4th INTERNATIONAL CONFERENCE ON RISK ASSESSMENT OF PHARMACEUTICALS IN THE ENVIRONMENT

Barcelona, 9 - 10 October 2023

TiO_2/Carbon dots nanocomposites: Solar driven photocatalysts for the removal of antibiotics from aquaculture effluents

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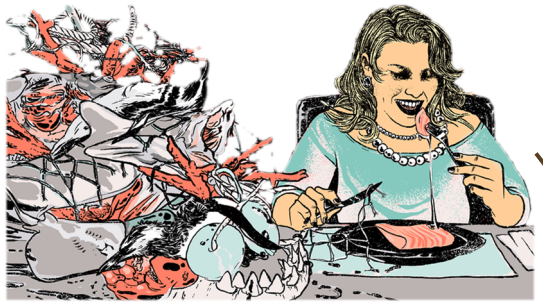
Introduction



Fish consumption

Overexploitation

Aquaculture growth

Infection treatment
or
Prophylactic treatment

Aquatic environment

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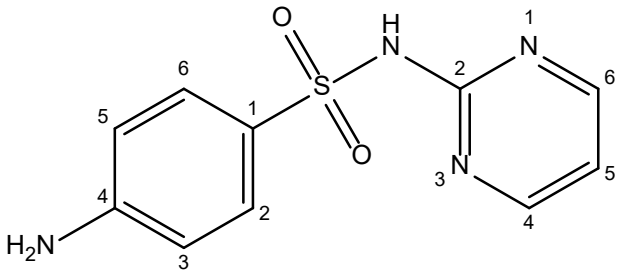
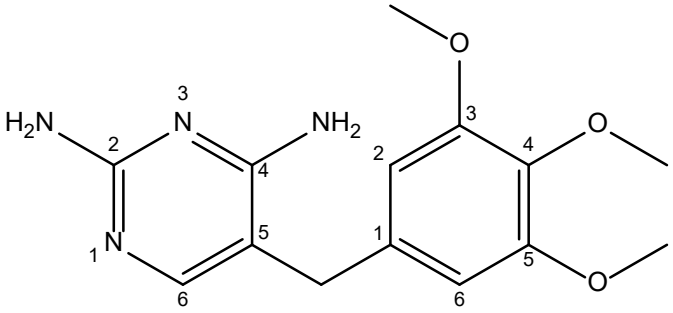
Introduction

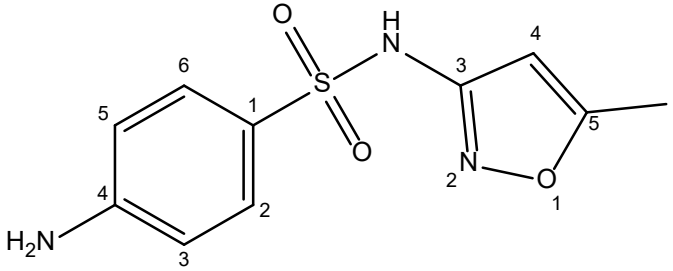
Antibiotics



Sulfadiazine (SDZ)

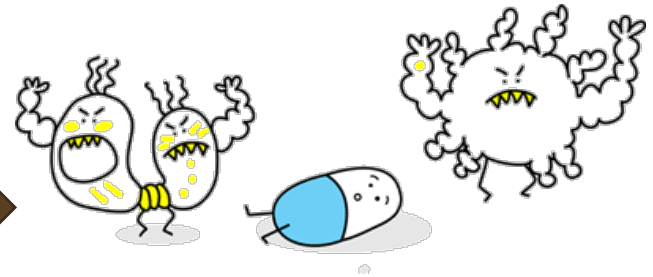


Trimethoprim (TMP)



Sulfamethoxazole (SMX)

In the aquatic environment



Bacterial resistance

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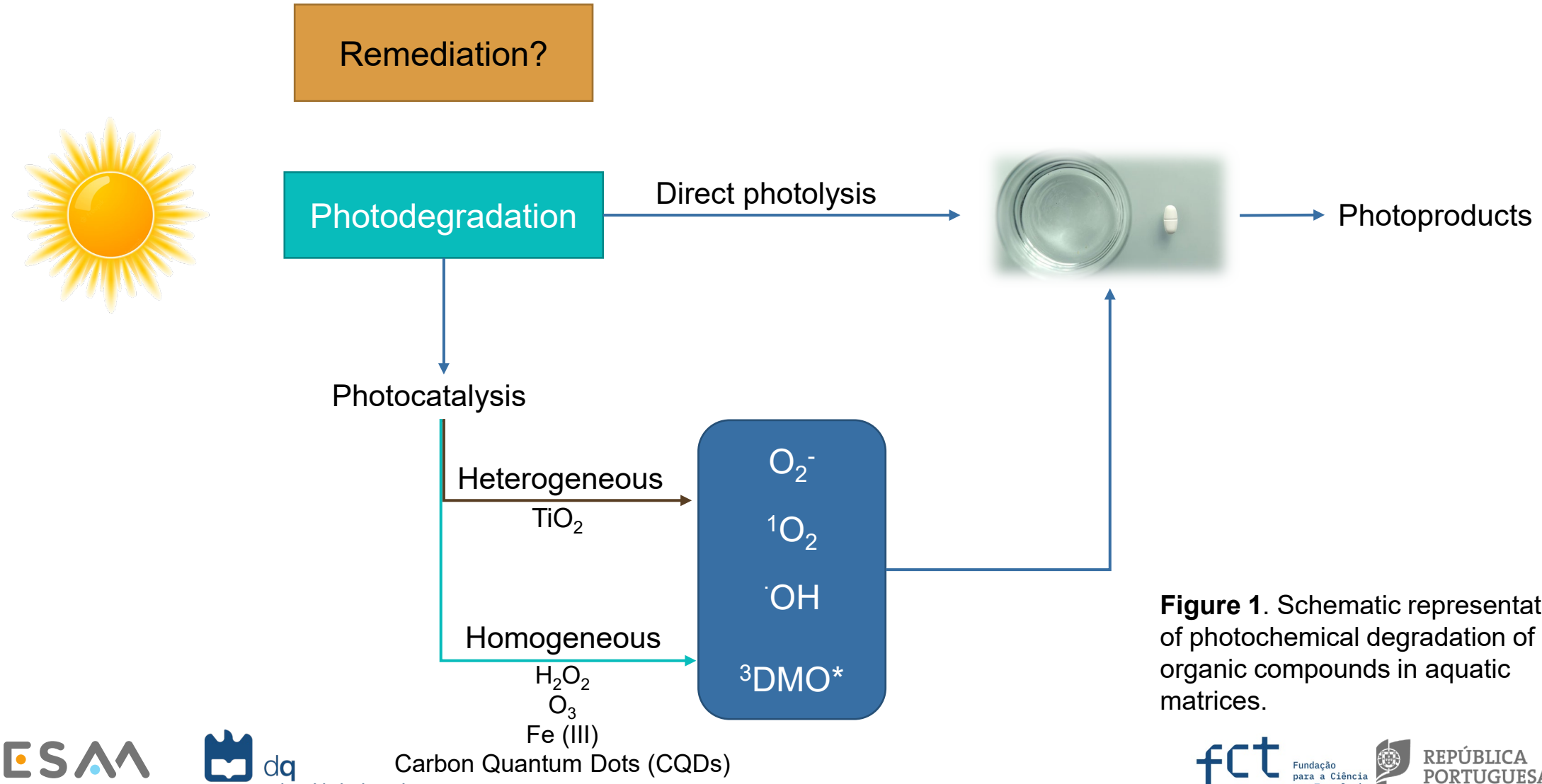

Figure 1. Schematic representation of photochemical degradation of organic compounds in aquatic matrices.

