Preparation of Al/Fe-PILC clay catalyst from concentrated precursors: process intensification towards scaling-up

Carlos-Andrés Vallejo[a], Claudia-Lucero Cabrera[a], Antonio Gil[b], Raquel Trujillano[c], Miguel-Ángel Vicente[c], Luis-Alejandro Galeano[a,*]

* Corresponding author: alejandrogaleano@udenar.edu.co
[a] Research Group on Functional Materials and Catalysis *(GIMFC)*. Department of Chemistry, University of Nariño, Pasto, Colombia.
[b] Department of Applied Chemistry, Public University of Navarra, Pamplona, Spain.
[c] Department of Inorganic Chemistry, Chemical Science Faculty, Salamanca University, Salamanca, Spain.

Introduction

The Catalytic Wet Peroxide Oxidation (CWPO) is one of the Advanced oxidation processes (AOPs) useful to deplete low concentrated, hazardous compounds in water effluents. CWPO is based on the continuous generation of hydroxyl radicals (HO•) carried out by immobilized cations of transition metals like Fe in presence of peroxide[1]. Structural modification of bentonites by pillaring with Al/Fe mixed oxides at nanometric scale leads to highly porous materials with the corresponding higher exposure of the catalytic active sites; although it has provided excellent catalytic response in the CWPO degradation of organic pollutants in wastewaters, it might also display interesting potential polishing surface waters for production of drinking water[2]. However, in order to make it possible at a real-scale, the scaling-up of the catalyst's preparation from both *(i)* high-concentrated dissolved metals and *(ii)* clay precursors, is mandatory. Thus, this research was devoted at first to compare the preparation of highly concentrated Al/Fe solutions by two methodologies against the very widely reported diluted one. The best performing concentrated solution was then used to study in a second step, three procedures for the mineral swelling yielding the pillared clays at 50 g scale. Whereas, the effect of previous refining (C2-R) of the natural clay mineral (C2-N) was determined. Every prepared material was characterized by standard physicochemical methodologies and assessed for their catalytic properties in the CWPO reaction of phenol (PhO) degradation.

Experimental Materials & Methods

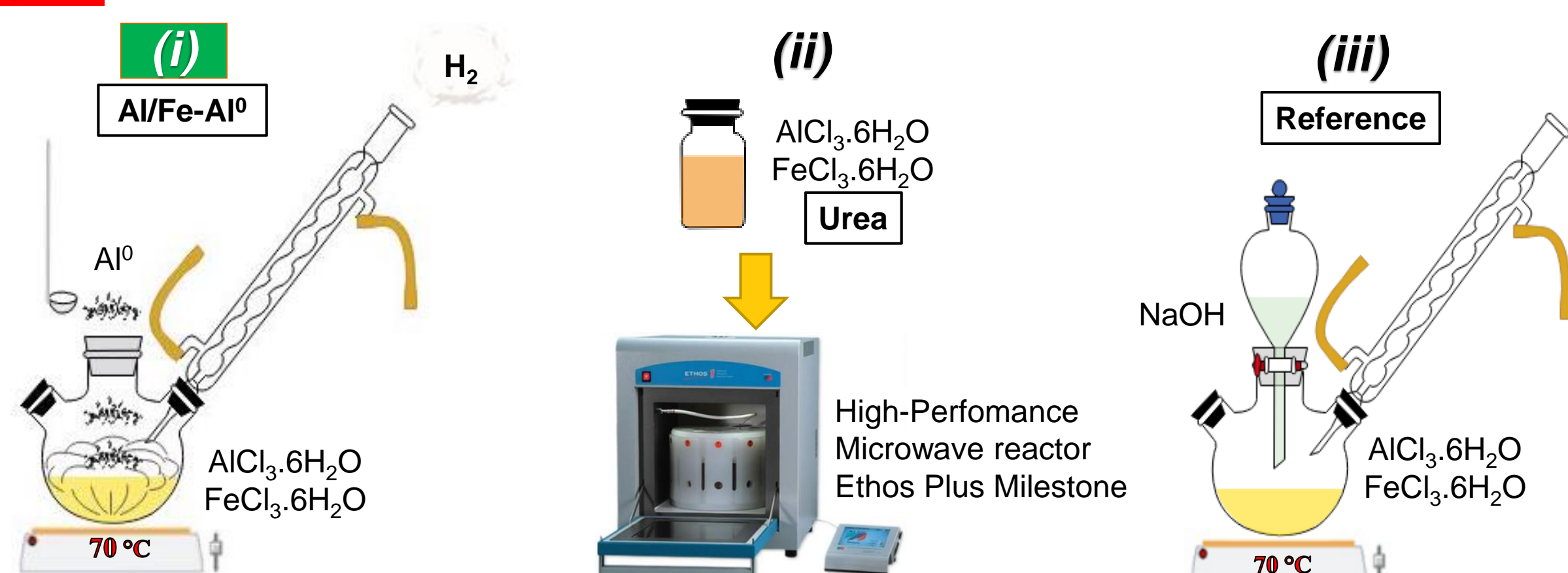### step 1 Preparation of highly-concentrated Al/Fe interlayering solution

