Implementation of Electro-Fenton technology for environmental remediation: application for soil and water restoration

Marta Pazos and M. Ángeles Sanromán

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2nd Summer School on Environmental Applications of AOPs
Porto
July 10-14, 2017

AOPs PhD School

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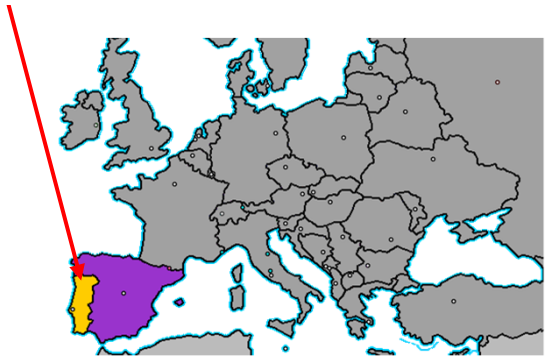

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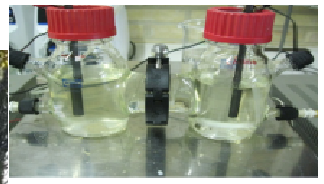
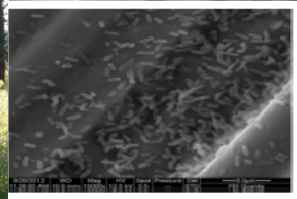
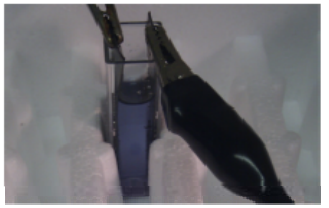
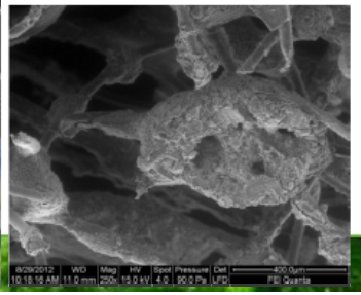
Research lines

- *Green Chemistry*
- *Applied Biotechnology*
- *Environmental Technology*







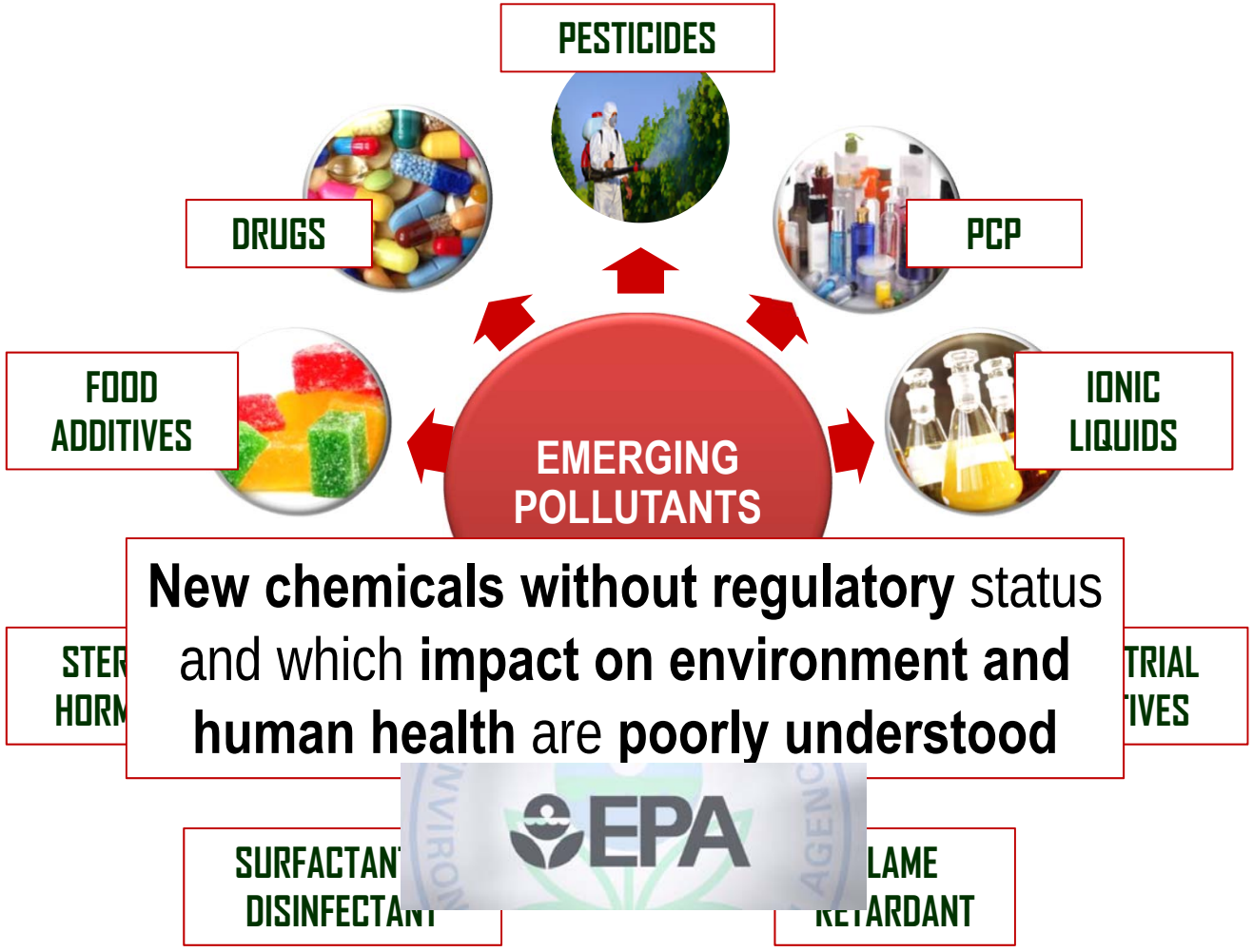


Implementation of Electro-Fenton technology for environmental remediation: application for soil and water restoration

1. Introduction
2. Electro-Fenton for effluent treatment
3. Electro-Fenton for soil remediation
4. Conclusions

AOPs PhD School

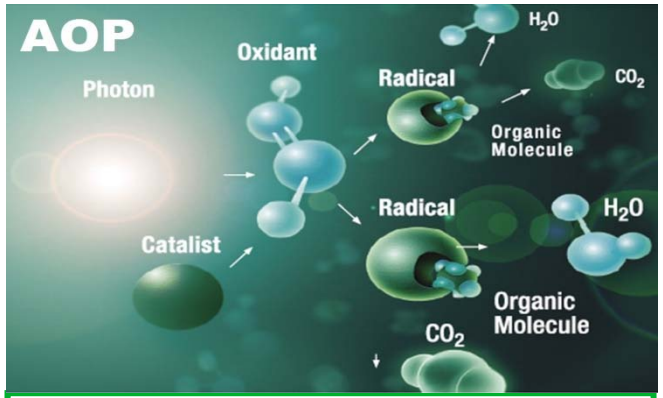
1. Introduction



1. Introduction

Environmental problem

TREATMENT REQUIRED



·OH

Fenton based process

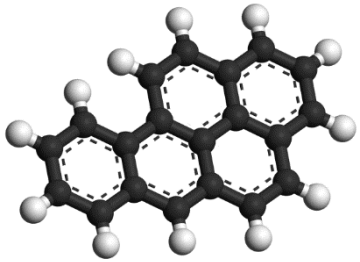
PROBLEM OF GREAT ENVIRONMENTAL IMPACT

1. Introduction

(1894) Henry John Horstman Fenton

Fenton's Reaction

$$Fe^{2+} + H_2O_2 \xrightarrow{H^+} Fe^{3+} + \bullet OH + HO$$



- Constant addition of Fe^{2+}
- Constant addition of H_2O_2
- Generation of Fe-complexes
- Fe-sludge formation

