

# Continuous Flow Photooxidative Degradation of Water Pollutants with fish waste-derived Carbon Dots

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Università  
Ca' Foscari  
Venezia



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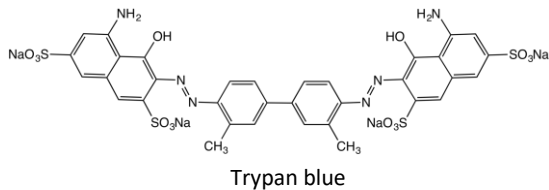
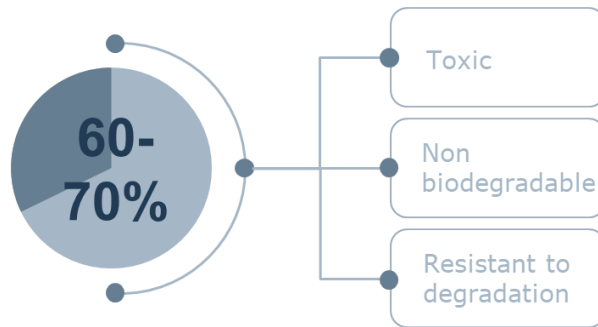
MYCS  
2022

# Context: Azo Dyes



The **60-70%** of the dyes used in the textile industry is constituted by **azo dyes**.

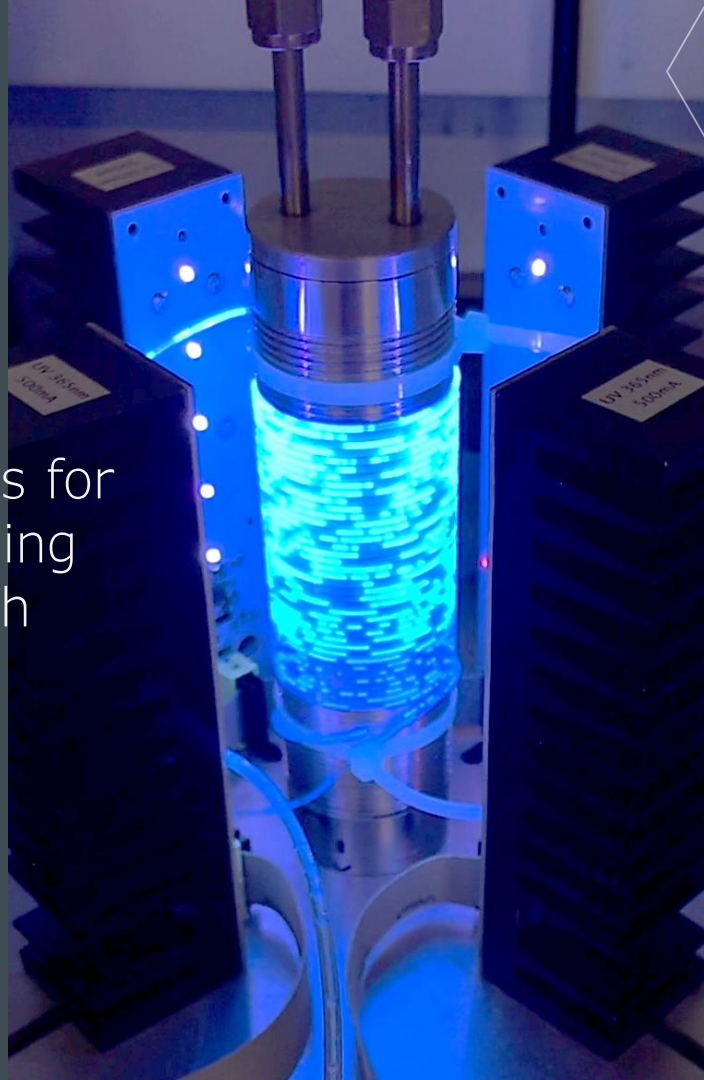
Synthetic dyes are one of the most serious sources of **environmental contaminants**.



