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Sediment continuum: applying an integrated management approach

SedNet

Exploring unconventional approaches to sediments decontamination: A spanish project

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Motivation…

- Dredged sediments are a **valuable resource**. However, **pollution turns them into a waste**
- Sediments usually have a **complex mix of different types of pollutants**, including Persistent Organic Pollutants (POPs), microplastics and heavy metals among others.
- The organic and inorganic contaminants can be **adsorbed simultaneously** on the soil particles and organic matter of the sediment, or **precipitated** as a different solid phases.
- Decontamination technologies rely on the desorption and dissolution of the contaminants. Both **sorption/desorption and precipitation/dissolution processes depend on** the type of contaminant, its concentration, type of sediment and its surface characteristics, the chemistry of pore fluid, pH and other parameters.
- To reuse sediments, **threshold limits are more and more restrictive**, as in the case of TBT

This makes sediment decontamination a serious technological challenge.
No effective technologies for decontamination of multiple-polluted sediments have been developed so far

This is attributed to the **incompatibility of the technologies used for different types of pollutants**, a decrease in the overall effectiveness of the remediation processes for the mixture of pollutants for competition effects

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Some examples to illustrate the problem

 

Heavy metals

Anolito	Catolito	Cu	Cd	Cr	Pb	Ni	Zn
		Extracción máxima (%)					
Agua destilada	Agua destilada	-	-	-	-	-	-
Agua destilada	Agua destilada	2	24	9	0	75	29
Agua destilada	Ácido cítrico 0,3M	16	64	1	14	48	35
Agua destilada	Acido acético 0,5M	26	64	14	27	89	81
Agua destilada	AEDT 0,1M	0	0	6	63	45	58
Agua destilada	Ácido acético 0,2M	19	0	19	11	33	23
Agua destilada	Ácido acético 0,05M	5	0	20	0	0	2
Ácido cítrico 0,3M	Ácido cítrico 0,3M	22	0	74	2	58	48
Ácido acético 0,1M	Ácido acético 0,1M	23	64	47	42	54	53
Agua destilada	Ácido húmico 1g/L	13	64	41	11	85	63
Agua destilada	Ácido acético 0,1M	8	64	6	8	60	19
Ácido acético 0,1M	Ácido acético 0,1M	19	74	18	17	67	33

There is not a general treatment able to remove the 6 metals simultaneously

ELECTROKINETIC Decontamination

- Clean sandy sediment
- Spiked contaminants
- Metals OR fuel
- Enhancing solutions/surfactants

Fuel

Ensayo	Anolito	Catolito	Pretratamiento	Extracción máxima (%)
O1	-	-	Biosurfactante	55
O2	-	-	Surfactante B	16
O3	-	-	Surfactante C	16
O4	-	-	Surfactante D	25
O5	**-**	**-**	**Agente complejante**	**73**
O6	Agua destilada	Biosurfactante	NO	8
O7	Agua destilada	Surfactante B	NO	31
O8	**Agua destilada**	**Surfactante C**	**NO**	**91**
O9	Agua destilada	Surfactante D	NO	34
O10	Agua destilada	Agente complejante	NO	5
O11	Agua destilada	Agua destilada	NO	6
O12	Agua destilada	Agua destilada	NO	-
O13	**Agua destilada**	**Surfactante C**	**NO**	**92**
O14	Agua destilada	Biosurfactante	Biosurfactante	-
O15	Agua destilada	Surfactante B	Surfactante B	40
O16	Agua destilada	Surfactante C	Surfactante C	38
O17	Agua destilada	Surfactante D	Surfactante D	26
O18	Agua destilada	Agente complejante	Agente complejante	-
O19	Agua destilada	Ácido acético 0,5M	NO	29
O20	Agua destilada	Ácido acético 0,5M	Surfactante C	31
O21	Agua destilada	Surfactante C/Ácido acético 0,5M	NO	34
O22	Surfactante C	Ácido acético 0,5M	NO	26

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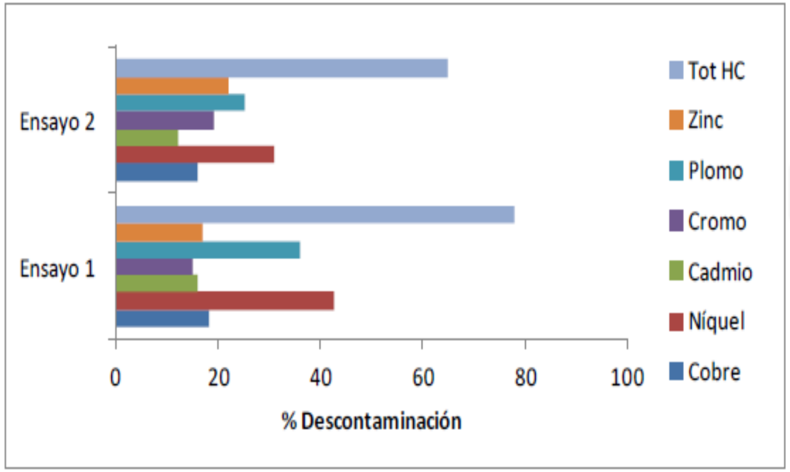
Mixed Contamination