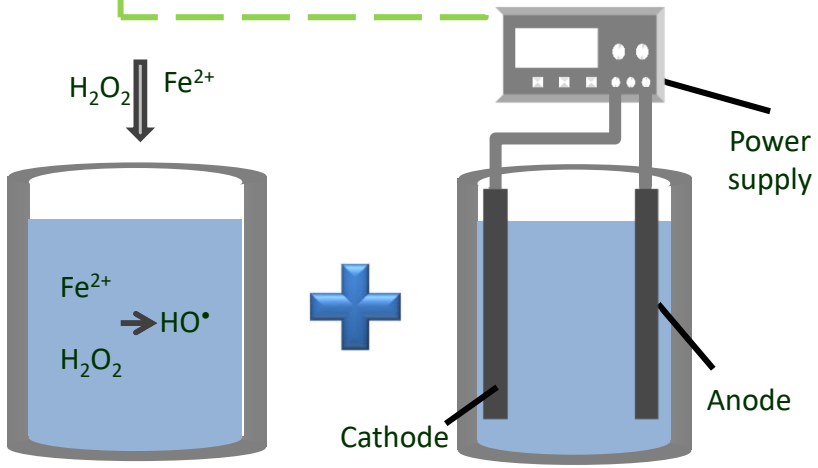
Organic compounds

HYBRID PROCESSES

$CO_2 + H_2O$ …

1. Introduction

HYBRID PROCESSES

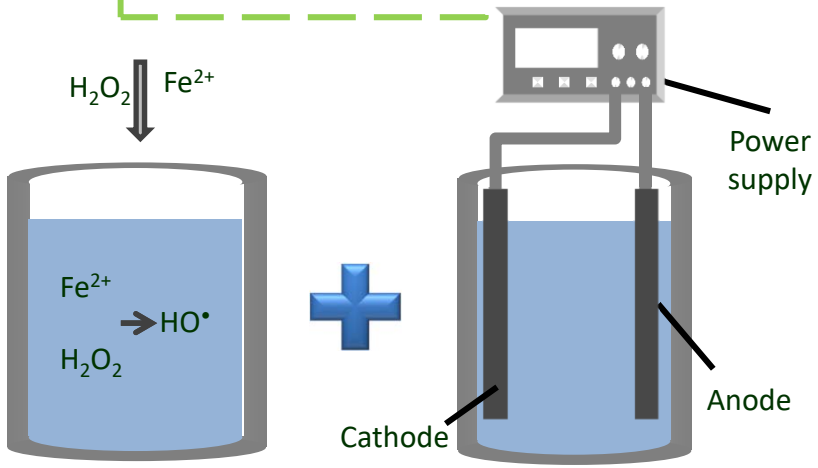


Fenton Process

Electrochemical Process

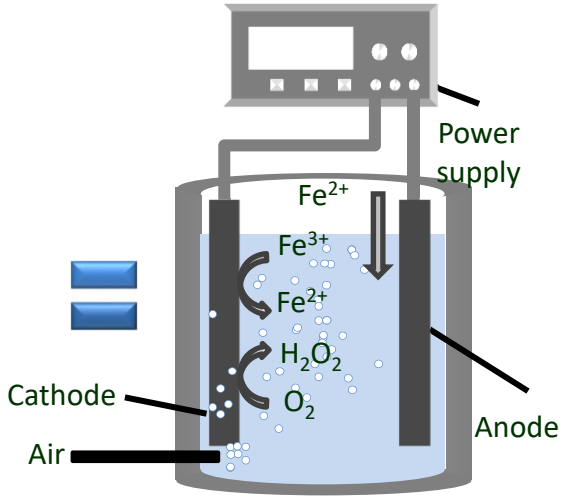
1. Introduction

HYBRID PROCESSES



Fenton Process

Electrochemical Process



Electro-Fenton Process

$O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$

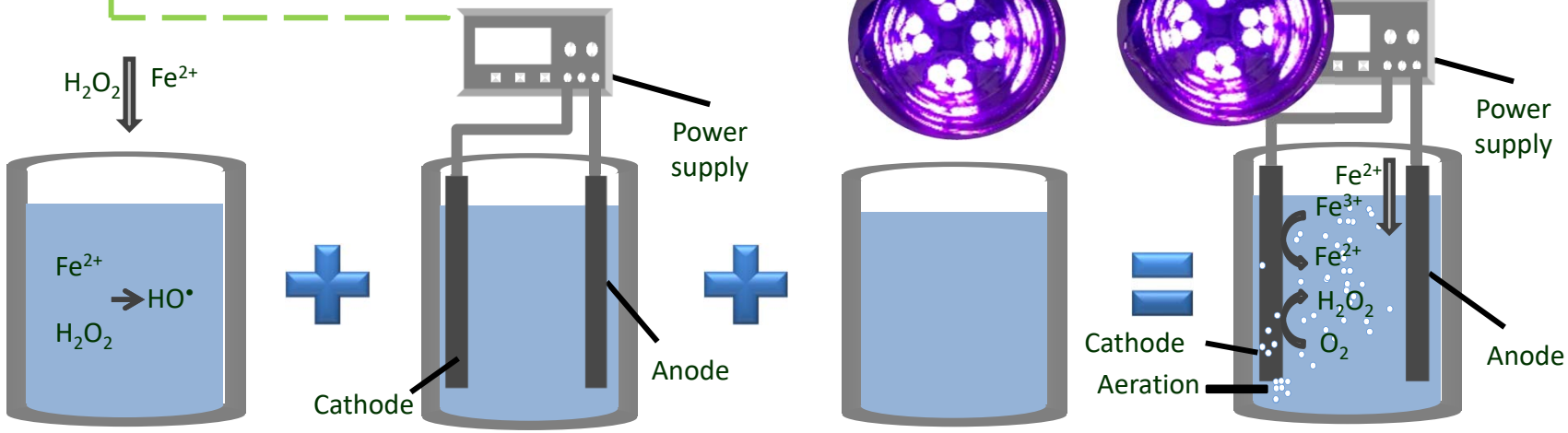
$Fe^{3+} + e^- \rightarrow Fe^{2+}$

- *In situ* generation H_2O_2
- Fe^{2+} regeneration
- No Fe-sludge

- Fe-complexes

1. Introduction

HYBRID PROCESSES



Fenton Process | **Electrochemical Process** | **Photolysis** | **Photo-electro Fenton**

- *In situ* generation H_2O_2
- Fe^{2+} regeneration
- No Fe-sludge
- No Fe-complex

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$
$$H_2O_2 + h\nu \rightarrow 2\,{\bullet}OH$$
$$Fe^{3+} + h\nu \rightarrow Fe^{2+}$$

Implementation of Electro-Fenton technology for environmental remediation: application for soil and water restoration

1. Introduction

2. Electro-Fenton for effluent treatment

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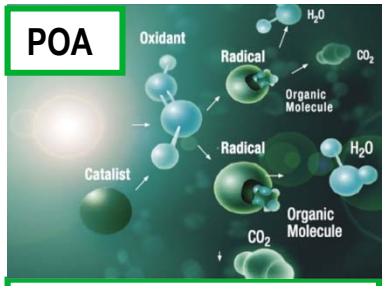
2. Electro-Fenton for effluent treatment

POA



·OH
Fenton

GOOD RESULTS LAB SCALE

INDUSTRIAL USE

DRAWBACKS

- ✘ Scarce reactor designs suitable for industrial scale
- ✘ Continuous treatment of high volumes (Fe release)

2. Electro-Fenton for effluent treatment

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HETEROGENEOUS CATALYST

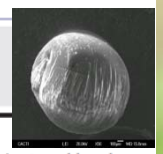
REACTOR DESIGN

Journal of Hazardous Materials 213–214 (2012) 369–377

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Decolourisation of dyes under electro-Fenton process using Fe alginate gel beads

Applied Catalysis B: Environmental 144 (2014) 416–424

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

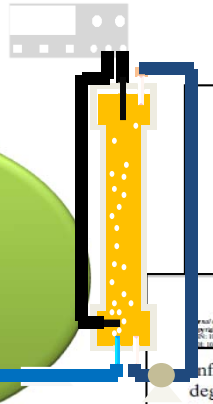
Electro-Fenton oxidation of imidacloprid by Fe alginate gel beads

Environ Sci Pollut Res (2013) 20:2172–2183
DOI 10.1007/s11356-012-1035-5

RESEARCH ARTICLE

Optimisation of decolourisation and degradation of Reactive Black 5 dye under electro-Fenton process using Fe alginate gel beads

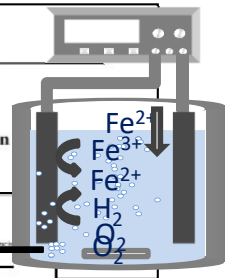
O. Iglesias · M. A. Fernández de Dios · E. Rosales · M. Pazos · M. A. Sanromán



Environ Sci Pollut Res (2012) 19:1738–1746
DOI 10.1007/s11356-011-0668-0

RESEARCH ARTICLE

Application of central composite face-centered design and response surface methodology for the optimization of electro-Fenton decolorization of Azure B dye



nfluence of operational parameters on electro-Fenton degradation of organic pollutants from soil

Chemical Engineering Journal 155 (2009) 62–67

Contents lists available at ScienceDirect

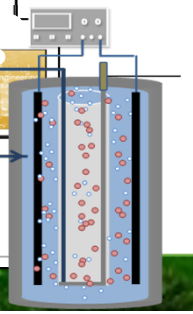
Chemical Engineering Journ

journal homepage: www.elsevier.com/loca

Electro-Fenton decoloration of dyes in a continuous reactor: A promising technology in colored wastewater treatment

E. Rosales, M. Pazos, M.A. Longo, M.A. Sanromán*

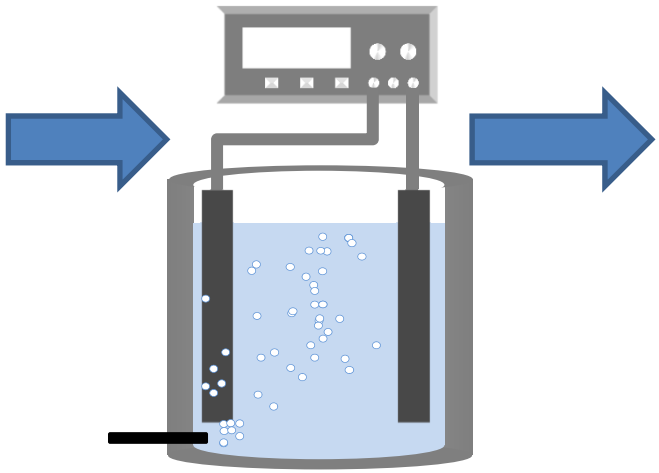
Department of Chemical Engineering, University of Vigo, Isaac Newton Building, Campus As Lagoas, Marcosende 36310,Vigo, Spain



2. Electro-Fenton for effluent treatment

REACTOR DESIGN

STIRRED TANK REACTOR

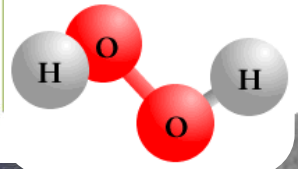


2. Electro-Fenton for effluent treatment

OPTIMIZATION

- Operational conditions: Voltage, air supply, Fe dosage ..
- Electrode material

H_2O_2



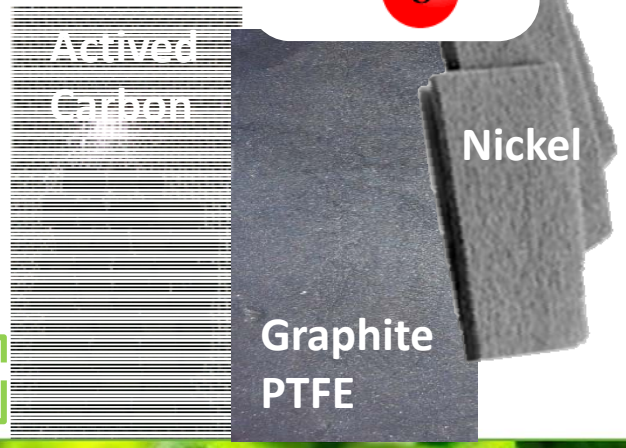
ANODIC MATERIAL

$$BDD + H_2O \rightarrow BDD \times (HO^{\bullet}) + H^+ + e^-$$

$$BDD \times (OH^{\bullet}) + R \rightarrow BDD + CO_2 + H_2O$$

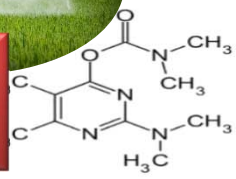
Boron-Doped Diamond (BDD)

