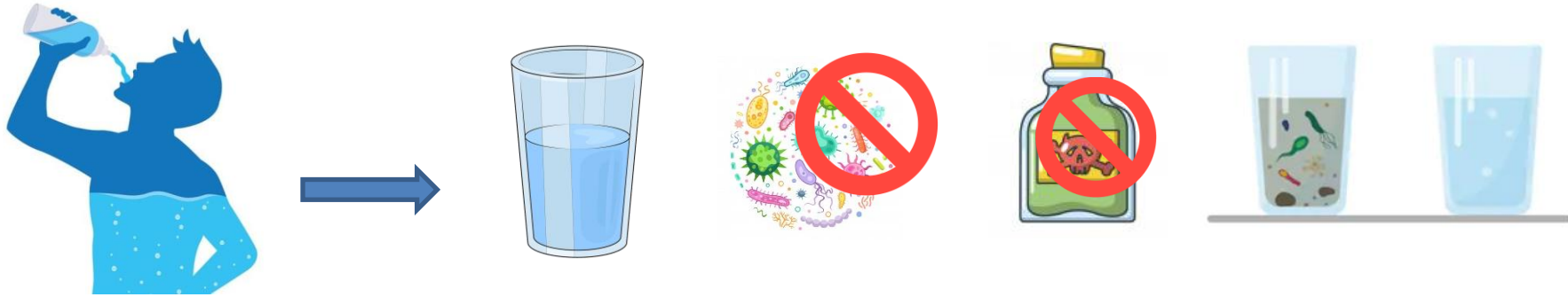# Application of catalytic hydrodehalogenation for the removal of the DBPs haloacetic acids.

*Julia Nieto-Sandoval, Esther Gómez-Herrero, Macarena Munoz, Zahara M. de Pedro and Jose A. Casas*
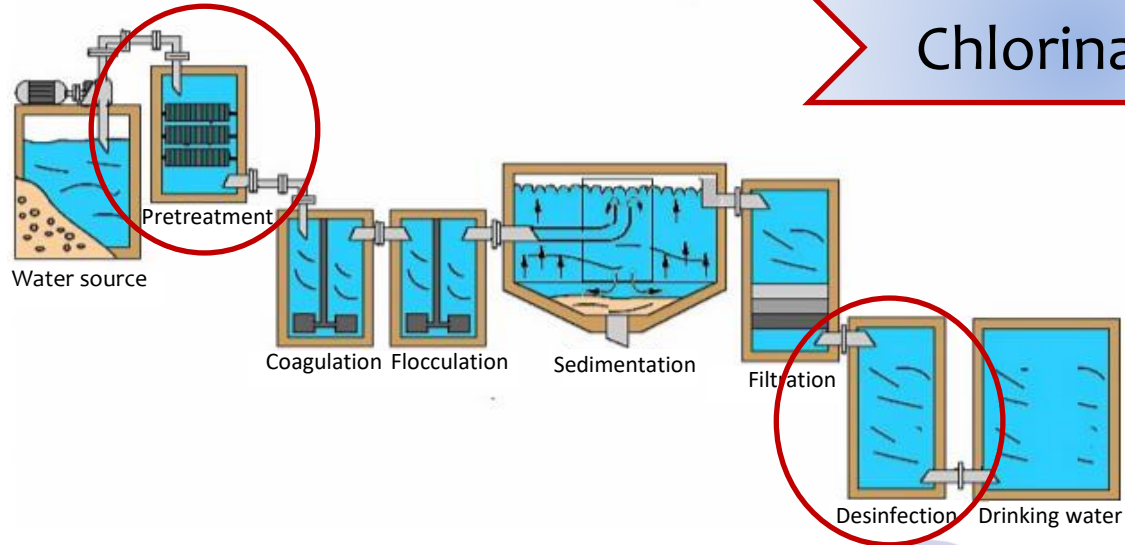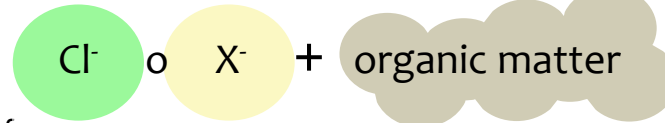


UAM
Universidad Autónoma de Madrid

Workshop "*Innovative technologies for sustainable management of urban and industrial waste streams*"

REMTAVARES

EM
La Suma de Todos

## Drinking water



## Drinking water treatment plant (DWTP)



Chlorination

Water source

Pretreatment

Coagulation  Flocculation

Sedimentation

Filtration

Desinfection  Drinking water

**Catalytic hydrodehalogenation (HDH)**

$$C_x H_y X_z + zH_2 \xrightarrow{\text{catalyst}} C_x H_{y+z} + zHX$$



Nobel metal
**+**
Support
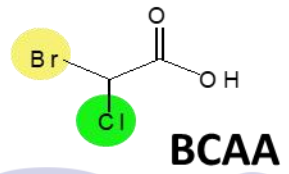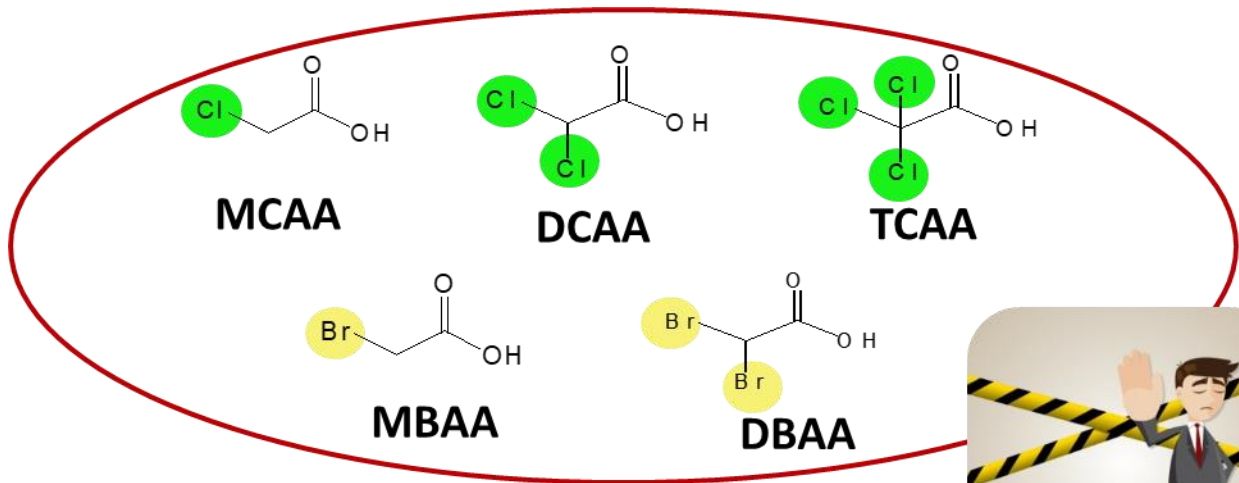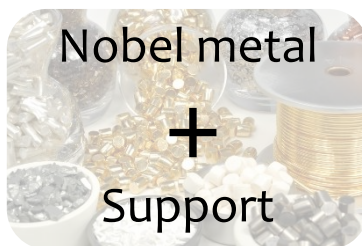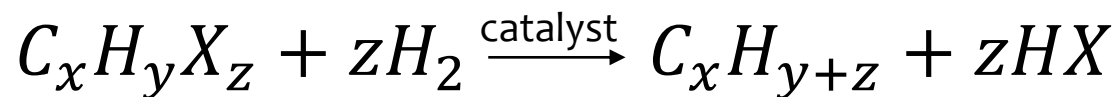
✓ Ecotoxicity abatement

