FACULTAD DE CIENCIAS
UNIVERSIDAD AUTÓNOMA DE MADRID

Sección Departamental de Ingeniería Química

# Catalytic Wet Peroxide Oxidation (CWPO): Potential applications and challenges

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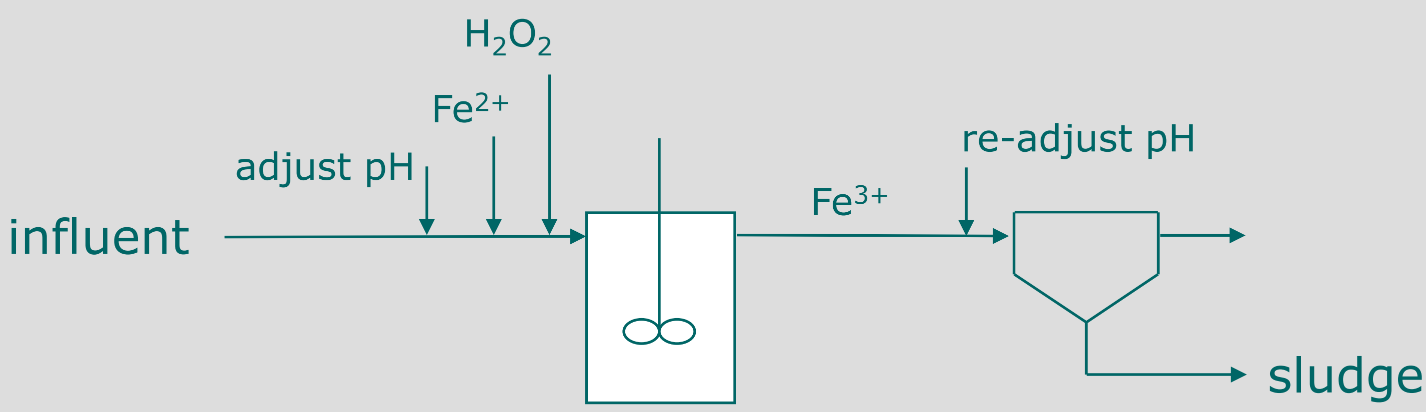
# THE FENTON PROCESS

## Homogeneous Fenton Process

High oxidation capacity

$$Fe^{2+} + H_2O_2 \xrightarrow{\text{acidic pH}} Fe^{3+} + OH^- + OH^\bullet$$

$$COD_{initial} + H_2O_2 \xrightarrow{Fe^{2+}} \text{PARTIALLY OXIDIZED COMPOUNDS} + H_2O_2 \xrightarrow{Fe^{2+}} \begin{array}{l} CO_2 + H_2O \\ \text{INORGANIC SALTS} \\ \text{REFRACTORY COMPOUNDS} \end{array}$$



# SOME WORKS IN CATALYTIC WET PEROXIDE OXIDATION

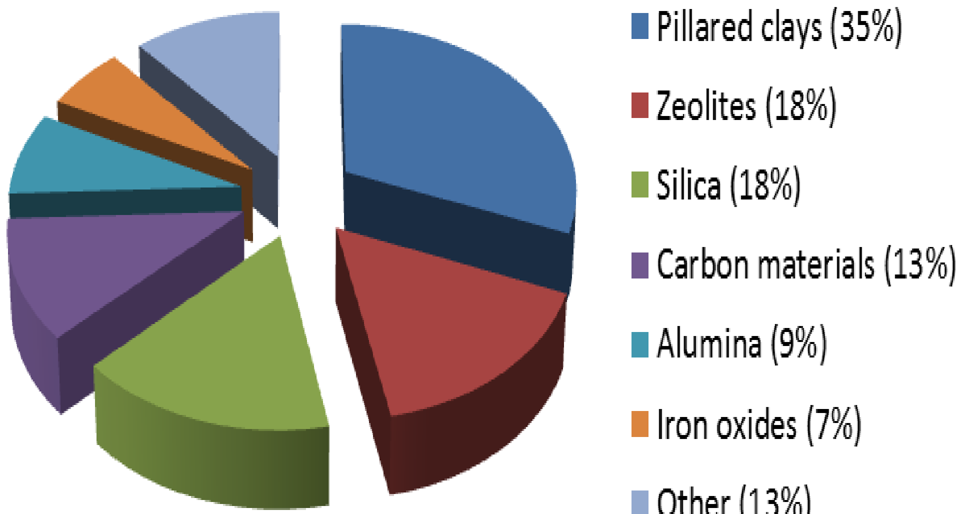
## AC-based catalysts

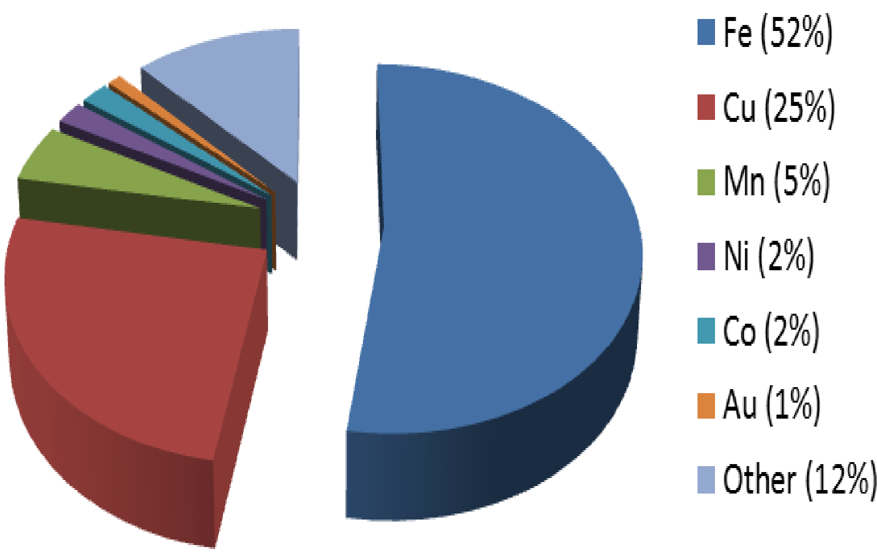
- J.A. Zazo, J.A. Casas, A.F. Mohedano, J.J. Rodriguez. ***Catalytic wet peroxide oxidation of phenol with a Fe/active carbon catalyst***. Appl. Catal. B., 65 (2006) 261-268.
- C.M. Domínguez, P. Ocón, A. Quintanilla, J.A. Casas, J.J. Rodriguez. ***Highly efficient application of activated carbon as catalyst for wet peroxide oxidation***. Appl. Catal. B., 65 (2006) 261-268.
- R.S. Ribeiro, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes. ***Removal of 2-nitrophenol by catalytic wet peroxide oxidation using carbon materials with different morphological and chemical properties***. Appl. Catal. B., 140-141 (2013) 356-362.
- R.S. Ribeiro, Z. Frontistis, D. Mantzavinos, D. Venieri, M. Antonopoulou, I. Konstantinou, A.M.T. Silva, J.L. Faria, H.T. Gomes. ***Magnetic carbon xerogels for the catalytic wet peroxide oxidation of sulfamethoxazole in environmentally relevant water matrices***. Appl. Catal. B., 199 (2016) 170-186.

## Other materials

- C.B. Molina, A.H. Pizarro, V.M. Monsalvo, A.M. Polo, A.F. Mohedano, J.J. Rodriguez. ***Integrated CWPO and biological treatment for the removal of 4-chlorophenol from water***. Sep. Sci. Technol., 45 (2010) 1595-1602.
- M. Munoz, Z.M. de Pedro, N. Menendez, J.A. Casas, J.J. Rodriguez. ***A ferromagnetic $\gamma$-alumina-supported iron catalyst for CWPO. Application to chlorophenols***. Appl. Catal. B., 136-137 (2013) 218-224.

# CATALYTIC WET PEROXIDE OXIDATION



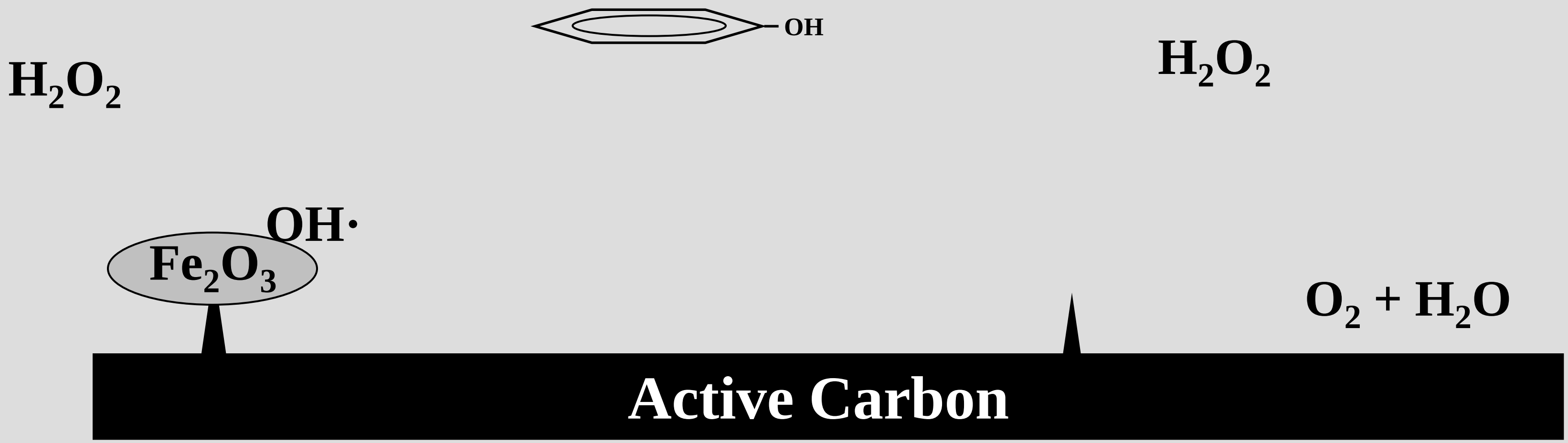
# HIGHTLIGHT RESULTS IN CWPO OF PHENOL

| CATALYST | Fe (%, wt.) | $W_{CAT}$ (g/L) | Phenol (mM) | $H_2O_2$/Phenol (stoich) | T (ºC) | $pH_0$ | Time (min) | $X_{Ph}$ (%) | $X_{TOC}$ (%) | $Fe_{Leach}$ (mg/L) | Ref. Author |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Fe_2O_3/CeO_2$ | **5** | **1** | **53** | **1.32** | **70** | **---** | **240** | **78** | **57** | **<0.25** | Massa et. al., 2008 |
| Fe-ZSM-5 | **2** | **0.35** | **69** | **1.5** | **70** | **3.5** | **180** | **81** | **17** | **1** | Fajerwerg et. al., 1996 |
| Fe-Al-PILC | **3.01** | **5** | **0.5** | **1.1** | **25** | **3.7** | **240** | **100** | **65** | **0.2** | Guelou et. al., 2003 |
| Fe-Al-PILC | **7.2** | **0.5** | **1.06** | **1** | **25** | **3.5** | **240** | **100** | **60** | **2.0** | Molina et al. 2006 |
| $Fe/Al_2O_3$ | **7.67** | **1** | **1** | **1.1** | **---** | **---** | **120** | **100** | **60** | **6.5** | Al Hayek et. al., 1984 |
| $Fe/SiO_2$ | **1.5** | **0.35** | **69** | **1.5** | **70** | **3.5** | **180** | **65** | **19** | **5** | Fajerwerg et. al., 1996 |
| Fe-Resin | **27.5** | **5** | **10.6** | **0.67** | **80** | **3** | **120** | **100** | **76** | **---** | Liou et. al., 2005 |
| Fe/AC | **4** | **0.5** | **1.06** | **1** | **50** | **3** | **120** | **100** | **78** | **1.1** | Zazo et. al., 2006 |

# Fe/AC CATALYST

| | AC | Fe/AC |
|---|---|---|
| $S_{BET}$ ($m^2/g$) | 974 | 781 |
| Pore volume ($cm^3/g$) | 0.75 | 0.67 |
| Micropore | 0.34 | 0.27 |
| Mesopore | 0.19 | 0.16 |
| Macropore | 0.22 | 0.24 |
| Fe content (% w/w ) | - | 4 |

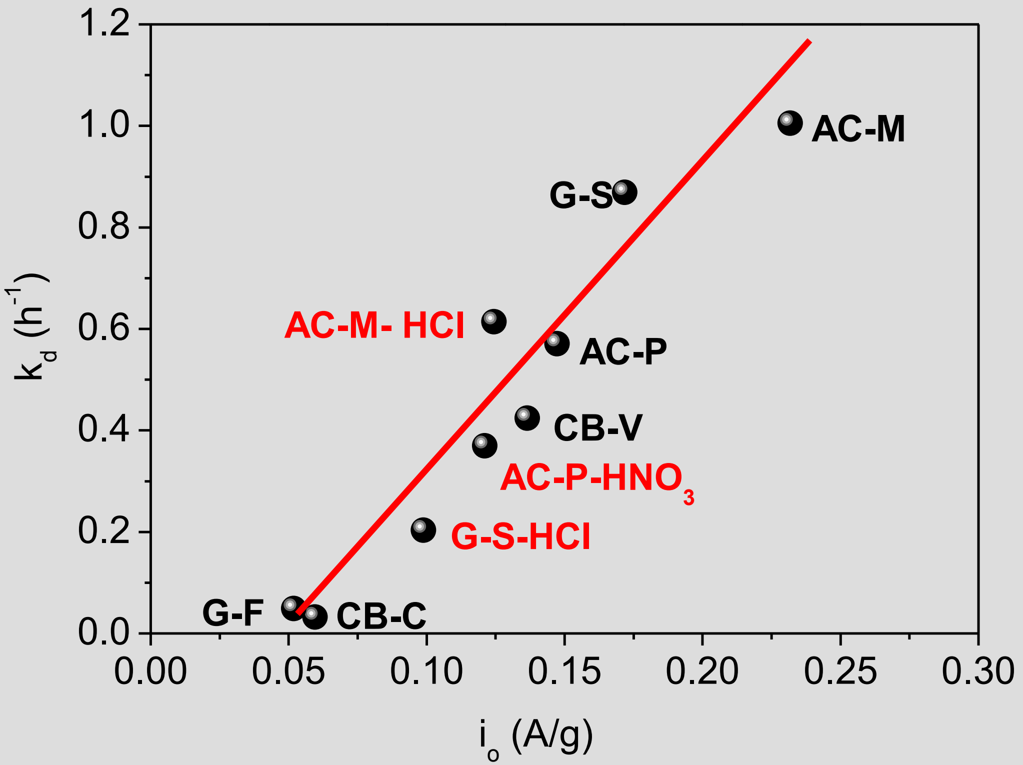
How is it expected to work?



