



3<sup>er</sup> Congreso Iberoamericano  
4<sup>to</sup> Congreso Latinoamericano  
2<sup>do</sup> Simposio Internacional de Materiales Lignocelulósicos

# Biorrefinerías

Ciencia, Tecnología e Innovación para la Bioeconomía  
23 al 25 de noviembre de 2015, Concepción - Chile

## Kinetic model for the oxidation of hazardous compounds in an industrial effluent from forest biomass processing

Laura Covinich, Fernando Felissia, Rosa Fenoglio, María C. Area.

CONICET  
  
INTEMA



PROCYP

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# ADVANCED OXIDATION PROCESSES

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The main advantage of the Fenton process is that the reagents are safe to handle and environmentally benign.



It does not require highly complicated devices or pressurized systems for the oxidation process, making it technologically a viable for direct application on any scale.

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Therefore...



**The principal objective of this work was to propose a kinetic model for the reaction.**

## Experimental

**Black Liquor: 2mL**  
**Temp: 45/70/80°C**  
**[H<sub>2</sub>O<sub>2</sub>]: 1.78/2.43/3.54 g/L**  
**Catalyst mass: 0.5 g**

### Chemical properties of the effluent

Total Soluble Solids (g/L)	61.1
pH	7.4
COD (ppm)	46550
TOC (ppm)	21665
Ashes at 525°C (% of Total Soluble Solids)	52.3
Acetic acid (g/L)	23.6
Formic acid(g/L)	0.3
Propionic acid (g/L)	0.6

pH and  
temperature  
control



Preparation of the catalysts  
(incipient wetness  
impregnation)



Copper oxide  
supported on  
alumina

Batch  
Reactor  
250 mL

M00 sample

COD: 931 ppm  
TOC: 433 ppm

The final effluent  
(D: 1/50) was generated  
by dilution of the black  
liquor

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**240 min of  
oxidation  
reaction**

<b>Oxidation reaction</b>	<b>Temperature °C</b>	<b>[H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> g/L</b>
Ox 1	45	1.786
Ox 2	60	1.786
Ox 3	70	1.786
Ox 4	80	1.786
Ox 5	45	2.437
Ox 6	60	2.437
Ox 7	70	2.437
Ox 8	80	2.437

## **Catalytic reaction**

**Beginning**

**End**

**Oxidant  
dosage  
strategy**



**Time 0**

**Time 1**

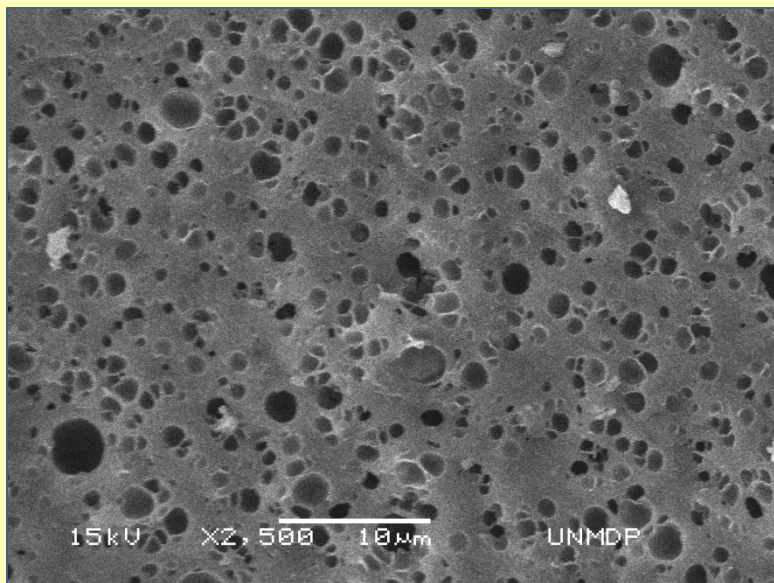
**Time n-1**

**Time n**

**240 min of  
oxidation  
reaction**

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# Catalysts characterization