Figure 1. *(i)* Addition of elemental aluminum on the starting dissolved 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).
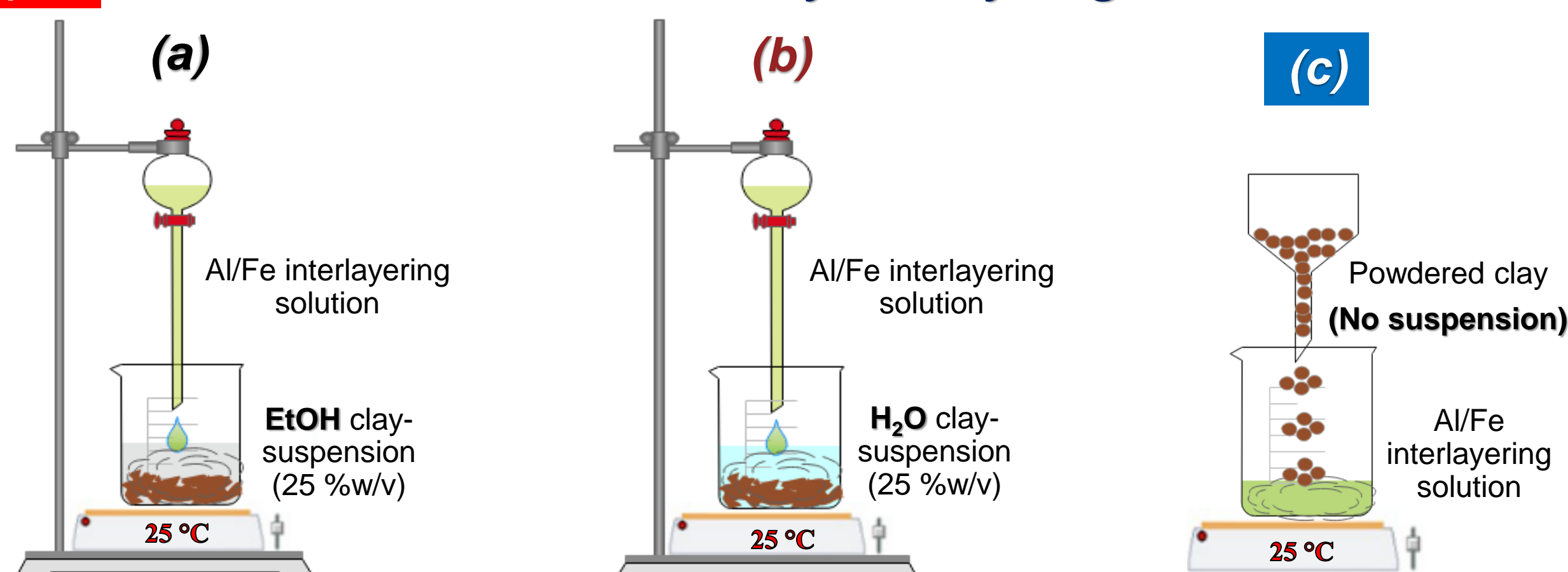
step 2 Methods of clay-interlayering

Figure 2. *(a)* Addition of interlayering solution on ethanol clay-suspension (25 % w/v); *(b)* the same as *(a)* but using water instead of ethanol; and *(c)* clay powder (either C2-N or C2-R) added straightforwardly on interlayering solution (without previous clay-suspension).

