



UNIVERSIDADE ESTADUAL DE CAMPINAS

FACULDADE DE ENGENHARIA CIVIL, ARQUITETURA E URBANISMO

DEPARTAMENTO DE SANEAMENTO E AMBIENTE

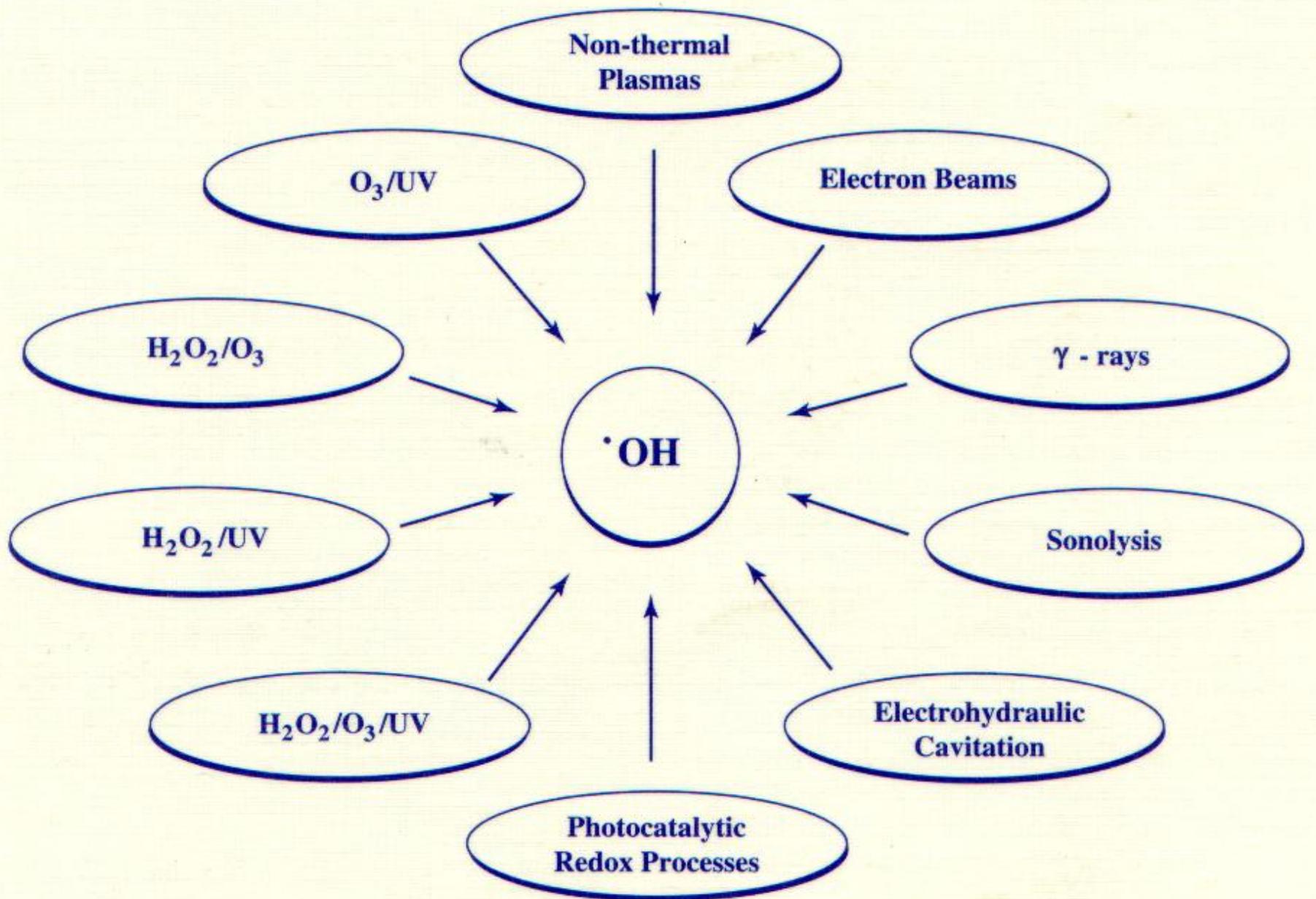
Processos Oxidativos Avançados

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Fórum-Recursos Hídricos: Oportunidades Tecnológicas
Conselho Regional de Química – IV Região
março/2013

PROCESSOS OXIDATIVOS AVANÇADOS

- 1886 – De Meritens: O_3 como desinfectante
- 1894 – Fenton: oxidação de ácido málico Fe^{2+}/H_2O_2
- 1972 – Fujishima e Honda: TiO_2/UV e $H_2O \Rightarrow O_2$ e H_2
- 1973 – “Tecnologias de Oxidação Avançadas”: UV/O_3 complexos de CN^-
- 1976 – 1º Artigo sobre FH
- 1988 – IQ-Unicamp, IC de M.M.Kondo. “FH de compostos halogenados”
- 1990 – M.M.Kondo, Mestrado. “FH de clorofórmio e uréia”
- 1991 - M.M.Kondo e W.F.Jardim . *Photodegradation of chloroform and urea using Ag-loaded titanium dioxide as a catalyst. Water Research.*
- 1998 – USEPA: “Handbook of Advanced Oxidation Process”
- 2011 – “VI Encontro sobre Aplicações Ambientais de Processos Oxidativos Avançados” (VI EPOA)
- 2013 – ICIPOA “Congresso Iberoamericano de Processos Oxidativos”



PRINCIPAIS RADICAIS LIVRES

HO^\bullet \Rightarrow radical hidroxila

HO_2^\bullet \Rightarrow radical hidroperoxila

$\text{O}_2^{\bullet-}$ \Rightarrow radical superóxido

POTENCIAL REDOX EM ÁGUA

Oxidante **Potencial de oxidação (eV)**

F_2	3,03
$\bullet OH$	2,80
$O(^1D)$	2,42
O_3	2,07
H_2O_2	1,77
HO_2^\bullet	1,70
MnO_4^-	1,67
ClO_2	1,50
Cl_2	1,36
O_2	1,23

Radiação ultravioleta (UV)

Fotólise: radiação \Leftrightarrow ligações moleculares \Rightarrow dissociação em fragmentos.

$$E = hc/\lambda = h\nu$$

Espectro de ultravioleta

- UV-A: 315 a 400 nm;
- UV-B: 280 a 315 nm;
- UV-C: 200 a 280 nm;
- UV-Vacuum: 100 a 200 nm



Elétron aquoso (baixo rendimento): $\text{H}_2\text{O} + h\nu \rightarrow \bullet\text{OH} + \text{H}^+ + \text{e}^-(\text{aq})$

Radicais secundários (rápido): $\text{O}_2 + \bullet\text{H} \rightarrow \text{HO}_2\bullet$



H₂O₂/UV



concentração de peróxido de hidrogênio; radiação ultravioleta; pH; estrutura da molécula; composição do efluente

Reagente de Fenton - H₂O₂/Fe²⁺



Mecanismo básico: oxidação por $\bullet\text{OH}$ e coagulação química de CO

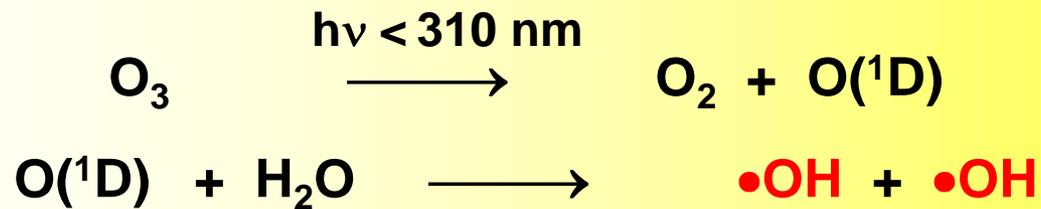
Foto-Fenton - H₂O₂/Fe²⁺/UV

Foto-redução do Fe³⁺ a Fe²⁺;

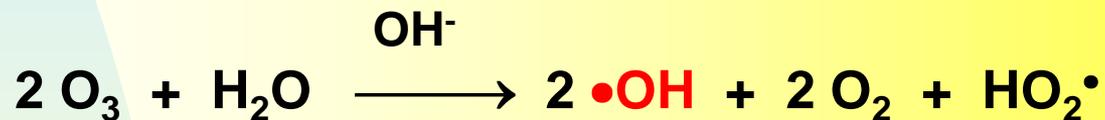
Foto-descarboxilação de complexos de carboxilato férrico;