# CWPO

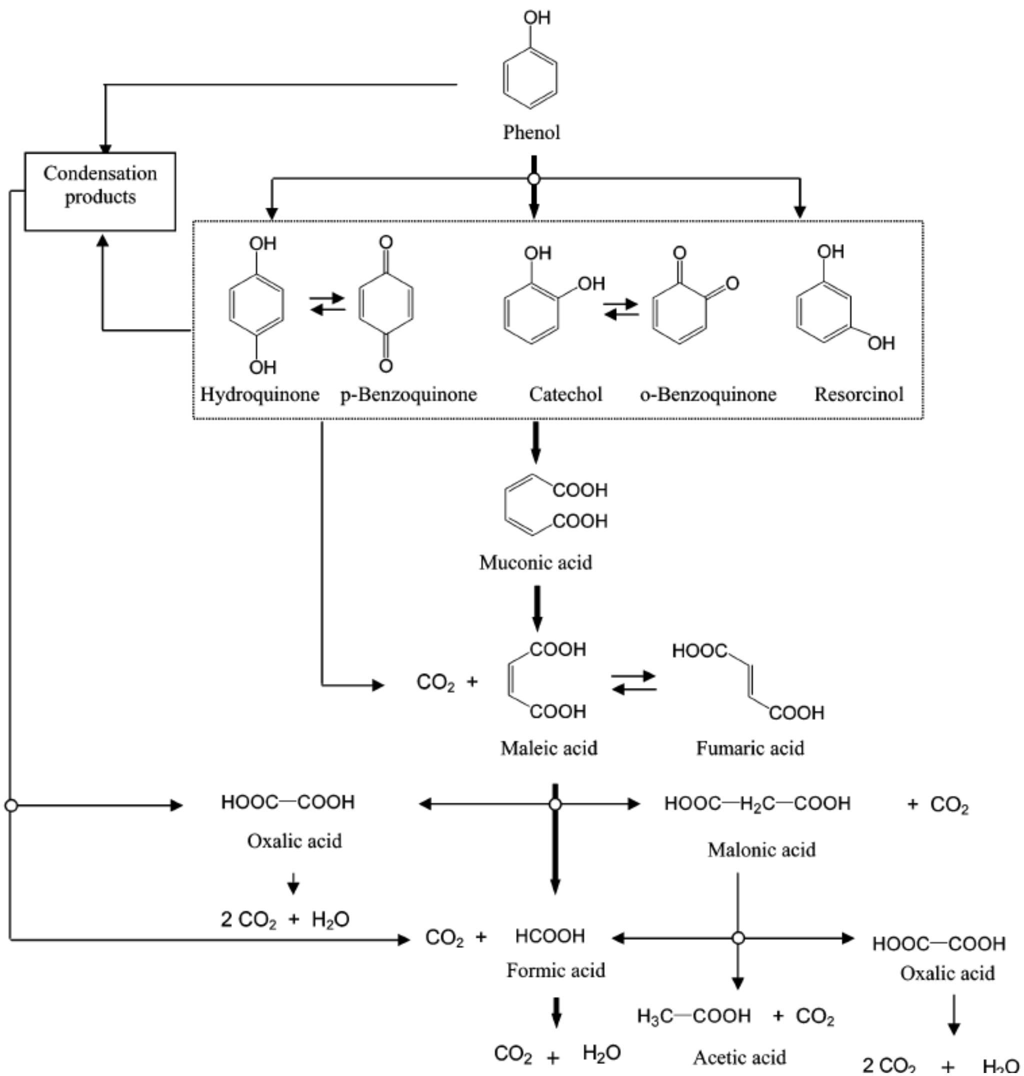
## CATALYTIC WET PEROXIDE OXIDATION

### Carbon materials as catalysts: activity prediction by redox properties




**Relationship between the current exchange ($i_o$) and the $H_2O_2$ decomposition ($k_d$) for the carbon materials tested**

# FENTON OXIDATION OF PHENOL: REACTIO PATHWAY




J.A. Zazo, J.A. Casas, A.F. Mohedano, M.A. Gilarranz, J.J. Rodriguez. Environ. Sci. Technol. 39 (2005) 9295-9302

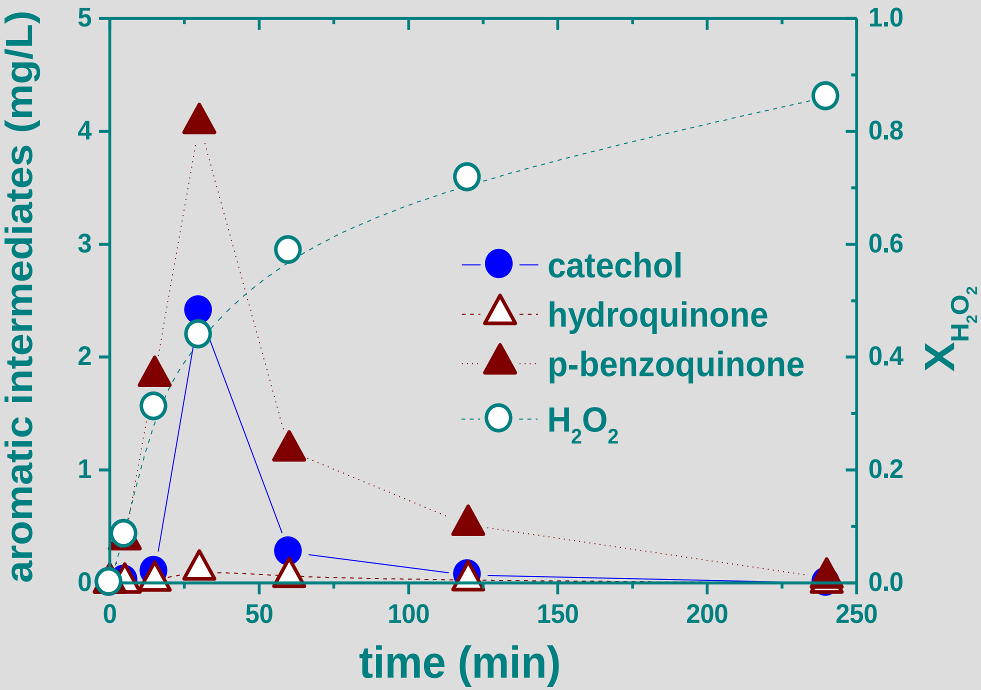
# CWPO OF PHENOL: ECOTOXICITY OF OXIDATION BYPRODUCTS

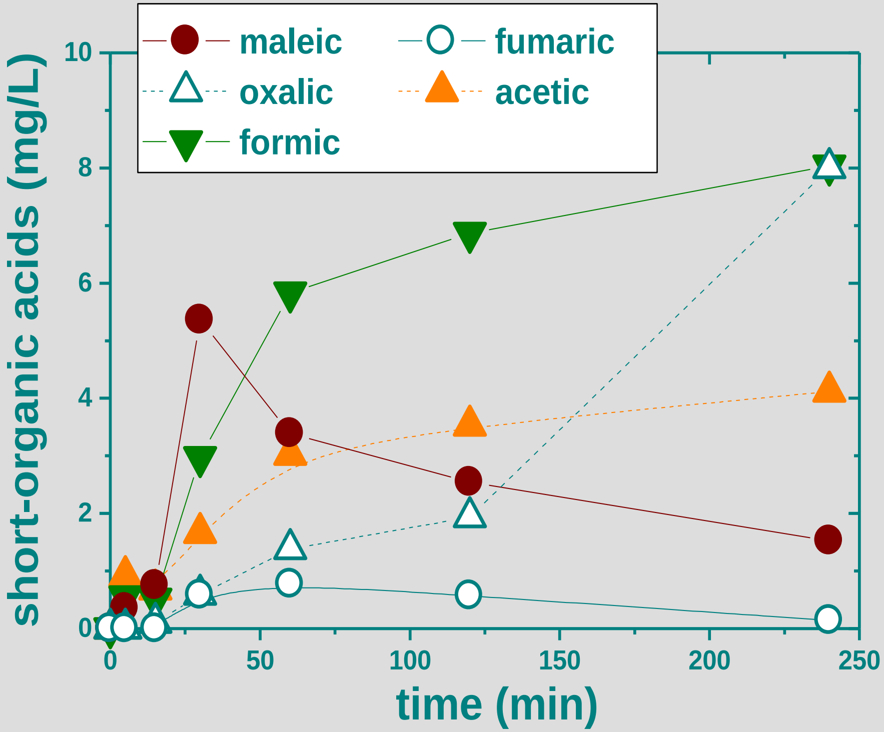
| Compound | | $EC_{50}$ (mg/L) | TU (100 mg/L) |
|---|---|---|---|
| Aromatics | Phenol | 16 | 6.3 |
| | Catechol | 8 | 12.5 |
| | Resorcine | 215 | 0.5 |
| | Hydroquinone | 0.041 | 2400 |
| | p-Benzoquinone | 0.1 | 1000 |
| Organic Acids | Muconic | 250 | 0.4 |
| | Maleic | 250 | 0.4 |
| | Fumaric | 250 | 0.4 |
| | Malonic | 450 | 0.2 |
| | Acetic | 130 | 0.8 |
| | Formic | 162 | 0.6 |
| | Oxalic | >450 | <0.2 |

CWPO

# Fe/AC CATALYST

## Batch experiments




**Operating cond:** T: 50ºC ; $pH_0$: 3; 100 mg/L phenol, 500 mg/L $H_2O_2$, 500 mg/L Fe/AC

J. A. Zazo, J. A. Casas, A.F. Mohedano, J. J. Rodriguez. Appl. Catal. B Environ. 65 (2006) 261-268

# HIGHTLIGHT RESULTS IN CWPO OF PHENOL

| CATALYST | Fe (%, wt.) | $W_{CAT}$ (g/L) | Phenol (mM) | $H_2O_2$/Phenol (stoich) | T (ºC) | $pH_0$ | Time (min) | $X_{Ph}$ (%) | $X_{TOC}$ (%) | $Fe_{Leach}$ (mg/L) | Ref. Author |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Fe_2O_3/CeO_2$ | **5** | **1** | **53** | **1.32** | **70** | **---** | **240** | **78** | **57** | **<0.25** | Massa et. al., 2008 |
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| Fe/AC | **4** | **0.5** | **1.06** | **1** | **50** | **3** | **120** | **100** | **78** | **1.1** | Zazo et. al., 2006 |

