UNIVERSIDAD COMPLUTENSE MADRID

WORKSHOP:

INNOVATIVE TECHNOLOGIES FOR SUSTAINABLE MANAGEMENT OF URBAN AND INDUSTRIAL WASTE STREAMS

Section I. Advanced oxidation processes for the removal of priority pollutants in wastewaters

RUTHENIUM AND PLATINUM SUPPORTED ON CARBON NANOSPHERES FOR THE DEGRADATION OF NAPROXEN BY CWAO: KINETICS, MECHANISM AND APPLICATION IN REAL MATRICES

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Remtavares P2018/EMT-4344

17th December 2020

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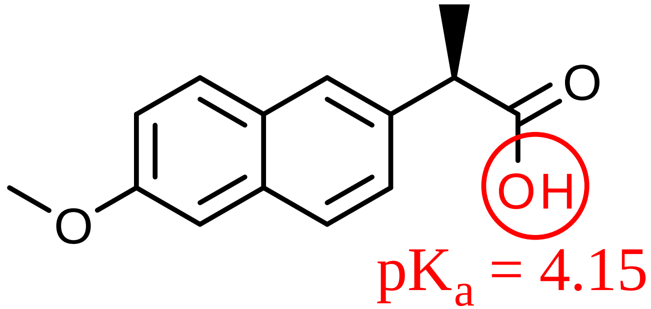
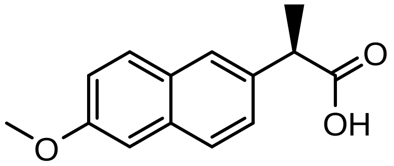
OBJECTIVE

Degradation of NPR

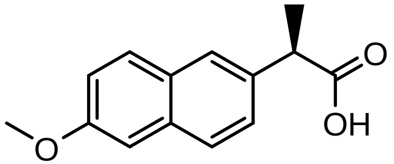


1. Group of non-steroidal anti-inflammatory drugs (NSAIDs)
2. Reduces levels of prostaglandins (chemicals responsible for pain, fever, and inflammation)
3. In 2016, 2nd NSAIDs after ibuprofen consumption in Spain (8.56 DHD/1000 inhabitants per day) according to the Spanish Ministry of Health
4. Pharmaceutical product detected in hospital effluents and surface waters because conventional WWTP does not degrade



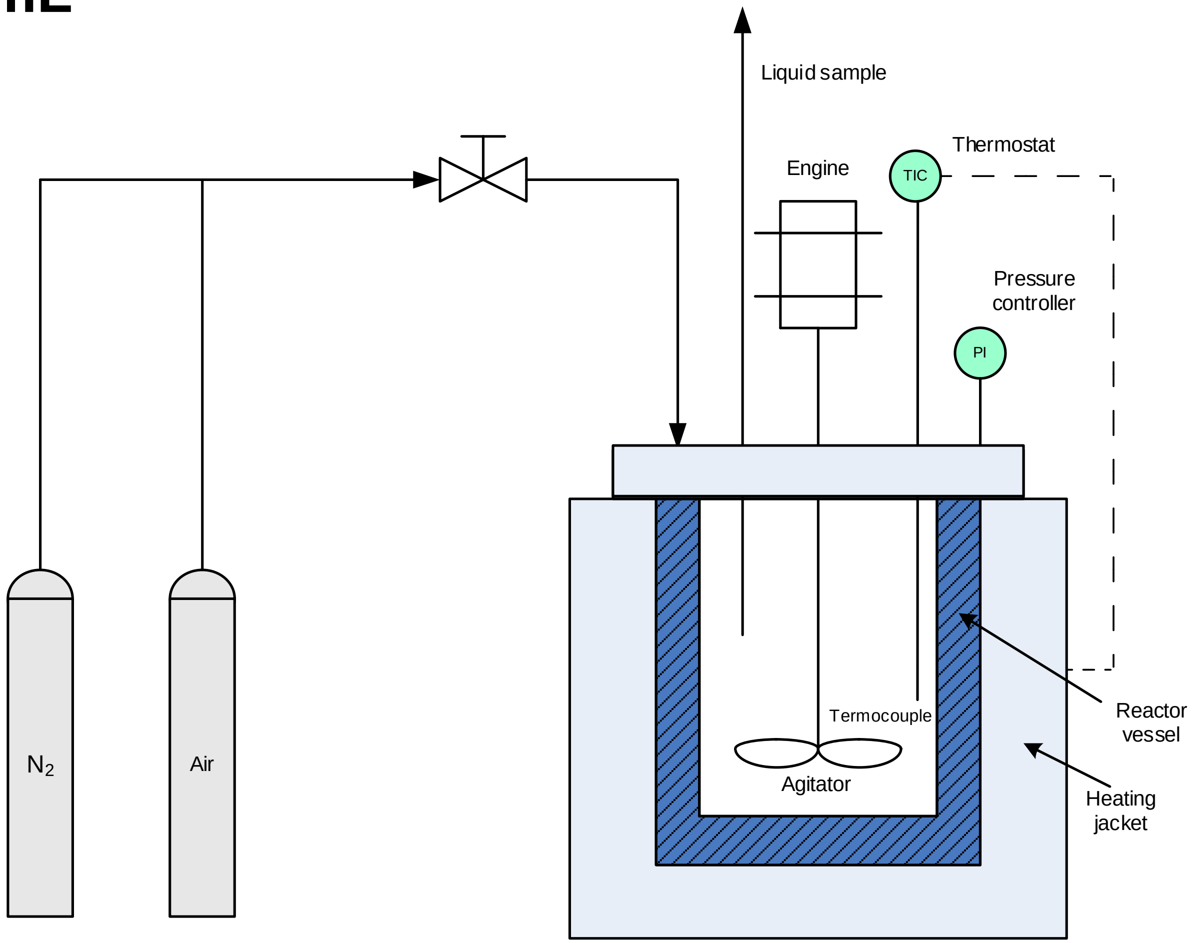
WORK PLAN

1. Catalyst synthesis (Ru supported on carbon nanospheres)
2. Catalyst characterization: SEM, TEM, TG, FT-IR, XRD
3. CWAO reaction: 3h → optimization conditions with Ru
4. Use of Pt at Ru optimal conditions
5. Reaction kinetic (Ea)
6. Reaction mechanism LC-MS
7. Application in real matrices



