

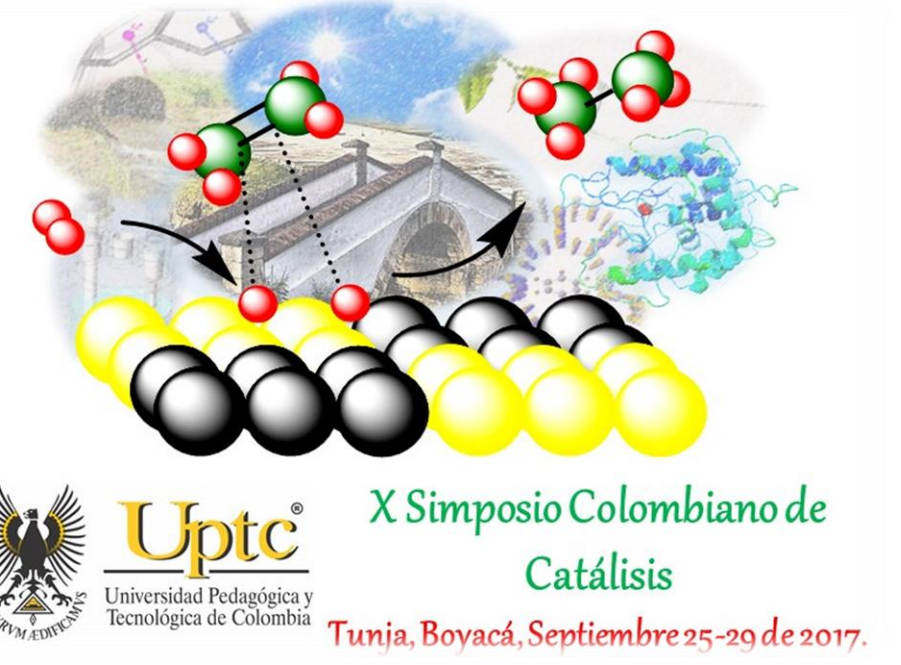
# CWPO Degradation of Natural Organic Matter: Synthetic Water vs. Real Surface Water

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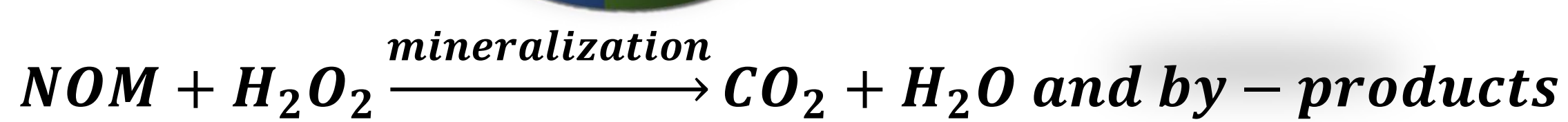
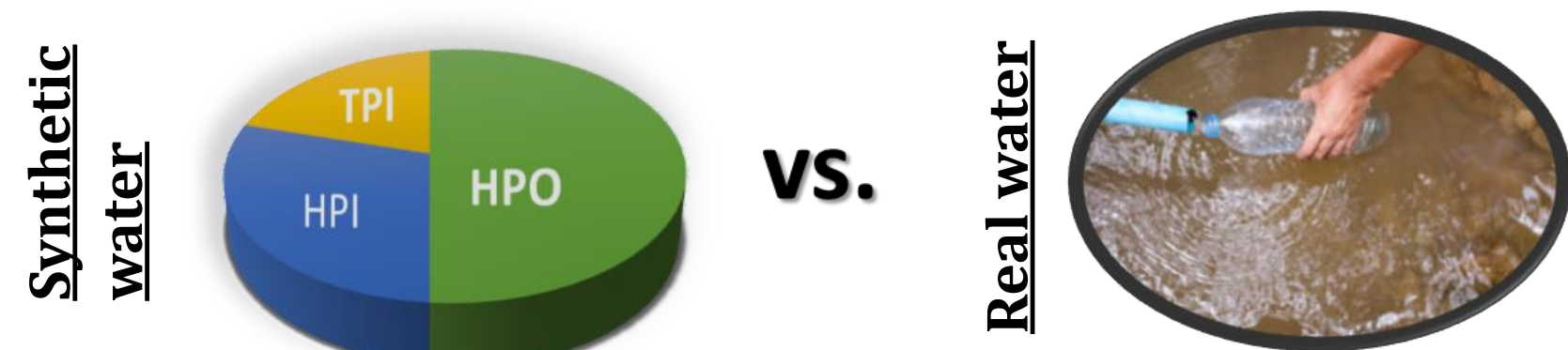
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## Introduction

