Treatment techniques for water containing cyanuric acid (CYA)

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Workshop 2020

INNOVATIVE TECHNOLOGIES FOR SUSTAINABLE MANAGEMENT OF URBAN AND INDUSTRIAL WASTE STREAMS

REMTAVARES
Red Madrileña de Tratamientos Avanzados de Aguas Residuales

P2018/EMT-4341 (Consejería de Educación y Ciencia de la Comunidad Autónoma de Madrid)

Comunidad de Madrid
CONSEJERÍA DE EDUCACIÓN E INVESTIGACIÓN

INTRODUCTION

SWIMMING POOL DISINFECTION

- …**Microorganisms** in swimming pool water can pose a **serious health issues**
- Threat and pool disinfection is therefore **compulsory by law**

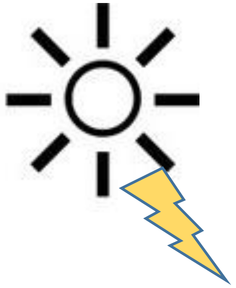
HClO Effective disinfection

Chlorine Disinfection

Chlorine as hypochlorous acid (HClO) in water

- Massively employed
- highly effective method of disinfection

$$NaClO + H_2O \leftrightarrow \mathbf{HClO} + Na^+ + OH^-$$
$$HClO + H_2O \leftrightarrow ClO^- + H_3O^+$$



HClO rapidly decomposed in presence of UV light:

- losing its bactericide effect
- continuous supply is needed to maintain safe levels
- The half-life of chlorine when exposed (Uv-light): 45´

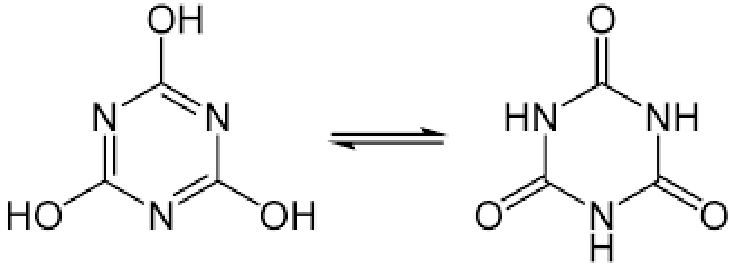
$$2\ HClO \rightarrow HCl + O_2$$
$$2\ ClO^- \rightarrow 2\ Cl^- + O_2$$

Cl^- Ineffective disinfection

WHAT IS CYANURIC ACID USED FOR?

CYANURIC ACID (CYA); cyclic trimer. The ring can readily interconvert between two structures.

- triol tautomer (may have aromatic character) predominates in solution.
- Deprotonation with base affords cyanurate salt



1 Cyanuric (triol) tautomer

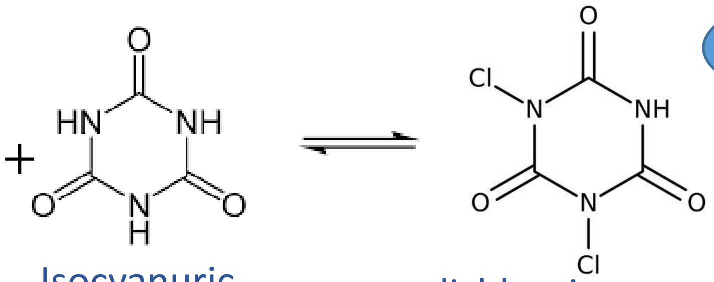
2 Isocyanuric (trione) tautomer

Cyanuric acid (CYA) as chlorine stabilizer (dichloroisocyanuric)

- Stabilises HClO and is added to pool water
- Slow down the degradation of HOCl by sunlight

Stable with sunlight

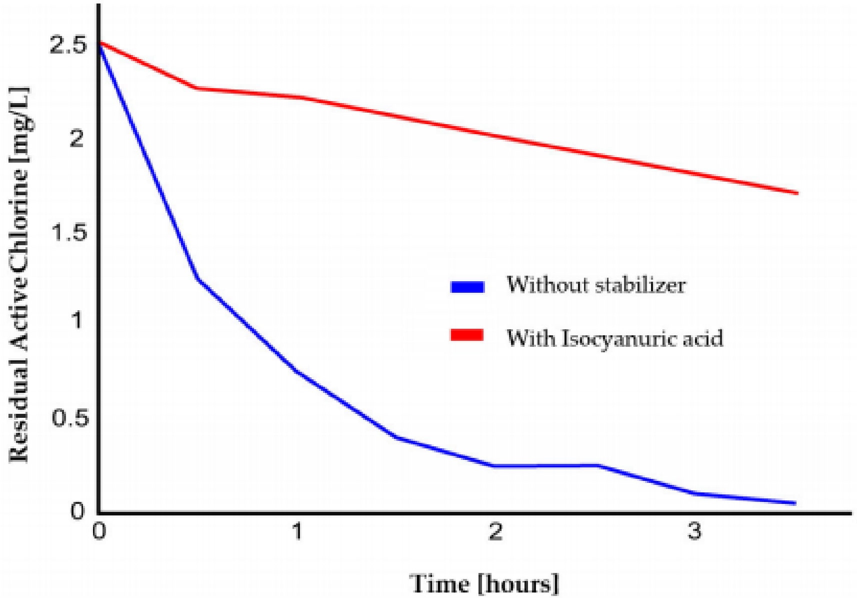
$2\ HClO +$



$+ 2\ H_2O$

Isocyanuric acid (CYA)

dichloroisocyanuric acid (DCC)