Fotólise de H₂O₂

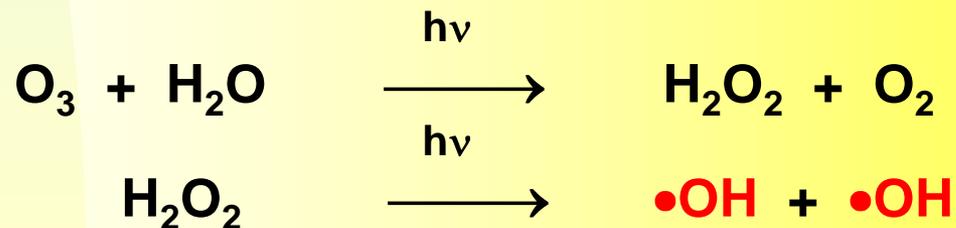
O_3 / UV



O_3 / OH^-

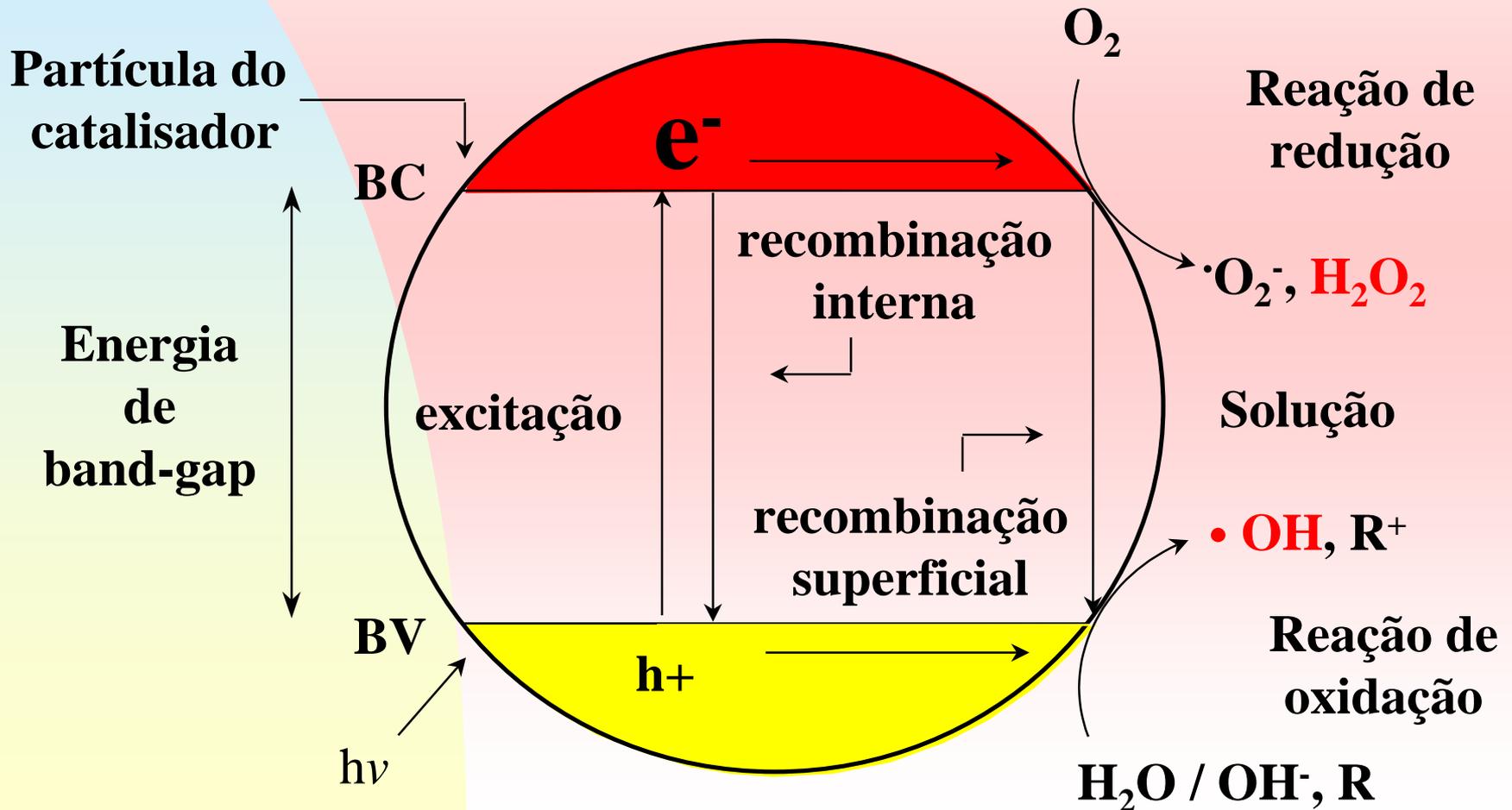


$O_3 / H_2O_2 / UV$

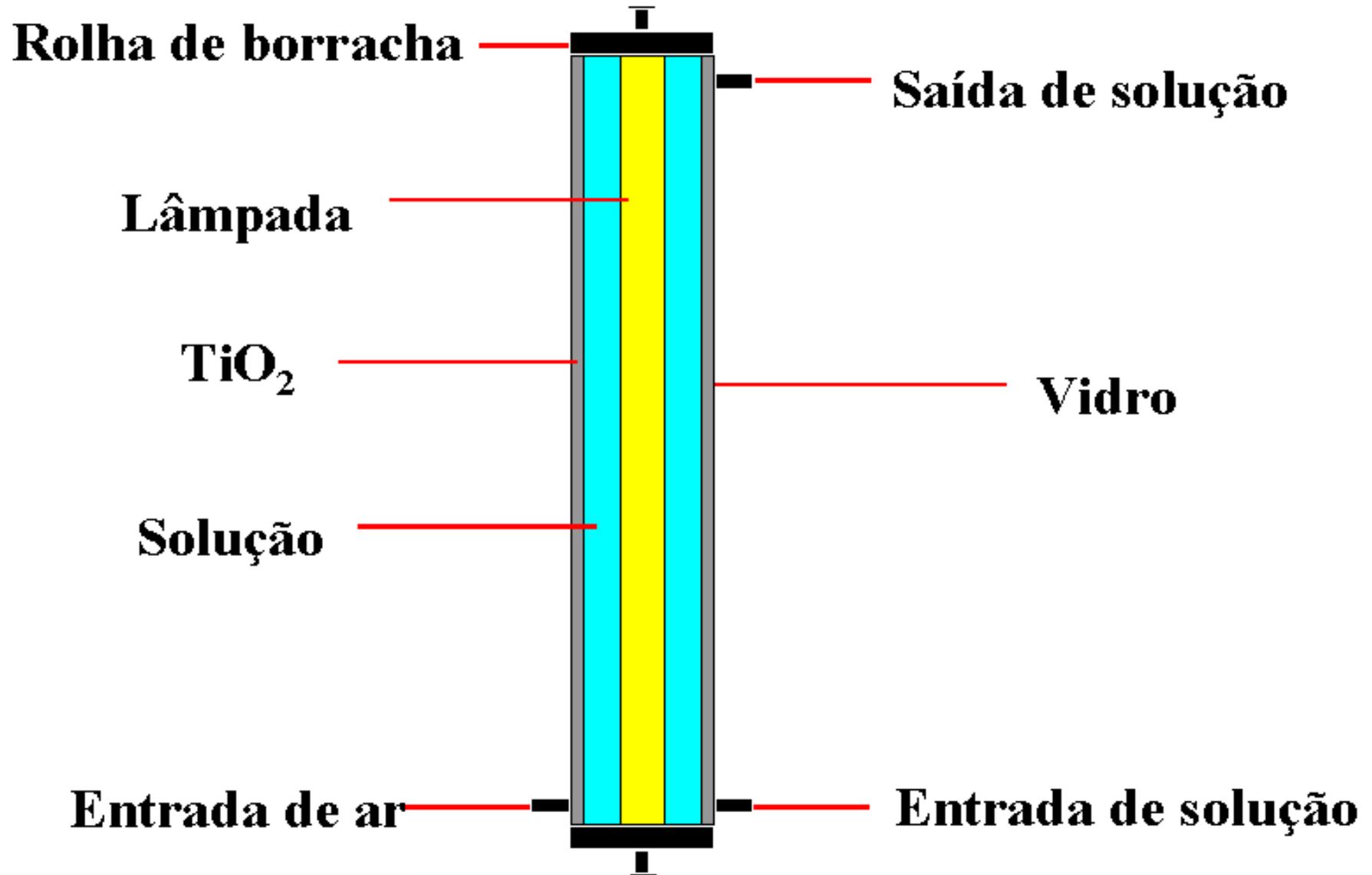


Fotocatálise Heterogênea

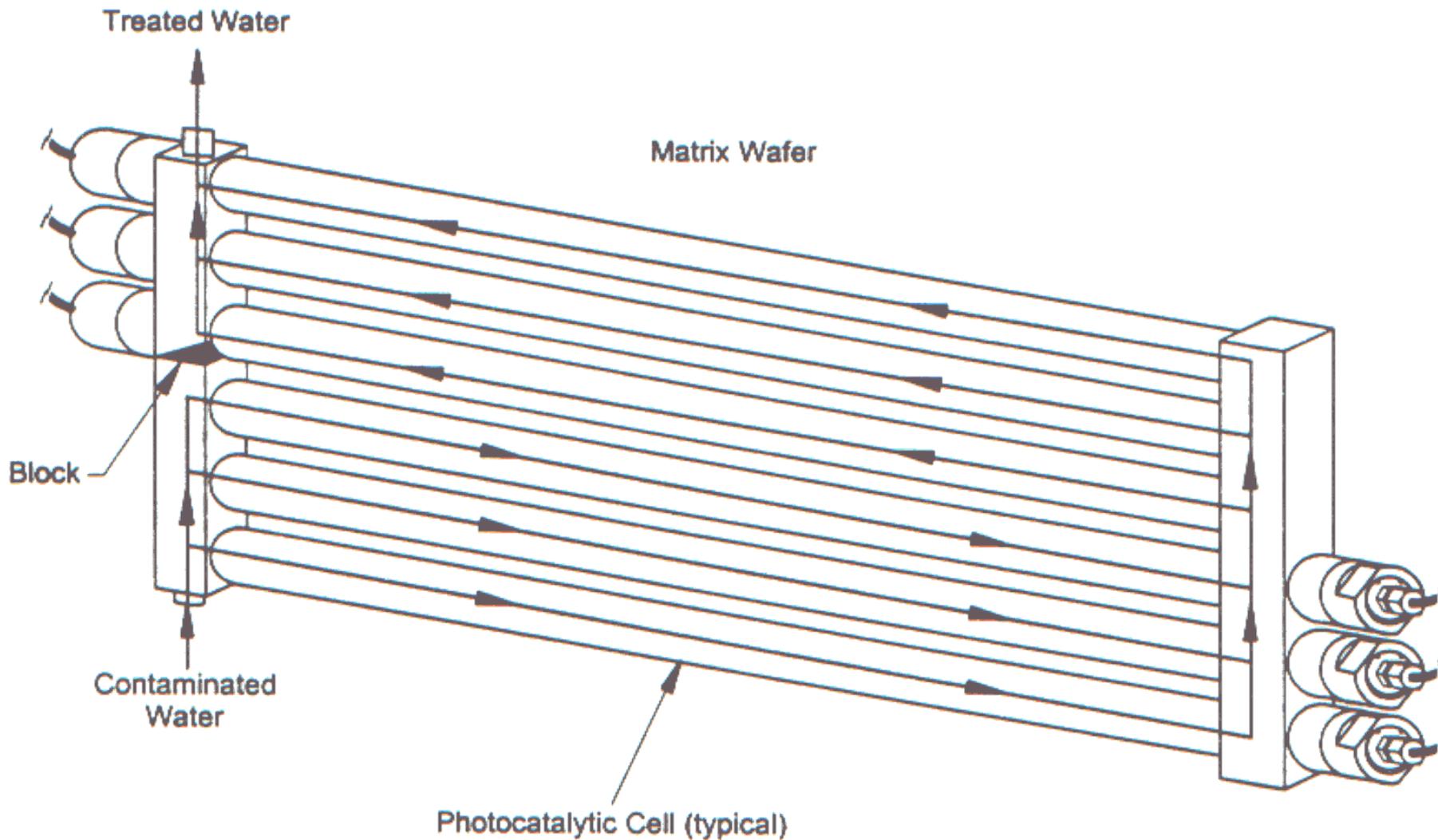
FOTOATIVACÃO DO CATALISADOR



REATOR FOTOCATALÍTICO



UV/TiO₂ (matrix system)



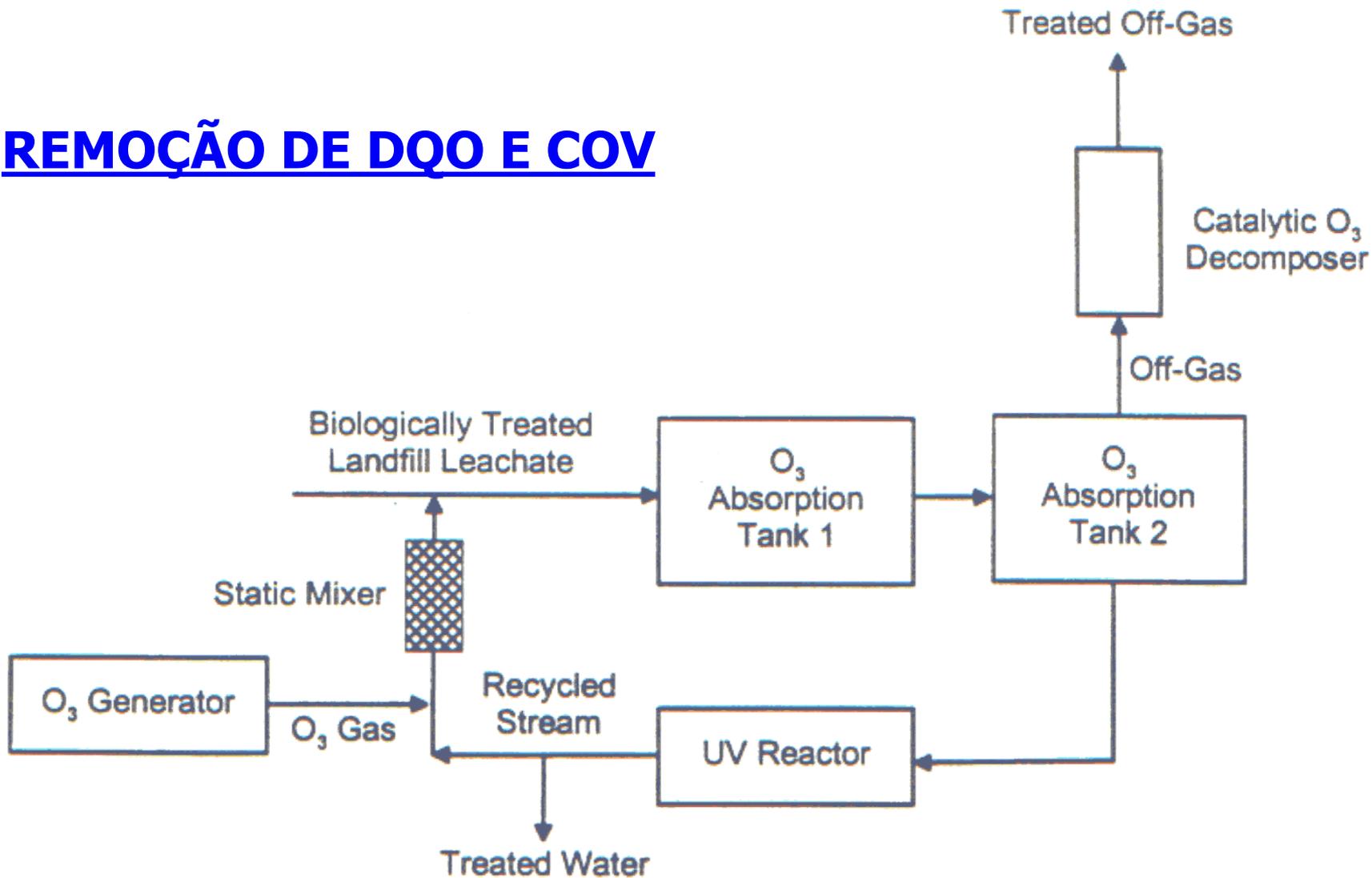
Lâmpada UV de 75 W; 254 nm, 1,75 m

Vazão de 0,8 L/min (cada cela)