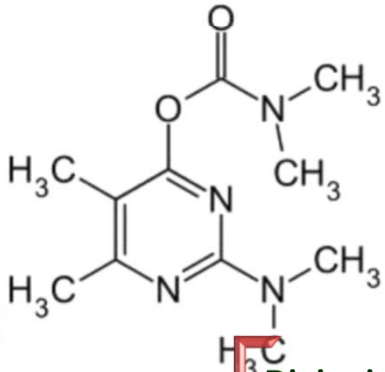
CATHODIC MATERIAL



2. Electro-Fenton for effluent treatment

PESTICIDES

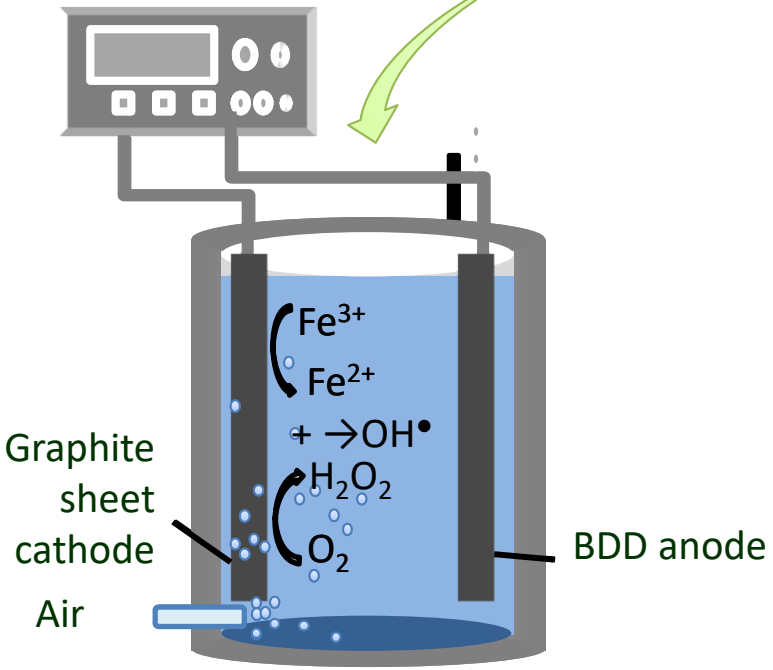




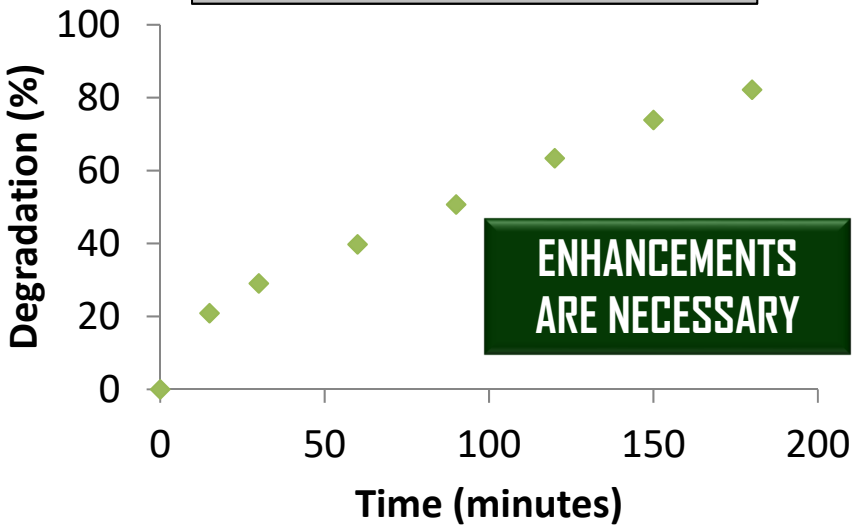
Pirimicarb

BDD | Graphite

Power supply



100 mg/L Pirimicarb
82% removal 3h

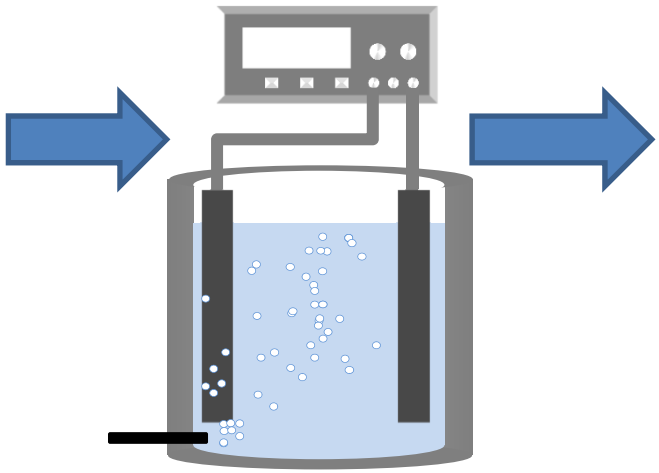


ENHANCEMENTS ARE NECESSARY

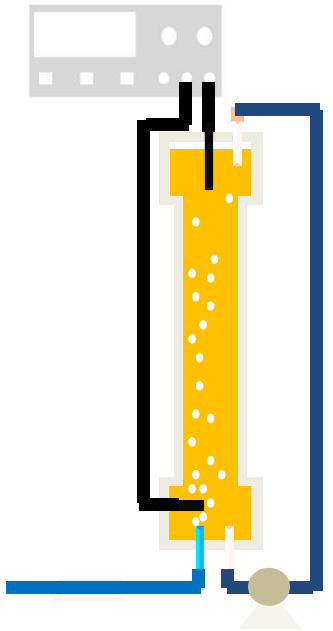
2. Electro-Fenton for effluent treatment

REACTOR DESIGN

STIRRED TANK REACTOR

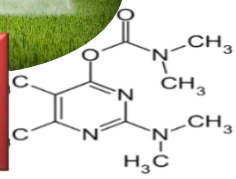


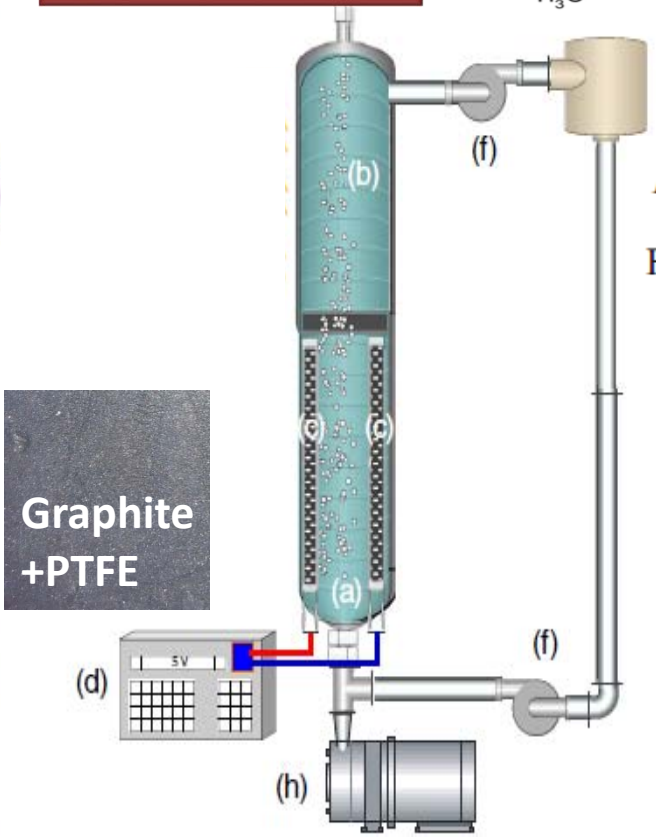
FLUIDIZED REACTOR



2. Electro-Fenton for effluent treatment

PESTICIDES





Graphite +PTFE

ENHANCEMENTS

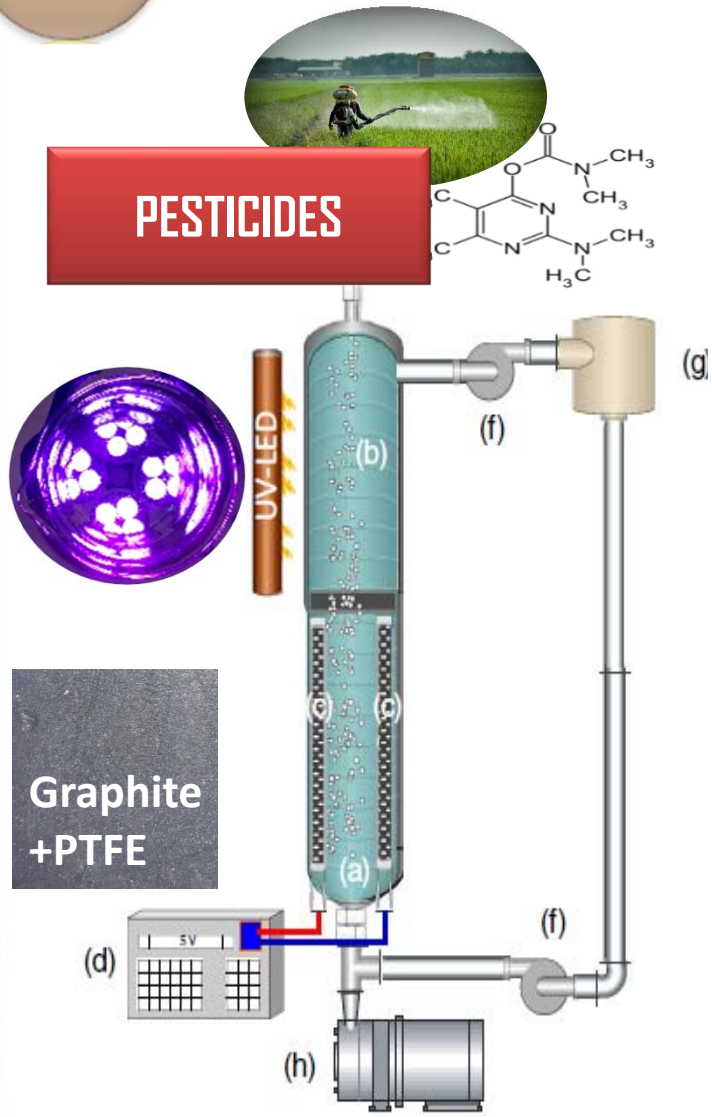
- Sequential fluidized reactor
- New electrodes Graphite-PTFE
- UV LED radiation

