Recent advances towards scaled-up preparation of Al/Fe-PILC clay catalysts: Potential application in CWPO oxidation to improve drinking water quality

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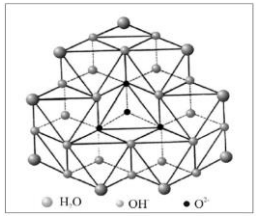
CWPO – Drinking Water

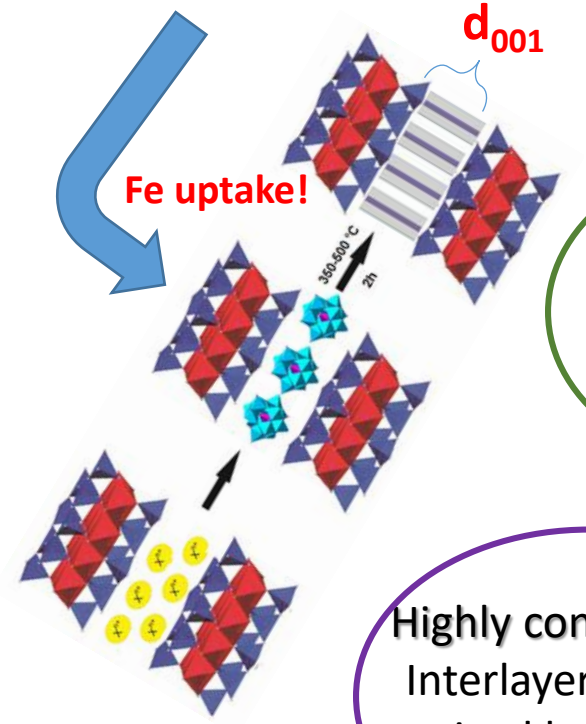


$[Al(Al_{12}O_4(OH)_{24}(OH_2)_{12}]^{7+}$

Al/Fe-PILC
Efficient CWPO active catalyst

Scaling-up

Intensification process



Catalyst shaping
Extrudates
Microspheres

CWPO

Catalytic potential
MO; PhO; NOM

Highly concentrated
Interlayering Al/Fe
mixed hydrolyzed
precursor

Simpler and
efficient clay
Interlayering
method

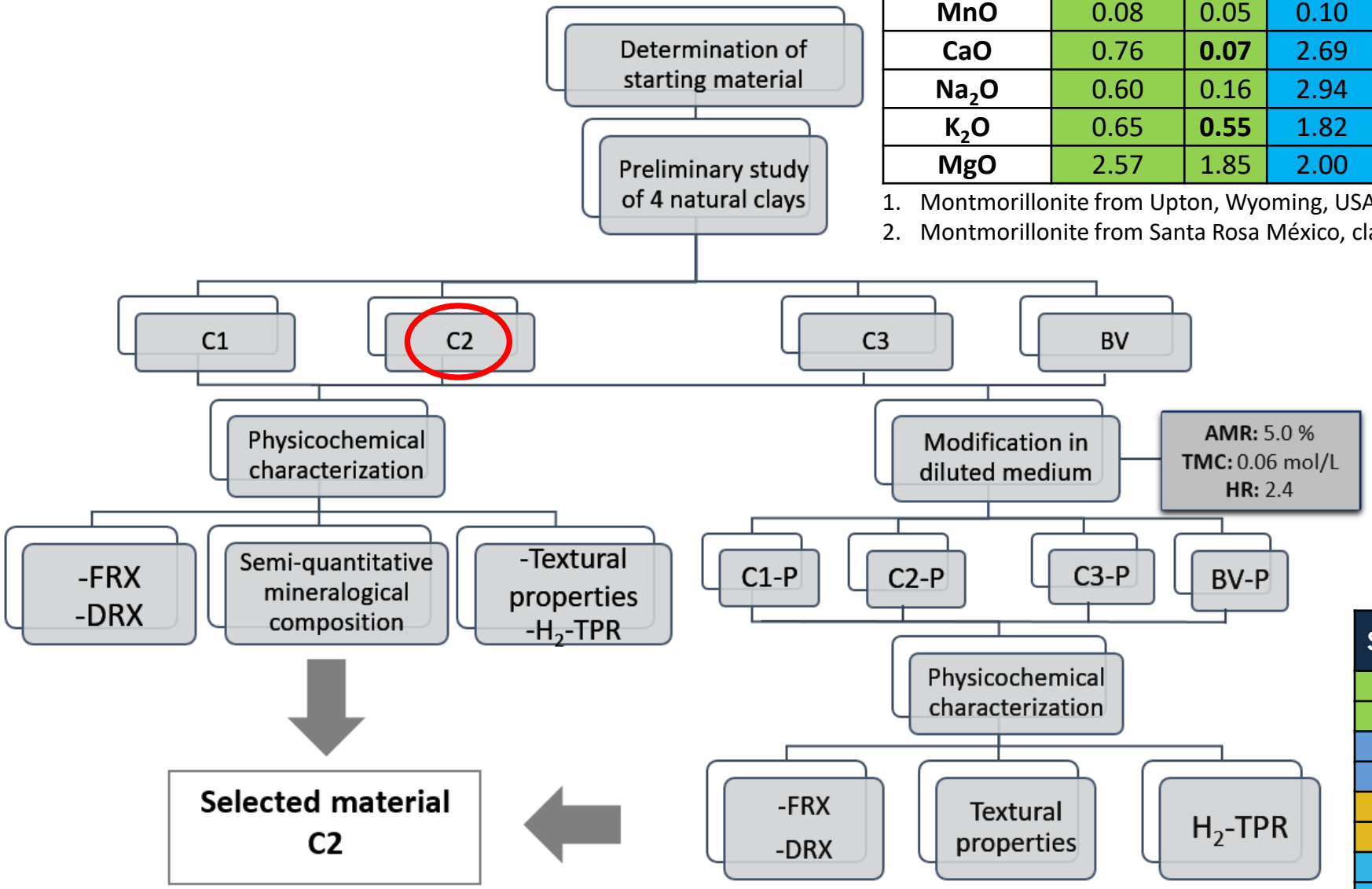
Galeano L.A., Gil A., Vicente M.A., *Appl. Catal. B* 100 **(2010)** 271–281.

Galeano L.A., Vicente M.A., Gil A., *Catal. Rev. Sci. Eng.* 56 (03) **(2014)** 239 - 287.

Al/Fe – PILC: Selection of the best starting natural bentonite

Content/ sample	BV	BV-P	C1	C1-P	C2	C2-P	C3	C3-P	1	2
Al_2O_3	18.9	28.7	15.4	25.0	16.5	26.5	14.0	**24.3**	20.6	21.2
Fe_2O_3	7.60	10.8	7.00	13.3	6.90	11.6	16.1	16.9	3.90	2.00
SiO_2	49.1	49.6	56.4	50.8	53.2	52.1	40.9	45.2	57.5	56.6
MnO	0.08	0.05	0.10	0.04	0.11	0.00	0.16	0.12	-	0.01
CaO	0.76	**0.07**	2.69	**0.13**	1.84	**0.08**	2.10	**0.30**	-	-
Na_2O	0.60	0.16	2.94	0.32	1.30	0.23	2.94	0.15	2.87	3.71
K_2O	0.65	**0.55**	1.82	**0.88**	0.83	**0.72**	0.14	**0.12**	-	-
MgO	2.57	1.85	2.00	1.86	2.22	1.79	2.48	2.26	2.45	3.46