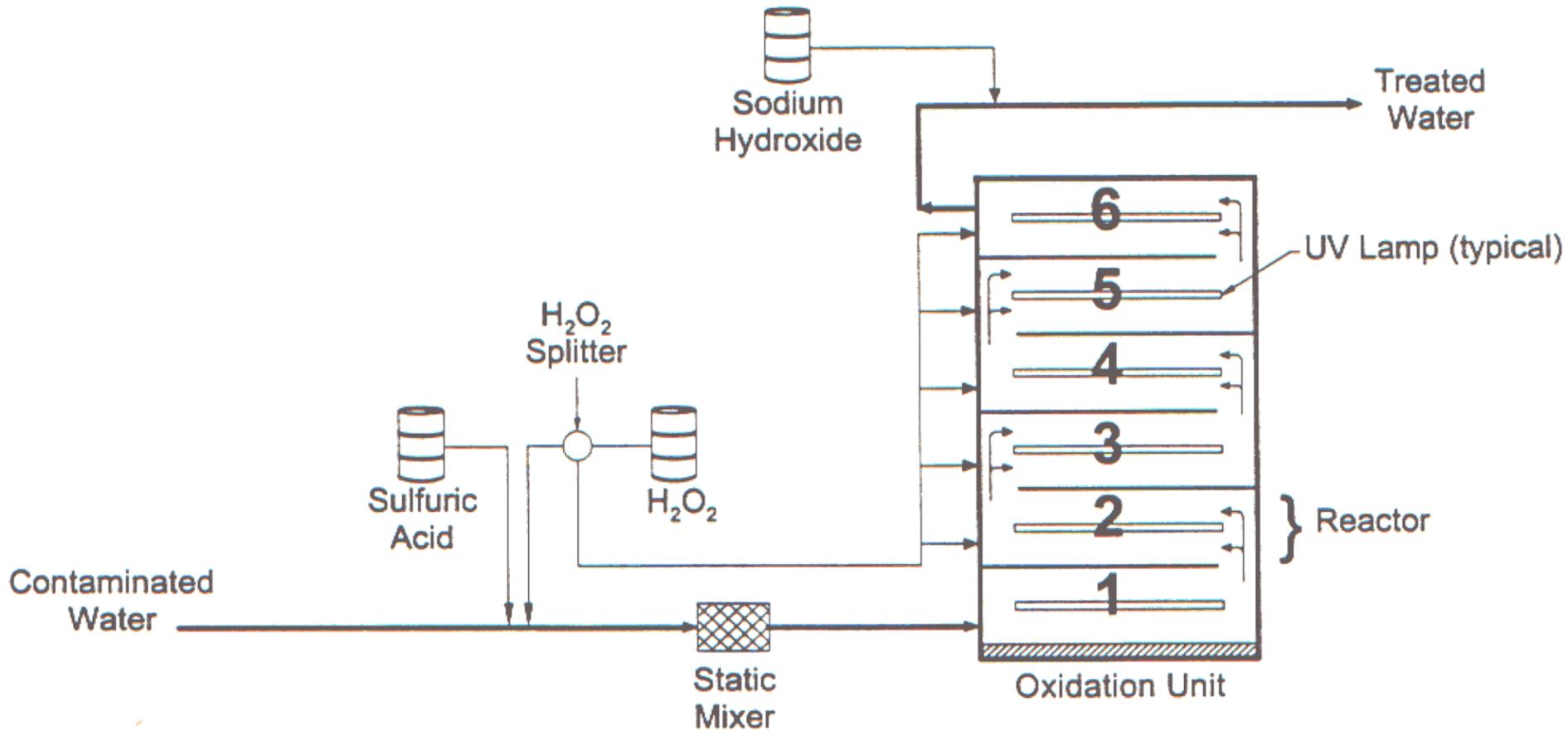
UV/O₃ (WEDECO)

Lixiviado de aterro sanitário tratado biologicamente

REMOÇÃO DE DQO E COV

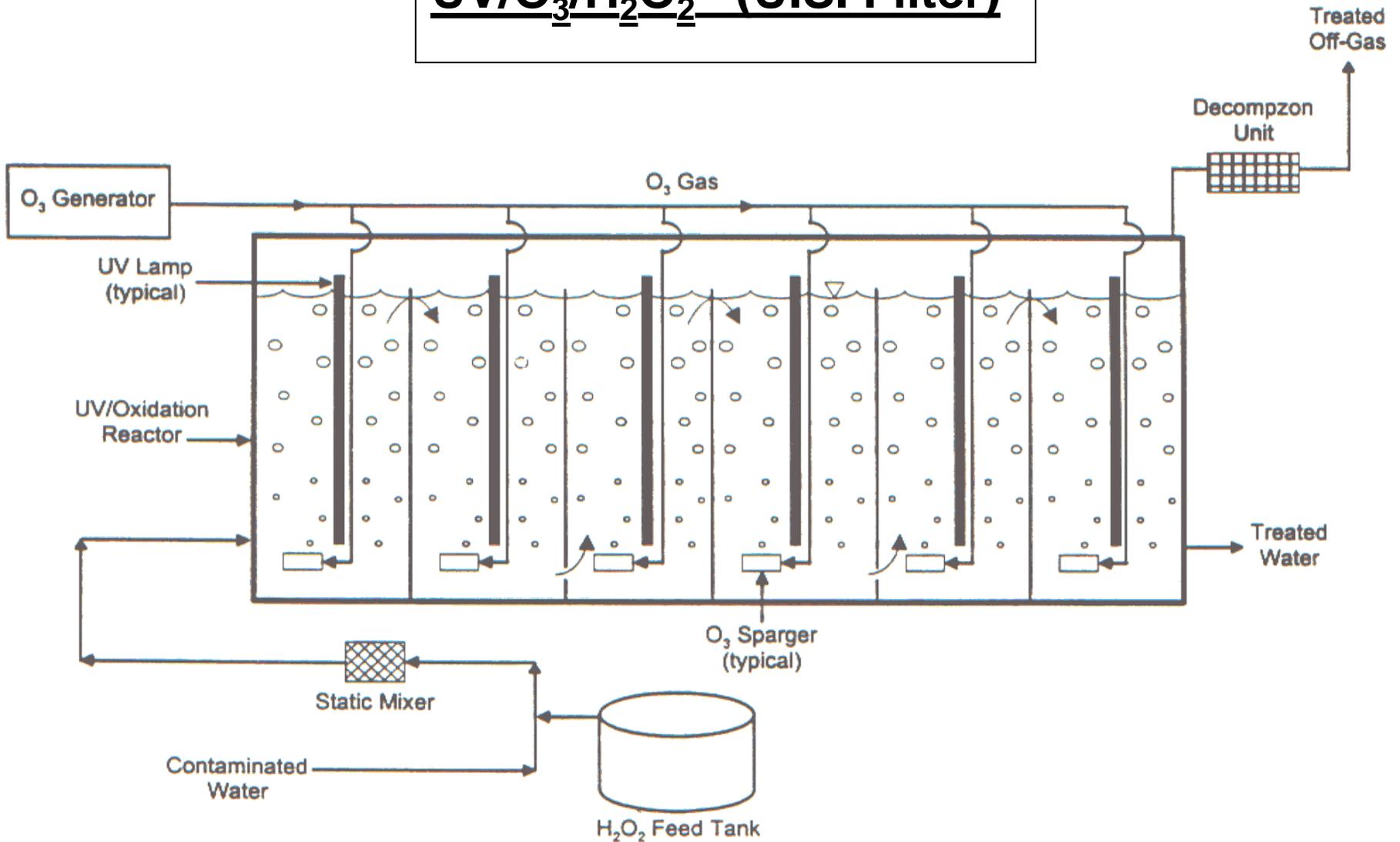


UV/H₂O₂ (Calgon)



Lâmpada UV ⇒ 15 kW e Reator ⇒ 55 L

UV/O₃/H₂O₂ (U.S. Filter)



V_{REATOR} = (1 x 0,5 x 2) m; 24 lâmpadas UV (65 W)

UV/TiO₂

Fenol; mono,
di e triclorofenol:

1,0 x 10⁻³ mol/L

tetra e pentaclorofenol:

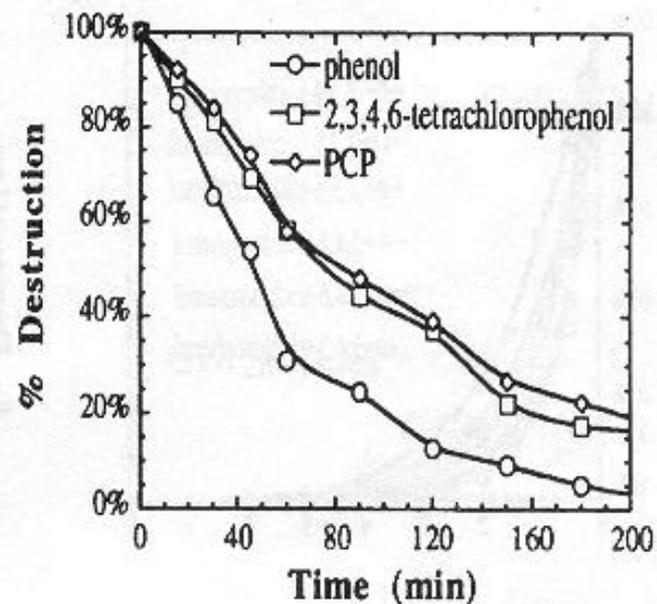
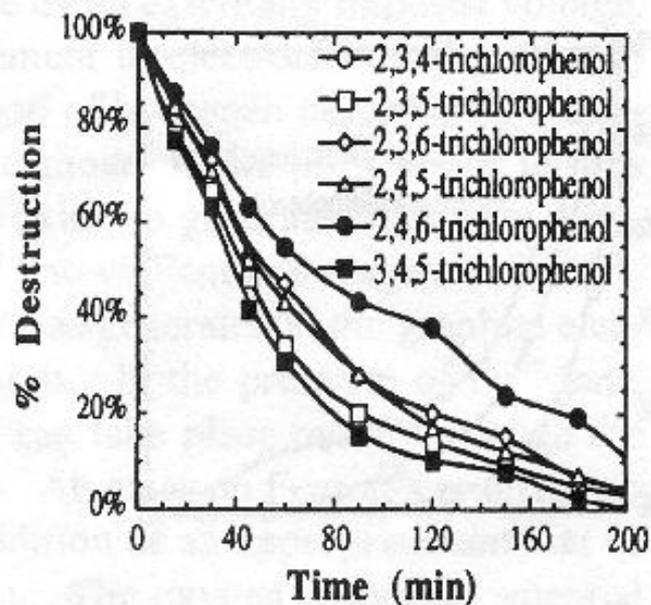
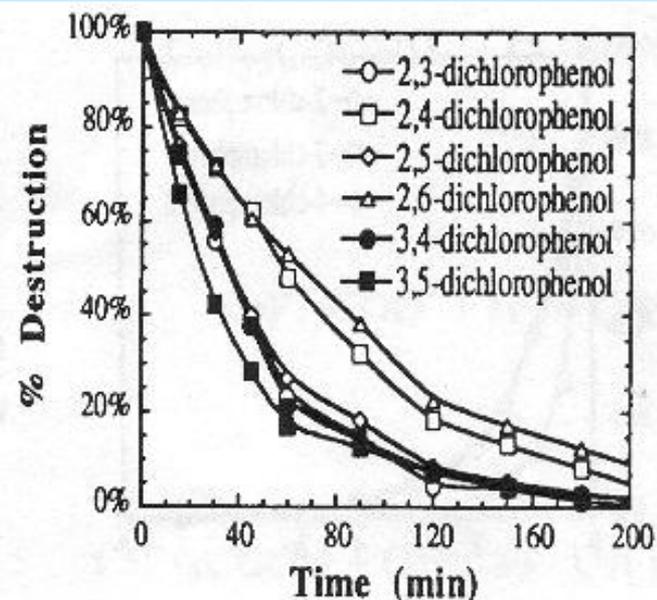
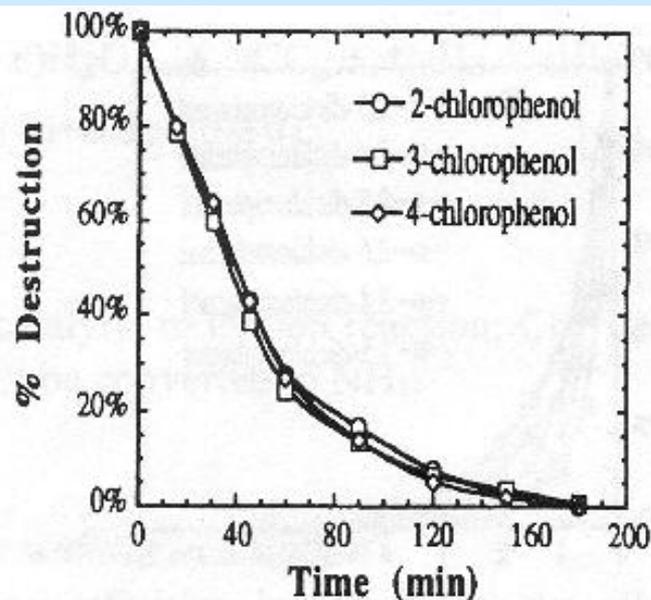
5,0 x 10⁻⁵ mol/L

TiO₂ : 1,0 g/L

pH: 3,0

I: 5,0 x 10⁻² mol/L

(NaNO₃)



UV/H₂O₂

Fenol; mono,
di e triclorofenol:

1,0 x 10⁻³ mol/L

tetra e pentaclorofenol:

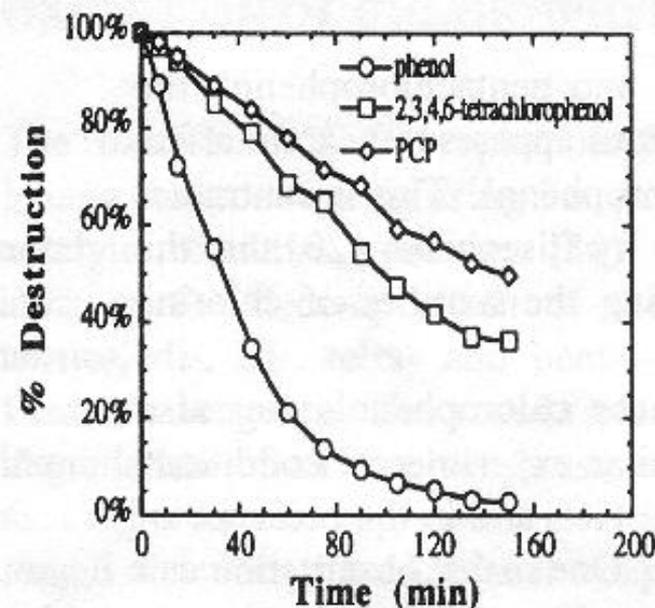
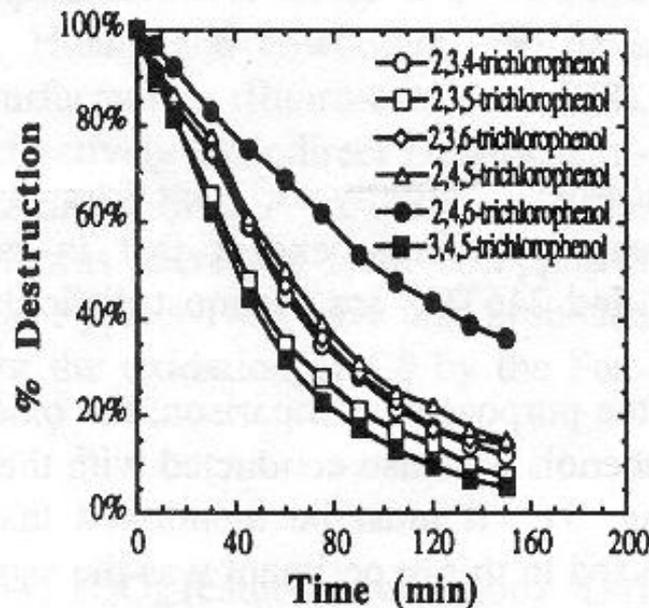
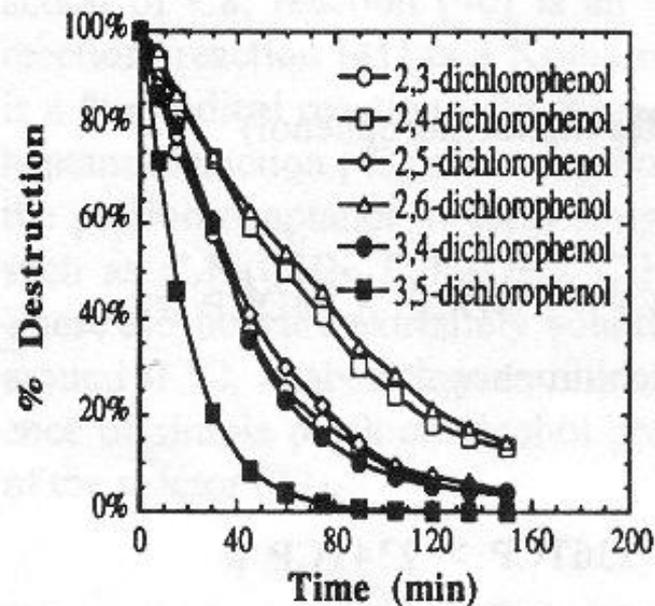
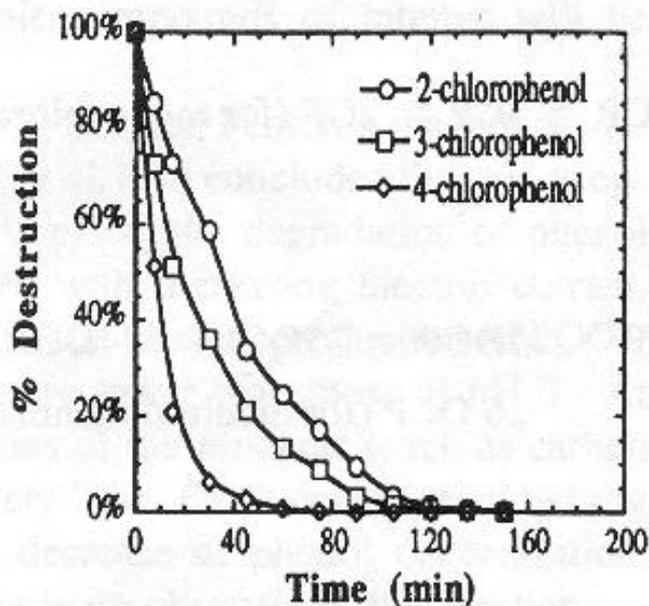
5,0 x 10⁻⁵ mol/L

H₂O₂ : 0,1 mol/L.min

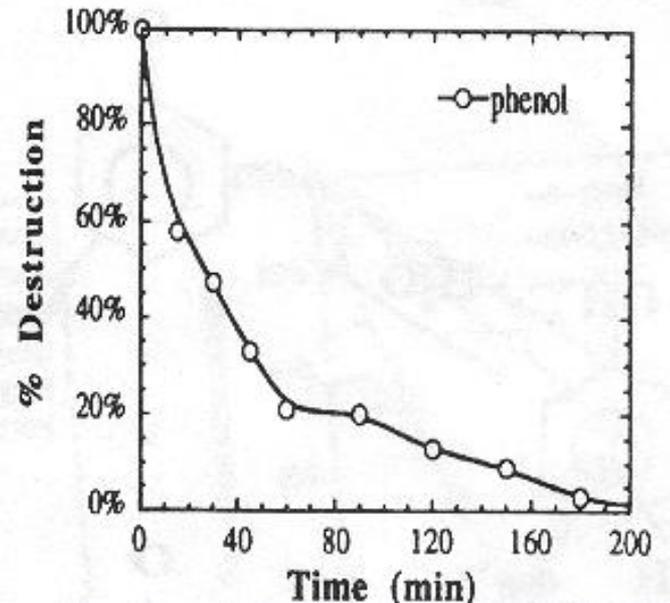
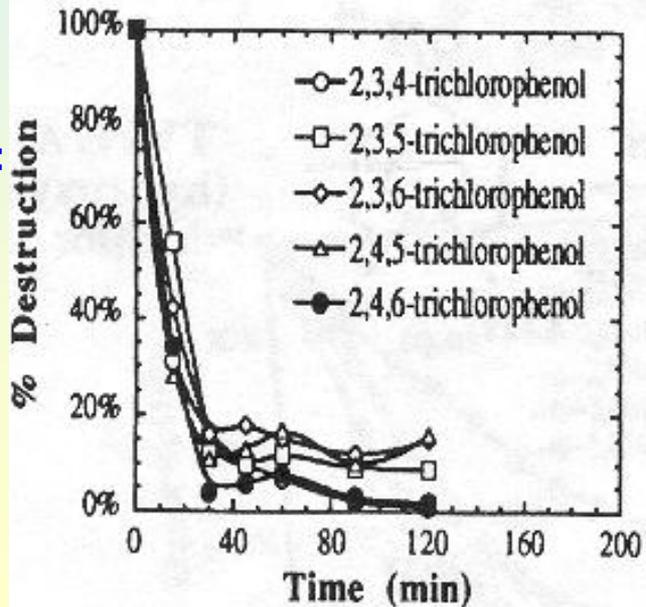
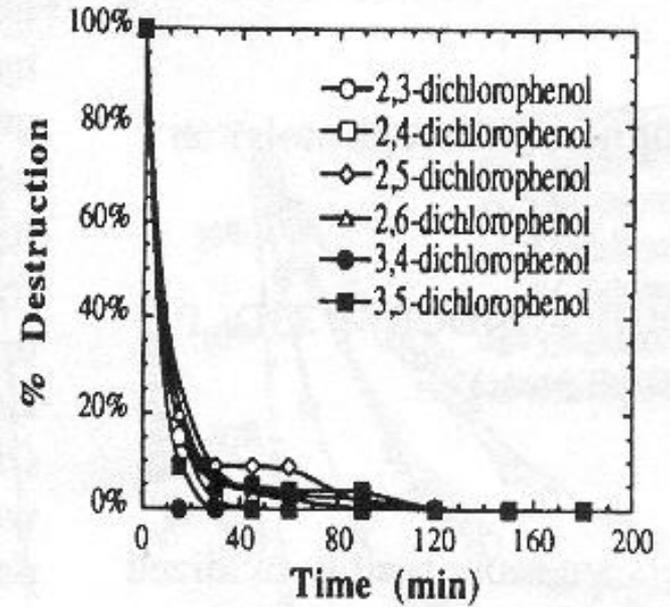
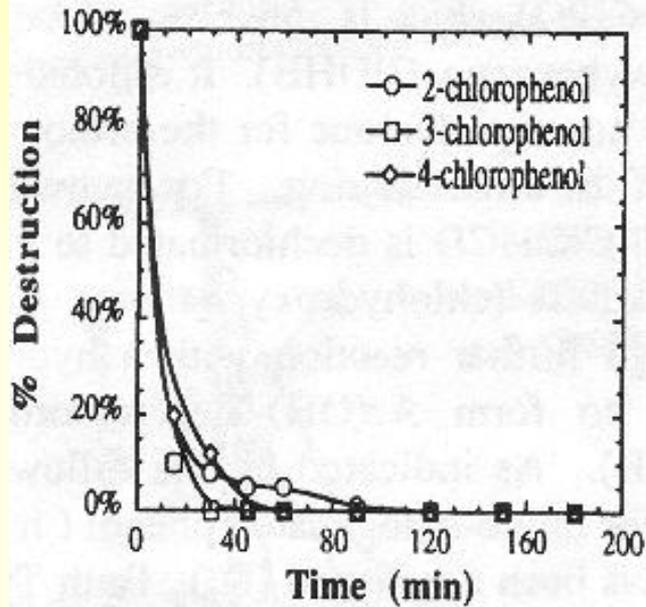
pH: 3,0

I: 5,0 x 10⁻² mol/L

(NaNO₃)



UV/TiO₂/H₂O₂



Fenol; mono,
di e triclorofenol:

$1,0 \times 10^{-3}$ mol/L

tetra e pentaclorofenol:

$5,0 \times 10^{-5}$ mol/L

TiO₂: 1,0 g/L

H₂O₂: 0,1 mol/L.min

pH: 4,0

I: $5,0 \times 10^{-2}$ mol/L

(NaNO₃)

REAGENTE DE FENTON

Fenol; mono,
di e triclorofenol:

$1,0 \times 10^{-3}$ mol/L

tetra e pentaclorofenol:

$5,0 \times 10^{-5}$ mol/L

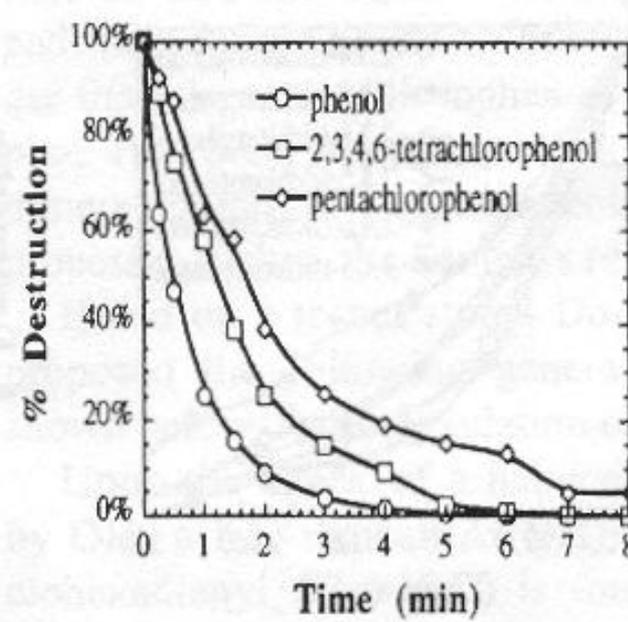
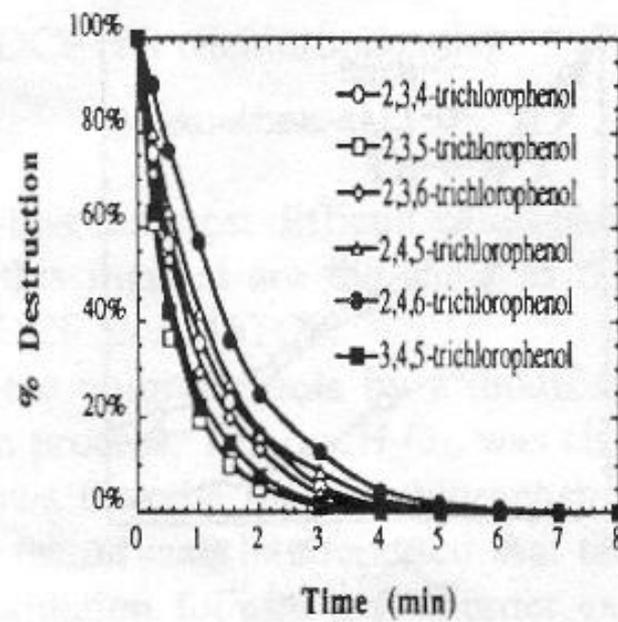
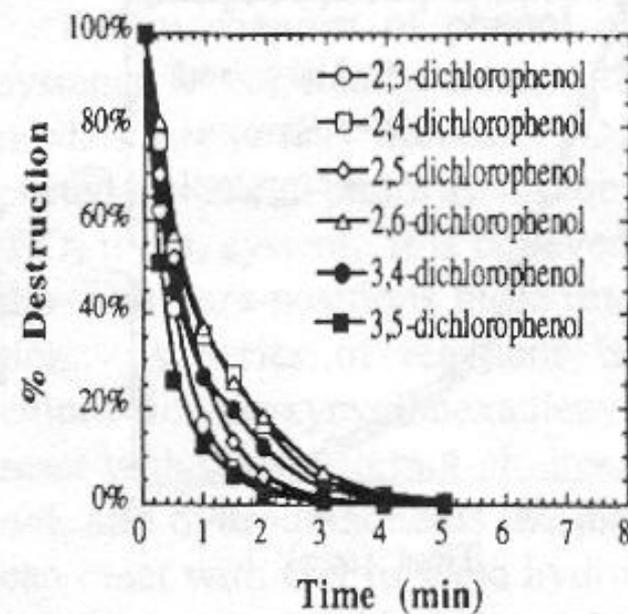
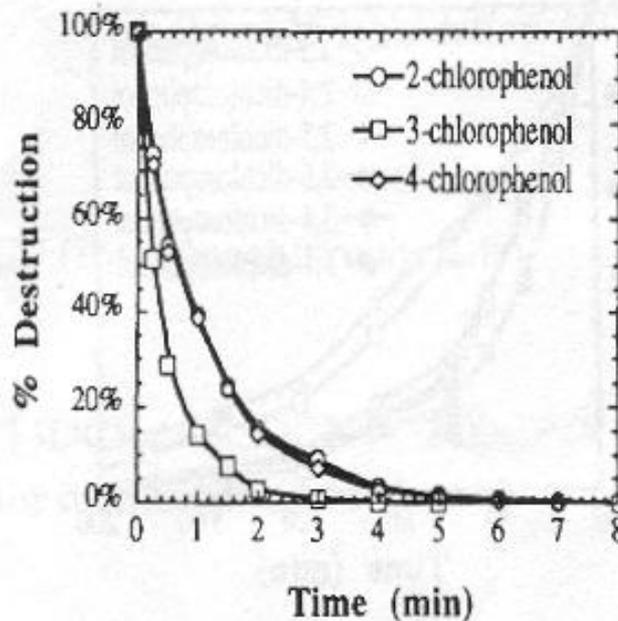
Fe^{2+} : $1,0 \times 10^{-3}$ mol/L

