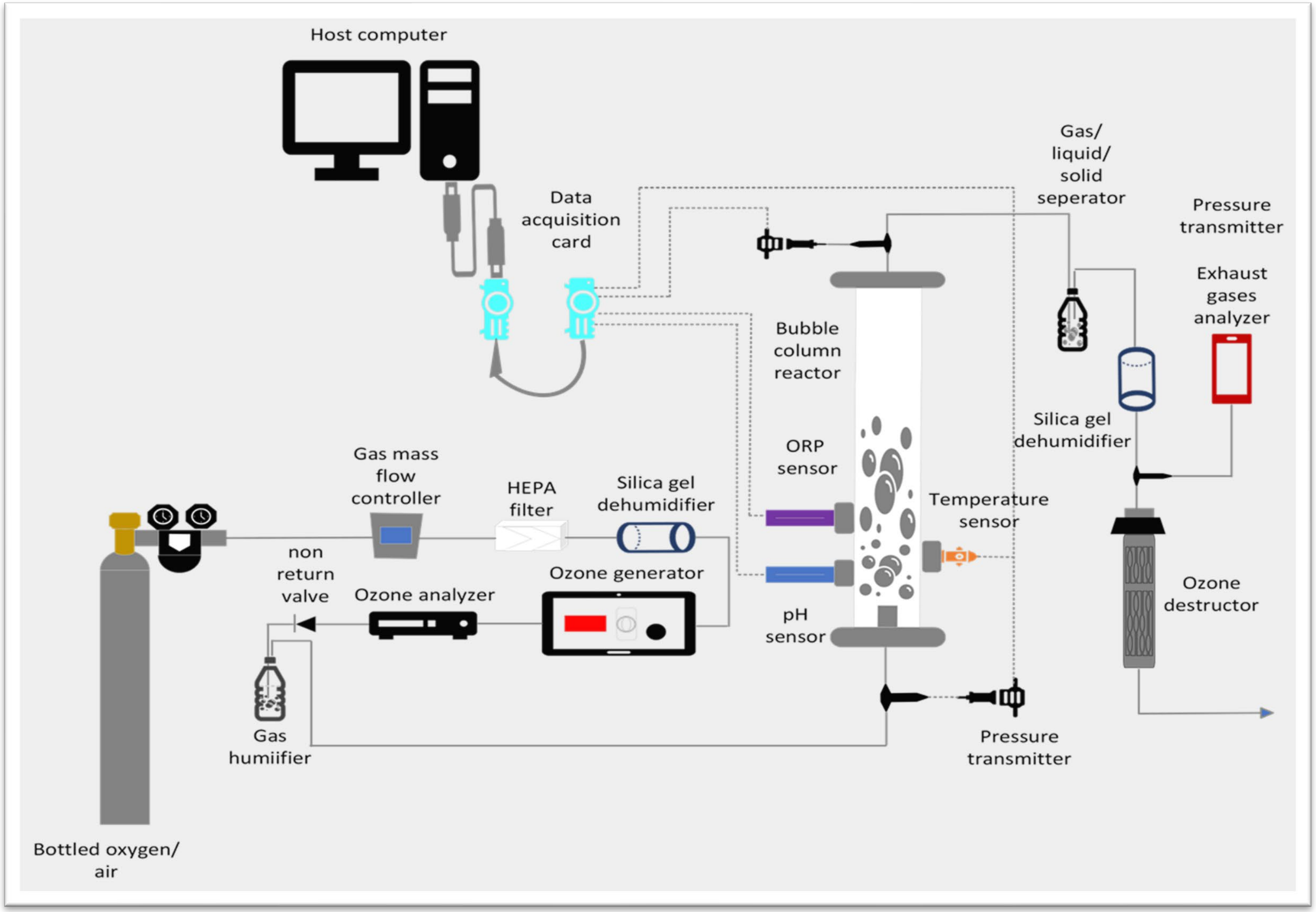
Ozonation of ODC

Experimental Setup

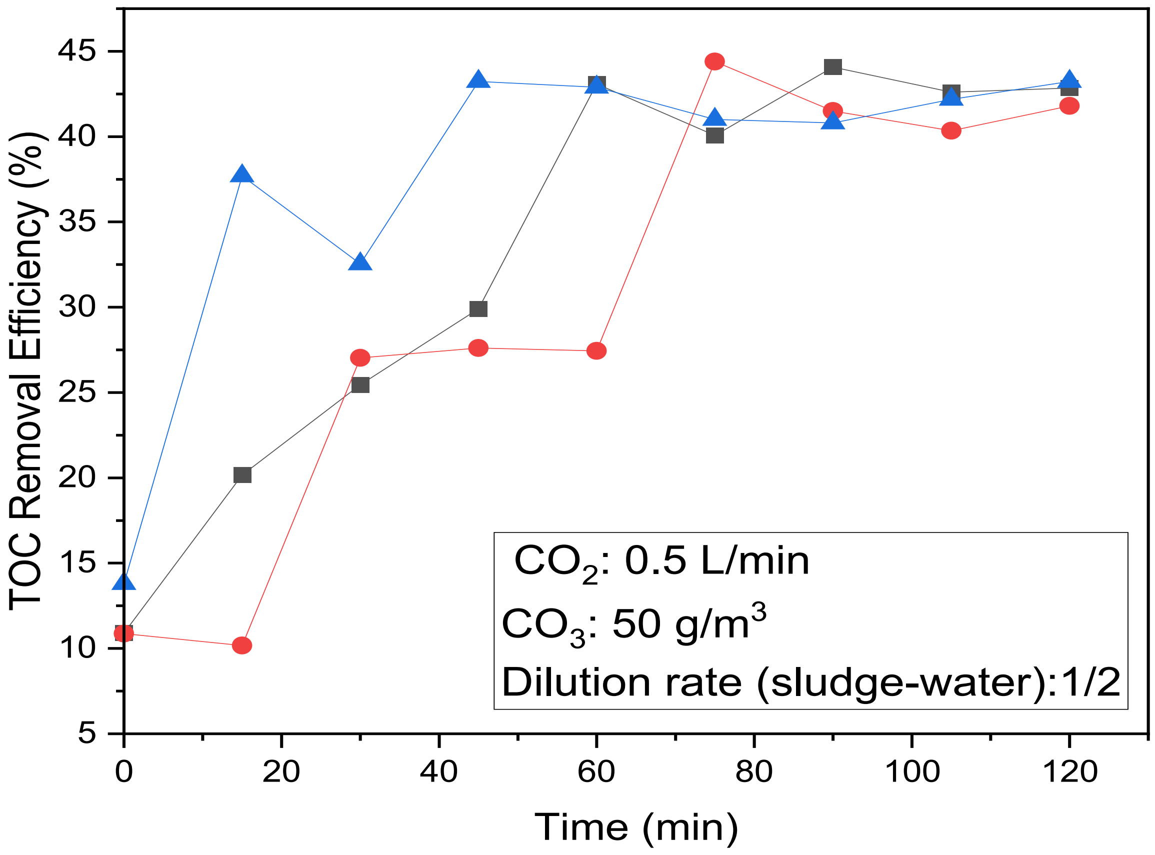
② Ozonation of the pretreated mud in a bubble column reactor

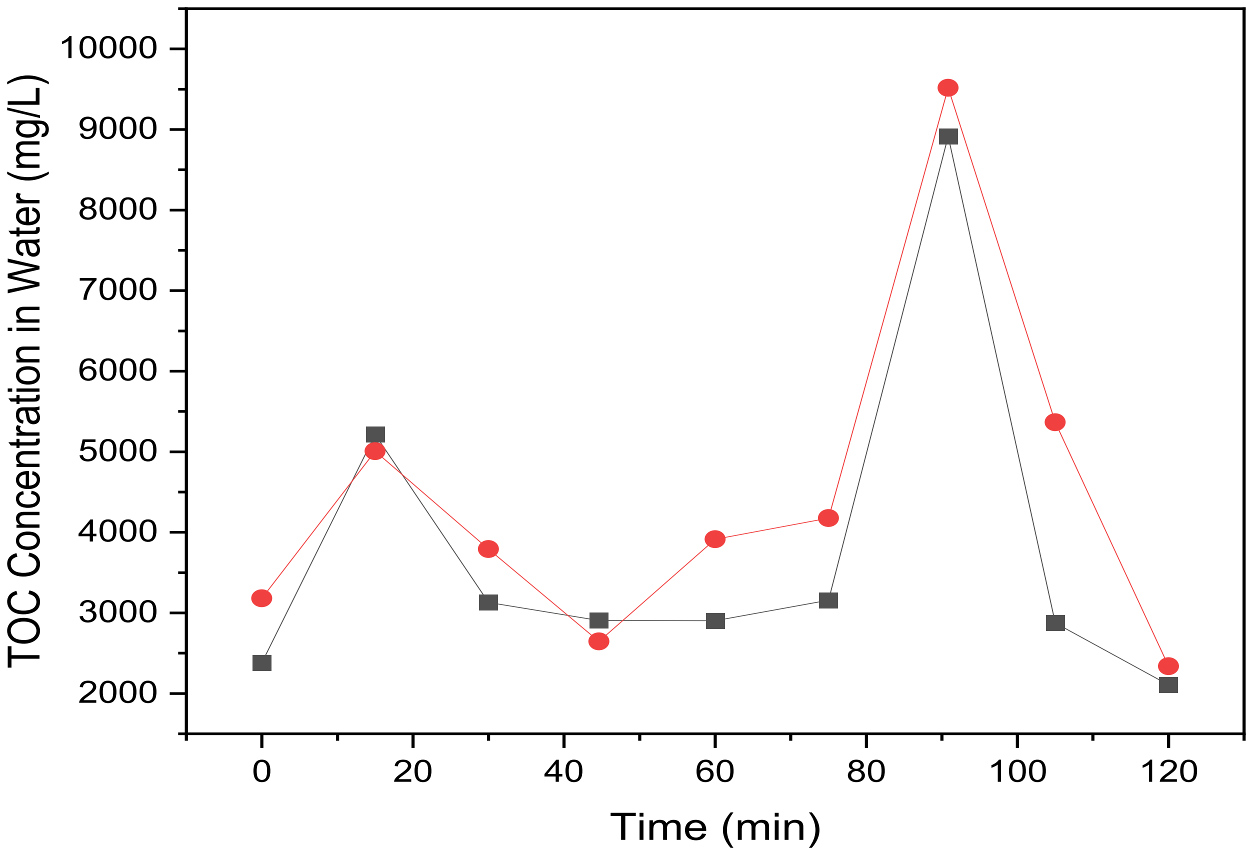
Measured Parameters (step 2)

Flow Rate of O_2
Concentration of O_3
Temperature
pH
Oxidation Reduction Potential
TOC Removal Efficiency in Solid Phase
TOC Removal Efficiency in Liquid Phase
TPH concentration
Gas Hold up



Reproducibility of Results





Removal ~41% of organic carbon (TOC).
Transfer of organic pollutants to the aqueous phase.
Oxidation by dissolved ozone and generated species .