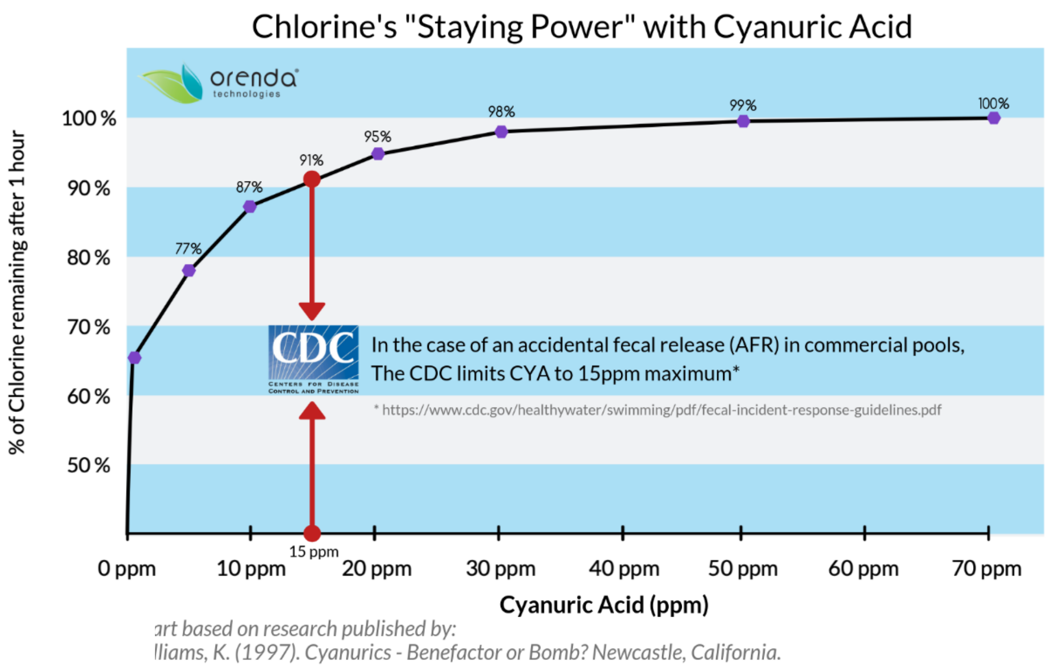
Water **2019**, *11*(4), 712

TOO MUCH CYA? Over-stabilization issues

OVER-STABILIZATION

CYA is extraordinarily stable in water

- **CYA concentration** therefore **rises** steadily over time.
- At high CYA levels**, chlorine is overstablished**, rendering it ineffective as a disinfectant.
- This increases the risk of **recreational water illnesses**
- **CYA** is therefore **regulated** by law
- CYN levels beyond **100 mg·L^{-1}** can cause **health issues to kids** due to drinking water (WHO)



BOE

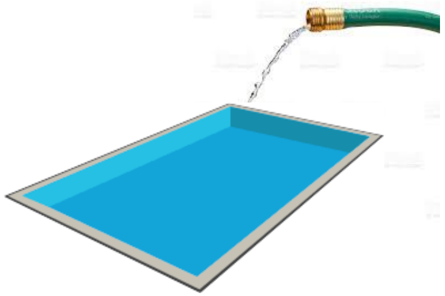
Real Decreto 742/2013, de 27 de septiembre, por el que se establecen los criterios técnico-sanitarios de las piscinas.

[CYA] ≤ 75 mg·L^{-1}

SOLUTION?

Currently only viable solution **replace some of the pool water with fresh water,**

- environmental concerns
- Economic concerns

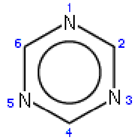


AIMS OF THIS WORK

OBJECTIVES

MOTIVATIONS:

- Absence of treatments devoted to treat cyanuric acid in recreational water environments and bathing water
- Unavailability of conventional AOPs to degrade s-triazine herbicides: absence of total mineralization observed in s-triazine herbicides final product obtained was essentially 1,3,5-triazine2,4,6, trihydroxy (cyanuric acid)