# Continuous experiments stirred tank reactor

## Working conditions

Q: 5 mL/min

Phenol: 100 mg/L

$H_2O_2$: 500 mg/L

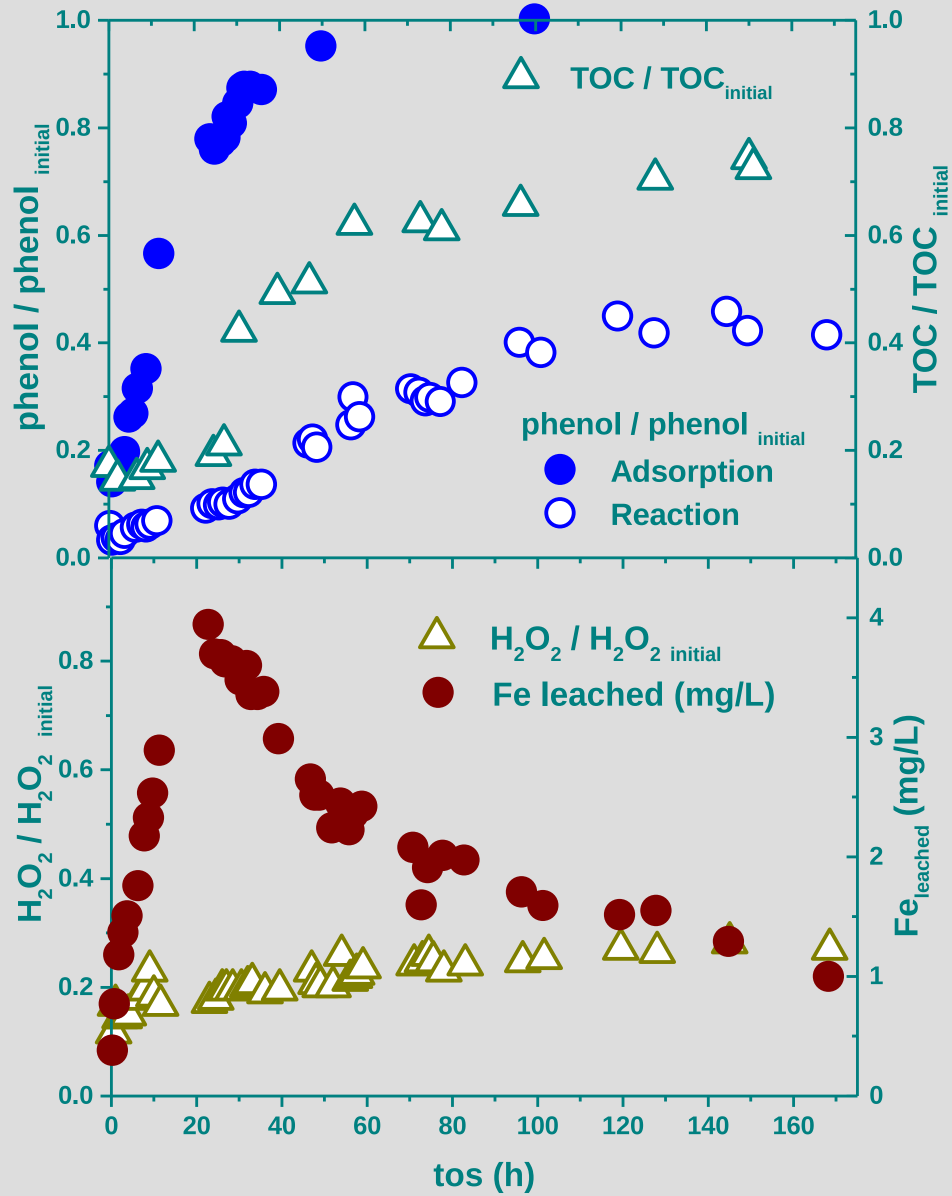
pH: 3

Temperature: 50 ºC

$V_{reaction}$: 0.92 L

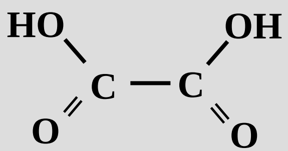
HRT: 184 min ; τ: 167 $g_{cat}.h/g_{Ph}$

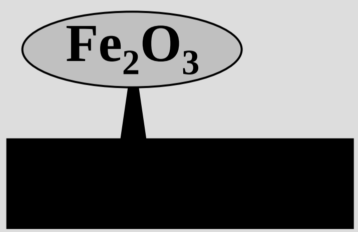
$W_{catalyst}$: 5.4 g/L




J. A. Zazo, J. A. Casas, A.F. Mohedano, J. J. Rodriguez. Appl. Catal. B Environ. 65 (2006) 261-268

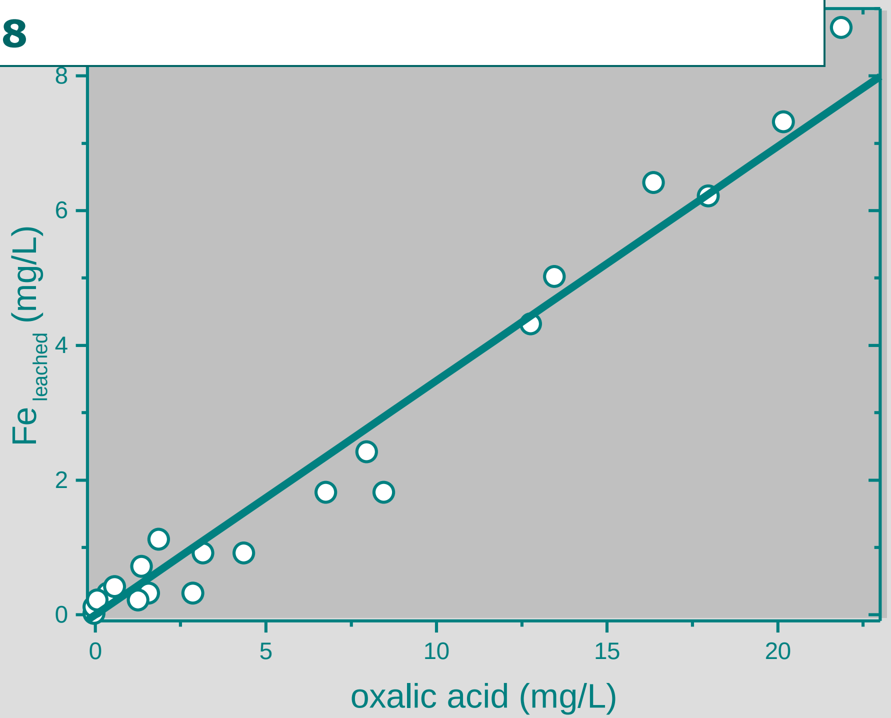
# CWPO





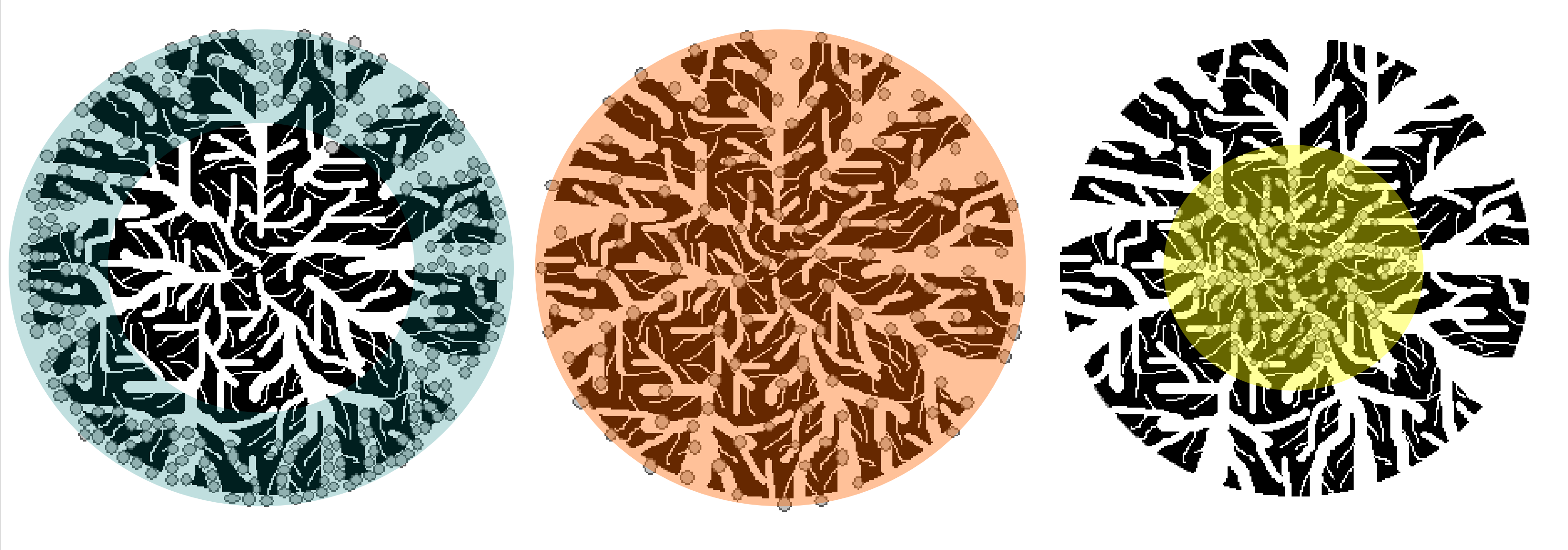

**Fe $_{leached}$ (mg/L): 0.35 · oxalic acid (mg/L)**

**r: 0.98**




**J. A. Zazo, J. A. Casas, A.F. Mohedano, J. J. Rodriguez. Appl. Catal. B Environ. 65 (2006) 261-268**

# Effect of Iron Precursor & AC support



Fe/C atomic ratios of catalysts

| Catalyst | $(Fe/C)_{BULK}$ | $(Fe/C)_{XPS}$ | |
|---|---|---|---|
| Fe/C1-N | 0.013 | 0.005 | egg-yolk |
| Fe/C2-N | 0.012 | 0.026 | egg-shell |
| Fe/C3-N | 0.013 | 0.045 | |
| Fe/C1-P | 0.009 | 0.013 | |
| Fe/C2-P | 0.010 | 0.013 | homogeneous |
| Fe/C3-P | 0.009 | 0.012 | |

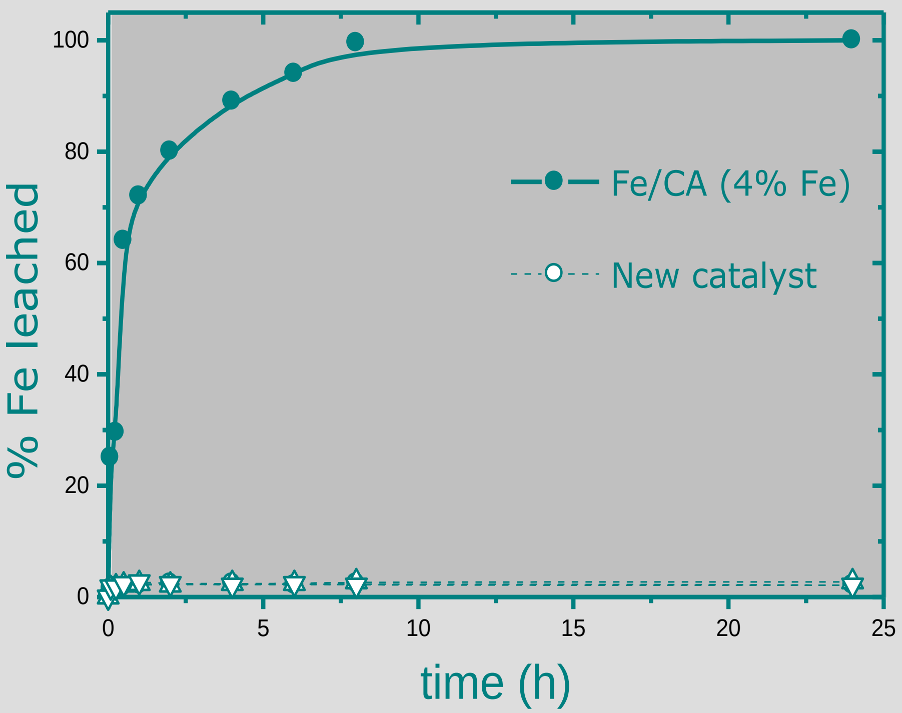
**Incipient wetness impregnation Fe: 4%**