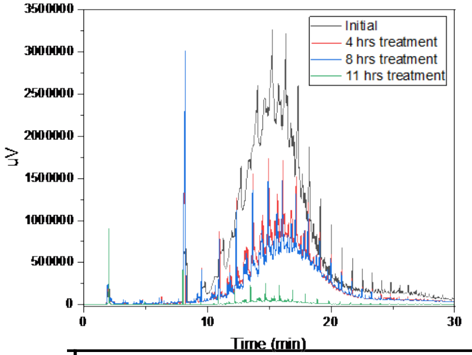
Formation of radicals

$O_3 + OH^- \rightarrow HO_2^- + O_2$
$O_3 + HO_2^- \rightarrow \cdot OH + \cdot O_2^- + O_2$
$O_3 + \cdot O_2^- \rightarrow \cdot O_3^- + O_2$
$\cdot OH + O_3 \rightarrow HO_2\cdot + O_2$
$\cdot O_3^- + H_2O \leftrightarrow O_2 + \cdot OH + OH^-$

Oxidation of alkanes

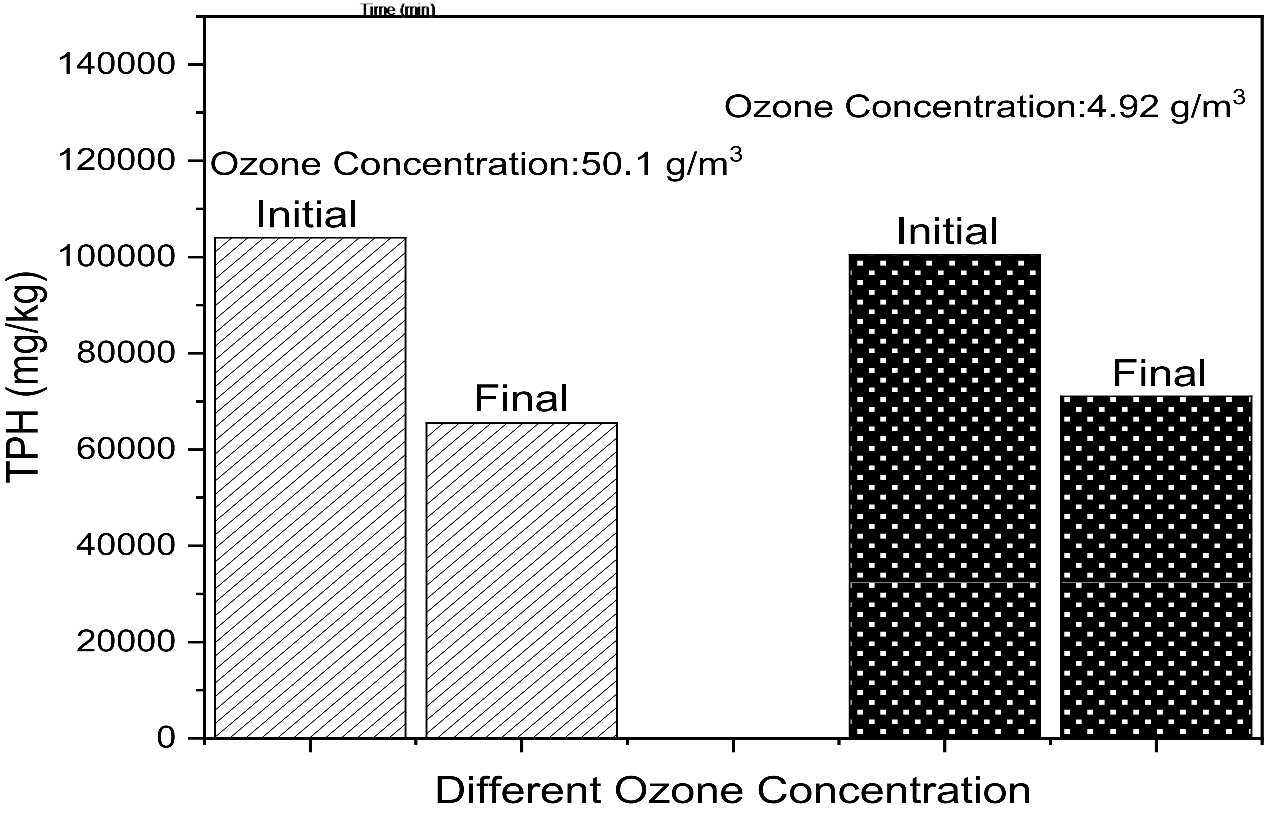
$RH + O_3 \rightarrow I \leftrightarrow II$
$I \rightarrow R\cdot + \cdot OH + O \longrightarrow ROH + ketone + peroxides$
I or $II \rightarrow ROH + O_2$
$II \rightarrow ROOOH \rightarrow ROH + O_2$

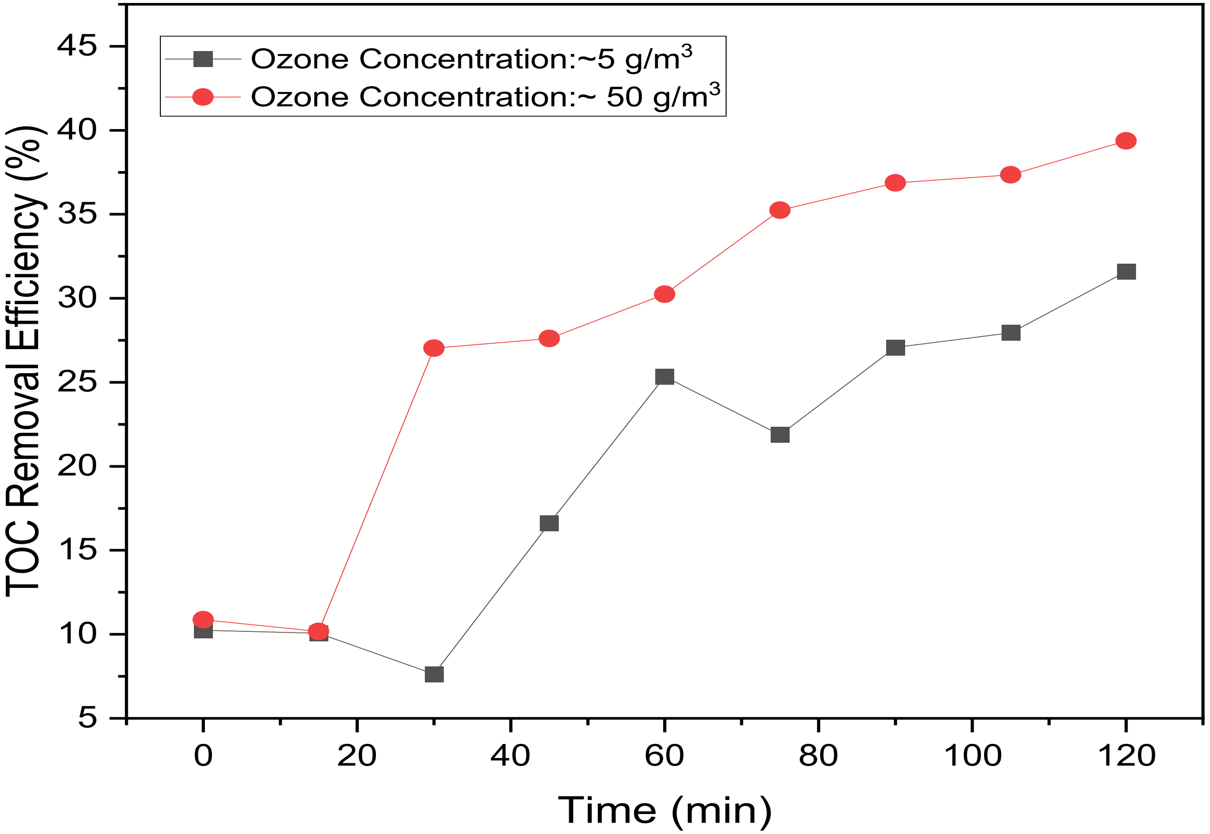
Effect of O_3 concentration on TPH and TOC removal efficiency