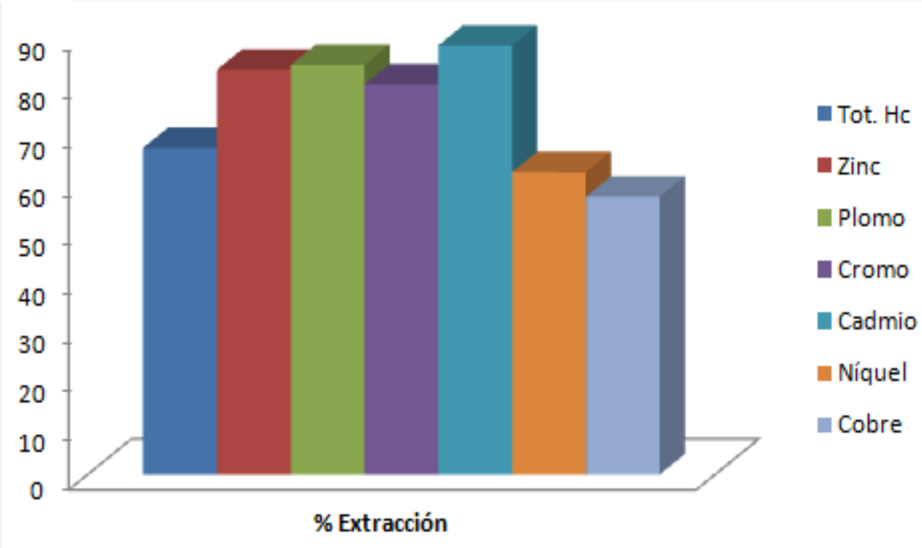
- Sandy sediment
- Spiked contaminants
- Metals AND fuel
- Enhancing solutions/surfactants



Lower results for heavy metals
Lower results for fuel

Multi-step treatment

1) **Organic compounds**
2) **Heavy metals**



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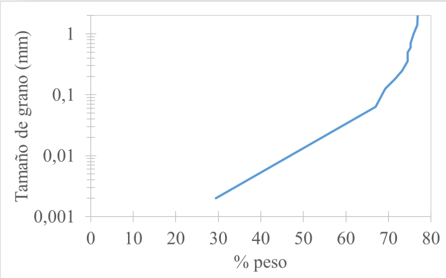
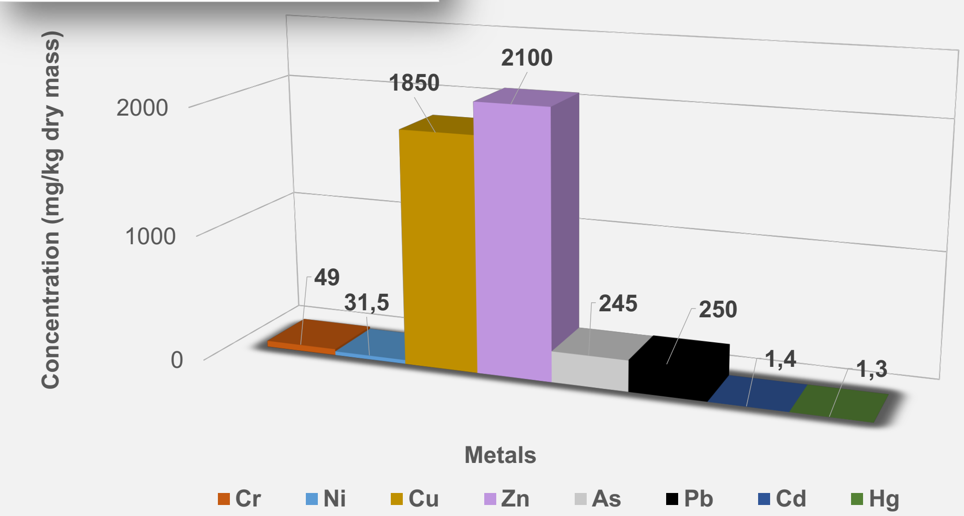
A different marine sediment. Polluted with heavy metals and organic compounds

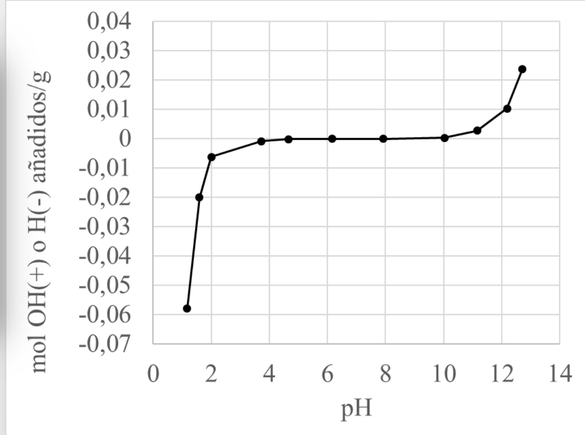


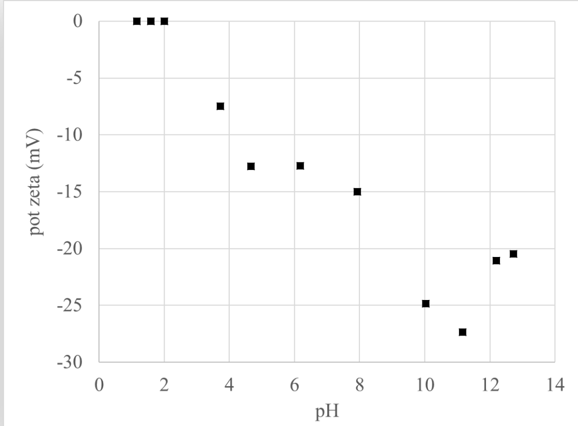
Sediment composed mainly of clays and silts:
67% weight fraction < 63 µm



$CaCO_3$ (g/kg)	Total organic carbon (TOC) (g/kg)	Solids concentration (mass %)	Agglomerated mass (g)	Dry matter (mass %)	Microtox solid phase test
10,2	21	33	0	34,85	>16 g/L of sediment