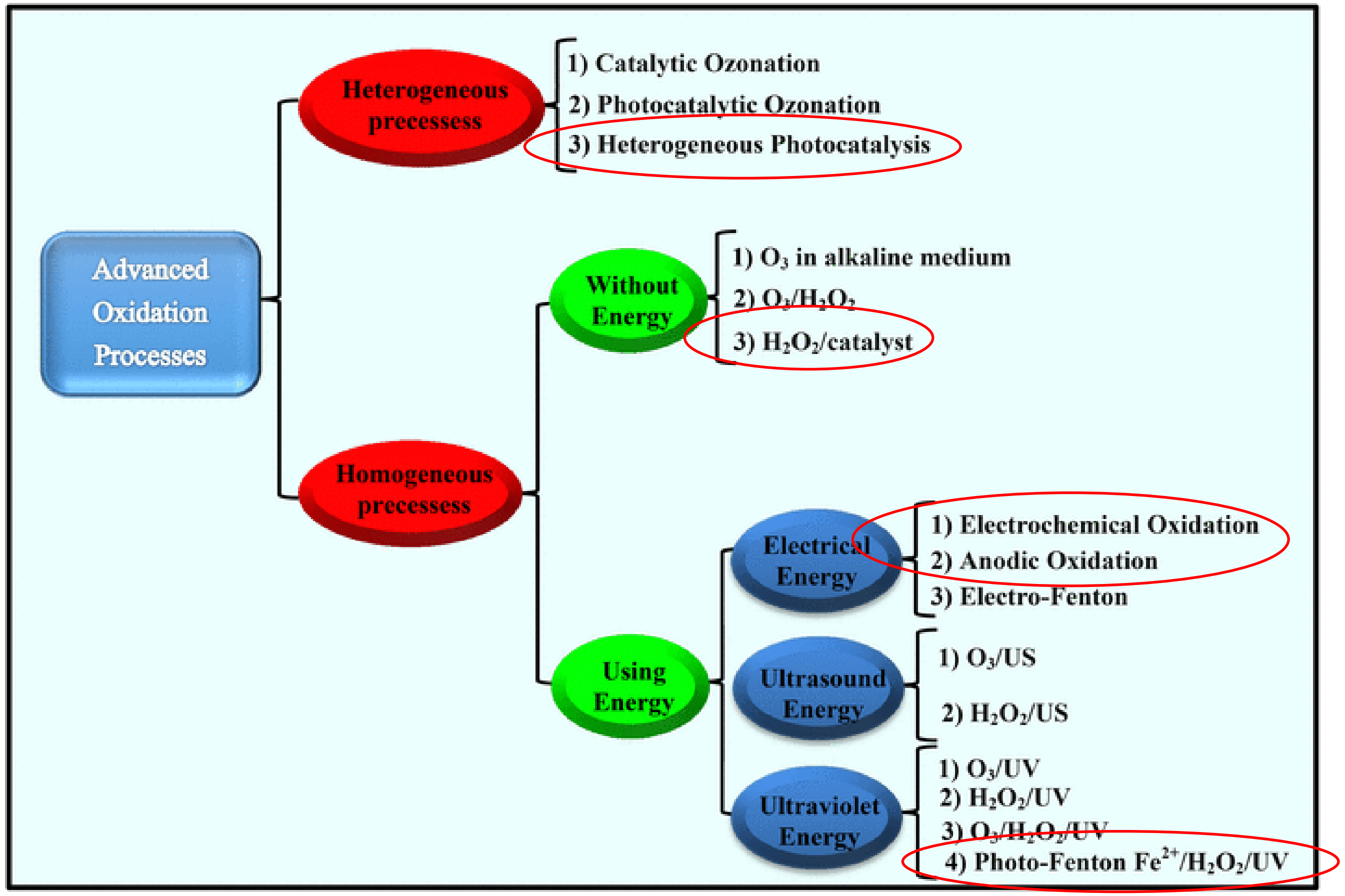


1,3,5-triazine
or
s-triazine

OBJECTIVES:

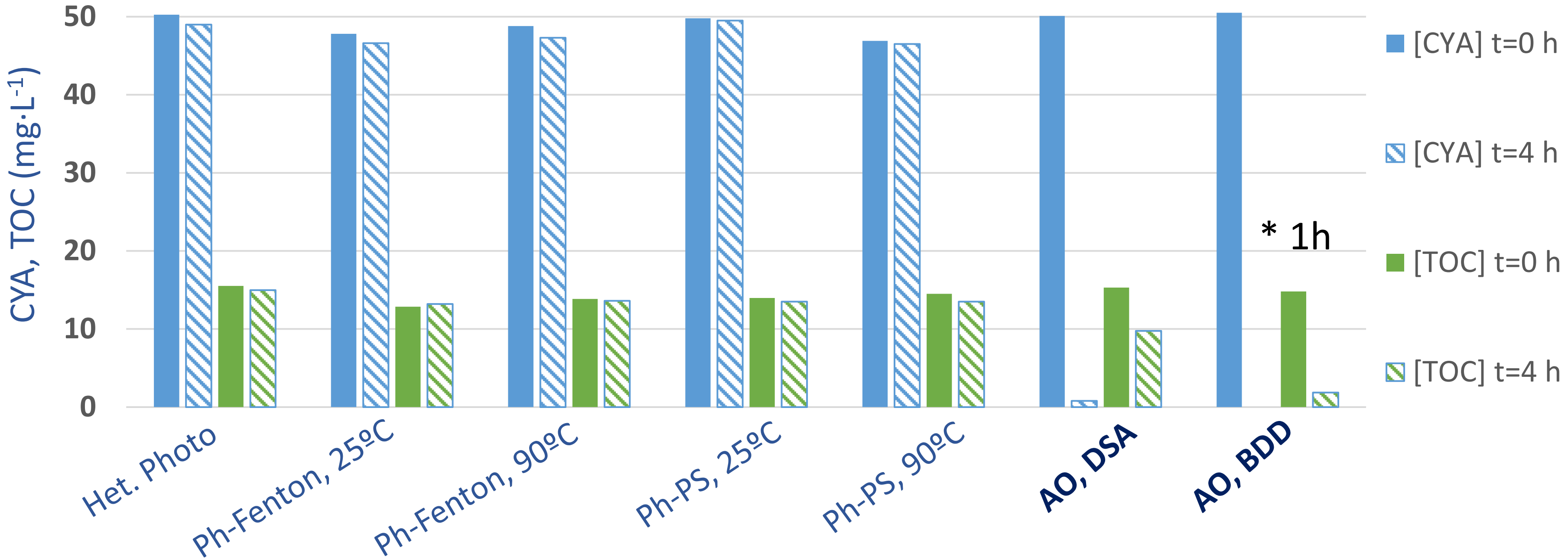
- To assess the possibility to **treat cyanuric acid by AOPs intensification**.

