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REMEDIATION OF HCHS-POLLUTED SOILS BY SURFACTANT-ENHANCED WASHING AND ACTIVATED PERSULFATE OXIDATION

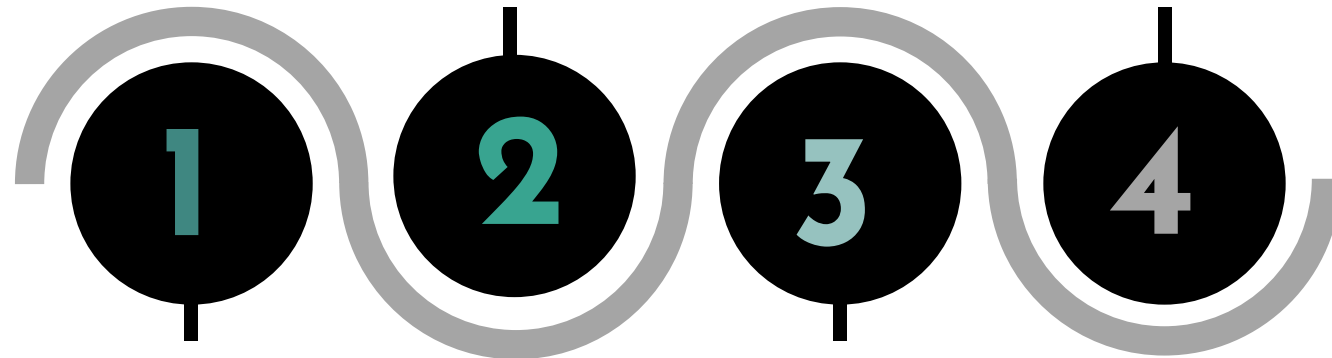
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SUMMARY

EXPERIMENTAL 

CONCLUSIONS 



INTRODUCTION 

RESULTS 



SUMMARY

EXPERIMENTAL 

CONCLUSIONS 



INTRODUCTION 

RESULTS 



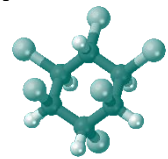
INTRODUCTION



PESTICIDES
SOIL
POLLUTION → **Major environmental problem** !

CASE STUDY

Lindane
(γ -HCH)
wastes
pollution



i) **Liquid**
↓
Dense non-aqueous
phase liquid (DNAPL)



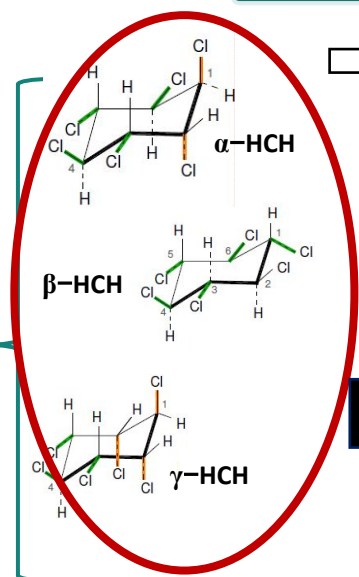
ii) **Solid:** HCHs isomers
without insecticidal
properties



**Objective
of this work**



HCH-polluted
superficial soil



Adverse effects on:
○ Ecosystems
○ Human beings

High refractoriness

**Chemical
Oxidation
treatments**

Degradation



DIFFICULT

Low solubility



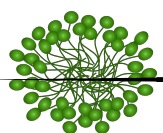
**Urgent need to remediate
HCHs-polluted sites**





INTRODUCTION

HCHs-polluted soil



Surfactants

- Emulsification of organic pollutants
- Anphiphilic nature:

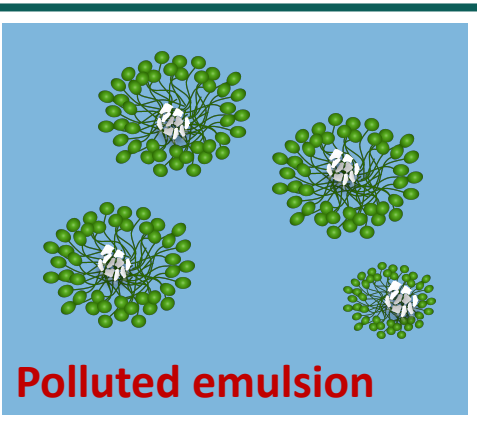
Hydrophilic group

Hydrophobic group

Surfactant-enhanced pollutants
solubilization

On-site

"clean" soil



Polluted emulsion

PS-Fe



pH=7

PS-T

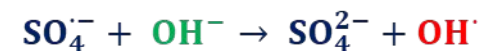


pH=7

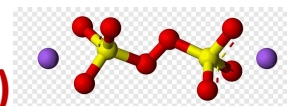
PS-NaOH



pH>12



Activated
Persulfate (PS)



Chemical Oxidation Processes





INTRODUCTION



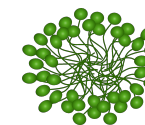
OBJECTIVE

Application of *surfactants* with *PS-oxidation treatments*

1

Soil washing (SW) experiments

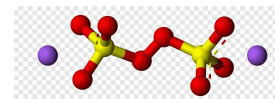
- ✓ Surfactant ability to solubilize the soil pollutants
- ✓ Selection SW conditions: surfactant, pH, reagents concentration, number of washing cycles, etc.



2

Oxidation of polluted emulsion (PE)

- ✓ Maximum degradation of pollutants
- ✓ Moderate oxidant consumption





SUMMARY

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INTRODUCTION



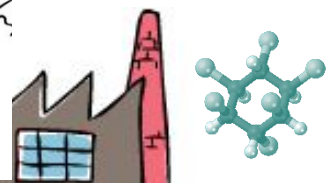
RESULTS





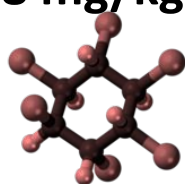
EXPERIMENTAL

Bailín landfill
(Sabiñánigo, Spain)

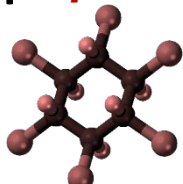


HCHs-polluted superficial soil

298 mg/kg soil β -HCH



α -HCH



49 mg/kg soil

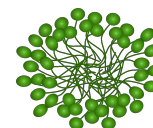
Collected: 0-0.3 m
 $d_p = 0.02-0.25$ mm

Pollution

- Particulate matter $\Sigma\gamma$ -HCH, δ -HCH, ϵ -HCH=26 mg/kg soil
- Adsorbed into the soil

1 SW experiments

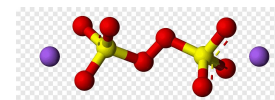
Surfactants



- Anionic: Sodium dodecyl sulfate (SDS)
- Non-Ionic: Tween-80 (T80), Emulse-3 (E3)

2 Oxidation experiments

PS activated by NaOH and T





EXPERIMENTAL

1

Soil washing (SW) experiments

Effect of the main variables of the SW process

24 h
(equilibrium)
100 rpm



30 ml
aqueous
phase

15 g
polluted
soil



Objective	Surfactant	C_{surf} (g/L)	C_{NaOH} (g/L)	Number of solubilization cycles
Effect of surfactant and pH	No surfactant SDS, E3, T80	10	0 (pH=7) 13.5 (pH>12)	1
Effect of alkali concentration	SDS, E3, T80	10	2.5, 4, 13.5	1
Effect of surfactant concentration	SDS, E3	2, 5, 10	10	1
Successive solubilization cycles	SDS, E3	SW1=5 SW2=2.5 SW3=1.25	SW1=4 SW2=0 SW3=0	3



EXPERIMENTAL

1

Soil washing (SW) experiments

Analytical techniques

Slurry system



After 24 h (equilibrium)



Centrifugation



10 min, 900 rpm



EXPERIMENTAL

1

Soil washing (SW) experiments

Analytical techniques



Polluted emulsion

Soil phase

- Chlorinated Organic Compounds (COCs) concentration

- No surfactant: L-L extraction (hexane, 1/1)
- SDS: NaCl + L-L extraction (hexane, 1/1)
- E3 and T80: MeOH dilution (1/10)



Gas chromatography
(GC-FID/ECD)