**PHOTOCATALYSIS**  
Advanced Oxidation Process  
Effective technique

# >AIM

Develop a green, quick and efficient process for azo dyes removal combining CF and photocatalysis with CDs and oxygen



01.

## **Introduction**

Continuous Flow Chemistry  
Carbon Dots

02.

## **Carbon Dots**

Synthesis from fishery waste

03.

## **Carbon Dots**

Characterization

04.

## **Azo Dyes Degradation**

Batch experiments

05.

## **Azo Dyes Degradation**

CF Setup and experiments

06.

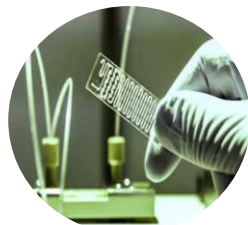
## **Azo Dyes Degradation**

Mechanisms



# >Continuous Flow Chemistry

Reactions run in a  
continuous flowing stream



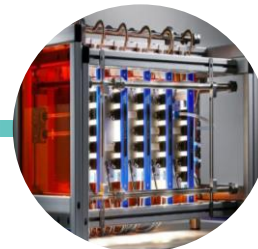
Efficient **mixing**  
Efficient **heat** management



Precise control over the  $R_t$   
Improve **safety** and **efficiency**



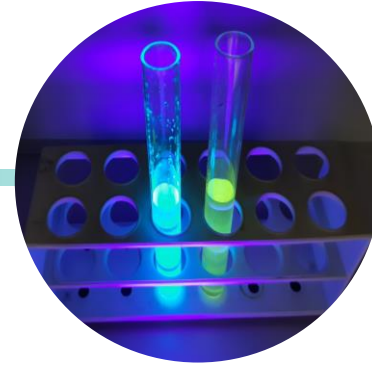
**Scalability** (decreasing process space and time frames)  
Enabling hazardous or difficult processes



# > Carbon Dots

Spherical carbon nanoparticles with  $d < 10\text{nm}$  and functionalised surface

- Highly biocompatible
- Water soluble
- Non toxic
- Tunable fluorescence
- Chemically stable
- Easy to functionalize/dope
- Cheap precursors and synthesis