H_2O_2 : $6,7 \times 10^{-4}$
mol/L.min

pH: 3,0

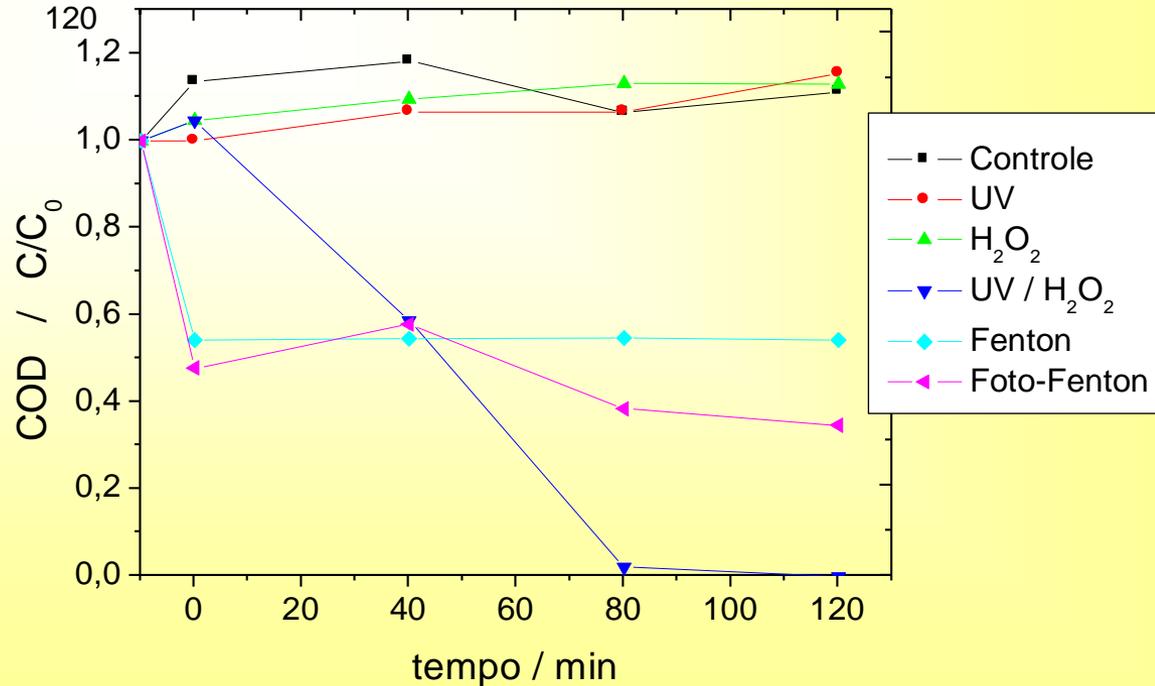
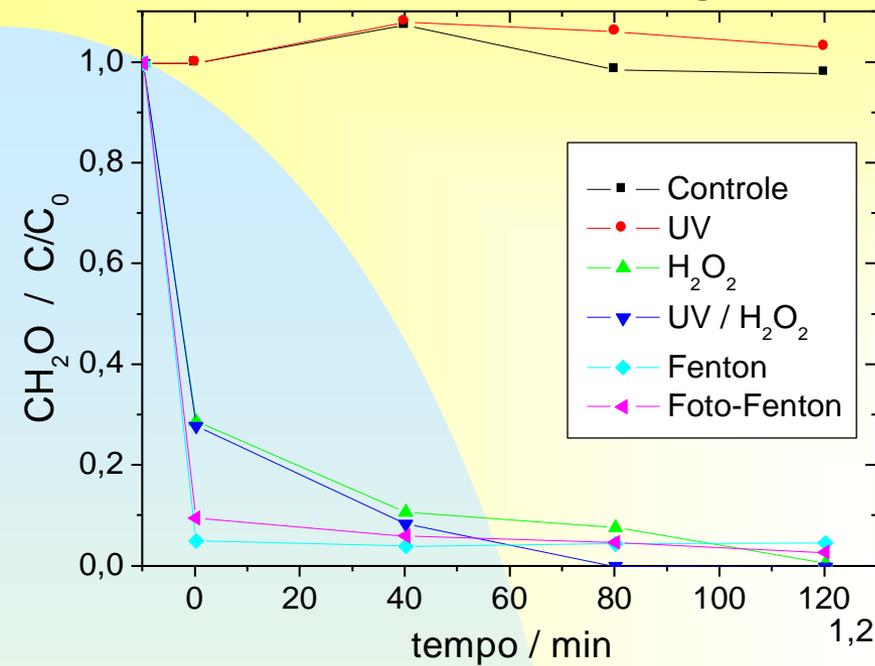
I: $5,0 \times 10^{-2}$ mol/L

(NaNO_3)



DEGRADAÇÃO DE FORMOL (400 mg L⁻¹)

JR Guimarães; CRT Farah; MG Maniero; PS Fadini
Journal of Environmental Management,
v. 107, p. 96-101, 2012



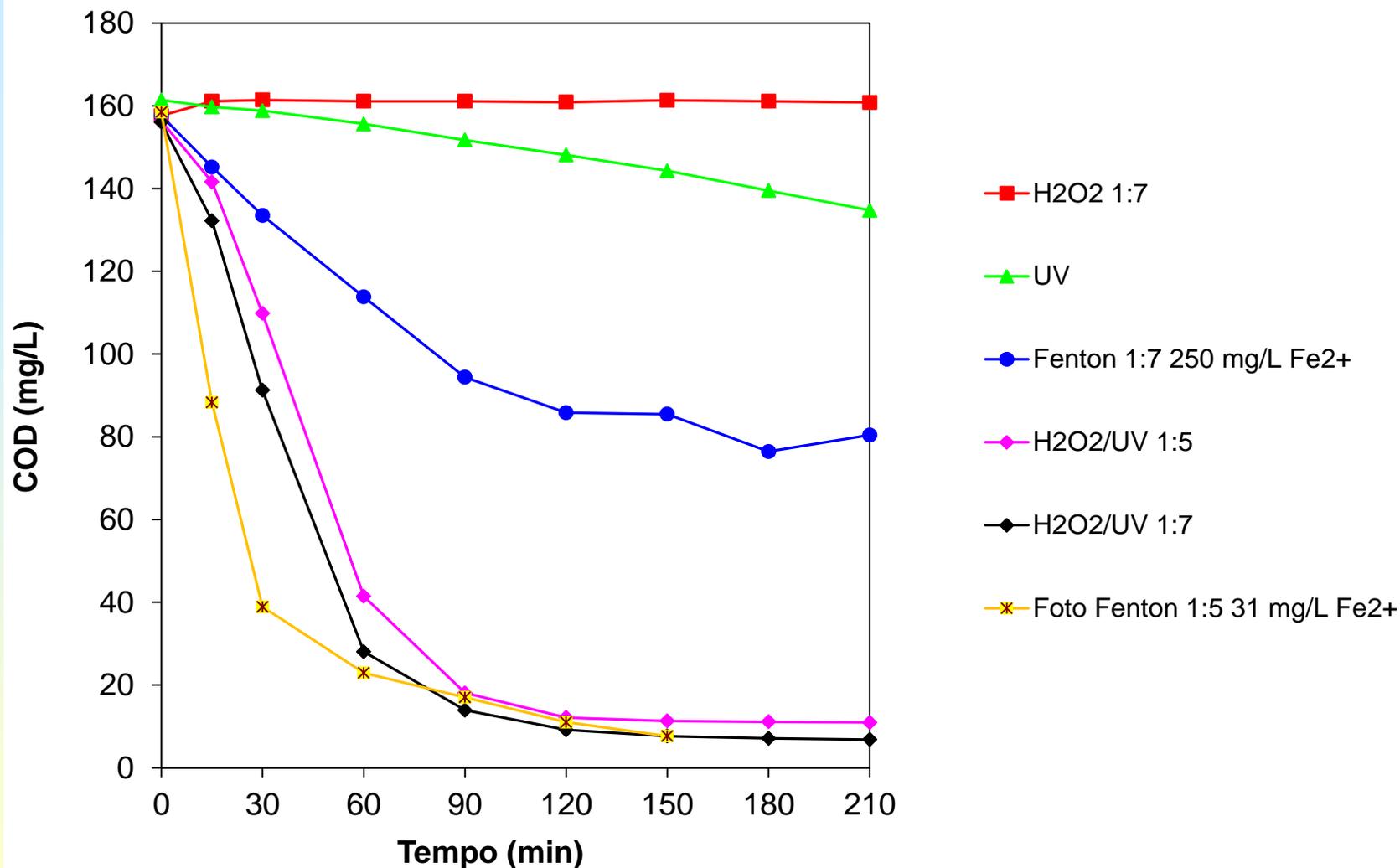
degradação de formol

Processo UV/H ₂ O ₂			
Solução de formol	Tempo de recirculação*	% red. COD	% red. CH ₂ O
1.200	210	91	91
3.000	300	83	99
6.000	270	70	98
12.000	480	65	-

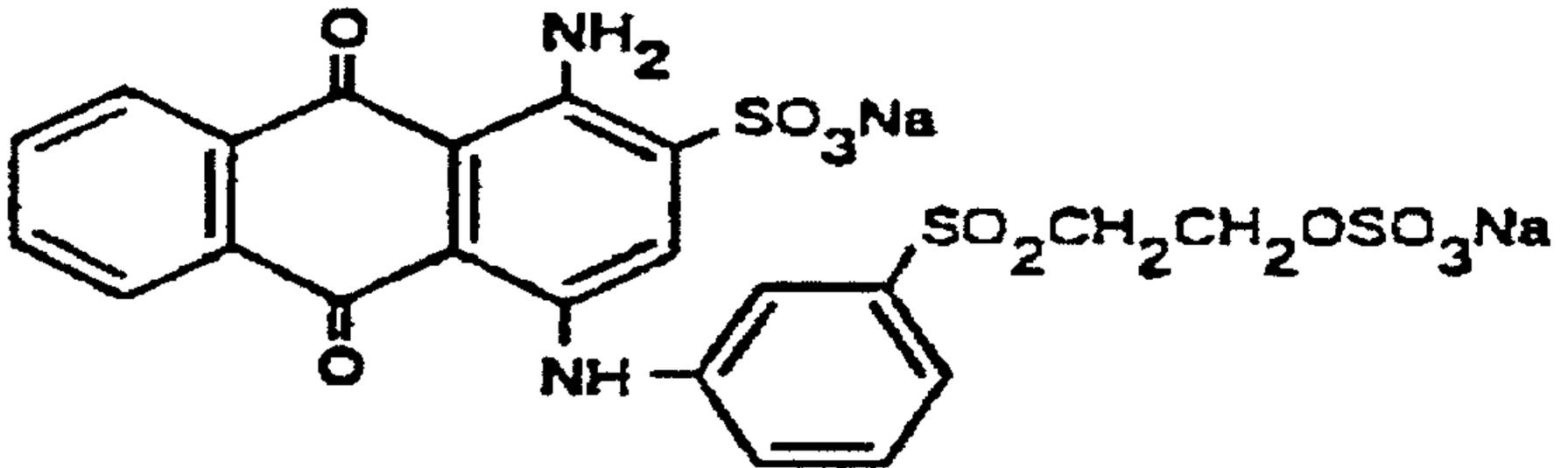
Processo Foto-Fenton			
Solução de formol	Tempo de recirculação*	% red. COD	% red. CH ₂ O
1.200	90	63	-
3.000	120	58	-
6.000	180	64	99
12.000	390	65	99