Advanced Oxidation Processes (AOPs) are feasible and very promising methods to oxidize NOM from raw waters. Catalytic Wet Peroxide Oxidation (CWPO) degradation of NOM present in (i) a synthetic model water and (ii) raw surface, real water was carried out in order to determine the efficiency of NOM removal.



## Materials and methods

**Table 1.** Preparation of synthetic water surrogate based on standards of different polarity.

Reagent <sup>1</sup>	NOM-fraction modelled <sup>2</sup>	Molecular weight (Da)	Abundance in synthetic water (TOC %)
Polyacrylic acid (PAA)	TPI	130.000	20
Polystyrene sulfonate (PSS)	PSS-1	1'000.000	12.5
	PSS-2	200.000	12.5
Polygalacturonic acid (PGUA)	HPI	25.000-50.000	30
Humic acids (HA)	HPO	-	25

<sup>1</sup>All reagents Sigma-Aldrich used as received  
<sup>2</sup>HPI: hydrophilic; TPI: transphilic; HPO: hydrophobic



**Fig. 1** Preparation of synthetic water.

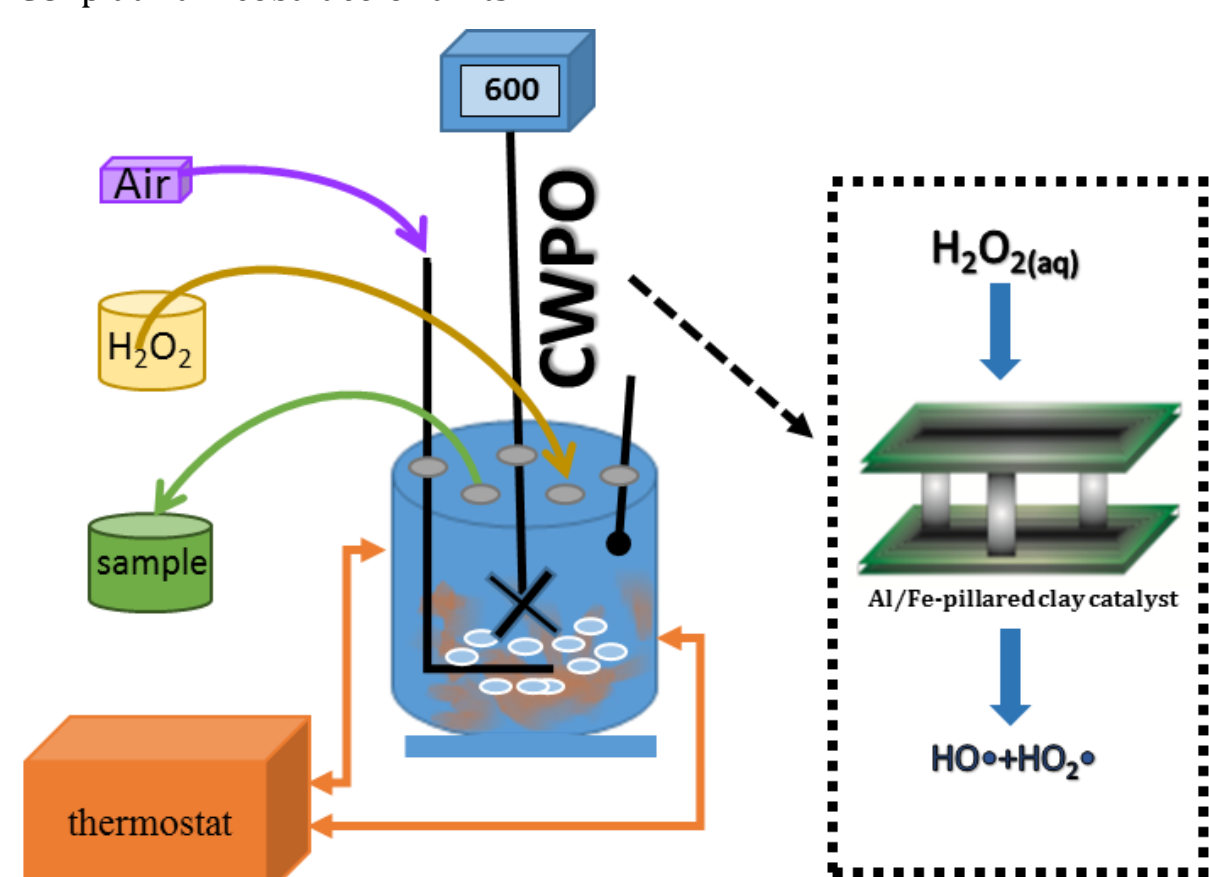
**Table 2.** Physicochemical properties of real and synthetic water samples.