TPH
50.1 g/m^3 → 37.01 %
4.92 g/m^3 → 29.20 %

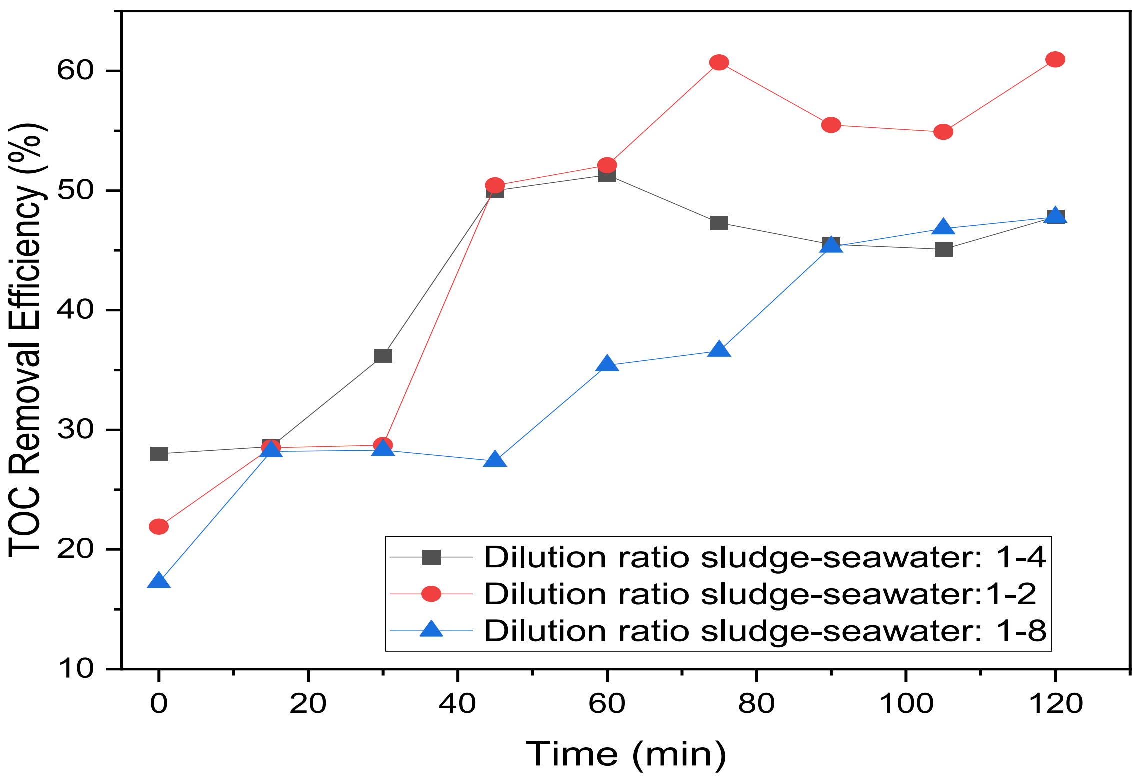
TOC
50.1 g/m^3 → 39.37 %
4.92 g/m^3 → 32%





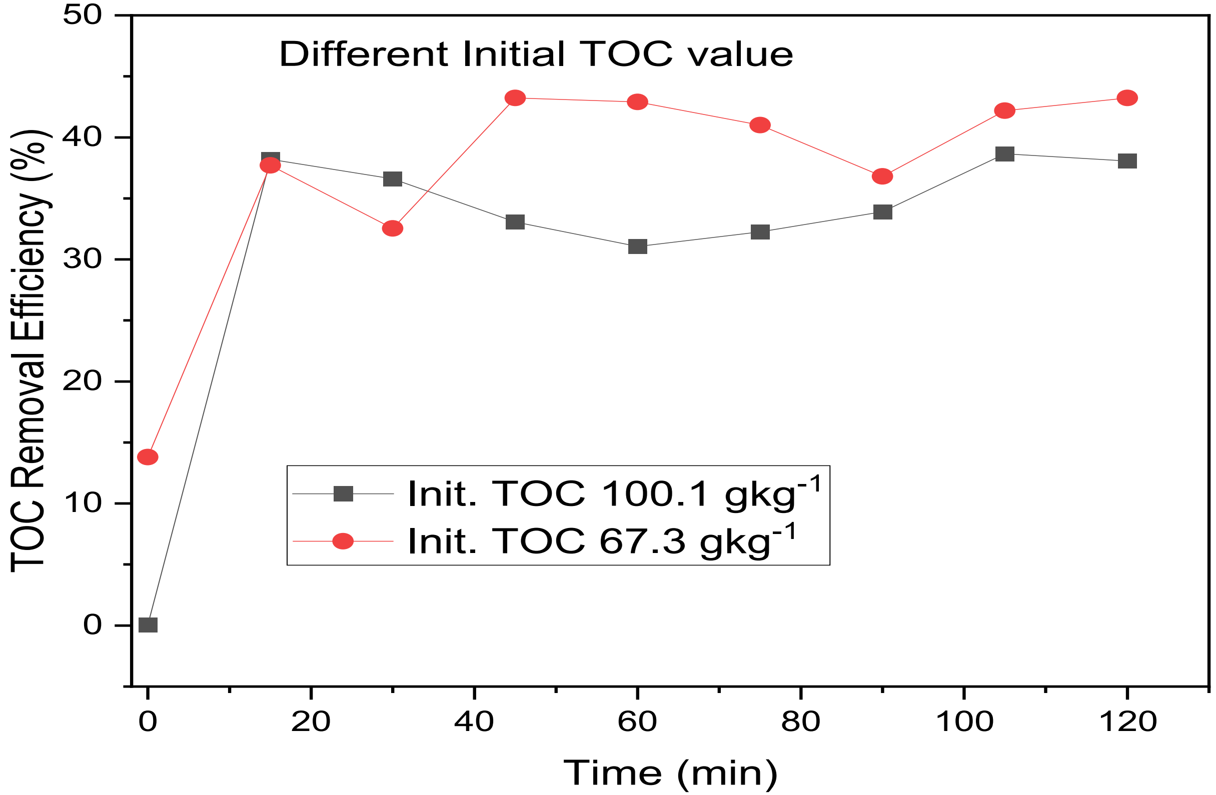
Effect of ODC/water ratio and initial TOC concentration

Effect of dilution ratio sludge/water



Dilution ratio ODC/water=1/2 → Maximum percentage of pollutants transferred to the aqueous phase.