✓ Ambient conditions
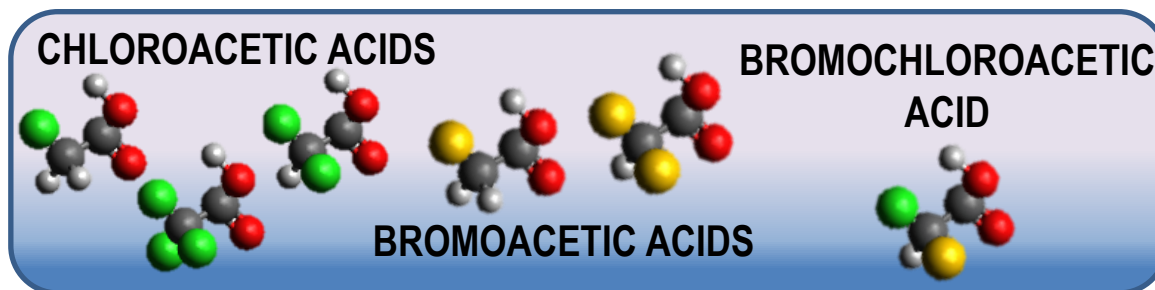
x High catalyst cost

x Catalytic deactivation

**Feasibility of HDH process for HAAs degradation.**



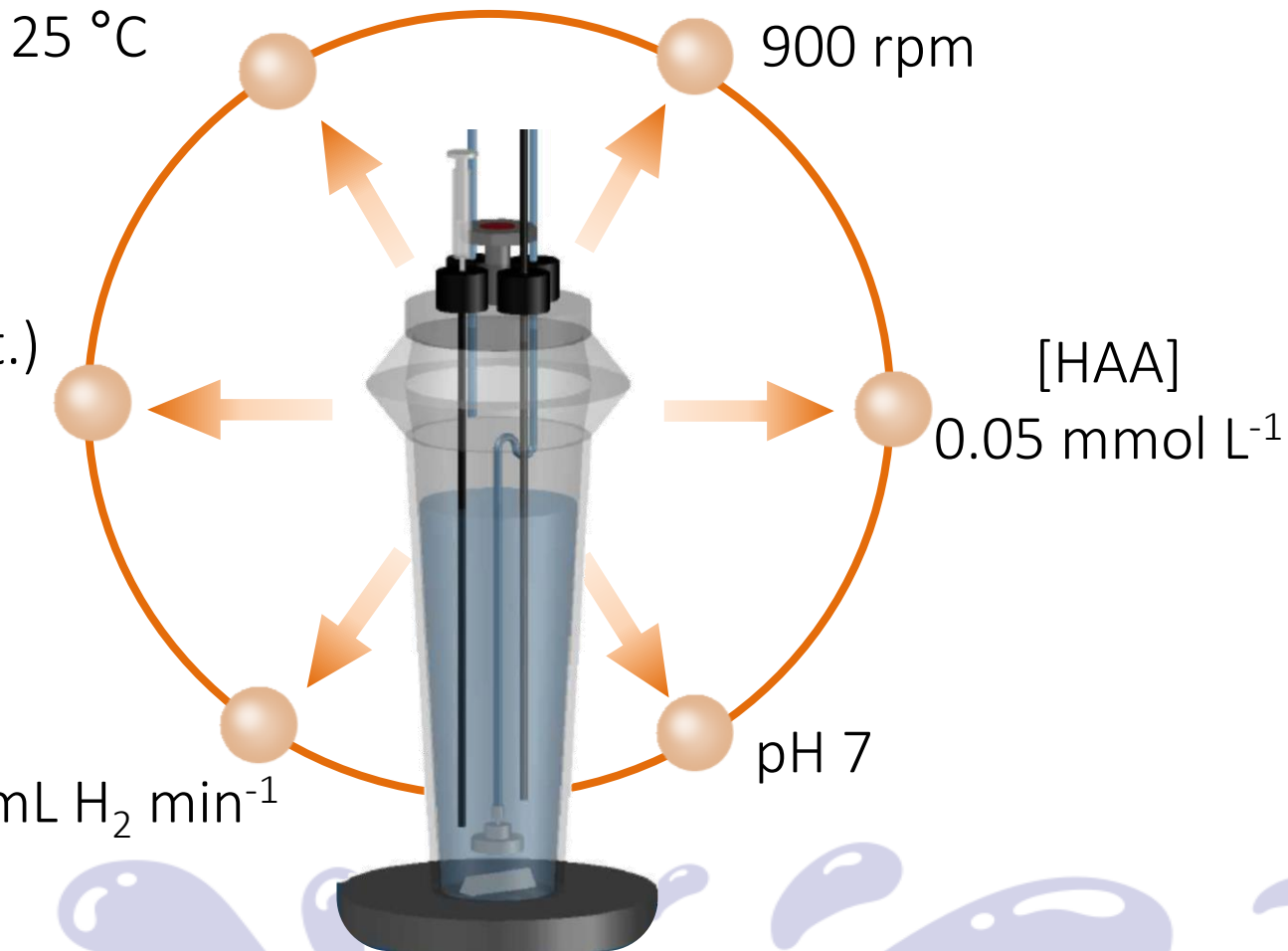- Effect of nature and number of subtituents.

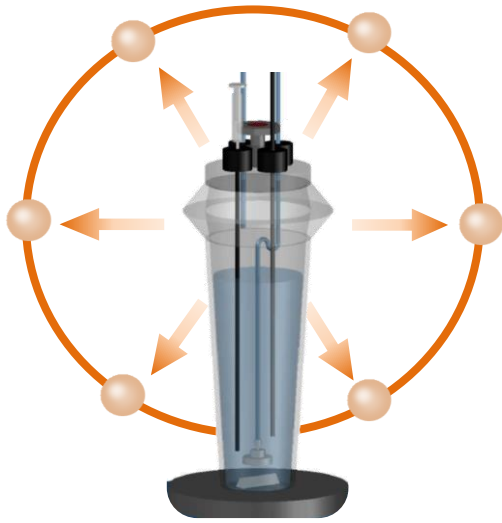- Reaction pathways of the HAAs.

- Kinetic model study.

# Materials and Methods



25 °C

900 rpm

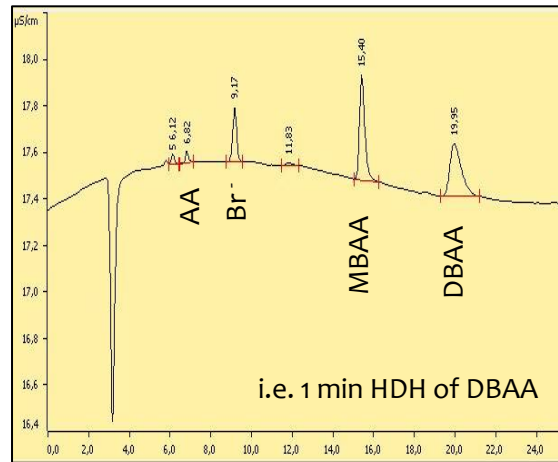Pd/Al$_2$O$_3$ (1% wt.)
(0.50 g L$^{-1}$)