- Surfactant concentration

TOC
concentration



TOC-V CSH analyzer

- COCs concentration

S-L extraction
(MeOH)
(1:2, 180 min, 45 °C,
US bath)



Gas chromatography
(GC-FID/ECD)



EXPERIMENTAL

2

Polluted emulsion (PE) oxidation experiments

*PS activated by alkali
and intensified by T*

Analytical techniques

Objective	PE employed	Surfactant	C _{PS} (g/L)
COCs oxidation	Surfactant		
	PE-SDS-1	SDS	40
	PE-SDS-1,2,3		
	PE-E3-1	E3	
	PE-E3-1,2,3		



Molar ratio of NaOH:PS=2



Polluted
emulsion
(10 ml)

T=40 °C, 80 rpm

- PS concentration → Spectrophotometry



- COCs concentration →



Gas chromatography
(GC-FID/ECD)



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RESULTS 



1

Selection SW conditions

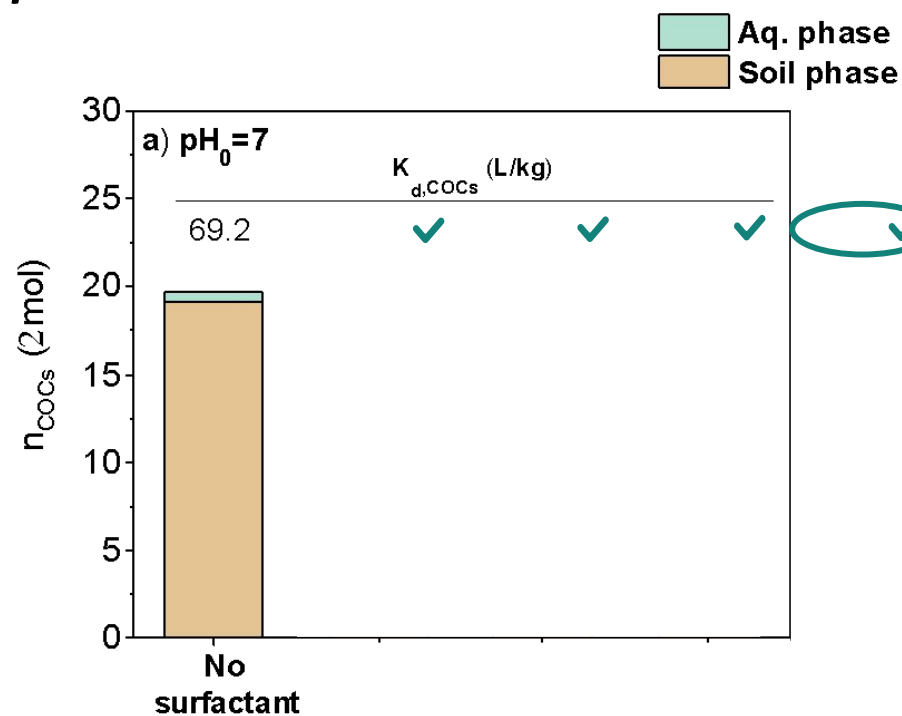
1.1. Effect of surfactant and pH

Partition coefficient

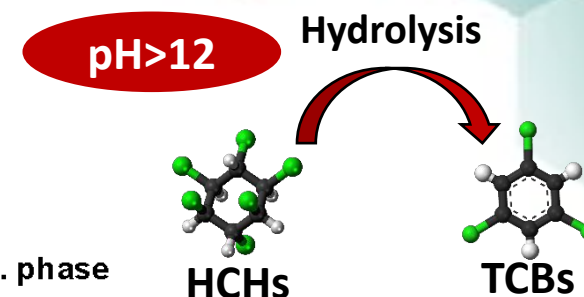
$$K_{d,COCs} = \frac{COCs_{soil\ phase}}{COCs_{aqueous\ phase}}$$



Lower $K_{d,COCs}$ → Higher COCs solubilization ✓



RESULTS



✗ Lower T80 stability

SELECTED:

Alkaline conditions (pH>12)



Experimental conditions:

$C_{surfactant} = 10$ g/L, $V_L/W_{soil} = 2$, 100 rpm, 24 h, 20 °C

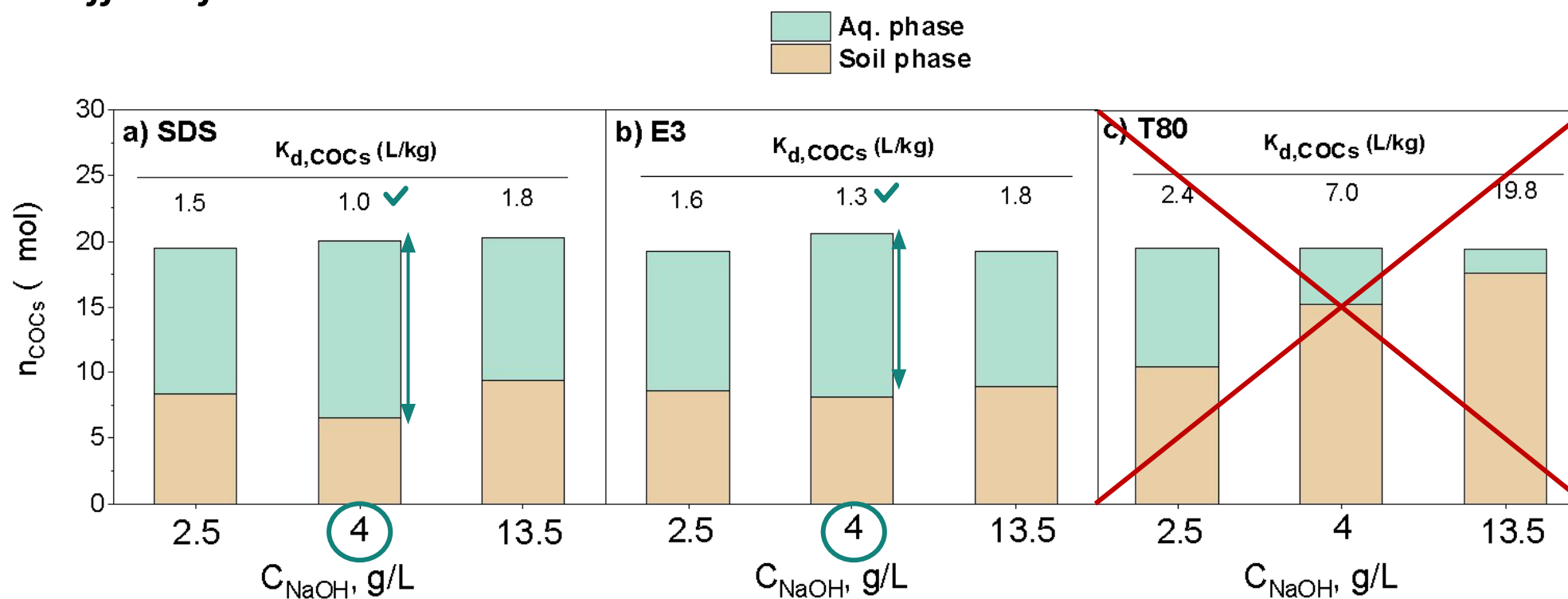


RESULTS

1

Selection SW conditions

1.2. Effect of NaOH concentration



Experimental conditions:

$C_{surf}=10\text{g/L}$, $V_L/W_{soil}=2$, 100 rpm, 24 h, 20 °C, **pH>12**

SELECTED:

- SDS and E3
- $C_{NaOH}=4\text{ g/L}$



RESULTS

1

Selection SW conditions

1.3. Effect of surfactant concentration

- Excessive $C_{\text{surfactant}}$:

- Reduces COCs availability towards oxidation
- Compete with contaminants for radicals