Results

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

Interlayering solution	$[Al]^{(w,x)}$ (mol/dm³)	$[Fe]^{(w,x)}$ (mol/dm³)	$TMC^{(w)}$ (mol/dm³)	$pH^{(w)}$ (final)	$\rho^{(w)}$ (g/mL)	$EC^{(w)}$ (mS/cm)
Al/Fe-Al⁰*	3.98	0.27	4.25	3.32	1.330	58.6
Al/Fe-U	2.20	0.12	2.32	-0.33	1.410	47.8
Al/Fe-OH⁻	0.054	0.002	0.06	3.86	0.999	22.4

TMC: Total final Metal Concentration; ρ: density; EC: electric conductivity. W: Experimental values for each highly-concentrated Al/Fe interlayering solution. X: Amount needed to reach Atomic Metal Ratio **AMR** = 5.0 %Fe determined by AAS. * Interlayering solution used to study clay-interlayering methods at step 2.
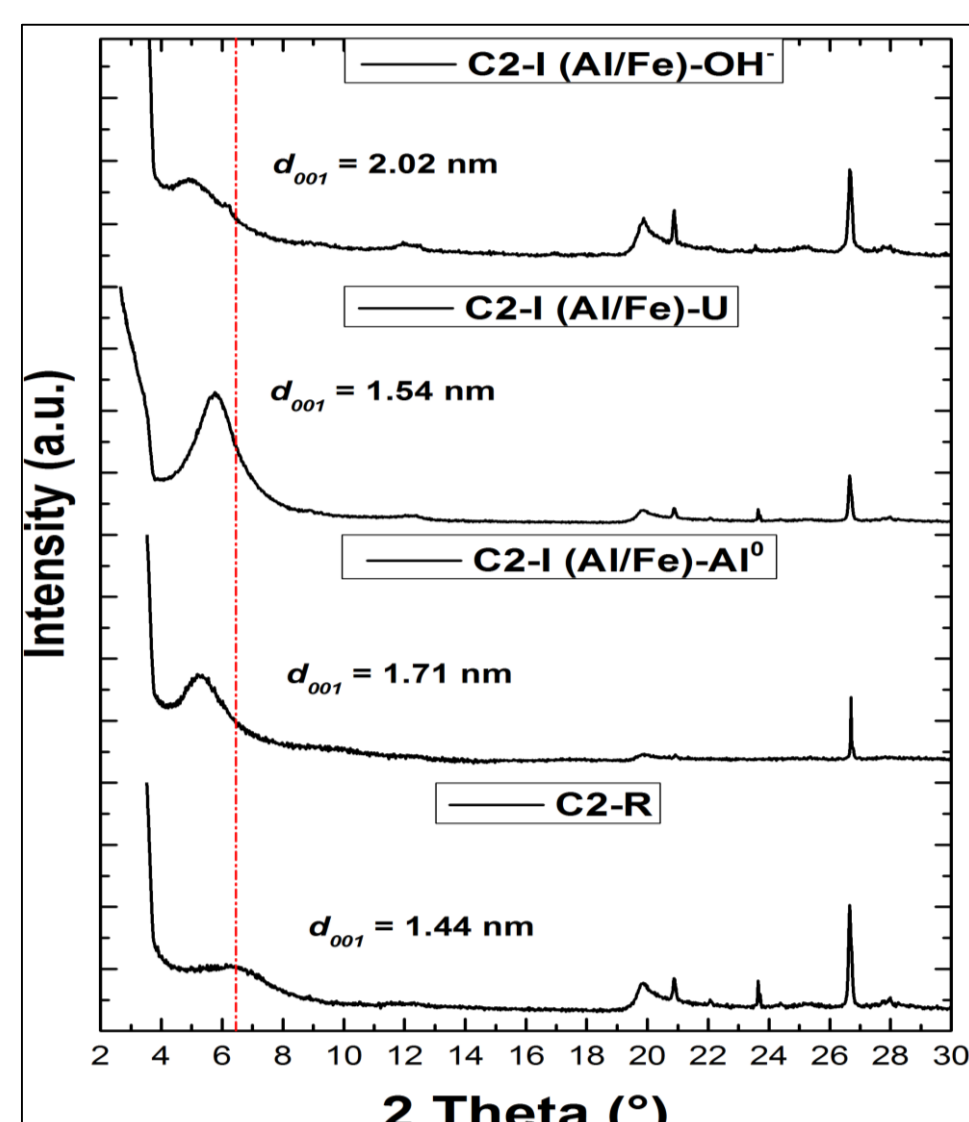