[HAA]
0.05 mmol L$^{-1}$

50 N mL H$_2$ min$^{-1}$

pH 7

# Materials and Methods

**1** Catalyst separation: **centrifugation**

**2** Analysis method: **Ionic cromathography**

i.e. 1 min HDH of DBAA
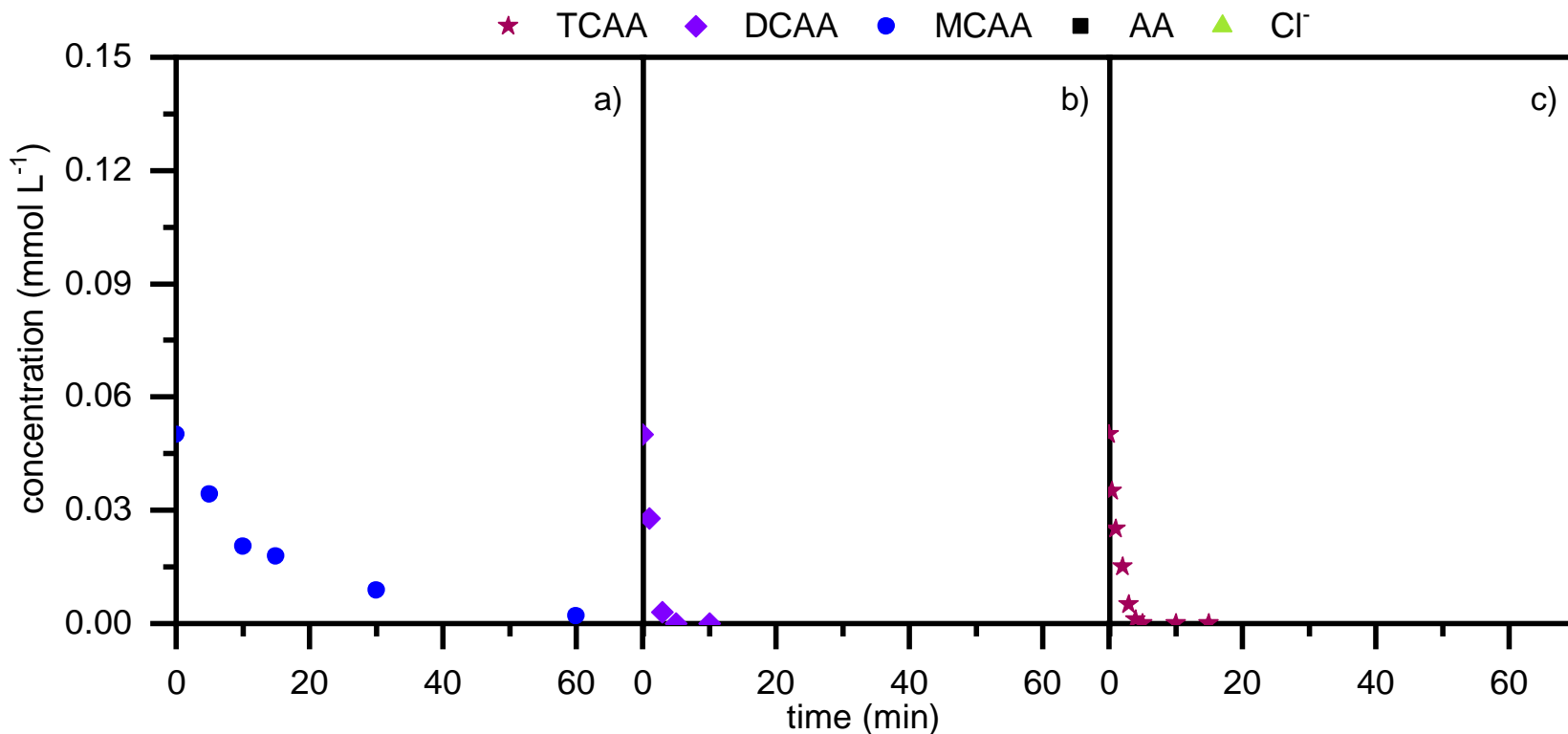
# Results

## CHLOROACETIC ACIDS

- **Adsorption < 20%**

# Results

## CHLOROACETIC ACIDS

Operating conditions
$[HAA]_0 = 0.05$ mmol $L^{-1}$
$[Pd/Al_2O_3] = 0.5$ g $L^{-1}$
$H_2 = 50$ N mL $min^{-1}$
T= 25 °C