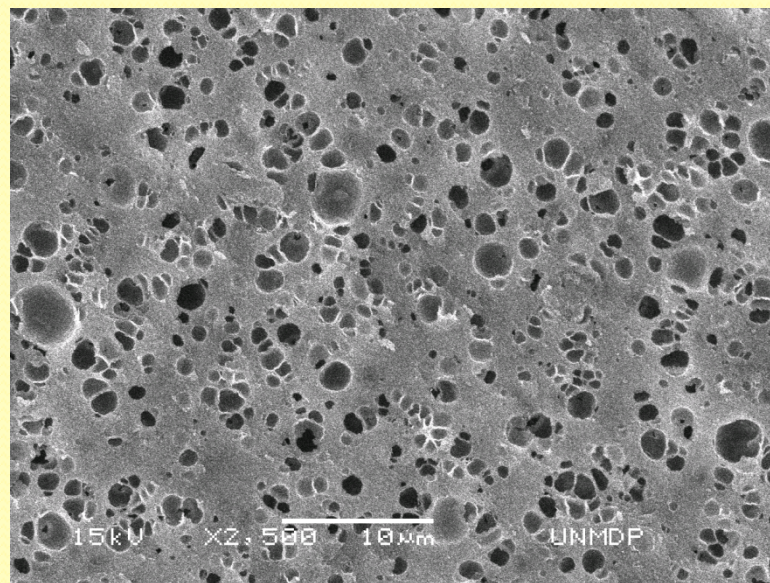
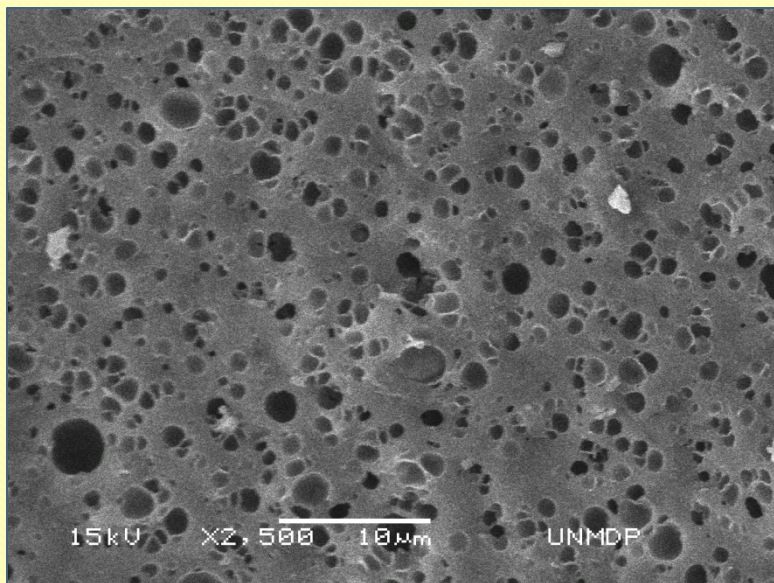


$\gamma\text{-Al}_2\text{O}_3$

200 m<sup>2</sup>/g

BET area (m<sup>2</sup>/g)

# Catalysts characterization



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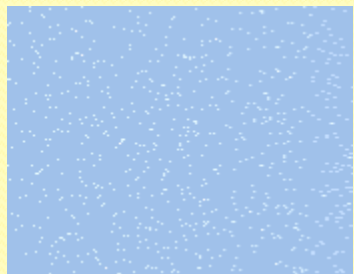
**$\text{CuO}/\gamma\text{-Al}_2\text{O}_3$**

**170 m<sup>2</sup>/g**

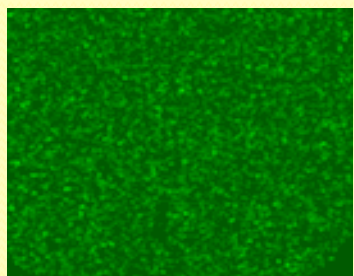
BET area (m<sup>2</sup>/g)

The catalysts show acceptable surface areas after calcination (900°C)