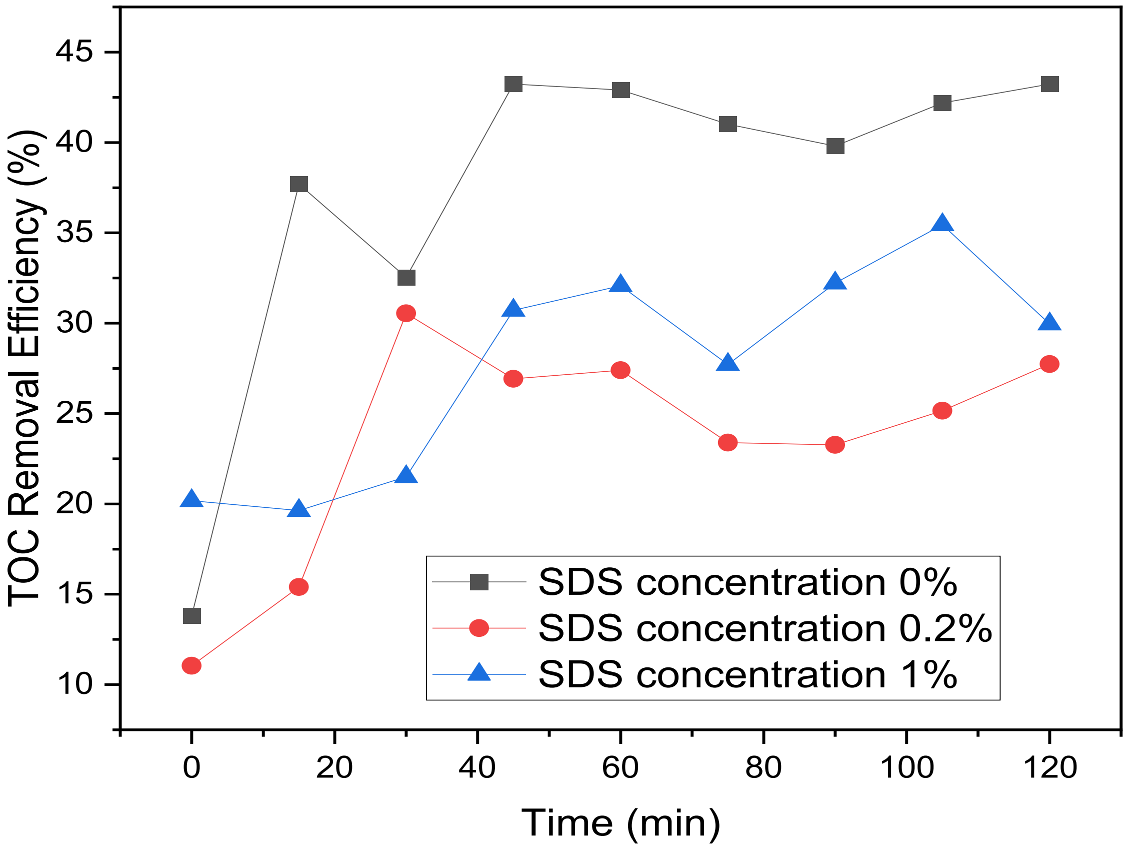
Effect of initial TOC concentration

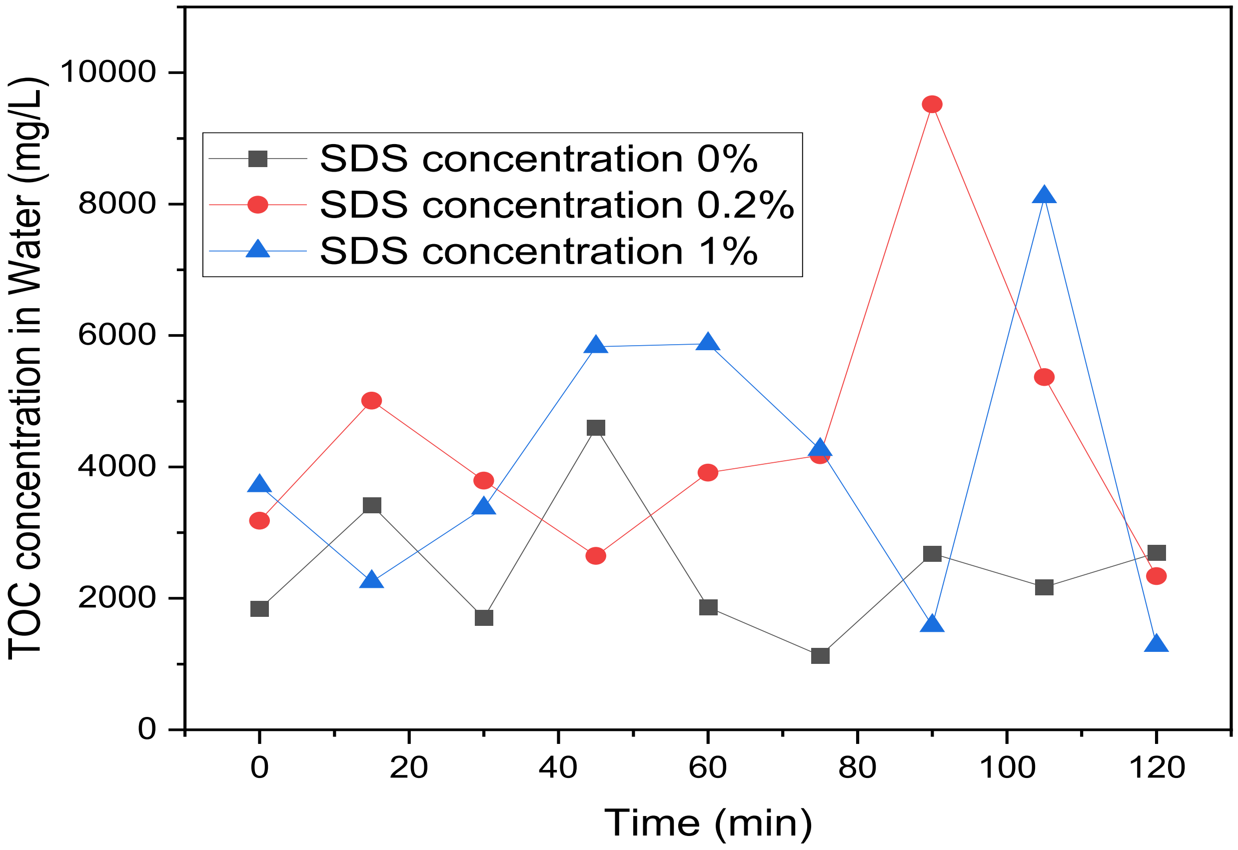


Lower initial TOC → Higher TOC removal

Process efficiency is not affected by initial TOC value

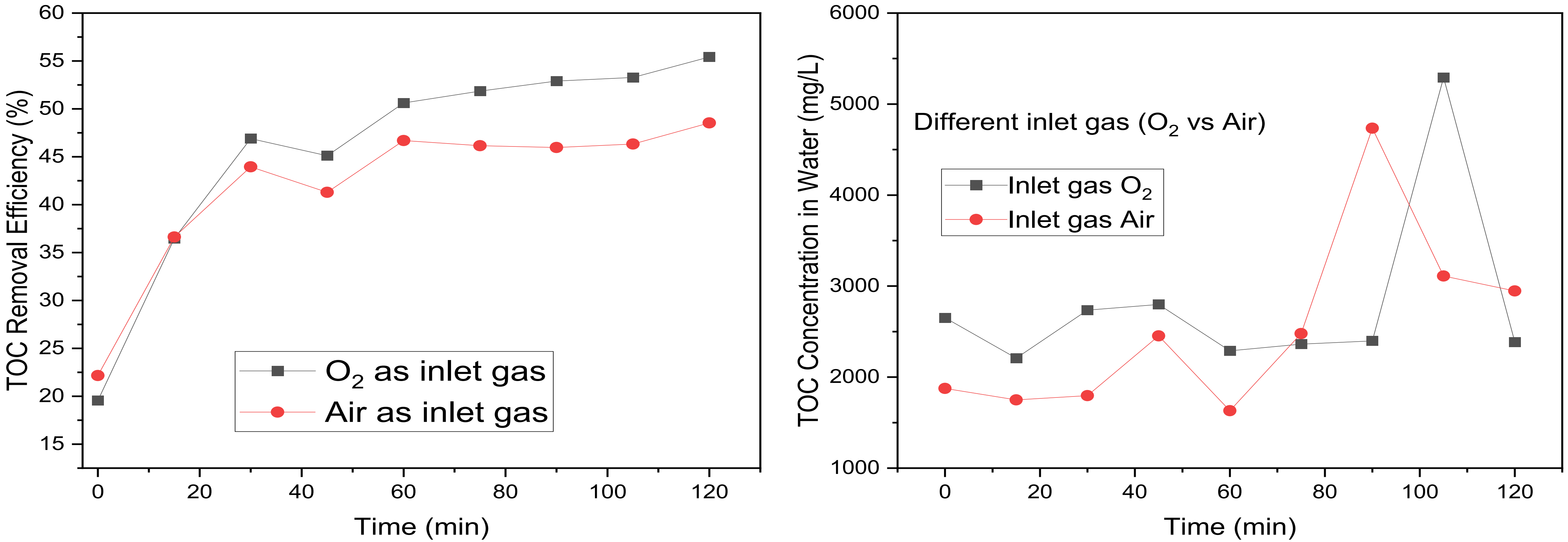
Effect of SDS concentration





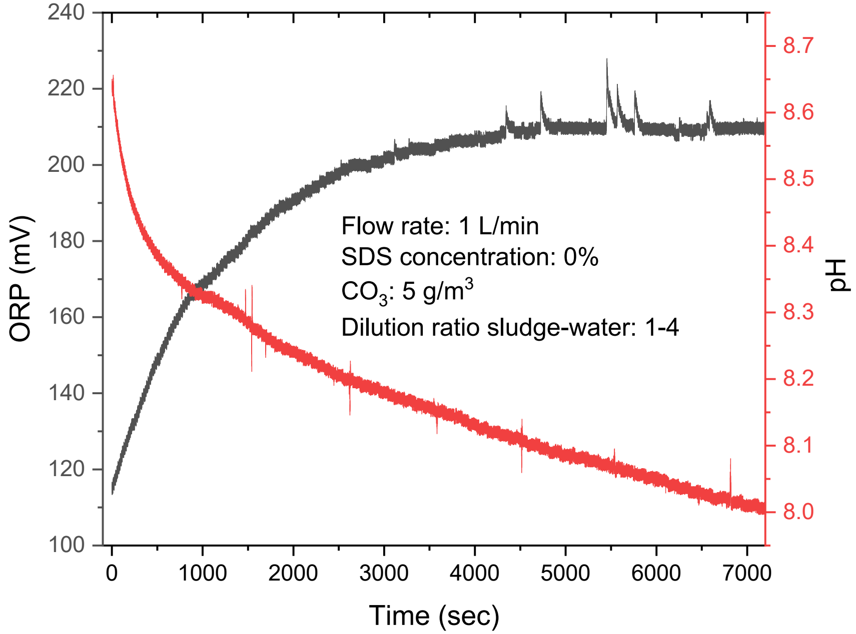
The presence of SDS enhances the foaming and the percentage of organics in aqueous phase, without increasing the TOC removal efficiency in solid phase