Parameters	Raw water (RW) <sup>1</sup>	Synthetic water (SW)
UV <sub>254</sub> (cm <sup>-1</sup> )	0.385	0.418
Color <sub>456</sub> (PCU) <sup>2</sup>	0.021	0.047
TOC (mg C/L)	18.1	15.4
DOC (mg C/L)	10.9	15.4
SUVA (L mg <sup>-1</sup> m <sup>-1</sup> )	3.526	2.709
Alcalinity (mgCaCO <sub>3</sub> /L)	46	---
Conductivity (μS/cm)	16.9	17.9
Turbidity (UNT)	173.0	---
Dissolved oxygen (mg/L)	159	11

<sup>1</sup>Raw water was collected from Vereda Charandú surface source, near Ipiales – Nariño, Colombia  
<sup>2</sup>PCU: platinum cobalt color units



**Fig. 2** DAX-8 and XAD-4 resins packed columns.



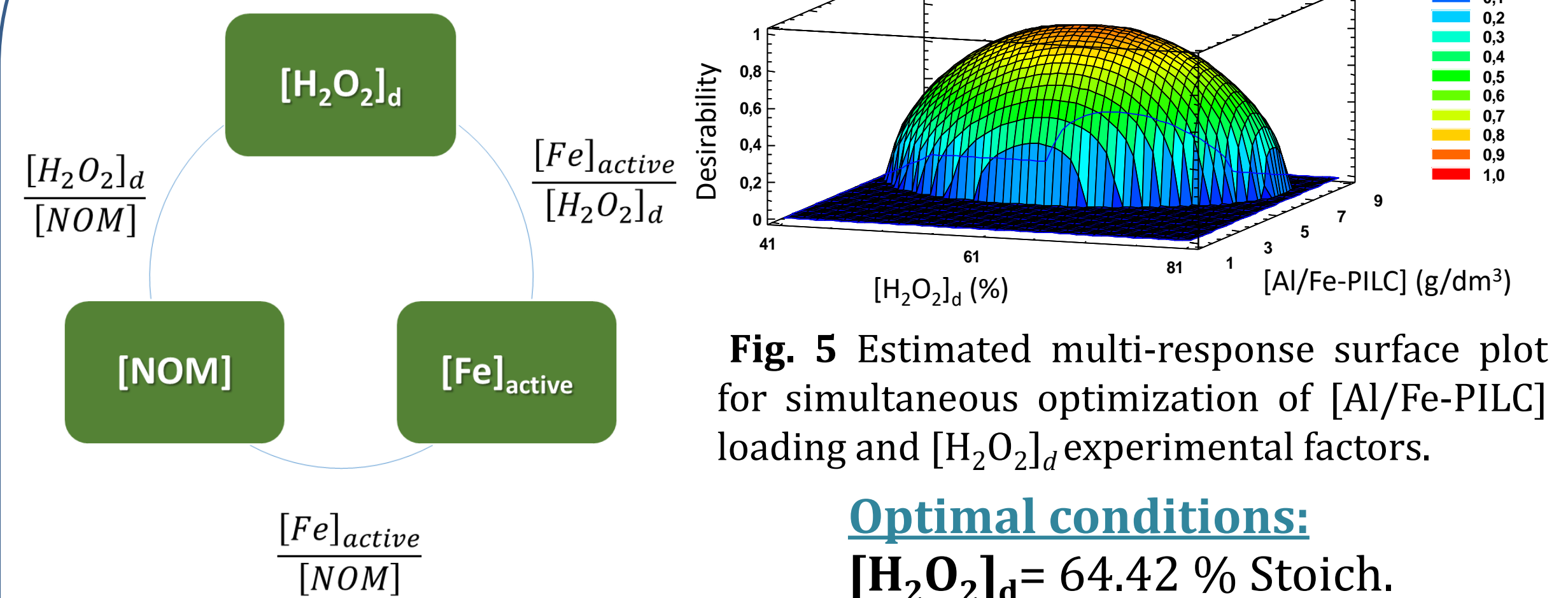
**Fig. 3** Schematic (left) and real laboratory (right) set-up for CWPO-degradation of NOM. Experimental parameters: Peroxide Dose  $[\text{H}_2\text{O}_2]_d = 64.42\%$  stoichiometric (SW: 87 mg/L, RW: 50 mg/L); Catalyst concentration  $[\text{Al/Fe-PILC}]^*$ : 5.1 g/L;  $\text{pH}_{\text{SW}} 7.0$  and  $\text{pH}_{\text{RW}} 7.3$ ; Temperature<sub>SW</sub>: 25 °C and Temperature<sub>RW</sub>: 14 °C (RT on sampling); full reaction time: 180 min; full recorded time: 240 min.