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO\cdot$$

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R$$

Diez, Sanromán, Pazos (2017) Environ Sci Pollut Res (2017) 24:1137–1151

2. Electro-Fenton for effluent treatment



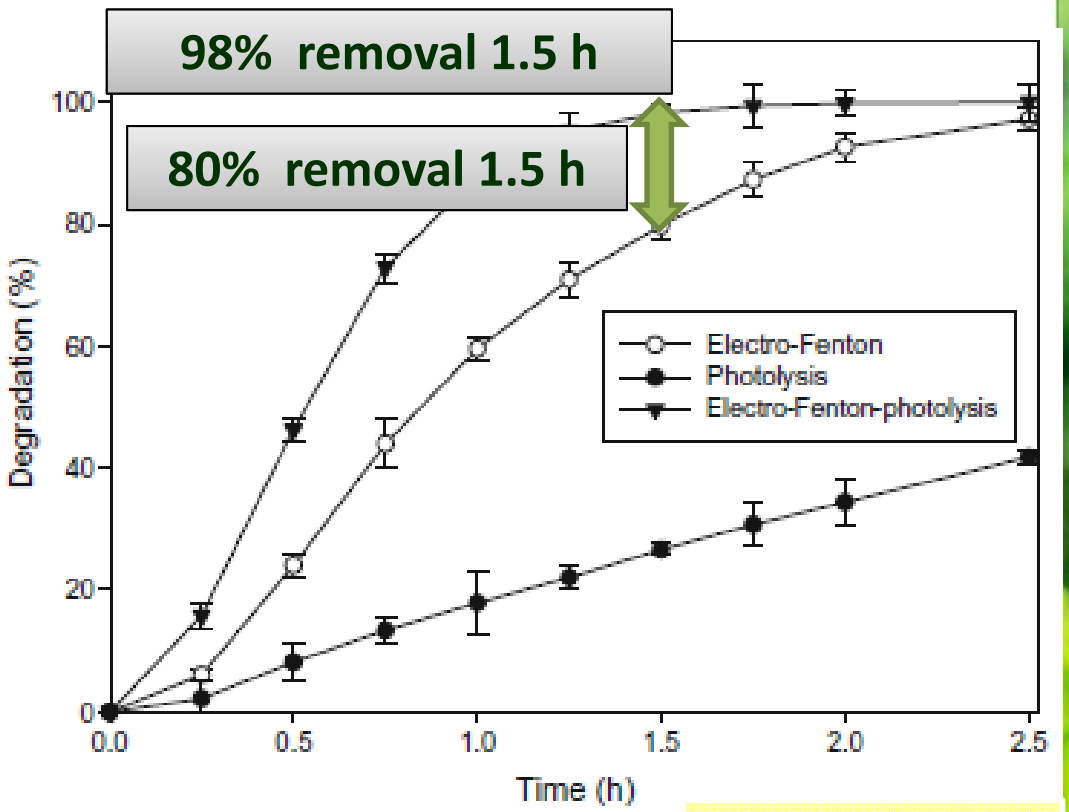
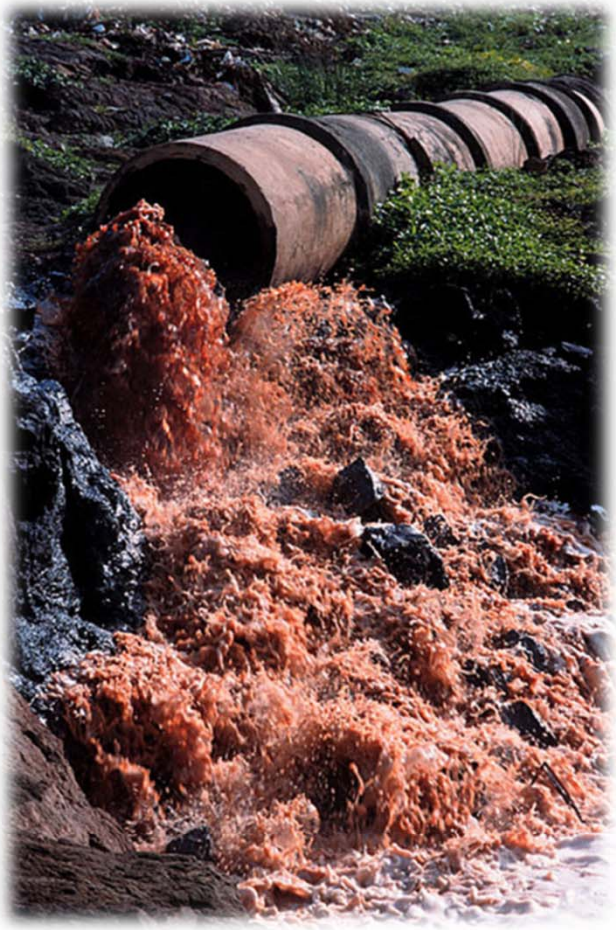


Fig. 2 Degradation by using different AOPs of 100 mg L^{-1} of pirimicarb solution with 0.01 M Na_2SO_4, pH 2, and by adding 75 mg L^{-1} of Fe^{+2} in the Fenton processes, the electrochemical field was 5 V when needed

Diez, Sanromán, Pazos (2017) Environ Sci Pollut Res (2017) 24:1137–1151

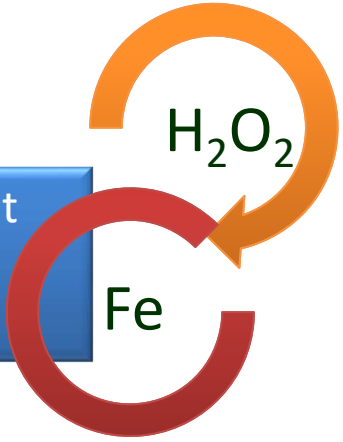
2. Electro-Fenton for effluent treatment



HETEROGENEOUS CATALYST

Huge amount of effluents is generated

Request to design processes that permit their remediation in continuous mode



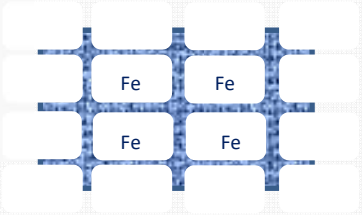
2. Electro-Fenton for effluent treatment

HETEROGENEOUS CATALYST

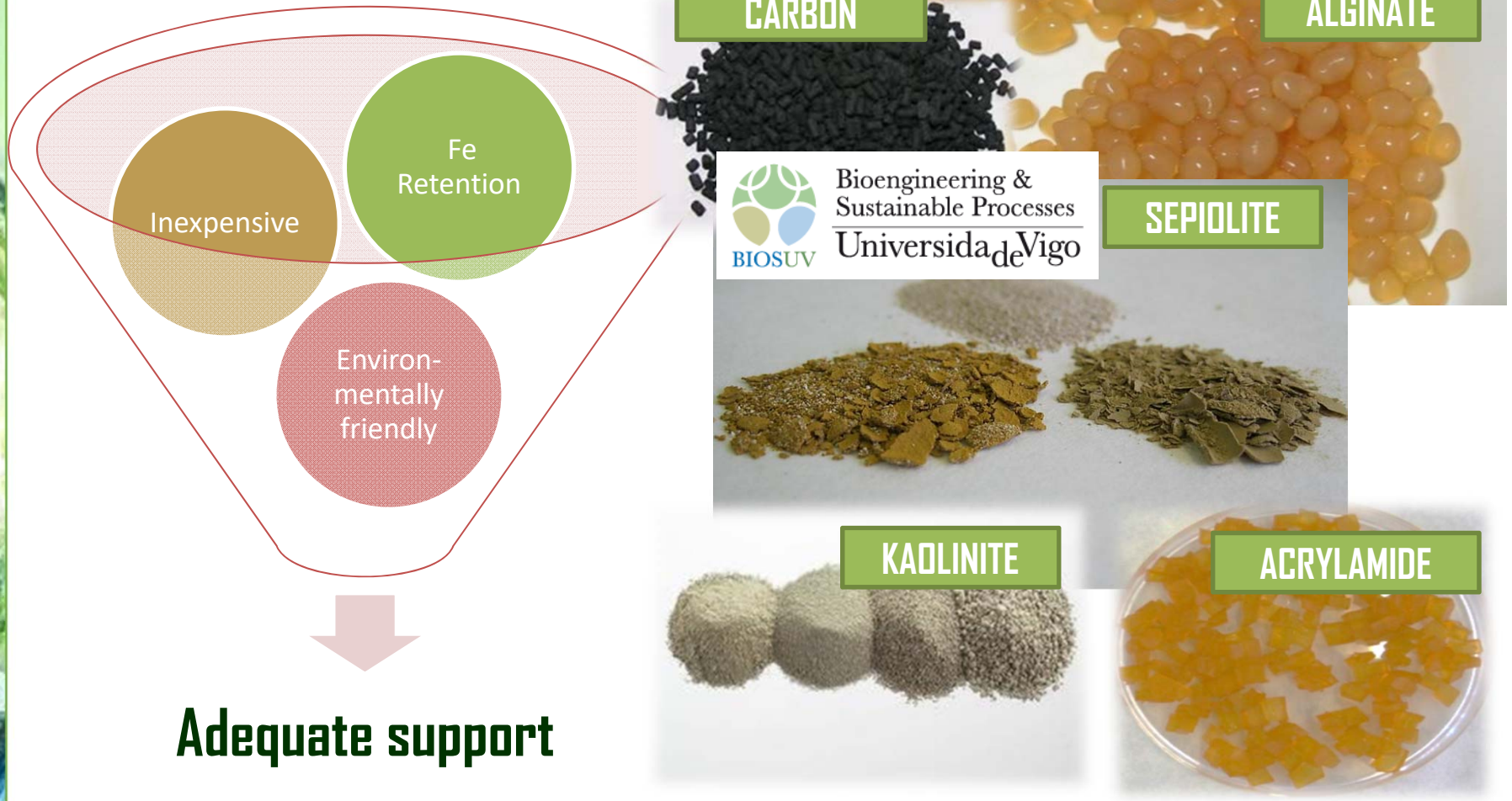
Fe

How to avoid Fe release due to the flow system?