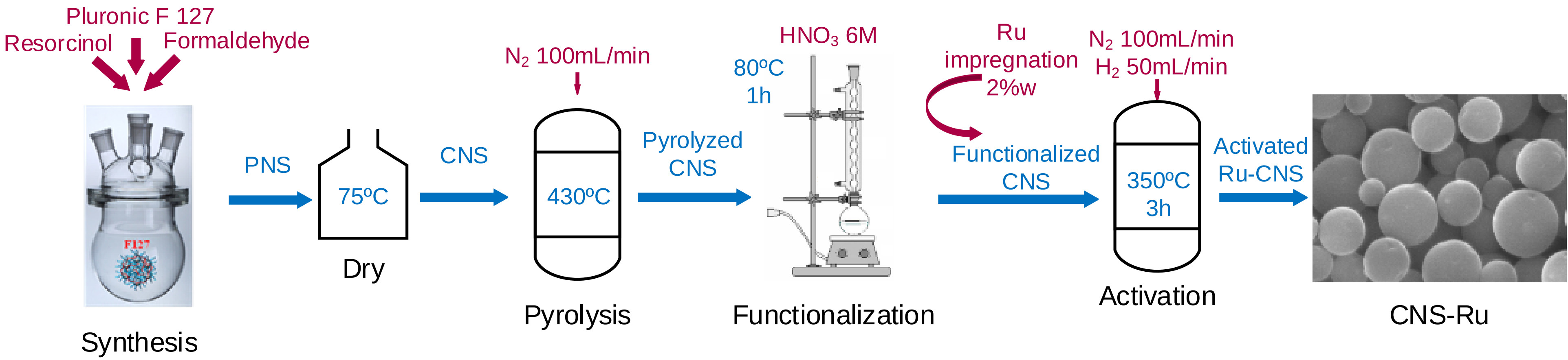
WAO/CWAO DISCONTINUOUS REACTOR

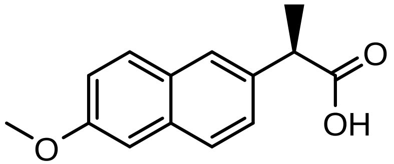
V = 100 mL

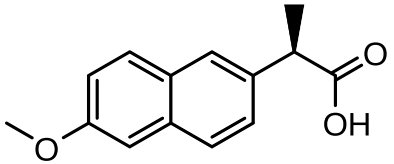


CATALYST SYNTHESIS

Modified method of Zhu et al., 2016







CWAO REACTION

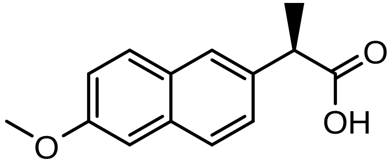
1. Reaction time: 3h → optimization conditions (5 variables)
2. Loadings of Ru (1-10%) and catalyst reuse
3. Analysis by:
   - HPLC
   - ICP
   - Elemental analysis
   - TG
   - FT-IR

Operating conditions:

- ✓ Volume = 100 mL
- ✓ Agitation speed = 700 r.p.m.

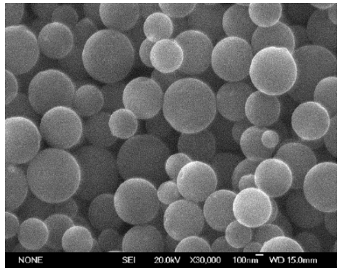
Variables to optimize:

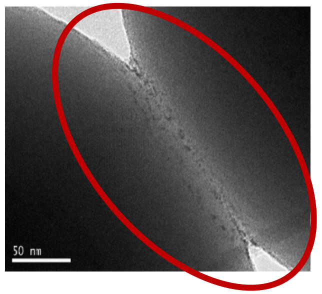
1. Temperature: 110 - 160 ºC
2. Pressure: 20 - 50 bar
3. m_{CNS-Ru}: 50 - 150 mg
4. $[NPR]_0$: 5 - 30 mg / L
5. Initial pH: 4 - 9