- Analyse the efficacy of the selected process to **treat CYN in a real swimming pool water**.



RESULTS

CYA DEGRADATION BY AOPs INTENSIFICATION

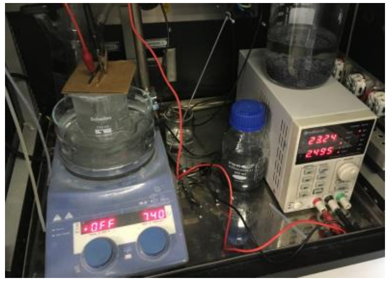


AOP PROCESS	OPERATIONAL CONDITIONS	CYA REMOVAL (%)*		TOC REMOVAL (%)*
Heterogeneous Photocatalysis (P25)	[TiO2]=0.5 g·L^{-1}; pH$_0$ = 6.7, T=25º, Hg lamp, V=750 mL	-	✗	-
Photo-Fenton	[H2O2]$_0$=Stoich. dose, [Fe^{2+}]$_0$ = 10 mg·L^{-1} pH$_0$ = 3, T=25-90 ºC, V=750 mL, Hg lamp	-	✗	-
Photo-Persulfate	[PS]$_0$=Stoich. dose, pH$_0$ = 6.7, T=25-90 ºC, V=750 mL	-	✗	-
Anodic Oixidation ,DSA Anode Ti 70 % TiO_2/30 % RuO_2 coated	Current density: 40 mA·cm$^{-2,}$ V=250 mL, L^{-1}, [NaCl]= 4 g/L, pH$_0$ = 6.7	**98.4**	✓	**36.2**
Anodic Oxidation, BDD coated Ti Anode		**100**	✓	**87.5**

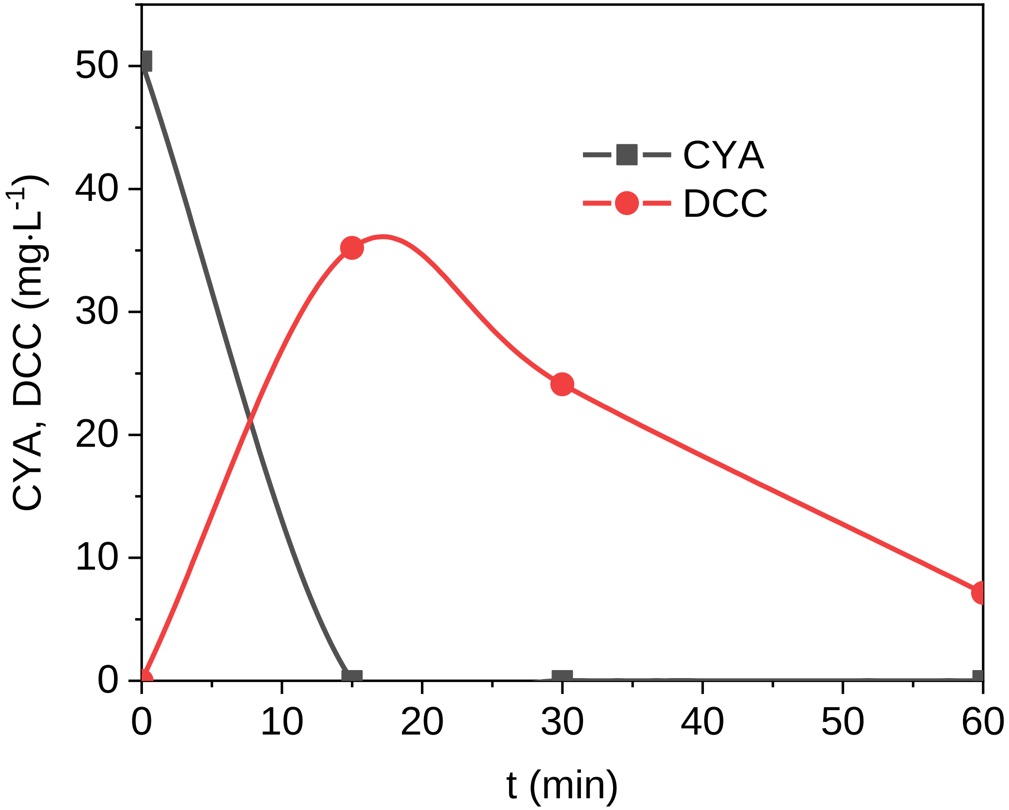
* After 4h of treatment except AO, BDD (1h)