Figure 3. Oriented XRD patterns of Al/Fe-interlayered **(I)** C2-R-material as a function of the interlayering solution. (60 °C)
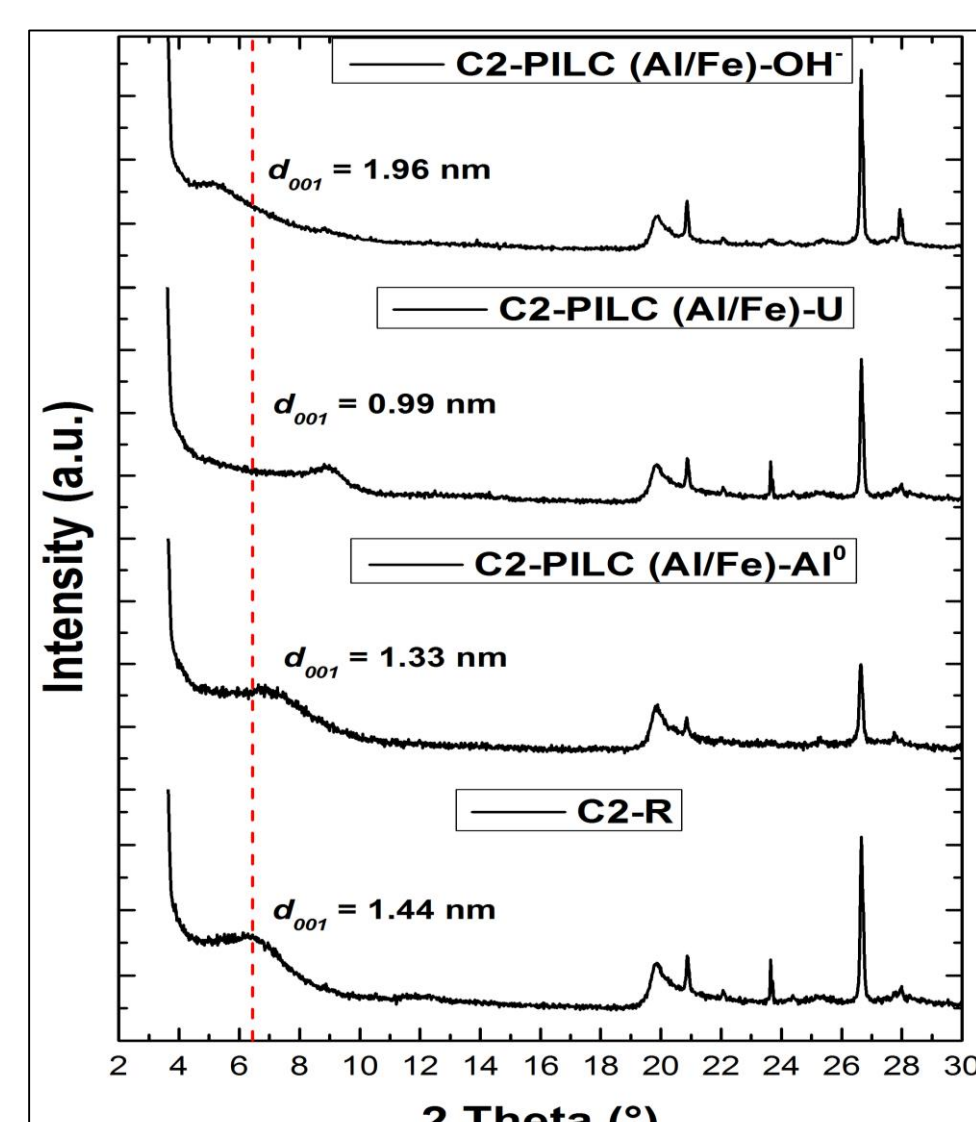