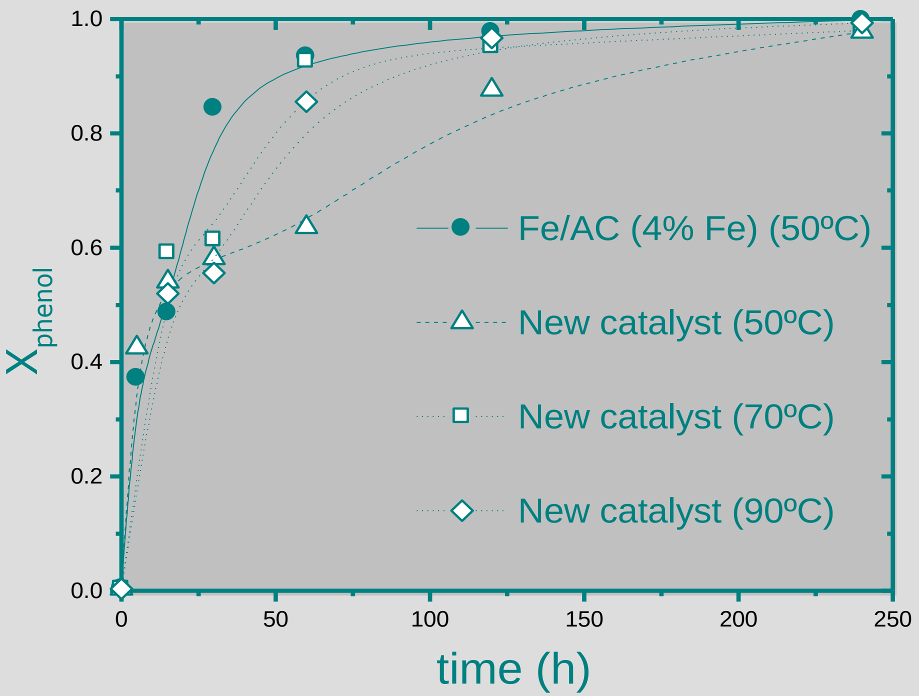
**Iron nitrate (N) → aqueous solution**

**Iron pentacarbonyl (P) → organic medium**

A. Rey, M. Faraldos, J. A. Casas, J. A. Zazo, A. Bahamonde, J. J. Rodríguez. Appl. Catal. B Environ. 86 (2009) 69

# CWPO

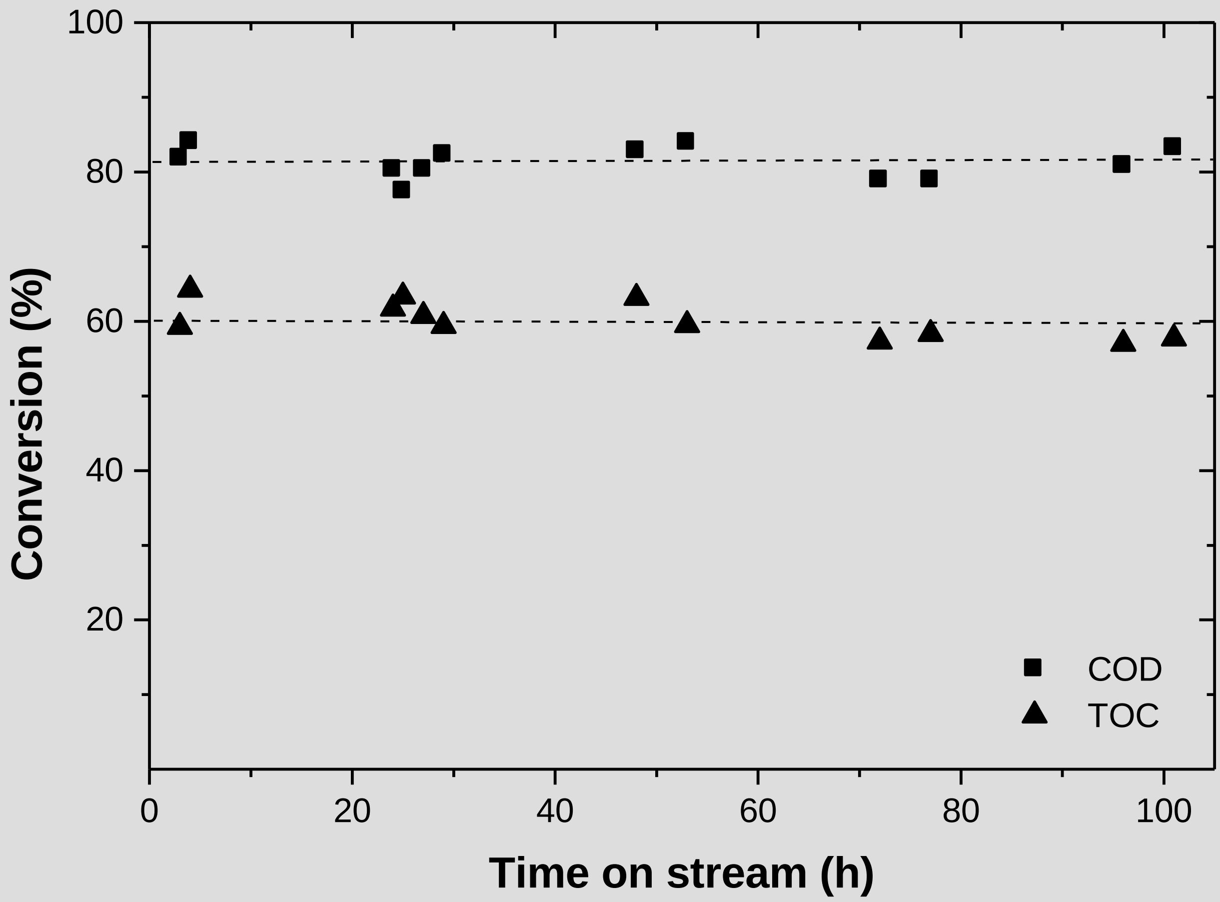



**% Fe $_{leached}$ from Fe/AC and the new catalyst in presence of oxalic acid (100 mg/L)**

**Comparision of the catalytic activity of Fe/AC and the new catalyst**

# Cosmetic wastewater with Fe/γ-$Al_2O_3$




Long-term stability of the Fe (4%)/γ-$Al_2O_3$ catalyst in CWPO of cosmetic wastewater T = 85 ºC; space-time: 9.8 kg cat.h/kg COD

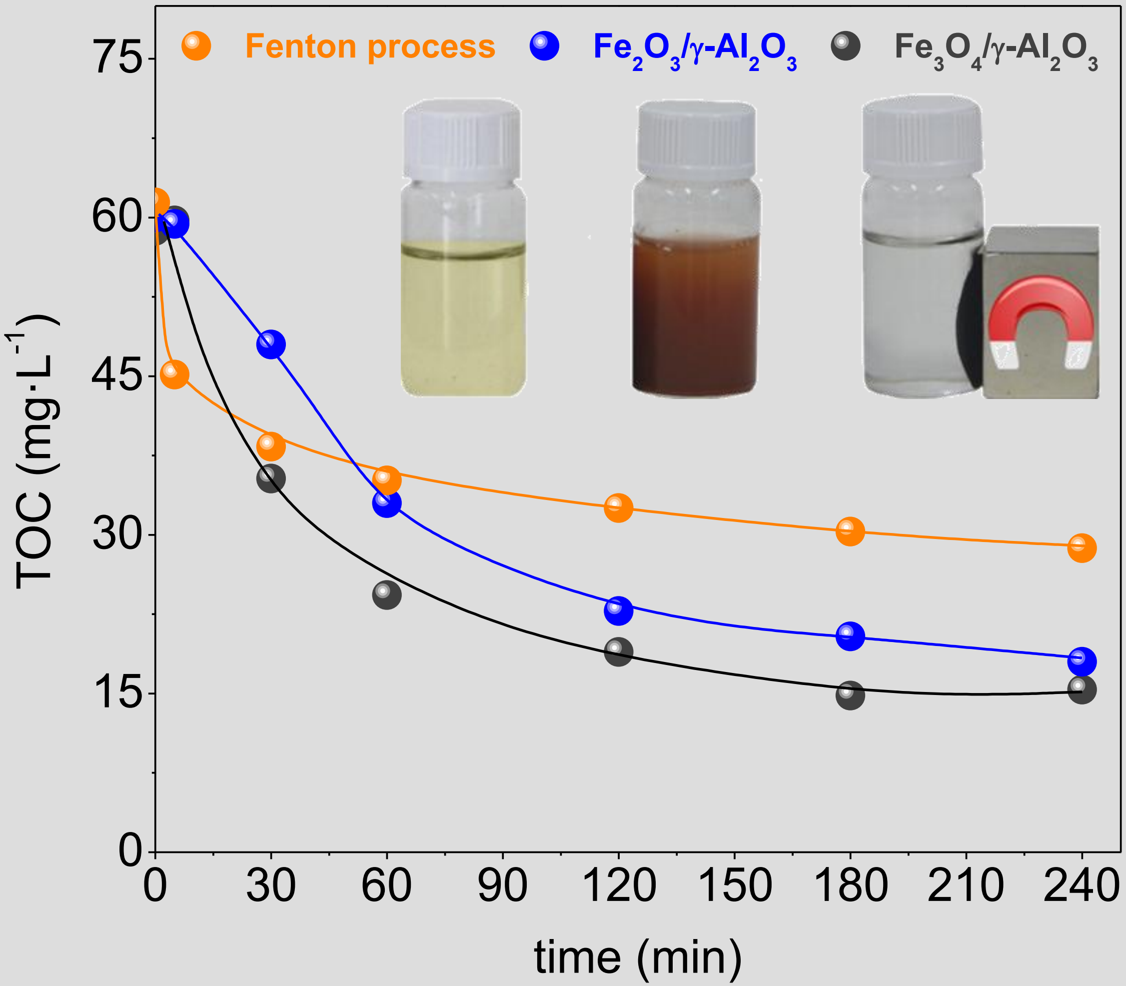
# Economic Analysis (€ /m³)

| | Fenton (homogeneous) | CWPO with Fe/γ-$Al_2O_3$ |
|---|---|---|
| **Investment** | **1.35** | **1.40** |
| **Operation & Maintenance** | | |
| $H_2O_2$ | **2.20** | **1.80** |
| Catalyst | **0.10** | **0.06** |
| Other | **0.20** | **0.20** |
| Electricity (1.9 kW-h/m³) | **0.17** | **0.17** |
| Heat (32 MJ/m³) | | **0.25** |
| Sludge treat & disposal (30 €/t) | **0.30** | |
| | **4.32** | **3.88** |
| Cosmetic wastewaters (100 m³/d) | | |
| $COD_0$: 3000 mg/L | 200 mg/L $Fe^{2+}$ | 5g/L Fe/AC, 100 h |
| $COD_f$: 1200 mg/L | 3800 mg/L $H_2O_2$ | 2900 mg/L $H_2O_2$ |