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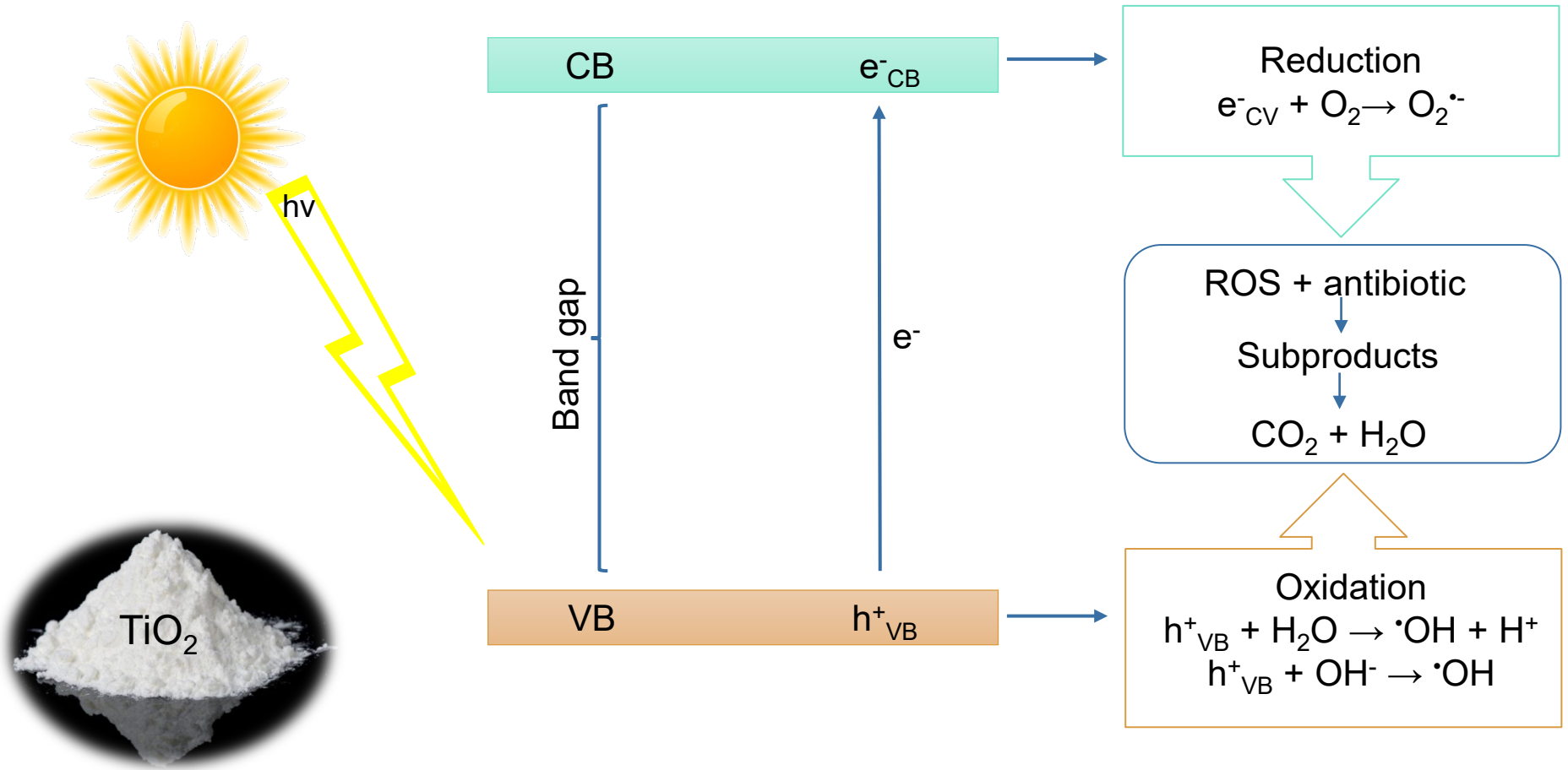

Figura 2. Schematic representation of photocatalytic mechanism of heterogeneous photocatalysis conducted by semiconductors.

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Introduction

Photoactivity can be improved

- Band gap is large
- Fast electron-hole recombination

Incorporation of CQDs

Figure 3. Real picture of luminescent Carbon Quantum Dots (CQDs) produced in the laboratory.

- Size (below 10 nm)
- Wavelength-dependent luminescence emission
- Good biocompatibility
- Resistance to photobleaching
- Environmentally friendly
- Highly hydrofilic
- Wider absorption spectrum

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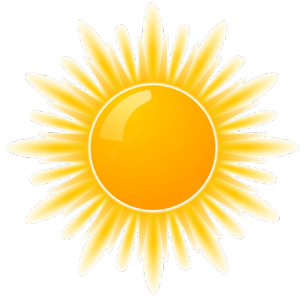
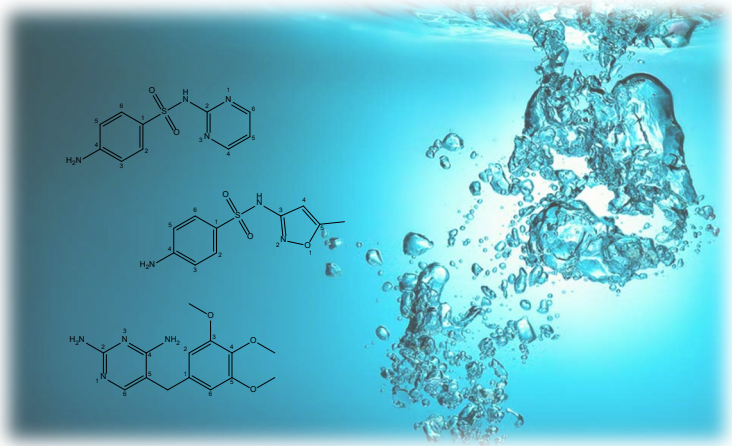
Aims

Determination of the most efficient TiO_2/CQDs photocatalyst and corresponding dose for the removal of each antibiotic in each condition.

Compare the photodegradation kinetic of each antibiotic in the presence and absence of photocatalyst in:

- ✓ Simulated fresh water;
- ✓ Simulated brackish water.





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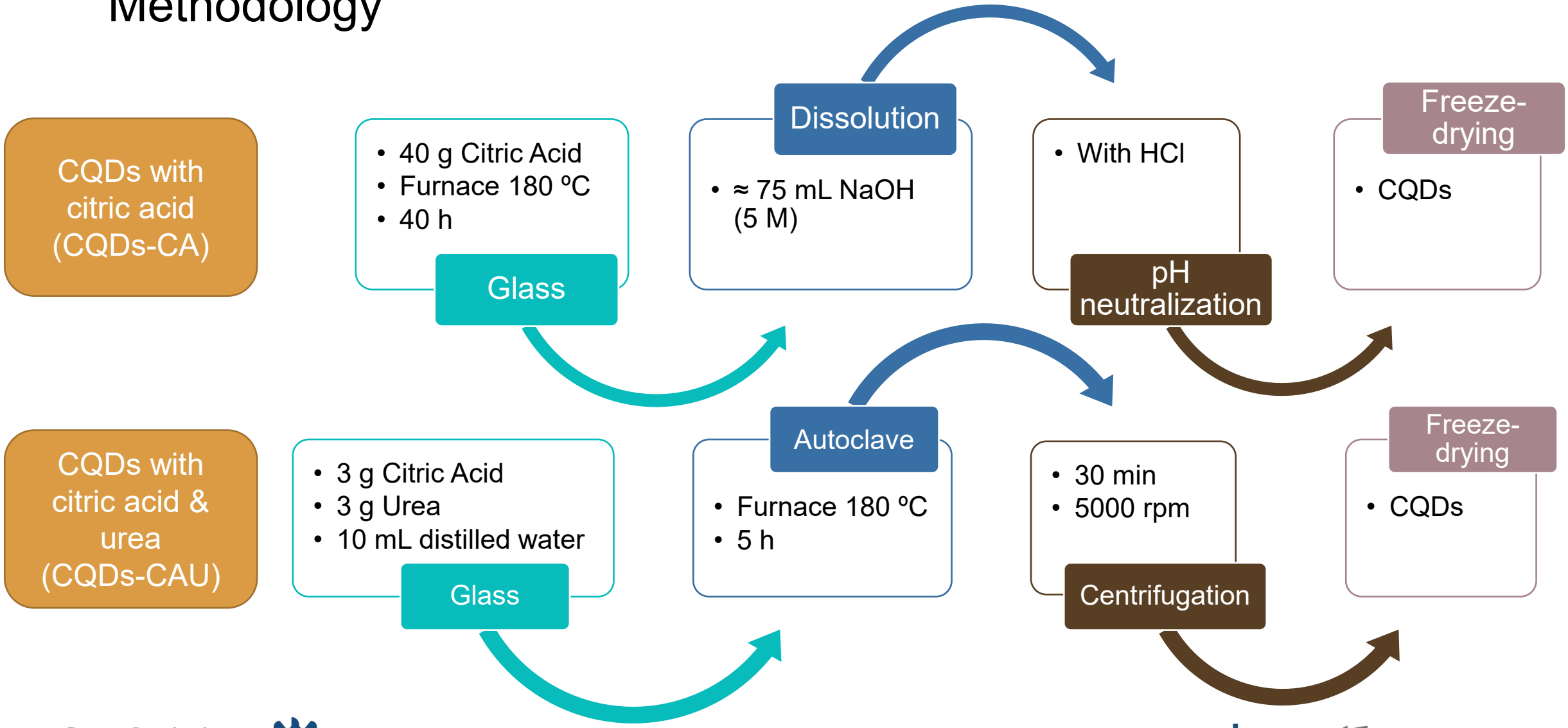
Methodology