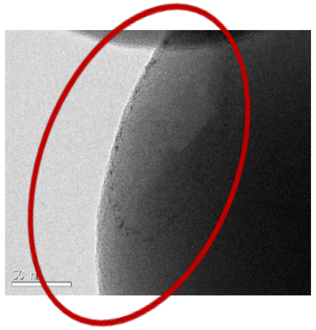


CHARACTERIZATION OF THE CATALYST

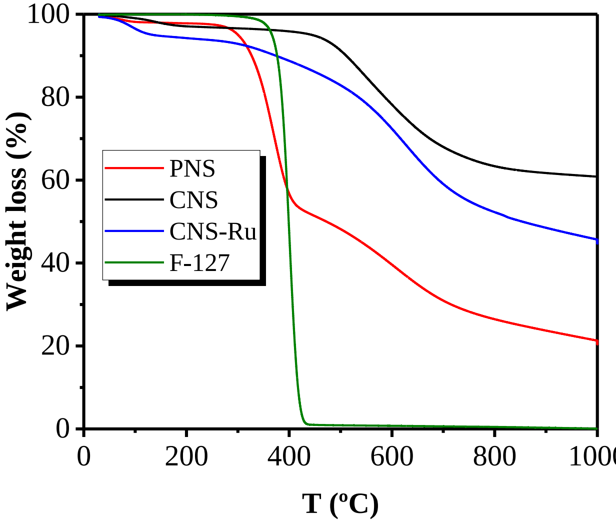
1. SEM and TEM



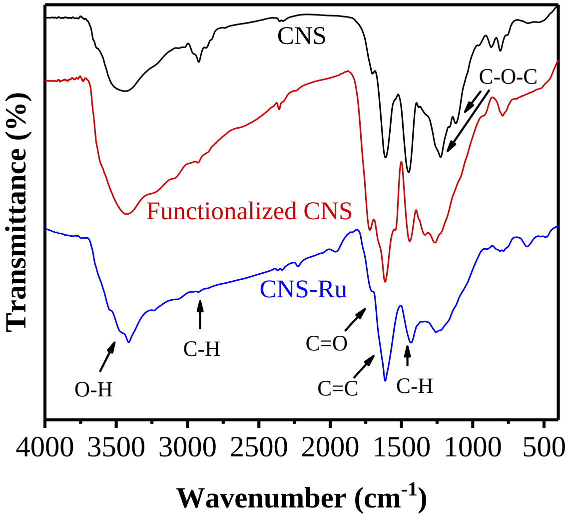




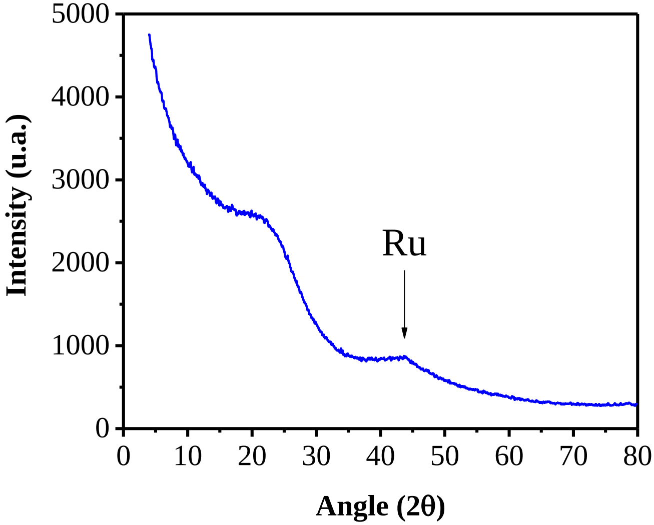
2.TG

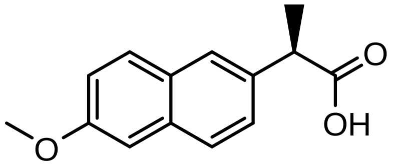


3. FT-IR



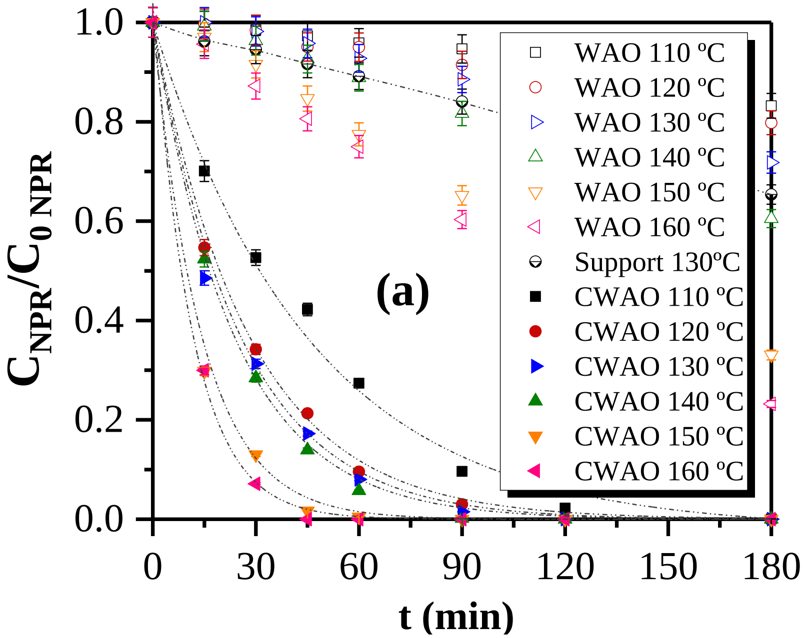
4. XRD





CWAO REACTION: OPTIMIZATION VARIABLES

- T influence



Conditions:

P = 20 bar

$m_{CNS\text{-}Ru}$ = 100 mg

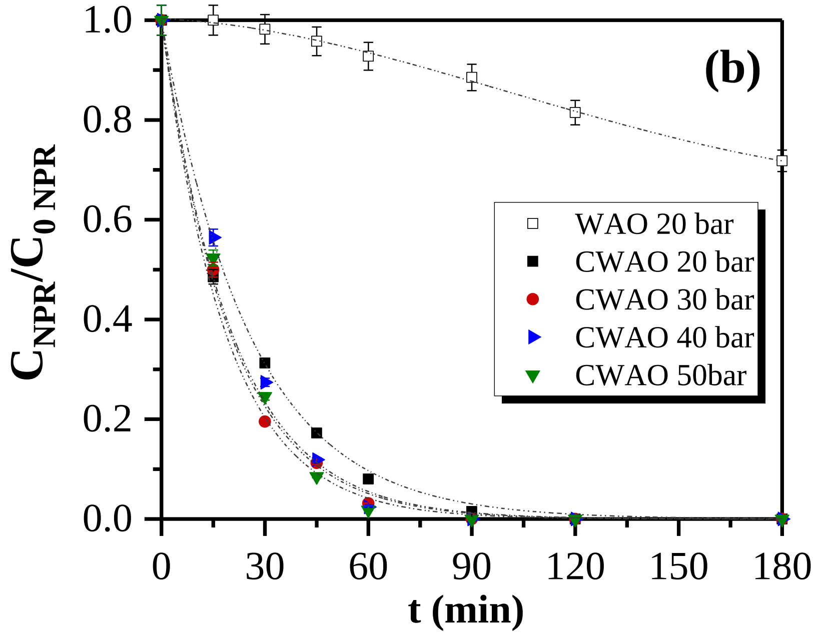
$[NPR]_0$ = 20 mg/L

pH_0 = neutral

Toxicidad

110°C	4,0 UT (5min)
160°C	2,1 UT (5min)

- P influence



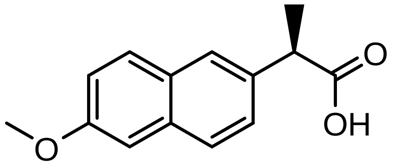
Conditions:

T = 130 °C

$m_{CNS\text{-}Ru}$ = 100 mg

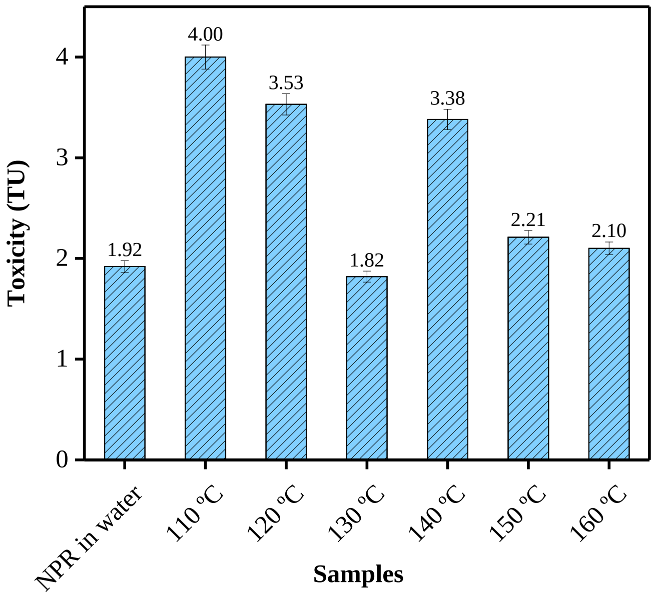
$[NPR]_0$ = 20 mg/L

pH_0 = neutral

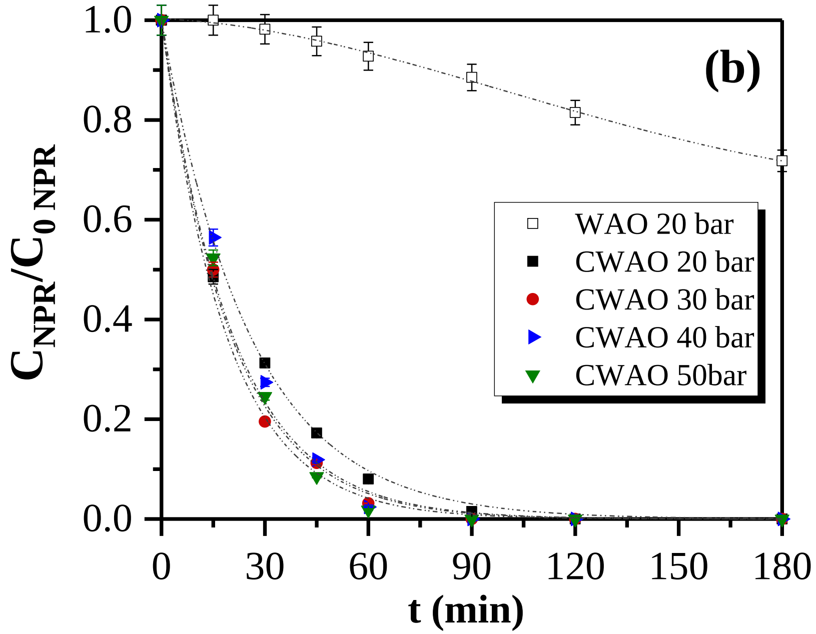


CWAO Reaction: optimization variables

- T influence



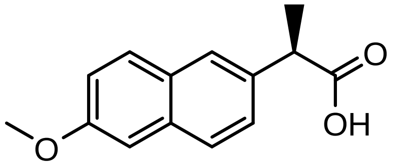
- P influence



Conditions:
P = 20 bar
m_{CNS-Ru} = 100 mg
$[NPR]_0$ = 20 mg/L
pH_0 = neutral

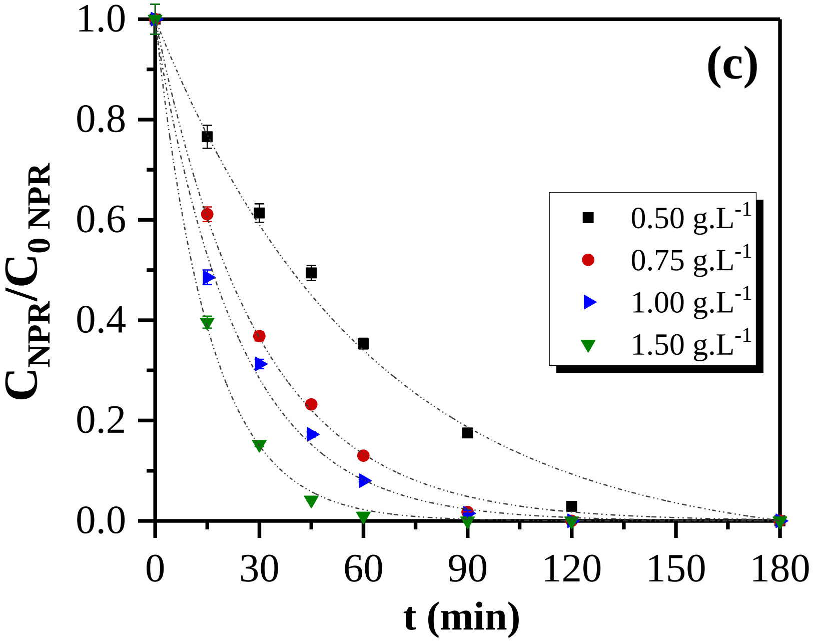
Toxicidad	
110°C	4,0 UT (5min)
160°C	2,1 UT (5min)

Conditions:
T = 130 °C
m_{CNS-Ru} = 100 mg
$[NPR]_0$ = 20 mg/L
pH_0 = neutral



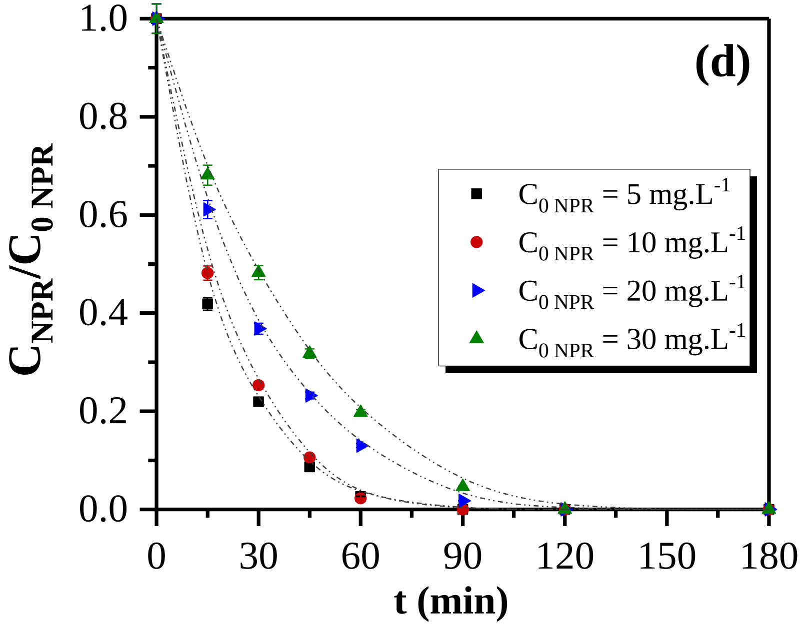
CWAO REACTION: OPTIMIZATION VARIABLES

- m_{CNS-Ru} influence

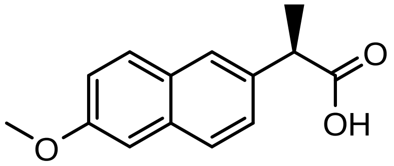


Conditions:
T = 130 °C
P = 20 bar
$[NPR]_0$ = 20 mg/L
pH_0 = neutral

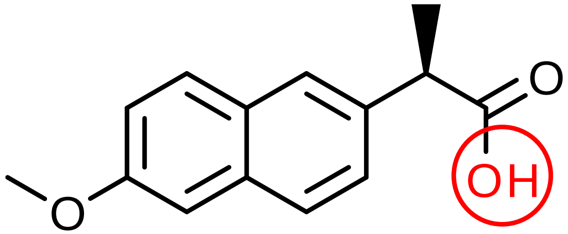
- $[NPR]_0$ influence



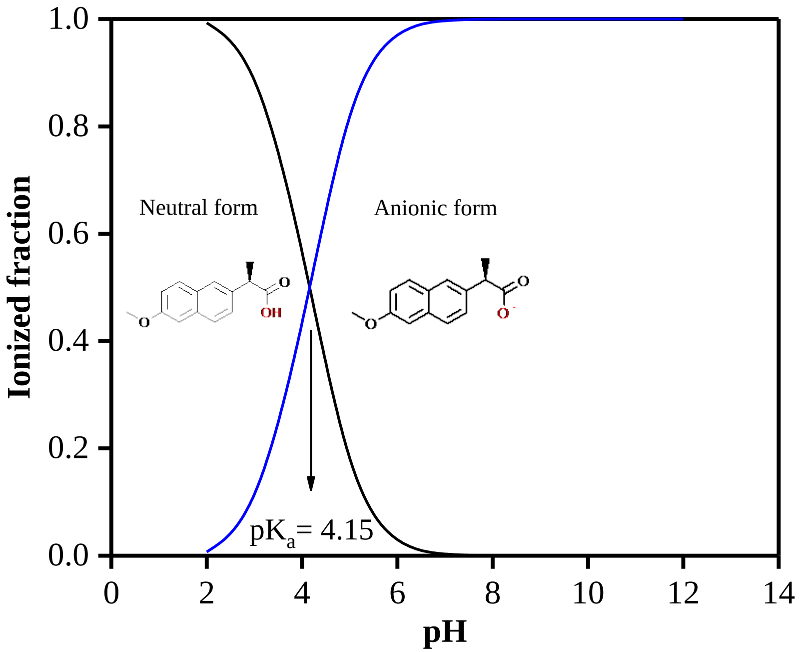
Conditions:
T = 130 °C
P = 20 bar
m_{CNS-Ru} = 75 mg
pH_0 = neutral



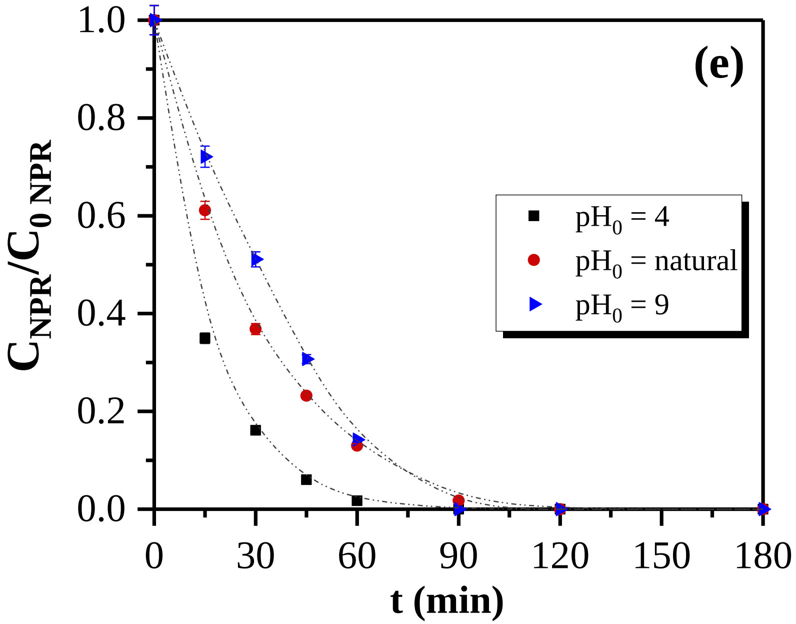
CWAO REACTION: OPTIMIZATION VARIABLES



pKa = 4.15



- pH$_{inicial}$ influence



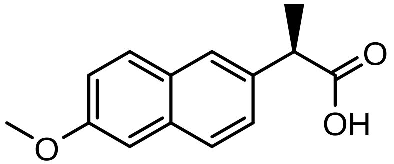
Conditions:

T = 130 °C

P = 20 bar

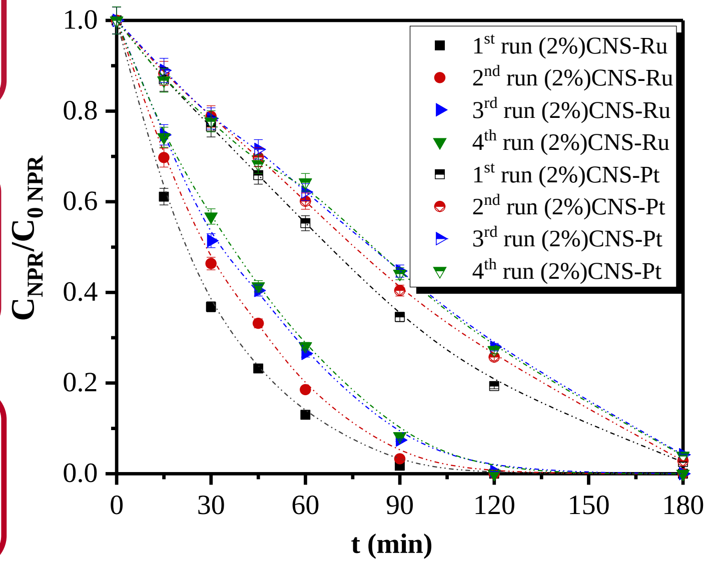
m_{CNS-Ru} = 75 mg

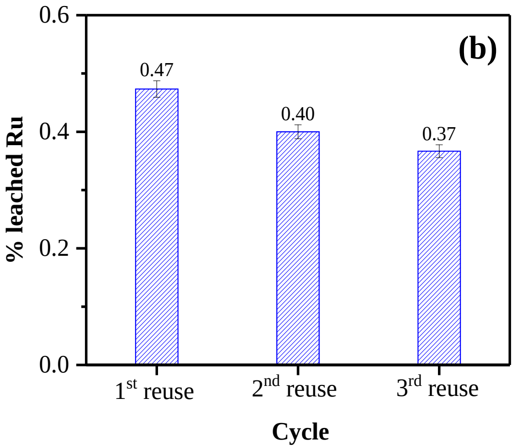
$[NPR]_0$ = 20 mg/L

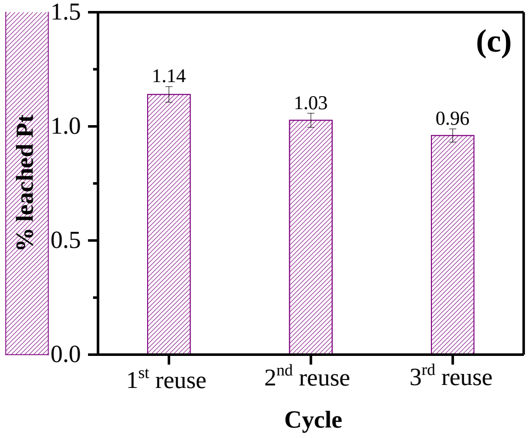


CWAO REACTION: CATALYST REUSE

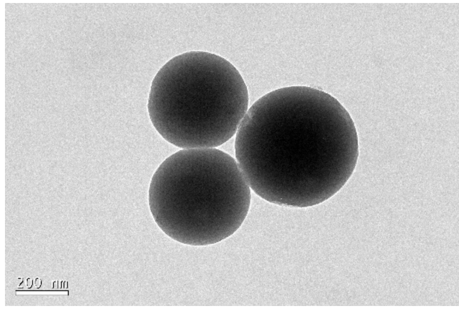
Optimized conditions: T = 130 °C, P = 20 bar, m_{CNS-Ru} = 75 mg, $[NPR]_0$ = 20 mg/L, $pH_{initial}$ = neutral



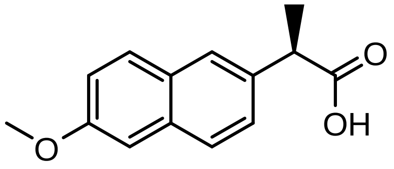




- **Carbon deposits are not formed (confirmed by elemental analysis)**
- **Morphology and structure of the catalyst is not altered after reuse**
- **Leaching of Ru and Pt in liquid final phase: less than 2% detected – ICP analysis**