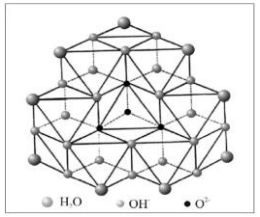
1. Montmorillonite from Upton, Wyoming, USA, clay fraction, air-dried (Newman, 1987).
2. Montmorillonite from Santa Rosa México, clay fraction, air-dried (Newman, 1987)



Sample	S_{BET} (m^2/g)	$V_{\mu p}$ (cm^3/g)	$S_{Ext.}$ (m^2/g)
BV	85	20	-
BV-P	138	32	25
C1	42	10	-
C1-P	144	33	25
C2	62	14	-
C2-P	**194**	**45**	29
C3	108	25	-
C3-P	185	42	48

Sample	Fe_2O_3 (% w/w)	$Fe_{inc.}$ (% w/w Fe_2O_3)	Reduction of $Fe_{inc.}$ (%)
BV	7.63	-	-
BV-P	10.85	3.22	1.71
C1	7.04	-	-
C1-P	13.34	6.30	1.64
C2	6.86	-	-
C2-P	11.56	4.70	0.89
C3	16.06	-	-
C3-P	16.95	0.89	> 100

Al/Fe – PILC: Comparison of methods for Concentrated Interlayering solution



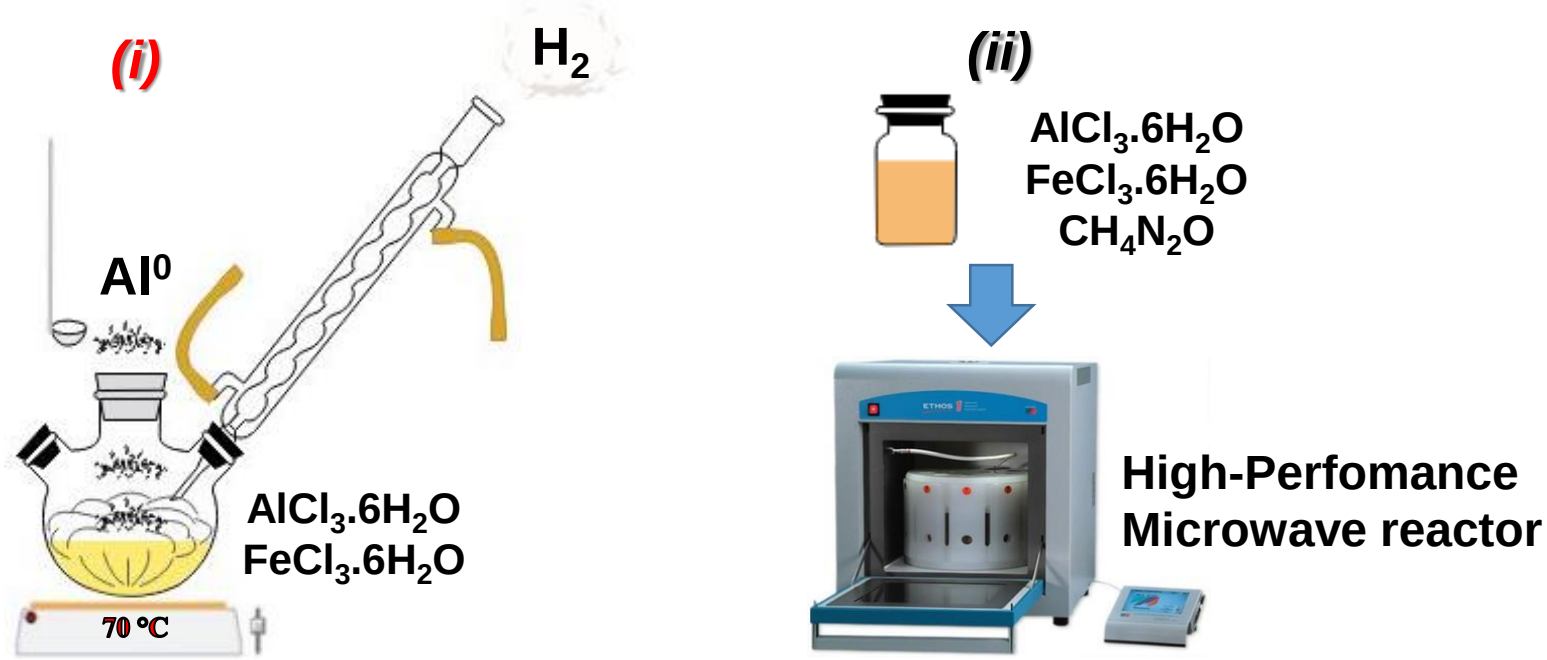
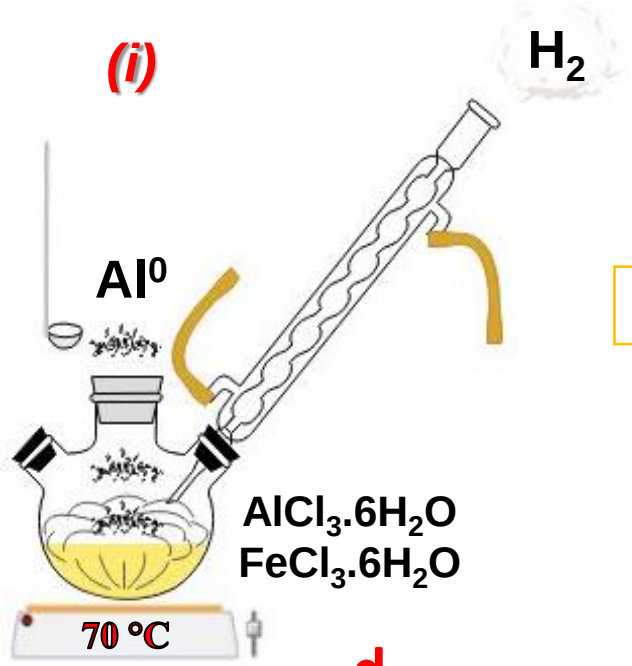


Figure 1. ***(i)*** Addition of elemental aluminum on the starting metal chlorides; ***(ii)*** microwave-assisted hydrolysis of the metals via urea decomposition and ***(iii)*** basic hydrolysis by addition of sodium hydroxide under diluted conditions (reference solution).

Table 1. Physicochemical properties of highly-concentrated Al/Fe interlayering solutions

Interlayering solution	$[Al]^{(w,x)}$ (mol/dm^3)	$[Fe]^{(w,x)}$ (mol/dm^3)	$TMC^{(w)}$ (mol/dm^3)	$pH^{(w)}$ (final)	$\rho^{(w)}$ (g/mL)	$EC^{(w)}$ (mS/cm)
(i) Al/Fe-Al^{0*}	**3.98**	**0.27**	**4.25**	**3.32**	**1.330**	**58.6**
(ii) Al/Fe-U	2.20	0.12	2.32	-0.33	1.410	47.8
(iii) Al/Fe-OH$^-$	0.054	0.002	0.06	3.86	0.999	22.4