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Methodology

TiO_2/CQDs

In aluminum crucible with magnetic agitation

- 1 g TiO_2 (P25)
- 30 mL ethanol
- Homogenize

In aluminum crucible with magnetic agitation

- CQDs solution
- Homogenize

- TiO_2/CQDs 4% (*w*/*w*)
- TiO_2/CQDs 5% (*w*/*w*)
- TiO_2/CQDs 6% (*w*/*w*)
- TiO_2/CQDs 8% (*w*/*w*)

Furnace

- 75 ºC to evaporate overnight

Muffle

- 300 ℃ for 3 h

Controls

This calcination (C) procedure was applied to obtain:

i) TiO_2C
ii) CQDs-CAC
iii) CQDs-CAUC

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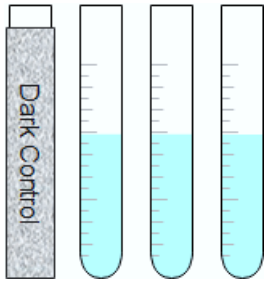
Methodology

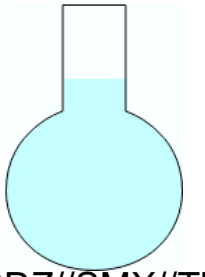
photocatalyst



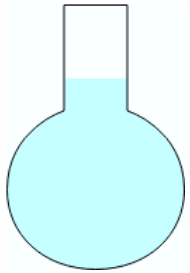
Quartz tubs

λ range: 290-800 nm

Antibiotic analysis by HPLC-UV



SDZ//SMX//TMP in phosphate buffer (PBS)



SDZ//SMX//TMP in synthetic sea salts (SSS)

Experimental data were fitted to the pseudo first-order kinetic equation:

$$C/C_0 = e^{-kt}$$

$$t_{1/2} = \ln(2)/k$$

Test sequence

i) TiO_2/CQDs selection
ii) Photocatalyst dosage
iii) Kinetics comparation

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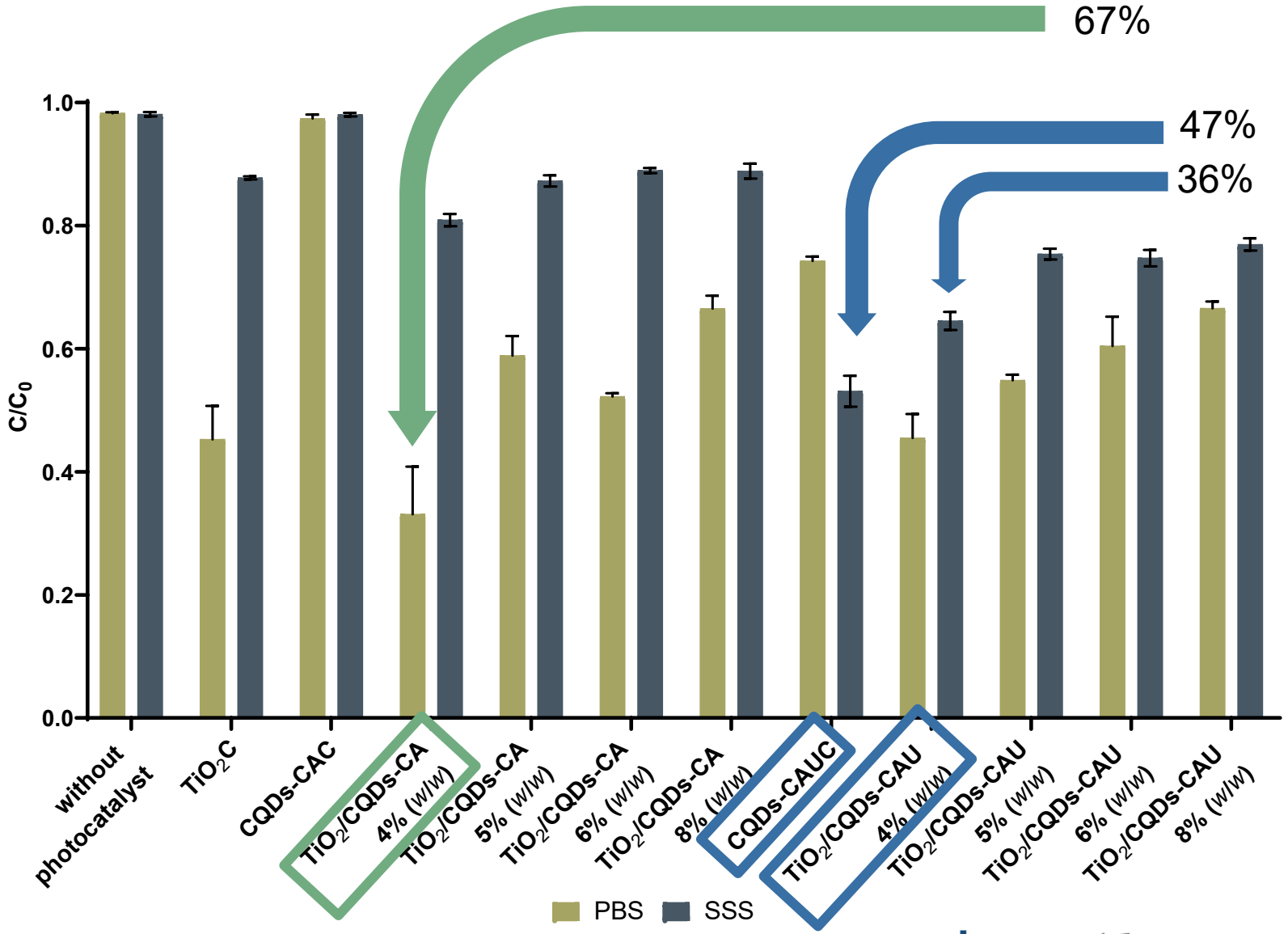
Results

TiO_2/CQDs selection

SDZ

PBS
TiO_2/CQDs-CA 4% (*w/w*)

SSS
CQDs-CAUC and
TiO_2/CQDs-CAU 4% (*w/w*)