- **Adsorption < 20%**

**Operating conditions**

$[HAA]_0 = 0.05$ mmol $L^{-1}$
$[Pd/Al_2O_3] = 0.5$ g $L^{-1}$
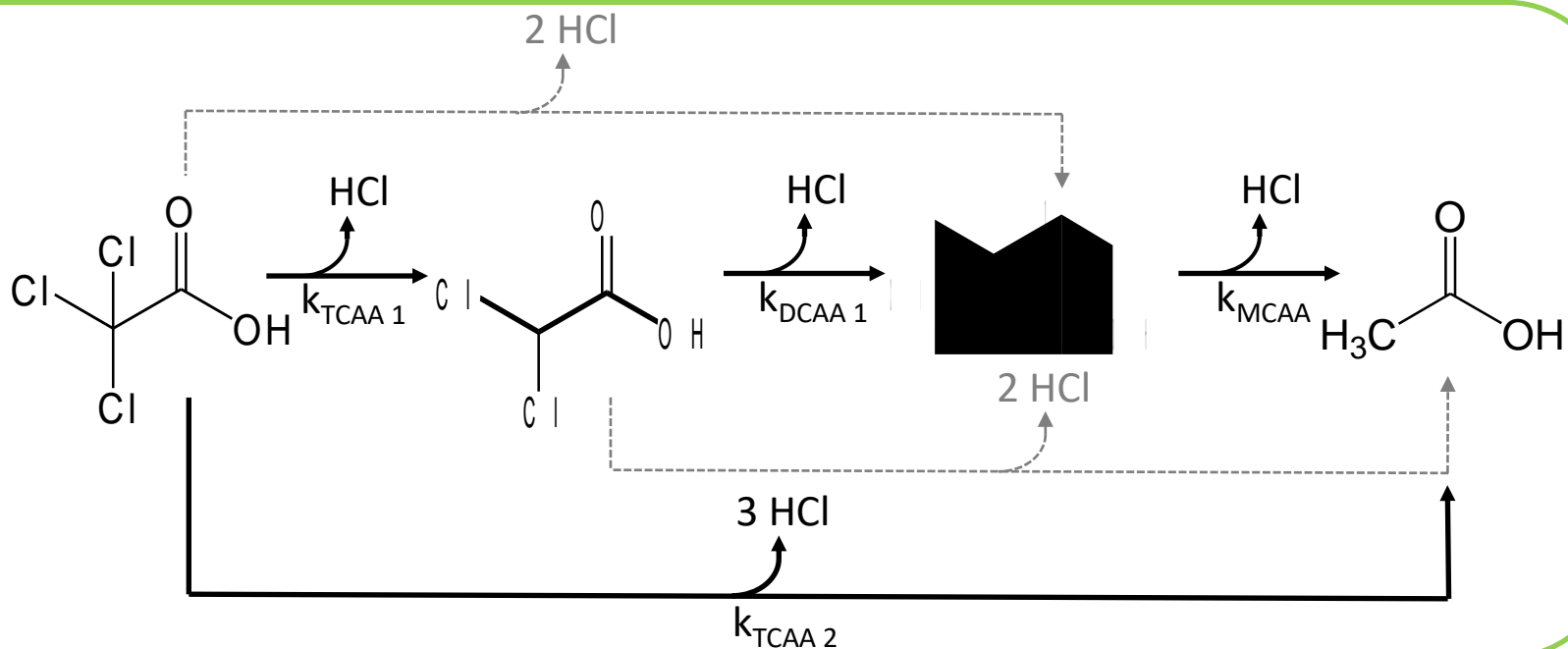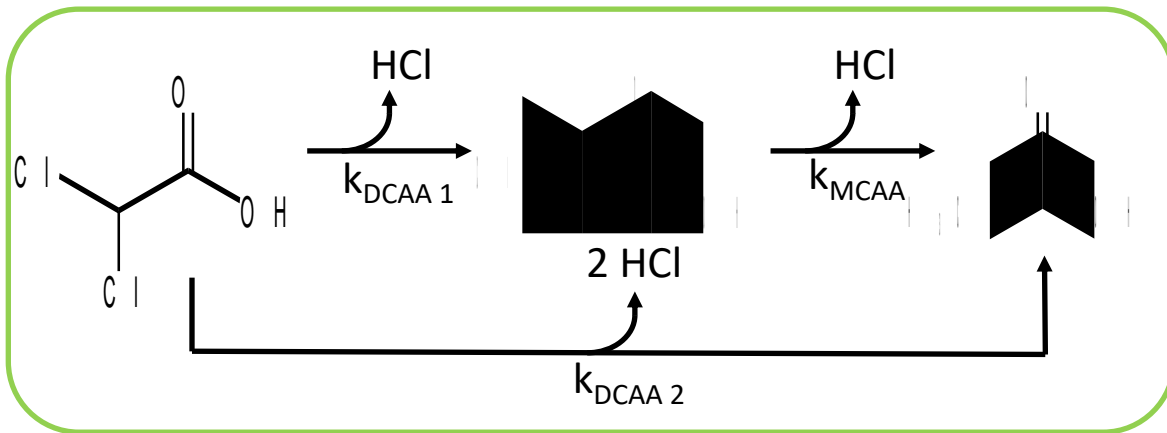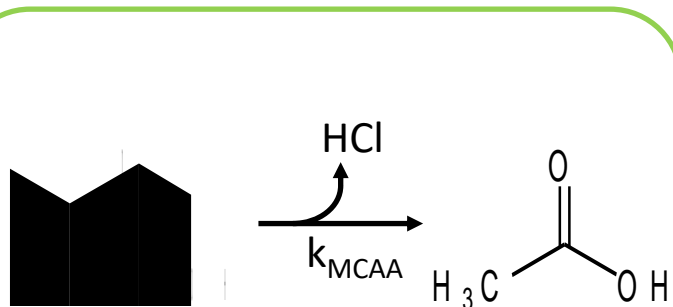$H_2 = 50$ N mL $min^{-1}$
$T= 25$ ºC
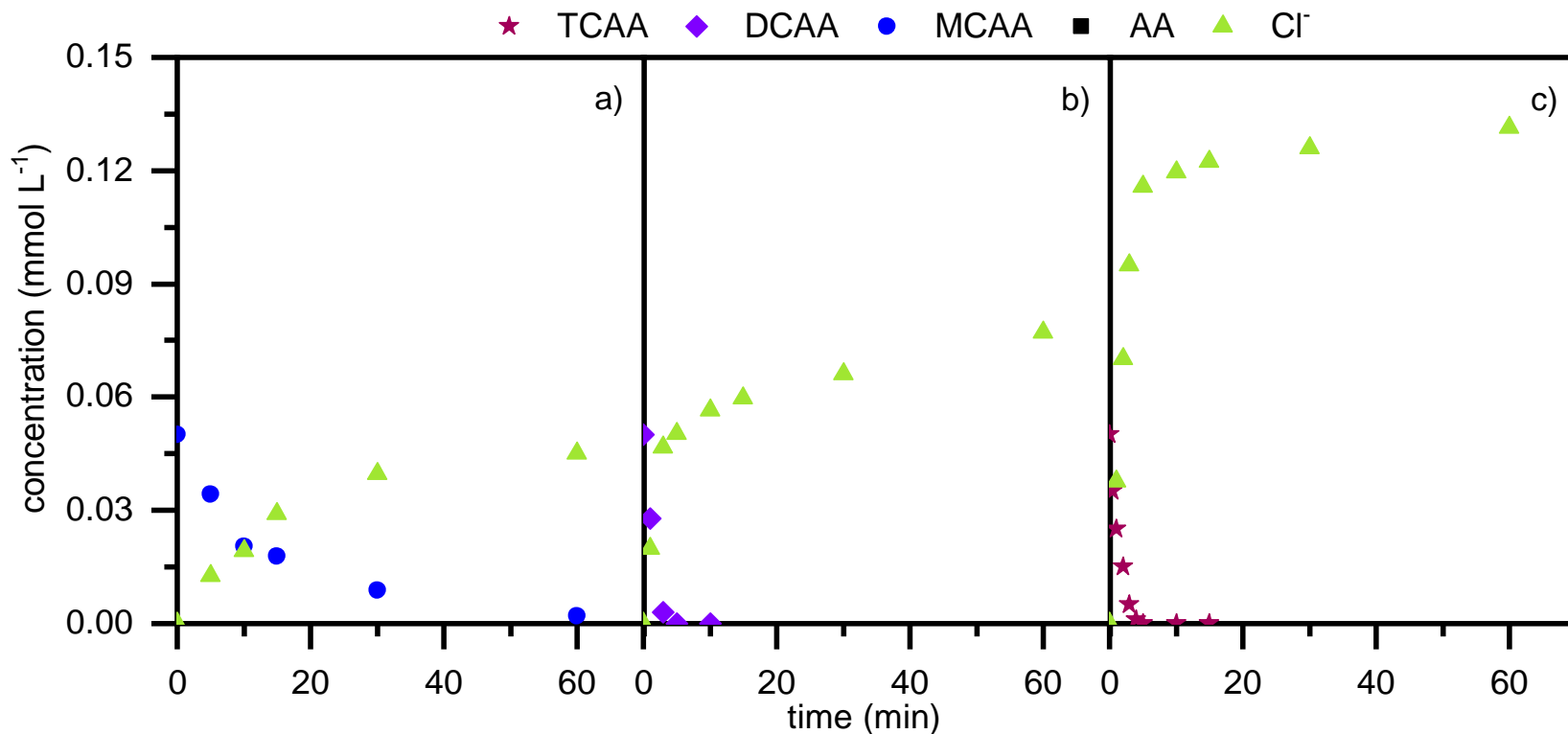
## CHLOROACETIC ACIDS

- **Adsorption < 20%**
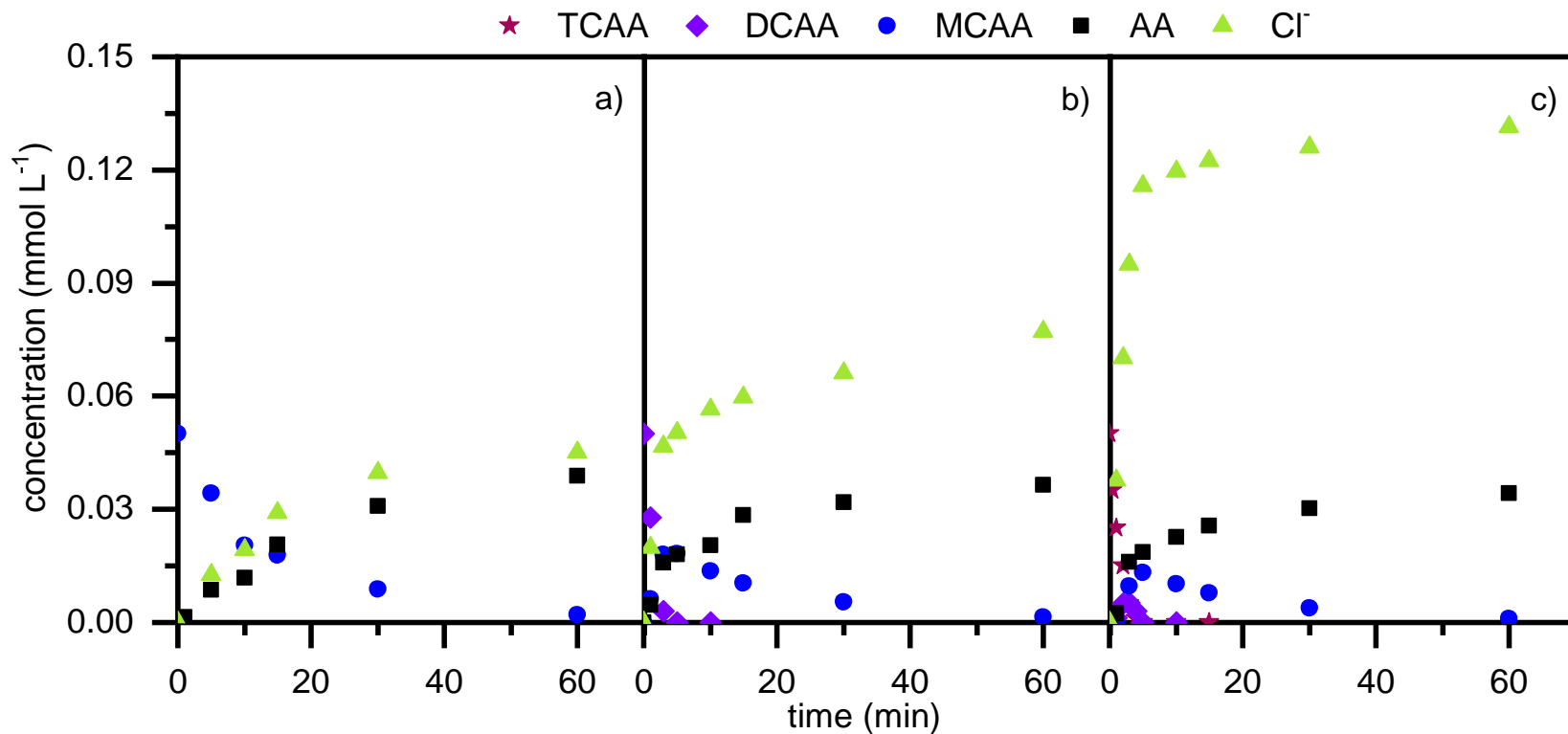
# Reaction pathways