Al/Fe – PILC: Statistical optimization of self-hydrolysis method



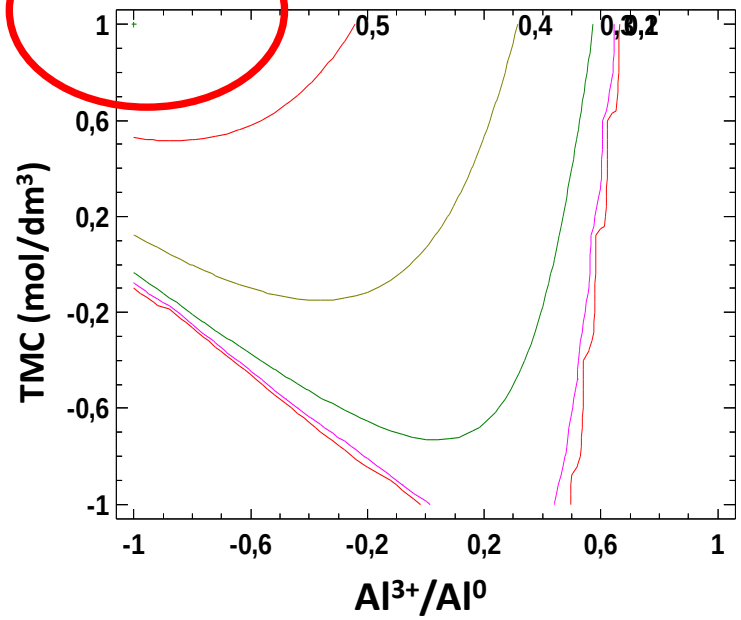
Series 1

14 samples

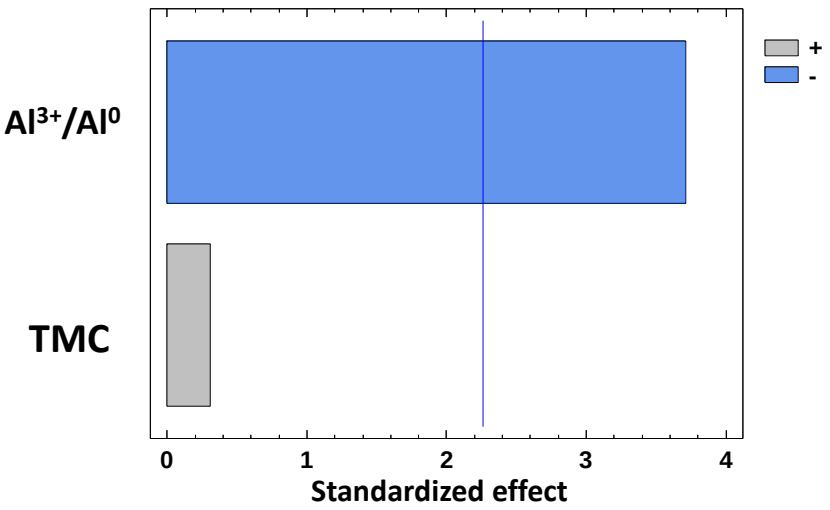
Factors	Levels	Responses	Goal
- **TMC:** (1.0 – 5.0 mol/L) - **Al^{3+}/Al^0:** (100/0 – 50/50)	(+1) (-1)	(1) pH (2) Density (3) d_{001} (4) hhpw	Maximize (1) to (3) + Minimize (4)

- Co-variable: Aging time

Contour diagram of the estimated response surface



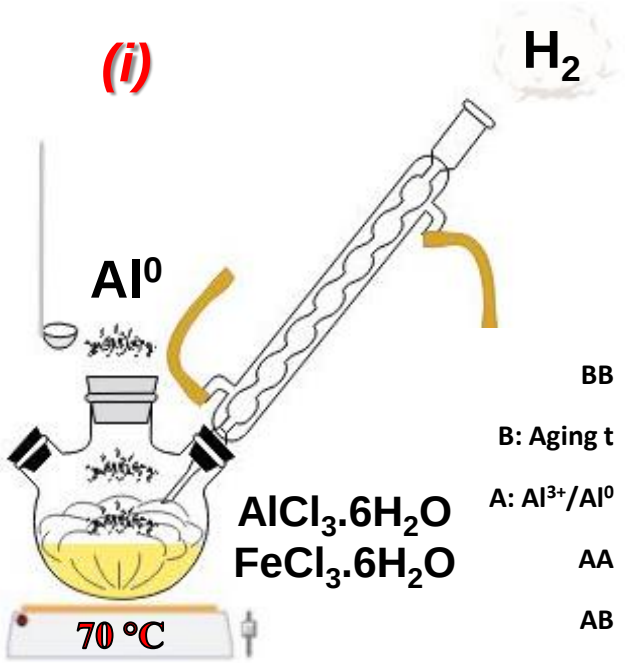
d_{001}



Main result Series 1

Factor	Optimal
Al^{3+}/Al^0	**50/50**
TMC (mol/dm³)	**4.41**

Al/Fe – PILC: Statistical optimization of self-hydrolysis method



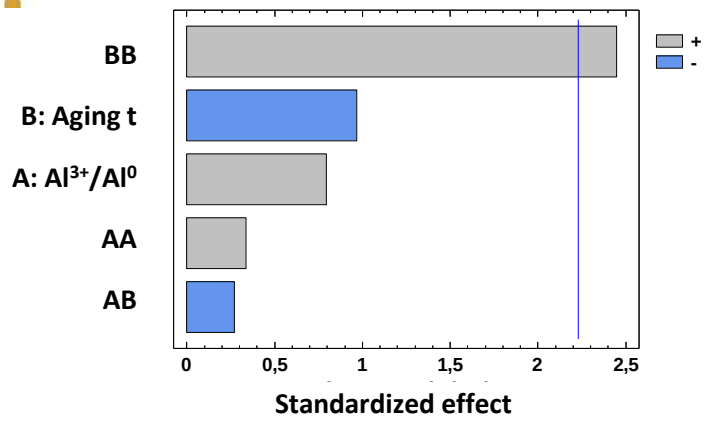
Series 2

16 samples

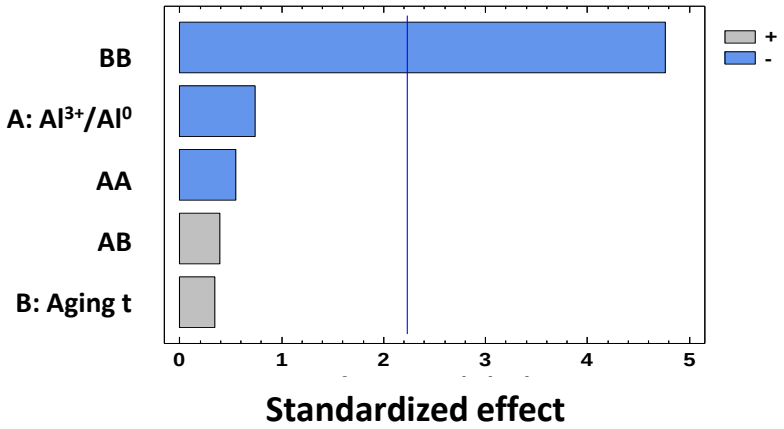
Factors	Levels	Responses	Target
- **Al^{3+}/Al^0:** (20/80 – 50/50) - **Aging t:** (2 h – 8 h)/70 °C	(+1) (-1)	(1) TOC (mg/dm^3) (2) PhO elim. (%) (3) S_{BET} (4) $S_{\mu p}$ (*t-plot*)	Maximize (2) to (4) and minimize (1)