RESULTS

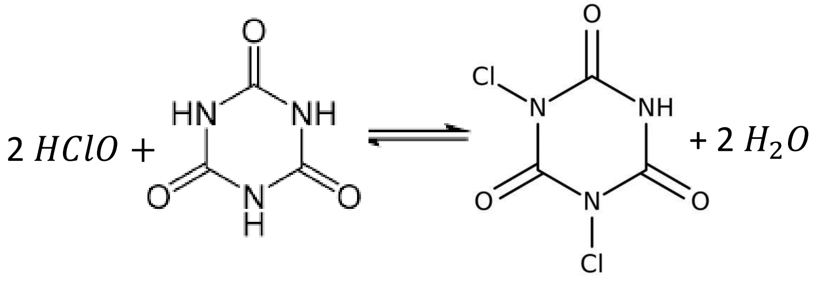
CYA DEGRADATION BY AO (BBD)



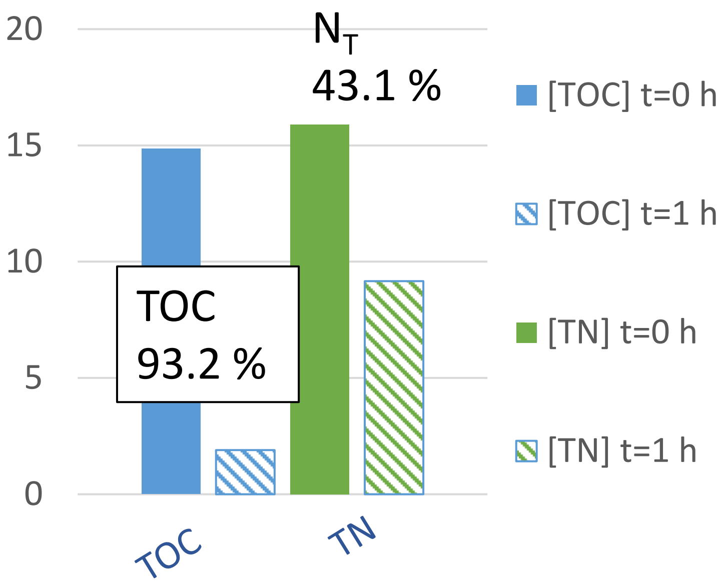
Treatment of 50 mg·L^{-1} CYA by AO, Boron Doped Diamond (BDD) electrode_[NaCl] = 4 g·L^{-1}



Operational Conditions: [CYN]= 50 mg·L^{-1} Current density: 40 mA·cm^{-2}, V=250 mL, L^{-1}, [NaCl]= 4 g·L^{-1}, pH$_0$ = 6.7



TOC and Total N evolution (ppm)