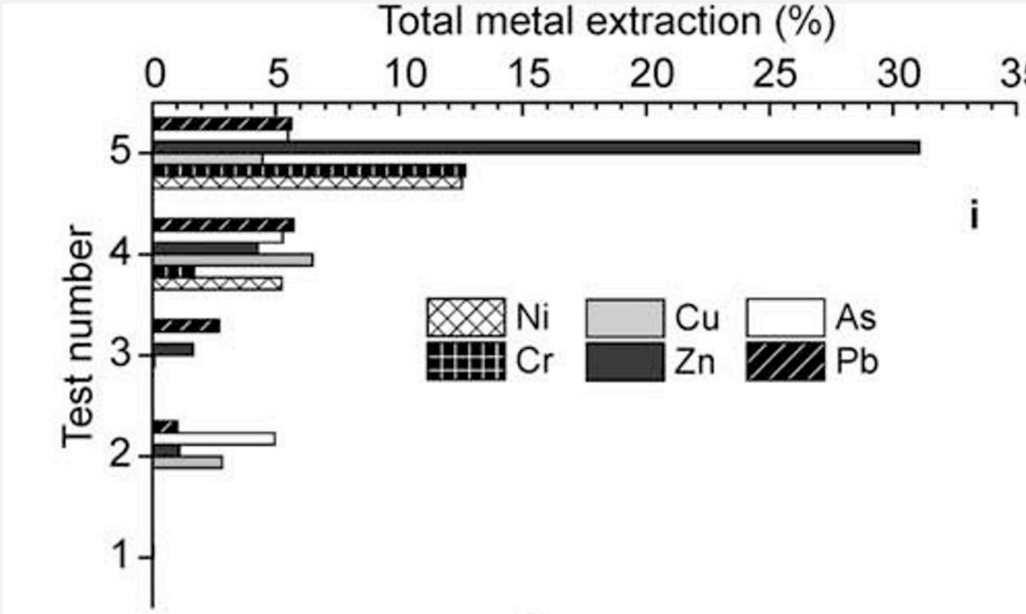
	Contaminante	Análisis
Hidrocarburo de petróleo (mg/kg ms)	TPH >C10-C12	<6,0
	TPH >C12-C16	<10
	TPH >C16-C21	**20**
	TPH >C21-C30	**45**
	TPH >C30-C35	**16**
PAH (mg/kg ms)	**Fluoranteno**	**0,018**
	Fenantreno	**0,02**
	Antraceno	<0,010
	Pireno	<0,010
	Benzo(a)antraceno	<0,010
	Criseno	0,012
	Benzo(a)pireno	<0,010
	Benzo(ghi)perileno	<0,010
	Indeno(1,2,3-cd)pireno	<0,010
	HAP 9 (suma)	<0,090
PCB (mg/kg ms)	PCB 28	<0,0010
	PCB 52	<0,0010
	PCB 101	<0,0010
	PCB 118	<0,0010
	PCB 138	<0,0010
	PCB 153	<0,0010
	PCB 180	<0,0010
	PCB (som 7)	<0,0070
	Materia seca	21,9
Organoestánnico (µg/kg ms)	Monobutyltin (MBT)	<2,2
	Dibutyltin (DBT)	**8,1**
	Tributyltin (TBT)	**68**
	Tetrabutyltin (TTBT)	<2,2
	Monooctyltin (MOT)	<2,2
	Dioctyltin (DOT)	<2,2
	Tricyclohexyltin (TCyT)	<4,4
	Triphenyltin (TPhT)	<2,2





Very high **buffer capacity** in the pH ranges 11-14 and 0-3.

Zeta potential decreases linearly with increasing pH, down to almost -30 mV at pH 11.



Poorer results even for metals

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For electrokinetic methods…

Simple problem

- Sandy sediment
- Spiked contaminants
- Metals
- Enhancing solutions

Simple problem

- Sandy sediment
- Spiked contaminants
- Fuel
- Surfactants

- Sandy sediment
- Spiked contaminants
- Metals and Fuel
- Enhancing solutions

Multi-step procedure

Complex problem

- Clay and silt sediment
- Consolidated real contaminants
- Metals, organics, POPs,..
- Enhancing solutions/surfactants
- Multi-step procedure