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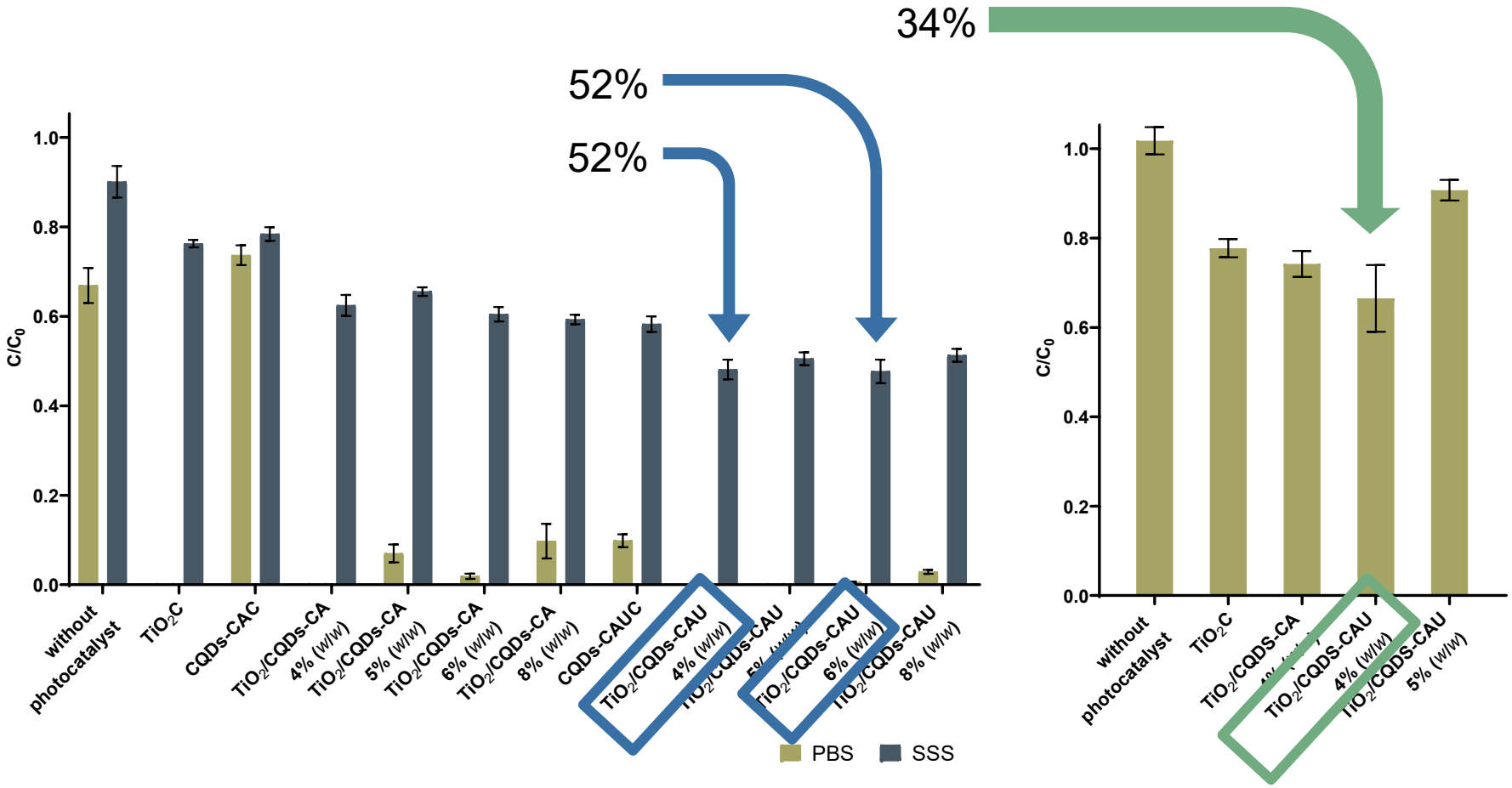
Results

Photocatalysts test

SMX

PBS
TiO_2/CQDs-CA 4% (*w/w*)

SSS
TiO_2/CQDs-CAU 4% (*w/w*) and TiO_2/CQDs-CAU 6% (*w/w*)



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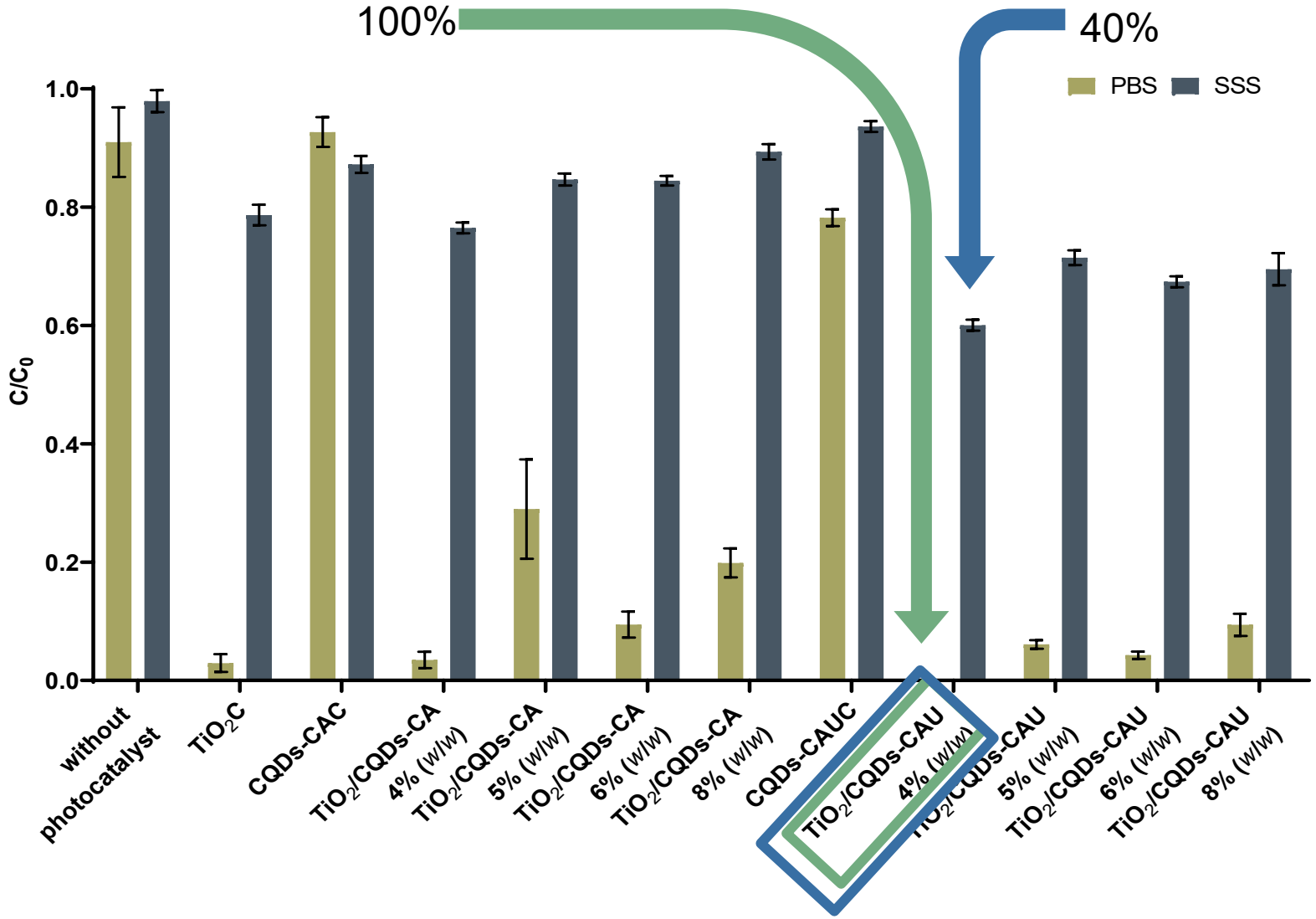
Results

Photocatalysts test

TMP

PBS
TiO_2/CQDs-CA 4% (*w/w*)

SSS
TiO_2/CQDs-CAU 4% (*w/w*)