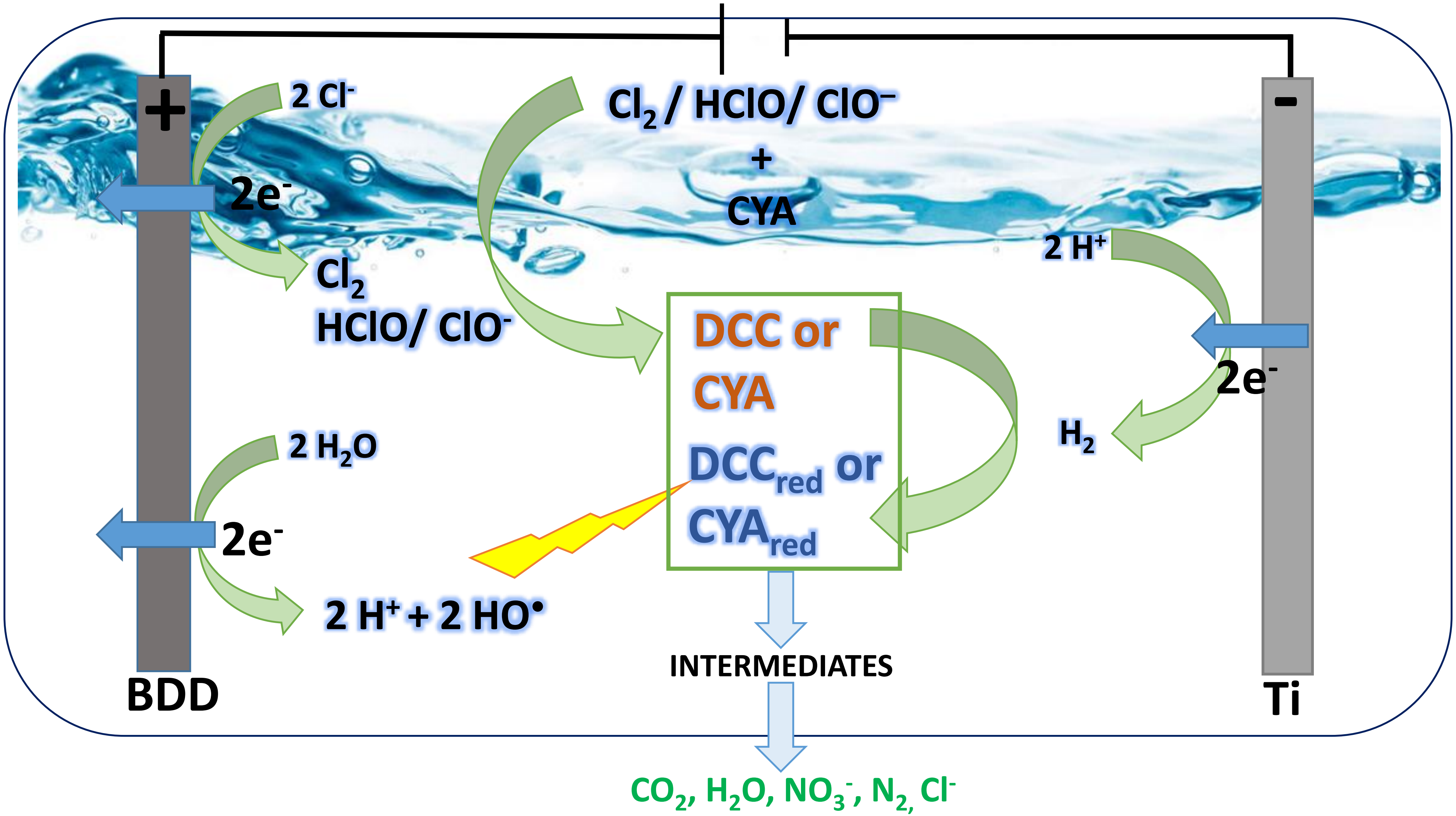


N_{NO3-} = 6.3 ppm
N_{NO2-} = 0.1 ppm
N_{NH4+} = 0.4 ppm

N_2 = 6.7 ppm
NO_x ?