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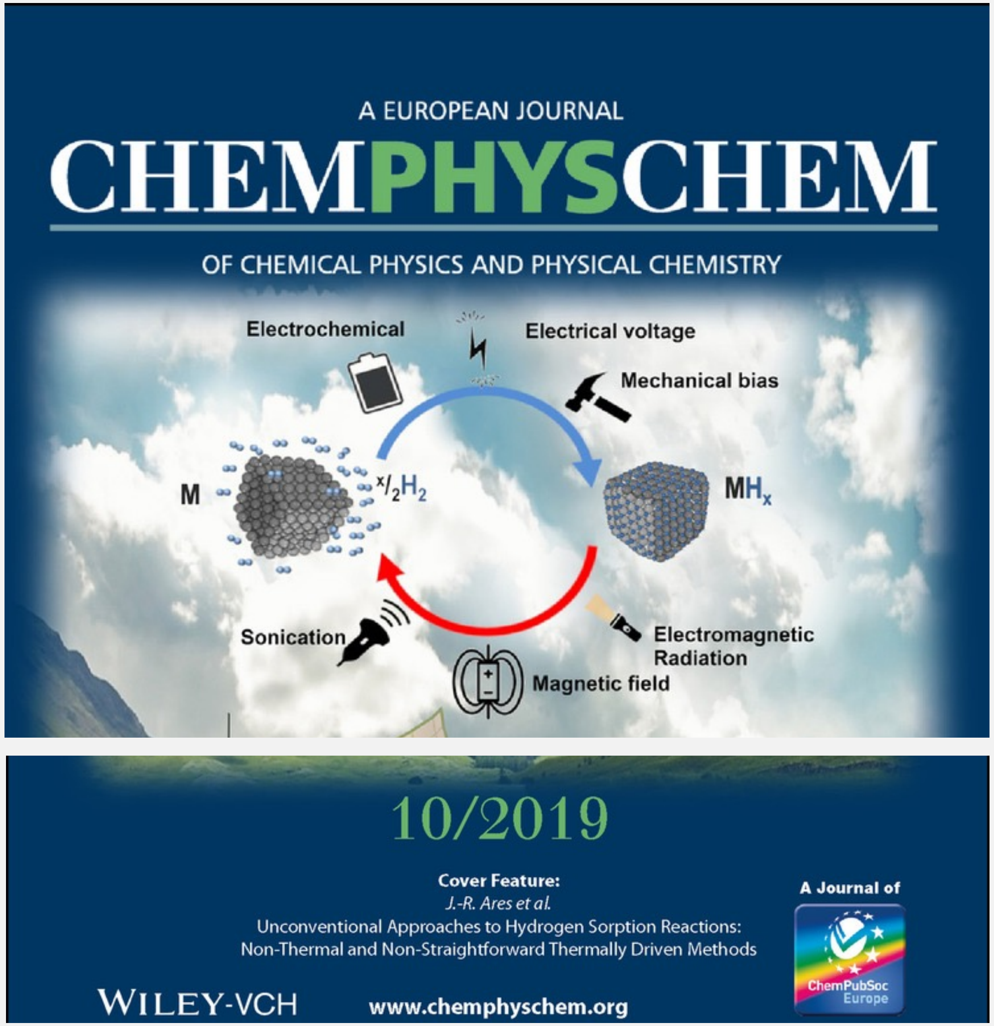
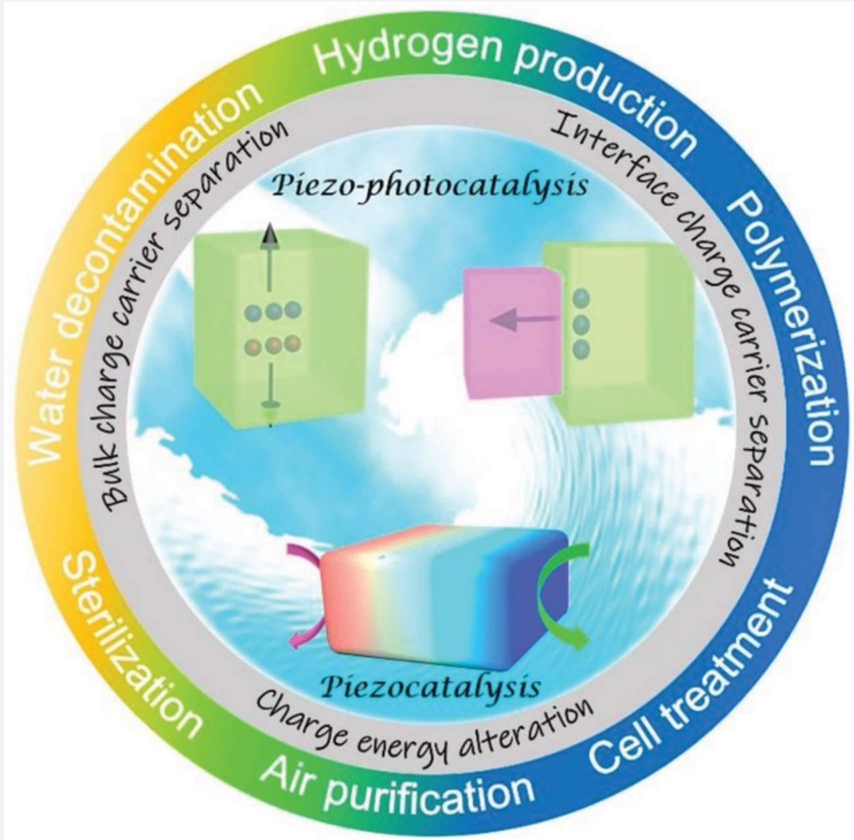
EXPLORATION OF DIFFERENT STRATEGIES FOR ACTIVATION OF CHEMICAL REACTIONS





Adv. Funct. Mater.2020, 30, 2005158

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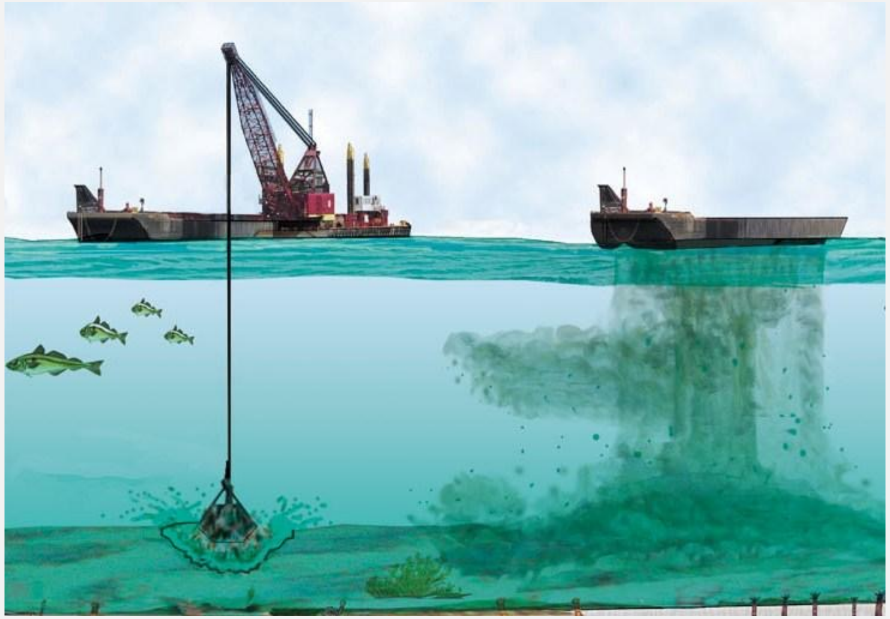
The project intends to tackle the whole decontamination of sediments