Figure 4. Powder XRD patterns of Al/Fe-pillared **(PILC)** C2-R-material as a function of the interlayering solution. (500 °C)

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

Material	$CC^{(w)}$ (%)	$Al_2O_3^{(w,x)}$ (wt.%)	$Fe_2O_3^{(w,x)}$ (wt.%)	$\%Fe_{inc.}^{(w,x)}$ (Fe_2O_3)	$S_{BET}^{(w)}$ (m²/g)	$S_{\mu p}^{(w)}$ (m²/g)	$S_{ext}^{(w)}$ (m²/g)	d_{001} (nm) 60 °C	d_{001} (nm) 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

CC: Compensated Cationic Exchange Capacity W: Experimental values for each clay modified with *(i)* Al/Fe-Al⁰ interlayering solution; X: Determined by XRF. The FTIR spectra revealed signals of the smectite minerals together with some minor quartz impurities. **C2-N-PILC** *(b)* was not prepared since this bentonite got spilled just once suspended in water at 25 %p/v.
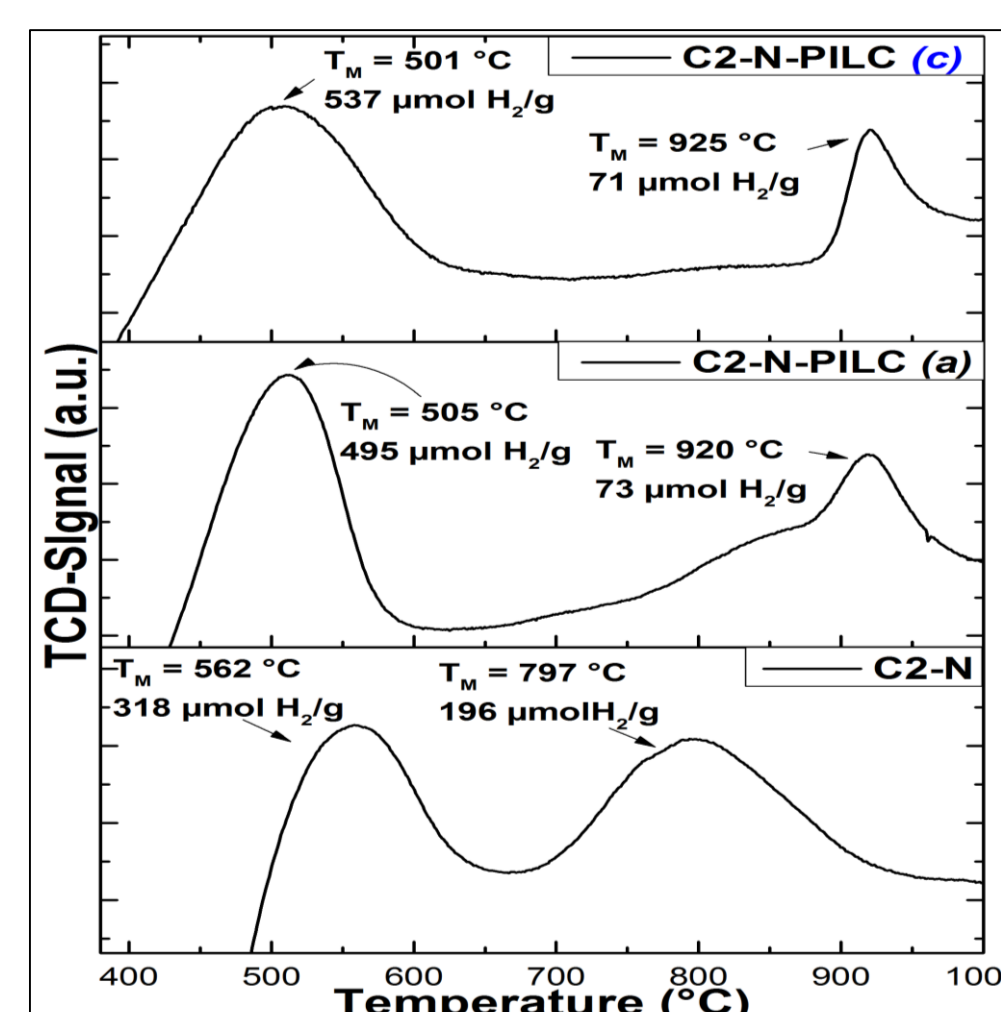