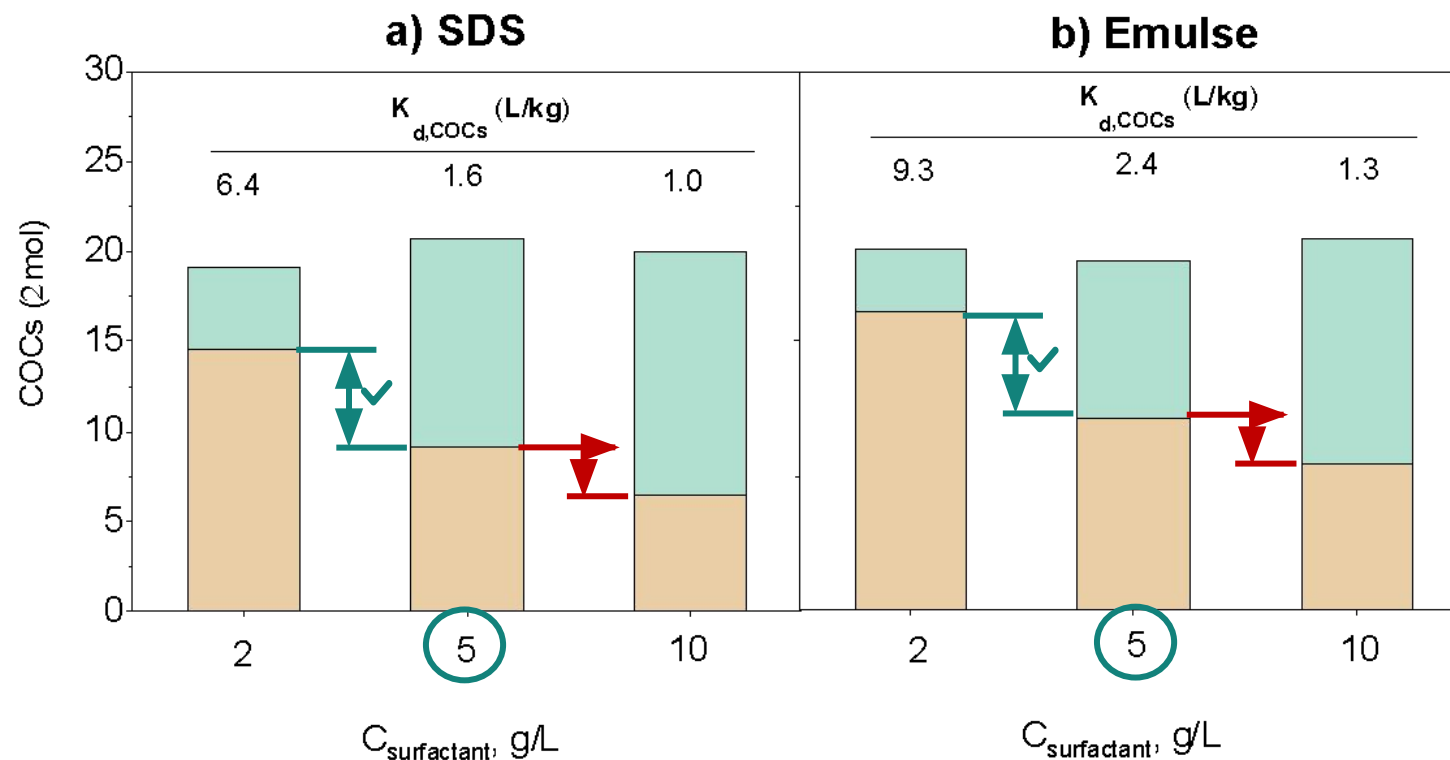
- Greater improvement from 2.5 to 5 g/L



SELECTED:

$C_{\text{surfactant}} = 5 \text{ g/L}$

Soil phase
Aqueous phase



Experimental conditions:

$V_L/W_{\text{soil}} = 2$, 100 rpm, 24 h, 20 °C, $\text{pH} > 12$, $C_{\text{NaOH}} = 4 \text{ g/L}$