\* (Al/Fe-PILC: Atomic Metal Ratio  $\text{AMR}_{(\text{Fe})} = 3.17\%$ ; Total Metal Concentration (TMC) = 5.73 mol/L; Interlayering solution: Auto-hydrolysis<sup>[1]</sup> with starting ratio  $(\text{Al}^{3+}/\text{Al}^0) = 14/86$ ; Final heating: 400 °C/2 h).  $\text{Fe}_{\text{active}}$  content: 0.62 wt. %.

## Conclusions

$\text{H}_2\text{O}_2$  was slightly more efficiently used by the catalytic system on RW, in good agreement with the highest percentage of color removal on this sample (~ 93 %); however, the NOM mineralization was significantly higher (75 %) on the SW against RW (37 %). It probably was related with higher fraction of more refractory hydrophilic substances formed in the real water (SUVA~ 3, HPI: 12.37 %, HPO: 30.88 %) vs. synthetic water (SUVA>4, HPI: 2.30 %, HPO: 14.63 %). Finally, the HPO fraction significantly decreased in both waters, but in RW the change was less significant due to the presence of more refractory substances than SW.

## Results



**Fig. 4** Relationship between three main factors in CWPO.

**Fig. 5** Estimated multi-response surface plot for simultaneous optimization of  $[\text{Al/Fe-PILC}]$  loading and  $[\text{H}_2\text{O}_2]_d$  experimental factors.