Figure 5. H_2-TPR diagrams of modified C2-N-PILC materials with *(i)* solution (Al/Fe)-Al⁰.
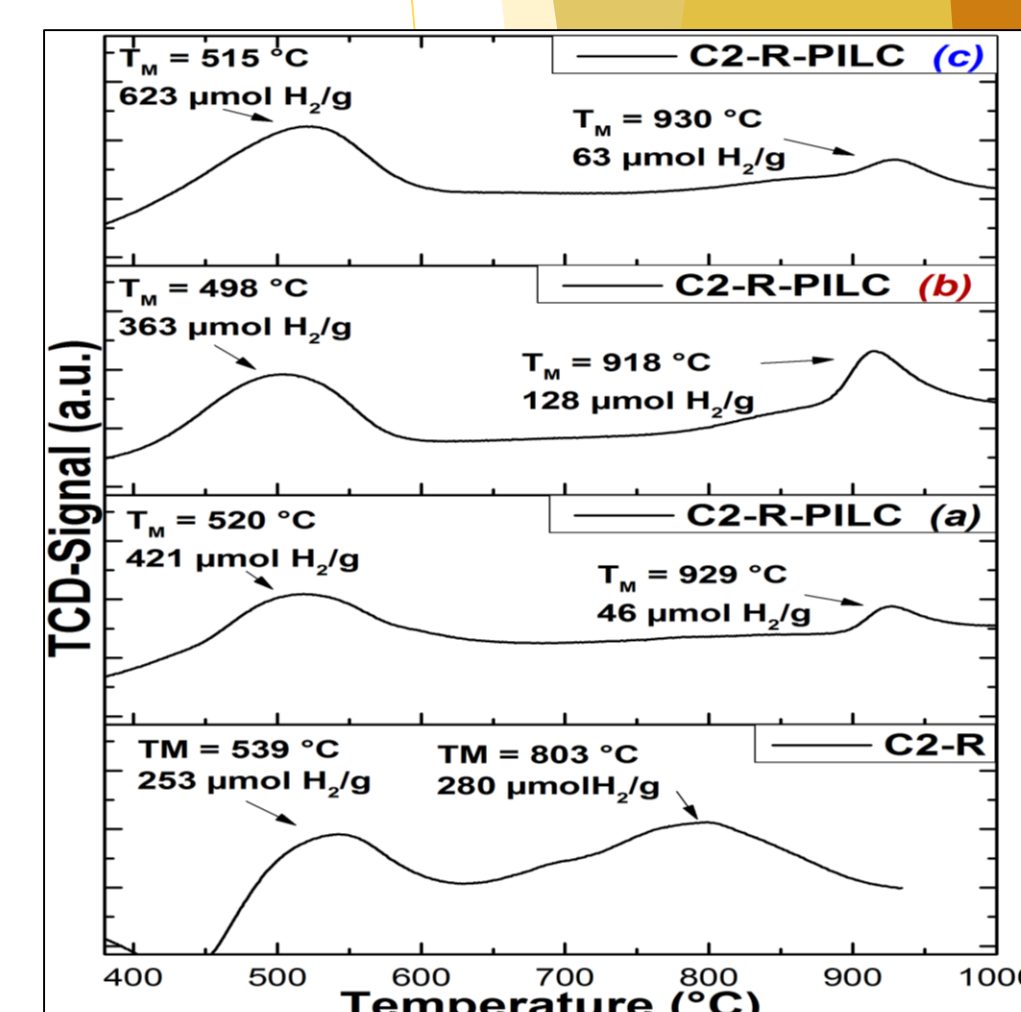

Figure 6. H_2-TPR diagrams of modified C2-R-PILC materials with *(i)*. (Al/Fe)-Al⁰.