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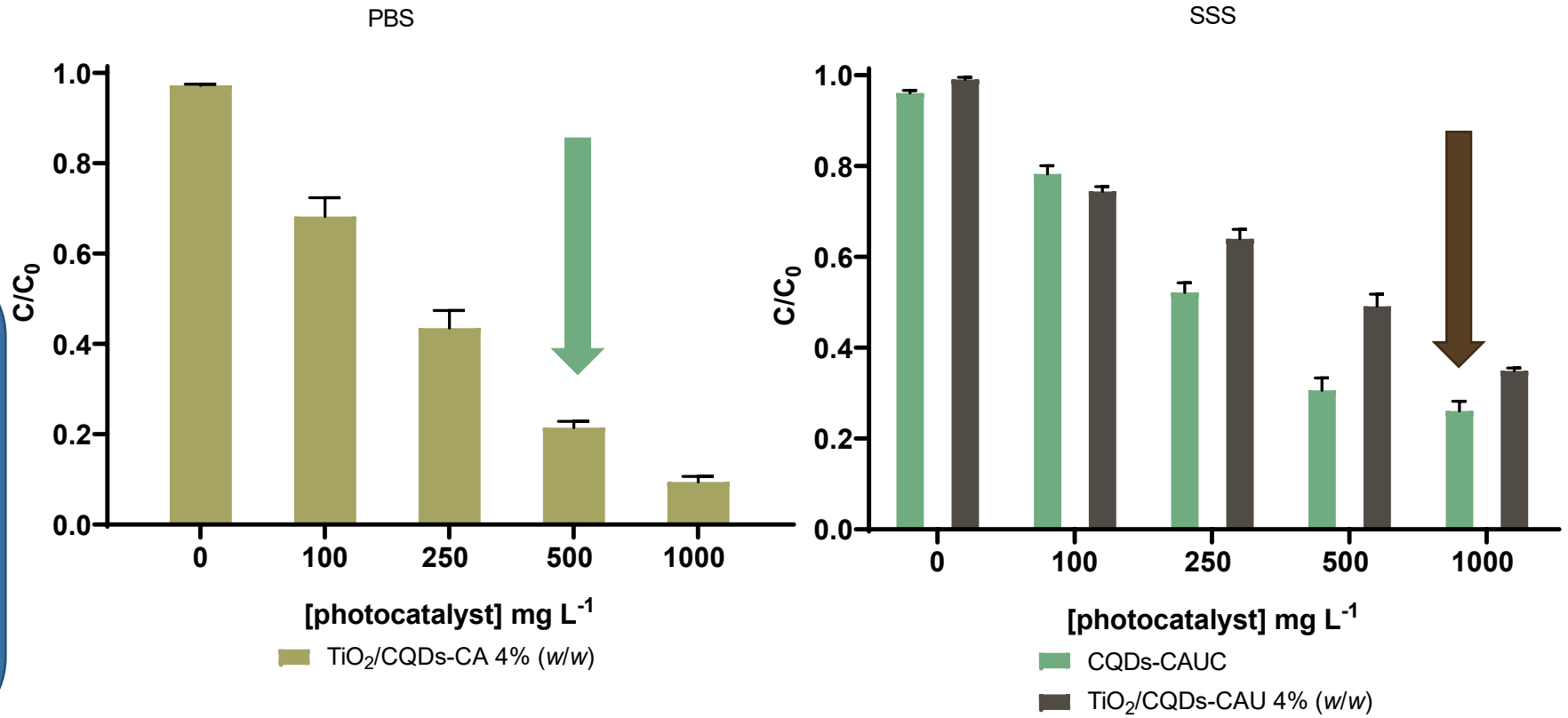
Results

Photocatalysts dosage

SDZ

PBS
500 mg L^{-1} TiO_2/CQDs-CA 4% (*w*/*w*)

SSS
1000 mg L^{-1}
TiO_2/CQDs-CAU 4% (*w*/*w*)



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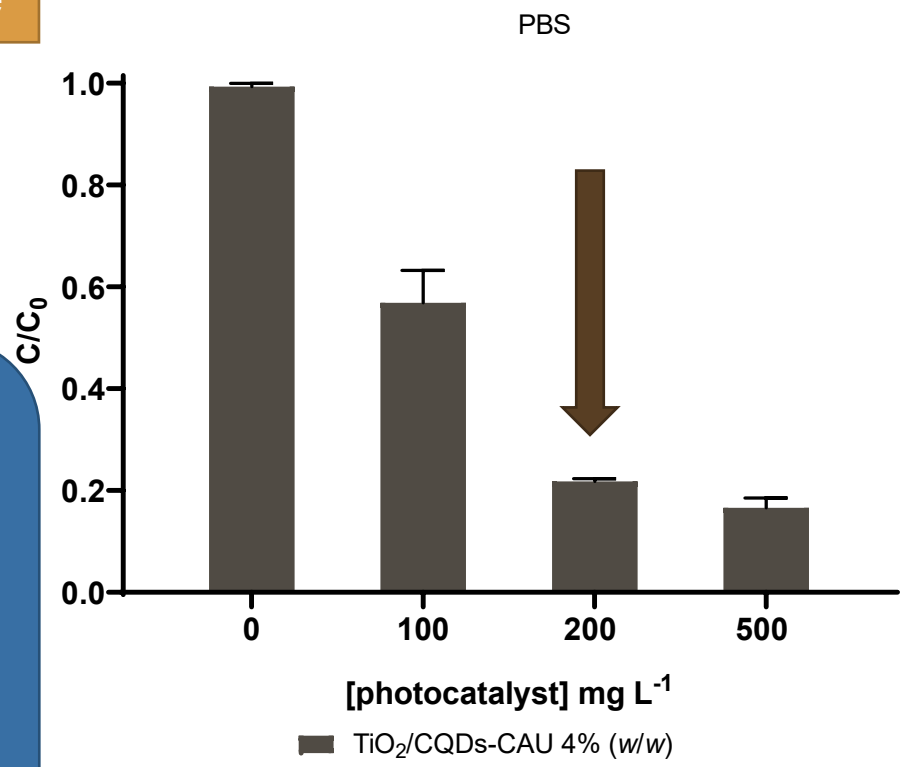
Results

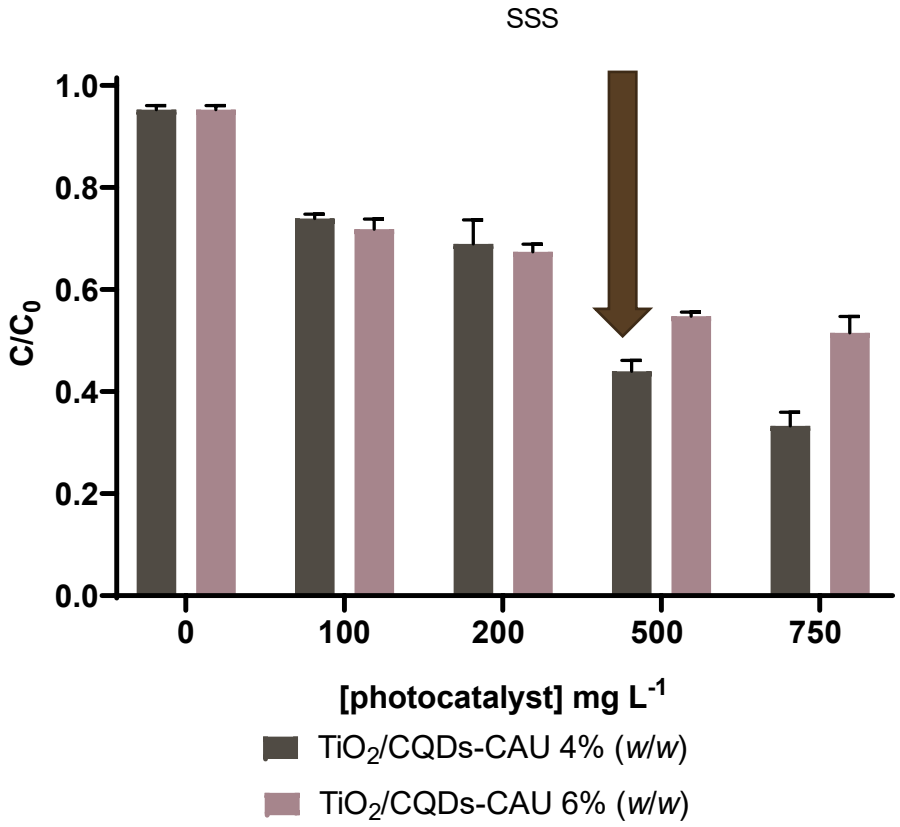
Photocatalysts dosage

SMX

PBS
200 mg L^{-1} TiO_2/CQDs-CA 4% (*w*/*w*)

SSS
500 mg L^{-1} TiO_2/CQDs-CAU 4% (*w*/*w*)