Immobilisation on different supports



2. Electro-Fenton for effluent treatment

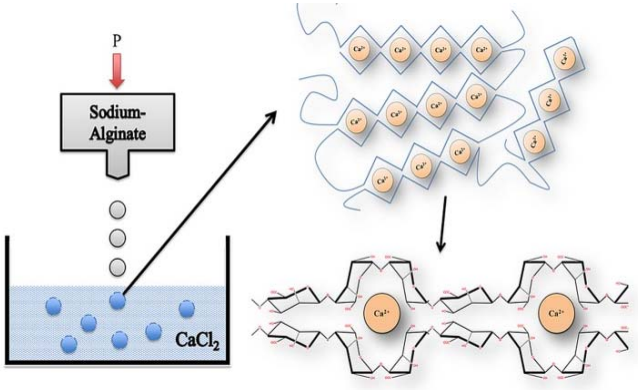


Adequate support

2. Electro-Fenton for effluent treatment

Fe-Alginate

Fe entrapment



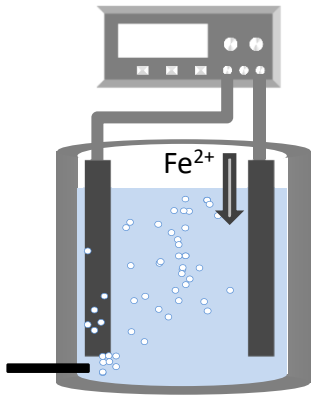
Fe adsorption

Fe-Sepiolite

Iglesias, Rosales, Pazos, Sanromán Environ Sci Pollut Res (2013) 20:2252–2261

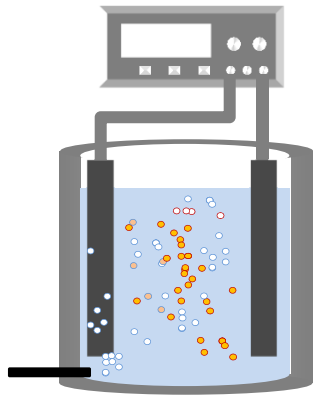
Iglesias, Fernández de Dios, Pazos, Sanromán Environ Sci Pollut Res Int (2013) 20:5983-93

2. Electro-Fenton for effluent treatment

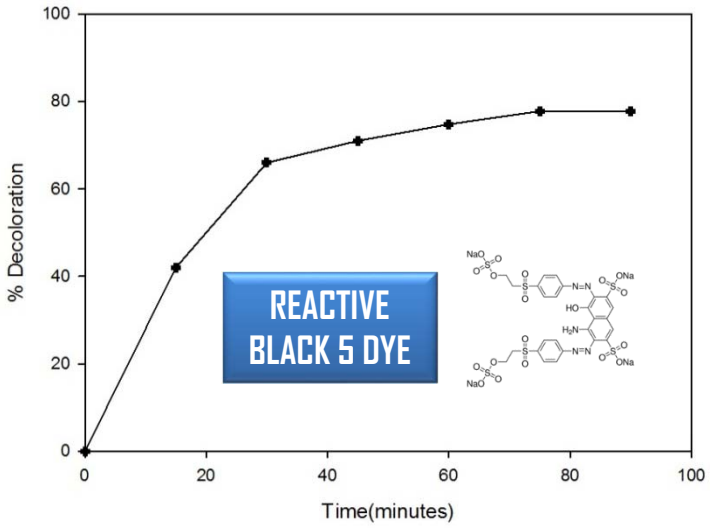


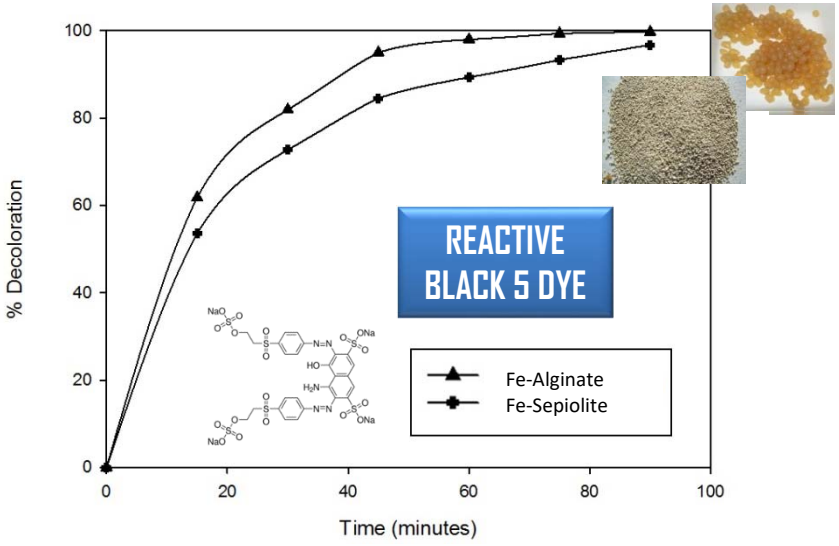
Homogenous Electro-Fenton

Heterogeneous Electro-Fenton



- Fast removal in heterogeneous
- Two stage process ads-degradation





Iglesias, Rosales, Pazos, Sanromán Environ Sci Pollut Res (2013) 20:2252–2261

Iglesias, Fernández de Dios, Pazos, Sanromán Environ Sci Pollut Res Int (2013) 20:5983-93

2. Electro-Fenton for effluent treatment

No adsorption after the process

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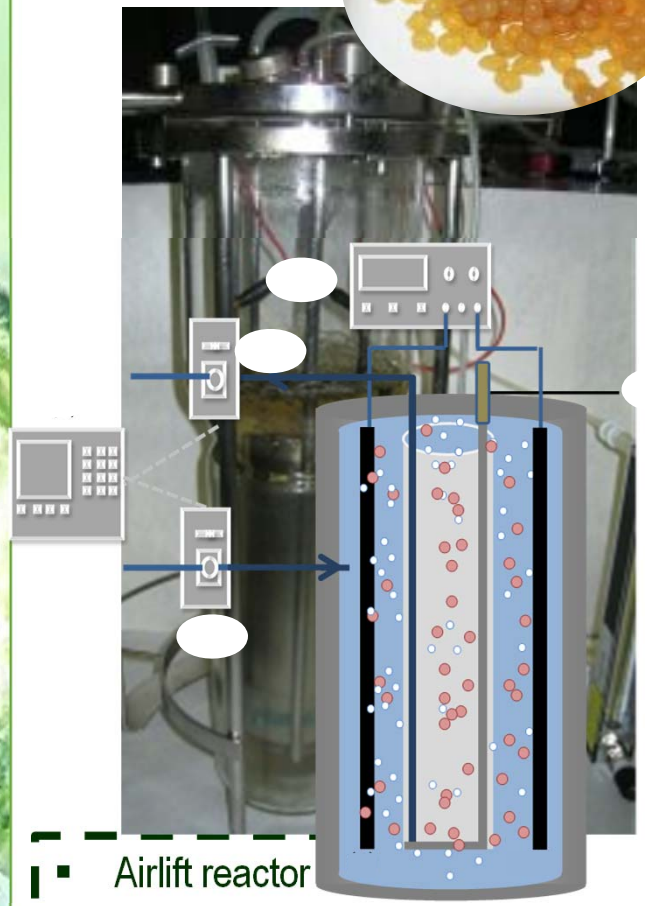
Iglesias, Fernández de Dios, Pazos, Sanromán Environ Sci Pollut Res Int (2013) 20:5983-93

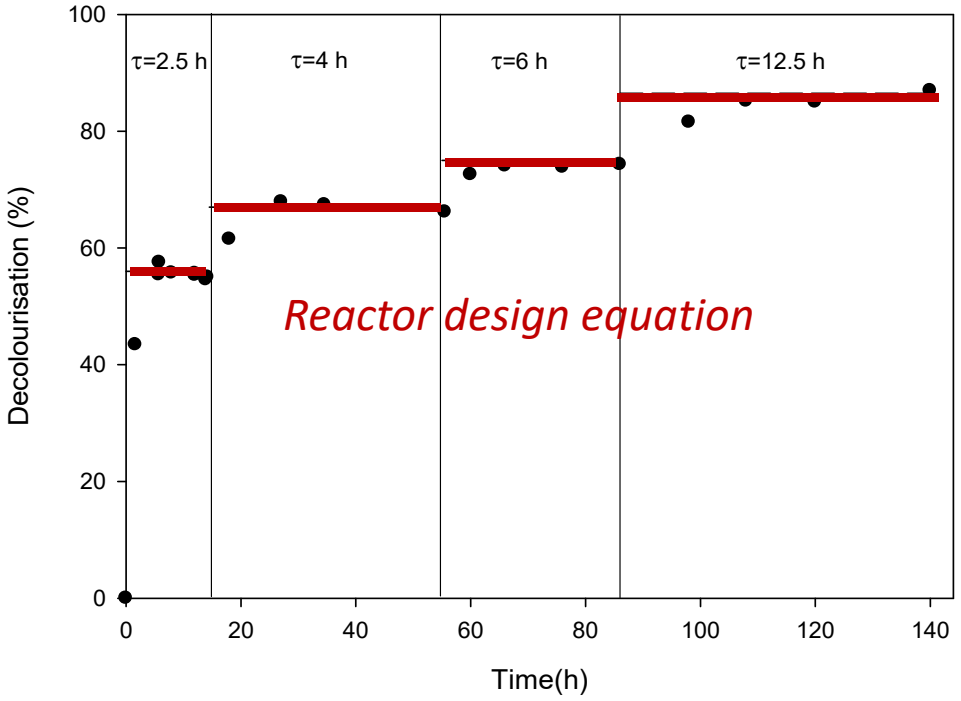
2. Electro-Fenton for effluent treatment