CWPO

# $Fe_xO_y/\gamma\text{-}Al_2O_3$ catalysts for CWPO

## Magnetic catalyst



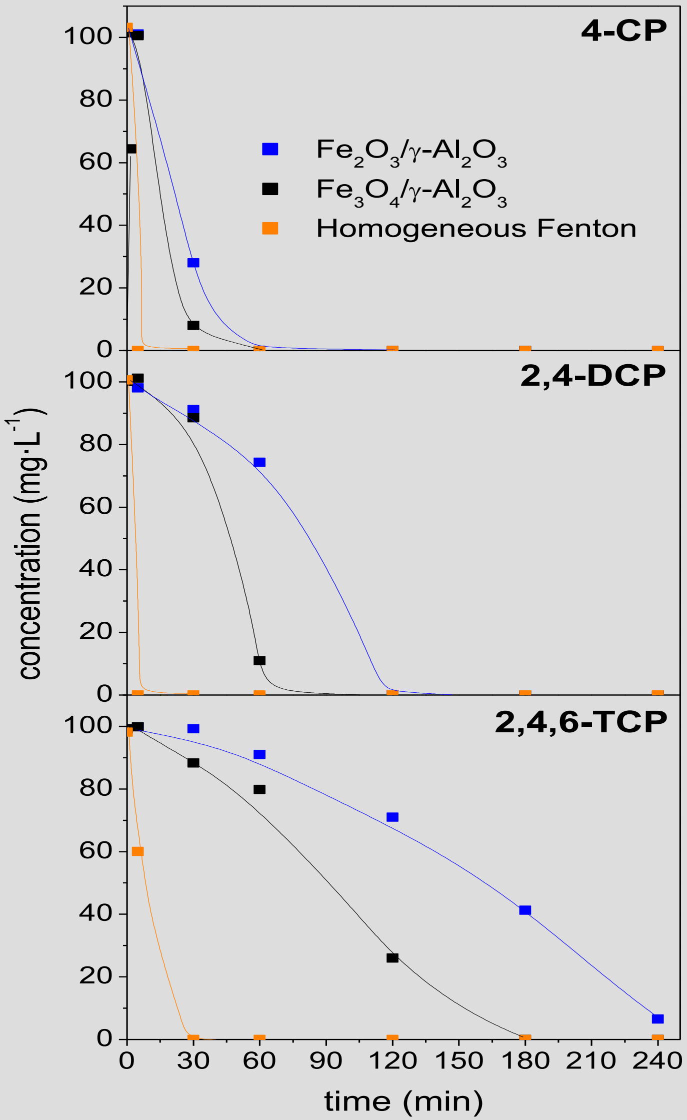

**4 % Fe**

**Incipient wetness impregnation with ferric nitrate**

**Calcination at 300 ºC**

**Magnetic catalyst: Reduction at 350 ºC**

# CWPO of CPs with $Fe_xO_y/\gamma\text{-}Al_2O_3$

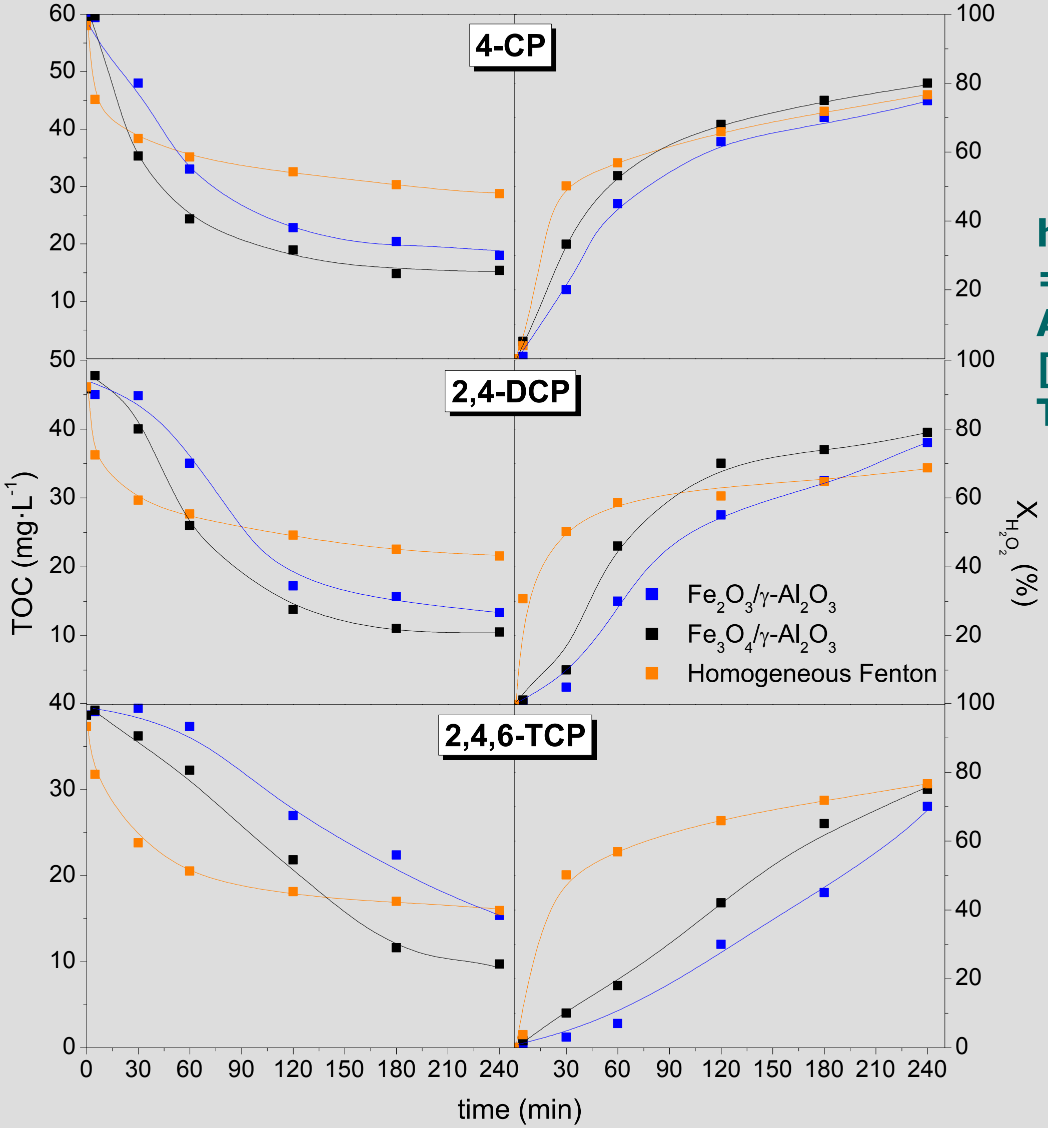



**Evolution of 4-CP, 2,4-DCP and 2,4,6-TCP upon homogeneous Fenton oxidation ($[Fe^{3+}]_0$ = 10 mg $L^{-1}$) and CWPO with $Fe_xO_y/\gamma\text{-}Al_2O_3$ (1 g $L^{-1}$); ($[CP]_0$ = 100 mg $L^{-1}$; $[H_2O_2]_0$ at stoichiometric dose; $pH_0$ = 3; T = 50 ºC).**

## Fenton provides more rapid conversion of the starting CP

**M. Munoz, Z.M. de Pedro, J.A. Casas, J.J. Rodriguez. Chem. Eng. J. 228(2013) 646-654**

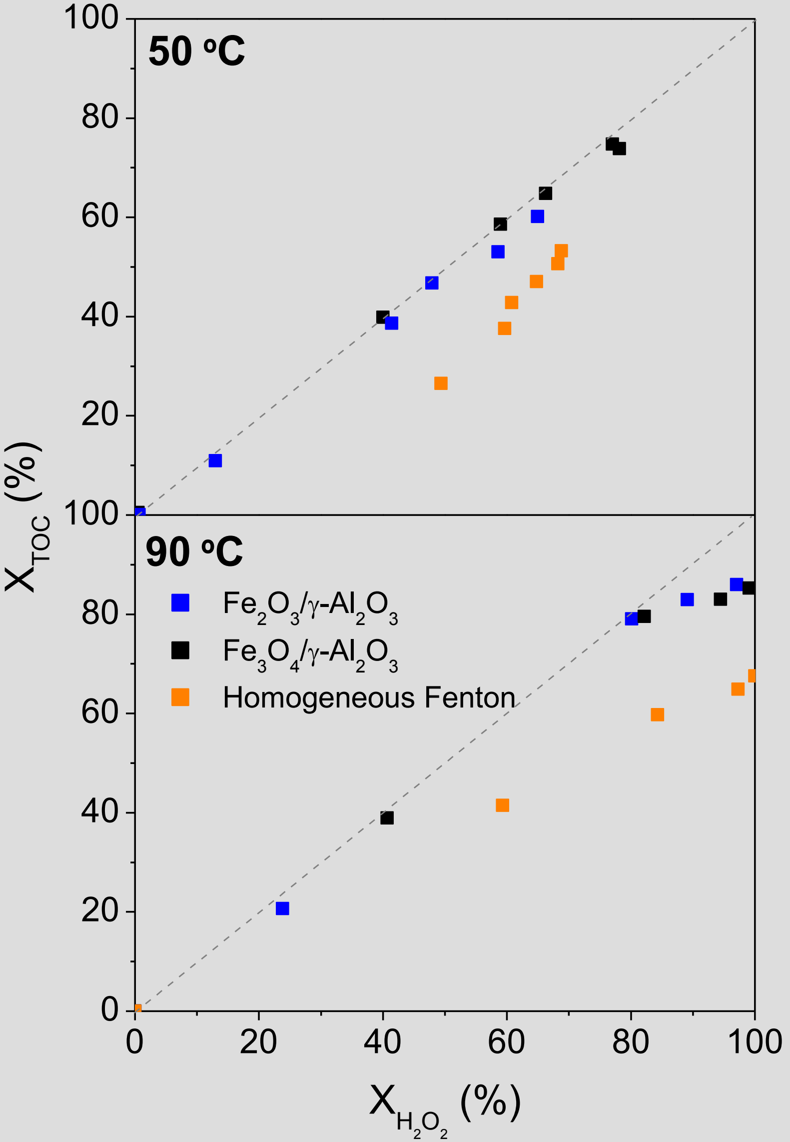
# CWPO of CPs with $Fe_xO_y/\gamma\text{-}Al_2O_3$




**Evolution of TOC and $H_2O_2$ upon homogeneous Fenton oxidation ($[Fe^{3+}]_0$ = 10 mg $L^{-1}$) and CWPO with FexOy/γ-$Al_2O_3$ (1 g $L^{-1}$); ($[CP]_0$ = 100 mg $L^{-1}$; $[H_2O_2]_0$ at stoichiometric dose; $pH_0$ = 3; T = 50 ºC).**

**CWPO more efficient than Fenton in terms of mineralization**

# CWPO of CPs with $Fe_xO_y/\gamma\text{-}Al_2O_3$




**Evolution of TOC vs. $H_2O_2$ conversion upon 4-CP breakdown by homogeneous Fenton oxidation ($[Fe^{3+}]_0$ = 10 mg $L^{-1}$) and CWPO with $Fe_xO_y/\gamma\text{-}Al_2O_3$ (1 g $L^{-1}$); ($[4\text{-CP}]_0$ = 100 mg $L^{-1}$; $[H_2O_2]_0$ = 350 mg $L^{-1}$; $pH_0$ = 3).**

## CWPO allows more efficient consumption of $H_2O_2$

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow HO\cdot + Fe^{3+} + H_2O$$

$$H_2O_2 + Fe^{3+} + H^+ \rightarrow HOO\cdot + Fe^{2+} + H^+$$

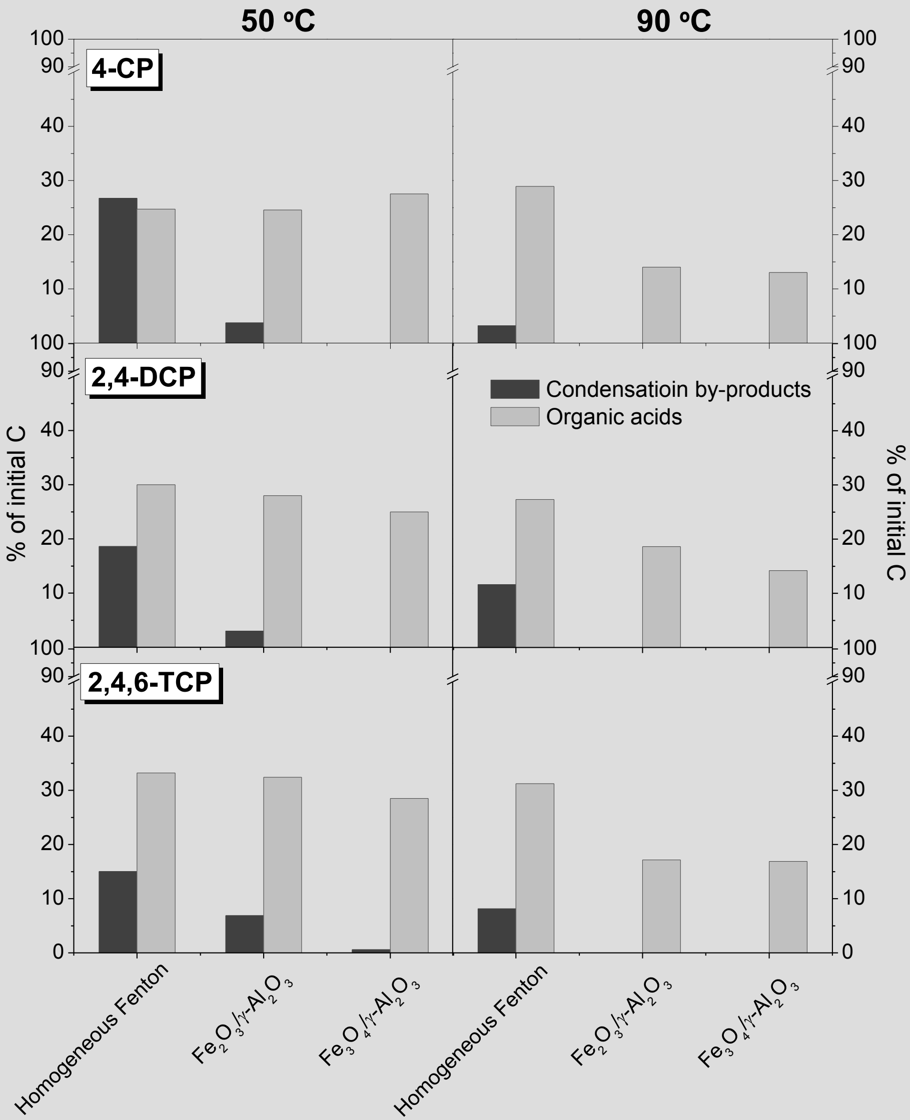
$$HO\cdot + HOO\cdot \rightarrow H_2O + O_2$$

$$HO\cdot + H_2O_2 \rightarrow H_2O + HOO\cdot$$

$$HOO\cdot + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+$$

$$HOO\cdot + Fe^{2+} \rightarrow Fe^{3+} + HOO^-$$

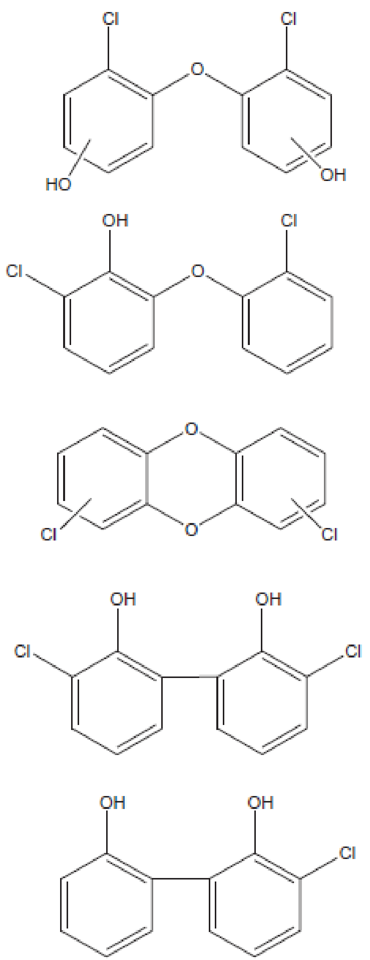
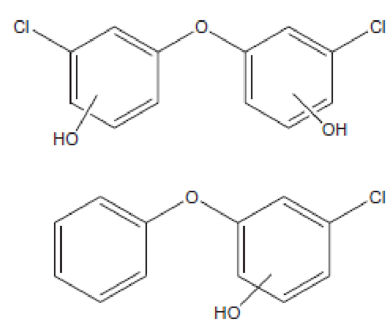
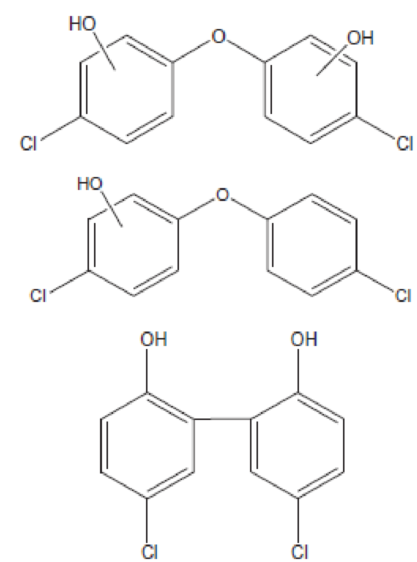
# CWPO of CPs with $Fe_xO_y/\gamma\text{-}Al_2O_3$




