RSM optimization of the catalytic wet peroxide oxidation of methyl orange and correlation with major intermediates and by-products

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Introduction

Figure 1. Contamination of natural water sources with azo dyes

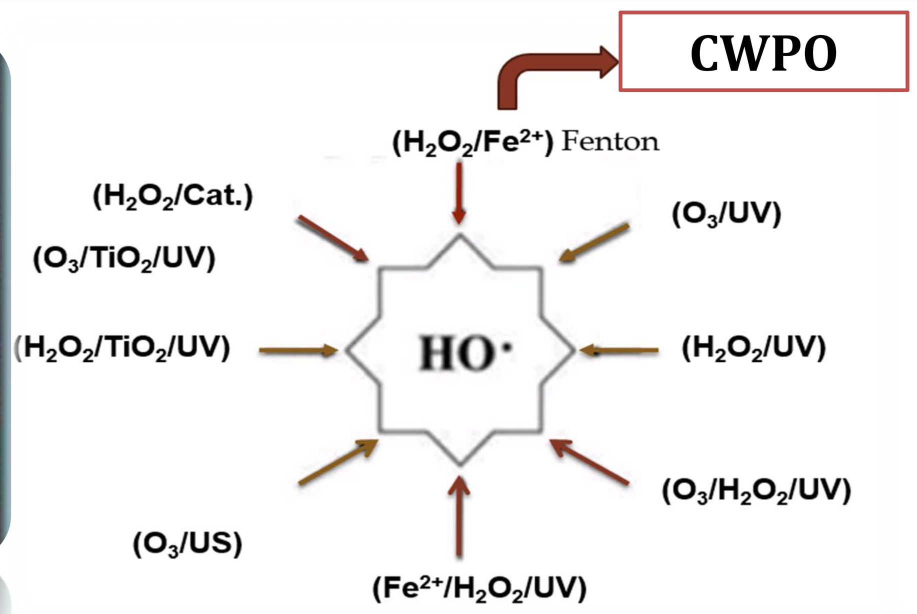

Figure 2. Advanced Oxidation Technologies [1]

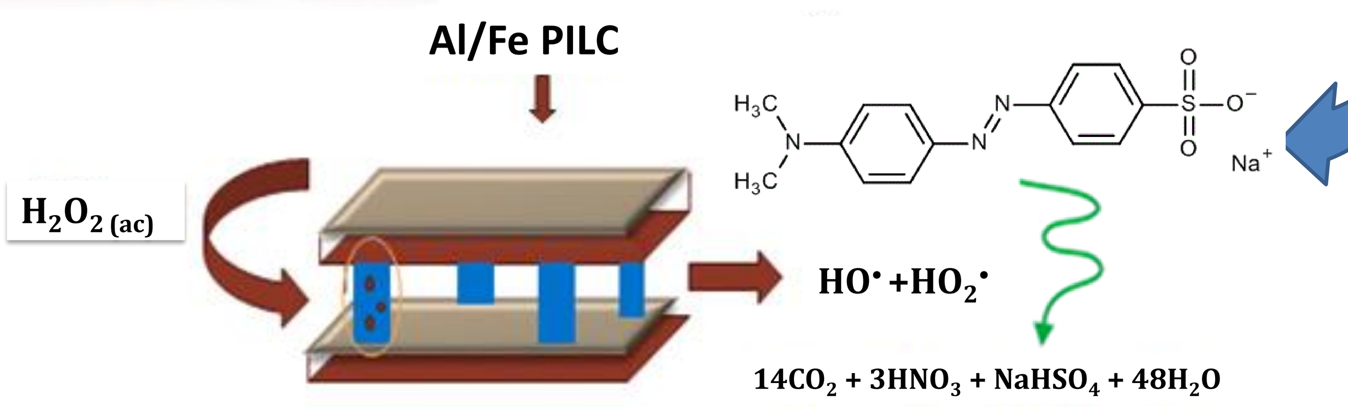

Figure 3. General Sketch of the CWPO technology catalyzed by pillared clays [2]

Statistical response surface methodology (RSM) was used to optimize the main parameters of the CWPO reaction in the catalytic degradation of methyl orange (MO) in a 1.5 L semi-batch reactor. Studied experimental variables were: *(i)* catalyst's concentration, *(ii)* dose of hydrogen peroxide and *(iii)* reaction time; Non-controllable variables were: starting pH, Temperature and initial [MO] loading (as Total Organic Carbon - TOC).