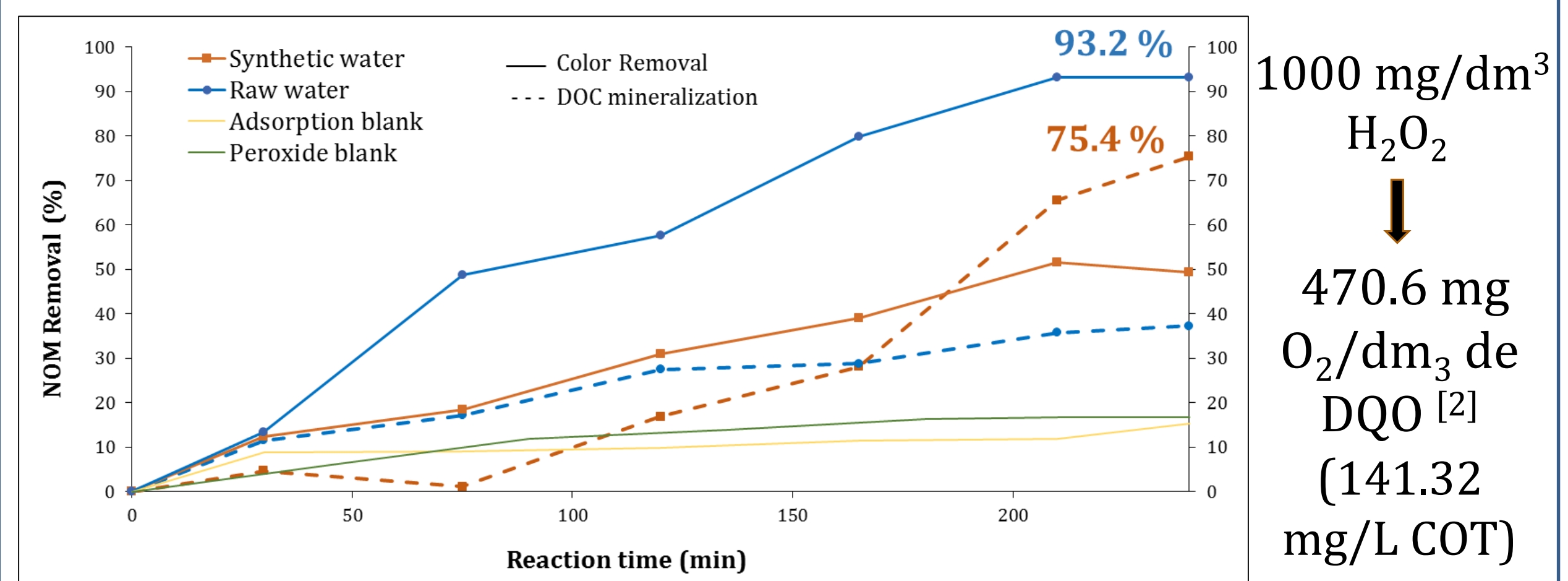
### Optimal conditions:

$[\text{H}_2\text{O}_2]_d = 64.42\%$  Stoich.