**CHLOROACETIC ACIDS**

# Kinetic model: DCAA

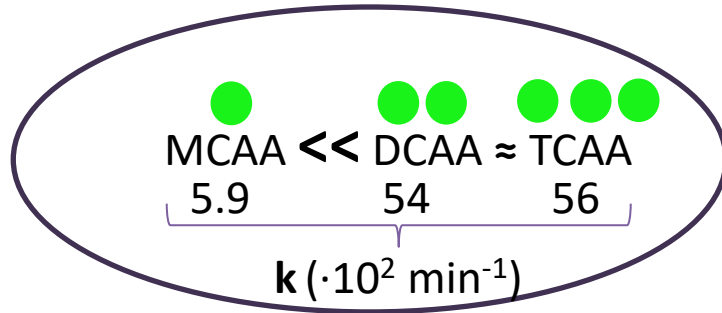$$\frac{dC_{DCAA}}{dt} = -(k_{DCAA\,1} + k_{DCAA\,2}) \cdot C_{DCAA}$$

$$\frac{dC_{MCAA}}{dt} = k_{DCAA\,1} \cdot C_{DCAA} - k_{MCAA} \cdot C_{MCAA}$$

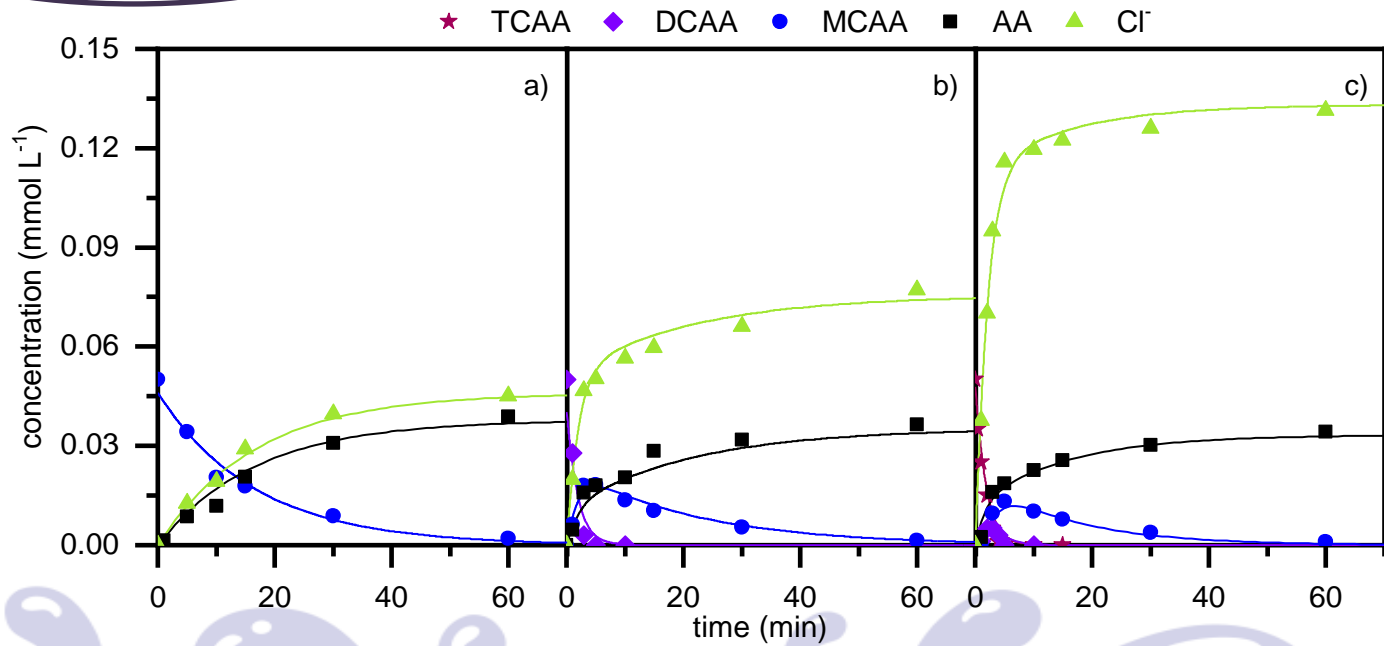$$\frac{dC_{AA}}{dt} = k_{DCAA\,2} \cdot C_{DCAA} + k_{MCAA} \cdot C_{MCAA}$$

$$\frac{dC_{Cl^-}}{dt} = (k_{DCAA\,1} + 2 \cdot k_{DCAA\,2}) \cdot C_{DCAA} + k_{MCAA} \cdot C_{MCAA}$$

Universidad Autónoma de Madrid

**CHLOROACETIC ACIDS**

MCAA **<<** DCAA ≈ TCAA
5.9      54      56

$k$ ($\cdot 10^2$ min$^{-1}$)

|  | MCAA | DCAA | TCAA |
|---|---|---|---|
| $k_{MCAA}$ ($\cdot 10^2$ min$^{-1}$) | 5.9 | 4.6 | 6.5 |
| $k_{DCAA\ 1}$ ($\cdot 10^2$ min$^{-1}$) |  | 36.3 | 60.0 |
| $k_{DCAA\ 2}$ ($\cdot 10^2$ min$^{-1}$) |  | 17.7 |  |
| $k_{TCAA\ 1}$ ($\cdot 10^2$ min$^{-1}$) |  |  | 25.7 |
| $k_{TCAA\ 2}$ ($\cdot 10^2$ min$^{-1}$) |  |  | 30.2 |
| $r^2$ | 0.98 | 0.99 | 0.99 |