Experimental Materials & Methods

Figure 4. Assembly used for CWPO catalytic experiments

Table 1. First experimental design (RSM -1) used to optimize main operating parameters of CWPO

Type of design	2^3	Optimization type	Central Composite	Number of runs	23

Experimental Variables	Experimental range	Central	Axial points
Peroxide dose $[H_2O_2]_d$ (Stoichiometric %)	50 – 150	100	15.9 - 184.1
Catalyst concentration **[C2P-Ext-PILC]*** (g/dm³)	0.34 – 1.21	0.775	0.05 – 1.5
Reaction time **(t_r)** (min)	60 -120	90	39.54 – 140.45
Non-controllable variables			
Starting MO concentration $[MO]_0$ TOC (mg C/dm³)	0–30	-	
Temperature of reaction **(T_r)** (°C)	1–35	-	
pH	6-9	-	

*C2Ext-PILC: Atomic Metal Ratio $AMR_{(Fe)}$ = 8.34 %; Total Metal Concentration (TMC) = 5.73 mol/L; Interlayering solution: Auto-hydrolysis with starting ratio (Al^{3+}/Al^0) = 14/86; Calcination: 400 °C.

Desirability: MO removal + $[H_2O_2]_f$ + MO mineralization

Responses

MO Removal (%) (Spectrophotometric)

$[H_2O_2]_f$ (%) (Spectrophotometric)

MO mineralization: TOC removal (%); Total Nitrogen removal (TN %)

Table 2. Second experimental design (RSM -2) used to optimize main operating parameters of CWPO

Type of design	2^2	Optimization type	Central Composite	Number of runs	10

Experimental Variables	Low (-1)	High (1)
Peroxide dose $[H_2O_2]_d$ (Stoichiometric %)	36.0	89.0
Catalyst concentration **[C2P-Ext-PILC]*** (g/dm³)	1.3	5.2
Non-controllable variables		
Starting MO concentration $[MO]_0$ TOC (mg C/dm³)	6.0	9.0
Temperature of reaction **(T_r)** (°C)	2.0	20.0
pH	5.0	25.0