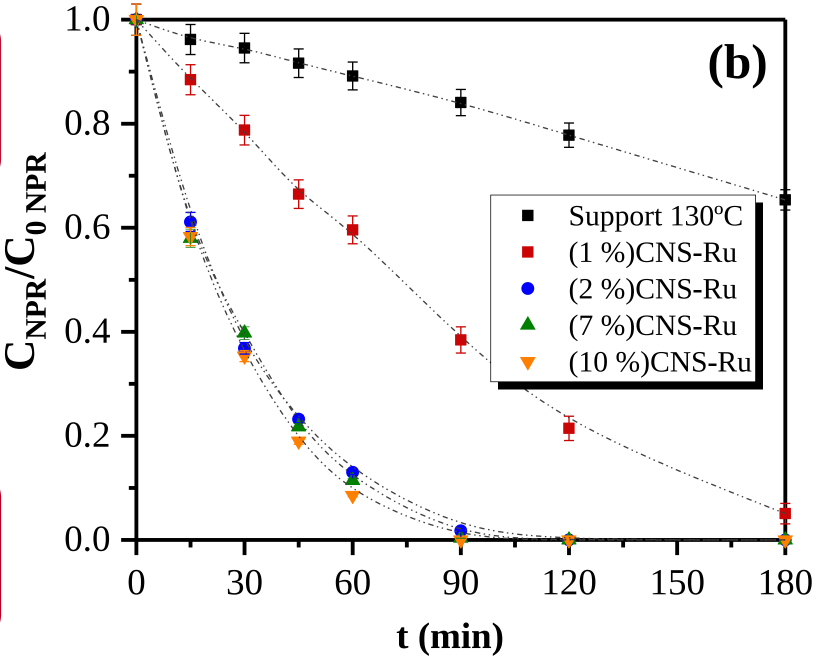


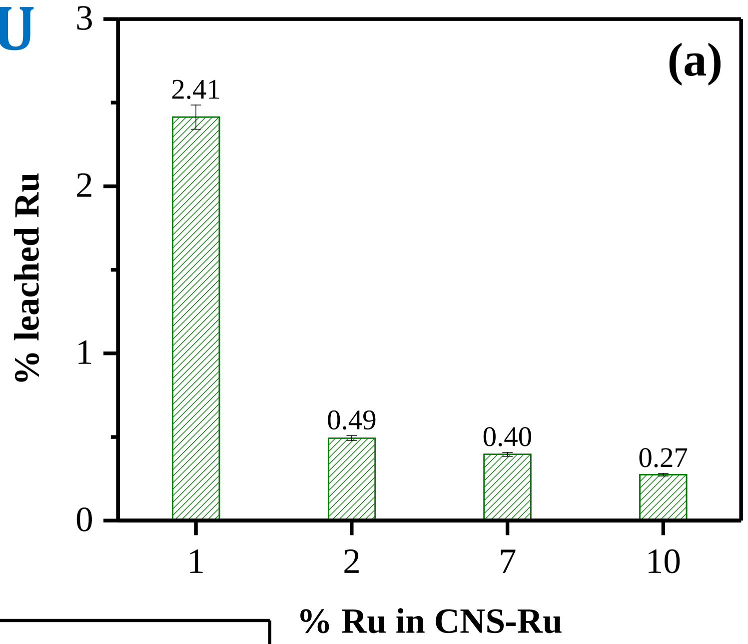
- INTRODUCTION
- MATERIALS AND METHODS
- **3 RESULTS AND DISCUSSION**
- CONCLUSIONS

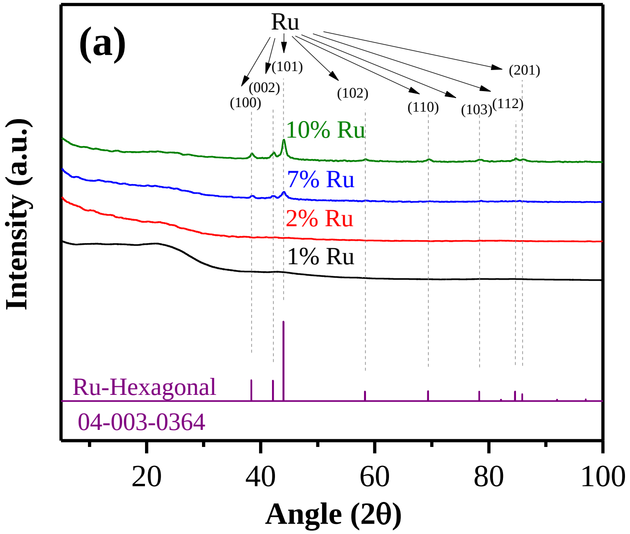


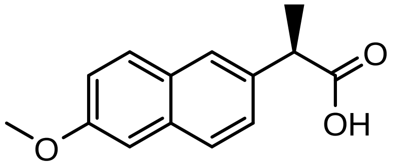
CWAO REACTION: LOADING OF RU

XRD analysis

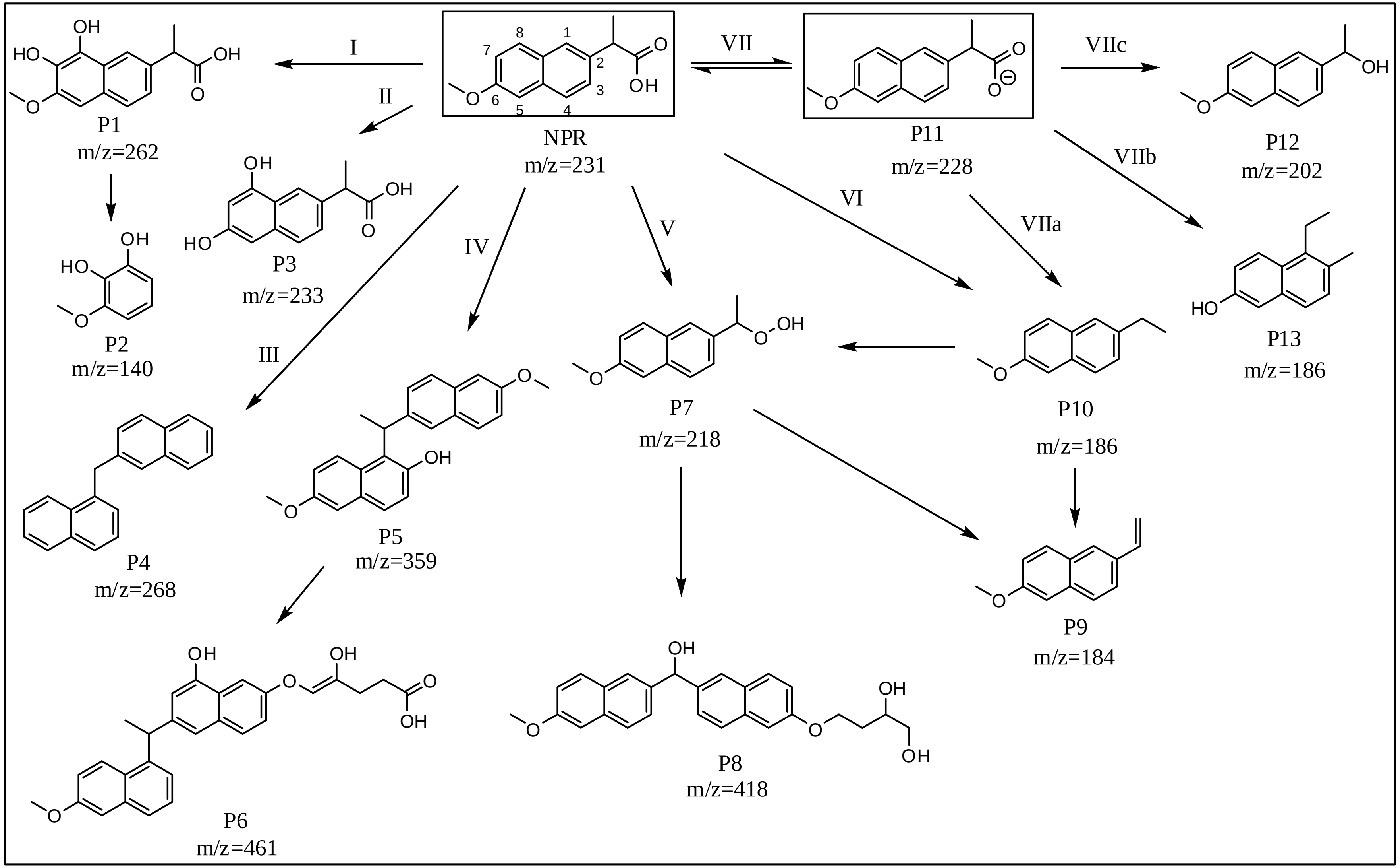








REACTION MECHANISM



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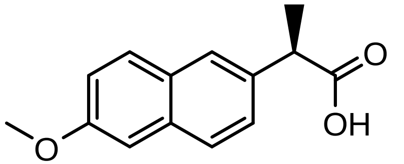


ACTIVATION ENERGY DETERMINATION AND KINETIC MODELS

$$r = k(T) \cdot C_{NPR}^{a}$$

$$r_{WAO} = \frac{R_{NPR}}{\nu_{NPR}} = \frac{dn_{NPR}}{\nu_{NPR} \cdot V \cdot dt} = \frac{-dC_{NPR}}{dt}$$

$$r_{CWAO} = \frac{R_{NPR}}{\nu_{NPR}} = \frac{dn_{NPR}}{\nu_{NPR} \cdot W \cdot dt} = \frac{V}{W}\left(\frac{-dC_{NPR}}{dt}\right)$$