# Results

## BROMOACETIC ACIDS

**Adsorption < 20%**

BROMOACETIC ACIDS

Operating conditions
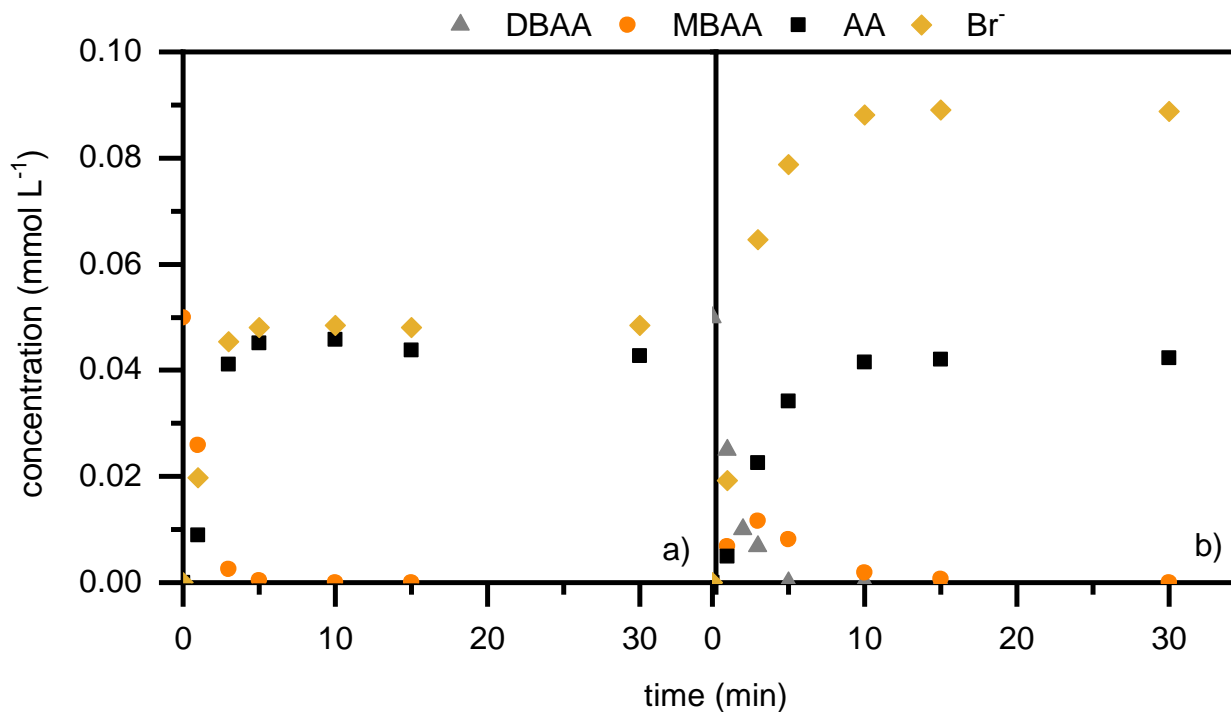$[HAA]_0 = 0.05$ mmol $L^{-1}$
$[Pd/Al_2O_3] = 0.5$ g $L^{-1}$
$H_2 = 50$ N mL $min^{-1}$
T= 25 ⁰C

Adsorption <20%

**BROMOACETIC ACIDS**

## Reaction pathways
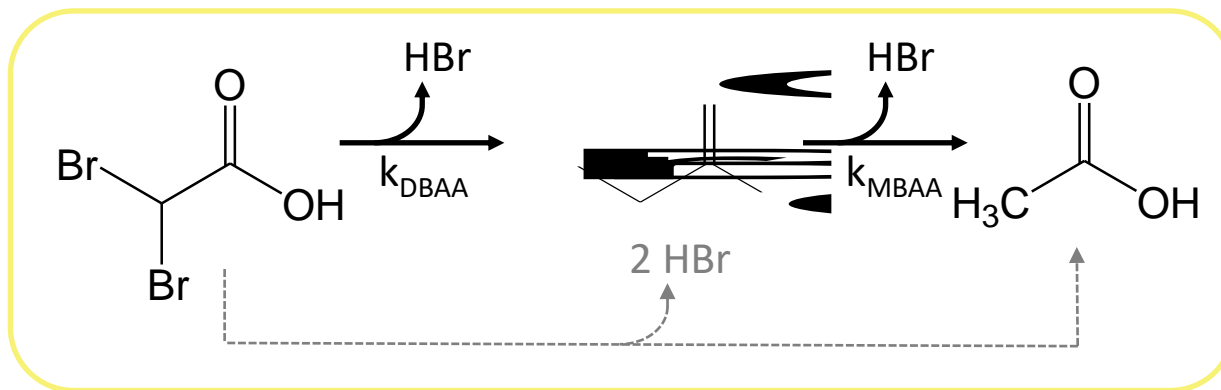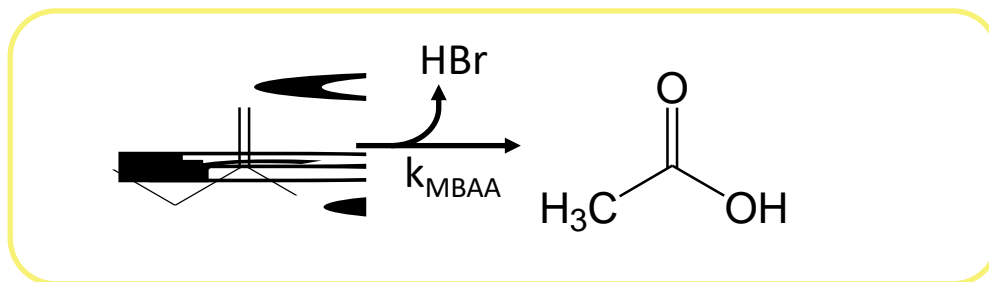
## Results

### BROMOACETIC ACIDS

MBAA ≈ DBAA

62.3      54

$k\,(\cdot 10^2\ min^{-1})$

MCAA << MBAA

5.9      62.3

$k\,(\cdot 10^2\ min^{-1})$

| | MBAA | DBAA |
|---|---|---|
| $k_{MBAA}\,(\cdot 10^2\ min^{-1})$ | 62.3 | 74.8 |
| $k_{DBAA}\,(\cdot 10^2\ min^{-1})$ | | 54.0 |
| $r^2$ | 0.98 | 0.99 |

DBAA ▲   MBAA ●   AA ■   Br⁻ ◆
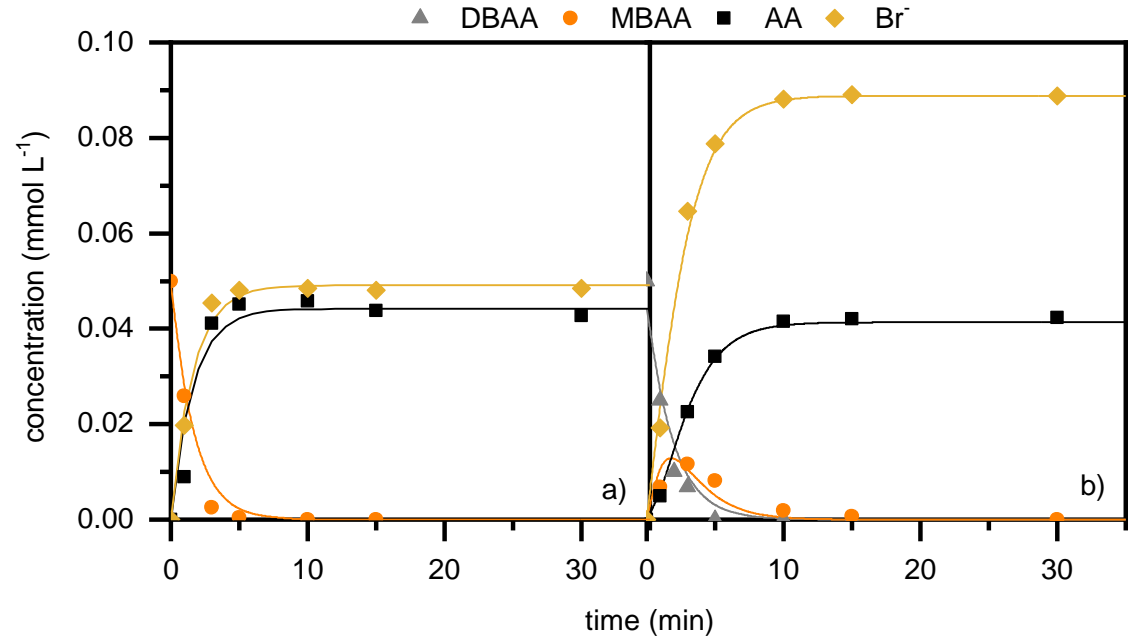
**Operating conditions**