It is based on the hypothesis that by using **unconventional reaction pathways**, it is possible to decontaminate dredged sediments from a **complex mix of pollutants** without generation of toxic residuals, so that contaminated sediments become a valuable resource contributing to the implementation of the precepts of the circular economy focusing on **revalorization of sediments as a raw material for its use in the construction sector and civil engineering**.



To do so…

1) To explore **new physicochemical approaches** including synergistic **mechanochemical, photocatalytic and electrochemical reactions**
2) conceptualization and proof of a the **technology allowing integral decontamination of multiply-contaminated dredged sediments** using the new approaches

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Mechanochemical energy

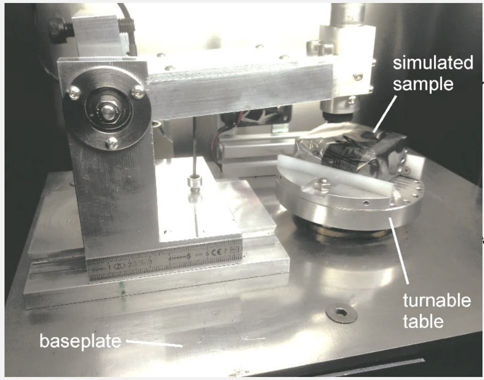
Direct coupling of mechanical energy to the energy landscape of chemical reactions

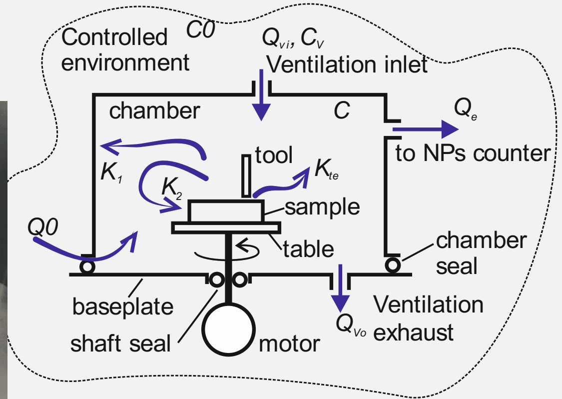
Unusual reactions paths and products: bond formation, bond dissociation, sliding of atomic layers…

Abrasion

small-scale laboratory test (MiniTribo)

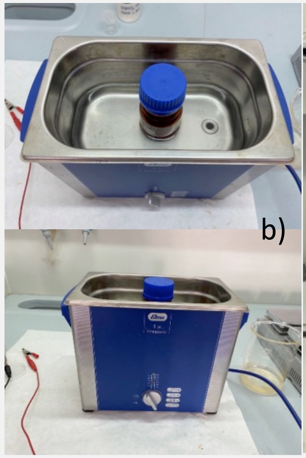
Pin-on-disk configuration
Load: 0.2-20 N range
Rot. speed 60-3000 rpm
Volume ~ 15 l





High energy milling

Ultrasounds

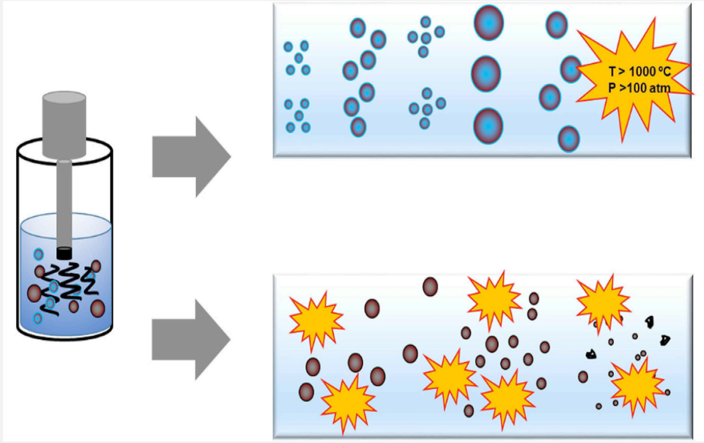


Bath

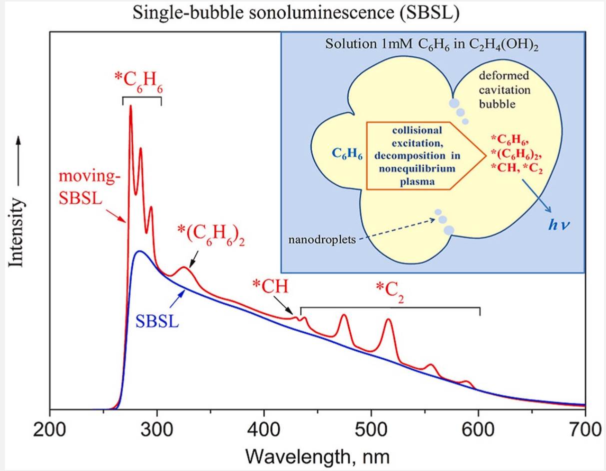
Sonicator

Sonochemistry:

Cavitation can be defined as small gas bubbles being grown, oscillated, and collapsed in a fluid. This causes a combination of mechanical stress, temperatura and electric gas discharge