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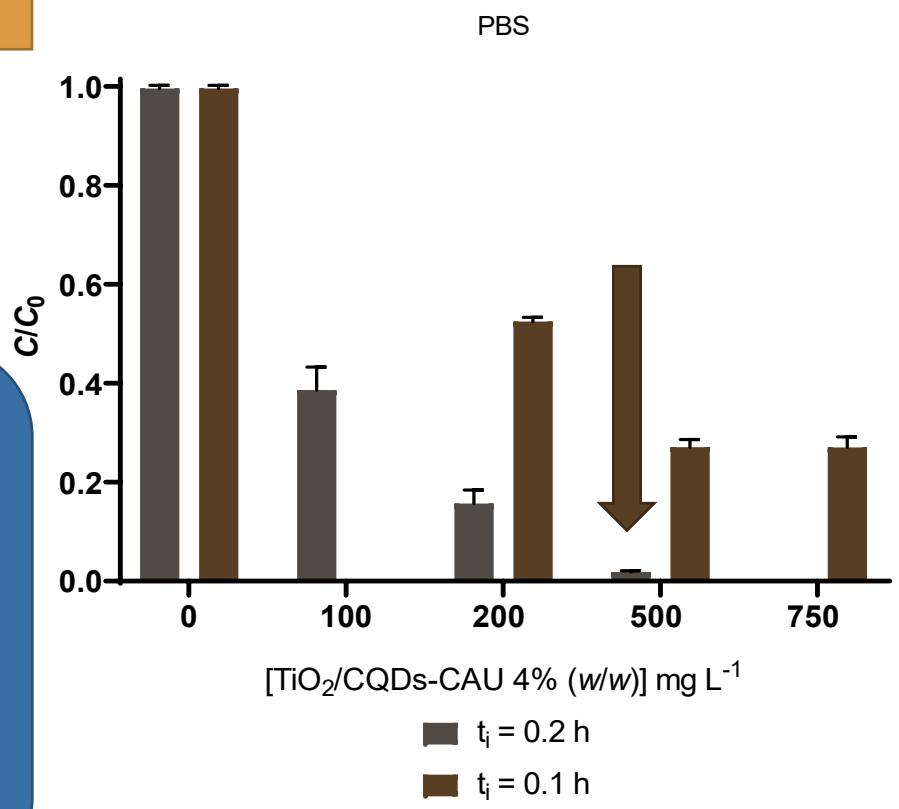
Results

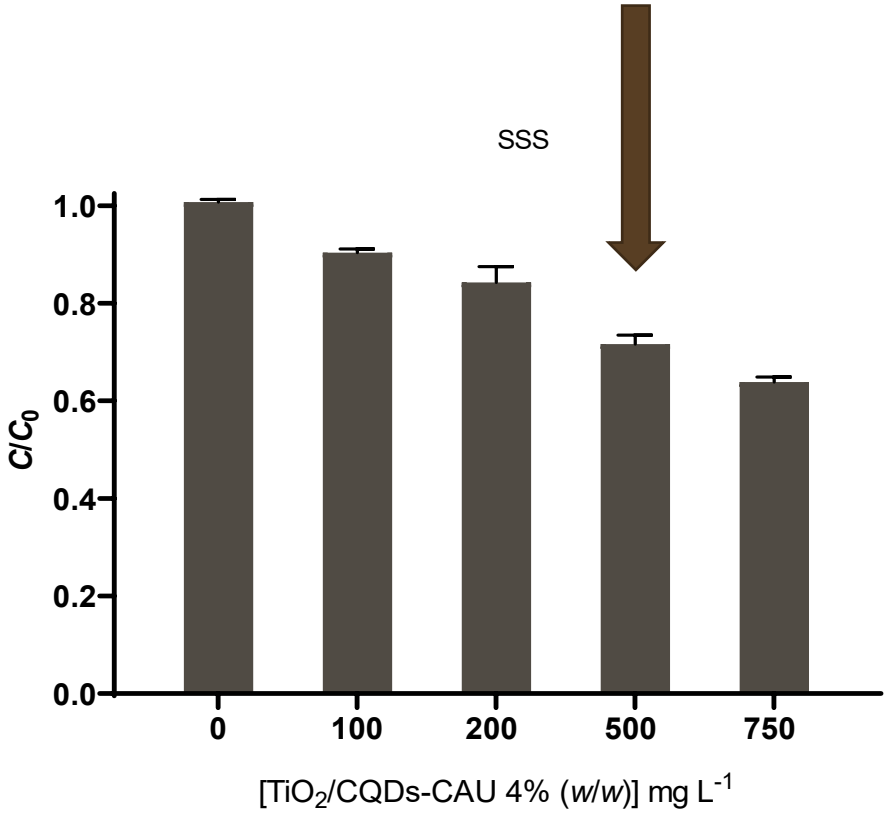
Photocatalysts dosage

TMP

PBS
500 mg L^{-1} TiO_2/CQDs-CA 4% (*w*/*w*)

SSS
500 mg L^{-1} TiO_2/CQDs-CAU 4% (*w*/*w*)





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Results

Antibiotic	Matrix	Photocatalysts	[Photocatalyst] mg L^{-1}
SDZ	PBS	TiO_2/CQDs-CA 4% (*w*/*w*)	500
	SSS	TiO_2/CQDs-CAU 4% (*w*/*w*)	1000
SMX	PBS	TiO_2/CQDs-CAU 4% (*w*/*w*)	200
	SSS	TiO_2/CQDs-CAU 4% (*w*/*w*)	500
TMP	PBS	TiO_2/CQDs-CAU 4% (*w*/*w*)	500
	SSS	TiO_2/CQDs-CAU 4% (*w*/*w*)	500

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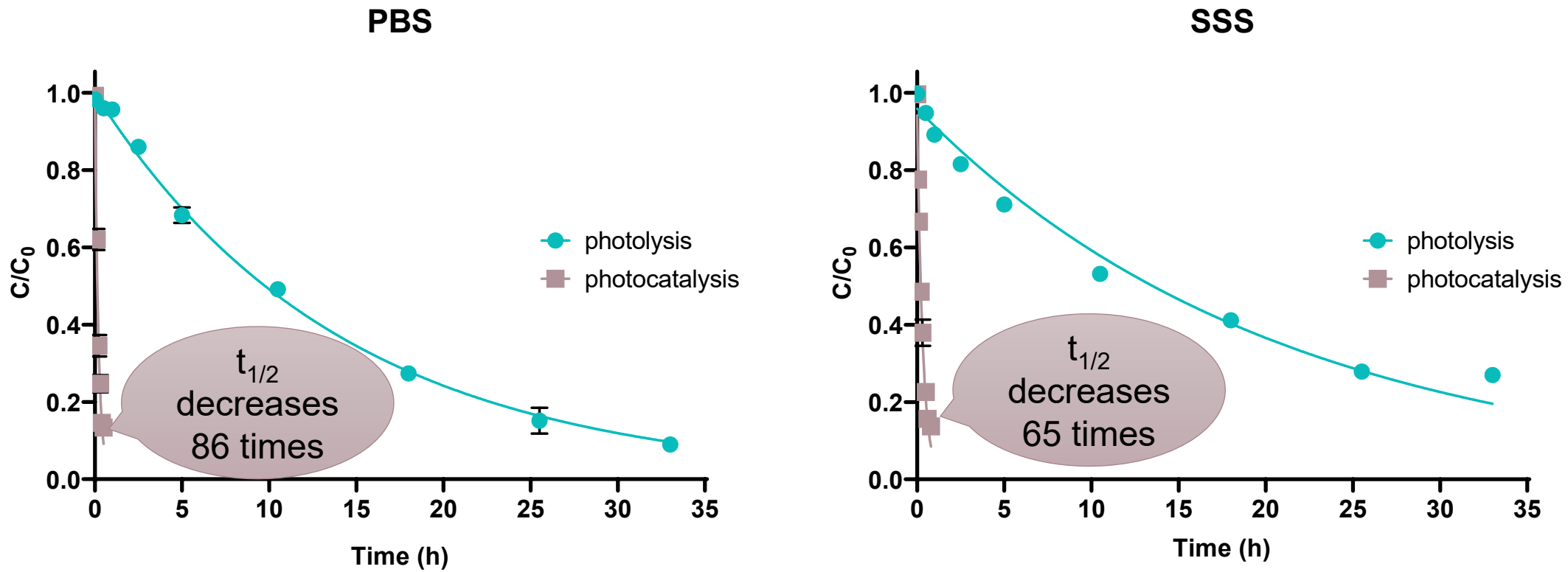
Results