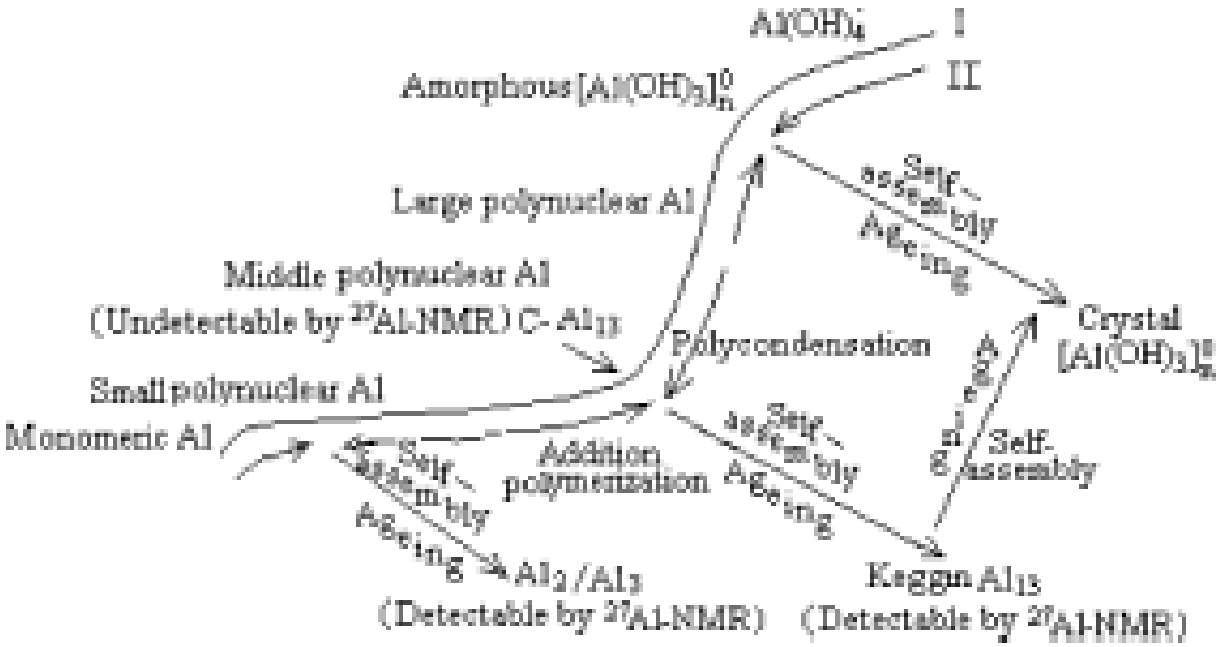
*Temperature of calcination: 2 Blocks **400 °C** vs. **500 °C**

TOC



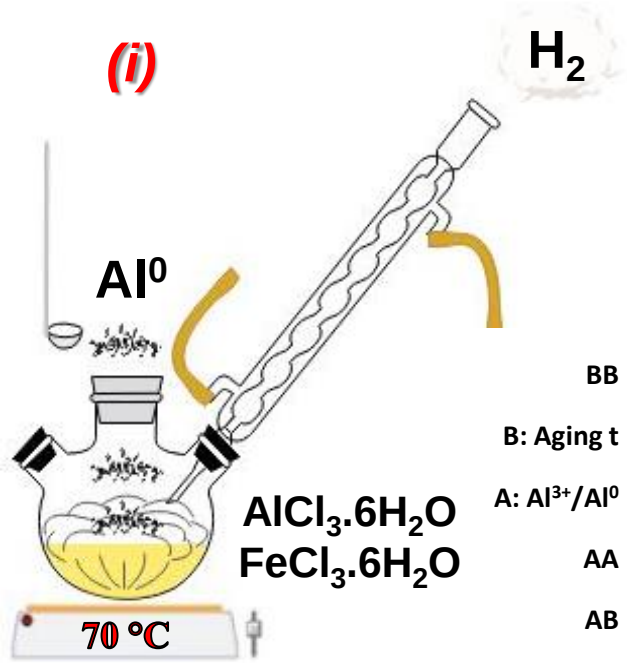
PhO elim.





Bi, S. et al., *Coord. Chem. Rev.* 248 **(2004)** 441–455.

Al/Fe – PILC: Statistical optimization of self-hydrolysis method



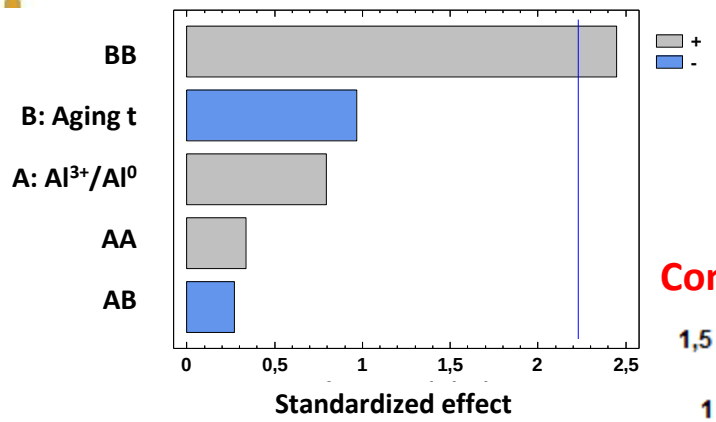
Series 2

16 samples

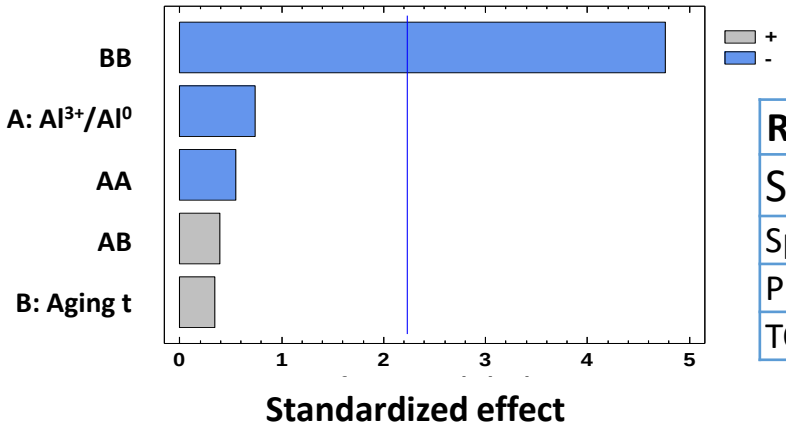
Factors	Levels	Responses	Target
- **Al^{3+}/Al^0:** (20/80 – 50/50) - **Aging t:** (2 h – 8 h)/70 °C	(+1) (-1)	(1) TOC (mg/dm^3) (2) PhO elim. (%) (3) S_{BET} (4) $S_{\mu p}$ (*t-plot*)	Maximize (2) to (4) and minimize (1)

*Temperature of calcination: 2 Blocks **400 °C** vs. **500 °C**

TOC



PhO elim.