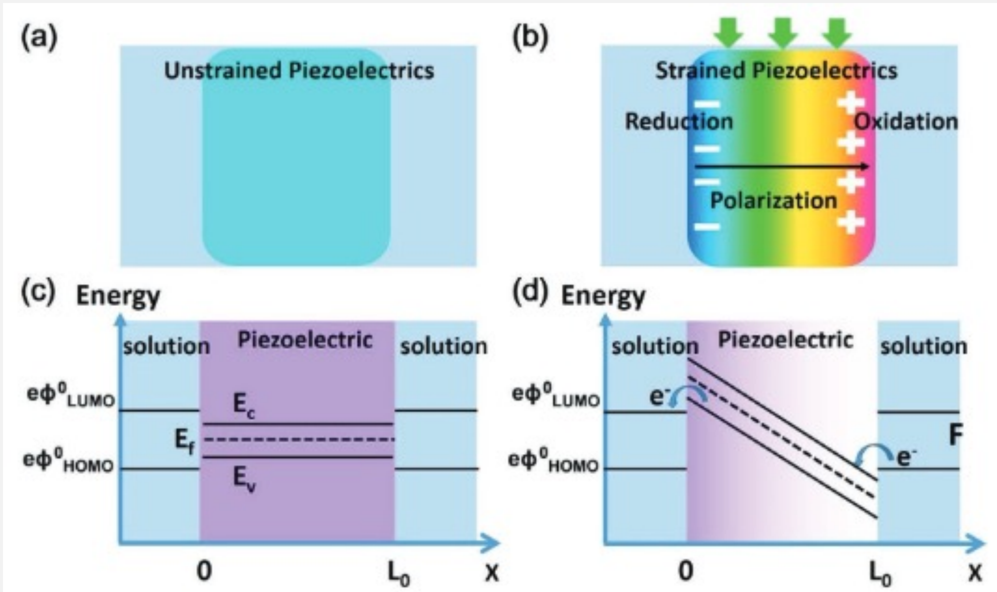


ChemPhysChem 2019, *20*, 1–14



G.L. Sharipov et al. Journal of Luminescence 238 (2021) 118279

Piezocatalysis



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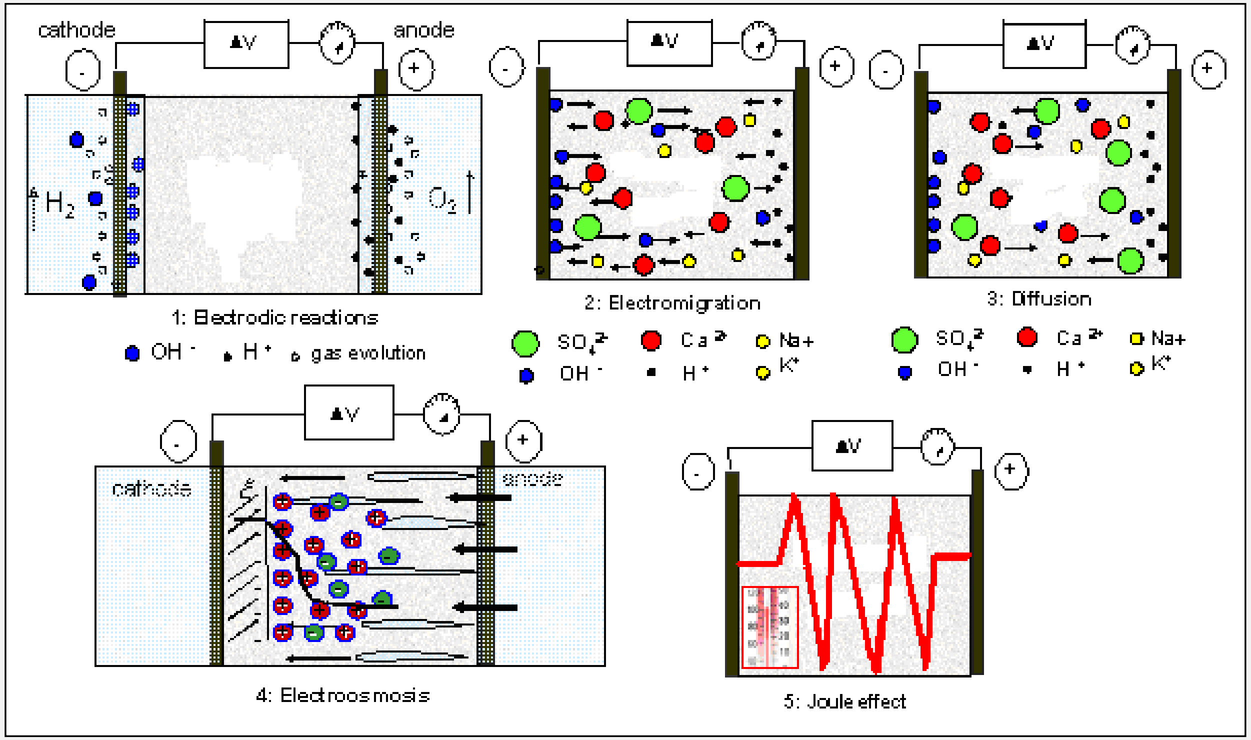
ELECTROKINETIC TECHNIQUES

FUNDAMENTALS → **Application of an electrical potential drop of low intensity directly on the contaminated material**



Electrodic Reactions

$$H_2O \rightarrow 1/2\ O_2 + 2H^+ + 2e^-$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