* Tempo necessário para o consumo do H₂O₂ – análise realizada na hora da coleta

Água ácida retificada - PETROBRAS

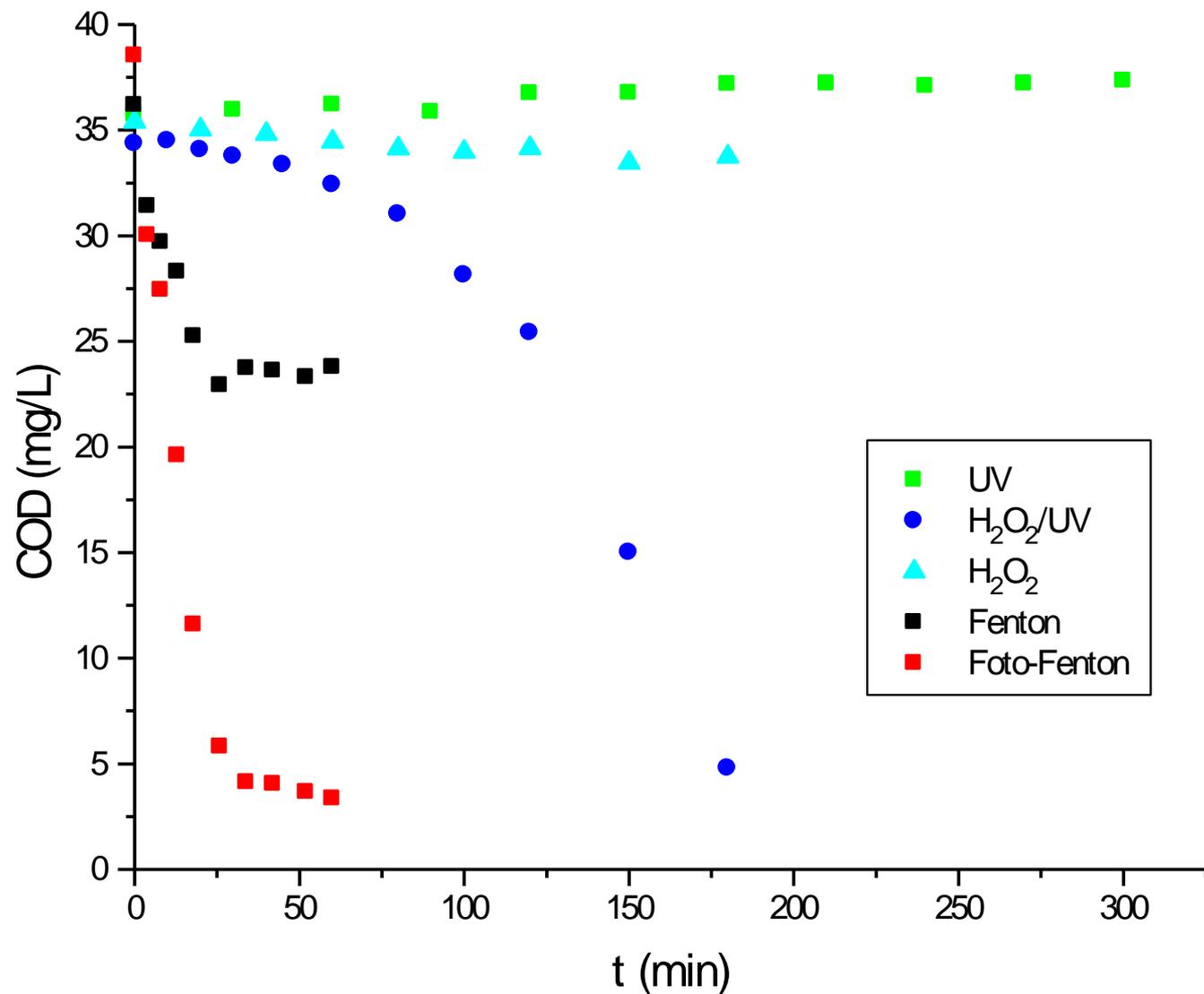


DEGRADAÇÃO DO CORANTE AZUL REATIVO 19



JR Guimarães; MG Maniero; RN Araújo

Journal of Environmental Management, v. 110, p. 33-39, 2012.



**VARIAÇÃO DE COD NA DEGRADAÇÃO DO CORANTE R-19,
 ($C_{\text{corante}} = 100 \text{ mg/L}$, $C_{\text{H}_2\text{O}_2} = 300 \text{ mg/L}$, $C_{\text{Fe}^{2+}} = 30 \text{ mg/L}$)**

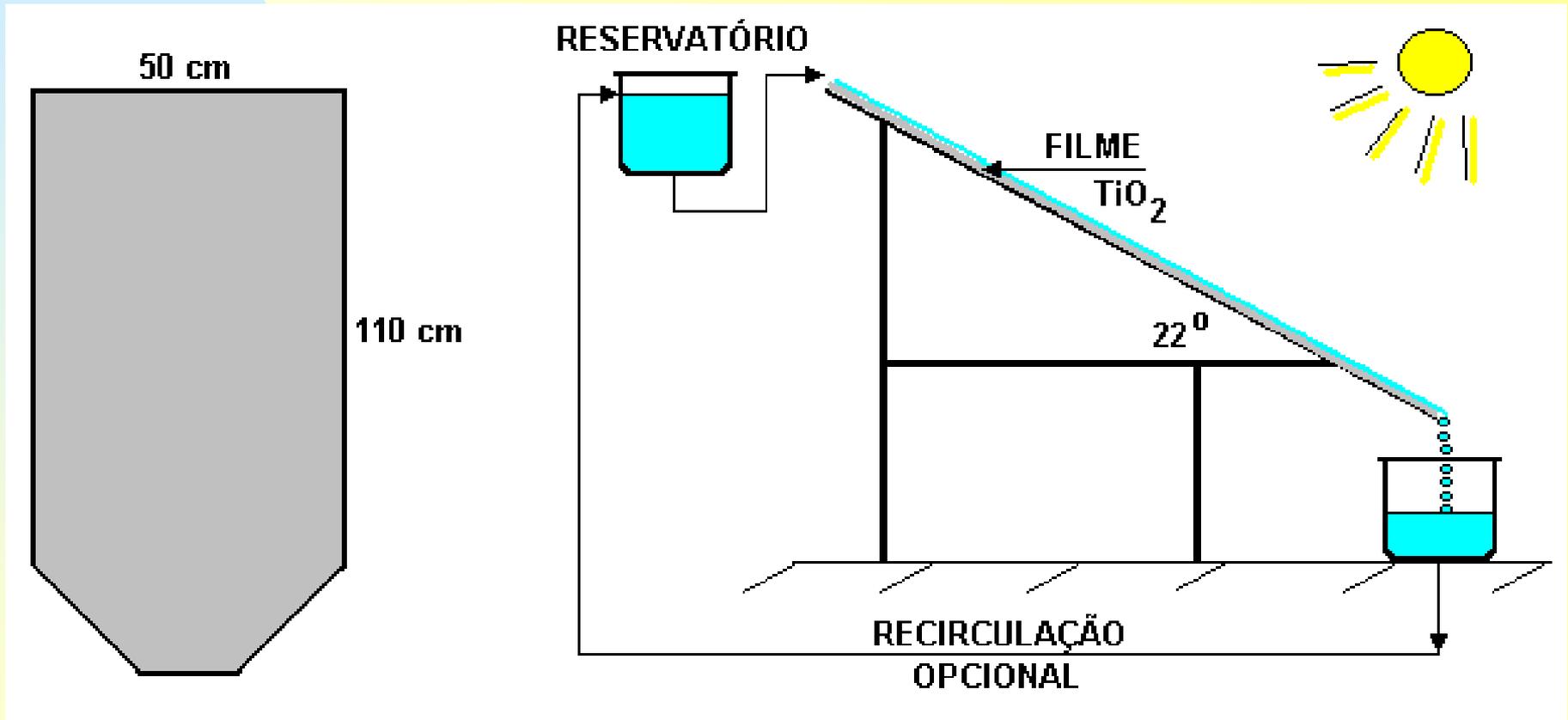
Processo Foto-Fenton



Solução de corante R-19 antes e após 1 hora de tratamento pelo processo Foto-Fenton