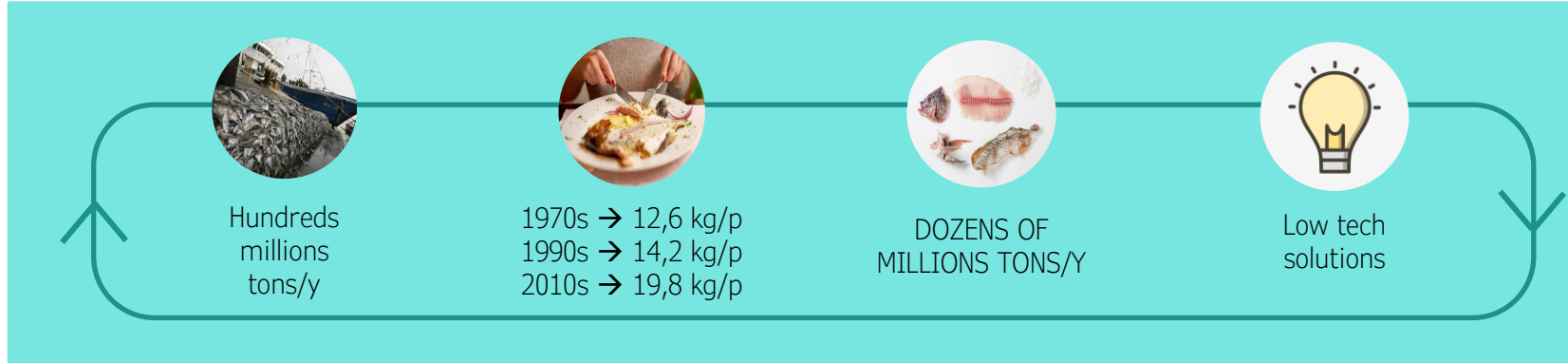


## > APPLICATIONS

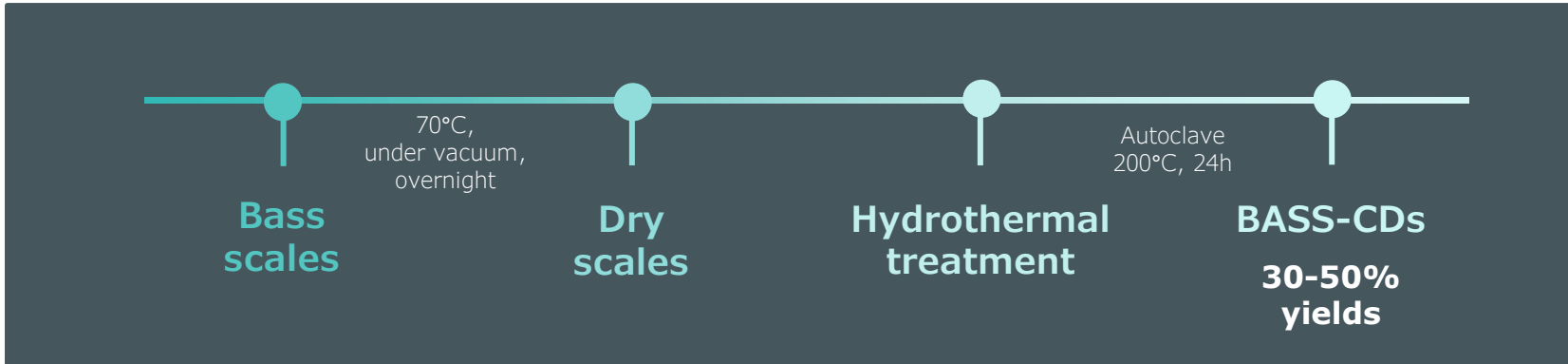
Bioimaging  
Sensing  
Photocatalysis  
Optoelectronics  
Photovoltaic  
Drug delivery

# Carbon Dots from Fishery waste

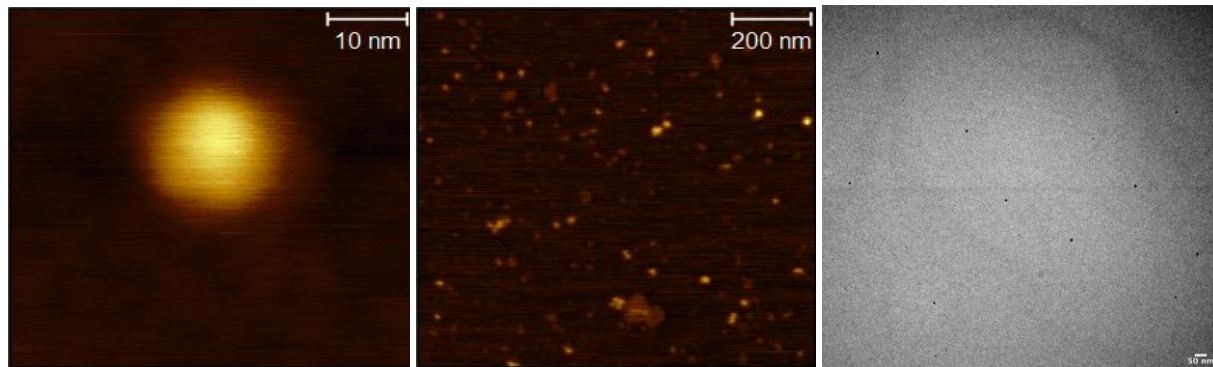
Why?