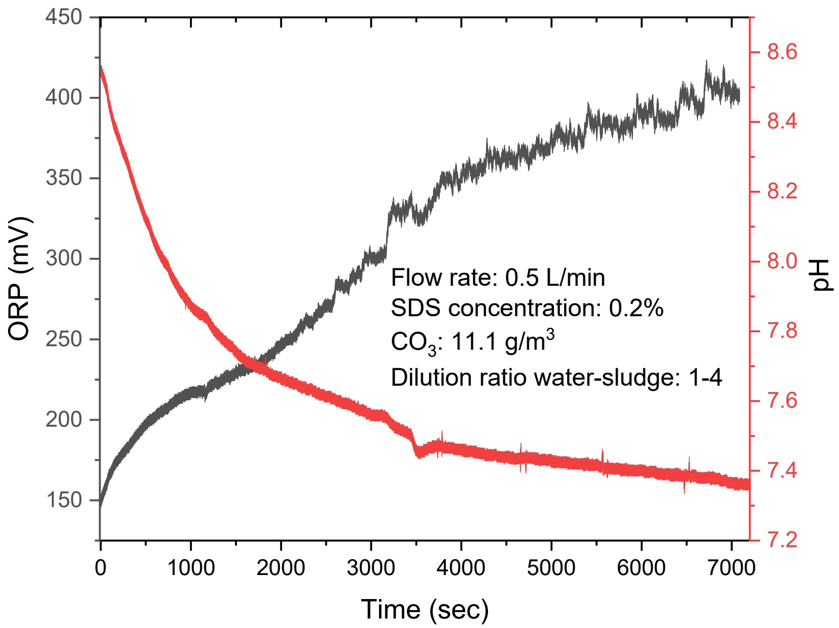
Effect of gas type

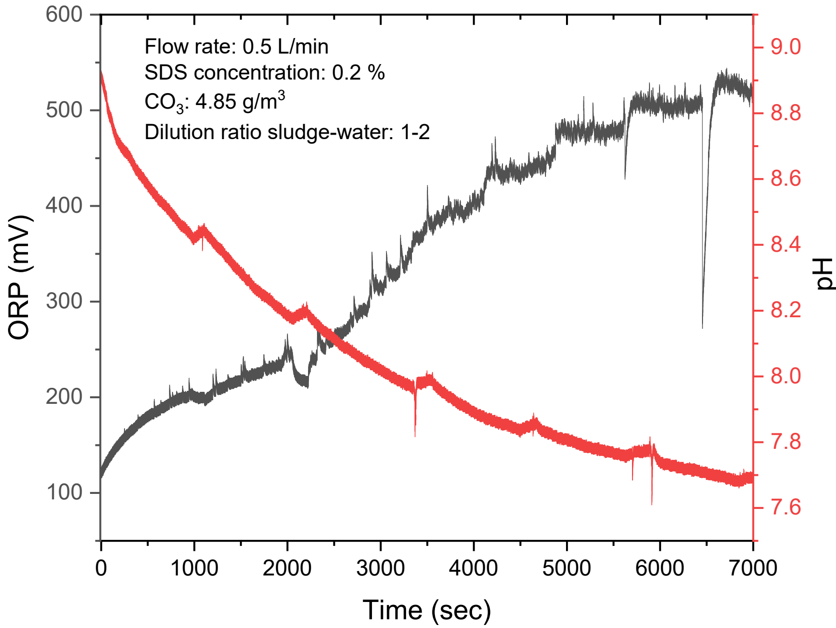


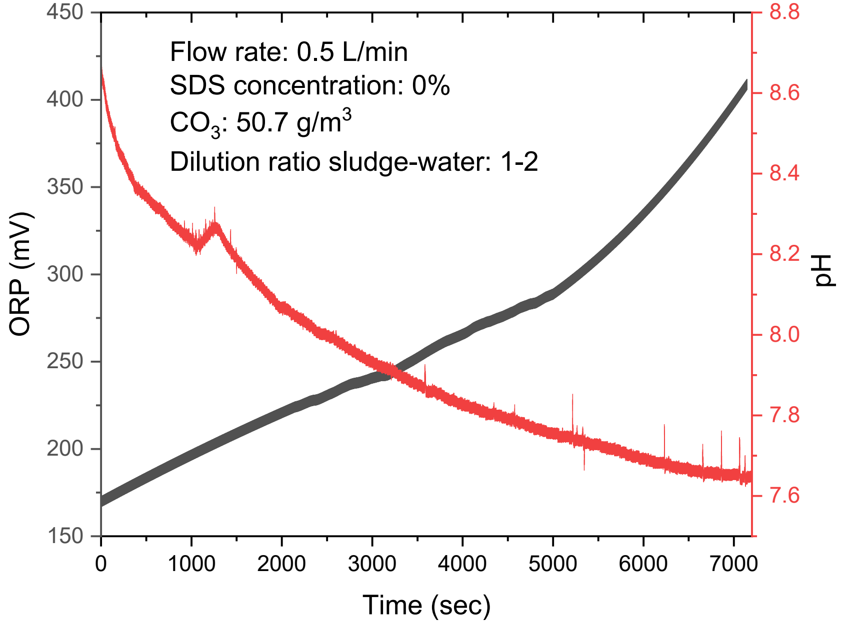
Oxygen → Higher ozone concentration is achieved.
Air → Production of NOx that act as oxidant

Transient variation of pH and ORP





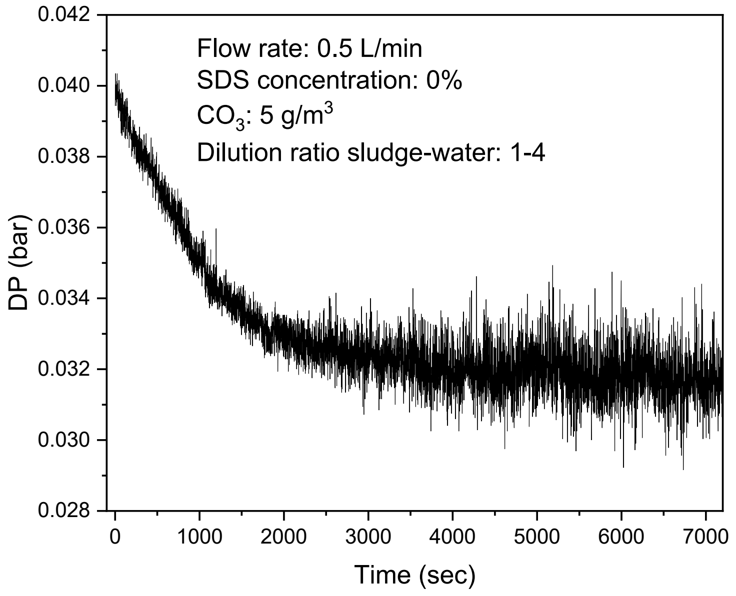




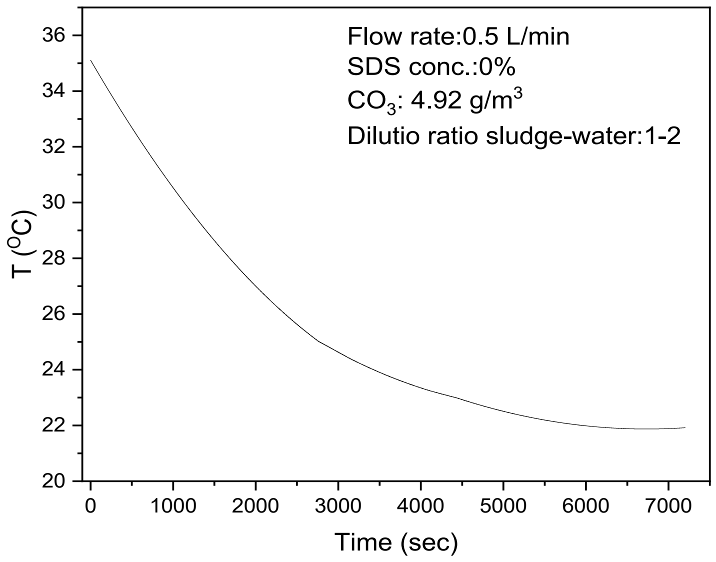
pH reduction → Formation of intermediate acidic species

ORP increment → Increment of oxidizing species by dissolved ozone

Transient response of pressure drop and temperature



Differential pressure → Hydrostatic Pressure
Initial high value → Capillary Pressure in gas diffuser pores
Pressure fluctuations → Frequency of bubbles formation



Initial high Temperature → Sonication process
Transient cooling → heat transfer to ambient

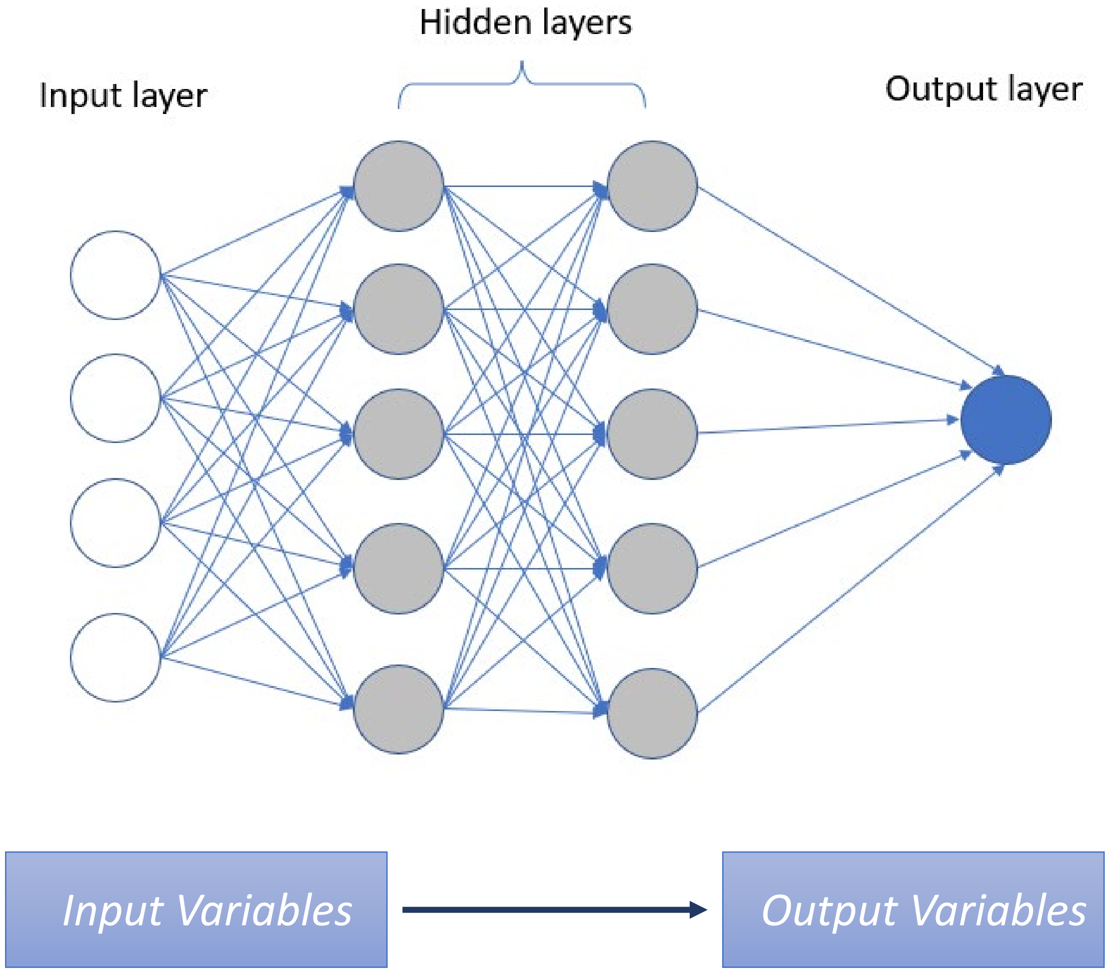
Heat generation due to exothermic oxidation/ desorption/ dissolution reactions.