Desinfecção de águas

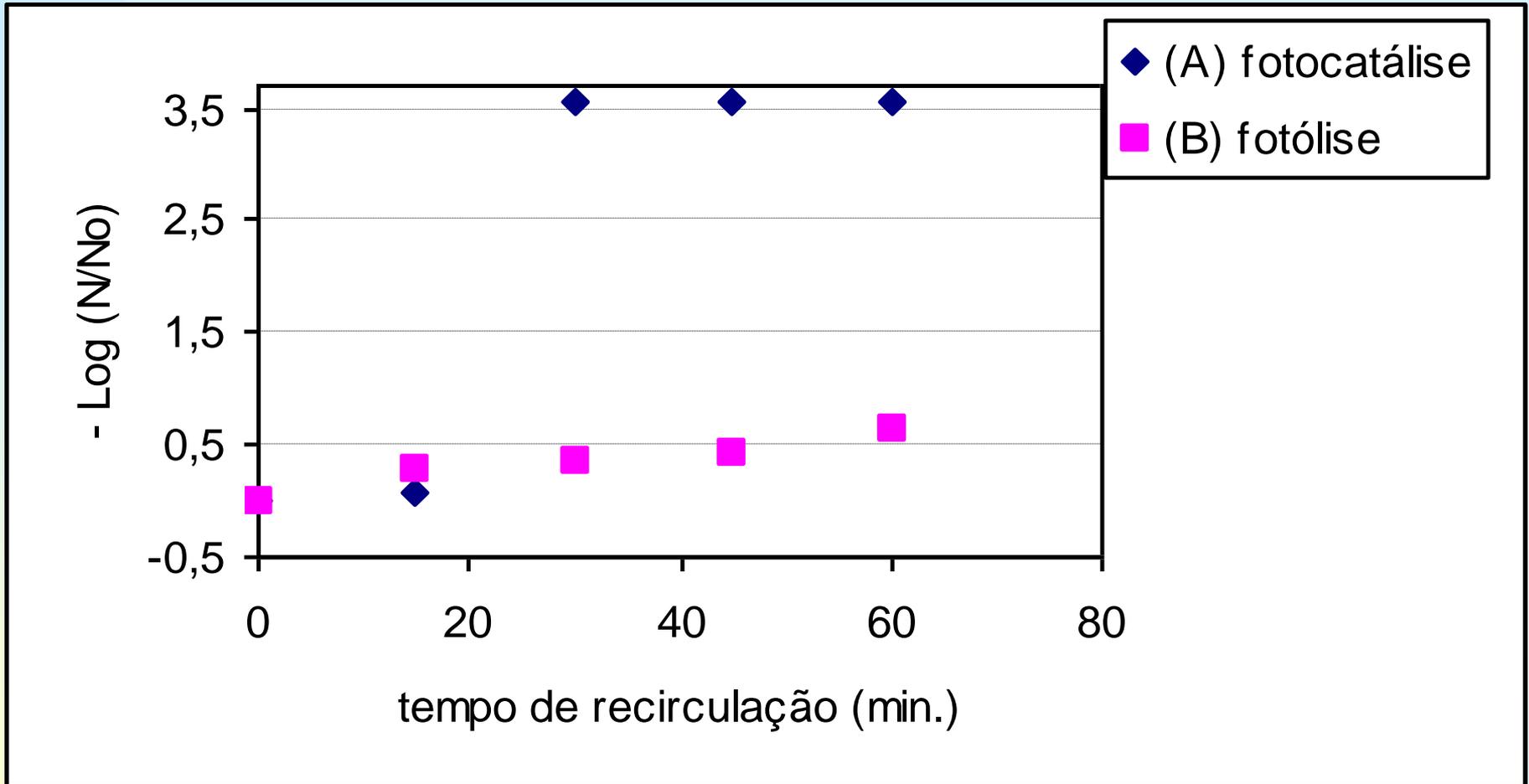
LEITO FIXO - SOLAR



CP Rodrigues ; RL Ziolli; JR Guimarães

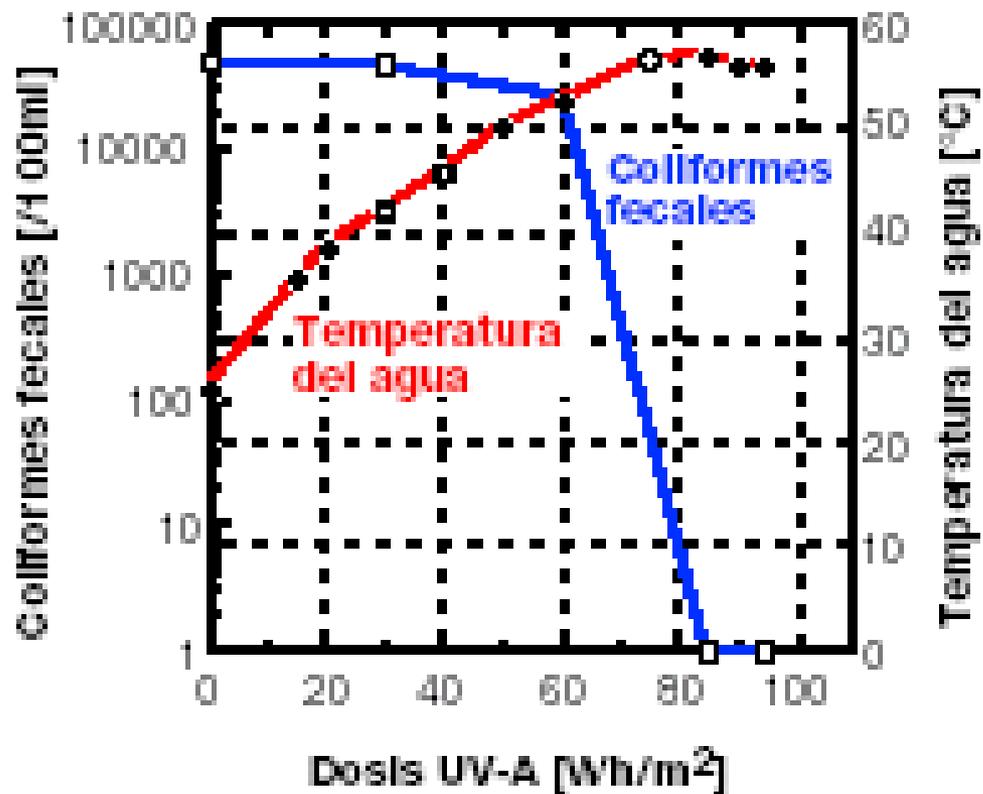
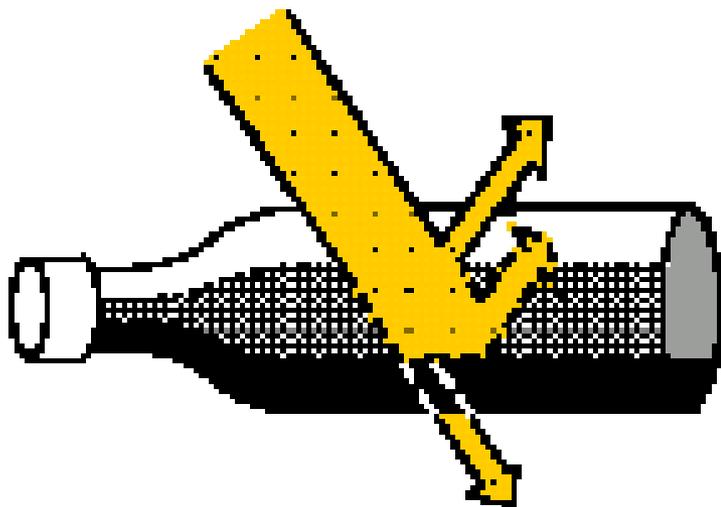
Journal of the Brazilian Chemical Society, v. 18, p. 126-134, 2007

Escherichia coli



$N_0 = 10^3 - 10^4$ NMP/100 mL

DESINFECÇÃO DE ÁGUA - SODIS



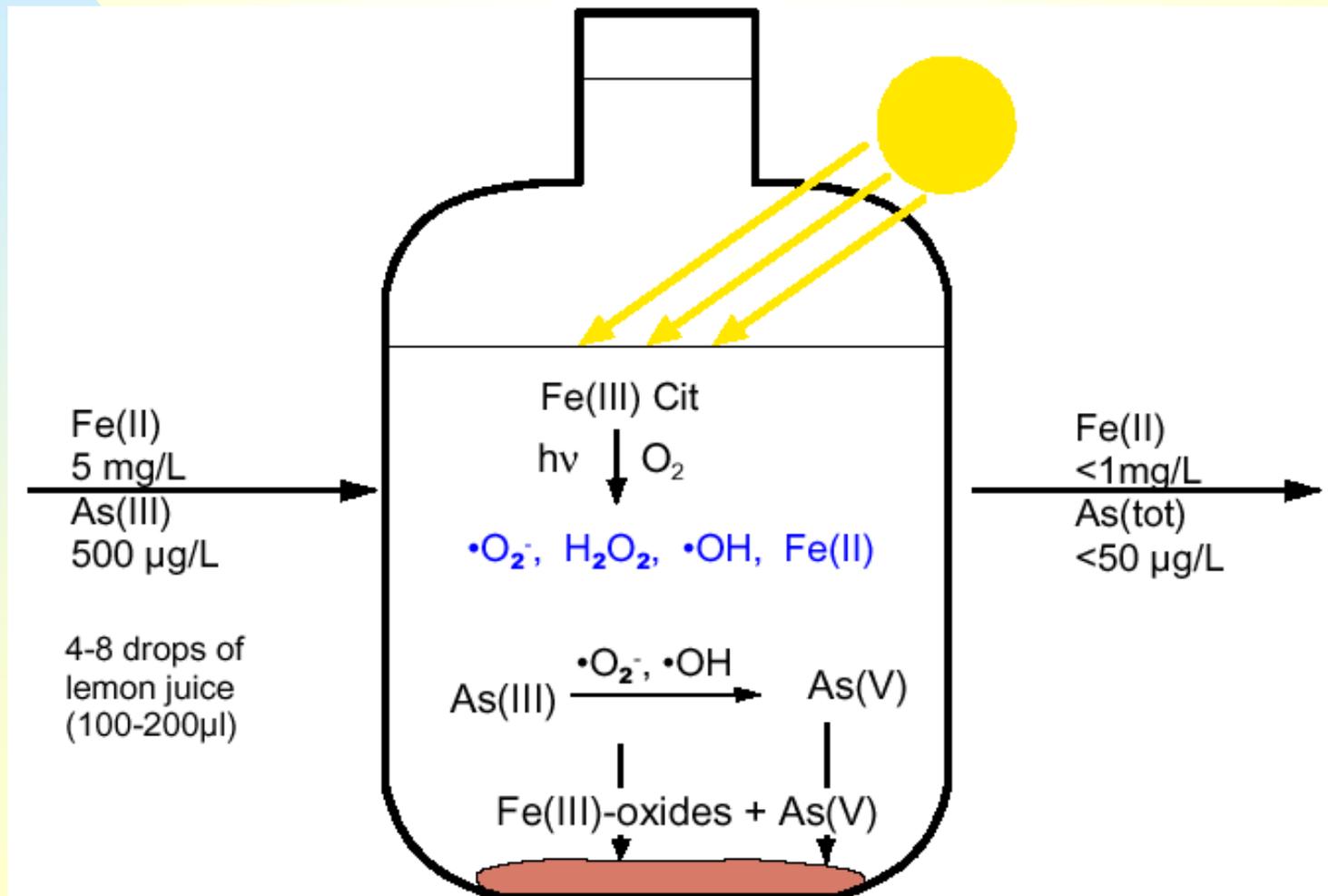
(EAWAG/SANDEC)

DESINFECÇÃO DE ÁGUA - SODIS



SOLAR OXIDATION AND REMOVAL OF ARSENIC

SORAS



Garrafas PET em exposição solar



A.H. Fostier, M.S.S. Pereira, S. Rath, J.R. Guimarães

Chemosphere , v. 72, p. 319-324, 2008

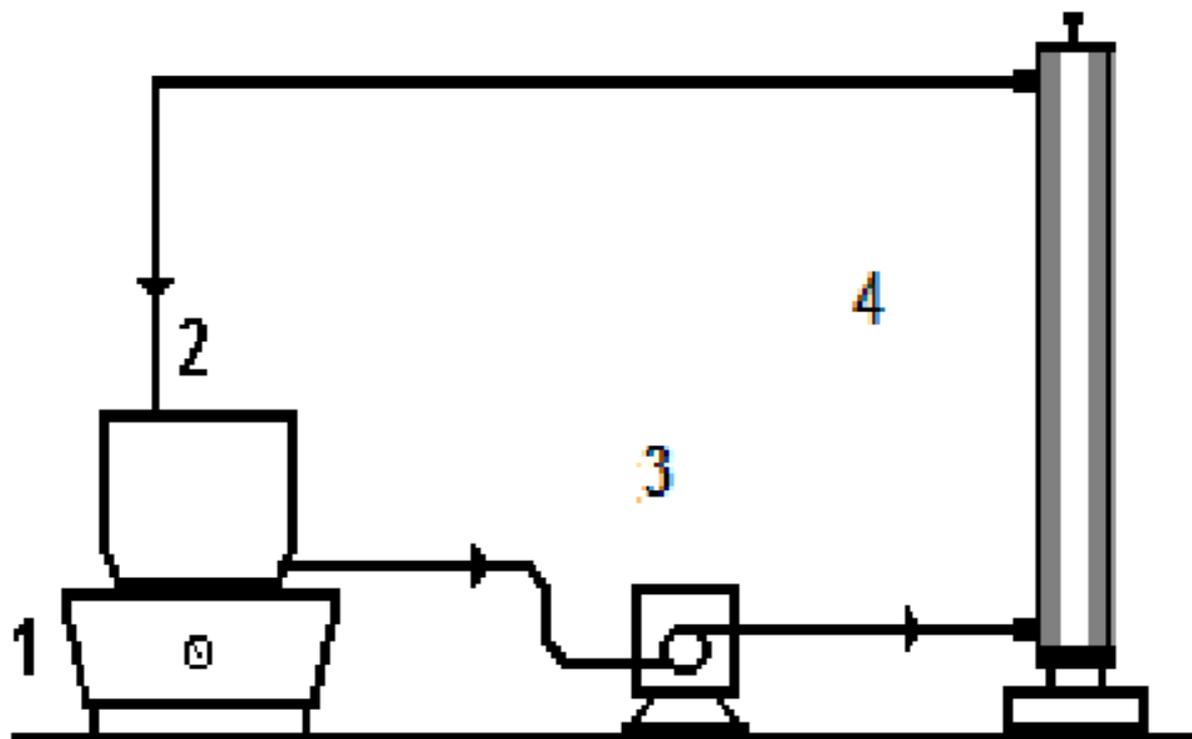
Remoção de As por SORAS em águas naturais

Amostra	As_i μg L⁻¹ media ±s*	As_f μg L⁻¹ media ±s*	% Remoção
Mina A(lago)	1200±50	100	92 %
Mina A (parede)	1100±25	< 2	>99%
Mina B	149±4	< 2	>99%
Mina C	363±10	< 2	>99%
Bica A	48±2	< 2	>99%
Bica B	40±2	< 2	>99%
Rio	96±2	< 2	>99%

AÇÃO DA PEROXIDAÇÃO ASSISTIDA POR LUZ ULTRAVIOLETA (H₂O₂/UV)
SOBRE OS PROTOZOÁRIOS PATOGENICOS DE VEICULAÇÃO HÍDRICA
Cryptosporidium spp. e *Giardia duodenalis*

CNPq: 471487/2007-4

FAPESP: 07/57068-5



Germicide Lamp: 15 W

λ_{\max} = 254 nm e; d.i.: 0,021 m

1) Agitador magnético; 2) Reservatório (1 L);

3) Bomba peristáltica e; 4) Reator

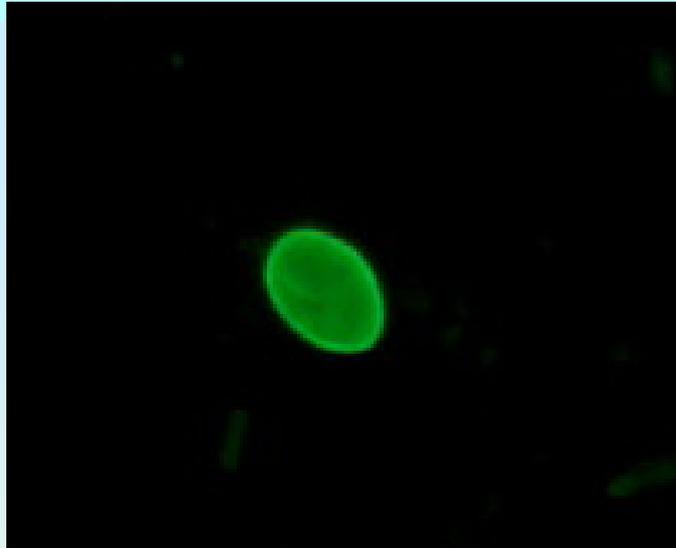
Reator: d.i.: 0,036 m;