- Airlift reactor
- 1.5 L
- Graphite electrodes

Applicability of these catalysts to operate in continuous mode

Kinetic model: First order
Hydrodynamic model: Stirred flow reactor



Iglesias, Rosales, Pazos, Sanromán Environ Sci Pollut Res (2013) 20:2252–2261

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1. Introduction
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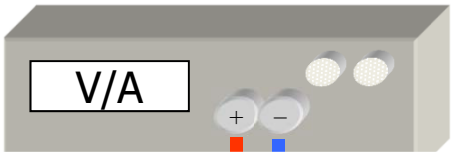
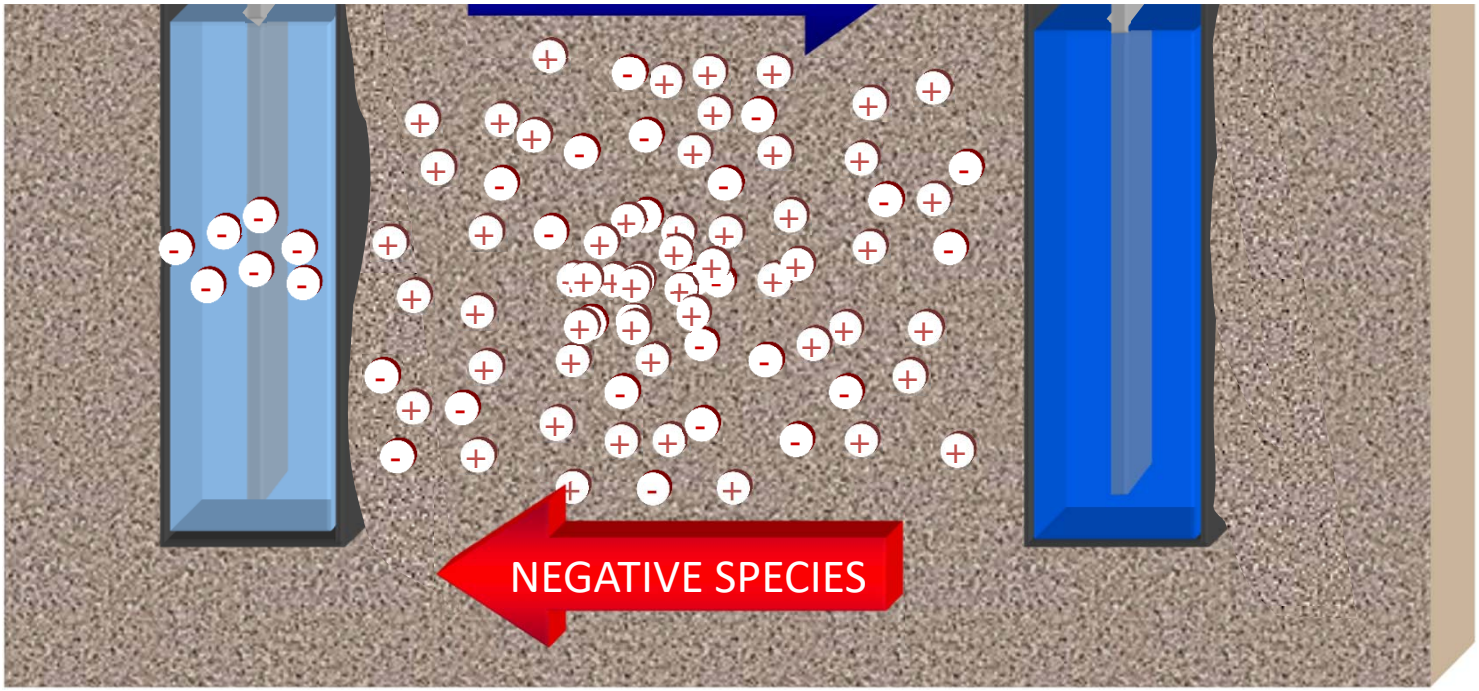
AOPs PhD School

3. Electro-Fenton for soil remediation

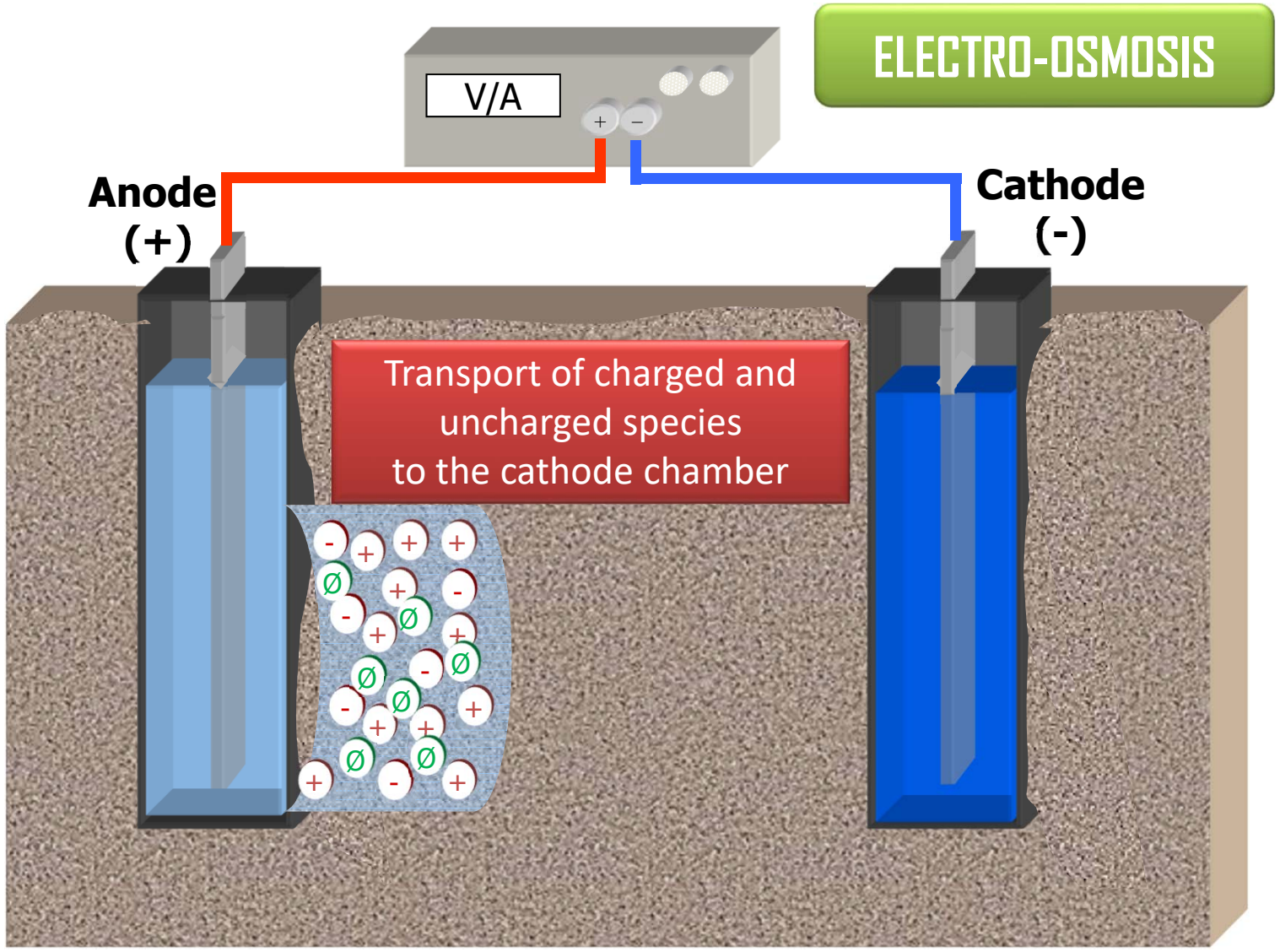
ELECTROMIGRATION



The principle of Electro-Remediation relies upon the application of a low-intensity direct current through the soil between a couple of inert electrodes