**Remaining by-products (4h) from chlorophenols oxidation by homogeneous Fenton ($[Fe^{3+}]_0$ = 10 mg $L^{-1}$) and CWPO with $Fe_xO_y/\gamma\text{-}Al_2O_3$ (1 g $L^{-1}$) at 50 and 90 ºC ($[CP]_0$ = 100 mg $L^{-1}$; $[H_2O_2]_0$ at stoichiometric dose; $pH_0$ = 3).**

# Chlorinated byproducts from Fenton oxidation of MCPs

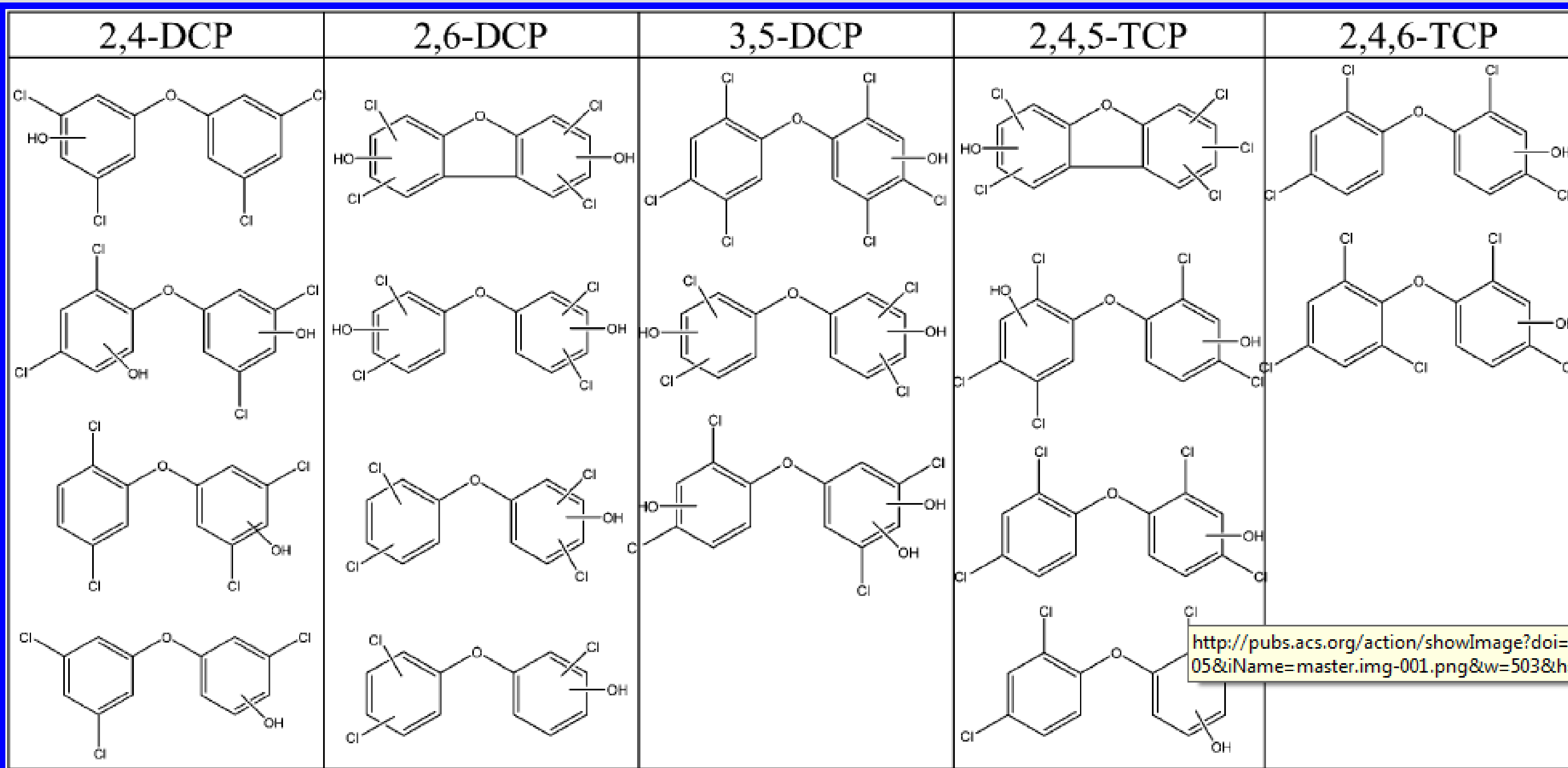
Chlorinated by-products identified by GC/MS from Fenton-like oxidation of monochlorophenols ($pH_0 = 3$, $T = 50\,^{\circ}C$, $[Fe^{3+}]_0 = 10$ mg/L; $[H_2O_2]_0 = 20\%$ of the stoichiometric dose).

| 2-CP | 3-CP | 4-CP |
|---|---|---|
|  |  |  |



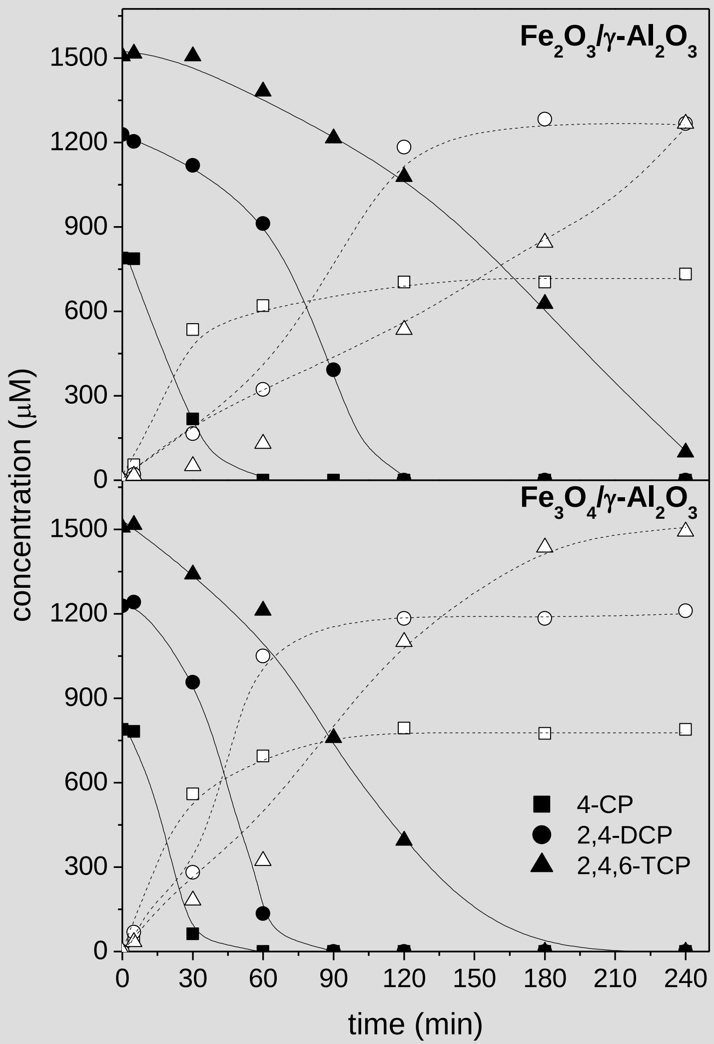
**M. Munoz, Z.M. de Pedro, J.A. Casas, J.J. Rodriguez. J. Haz. Mat. 190 (2011) 993-1000**

# Chlorinated byproducts from Fenton-like oxidation of PCPs




M. Munoz, Z.M. de Pedro, G. Pliego, J.A. Casas, J.J. Rodriguez. Ind. Eng. Chem. Res. 51 (2012) 13092-13099

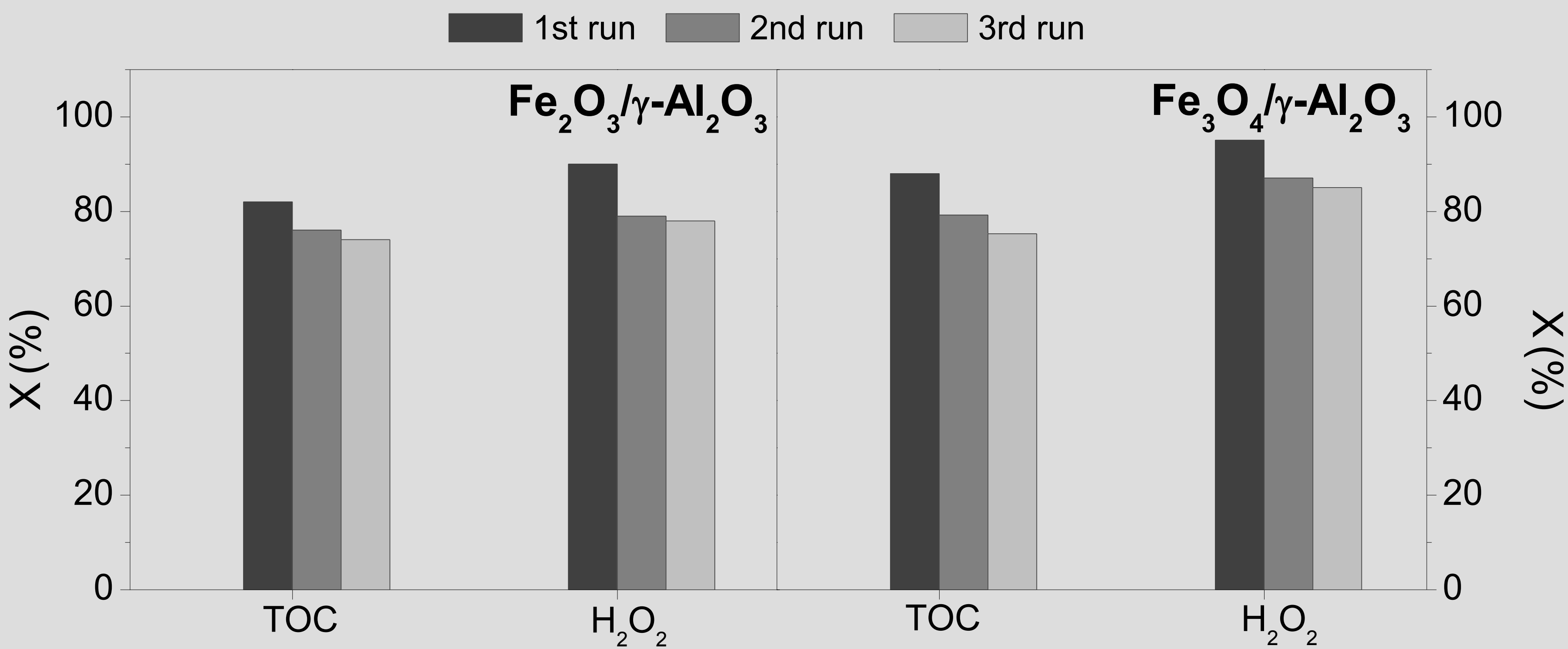
# CWPO of CPs with $Fe_xO_y/\gamma-Al_2O_3$




**Evolution of 4-CP, 2,4-DCP and 2,4,6-TCP (in equivalent Cl; solid symbols) and chloride ion (open symbols) concentration upon CWPO with $Fe_xO_y/\gamma-Al_2O_3$ catalysts. ($[CP]_0$ = 100 mg $L^{-1}$; $[Fe_xO_y/\gamma-Al_2O_3]_0$ = 1 g $L^{-1}$; $[H_2O_2]_0$ = stoichiometric dose; $pH_0$ = 3; T = 50 ºC).**