RESULTS

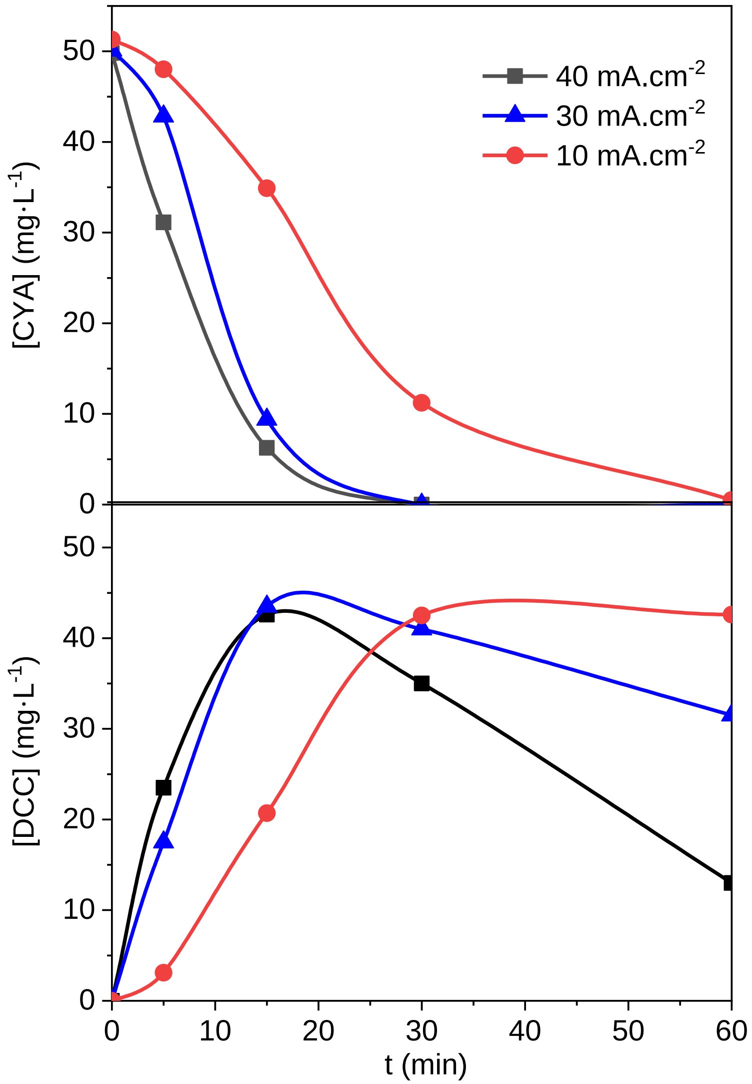
CYA DEGRADATION MECHANISM



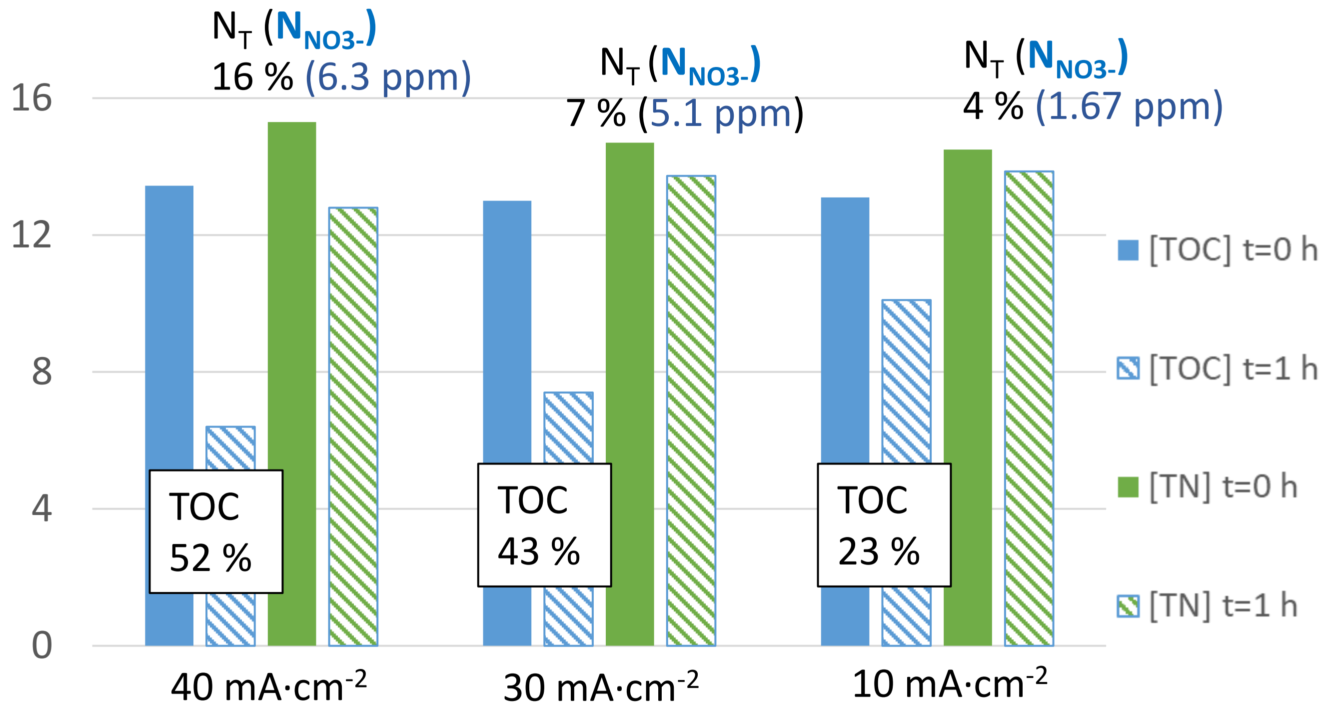
RESULTS

EFFECT OF CURRENT DENSITY

Treatment of [CYA] = 50 mg·L^{-1} by AO, Boron Doped Diamond (BDD) electrode_[NaCl] = 500 mg·L^{-1}



TOC, TN and NO_3^- evolution (ppm)