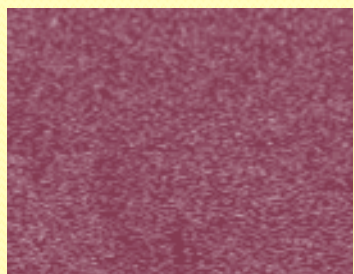
## Catalysts characterization



**Surface mappings reported a uniform distribution of copper onto the support**



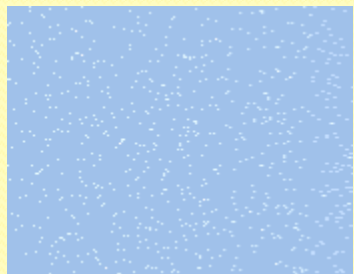
**Aluminium**



**Oxygen**

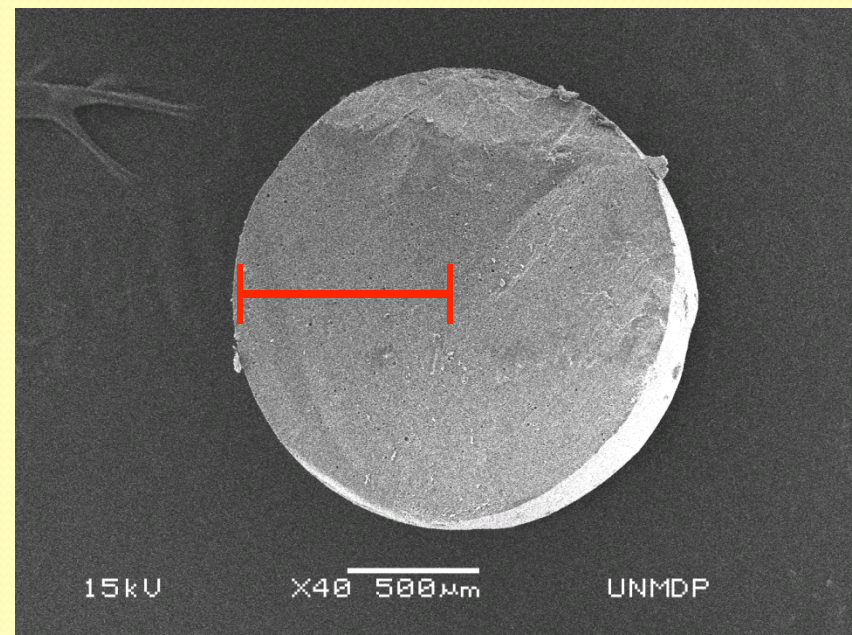
**$\gamma$ -Al<sub>2</sub>O<sub>3</sub> support**

## Catalysts characterization

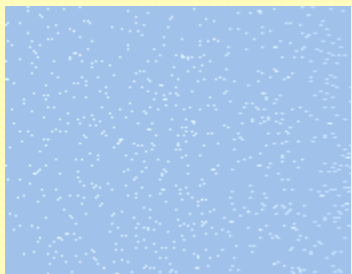


**Surface mappings reported a uniform distribution of copper onto the support**

**The composition of each catalyst was also determined as the average of 330 points from the surface to the center of the pellets, and remains almost constant through all the distance, indicating a uniform distribution of the active phase**