H : 0,42 m e; Vol.: 190 mL

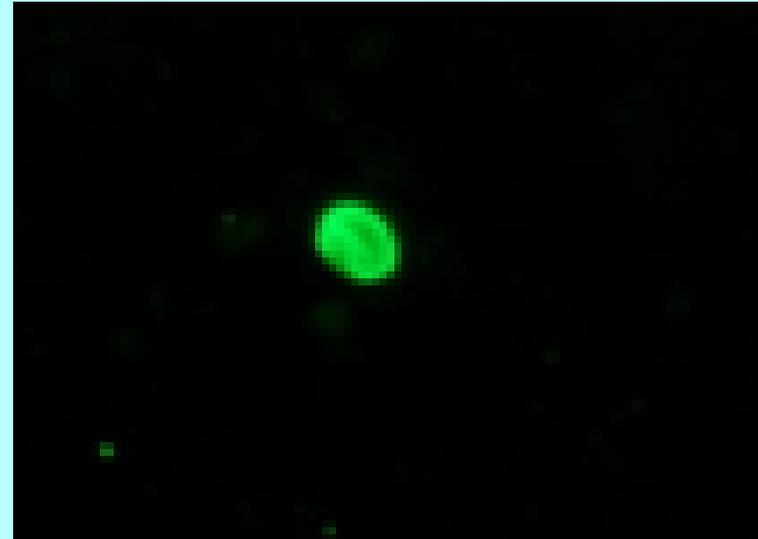
Dose: 44 mJ/cm²

C_{H₂O₂}: 15 mg/L

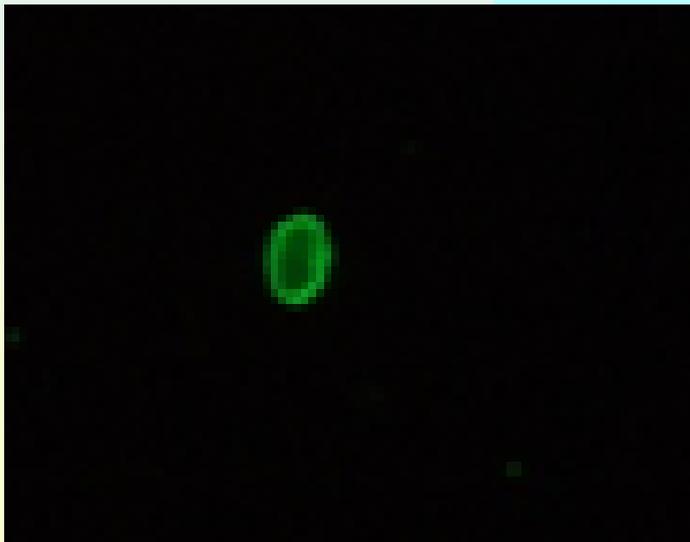
Giardia duodenalis cistos (8-12 μm)



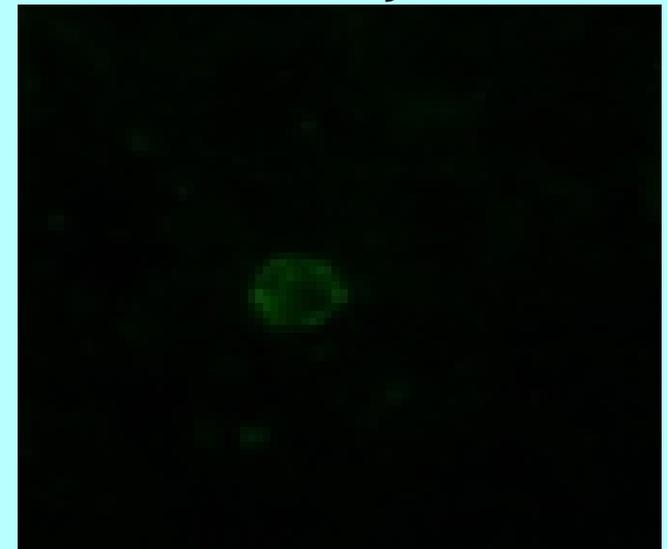
Sem tratamento



Peroxidação H_2O_2



Ultravioleta - UV



POA - H_2O_2 /UV

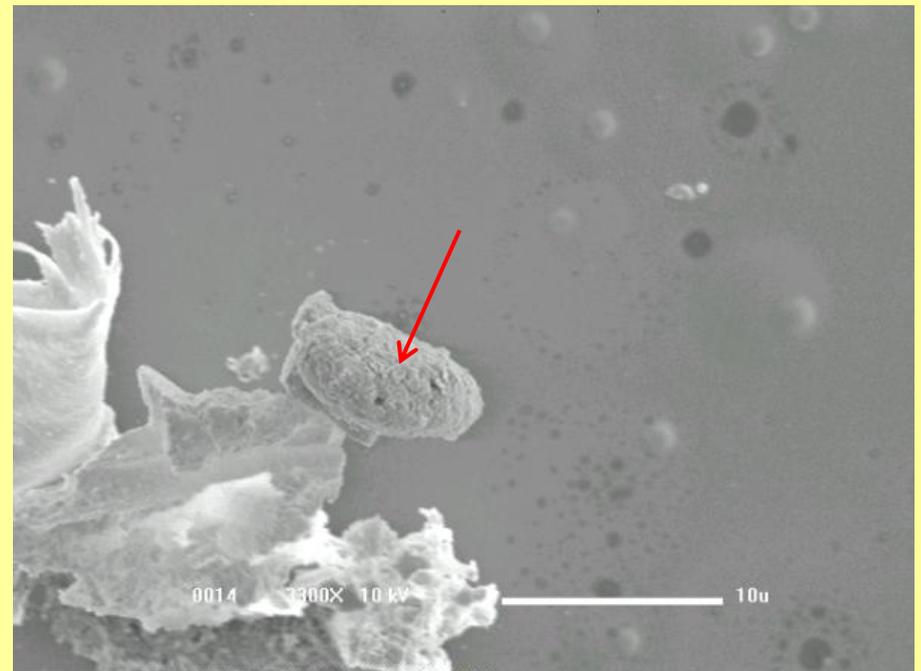
Imunofluorescência

Microscopia Eletrônica de Varredura

Giardia duodenalis cistos



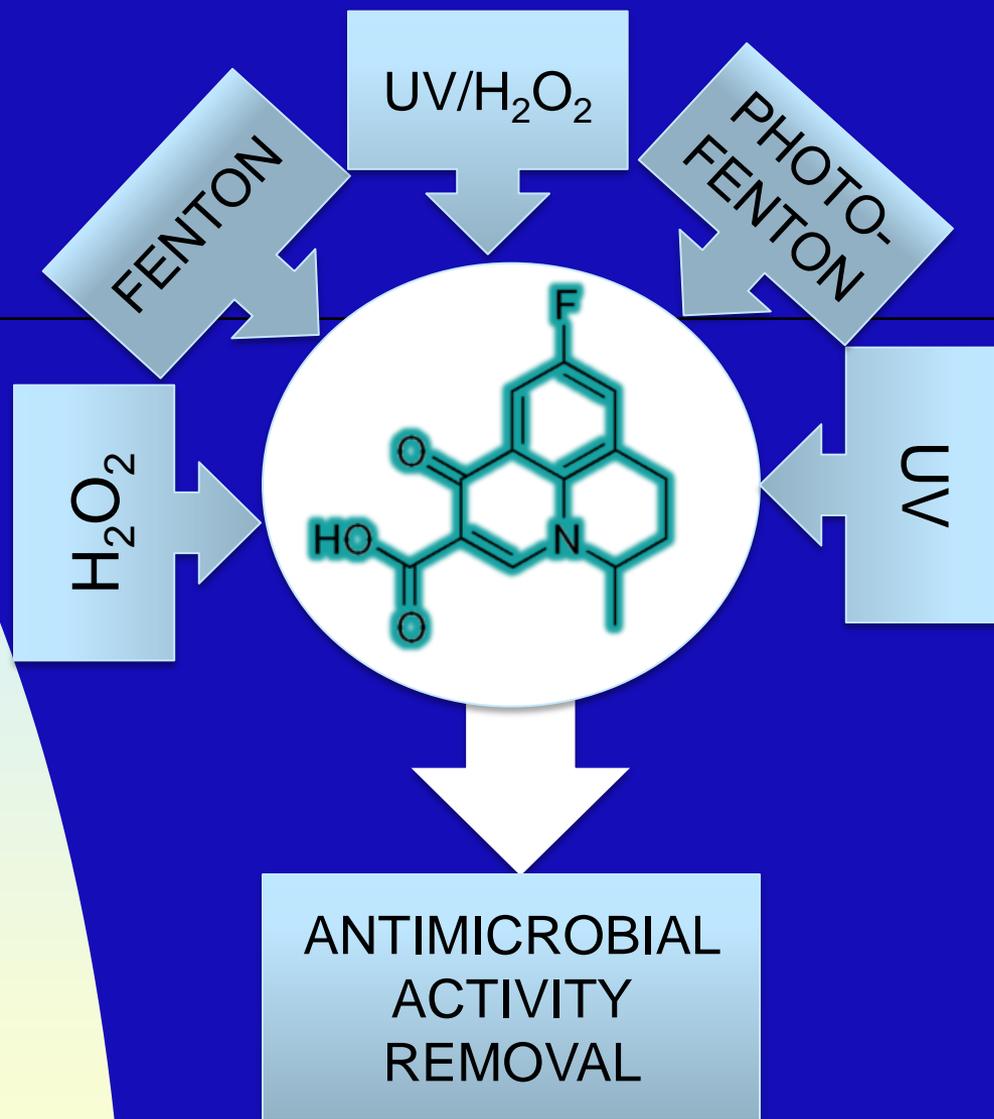
sem tratamento



após POA - H₂O₂/UV

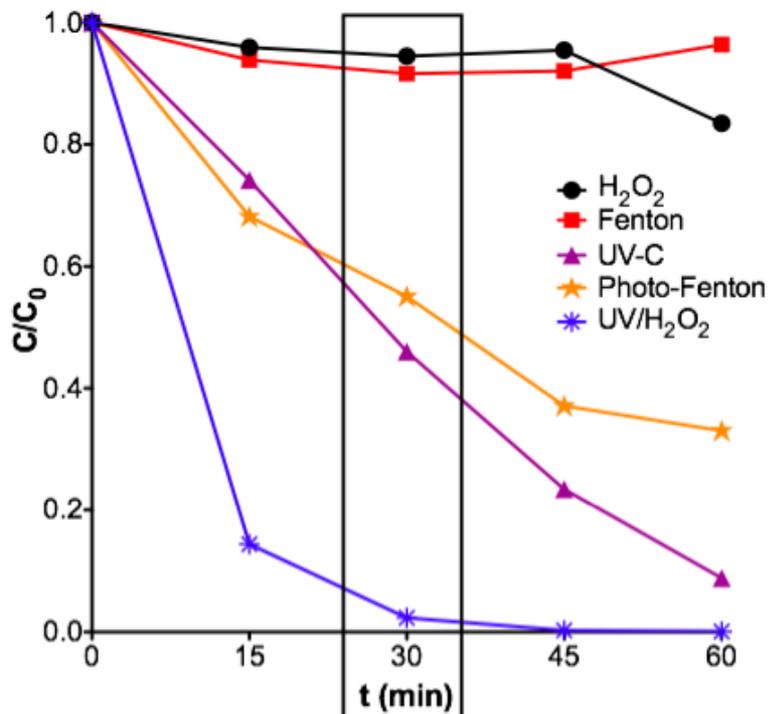
FEC/IQ

University of Campinas/Brazil

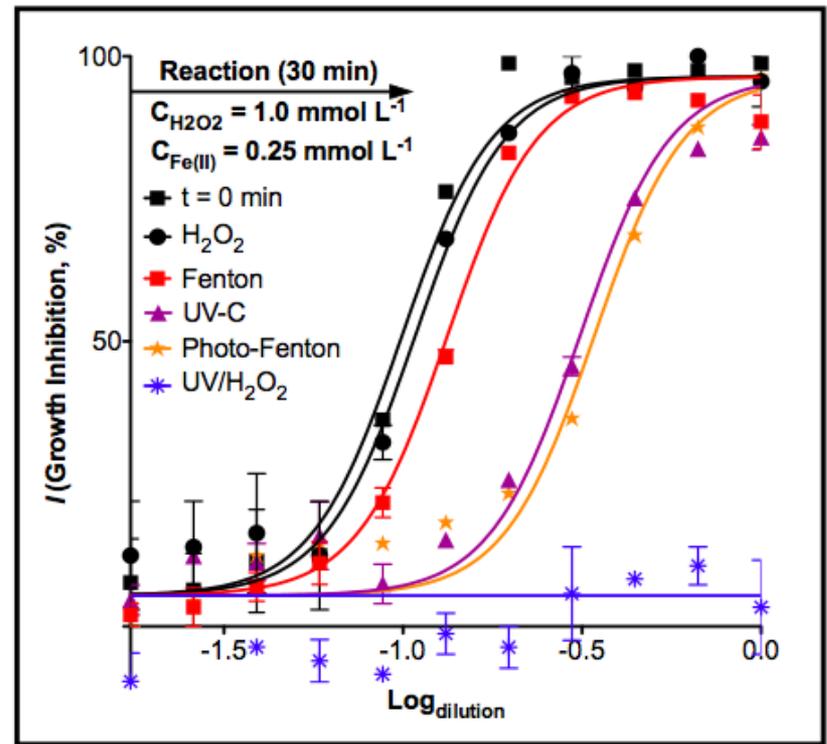


Silva, C.R.; Maniero, M.G.; Rath, S.; Guimarães, J.R.
Science of the Total Environment,
v. 445–446, p. 337-346, 2011

DEGRADATION



ANTIMICROBIAL ACTIVITY



$C_{\text{flumequinone}} = 500 \mu\text{g L}^{-1}$; $C_{H_2O_2} = 1.0 \text{ mmol L}^{-1}$; $C_{Fe(II)} = 0.25 \text{ mmol L}^{-1}$; UV-C (15 W)

Obrigado pela atenção



**Fórum-Recursos Hídricos:
Oportunidades Tecnológicas**

Conselho Regional de Química – IV Região - SP