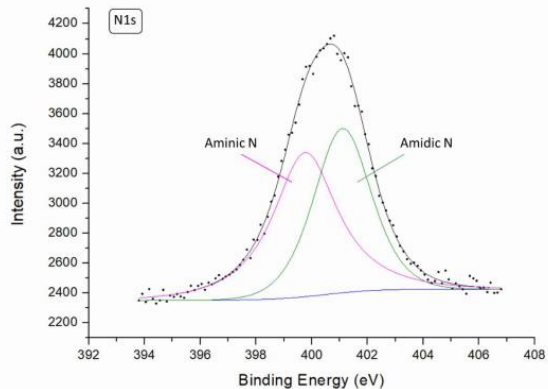
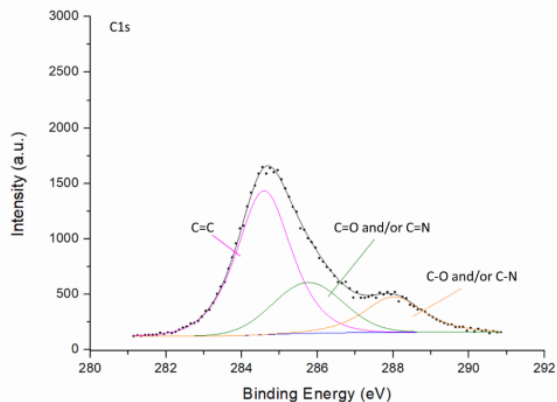
How?



# CDs characterization: Morphology



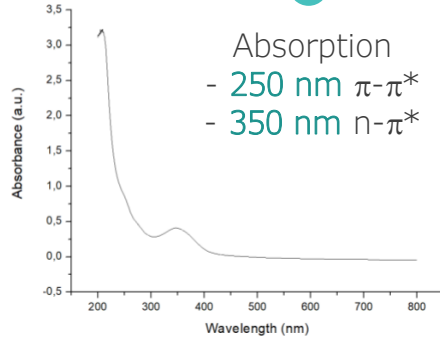
AFM, TEM, XPS, FT-IR, Elemental Analysis, SAXS, SLS



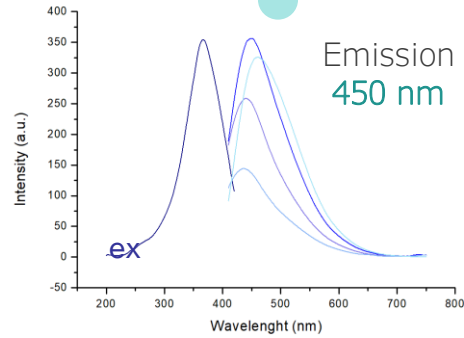
- Amorphous core
- Natural N-doping (C/N = 3.2)
- Surface functionalities (-OH, -NH<sub>2</sub>, -carboxyls, carbonyls, amides, -C=C)
- $d \approx 10$  nm

# CDs characterization: Optical

UV-Vis



PL-PLE



Excitation-dependent emission

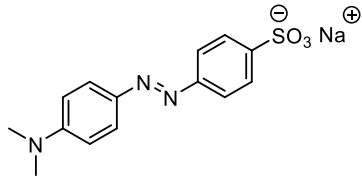
Time resolved PL,  
QY calculation



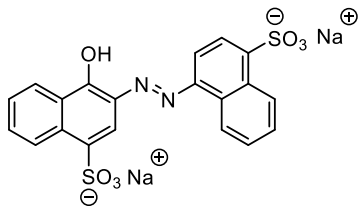
- Multiexponential decay
- $\tau = 7$  ns
- QY = 6%

# Degradations: Batch experiments

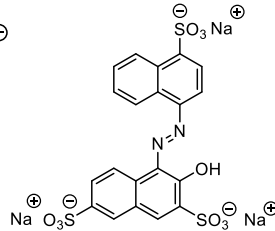
## 5 model azo dyes



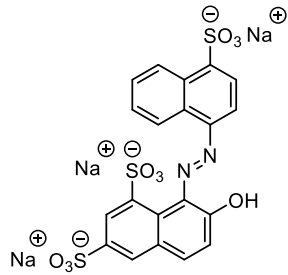
Methyl Orange  
(MO)