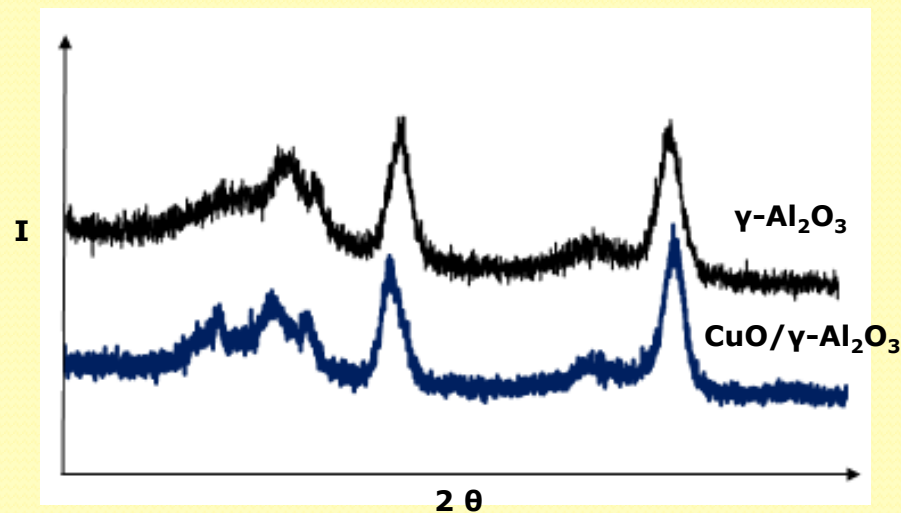


## Catalysts characterization



**Surface mappings reported a uniform distribution of copper onto the support**

**X-ray diffraction revealed only the presence of the characteristic peaks of the  $\gamma$ - $\text{Al}_2\text{O}_3$  phase, which means that the concentration of impregnated active phase is quite low and the formed particles are well dispersed copper oxides**



## **Kinetic study**

Variations of TOC in the performed oxidations can be divided into two stages

**"Seconds stage" and "Minutes Stage"**

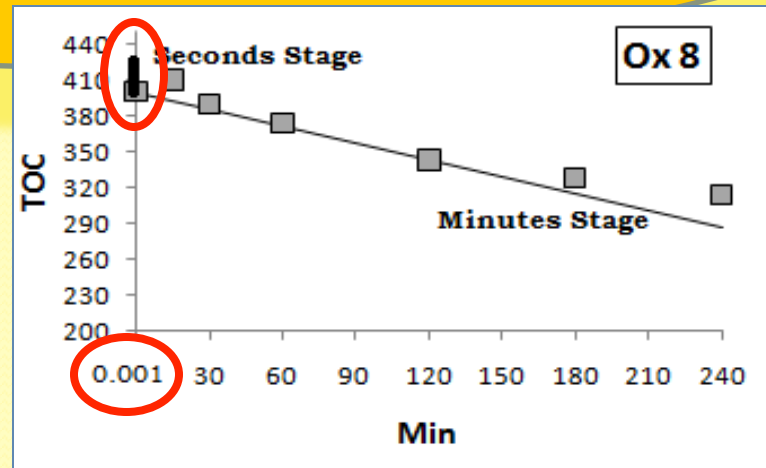


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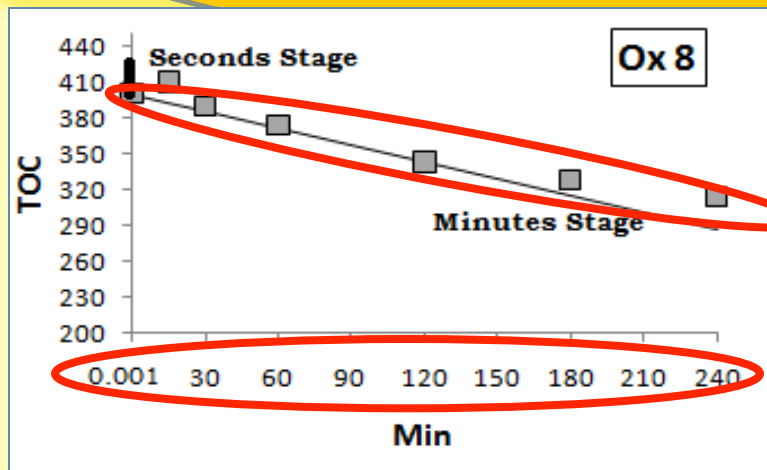
**The organic matter decreased abruptly**



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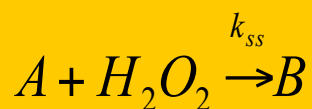
**“Seconds stage” and “Minutes Stage”**



**The organic matter decreased smoothly until the end of the reaction**

## Kinetic study

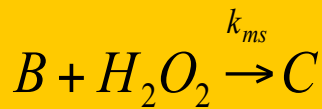
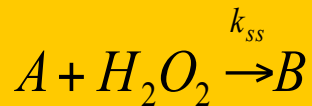
The "two step kinetic model" admits two sequential steps of oxidation, as follows:



Where unstable species easily oxidized are named as A, pollutants that are difficult to oxidize are designed as B, the desired final products (CO<sub>2</sub> and H<sub>2</sub>O) are commonly referred as C, and  $k_{ss}$  and  $k_{ms}$  correspond to the "seconds stage" and the "minutes stage" kinetics constants respectively.