Deep Neural Networks (DNNs)

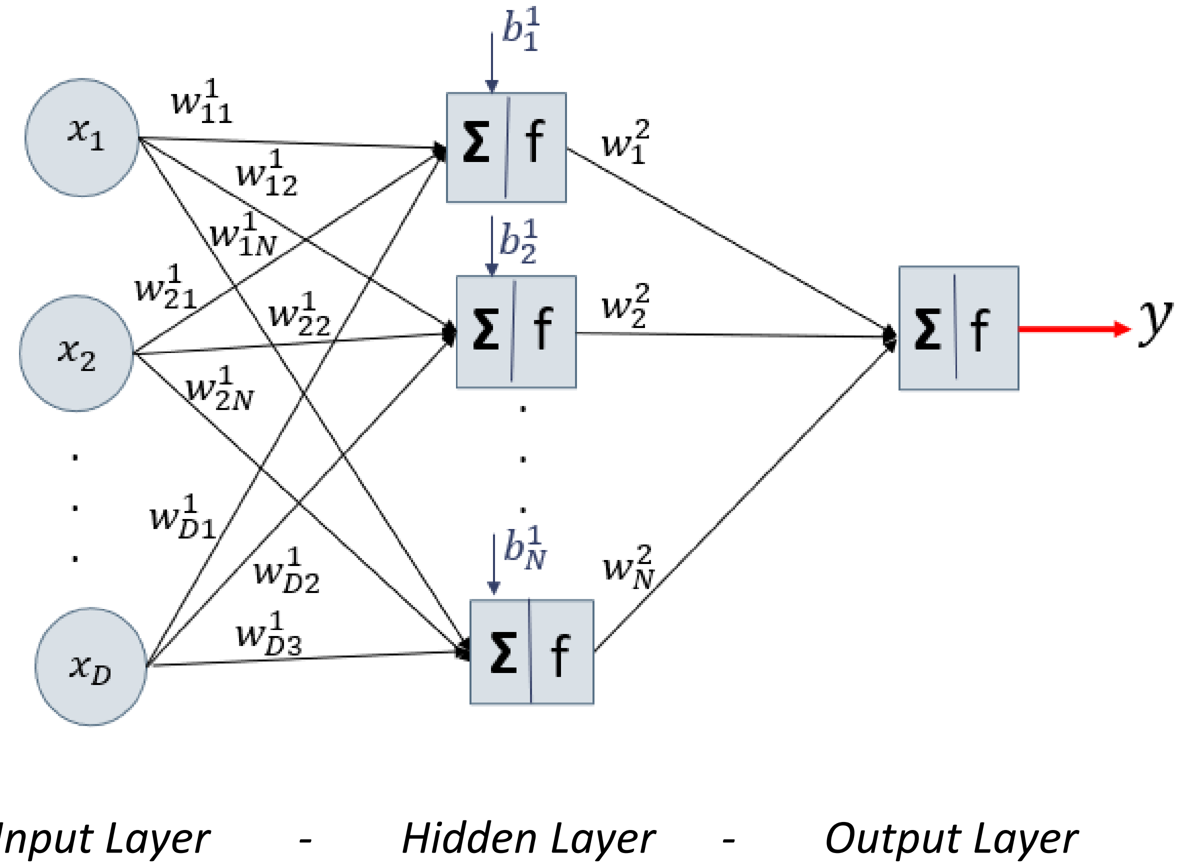
- Subclass of Artificial Neural Networks (ANNs) characterized by multiple hidden layers.

- A massively parallel distributed processor characterized by the ability:
  i. to store experimental knowledge,
  ii. to make it available for use.

- Implement nonlinear mappings from input data to output predictions.



How do the inputs correspond to the outputs?



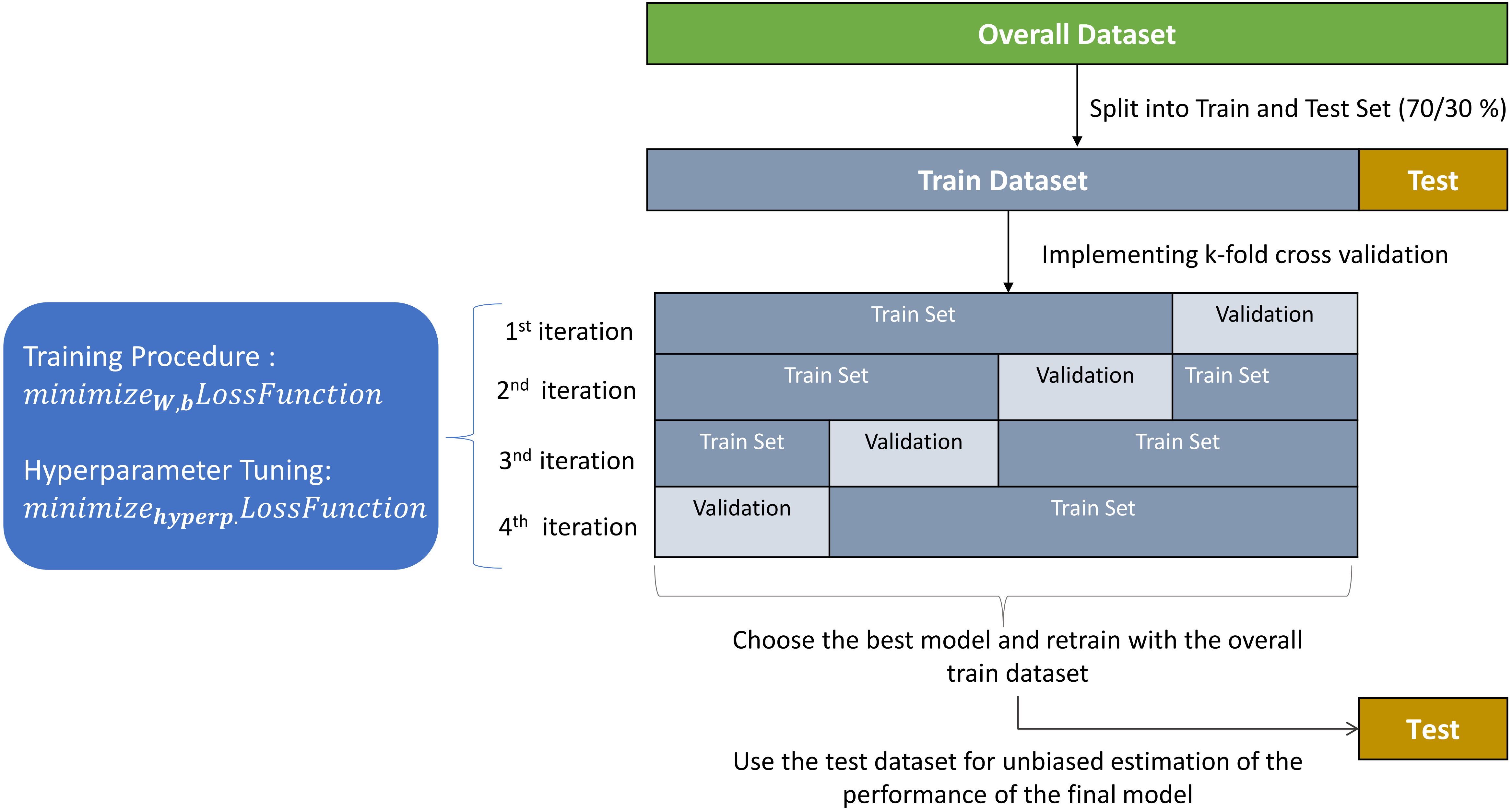
Model Parameters:

- $\boldsymbol{W}$**,** synaptic weights
- **b,** biases

Model Hyperparameters:

- f, activation function
- network depth
- width/hidden layer

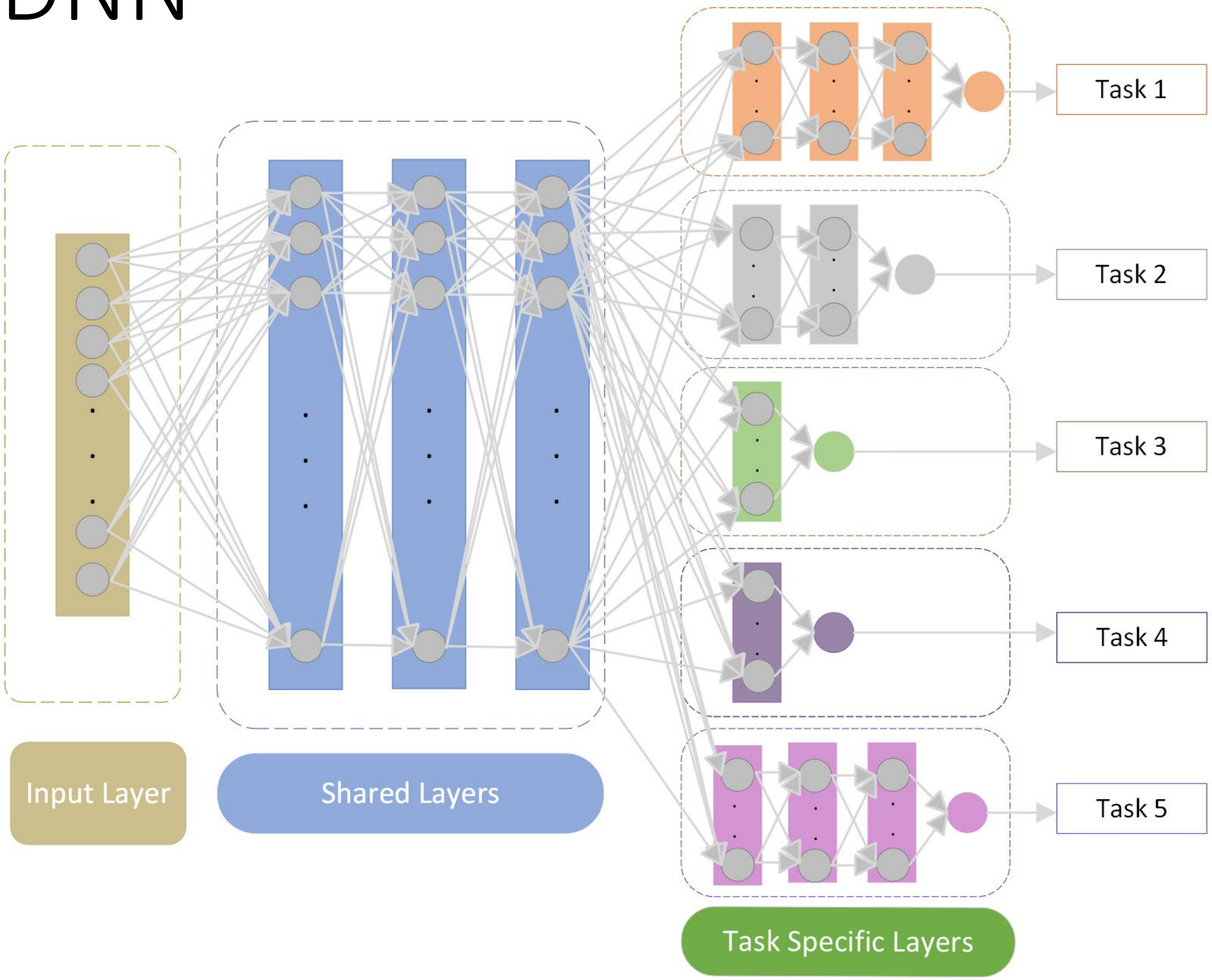
The Development of the DNN



Details of the final DNN

- Multitask Deep Neural Network:

Inputs	Tasks
t	R_{ES}
$C_{TOC,init}$	ΔP
C_{O_3}	pH
C_{SDS}	T
m_{ODC}	ORP
DR	
φ_G	
T_{init}	
F_{O_2}	



Details of the final DNN

- Parameters of the Model: 1,988,425
  Determined by the Training Process
  (44121 data points)

- Multitask Loss Function:

$$Loss = \sum_{i=1}^{5} g_i Loss_{Task_i} \, , \, g_i \in (0,1)$$

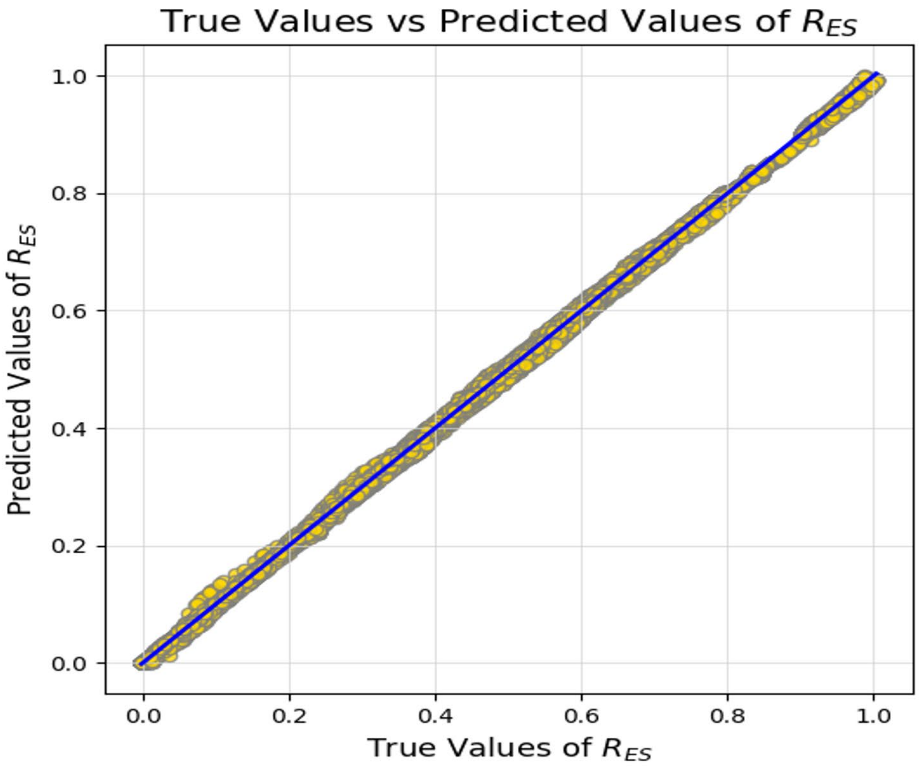
Hyperparameter	Value
No of shared layers	3
No of specific layers/task	(4,3,2,2,3)
No of nodes/shared layer	(1024,512,256)
No of nodes/specific layer	(1024,624,124,1), (624,182,1), (162,1), (824,624,124,1)
Activation function	ReLU, Linear
Learning rate	0.01
Optimizer	Adam
Batch size	100
Epochs	250
gamma	(0.25, 0.25, 0.1, 0.1, 0.3)

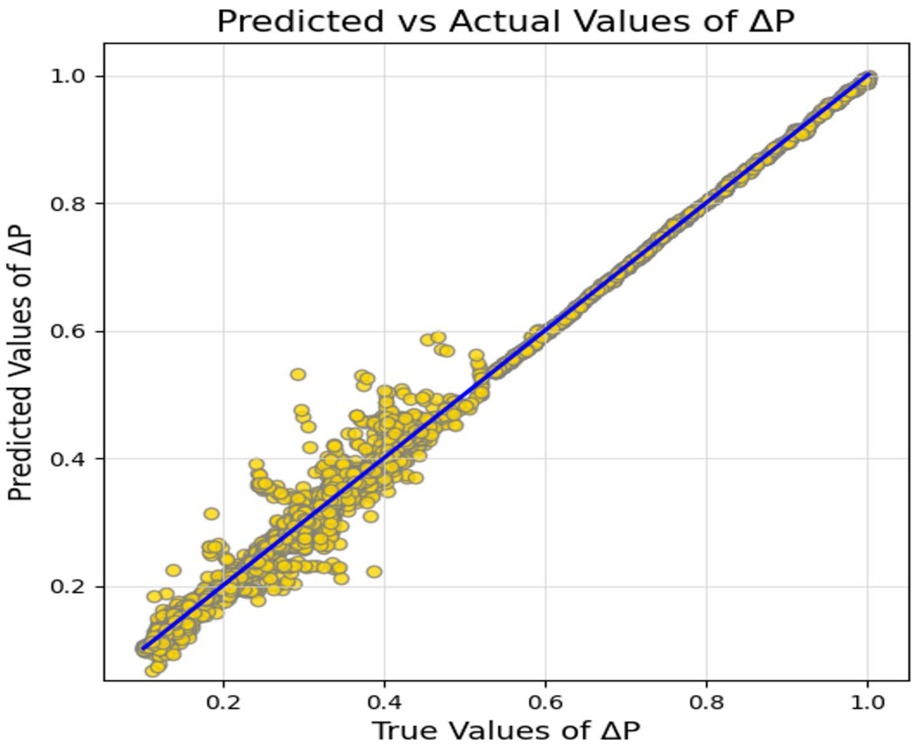
Performance of the DNN

- On the testing dataset (18910 data points)