Kinetics

SDZ



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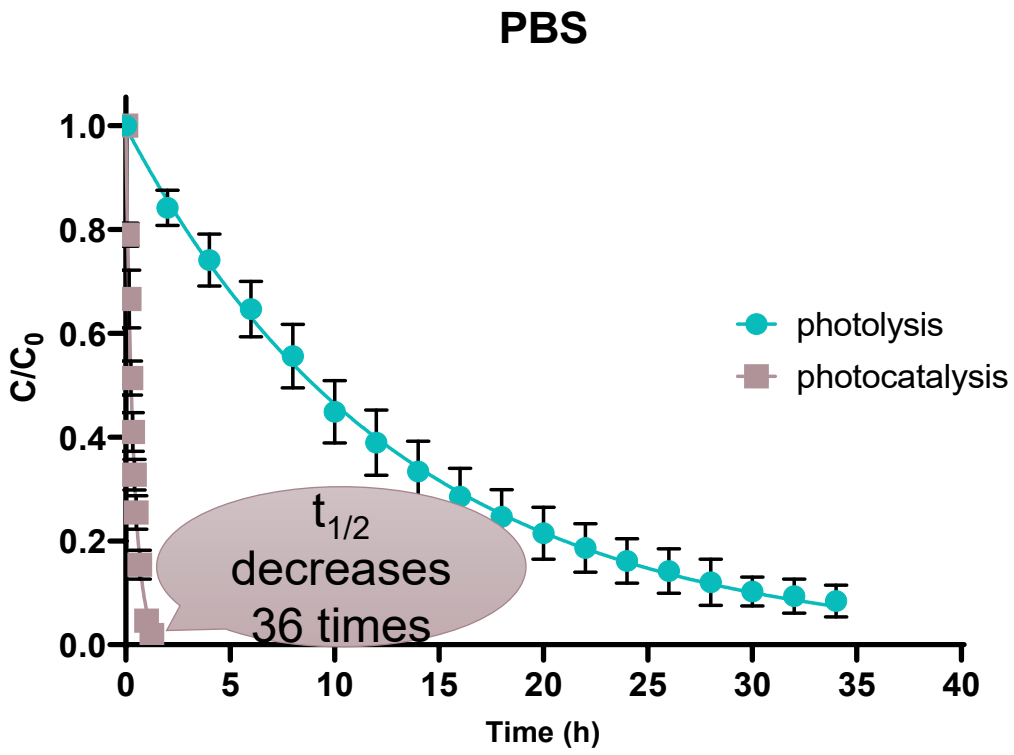
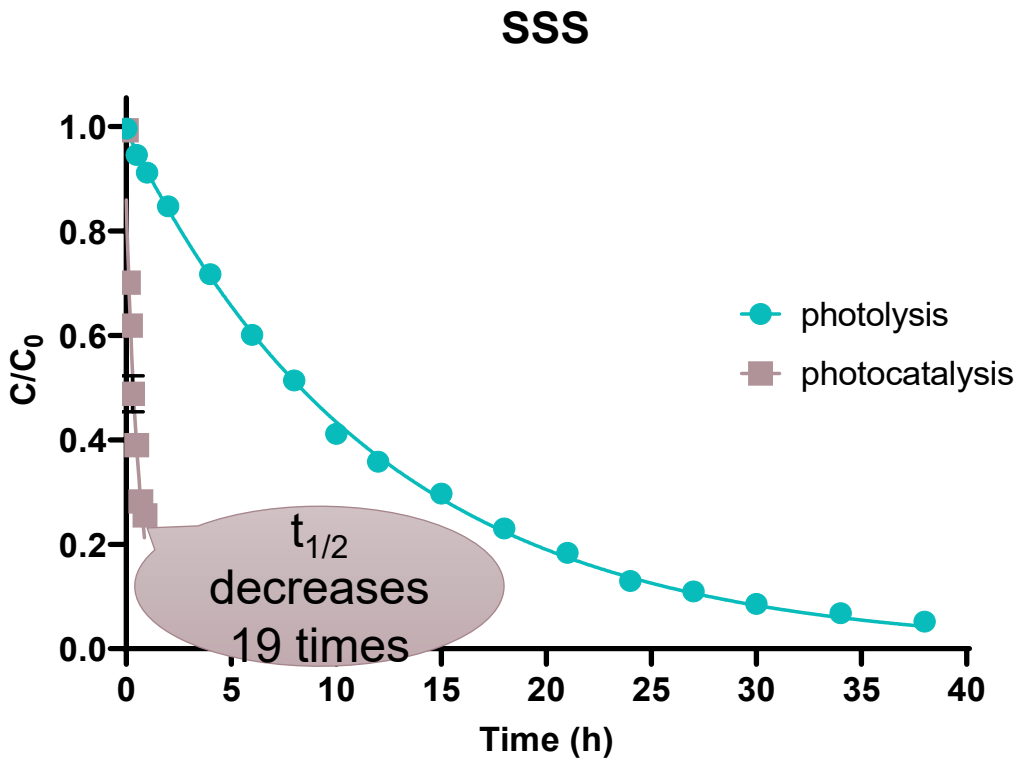
Results

Kinetics

SMX





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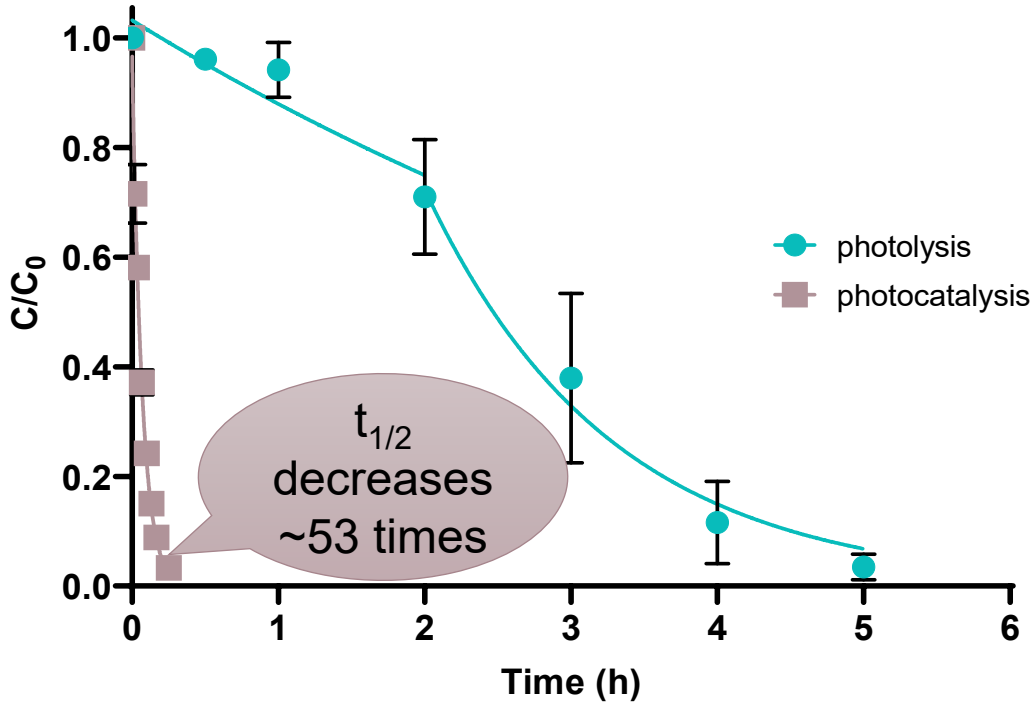
Results