Results

RSM-1

Maximal TOC removal = 20.5

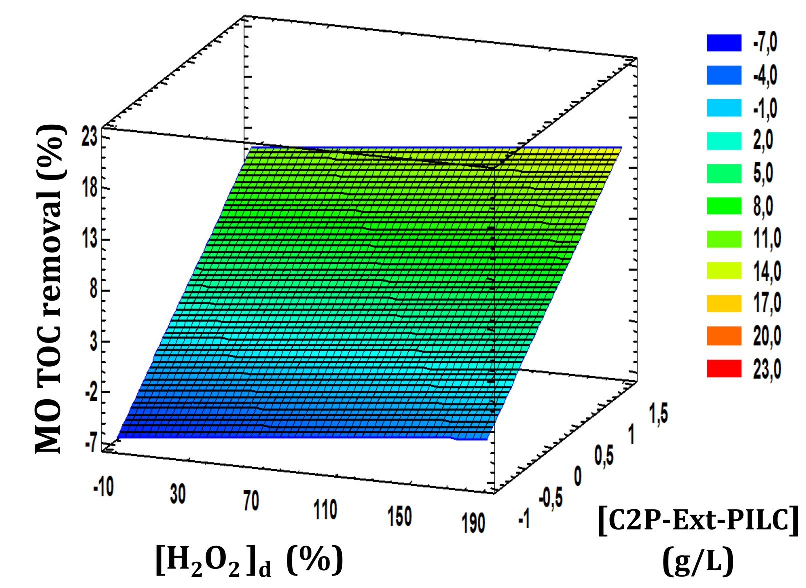

Figure 5. Response surface for MO mineralization (TOC removal) at final t_r

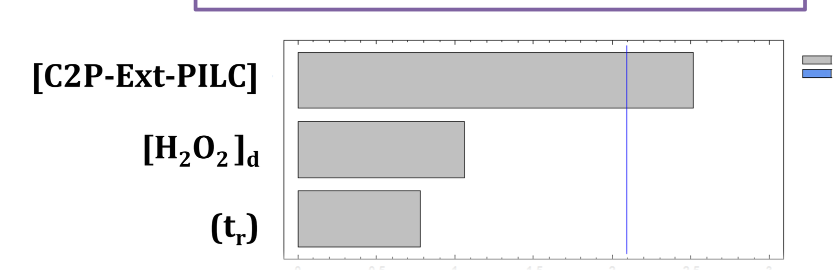

Figure 6. Pareto's diagram for TOC removal

Efficiency of MO degradation increased as a function of t_r

Table 4. Comparison between the $[Fe]/[H_2O_2]$ ratio used in RSM-1 against bibliography reports

Pollutant	Iron catalyst	Fe (mg/L)	$[H_2O_2]$ (mg/L)	[pollutant] (mg C/dm³)	$[H_2O_2]$/[pollutant] mg/mg TOC	$[Fe]/[H_2O_2]$	Elimination (%)	Reference
Linear alkyl benzene sulfonate (LAS) $C_{12}H_{25}NaO_4S$	$FeSO_4.7H_2O$ 98%	30.10	90.00	5.00	18.00	0.334	95.0 (COD)*	Lin *et al.* **(1999)**
NOM in drinking wáter	BVAlFe2C-EtOH25	190.6	1598	12.1	132.6	0.119	96.3 (COD)*	Galeano *et al.* **(2012)**
Catalyst concentration Upper Axial level	**C2Ext-PILC**	**17.40**	**506.6**	**5.97**	**84.90**	**0.034**	**13.7 (DOC)***	**RSM-1**

*COD: Chemical Oxygen Demand; DOC: Dissolved Organic Carbon

RSM-2

Optimized *desirability* = 0.892

$[C2P\text{-}Ext\text{-}PILC]_{optimal}$ = 6.0 g/dm³

$[H_2O_2]_{d\ optimal}$ = 100 %

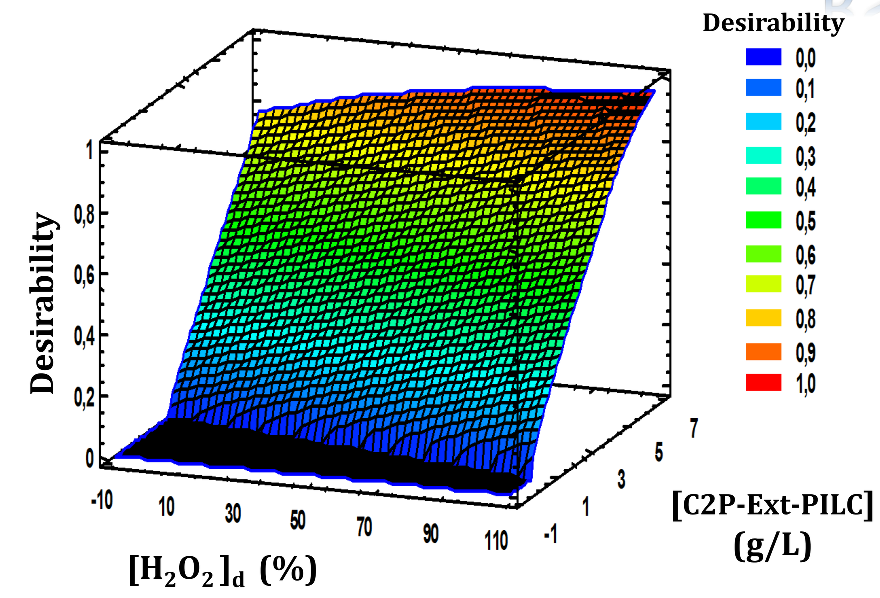

Figure 7. Multivariate Response surface

MO mineralization (%) = -4,55842 + 0,132927*$[H_2O_2]_d$+ 7,37861*[C2P-Ext-PILC]

Table 5. Influence of non-controlable variables in RSM-2

Parameter	Standard Error	Value t	Pr > |t|
$[MO]_0$	28.5	0.370	0.772
T_r	0.656	0.690	0.616
pH	0.381	5.62	0.112