3. Electro-Fenton for soil remediation

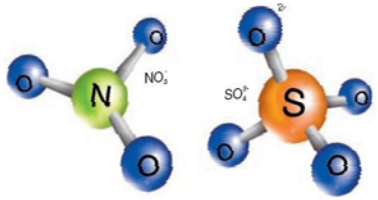


3. Electro-Fenton for soil remediation

Electrokinetic remediation

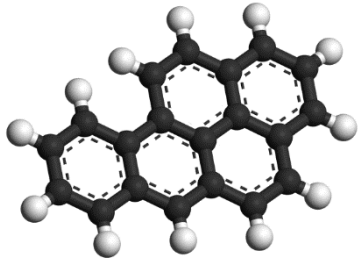
VALIDATED

- Inorganic cations: heavy metals
- Inorganic anions: sulphate, nitrates…



POOR RESULTS ORGANICS

- Low solubility
- Strongly attached to soil

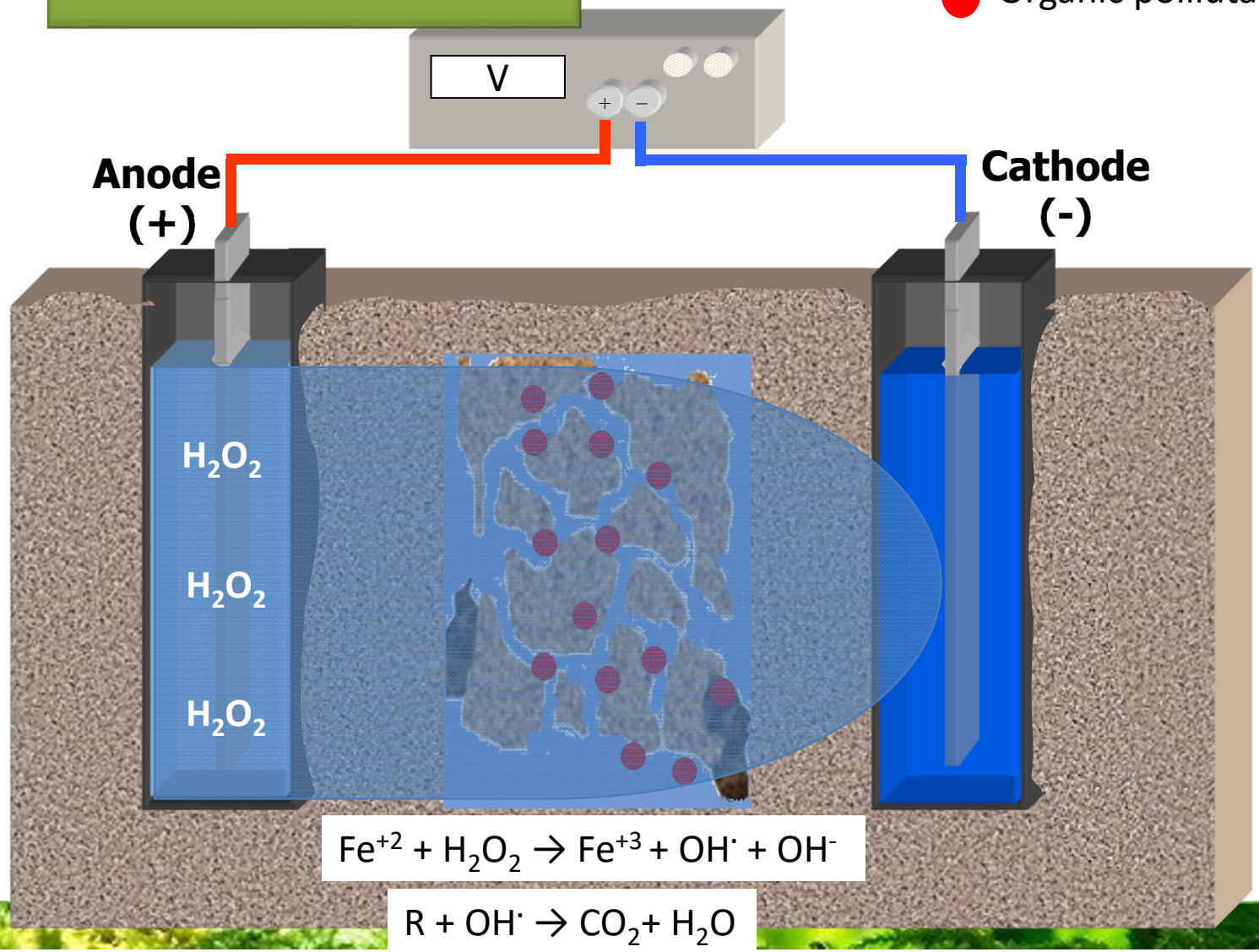


SOLUTION

- *IN SITU* degradation by Fenton reagent

3. Electro-Fenton for soil remediation

Electrokinetic-Fenton



$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\cdot} + OH^{-}$

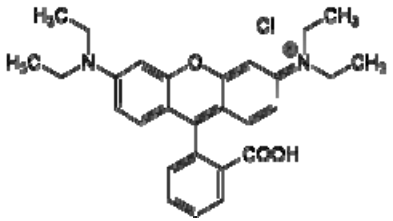
$R + OH^{\cdot} \rightarrow CO_2 + H_2O$

3. Electro-Fenton for soil remediation

Electrokinetic-Fenton

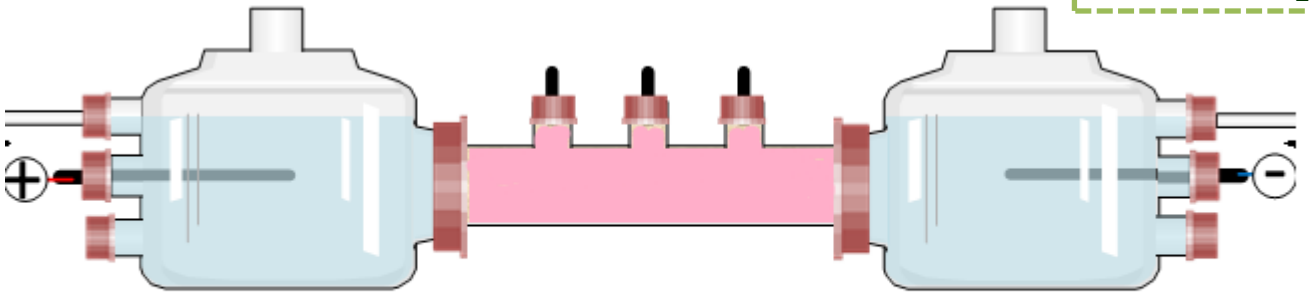
Experimental conditions	
Electrodes	Graphite bars
Electrochemical Field	30 V
Time	3 days
Fe contaminated clay	**3000 ppm**

RHODAMINE B DYE



FLUXING SOLUTION

- 0.1 M Na_2SO_4
- pH 3
- 10 % H_2O_2



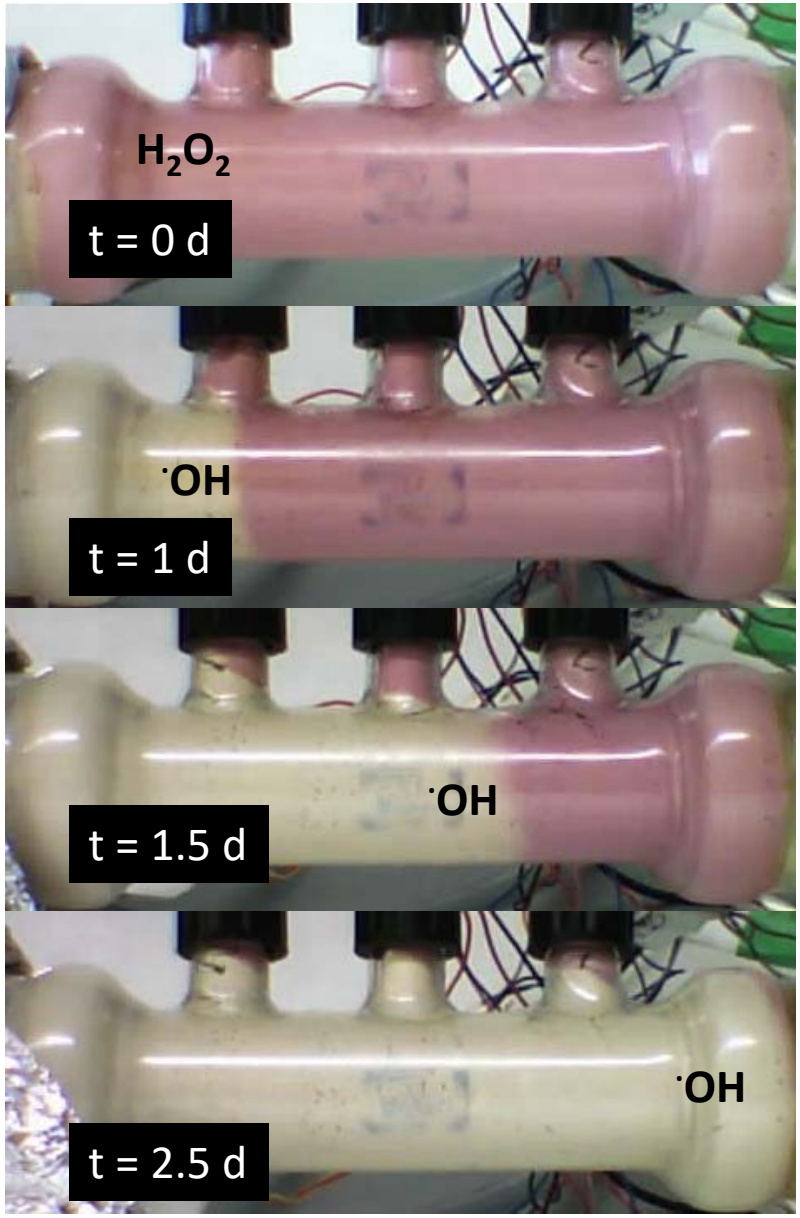
Popescu, Rosales, …, Pazos, Lazar, Sanromán Process Saf Environ Protec (2017) 108:99-107

3. Electro-Fenton for soil remediation

Electrokinetic-Fenton

Electro Kinetic cells (EK)

- Transportation of the H_2O_2 through the soil
- *In situ* degradation of pollutant



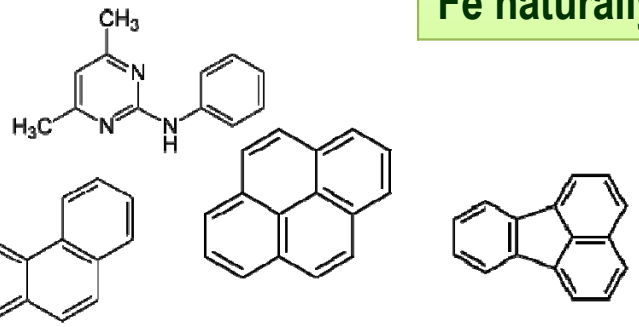
Popescu, Rosales, …, Pazos, Lazar, Sanromán Process Saf Environ Protec (2017) 108:99-107

3. Electro-Fenton for soil remediation

Electrokinetic-Fenton

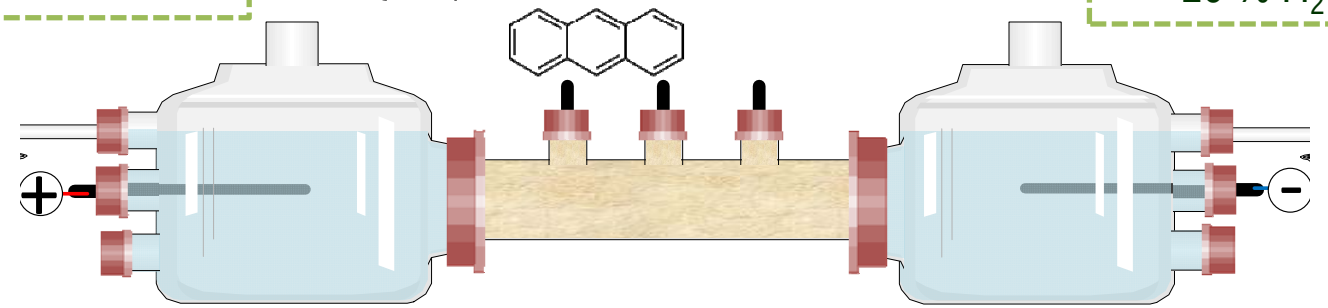
Experimental conditions	
Electrodes	Graphite bars
Electrochemical Field	30 V
Time	27 days
Fe naturally	**33594** ppm

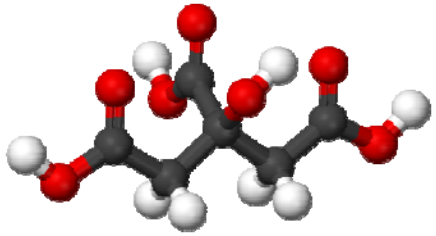
- Pyrimetanil
- Phenanthrene
- Anthracene
- Fluoranthene
- Benzo[a] anthracene
- Pyrene