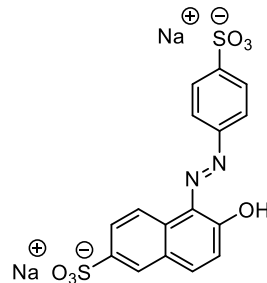
Chromotrope  
(CH)



Amaranth  
(AM)



Acid Red  
(AR)



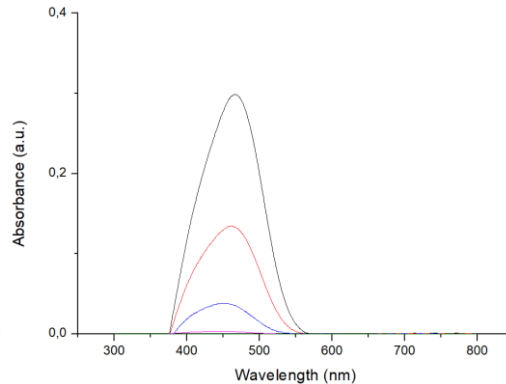
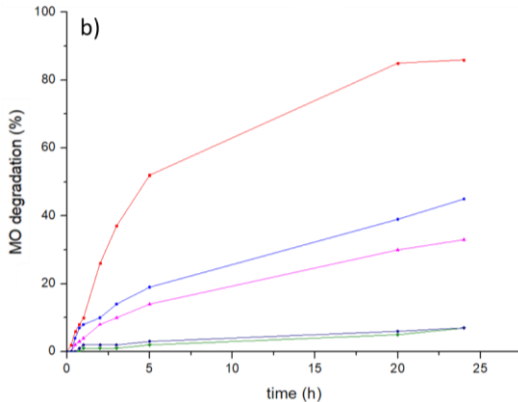
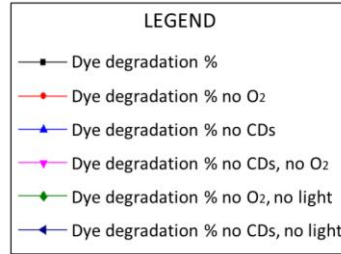
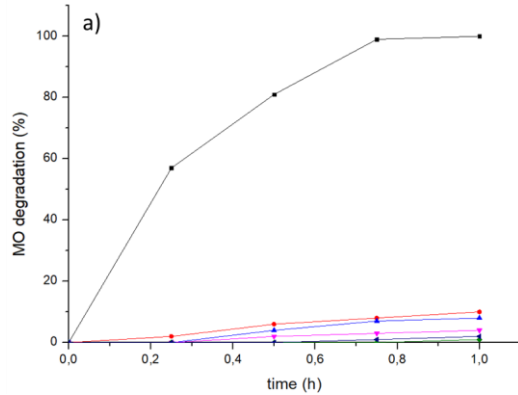
Sunset Yellow  
(SY)



## Conditions

- 2 mg/mL bass-CDs
- Oxygen
- In water
- At room temperature
- $\lambda = 365 \text{ nm}$
- No metals, S.D./S.A. etc