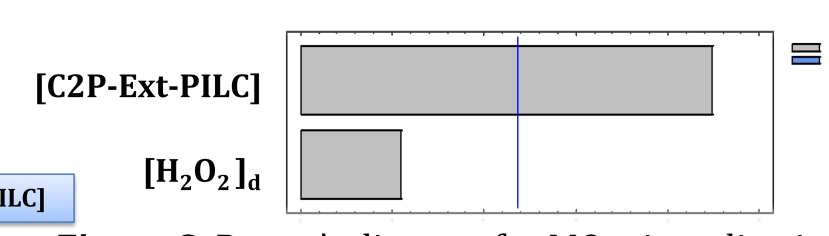

Figure 8. Pareto's diagram for MO mineralization

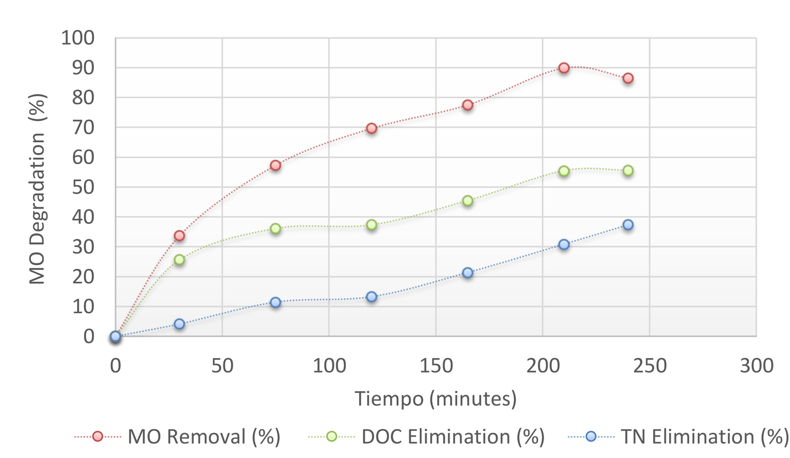

Figure 9. MO degradation in the best catalytic experiment

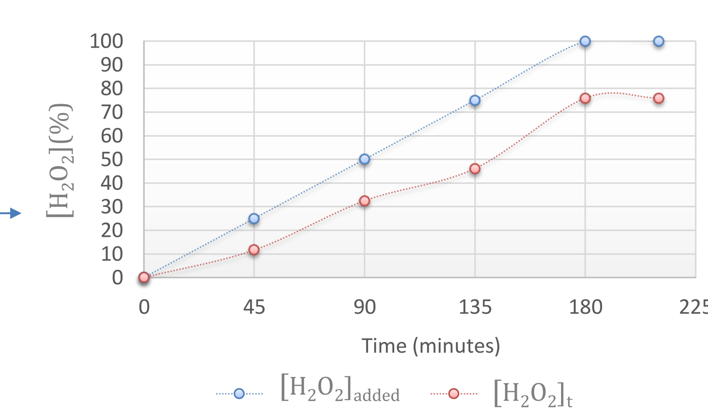

Figure 10. $[H_2O_2]_{added}$ Vs remaining $[H_2O_2]_t$

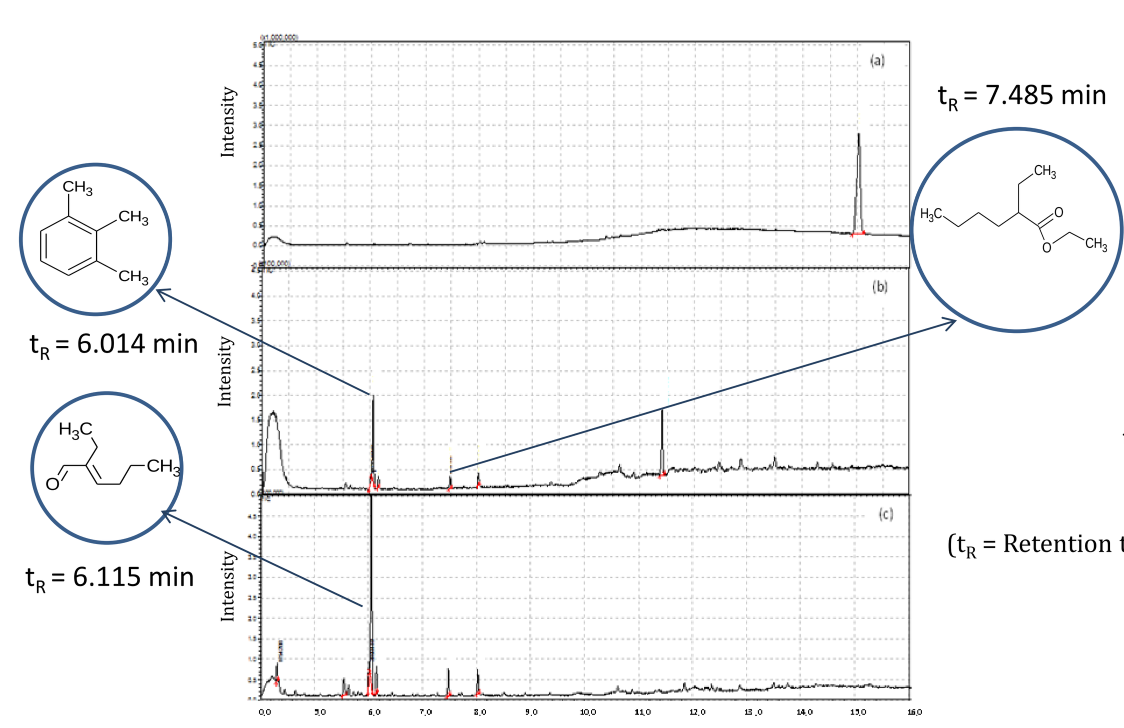

Figure 11. GC-MS for MO degradation at different reaction times: (a) 0 min; (b) 15 min; (c) 4 hours

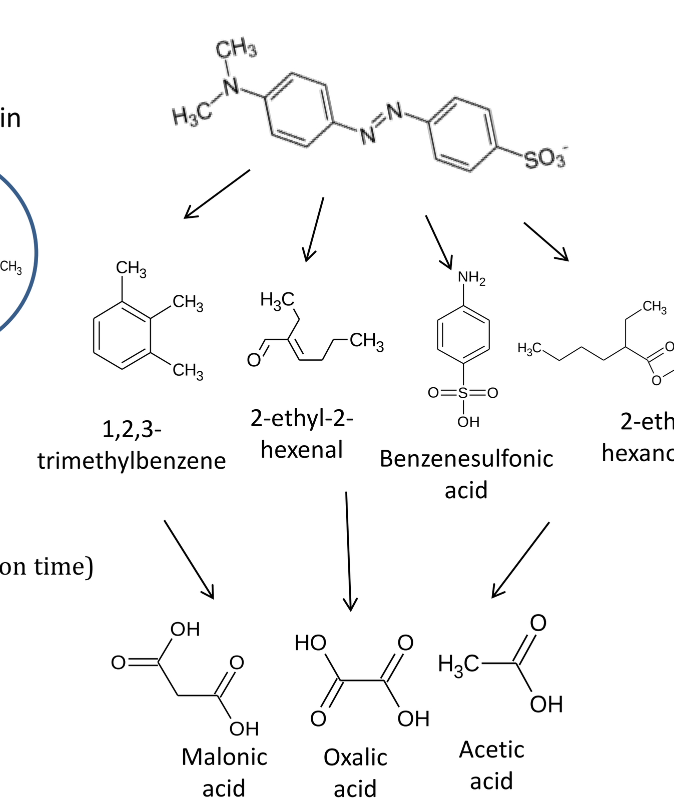

Figure 12. Proposed fragmentation profile for MO intermediates and by-products along CWPO

Conclusions

- The catalyst loading showed to exert the most influential effect on the overall performance of the CWPO degradation of MO, mainly in terms of TOC mineralization. Optimal values of the experimental variables promoted simultaneous maximal efficiency of added hydrogen peroxide to be achieved.
- The non-controllable variables were not statistically significant on the recorded response parameters, suggesting the CWPO catalyzed by pillared clays as promising technology for degradation of colored wastewaters under wide range of input physicochemical parameters.

Acknowledgement

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References

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