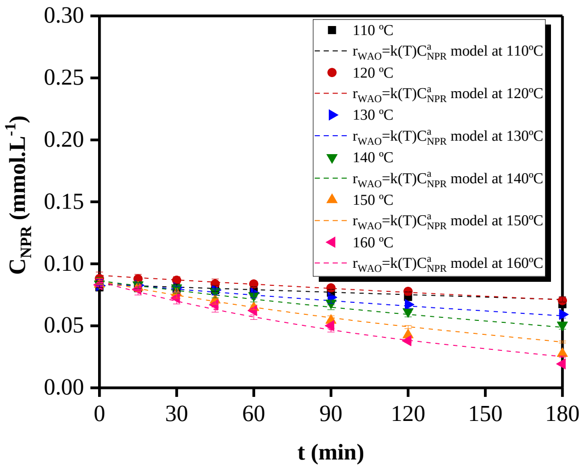
WAO

WAO reaction	Value
k_0 ($mmol^{1-a} \cdot L^{a-1} \cdot min^{-1}$)	4.298 x 10^4
E_a ($kJ \cdot mol^{-1}$)	56.48 ± 3.91
a	0.988 ± 0.003
R^2	0.966

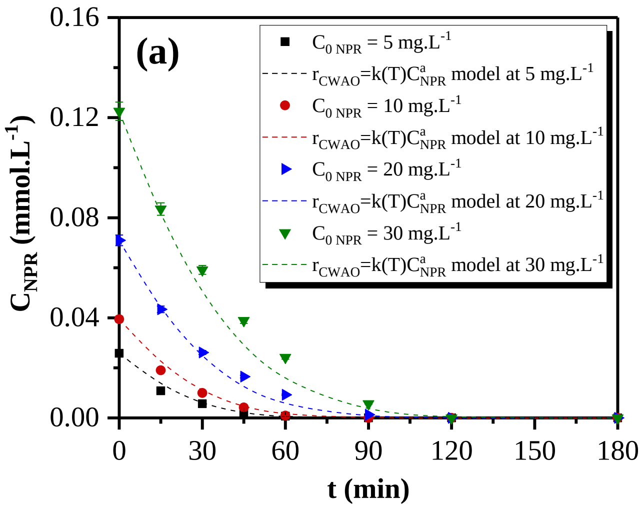
CWAO

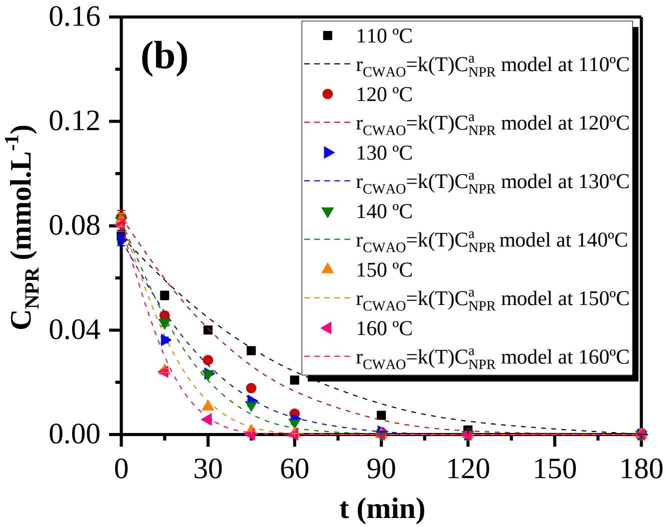
CWAO reaction	Value
k_0 ($mmol^{1-a} \cdot L^{a} \cdot g_{Ru}^{-1} \cdot min^{-1}$)	9.233 x 10^4
E_a ($kJ \cdot mol^{-1}$)	39.33 ± 2.08
a	0.72 ± 0.06
R^2	0.981

WAO: simulation ≠ T



CWAO: simulation ≠ T y ≠ C_0

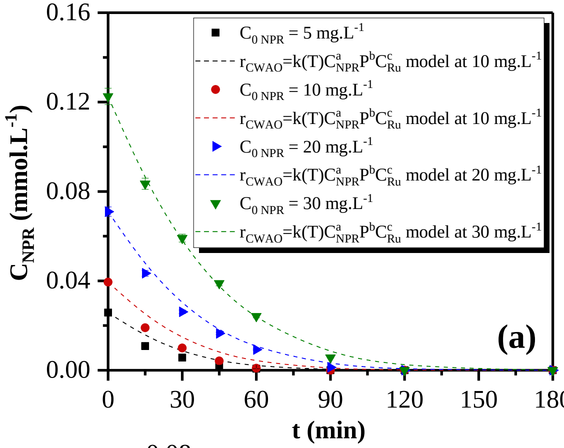


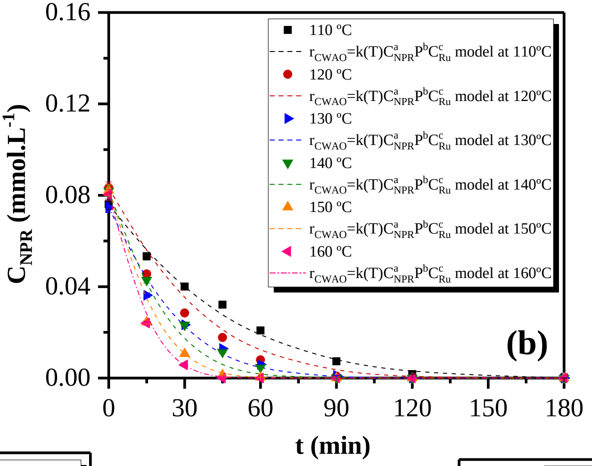


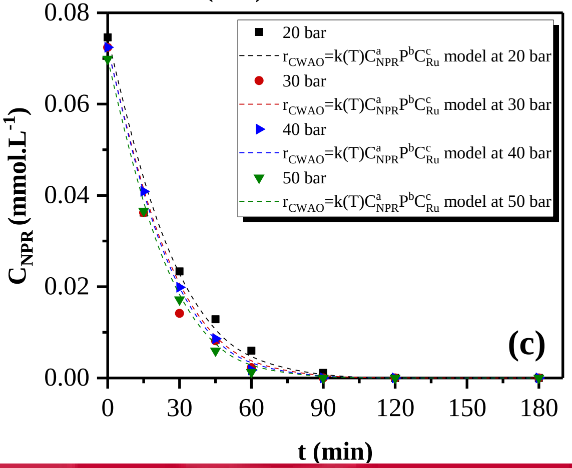
ACTIVATION ENERGY DETERMINATION AND KINETIC MODELS

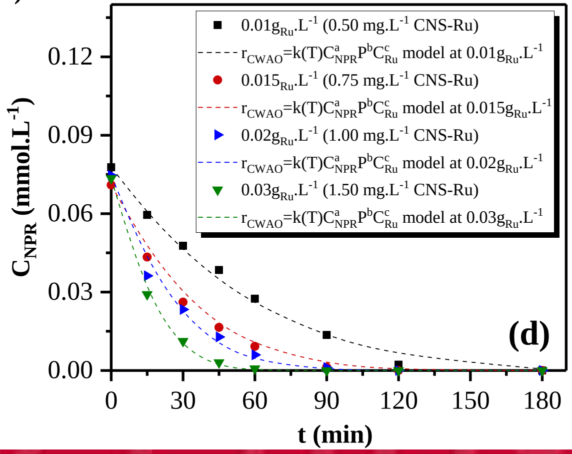
$$r = k(T)\cdot C_{NPR}^{\,a}\cdot P_{O_2}^{\,b}\cdot C_{Ru}^{\,c}$$