RESULTS

1

Selection SW conditions

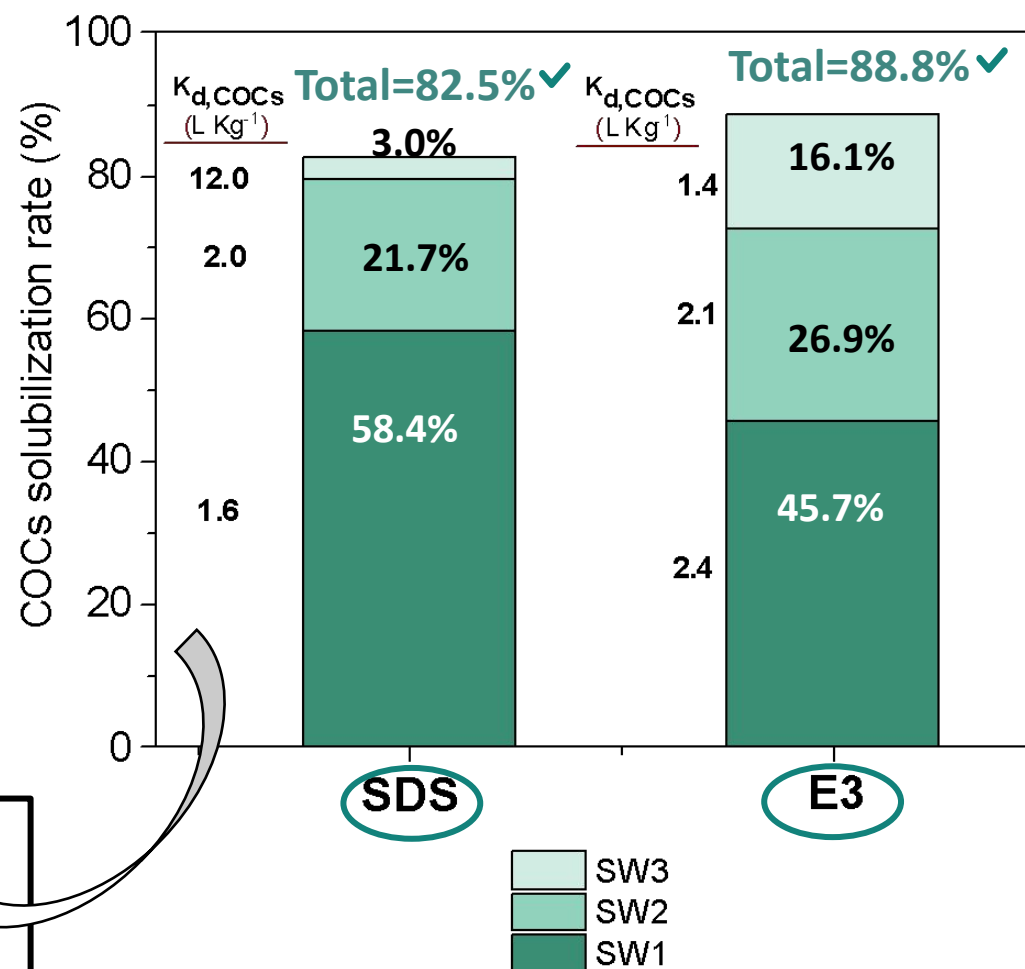
1.4. Successive solubilization cycles

$$\text{Solubilization rate (\%)} = \frac{\text{COCs}_{aq, phase} \cdot \frac{V_L}{W_S}}{\text{COCs}_{soil, phase}} \cdot 100$$

	C_{surf} (g/L)	C_{NaOH} (g/L)
SW1	4	0
SW2	2.5	0
SW3	1.25	0

$V_L/W_{soil} = 2, 100 \text{ rpm}, 24 \text{ h}, 20 \text{ }^{\circ}\text{C}$

PE employed for the
subsequent oxidation treatment:
SDS and E3 emulsions (after 1 and 3 SW cycles)