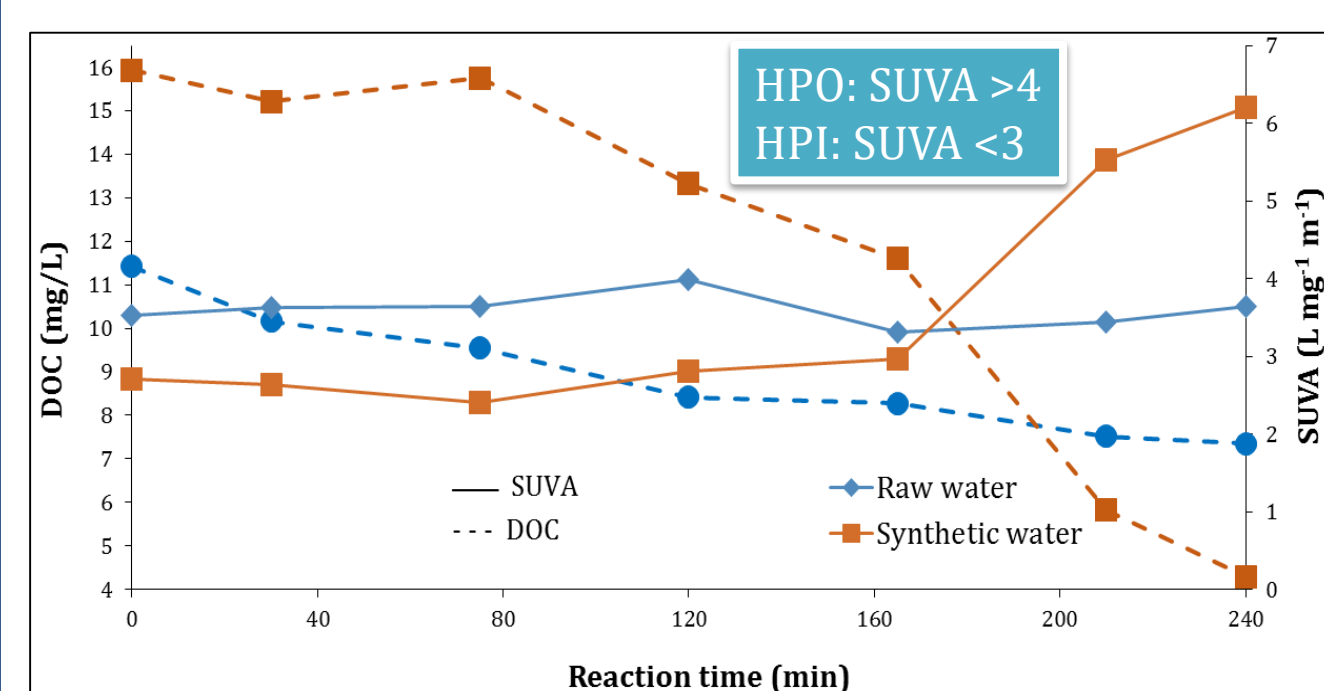
$[\text{Al/Fe-PILC}]$ : 5.1 g/L

$\text{RW}[\text{Fe}]_{\text{act}}/[\text{H}_2\text{O}_2]_d = 1.219$

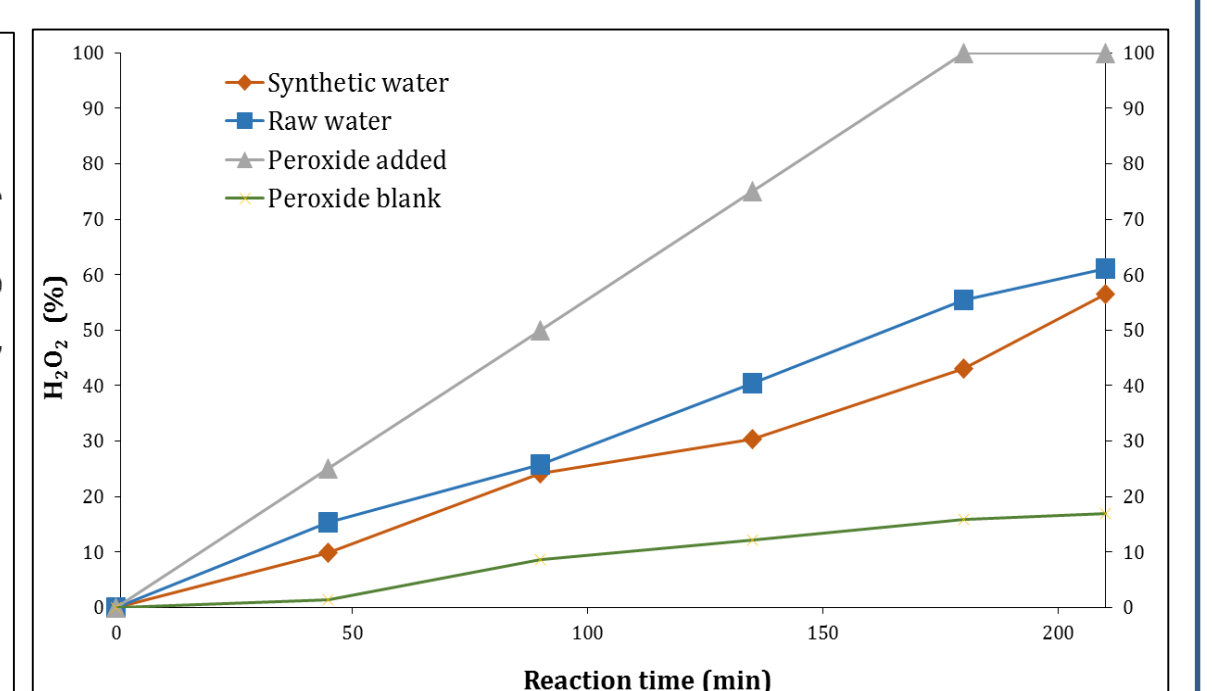
$\text{SW}[\text{Fe}]_{\text{act}}/[\text{H}_2\text{O}_2]_d = 0.701$