## Kinetic study

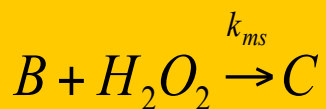
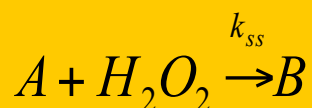
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The oxidation rates can be described by  
**pseudo-zero order kinetics.**

**This model is observed at catalyst surface saturation by the reactants**

**...and suggested that the rate of reaction in this study does not vary with their concentration.**

## Kinetic study

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Thus, kinetic reactions and the final kinetic expressions that are obtained from their integration can be represented as:

**"Seconds stage" and "Minutes Stage"**

$$-r_{TOC_A} = -\frac{dTOC_A}{dt} = f(TOC, k_{ss}) \rightarrow -\int_{TOC_A}^{TOC_B} \frac{dTOC_A}{f(TOC)} = k_{ss} \int_0^t dt$$

$$-r_{TOC_B} = -\frac{dTOC_B}{dt} = k_{ms} \rightarrow$$

$$TOC_C = TOC_B - k_{ms} * time$$

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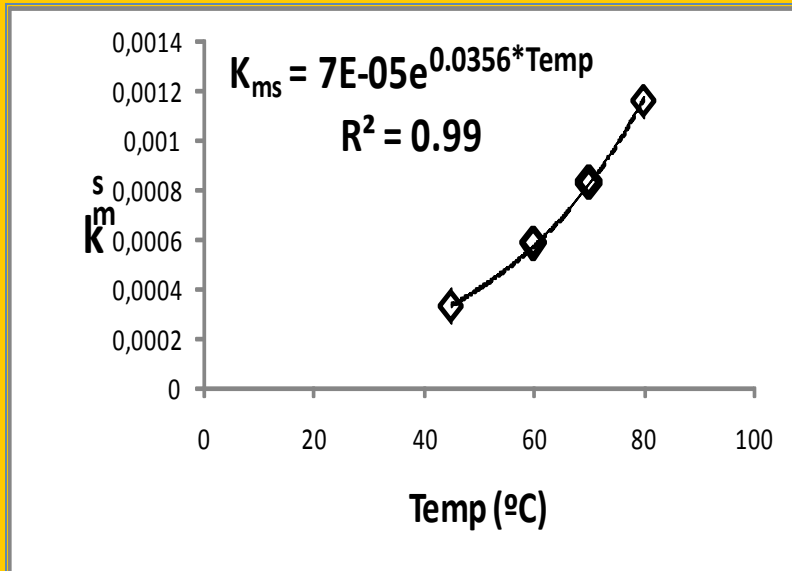
**"Seconds stage" and "Minutes Stage"**