Loss Function:	0.000015
Coefficient of Determination:	0.9997

Loss Function:	0.00016
Coefficient of Determination:	0.9938





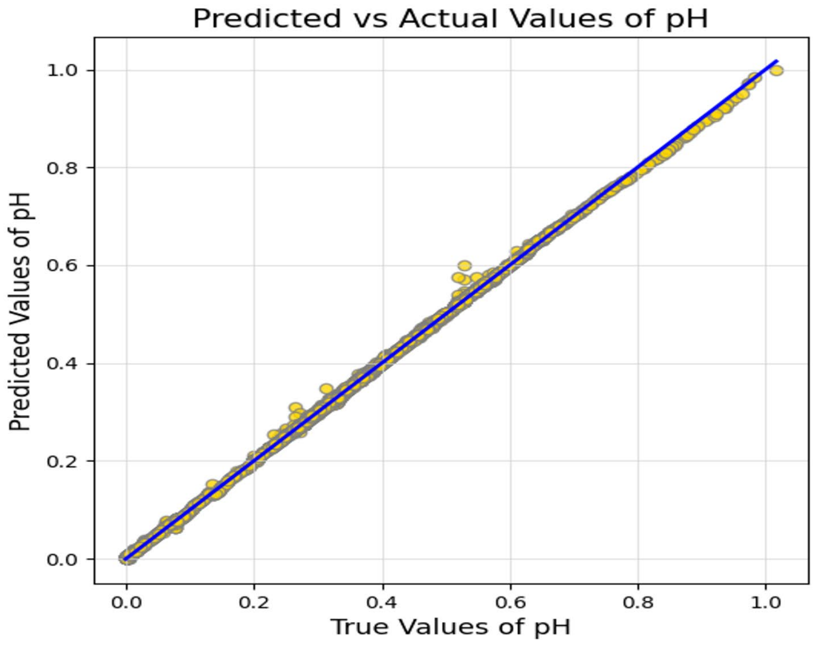
Performance of the DNN

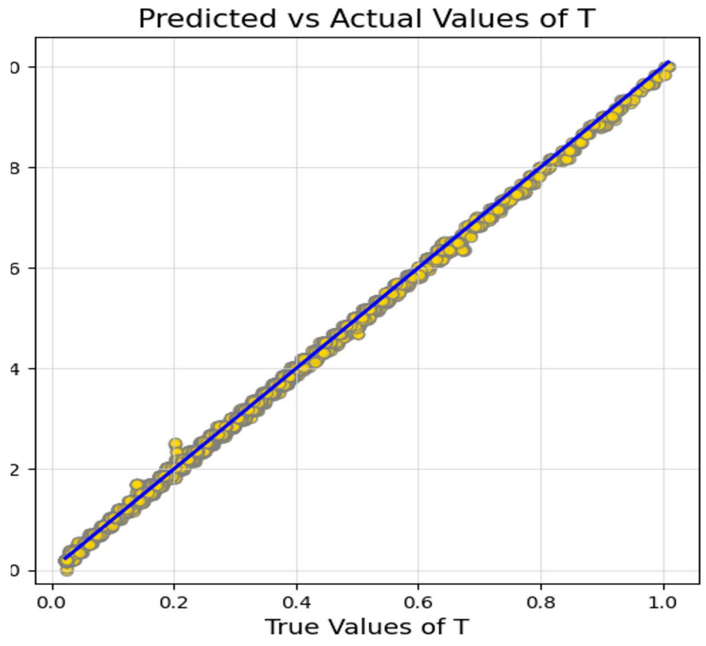
- On the testing dataset (18910 data points)

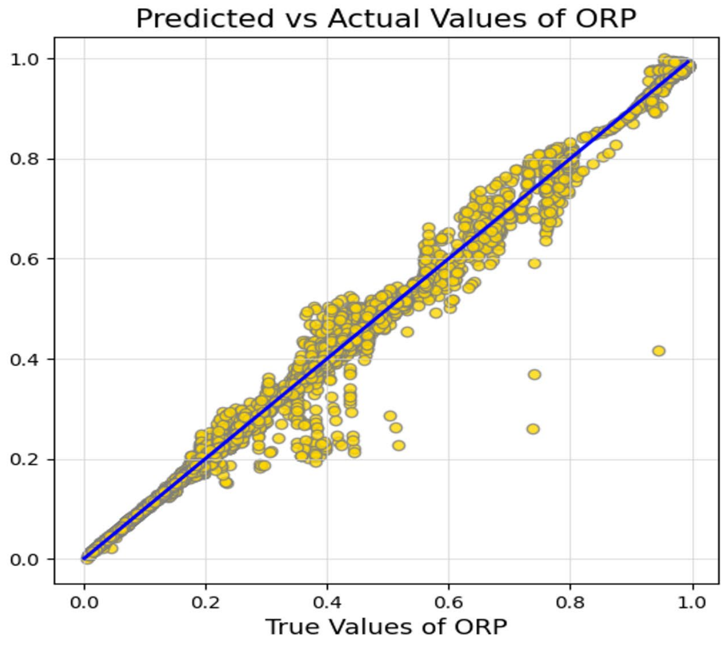
Loss Function_T3: 0.00000946
Coefficient of Determination_T3: 0.9995

Loss Function_T4: 0.0000287
Coefficient of Determination_T4: 0.9991

Loss Function_T5: 0.00026
Coefficient of Determination_T5: 0.9956





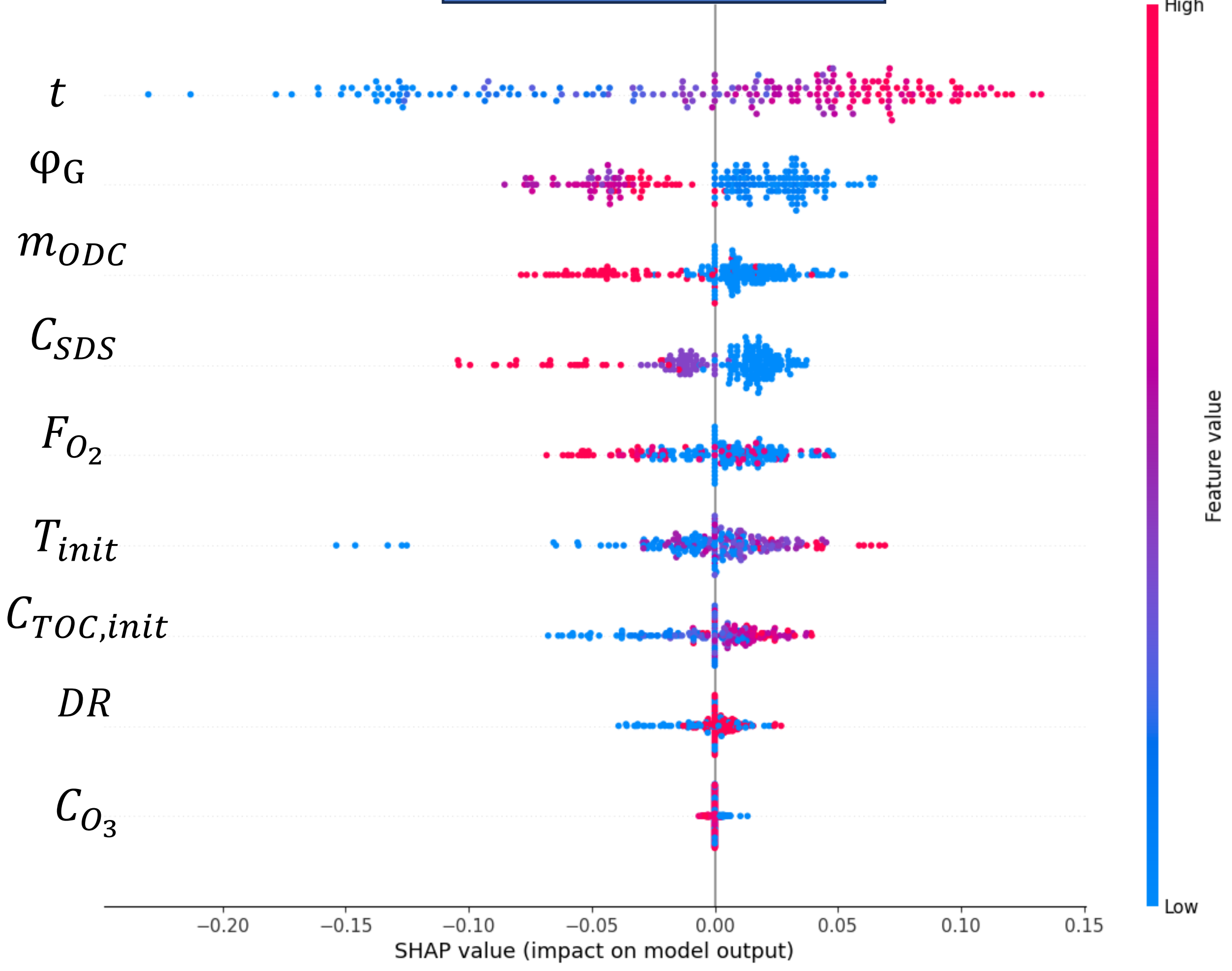


Interpretation of the DNN with XAI

- The input variables are ranked in decreasing order of influence on the R_{ES}.

- The TOC removal efficiency is favored when the:
  - ✓ treatment time is longer,
  - ✓ gas hold-up notes the smaller values,
  - ✓ mass of ODC corresponds to its smaller values,
  - ✓ SDS concentration is the lowest,
  - ✓ flow rate takes its smaller-medium values,
  - ✓ initial temperature is the highest,
  - ✓ initial TOC concentration is large.

Summary Plot of R_{ES}



Conclusions

Ozonation tests on bubble flow column reactors demonstrated:

- The organic pollutants are transferred to the aqueous phase and are oxidized by dissolved ozone and generated oxidative species (e.g. $OH^{\cdot}$).
- Oxygen as inlet gas and low flow rate favor the ozonation process.
- Dilution ratio higher than 1-1 leads to higher removal efficiency of TOC & TPH.
- Process efficiency seems to be independent of high ozone concentrations.
- Presence of surfactant (SDS) enhances foaming and oil solubilization without improving ozonation process.

Simulation of ozonation by deep neural network demonstrated:

- Accuracy of the multitask DNN exceeds 98% in each distinct task.
- Confirmation of the effect of SDS, flow rate and O_3 concentration by shap method and DNN.
- Longer treatment time, low values of gas hold up & ODC mass along with high initial TOC concentration and temperature favor the TOC removal efficiency in solid phase.

Acknowledgment

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SCENARIOS

HORIZON 2020

Earlier published work

Kalari K., K. Christodoulis, N. Bali, M. Theodoropoulou, C. D. Tsakiroglou, "An artificial neural network toward simulating the treatment of wastes in multiphase reactors by ozonation", *Chem. Eng. J.*, 471 (2023) 144433. https://doi.org/10.1016/j.cej.2023.144433

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