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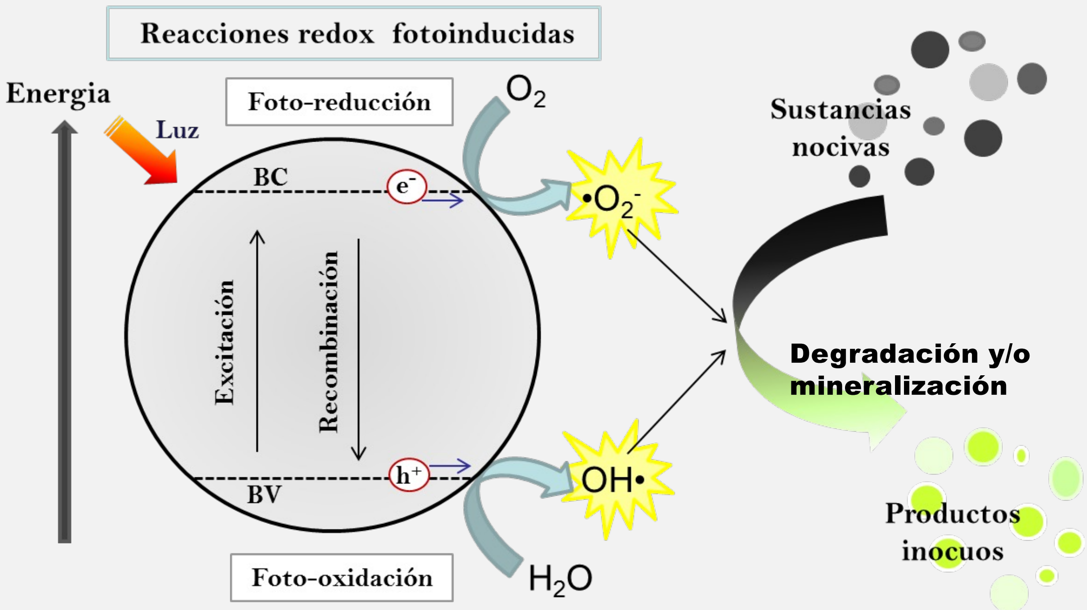
Photocatalysis

Technology based on the absorption of radiant energy (visible or UV) by a semiconductor acting as a photocatalyst. The catalyst induces the formation of redox pairs: highly oxidising species and excited electrons that can react with the organic and inorganic substances adsorbed on its surface, leading to their degradation and even mineralisation.



The
- band gap
- position of the bands

characterize the “potential” of the photocatalyst.

BV: Highest energy band in which all electronic levels are occupied.
BC: lowest energy band unoccupied by electrons.

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Thermodynamically:

VB holes can oxidise all adsorbed compounds whose redox potential is more negative

$h^+ + H_2O \rightarrow OH\bullet + H^+$

$h^+ + OH^- \rightarrow OH\bullet$

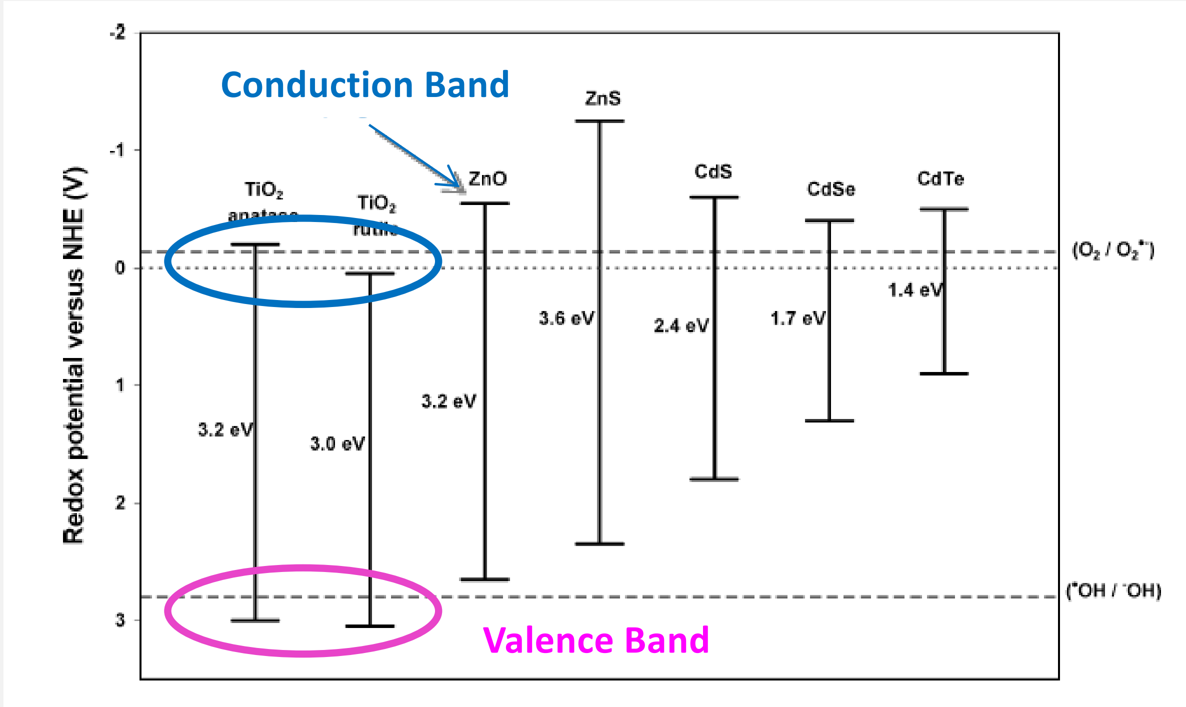
CB electrons can reduce all adsorbed compounds with a more positive redox potential

$$e^- + O_2 \rightarrow {}^\bullet O_2^-$$

$${}^\bullet O_2^- + 2H^+ + e^- \rightarrow H_2O_2$$

$$H_2O_2 + {}^\bullet O_2^- \rightarrow OH^\bullet + OH^- + O_2$$

In the absence of adsorbates: RECOMBINATION



TiO2: anatase holes and can oxidise OH to OH•

TiO2: anatase electrons can reduce molecular oxygen to superoxide radicals.