$$-r_{TOC_B} = \frac{k_{ms}}{R}$$

$$R = \frac{[H_2O_2]_{oWork}}{[H_2O_2]_{oStoichiometric}}$$



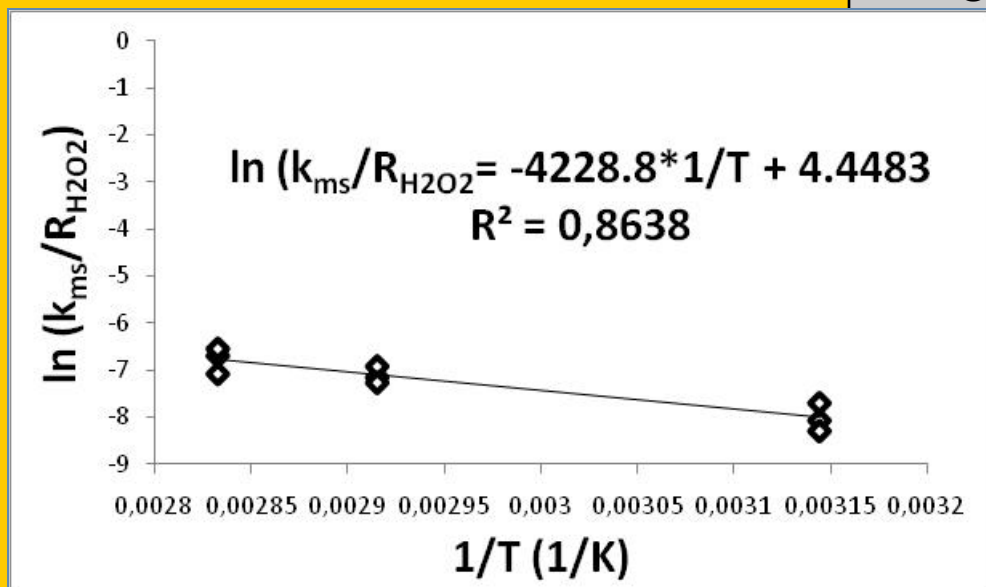
# Kinetic study



Oxidation reaction	$K_{ms} * R_{H2O2}$	$R^2$
Ox 1	5.36E-04	0.976
Ox 2	7.98E-04	0.943
Ox 3	1.33E-03	0.983
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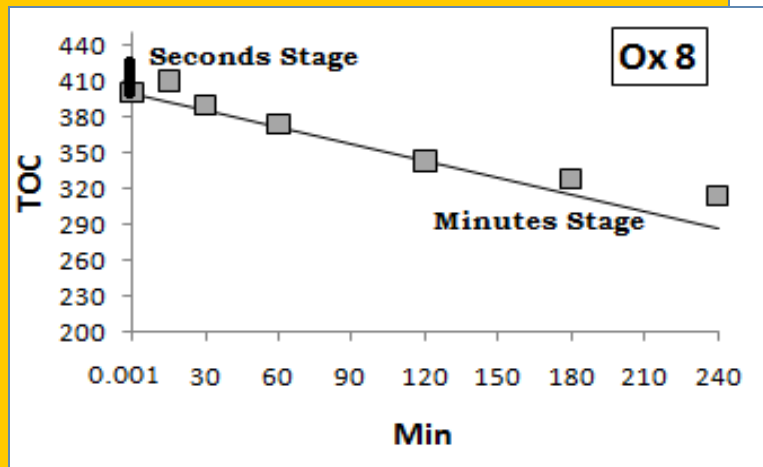
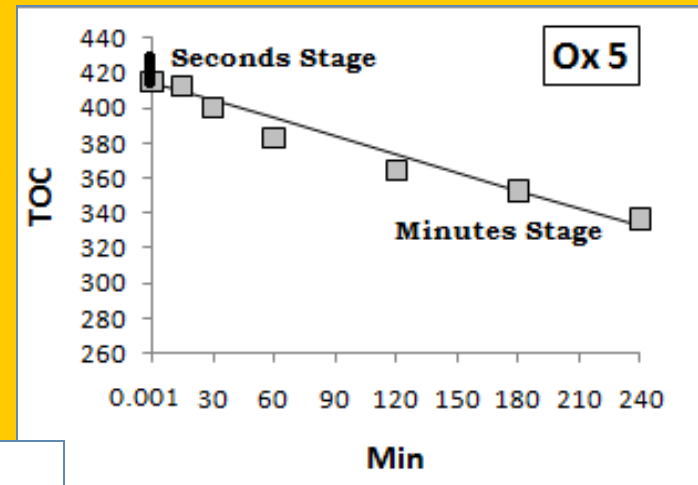
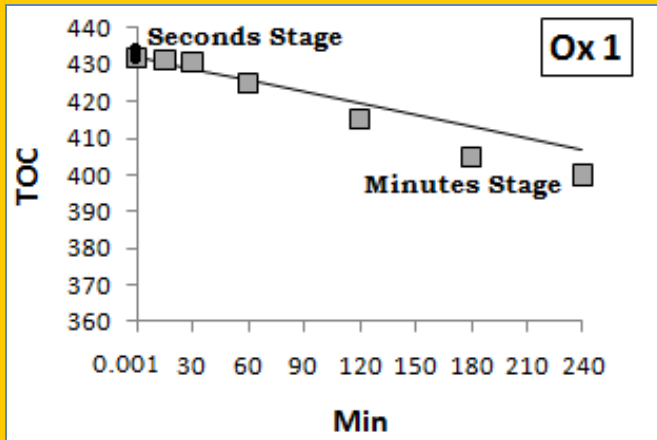
## Kinetic study