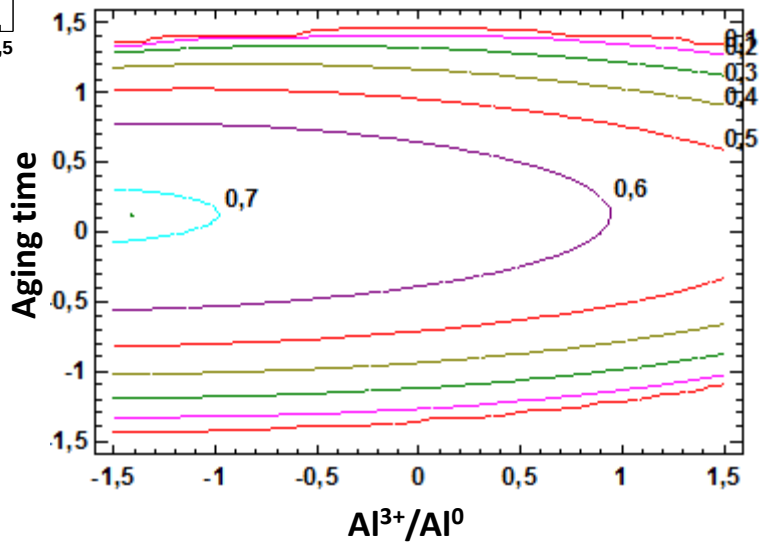


Response	Optimal
S_{BET}	120
$S_{\mu p}$	88
PhO elim.	67.8
TOC	16.7

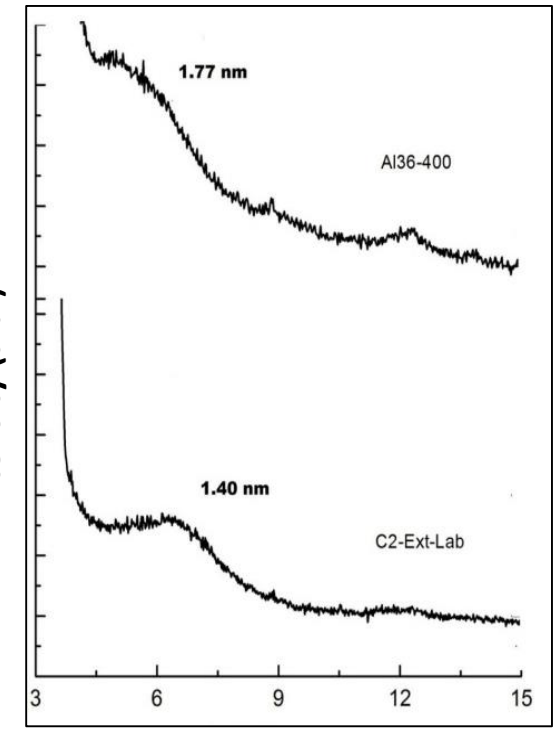
Factor	Optimal
Al^{3+}/Al^0	14/86
Aging t	5h 22min

Al/Fe-Al^0 interlayering solution

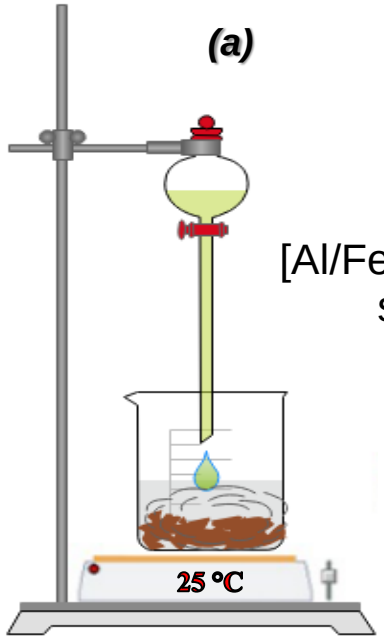
Contour of the estimated response surface



XRD

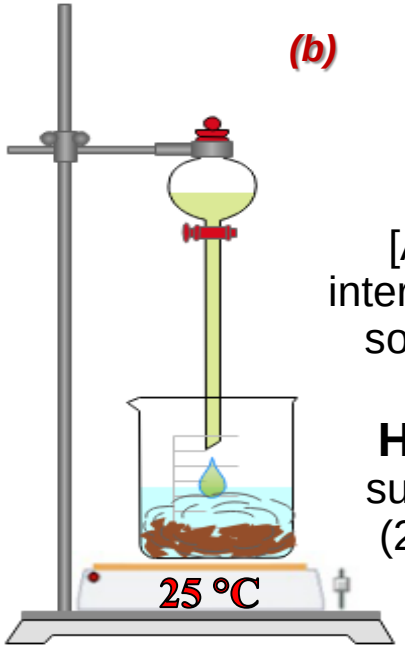


Al/Fe – PILC: Comparison of clay interlayering methods



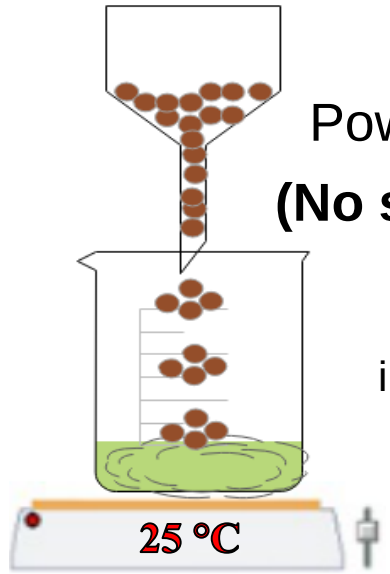
[Al/Fe interlayering solution]

EtOH clay-suspension (25 %w/v)



[Al/Fe interlayering solution]

H_2O clay-suspension (25 %w/v)



Powdered clay **(No suspension)**

[Al/Fe interlayering solution]

16 h Clay swelling

2 h Addition of Interlayering solution

2 h Aging

Total procedure 20 h

Powdered clay **(no suspension)**

Immediate clay addition

2 h Aging

Total procedure 2 h

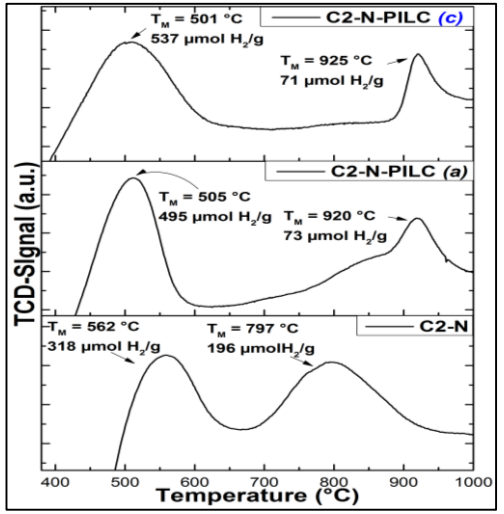
Galeano L.A., Gil A., Vicente M.A., *Appl. Catal. B* 111-112C **(2012)** 527-535.

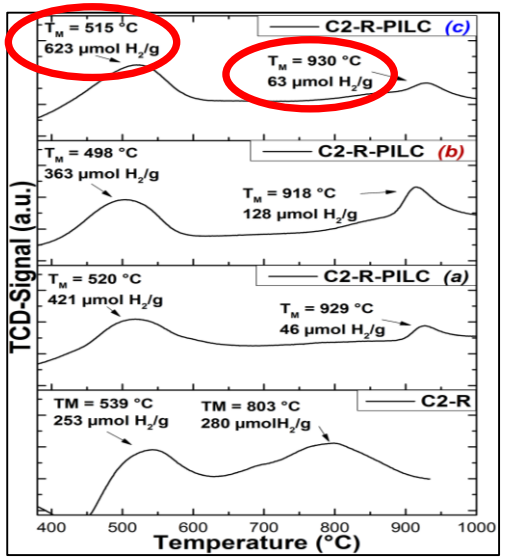
Al/Fe – PILC: Effect of previous vs. No-refining of starting clay