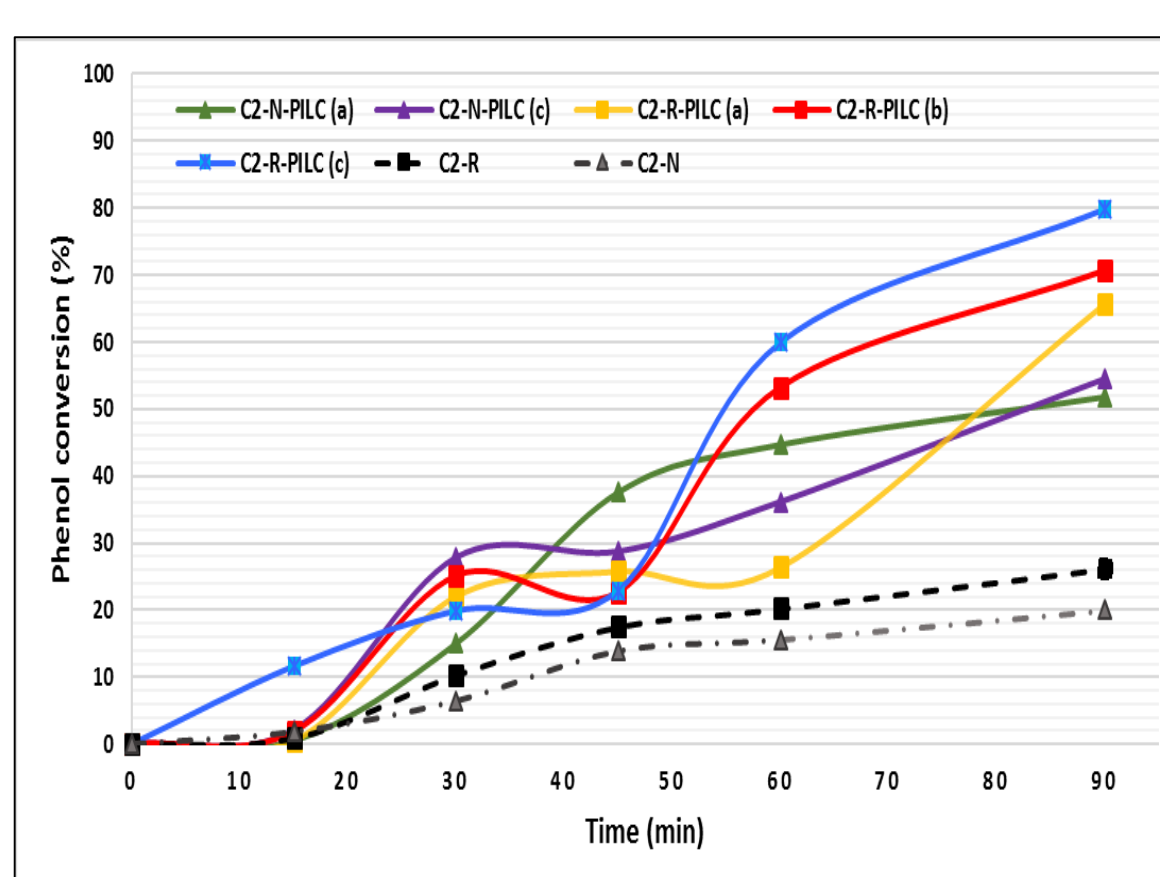## Catalytic properties in the CWPO degradation of phenol