**TOC evolution along the oxidation reaction can be determined according to:**

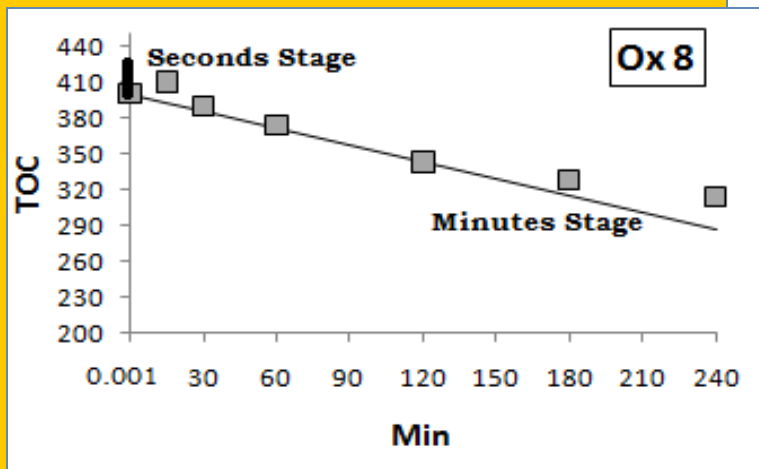
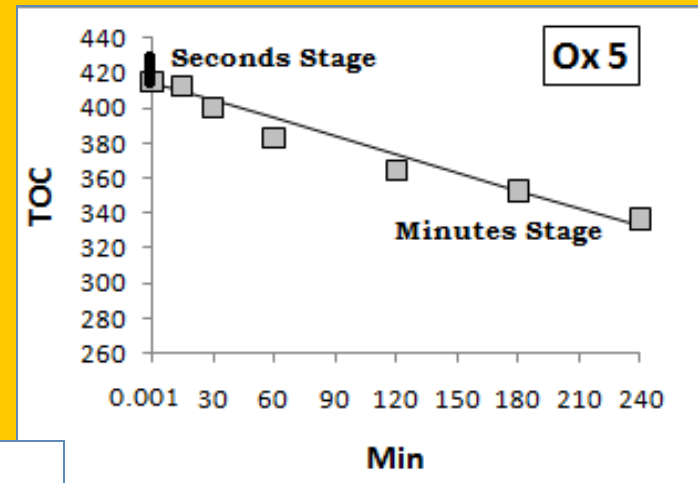
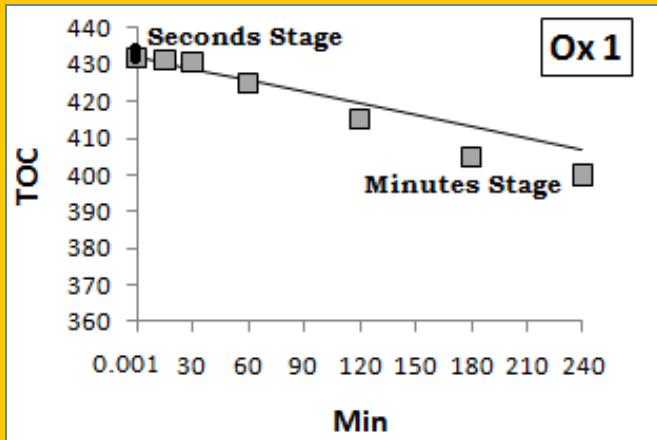
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$$\frac{TOC}{TOC_B} = \left(1 - \frac{A_o \exp\left(\frac{-E}{R * T}\right)}{R_{H_2O_2}} * time\right)$$