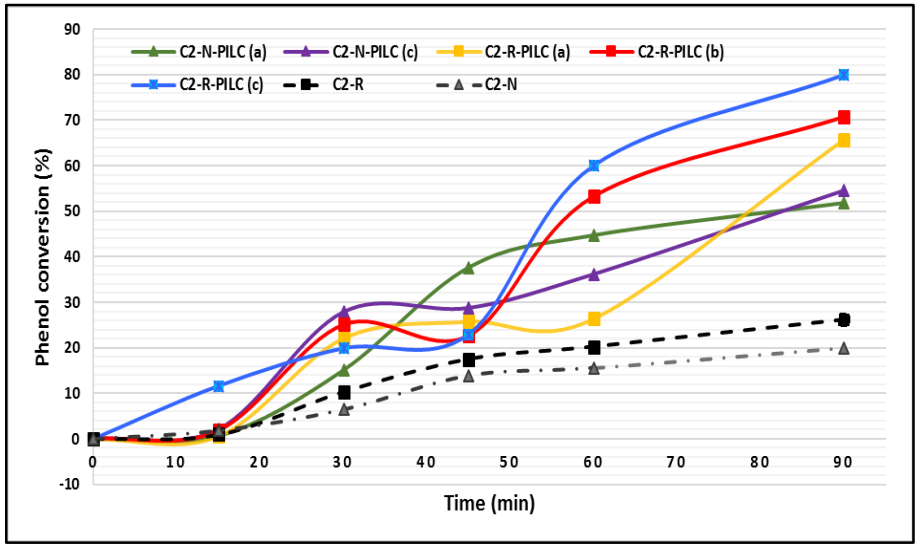
Table 2. Physicochemical characteristics of pillared clays from either raw (C2-N) or particle size refined (C2-R) obtained by three methods of clay-interlayering: ***(a)*** vs. ***(b)*** vs. ***(c)*** with ***(i)***

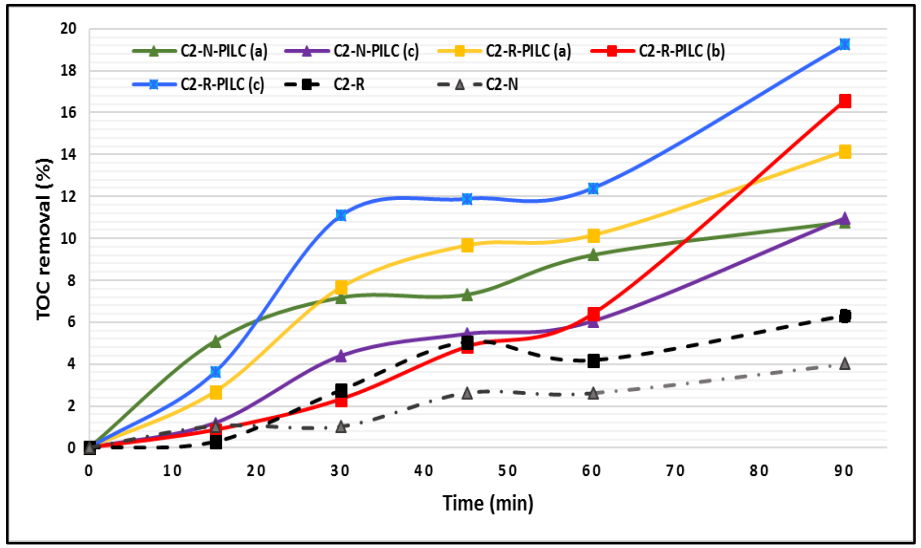
Material	CC$^{(w)}$ (%)	$Al_2O_3^{(w,x)}$ (wt.%)	$Fe_2O_3^{(w,x)}$ (wt.%)	% $Fe_{inc.}^{(w,x)}$ (Fe_2O_3)	$S_{BET}^{(w)}$ (m^2/g)	$S_{\mu p}^{(w)}$ (m^2/g)	$S_{ext}^{(w)}$ (m^2/g)	d_{001} (nm)	
								60 °C	500 °C
C2-N	--	16.52	6.86	--	36	10	26	1.53	1.53
C2-N-PILC *(a)*	64	25.90	8.42	1.56	71	48	23	1.67	1.38
C2-N-PILC *(c)*	34	26.39	8.02	1.16	85	73	12	1.70	1.40
C2-R	--	17.84	8.61	--	67	22	45	1.44	1.44
C2-R-PILC *(a)*	65	25.15	10.08	1.47	105	79	26	1.65	1.28
C2-R-PILC *(b)*	63	26.96	9.86	1.25	115	86	29	1.67	1.33
C2-R-PILC *(c)*	55	25.34	10.22	**1.61**	115	**93**	22	**1.71**	1.33

H_2-TPR diagrams of **C2-N-PILC** vs. **C2-R-PILC** materials with ***(i).*** (Al/Fe)-Al^0 interlayering solution.







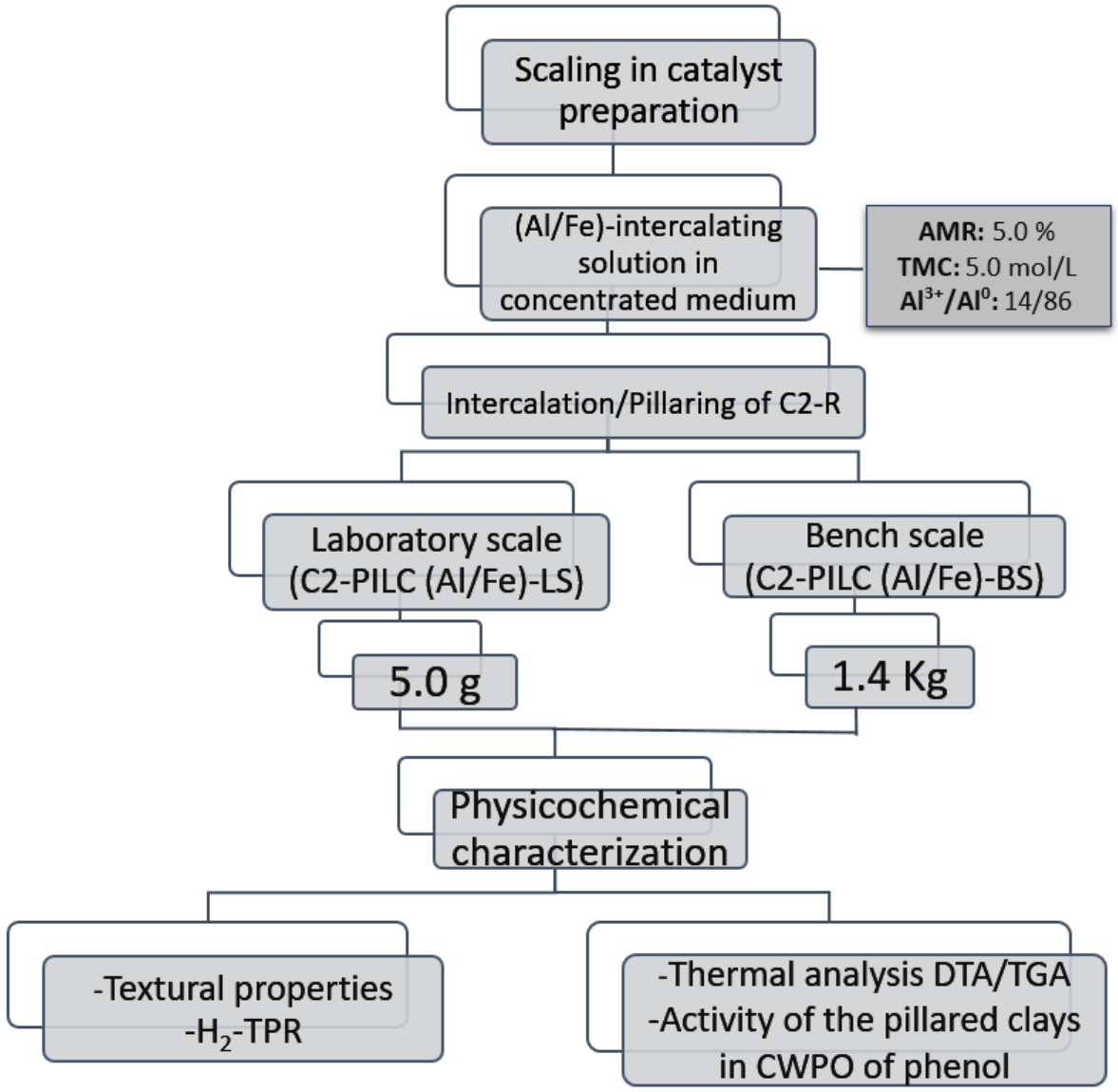


Best Interlayering Method

Powdered **refined** clay on concentrated interlayering solution **(No suspension)**