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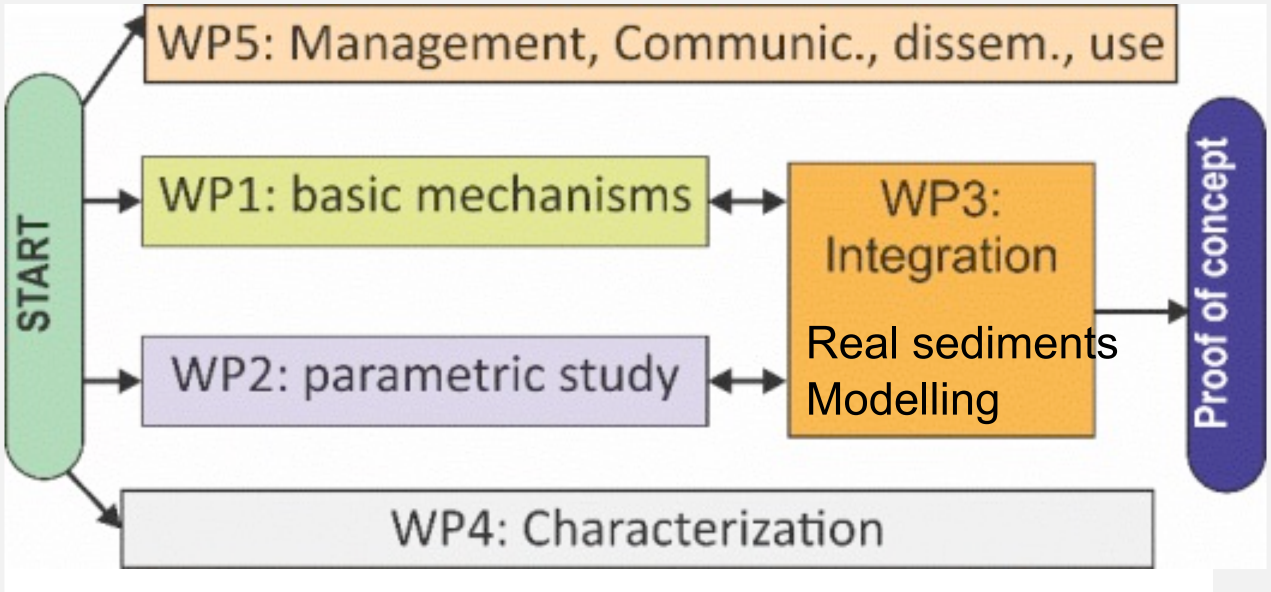
Objective

The **main objective** of the proposed project is **to explore new ways for integral, effective and environmentally friendly decontamination of dredged sediments from POPs, heavy metals and other pollutants using an interdisciplinary approach based on coupling or combining different unconventional techniques.**

Methodology and work plan



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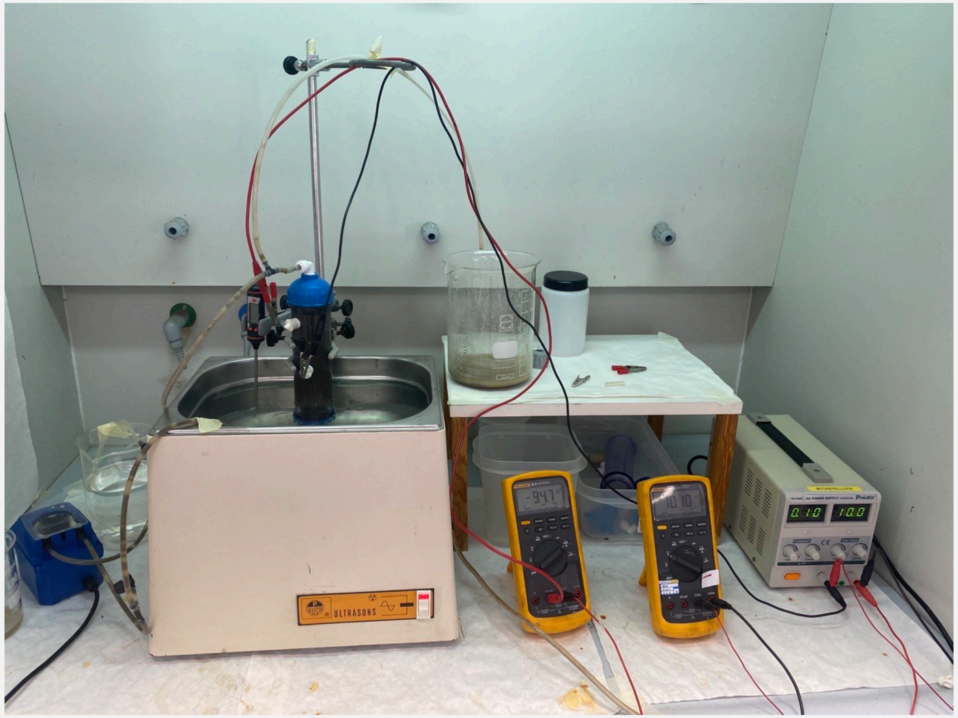
As a result… Complex decontamination of dredged sediments in the real world. Modelling will be used to connect physical and chemical mechanisms to the technological parameters. Then, it will be possible to determine the most appropriate type of energy (method) or combination of energies to apply in each case depending on the sediment characteristics.



Coupling electrokinetics with ultrasounds

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Thank you for your attention

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