# Kinetic study



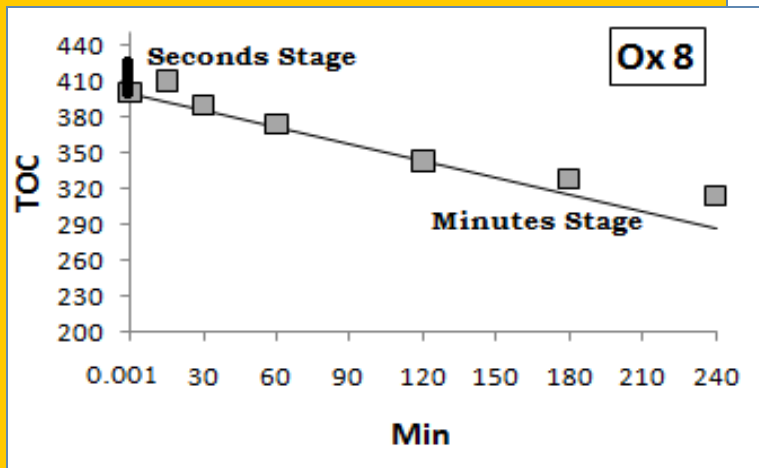
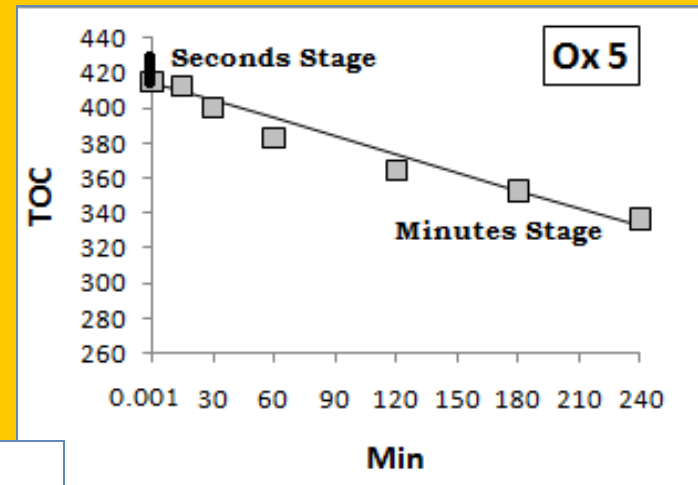
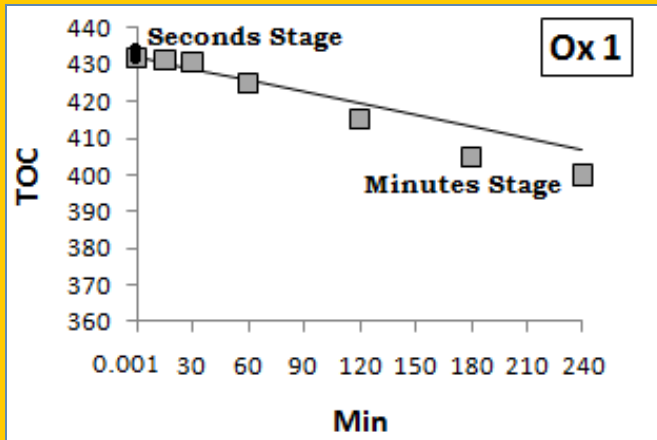
# Kinetic study



**Experimental TOC  
(points)**

**Calculated TOC (line)**

# Kinetic study



**Moo sample → 433 ppm**

**Time 0**

## **Conclusions**

**The obtained results are a clear indication that kinetic constants of black liquor degradation is significantly affected by reaction temperature and  $[\text{H}_2\text{O}_2]_0$  and that increased with the raising of these two parameters.**

# Conclusions

Suggests that the mobility of the reactants to the heterogeneous surface from the bulk medium and the converted products from the surface to the bulk medium are **more** favored by the applied thermal energy

are a clear constants of

black liquor degradation is significantly affected by reaction temperature and  $[H_2O_2]_0$  and that increased with the raising of these two parameters.



# Conclusions

**As  $\text{H}_2\text{O}_2$  concentration increases, the amount of hydroxyl radicals available for the oxidation of pollutants also increases and the removal of recalcitrant compounds increases as well.**

The obtained results indicate that the rate of black liquor degradation is significantly affected by reaction temperature and  $[\text{H}_2\text{O}_2]_0$ , and that increased with the raising of these two parameters.

## Conclusions

This model does not discriminate the presence of non-oxidizable matter in the initial mixture (mainly acetic acid). Being the remaining TOC along the reaction due to the presence of both, the refractory pollutants and oxidizable compounds.

## Conclusions

**Zero order** reactions are typically found when a material that is required for the reaction to proceed, such as a surface in **heterogeneous catalyst**.