# Degradations: Batch experiments



## Conditions

- 2 mg/mL bass-CDs
- Oxygen
- In water
- At room temperature
- $\lambda = 365$  nm
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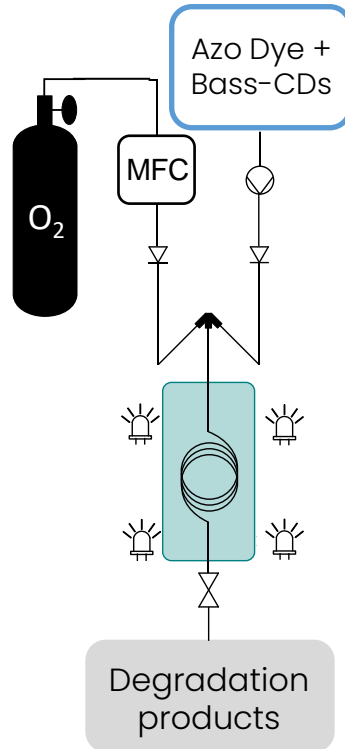
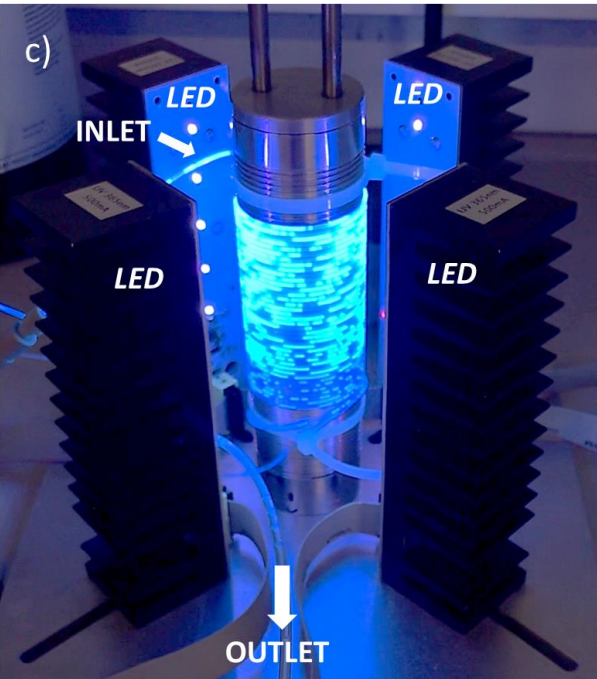
## RESULTS

With CDs + O<sub>2</sub>  
100% in 1-3h

Only CDs  
70-80% in 24h

Only O<sub>2</sub>  
30-50% in 24h

## Degradations: CF setup



### REACTOR

- HPLC pump
- PFA tubing 1/16 "
- $V_i = 2.6$  mL
- In water
- At room temperature
- $\lambda = 365$  nm

### FEED

- $[dye] = 5$  ppm
- $[bass-CDs] = 2$  mg/mL

### FLOWS

- $\Phi_{feed} = 0.5$  mL/min
- $\Phi_{oxygen} = 5.5$  mL<sub>N</sub>/min
- $\Phi_{oxygen\ real} = 0.78$  mL/min
- $\Phi_{tot} = 1.28$  mL/min
- $R_t = 2.03$  min

## Degradations: CF experiments

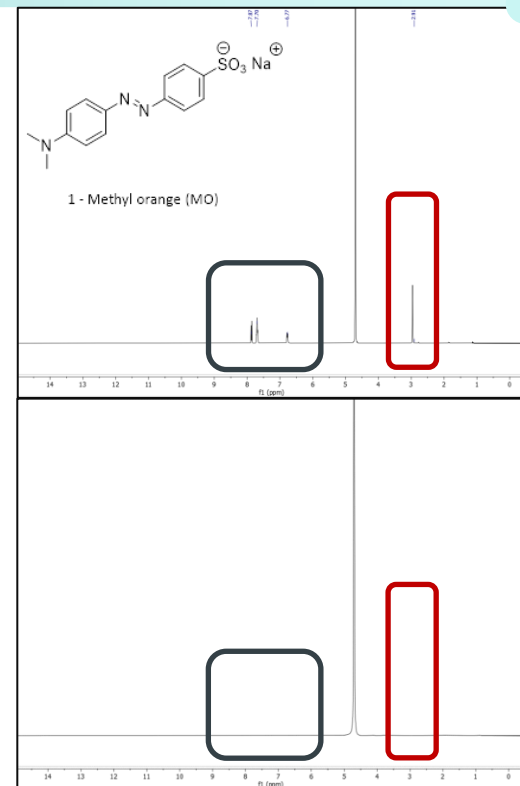
**COMPLETE  
MINERALIZATION  
in 2 minutes**