$[HAA]_0 = 0.05$ mmol $L^{-1}$

$[Pd/Al_2O_3] = 0.5$ g $L^{-1}$

$H_2 = 50$ N mL $min^{-1}$

T= 25 °C

## BROMOCHLOROACETIC ACID

**Adsorption 30%**
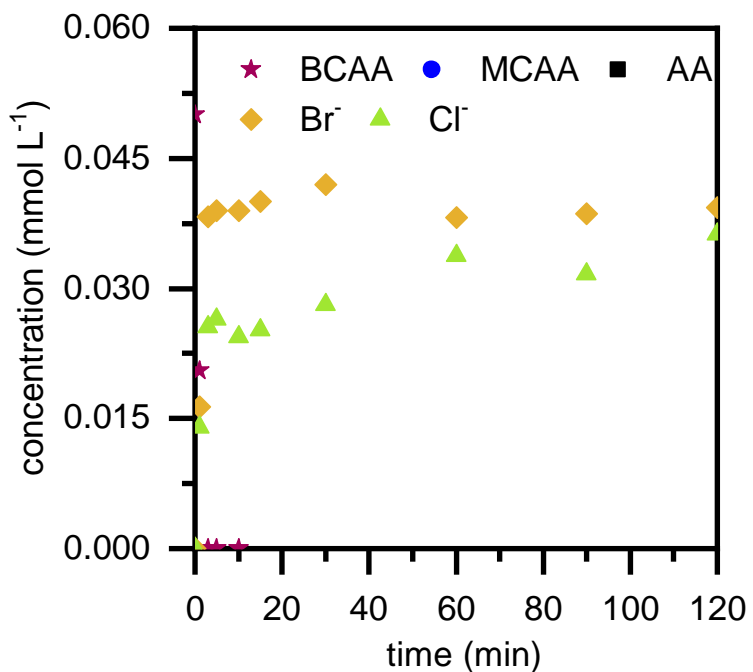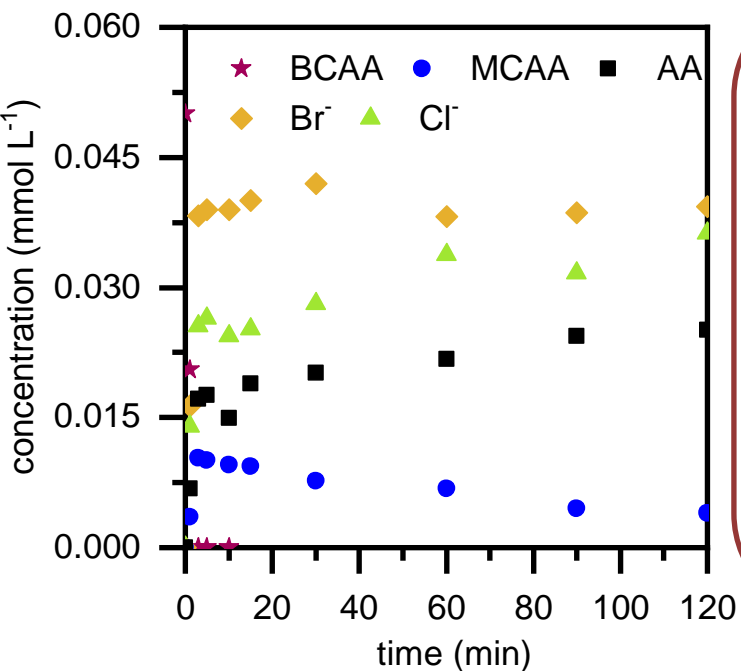


## Reaction pathway
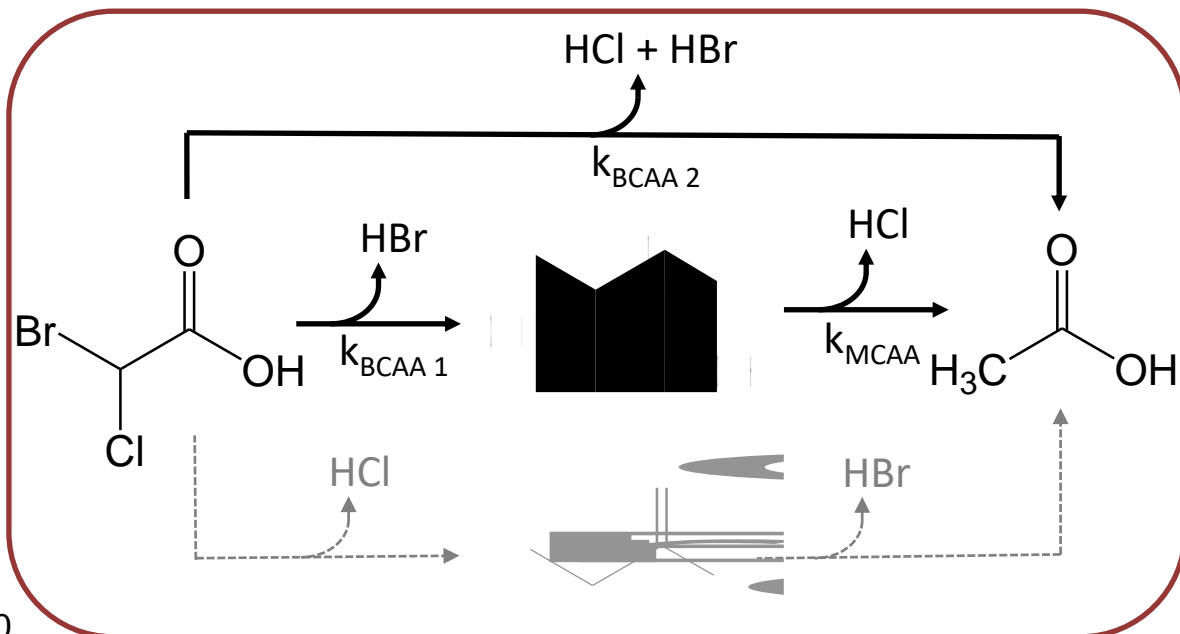
Results

BROMOCHLOROACETIC ACID
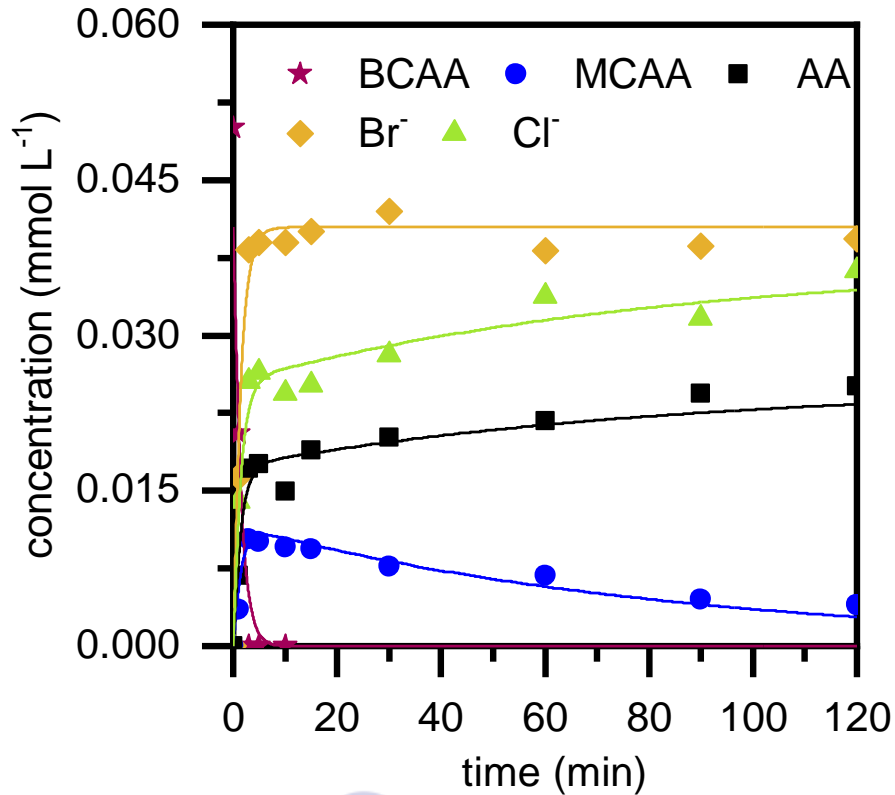
| | BCAA |
|---|---|
| $k_{MCAA}$ ($\cdot 10^2$ min$^{-1}$) | 1.2 |
| $k_{BCAA\ 1}$ ($\cdot 10^2$ min$^{-1}$) | 26.4 |
| $k_{BCAA\ 2}$ ($\cdot 10^2$ min$^{-1}$) | 46.0 |
| $r^2$ | 0.98 |

BCAA
$k$ ($\cdot 10^2$ min$^{-1}$) = 72.4

# Conclusions

**HDH** has a **potential** capability using Pd/Al$_2$O$_3$ catalyst to **eliminate the HAAs**.

- Influence of the **subtituents** number: TCAA ≈ DCAA >>MCAA

- Influence of **nature:** MBAA>>MCAA

- Sequencial and concerted reaction pathways.

- BCAA showed the highest degradation rate.

# Conclusions

Universidad Autónoma de Madrid

I&EC research
Industrial & Engineering Chemistry Research

Article

## Catalytic Hydrodehalogenation of Haloacetic Acids: A Kinetic Study

Julia Nieto-Sandoval,* Esther Gomez-Herrero, Ferdaus El Morabet, Macarena Munoz,* Zahara M. de Pedro, and Jose A. Casas

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Haloacetic acids (HAAs) are undesired halogenated byproducts commonly generated upon oxidation treatments carried out in drinking water treatment plants. In this work, the removal of a representative group of these hazardous species (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid, and bromochloroacetic acid) by catalytic hydrodehalogenation (HDH) was investigated and kinetic models were accordingly developed. Complete dehalogenation of all these pollutants (0.05 mmol $L^{-1}$) was achieved using a $Pd/Al_2O_3$ catalyst (0.5 g $L^{-1}$), although it was found that their reactivity depended on the nature and number of halogen substituents present in the HAA molecule. In general, bromoacetic acids showed higher reactivity than the chlorinated ones, which was attributed to the lower C-X bond dissociation energy. On the other hand, while the chloroacetic acid reactivity increased with the chlorination degree of the molecule, particularly from one to two Cl substituents, the bromoacetic acids did not show higher reaction rates with the increase in Br substituents. Based on the results obtained, different reaction pathways, via stepwise and/or concerted reactions, were proposed for the HDH of the HAAs. Consistent with those pathways, kinetic models were also developed, which allowed describing successfully the experimental data.
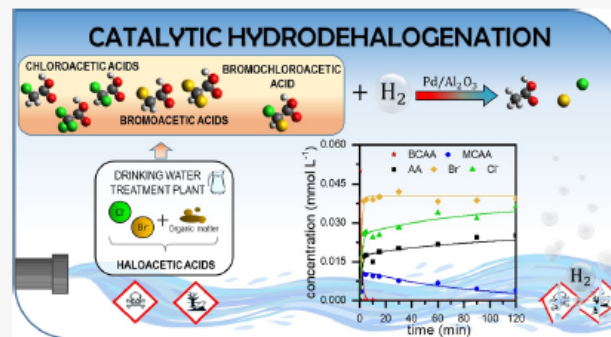
# Further investigation…

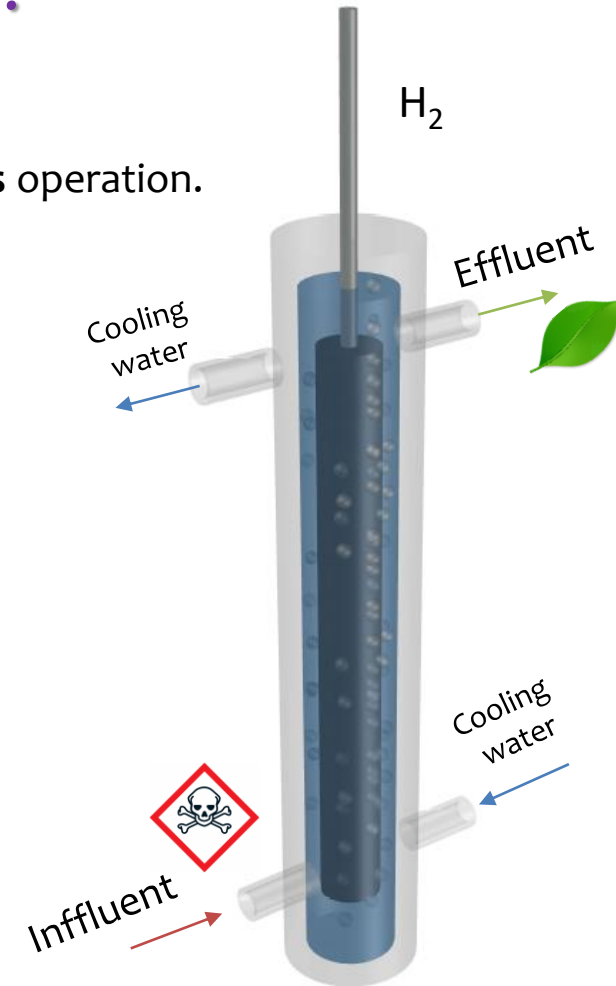Preparation of **CMR** (Catalytic membrane reactor) for **continuous** operation.

H$_2$

Effluent

Cooling water

Cooling water

Inffluent
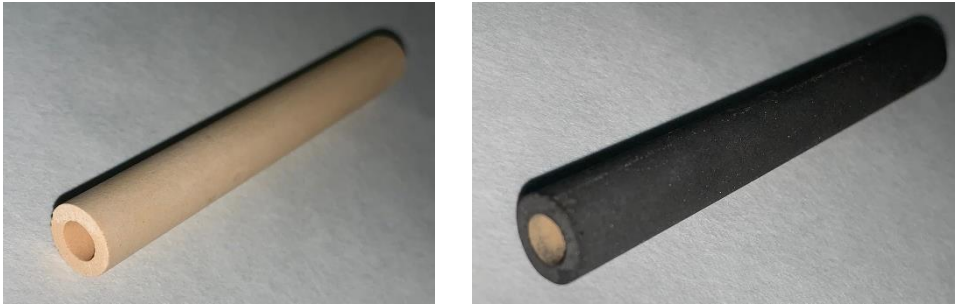
Adsorption of Pd

Calcination

Microwave drying

Reduction

# THANK YOU
# FOR YOUR ATTENTION

*julia.nieto-sandoval@uam.es*