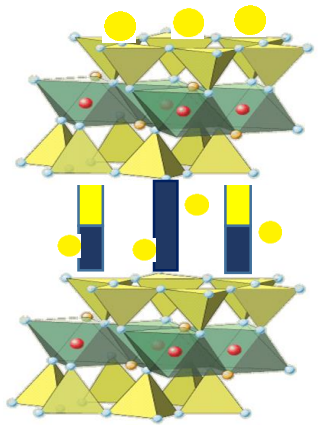
[Catalyst] = 50 mg/dm^3, $[PhO]_0$ (Sigma Aldrich 99.0-100.5 %) = 26.1 mg/dm^3, TOC_{PhO} = 20 mg/dm^3, $[H_2O_2]_{Stoich.}$ (Panreac 50 %) = 3.79 mmol/dm^3, $V_{H_2O_2}$ = 100 mL/h (dropping 30 - 90 min), pH = 3.7; temperature = 25 ± 2.0 ° C; pressure = 0.74 atm.

Al/Fe – PILC: Advances towards scaled-up preparation



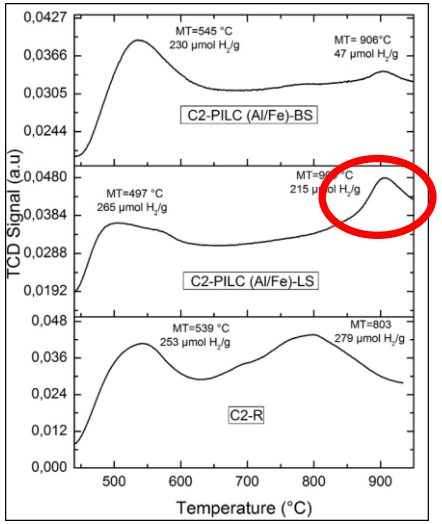
Sample	Textural Properties				
	S_{BET} (m^2/g)	S_{Ext} (m^2/g)	$S_{\mu p}$ (m^2/g)	Average pore diameter (1) (Å)	Average pore diameter (2) (Å)
C2-R	60	32	26	--------	--------
C2-PILC (Al/Fe)-LS	140	34	90	5.02	7.08
C2-PILC (Al/Fe)-BS	169	31	115	5.07	7.38

Sample	H_2 – TPR			
	AMR	Al_2O_3 (% w/w)	Fe_2O_3 (% w/w)	$Fe_{inc.}$ (% as Fe_2O_3)
C2-R	5.0 %	14.43	10.97	----
C2-PILC (Al/Fe)-LS	5.0 %	34.38	12.68	**1.71**
C2-PILC (Al/Fe)-BS	5.0 %	36.79	11.97	1.00

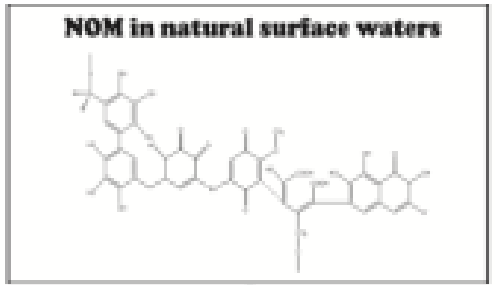


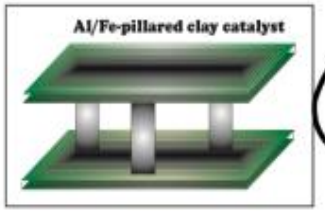
(Al_2O_3)-Pillar

($AlFeO_x$)-Mixed pillar



CWPO ←→ AlFe-PILC: Statistical optimization in NOM removal for drinking water





$H_2O_{2\,(aq)}$

$HO^{\cdot} + HO_2^{\cdot}$

[C_2P-Ext-PILC]*

Catalyst

GOAL: Minimize DOC and Color

Drinking water

Synthetic model of NOM

Number of runs: 10

Experimental factors: 2

Type of Desing: Factorial 2^2

Experimental design: Central Composite

Hydrogen Peroxide dose (%):
25.0 - 100.0

Catalyst concentration
(g/dm^3): 0.5 - 6.0

Non-controlable variables

pH
6.0 – 9.0

Starting NOM concentration $[NOM]_0$
TOC (mg C/dm^3): 2.0 – 20.0

Temperature of reaction (T_r)
(°C): 5.0 – 25.0

Responses: 3

Number of blocks: 1

NOM mineralization (TOC removal %)

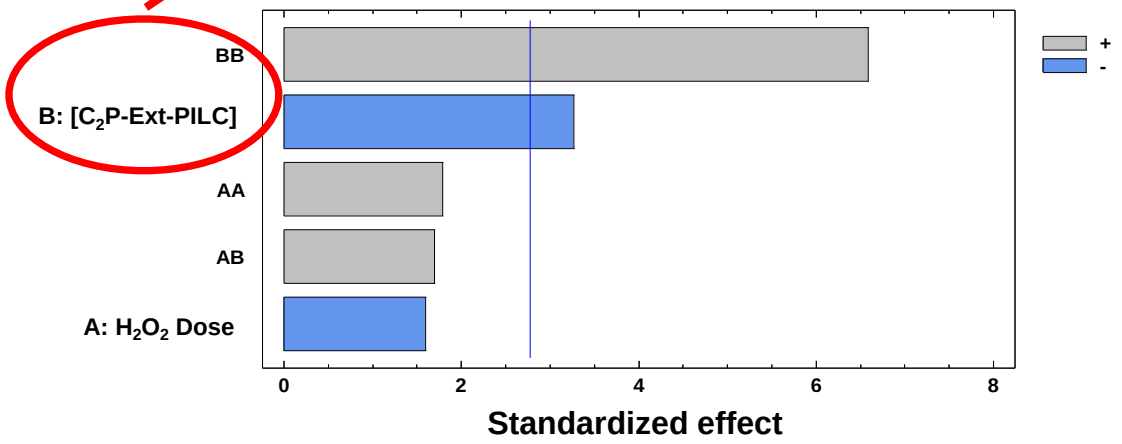
NOM Removal (%) (color)

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

Reaction time: 180 min

CWPO ←→ AlFe-PILC: Statistical optimization in NOM removal for drinking water

NOM mineralization (TOC removal %)



NOM Decolourization (%)