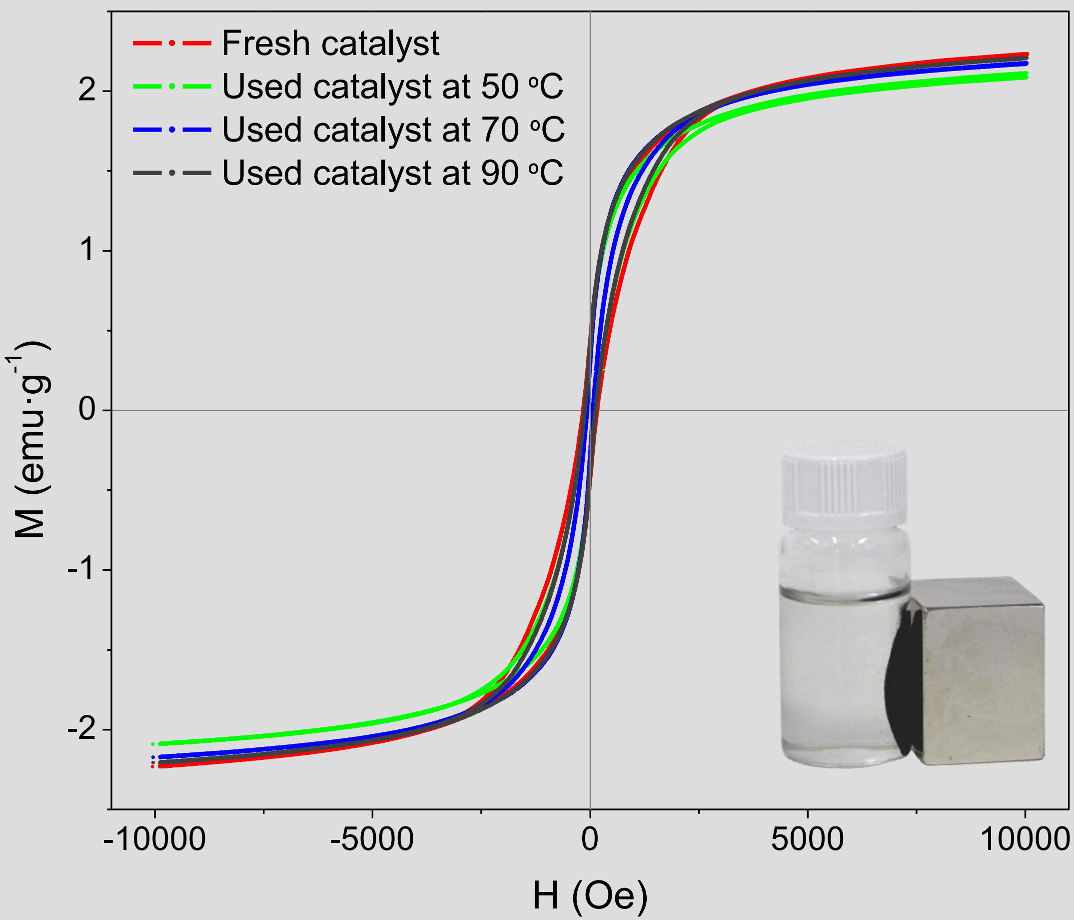
## Complete dechlorination

# CWPO of CPs with $Fe_xO_y/\gamma\text{-}Al_2O_3$



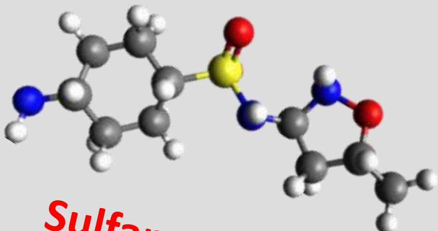

**TOC and $H_2O_2$ conversion (4 h) upon CWPO of 2,4,6-TCP with the $Fe_xO_y/\gamma\text{-}Al_2O_3$ catalysts in successive applications ($[Fe_xO_y/\gamma\text{-}Al_2O]_0$ = 1 g $L^{-1}$). ($[2,4,6\text{-}TCP]_0$ = 100 mg $L^{-1}$; $[H_2O_2]_0$ = 190 mg $L^{-1}$; $pH_0$ = 3; T = 90 ºC).**

# Magnetic Fe/$\gamma$-$Al_2O_3$ catalyst

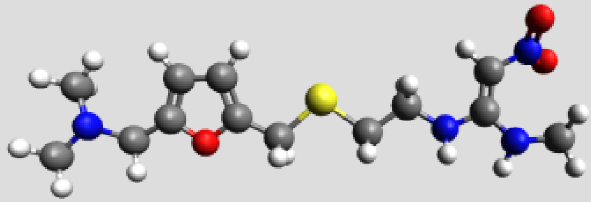



**Magnetization curves at room temperature of the $Fe_xO_y$/$\gamma$-$Al_2O_3$ catalyst before and after CWPO oxidation of 4-CP at different temperatures.**

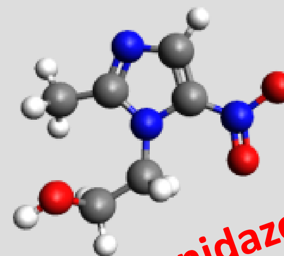
# CWPO OF REPRESENTATIVE DRUGS OVER $Fe_3O_4/\gamma\text{-}Al_2O_3$



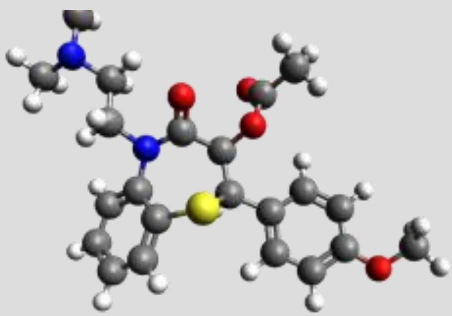
Sulfamethoxazole
SMX



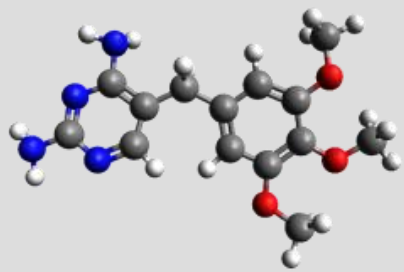
Ranitidine
RTD



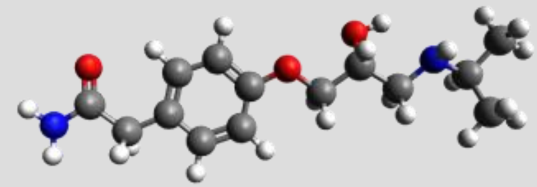
Metronidazole
MNZ



Diltiazem
DTZ



Trimethoprim
TMP



Atenolol
ATL

Operating conditions
$[\text{pharmaceuticals}]_0$ = 25 mg $L^{-1}$
$[H_2O_2]_0$ = stoichiometric amount
$[Fe_3O_4/\gamma\text{-}Al_2O_3]_0$ = 2 g $L^{-1}$
50 - 75 ºC
$pH_0$ = 3

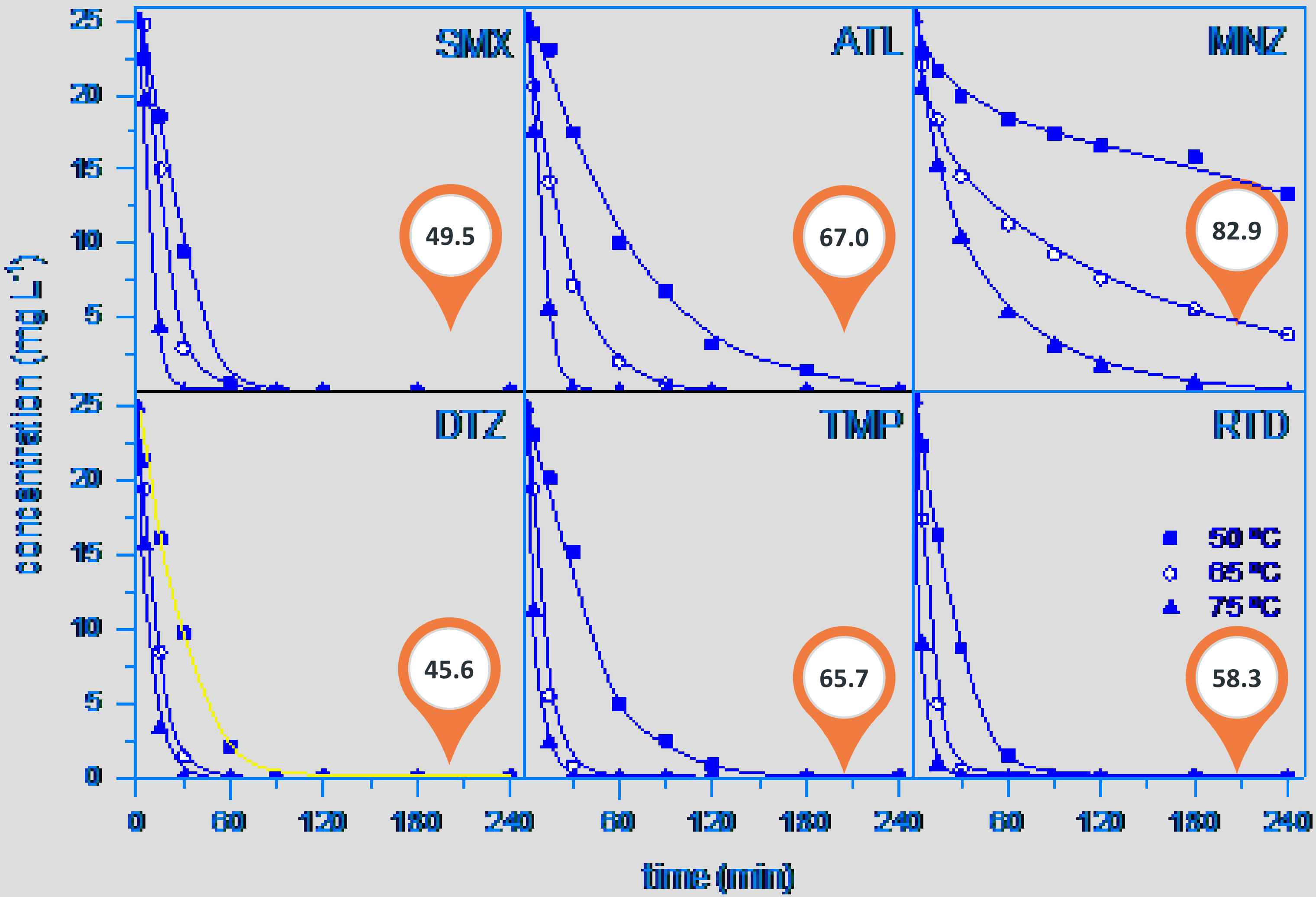
Antibiotics

β and calcium channel blockers

Antiulcer

Munoz et al., *J. Hazard. Mater.*, 331 (2017) 45-54.

# CWPO OF REPRESENTATIVE DRUGS OVER $Fe_3O_4/\gamma\text{-}Al_2O_3$

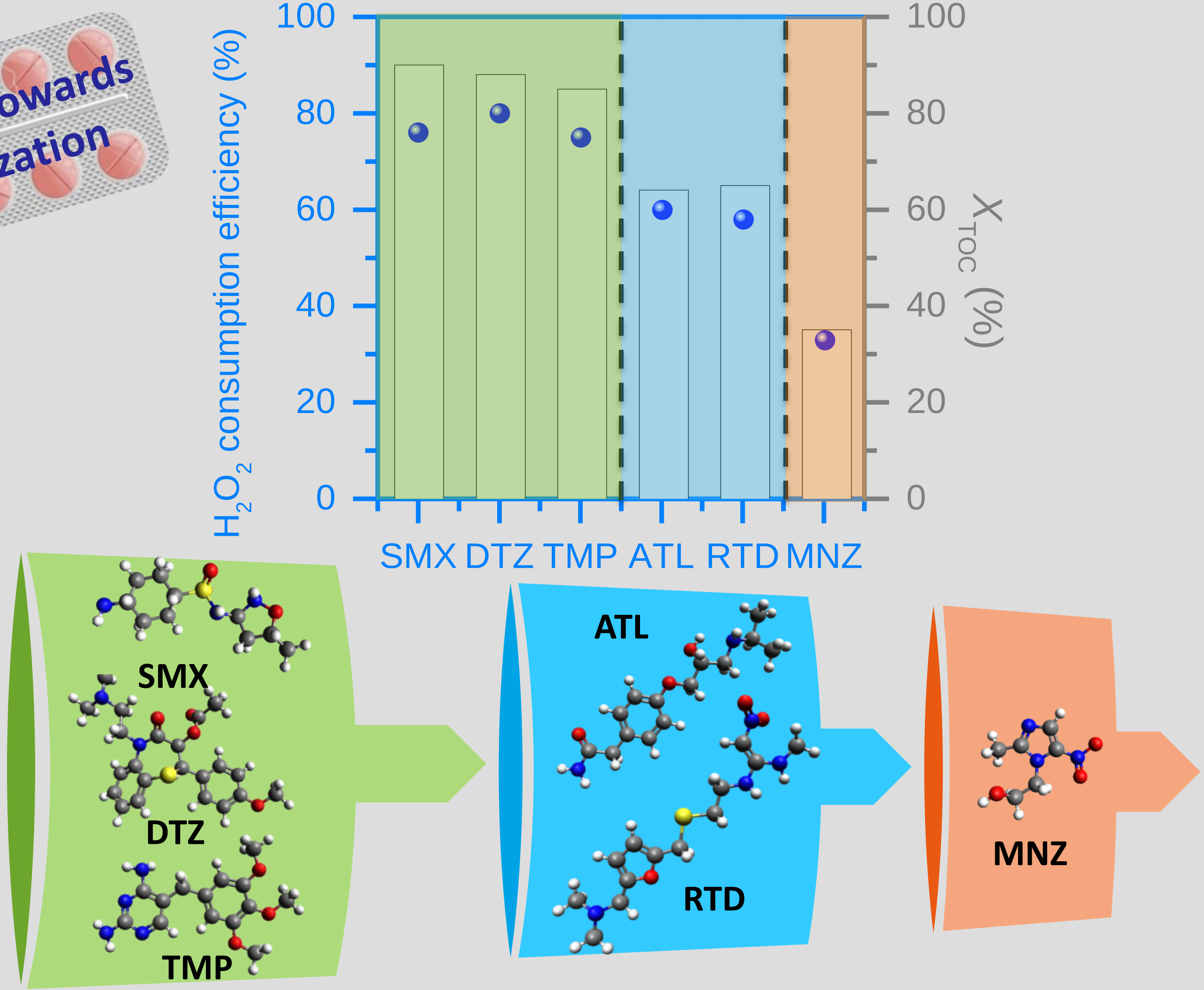



First order kinetics

Activation energy values (kJ $mol^{-1}$)