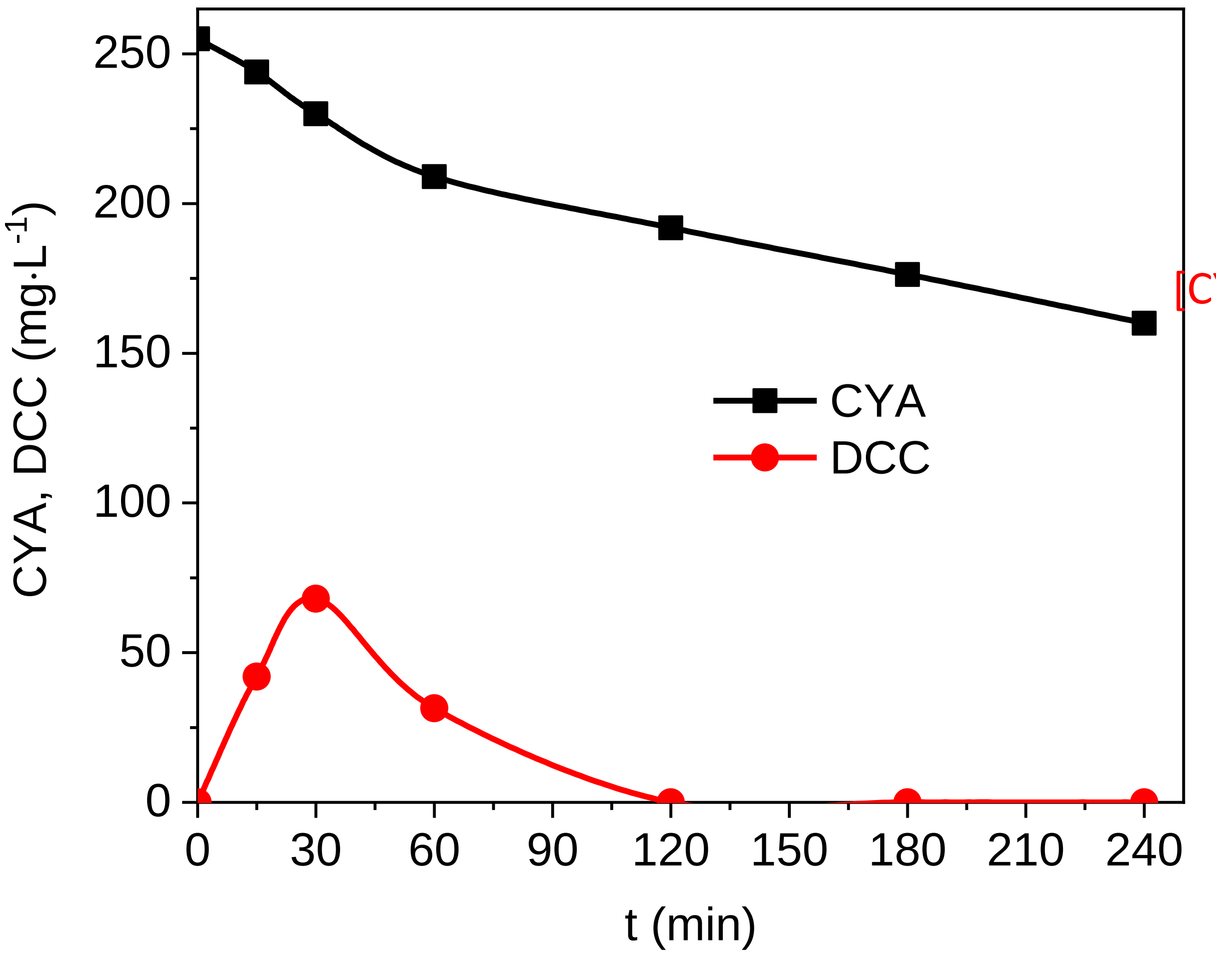
- As expected, the low the current density, the low the TOC and TN removal
- Nonetheless, still relatively high CYA removals can be achieved

Operational Conditions: [CYN]= 50 mg·L^{-1} Current density: 10-40 mA·cm^{-2}, V=250 mL, L^{-1}, [NaCl]= 500 mg·L^{-1}, pH_0 = 6.7

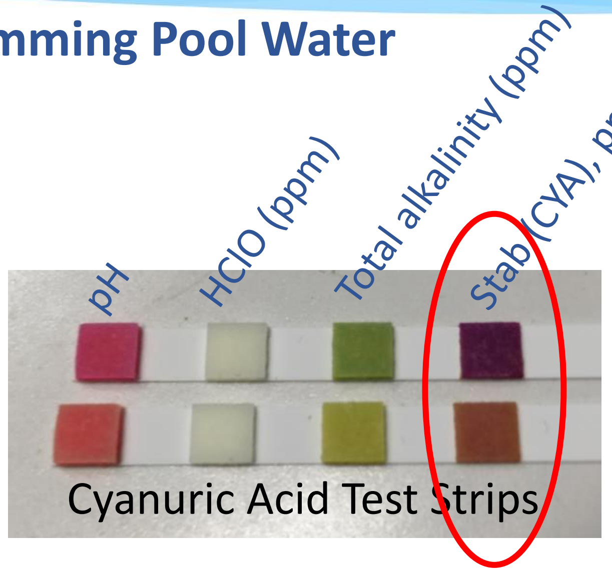
RESULTS

CYA REMOVAL: Real Swimming Pool Water

Boron Doped Diamond (BDD) electrode_Real Swimming Pool Water



$[CYA]_0$ = 250 ppm



1:2

Swimming Pool Water conditions:

t = 0 min: - pH_0 = 7.8, free chlorine = **0-0.5 ppm**; Total alkalinity = 80 ppm; **CYA = 150-300**

t = 240 min:- pH_0 = 8.2, free chlorine = **0-0.5 ppm**; Total alkalinity = 80 ppm; **CYA = 30-100**

Operational Conditions: Current density: 40 $mA \cdot cm^{-2}$, V=250 mL, L^{-1} pH_0 = 7.8

BDD AO was able to achieve a 37.2 % CYA removal even when $[CYA]_0$ = 250 ppm

CONCLUDING…

NEXT STEPS…

- Elucidate the CYA degradation by AO (HPLC-MS???)
- Test CYA degradation in real swimming pool water with DSA (Dimensionally Stable Anodes)
- Operate in continues mode (Anode stability)
- Cost assessment in CYA degradation by electrochemical Advances Oxidation Process

CONCLUDING …

- CYN in swimming pool water can be remove by AO processes.

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Acknowledgements

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