Figure 7. Phenol conversion by C2-N, C2-R and derived pillared clays with *(i)* solution (Al/Fe)-Al⁰.
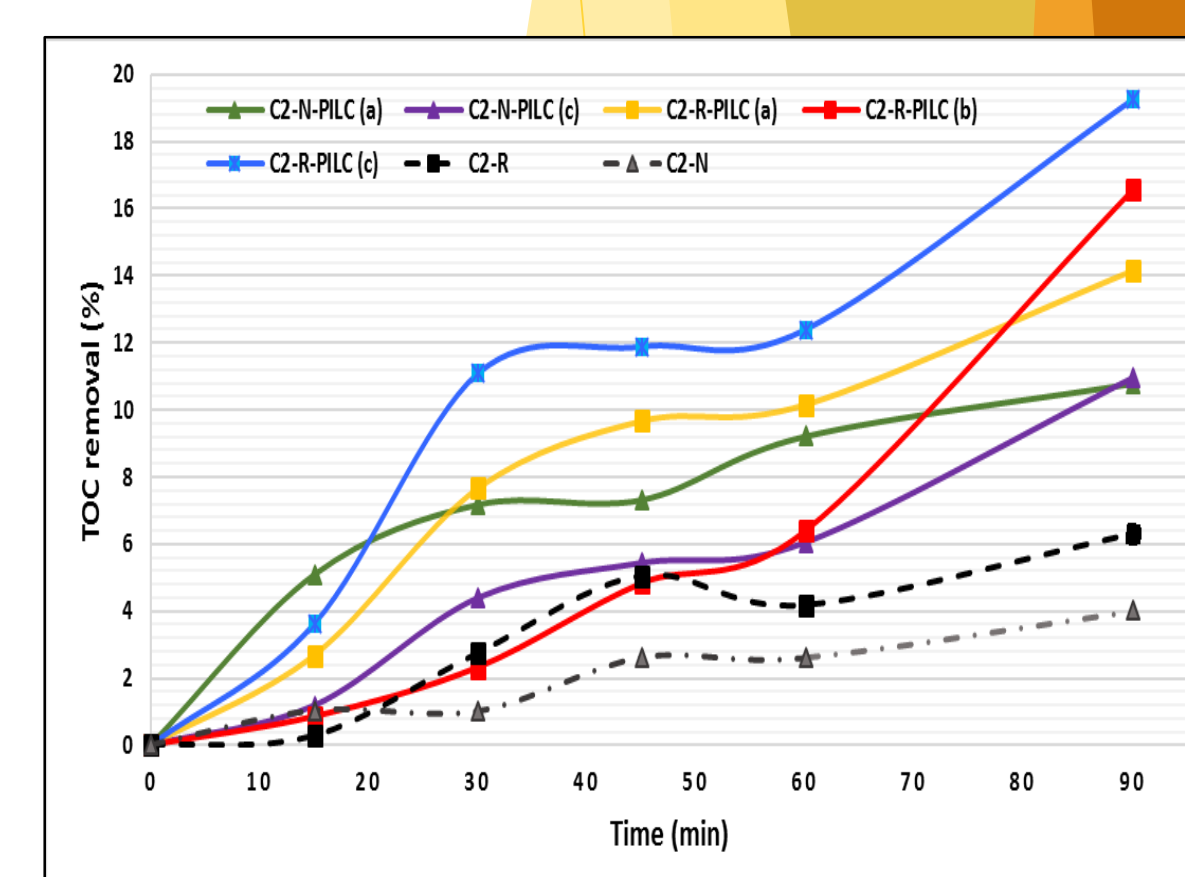

Figure 8. TOC removal by C2-N, C2-R and derived pillared clays with *(i)* solution (Al/Fe)-Al⁰.

[Catalyst] = 50 mg/dm³; $[PhO]_0$ (Sigma Aldrich 99.0-100.5 %) = 26.1 mg/dm³; $[TOC_{PhO}]_0$ = 20 mg/dm³; $[H_2O_2]_{Stoich.}$ (Panreac 50 %) = 3.79 mmol/dm³; $V_{H_2O_2}$ = 100 mL/h (dropping from 30 to 90 min); pH = 3.7; temperature = 25 ± 2.0 °C; pressure = 0.74 atm.

Conclusions

❖ The most suitable conditions for preparation of highly-concentrated Al/Fe mixed interlayering solution were established: *(i)* addition of elemental aluminum on the starting chlorides (Al/Fe)-Al⁰ ($[Al+Fe]_i$ = 5.0 mol/dm³; $(Al^{3+}/Al^0)_i$ = 50/50, AMR_{Fe} = 5.0 %).

❖ The most promising method for intensive clay-interlayering (20 meq (Al+Fe)/g clay) was found from clay modification at 50 g scale: *(c)* Straight addition of the powdered clay on the interlayering solution (no previous clay-suspension).

Acknowledgement

References

[1] Gil A., Korili S., Trujillano R., Vicente M.A., Pillared Clays and Related Catalysts. Springer Science+Business Media, LLC (2010).
[2] Galeano L.A., Bravo P., Luna C., Vicente M.A, Gil A., Appl. Catal. B: Environmental. Volumes 111 – 112 (2012) 527 – 535.

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