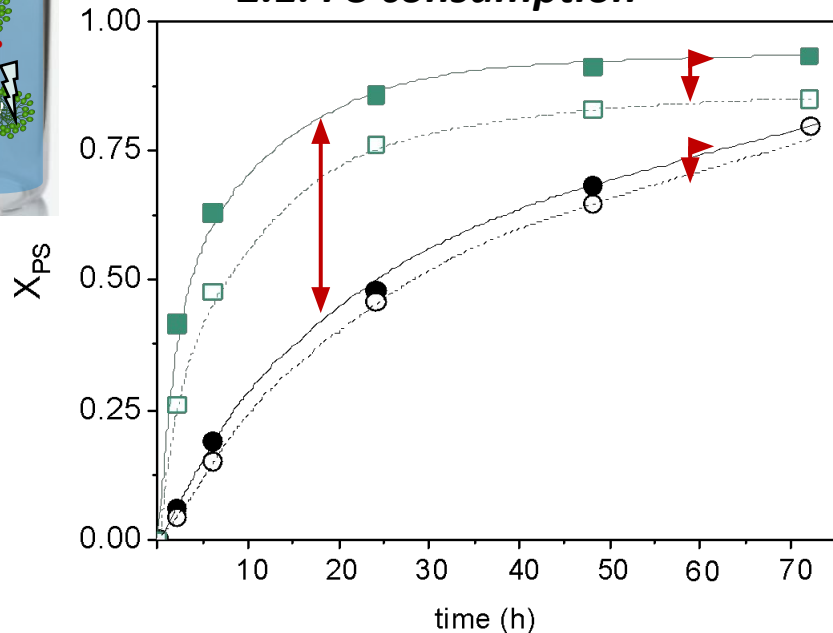


2

Oxidation of the polluted emulsion (PE)



2.1. PS consumption



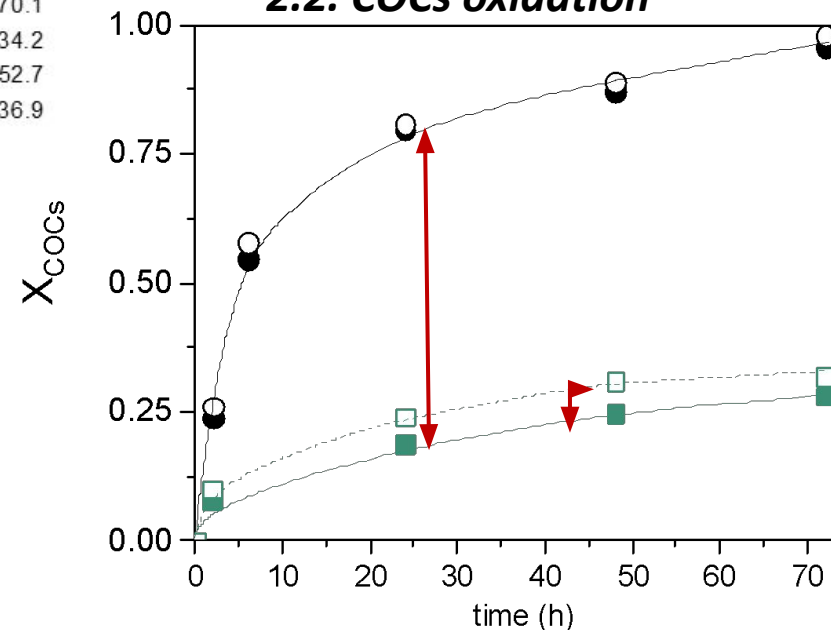
- **Higher PS** consumption in presence of **E3**
- **Higher PS** consumption **at higher $C_{surfactant}$**

RESULTS

PS activated by
NaOH and T \square OH^\bullet

PE	$C_{surf,0}$ (g L ⁻¹)	C_{COCs} (as TCBs) (mg L ⁻¹)
● SDS-1	4.1	70.1
○ SDS-1,2,3	2.7	34.2
■ E3-1	3.1	52.7
□ E3-1,2,3	2.3	36.9

2.2. COCs oxidation



- **Higher X_{COCs}** when treating **SDS**-emulsions
→ Independent of C_{surf}
- **Lower X_{COCs}** when treating **E3**-emulsions
with higher $C_{surfactant}$ → **Surfactant hindering effect**



SDS system

X_{COCs} = 96%, 72h
 X_{PS} = 75%, 72h

Experimental conditions:

Polluted emulsion, $T=40^\circ\text{C}$, $C_{PS}=40$ g/L, NaOH:PS=2, 100 rpm



SUMMARY

EXPERIMENTAL



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1

2

3

4

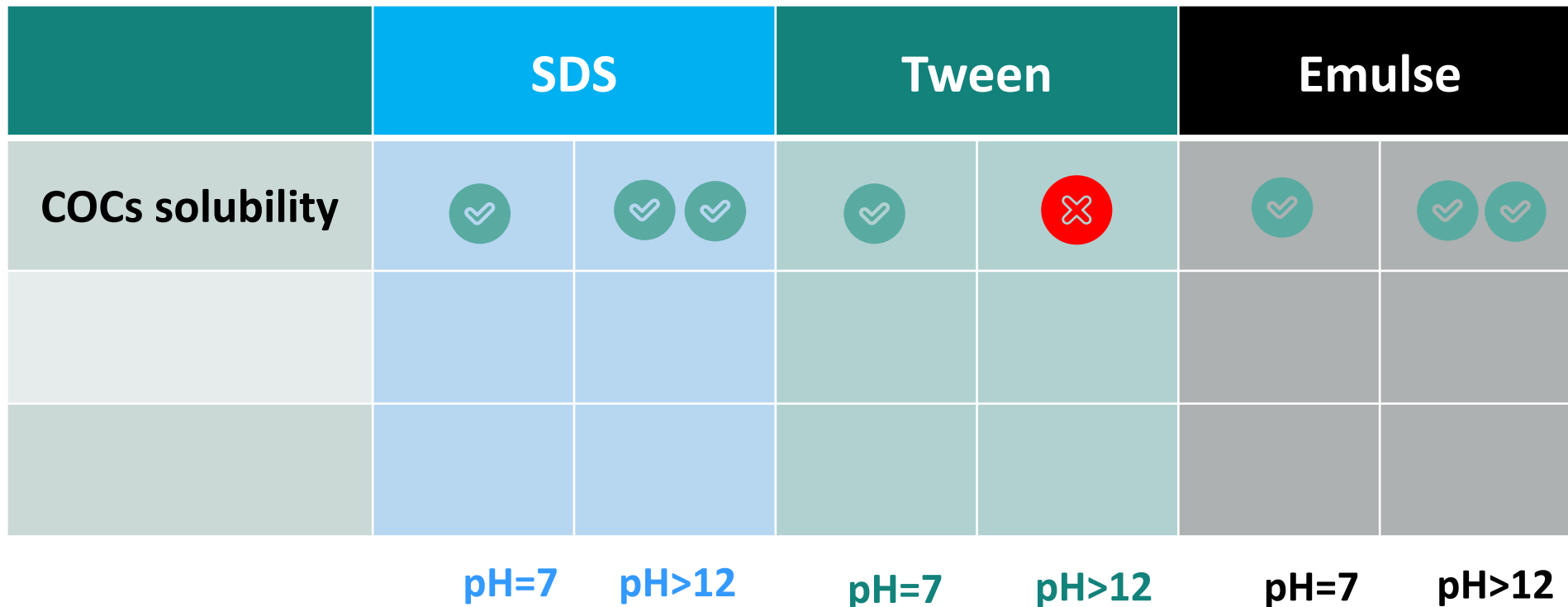
INTRODUCTION



RESULTS



- 



pH>12

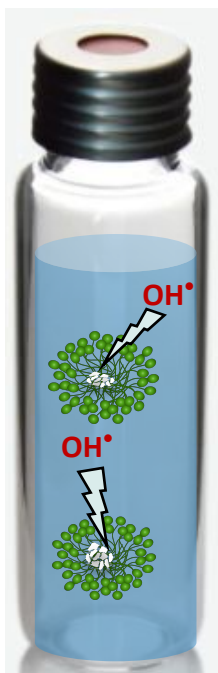



CONCLUSIONS

✗ Higher PS consumption when increasing surfactant concentration and in presence of **Emulse**

✓ Higher X_{COCs} when treating **SDS**-emulsions

(X_{COCs} =96%, 72h)



	 SDS		Tween		Emulse	
COCs solubility	✓	✓ ✓	✓	✗	✓	✓ ✓
PS consumption	-	✓ ✓	-	-	-	✗
COCs oxidation	-	✓ ✓	-	-	-	✗
	pH=7	pH>12	pH=7	pH>12	pH=7	pH>12

THANK YOU FOR YOUR ATTENTION

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INPROQUIMA



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