Confirmed via UV-Vis and NMR

Without oxygen max 66%  
Without CDs max 9%

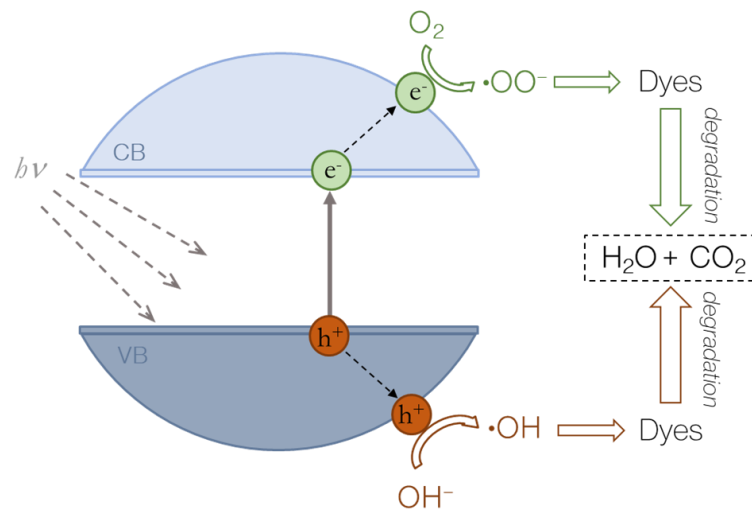
Entry	Azo dye	Conditions	Time to have 100% degradation
1	MO	Batch	1 h
2		CF	<b>2 min</b>
3	AR	Batch	1 h
4		CF	<b>2 min</b>
5	AM	Batch	2.5 h
6		CF	<b>2 min</b>
7	SY	Batch	2 h
8		CF	<b>2 min</b>
9	CH	Batch	3 h
10		CF	<b>2 min</b>

Feed: [dye] = 5ppm, [bass-CDs] = 2 mg/mL;  $\lambda = 365$  nm;  $\Phi_{\text{feed}} = 0.5$  mL/min,  
 $\Phi_{\text{oxygen}} = 5.5$  mL<sub>N</sub>/min,  $\Phi_{\text{oxygen real}} = 0.78$  mL/min,  $\Phi_{\text{tot}} = 1.28$  mL/min,  $R_t = 2.03$  min.



## Synergistic effect

- $CDs + h\nu \rightarrow CDs (e^-_{CB} + h^+_{VB})$
- $e^-_{CB} + h^+_{VB} \rightarrow \text{heat}$
- $h^+_{VB} + H_2O \rightarrow \cdot OH + H^+$
- $h^+_{VB} + \text{organic pollutants} \rightarrow \text{degraded products}$
- $e^-_{CB} + O_2 \rightarrow \cdot OO^-$
- $\cdot OO^- + H^+ \rightarrow \cdot OOH$
- $\cdot OH + \text{organic pollutant} \rightarrow \text{degraded products}$
- $\cdot OOH + \text{organic pollutant} \rightarrow \text{degraded products}$



# >CONCLUSIONS



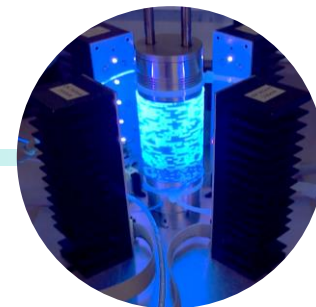
Valorisation of **fishery waste**  
for the production of CDs



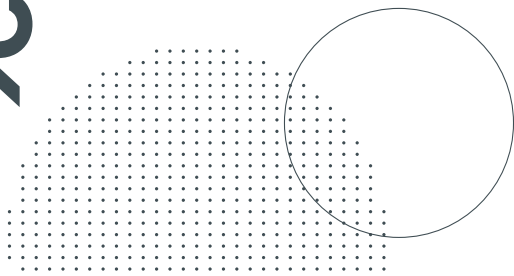
Production of  
**luminescent bass-CDs**  
with photocatalytic  
ability



Development of a easy,  
affordable and scalable **CF process**  
for wastewater pollutants removal



Complete **mineralization** of  
5 azo dyes in **2 min**



# Thank you for the attention

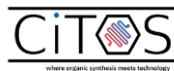


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