CWAO: simulation ≠ T, ≠ C_0, ≠ P and ≠ $m_{CNS\text{-}Ru}$ (g_{Ru}/L)



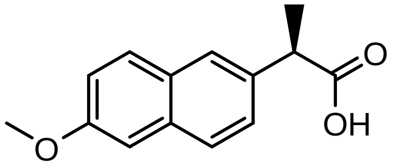






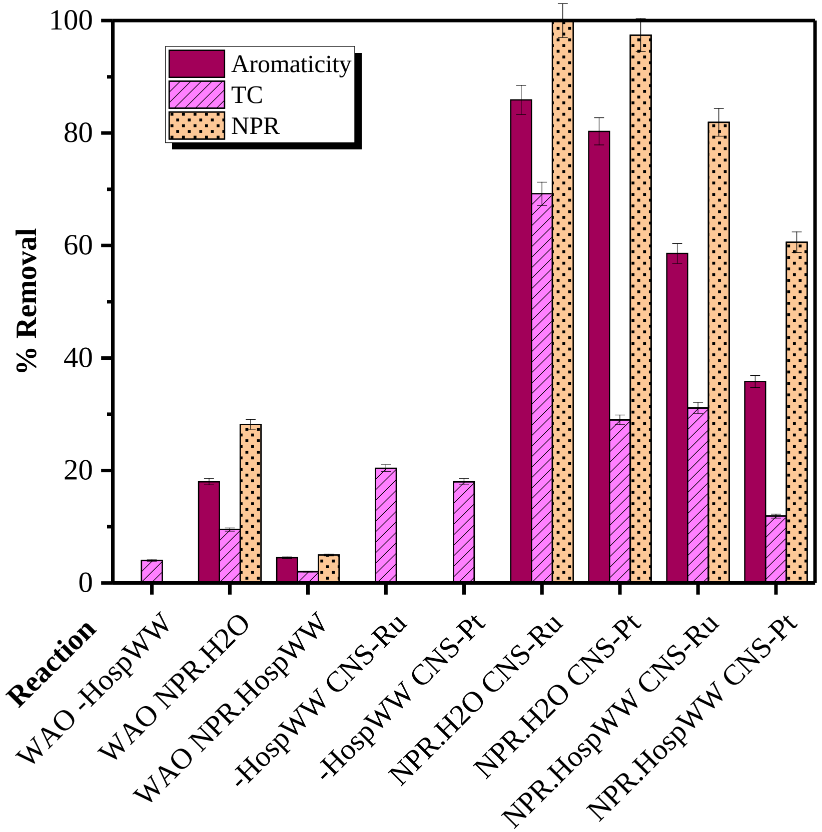
CWAO

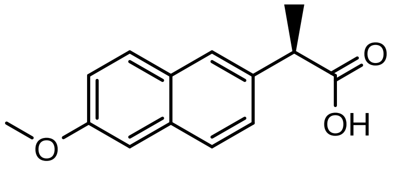
Variable	Value
k_0 (mmol^{1-a}·L^{a+c}·$g_{Ru}$$^{-1-c}$·min^{-1}·bar^{-b})	7.30 x 10^4
E_a (kJ·mol^{-1})	36.88 ± 1.37
a	0.77 ± 0.03
b	0.11 ± 0.05
c	1.13 ± 0.05
R^2	0.992



APPLICATION IN REAL MATRICES

Parameter	Value
pH	8.5
TC (mg·L⁻¹)	60
TN (mg·L⁻¹)	40
Conductivity at 20°C (mS·cm⁻²)	1.17
Aromaticity, $A_{254\ nm}$	0.17
NH^{4+} (mg·L⁻¹)	75
NO^{3-} (mg·L⁻¹)	0.64
COD (mg·L⁻¹)	365
Suspended solids concentration (mg·L⁻¹)	138
Phenolic compounds (mg·L⁻¹)	8.9

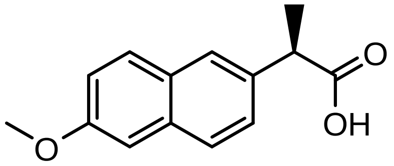




Aromaticity measured at 230 nm

NPR degradation in 180 min reaction time trend: *H_2O CNS-Ru* > *H_2O CNS-Pt* > *HospWW CNS-Ru* (82%) > *HospWW CNS-Pt* (61%) > *WAO H_2O* > *WAO HospWW*

TC removal: *NPR.H_2O CNS-Ru* > *NPR.HospWW CNS-Ru* (31.1%) > *NPR.H_2O CNS-Pt* (29%) > *-HospWW CNS-Ru* (20.4%) > *-HospWW CNS-Pt* (18%) > *NPR.HospWW CNS-Pt* (11.9%) > *WAO NPR.H_2O* (9.5%) > *WAO –HospWW* (4%) > *WAO NPR.HospWW* (2%)



CONCLUSIONS

- **Temperature**: the **highest influence** on the NPR degradation process.
- **Optimal conditions**: 130 °C, 20 bar and 75 mg of catalyst, being 20 mg / L the initial concentration of NPR and initial pH around the neutrality.

↓

Complete elimination of NPR in 90 min reaction time

- The **reuse of the catalyst**
- **Leaching** less than 2% and **formation of carbonaceous deposits** on the surface of the catalyst under the experimental conditions carried out.

↓

High stability CNS-Ru

- **Better activity CNS-Ru vs. CNS-Pt**
- **Applicability to real matrices**

ACKNOWLEDGMENTS

- Ph.D. Grant FPU2015/04075 to Ministerio de Educación, y Formación Profesional
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Effective removal of naproxen from aqueous solutions by CWAO process using noble metals supported on carbon nanospheres catalysts

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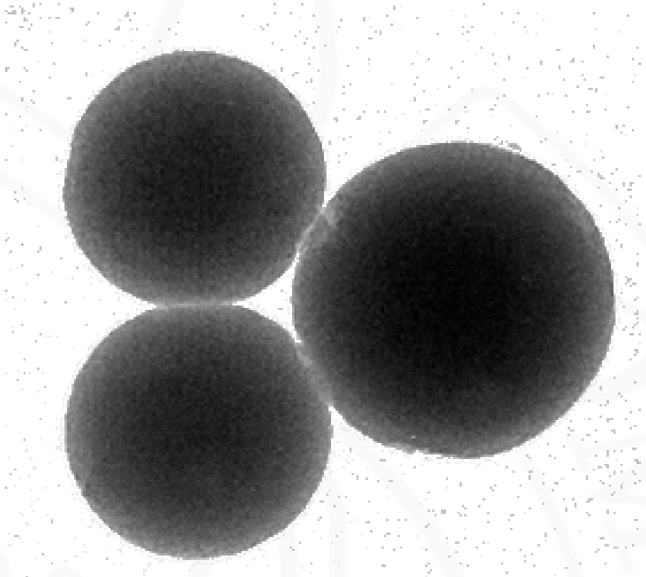

Thanks for your attention

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