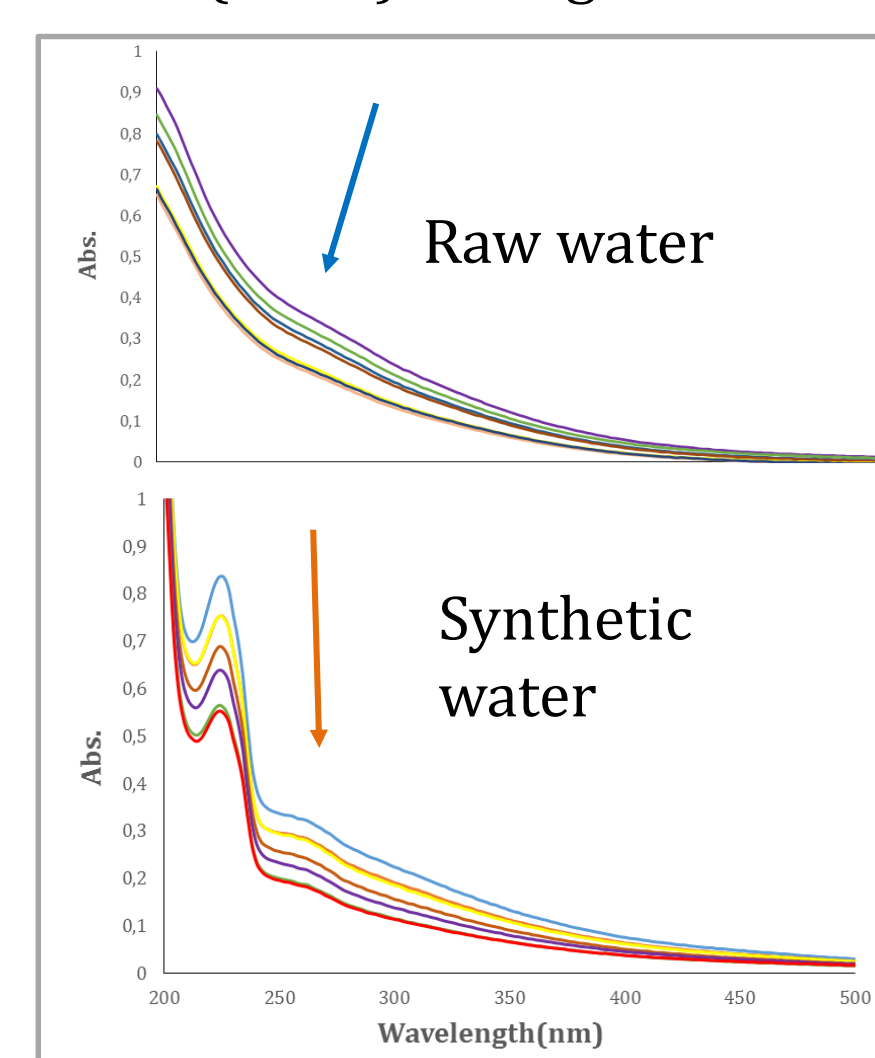
**Fig. 6** CWPO degradation of NOM: organic color removal at 456 nm (2120C-Standard Methods) and DOC mineralization (TOC-L Analyzer Shimadzu).