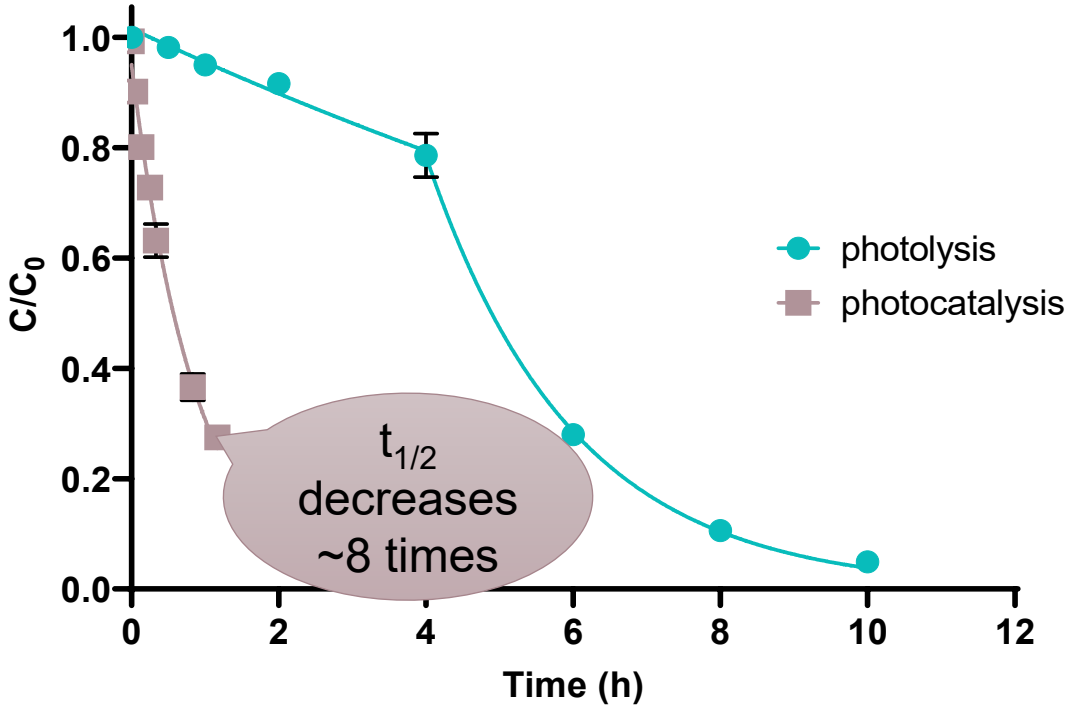
Kinetics

TMP

PBS



SSS



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Conclusions

- **TiO_2/CQDs** composites demonstrated that their presence in solution **accelerated the photodegradation** of SDZ, SMX and TMP, comparatively to photolysis.
- Differences in the photocatalysts' efficiency in PBS and SSS indicate that the **matrix influences the photodegradation** efficiency of the composites.
- The utilization of the synthetized photocatalysts **drastically decreased** the $t_{1/2}$ of the antibiotics in water.
- Among the synthesized photocatalysts, **TiO_2/CQDs-CAU 4% (*w*/*w*)** at a dosage of **500 mg L^{-1}** was the most efficient photocatalyst for the removal of the most considered antibiotics.
- The results herein reported indicate that the utilization of solar driven photocatalysis with **TiO_2/CQDs composites may be a suitable solution to remove SDZ, SMX and TMP from aquaculture** (fresh and brackish) effluents, especially when compared with the results found in literature.

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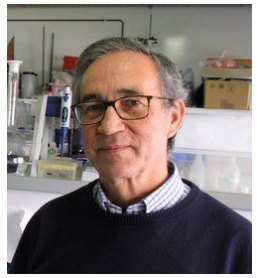
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THANK YOU

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Valentina Silva thanks support by the Fundação para a Ciência e a Tecnologia (FCT) PhD Grant (2022.10472.BD). Diana Lima acknowledges funding from FCT under the Scientific Employment Stimulus (2022.00570.CEECIND). The authors acknowledge financial support to CESAM by FCT/MCTES (UIDP/50017/2020+UIDB/50017/2020+LA/P/0094/2020), through national funds.

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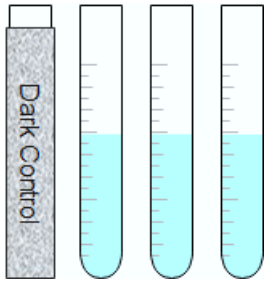
Methodology

≠ mg L^{-1} photocatalyst



Quartz tubs

0.1 h – 0.5 h irradiation
λ range: 290-800 nm
Irradiance: 550 W m^{-2}
1500 W arc Xe lamp

Antibiotic analysis by HPLC-UV
λ = 270 nm
Mobile phase:
SDZ CH_3OH : H_2O with 0.1% CH_2O_2 (20:80)
SMX C_2H_3N : H_2O with 0.1% CH_2O_2 (30:70)
TMP C_2H_3N : H_2O with 0.1% CH_2O_2 (15:85)
Stationary phase: C18

Experimental data were fitted using

Graphpad Prims 8.0.1 to the pseudo first-order kinetic equation:

$$C/C_0 = e^{-kt}$$

$$t_{1/2} = \ln(2)/k$$

10 mg L^{-1} SDZ//SMX//TMP in phosphate buffer (PBS) 0.001 mol L pH 8.6

10 mg L^{-1} SDZ//SMX//TMP in synthetic sea salts (SSS) 30 g L pH 8.6

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Results

Comparison with literature

Antibiotic	[Antibiotic] (mg L^{-1})	Matrix	Light source	Photocatalyst	[Photocatalyst] (mg L^{-1})	k (h^{-1})	Ref.
SDZ	10	PBS	simulated solar light irradiation 55 W m^{-2} (290–400 nm)	TiO_2/CQDs-CA 4% (*w*/*w*)	500	4.81 ± 0.06	This study
		SSS		CQDs-CAUC	500	3.17 ± 0.08	
	10	0.5 mol L^{-1} NaCl, pH 7	simulated solar light irradiation 60 mW cm^{-2} (320-780 nm)	AQ_2S@rGO	100	1.782	[22]
	1	Ultrapure water	simulated solar light irradiation 500 W m^{-2} (300-800 nm)	Cu-modified TiO_2	100	11.0 ± 0.6	[43]
	10	0.001 mol L^{-1} phosphate buffer, pH 7.3	simulated solar light irradiation 55 W m^{-2} (290–400 nm)	biochar-TiO_2 magnetic	100	0.062 to 0.236	[24]

DOI: 10.1016/j.cattod.2023.114150

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Results

Comparison with literature

Antibiotic	[Antibiotic] (mg L^{-1})	Matrix	Light source	Photocatalyst	[Photocatalyst] (mg L^{-1})	k (h^{-1})	Ref.
SMX	10	PBS	simulated solar light irradiation 55 W m^{-2} (290–400 nm)	TiO_2/CQDs-CAU 4% (w/w)	200	2.72 ± 0.06	This study
		SSS		TiO_2/CQDs-CAU 4% (w/w)	500	1.60 ± 0.06	
	1	ultrapure water	solar simulator, Xenon lamp (1.5 kW) 500 W m^{-2}	biobased-PET-TiO_2 P25 composite films	500	0.9	[45]
	1	deionized water, pH 6.0	solar simulation chamber, Xenon lamp (1.5 kW) (290-400 nm)	TiO_2 P25 (Degussa)	100	2.46	[46]
		simulated seawater, pH 8.2				1.2	

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Results

Comparison with literature

Antibiotic	[Antibiotic] (mg L^{-1})	Matrix	Light source	Photocatalyst	[Photocatalyst] (mg L^{-1})	k (h^{-1})	Ref.
TMP	10	PBS	simulated solar light irradiation 55 W m^{-2} (290–400 nm)	TiO_2/CQDs-CAU 4% (*w*/*w*)	500	14.6 ± 0.6	This study
		SSS		TiO_2/CQDs-CAU 4% (*w*/*w*)	500	1.13 ± 0.06	
	15×10^{-6}	treated wastewater	simulated solar light irradiation 500 W m^{-2} (350-840 nm)	TiO_2 powder	500	(100% removal after 3 h)	[49]
	121×10^{-3}	hospital wastewater	UV irradiation	porous geopolymer composite membranes with TiO_2 (10 wt%)	25000	0.108	[50]

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