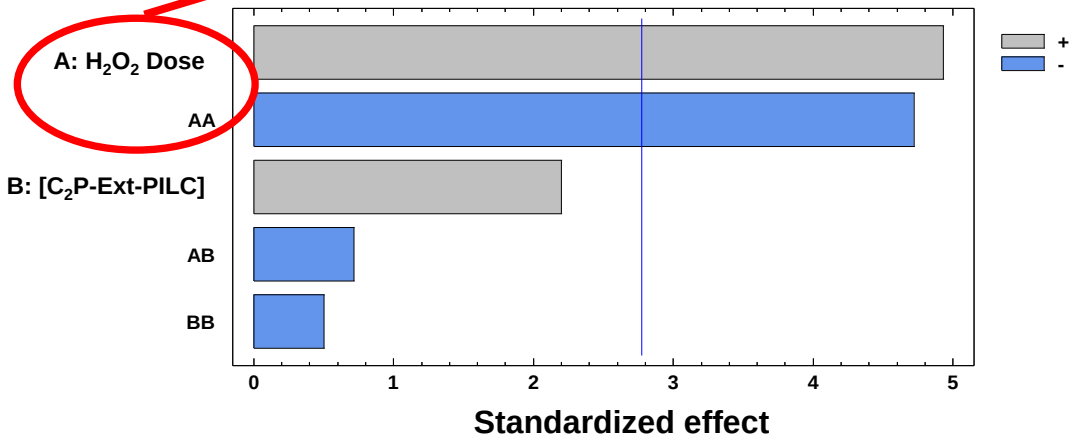
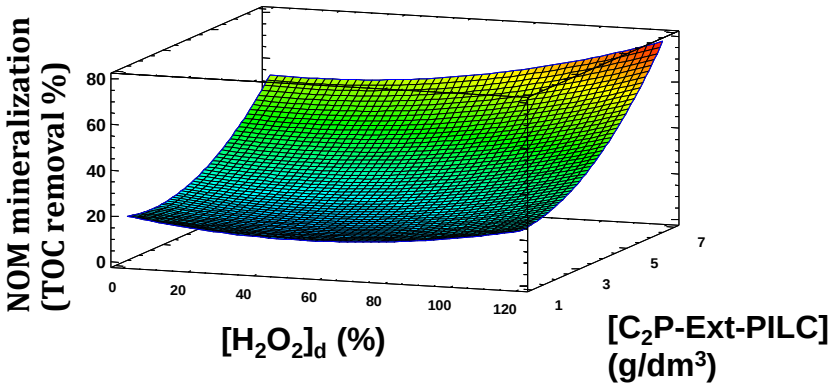


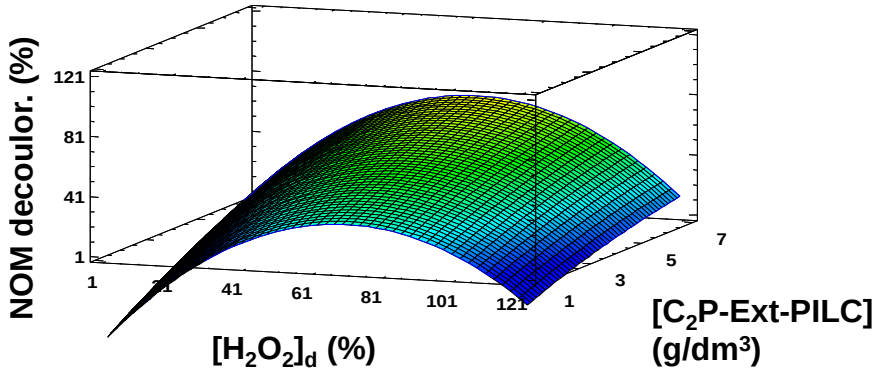
Table 5. Combining factor levels to maximize desired response

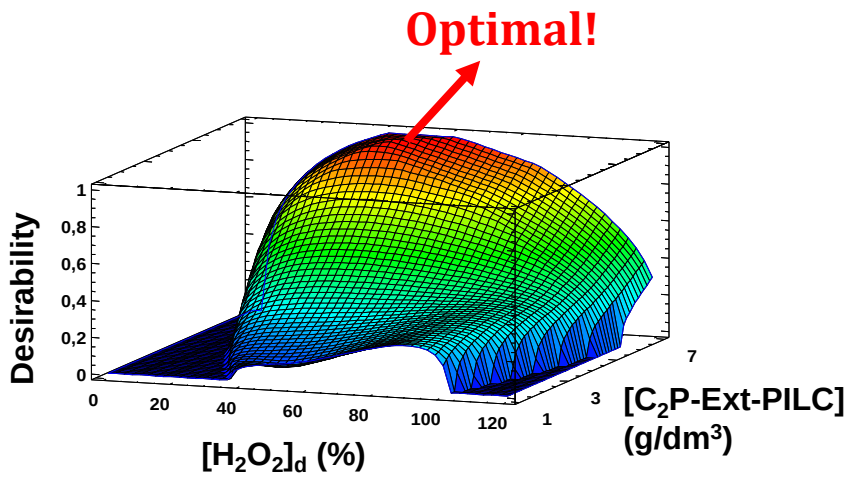
Response	H_2O_2 Dose (Stoich. %)	[C_2P-Ext-PILC] (g/dm^3)	Response Optimal (%)
NOM mineralization TOC removal (%)	100	6,0	**53.4**
NOM Decolourization (%)	64	6.0	**68.3**

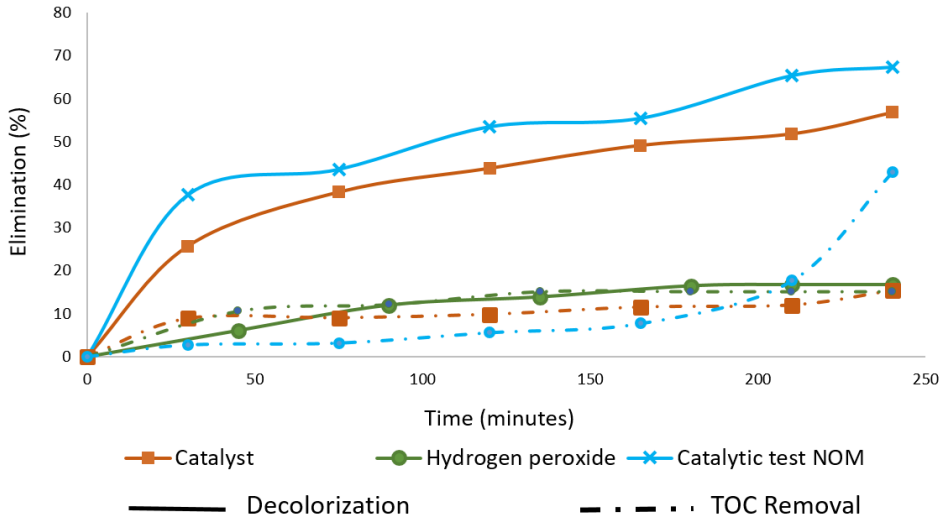
CWPO ←→ AlFe-PILC: Statistical optimization in NOM removal for drinking water

Desirability: NOM decoulorization + $[H_2O_2]_f$ + NOM mineralization









Optimized desirability = 0.90

$[C_2P\text{-}PILC]_{optimal}$ = 6.0 g/dm^3

$[H_2O_2]_{d\ optimal}$ = 46.21 %

[C_2-PILC]: 1.3 g/L, Reaction time: 180 minutes, Temperature: 8.5 °C, pH: 7.2. *Blanks:* [C_2-PILC]: 5.2 g/L, Reaction time: 180 minutes, Temperature: 25 °C, pH: 7.0

Departamento Administrativo de Ciencia, Tecnología e Innovación Colciencias
República de Colombia

SGR
Sistema General de Regalías

Gobernación de Nariño

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Desarrollo y aplicación de la Tecnología de Oxidación Avanzada PCFH para mejorar la calidad del agua potable en el Departamento de Nariño

GIMFC
GRUPO DE INVESTIGACIÓN EN MATERIALES FUNCIONALES Y CATÁLISIS

GIBIMMA

CEASE

EMPOPASTO

EMPOOBANDO E.S.P.

ACUAS YUNACO

EMPSA E.S.P.

AC MINERALES

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Thank you !