FLUXING SOLUTION

- 0.1 M Na_2SO_4
- pH 3
- 10 % H_2O_2



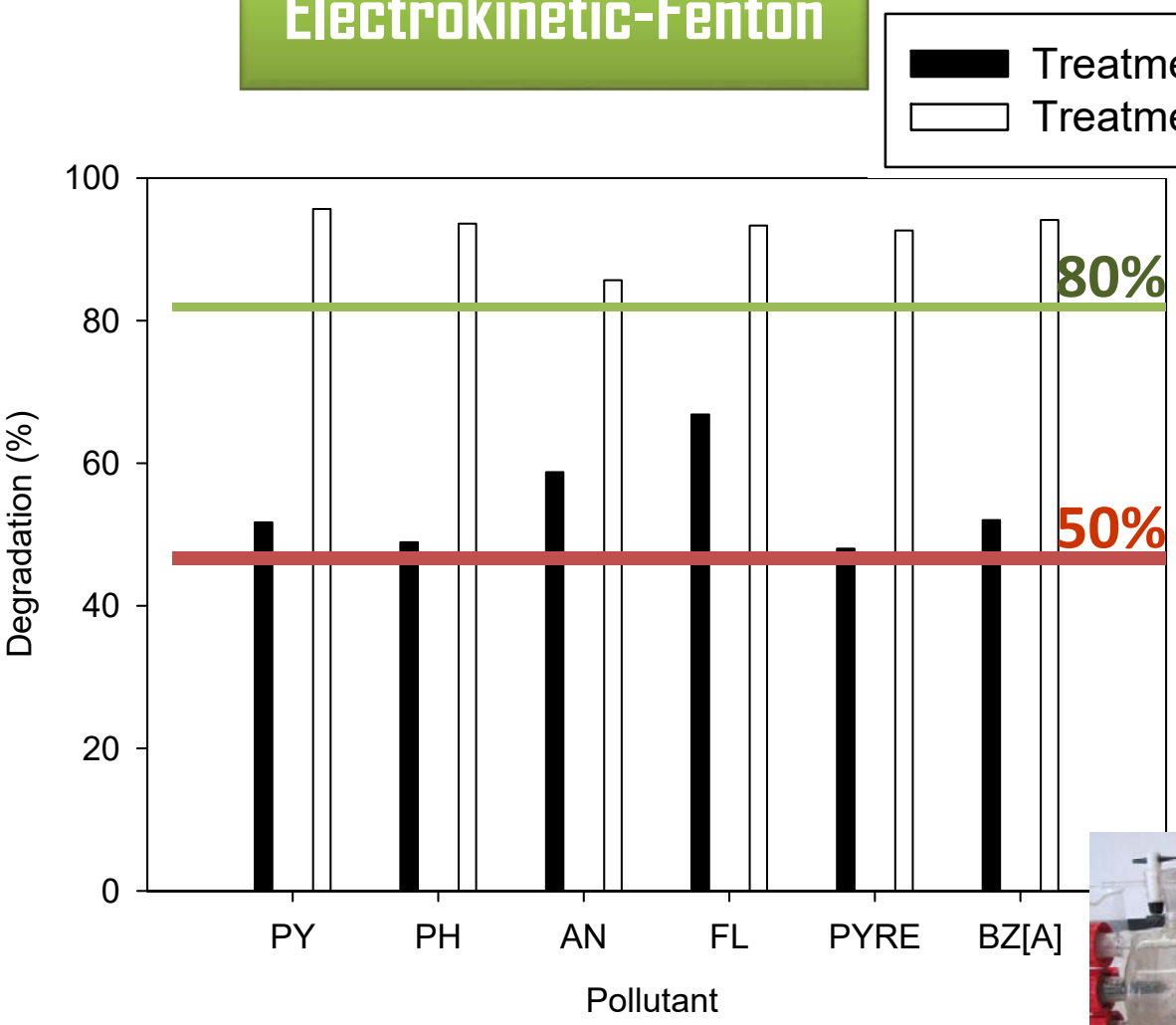


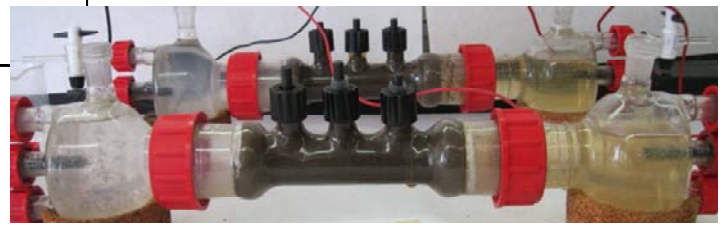
¿ citric acid ?

Bocos, Fernández, Pazos, Sanromán Chemosphere (2015) 125:168-174

3. Electro-Fenton for soil remediation

Electrokinetic-Fenton

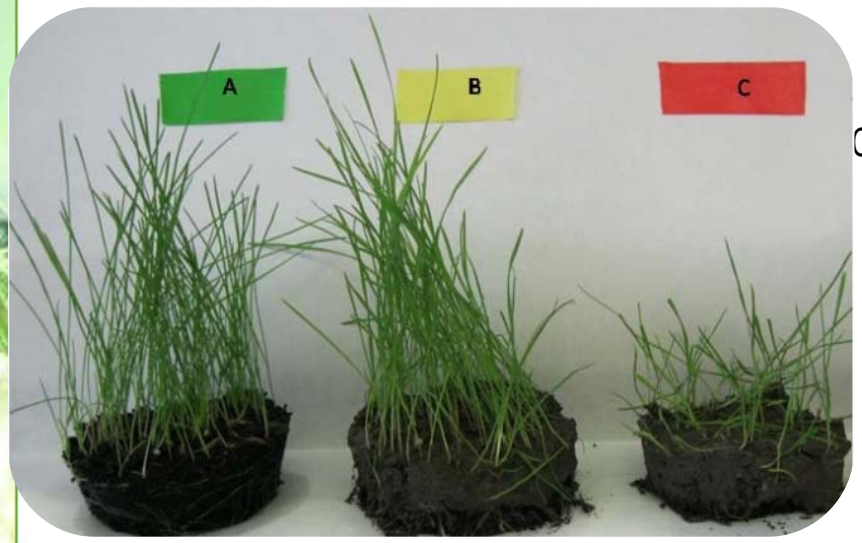


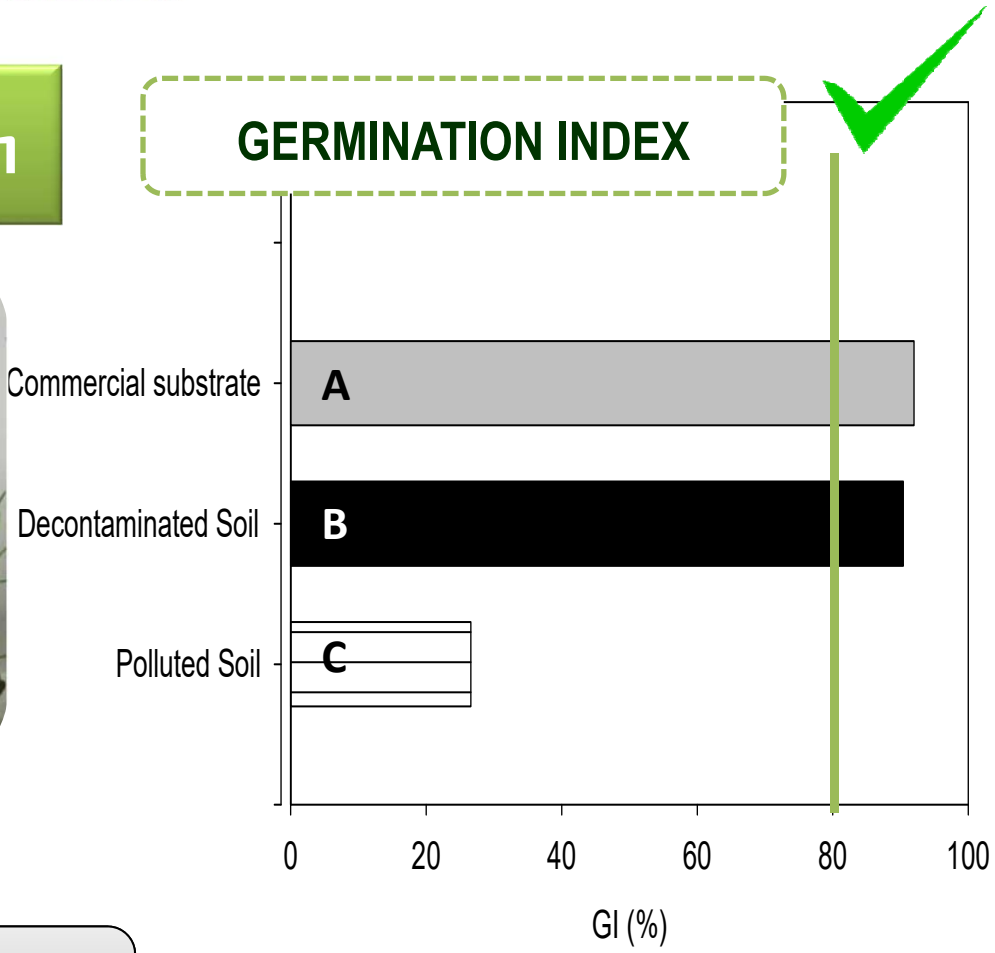


Bocos, Fernández, Pazos, Sanromán Chemosphere (2015) 125:168-174

3. Electro-Fenton for soil remediation

Electrokinetic-Fenton

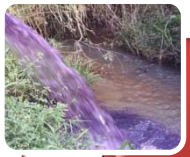




- **Phytotoxicity assays with *Lolium perenne***

Bocos, Fernández, Pazos, Sanromán Chemosphere (2015) 125:168-174

4. Conclusions



Electro-Fenton in aquatic environment

- The optimization of operational conditions and reactor design are necessary
- Heterogeneous catalyst useful for the treatment of continuous flow

Electro-Fenton in soils

- The electrokinetic phenomenon can be used to produce *in situ* Fenton reaction
- The presence of complexing agents enhances the treatment

BIOSUV
Bioengineering & Sustainable Processes
Universidade Vigo

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PhD Iglesias
PhD Rosales