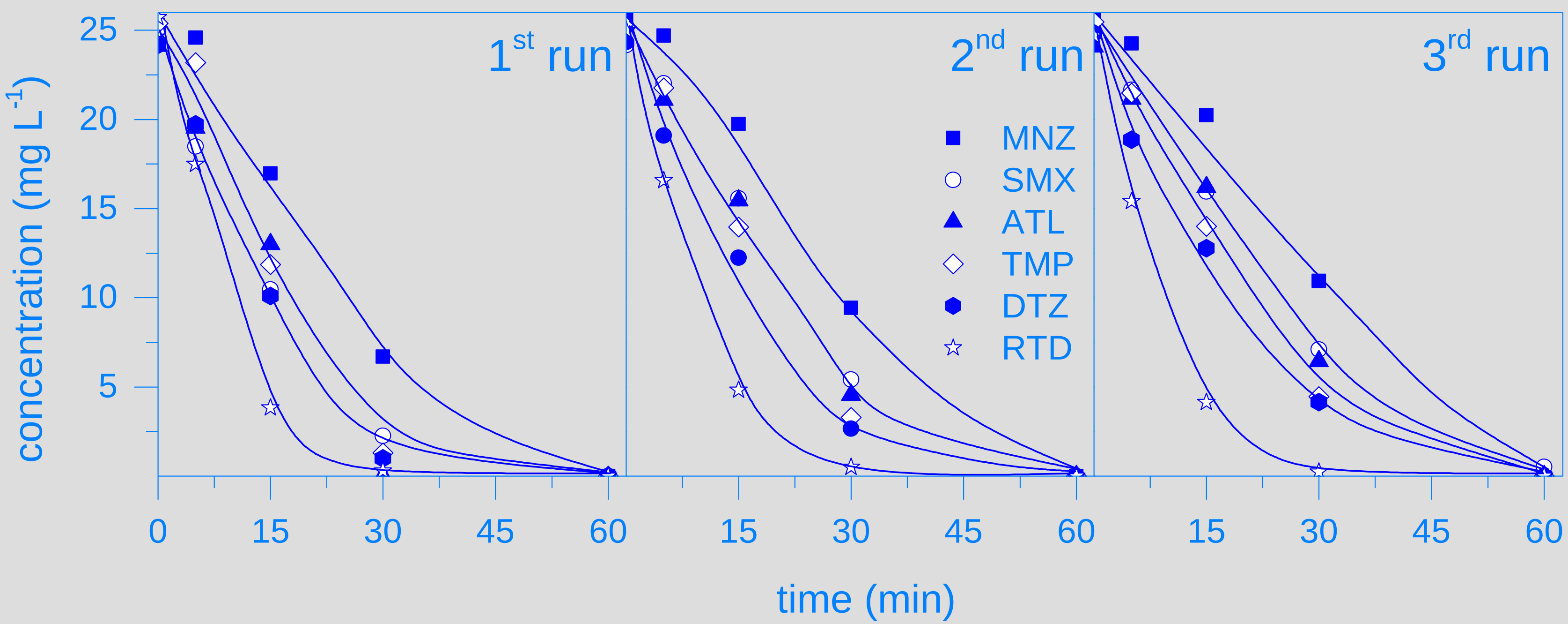
## CWPO

# CWPO OF REPRESENTATIVE DRUGS OVER $Fe_3O_4/\gamma$-$Al_2O_3$

CWPO

## STABILITY TESTS




Operating conditions

[pharmaceuticals]$_0$ = 25 mg $L^{-1}$

$[H_2O_2]_0$ = 730 mg $L^{-1}$

$[Fe_3O_4/\gamma\text{-}Al_2O_3]_0$ = 2 g $L^{-1}$

75 ºC

$pH_0$ = 3

**Iron leaching < 1.5% wt.**

**Surface area unchanged**

**Absence of carbon deposits**

CWPO

# OPERATION AT REPRESENTATIVE CONCENTRATIONS (μg $L^{-1}$)

**Hospital wastewater**

**WWTP effluent**

| | Concentration (μg $L^{-1}$) | |
|---|---|---|
| **SMX** | 2.6 | 1.2 |
| **ATL** | 4.5 | 7.6 |
| **MNZ** | 11.6 | 0.3 |
| **DTZ** | 0.9 | 0.1 |
| **TMP** | 1.6 | 3.1 |
| **RTD** | 2.4 | 0.5 |

Operating conditions

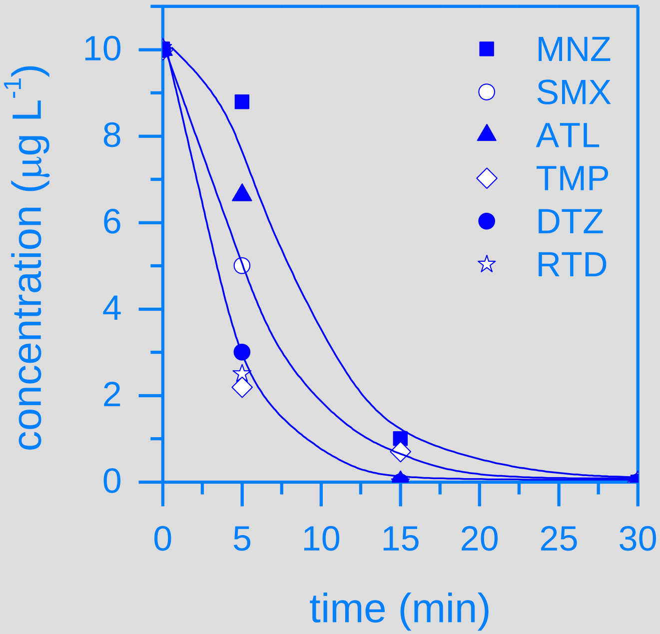
$[\text{pharmaceuticals}]_0 = 10$ μg $L^{-1}$

$[H_2O_2]_0 = 100$ mg $L^{-1}$

$[Fe_3O_4/\gamma\text{-}Al_2O_3]_0 = 2$ g $L^{-1}$

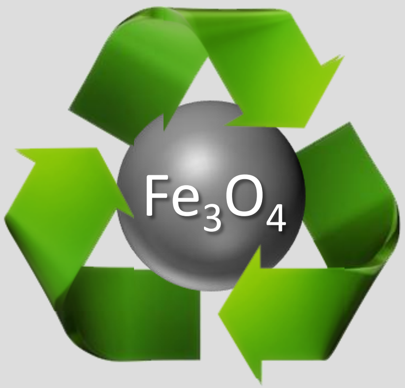
75 ºC

$pH_0 = 3$

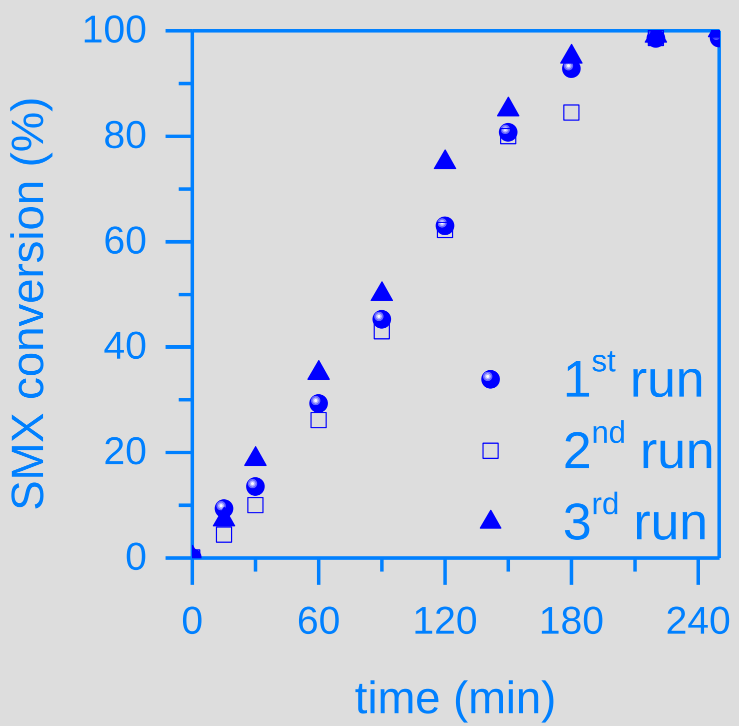



**Complete removal of pharmaceuticals (30 min)**

# CWPO OF SULFOMETHOXAZOLE WITH NATURAL MAGNETITE




Catalyst reuse
(3 consecutive runs)




Operating conditions
$[SMX]_0 = 5$ mg $L^{-1}$
$[H_2O_2]_0 = 25$ mg $L^{-1}$
$[Fe_3O_4]_0 = 1$ g $L^{-1}$
25 ºC
$pH_0 = 5$

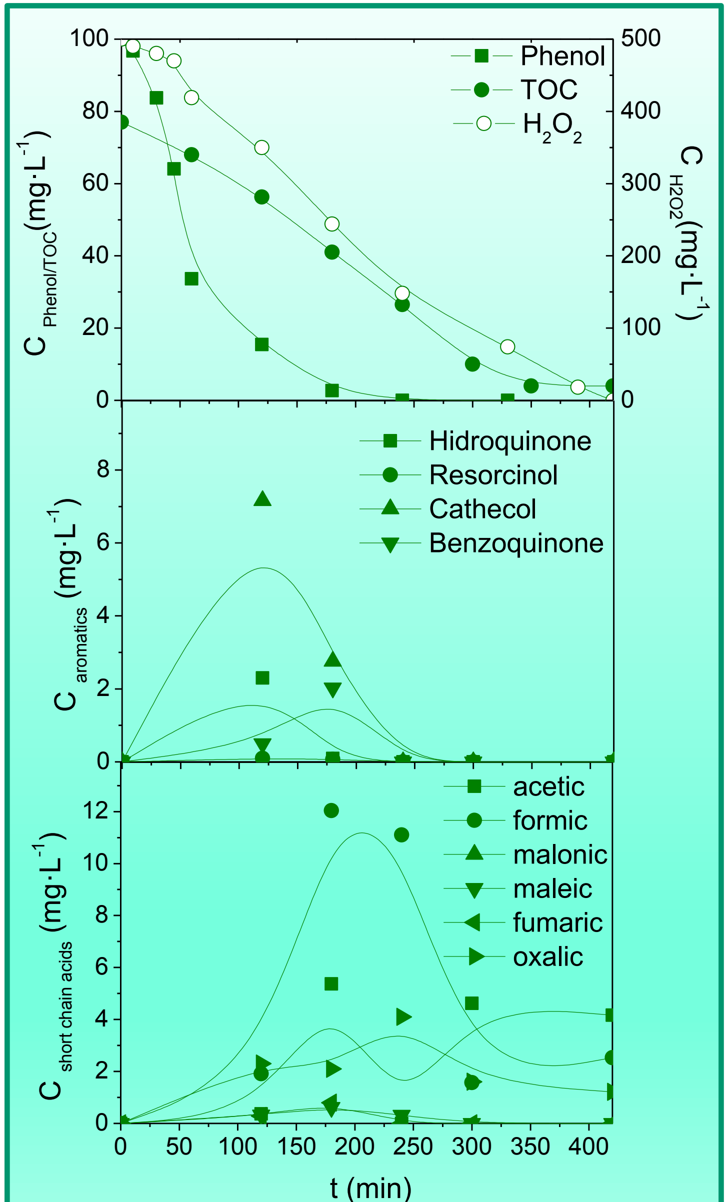
**Iron leaching < 0.5 mg $L^{-1}$**

**Absence of carbon deposits (<0.1% wt.)**

**Surface area and magnetic properties unchanged**

# CWPO/solar with ilmenite

**P. García-Muñoz, G. Pliego, J.A. Zazo, A. Bahamonde, J.A. Casas. Journal of Environmental Chemical Engineering 4 (2016) 542-548.**




**$X_{TOC}$>97%**

**$Fe_{leach}$< 1 mg·L$^{-1}$**

Conditions

25 ºC

$pH_0 = 3$

I=550 W·m$^{-2}$

[Phenol]$_0$ = 100 mg·L$^{-1}$

$[H_2O_2]_0$ = 500 mg·L$^{-1}$

[ILM-Fe(x)] = 450 mg·L$^{-1}$

UAM

FACULTAD DE CIENCIAS
UNIVERSIDAD AUTÓNOMA DE MADRID

Sección Departamental de Ingeniería Química

# Thank you!

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