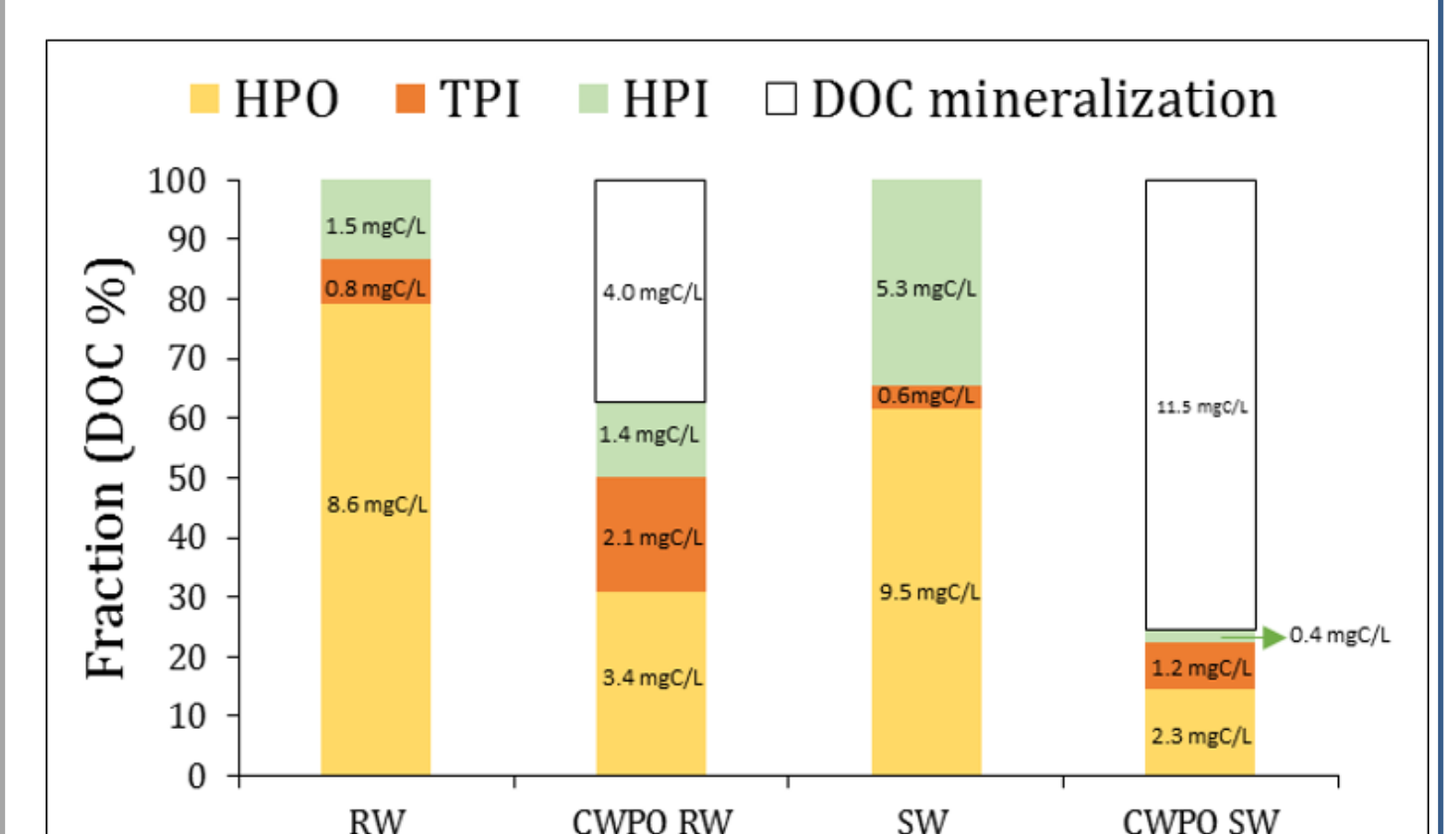
**Fig. 7** Evolution of DOC and Specific UV Absorbance (SUVA) through the CWPO tests.



**Fig. 8** Fraction of  $\text{H}_2\text{O}_2$  reacted vs. added through the CWPO catalytic tests.



**Fig. 9** RW and SW UV-Vis spectra through the CWPO catalytic experiments.



**Fig. 10** DOC resin-fractionation of synthetic and real water before and after (240 min) of the CWPO catalytic tests.

## Acknowledgment

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## References

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