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Application of an autocatalytic Fenton process for the pre-treatment of an oily sludge: a sustainable management for refinery wastes

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Refinery industry

Oily sludge is one of the most significant solid wastes generated in the petroleum industry

It is necessary the development of technologies to treat and valorize them properly within the framework of circular economy and sustainability.

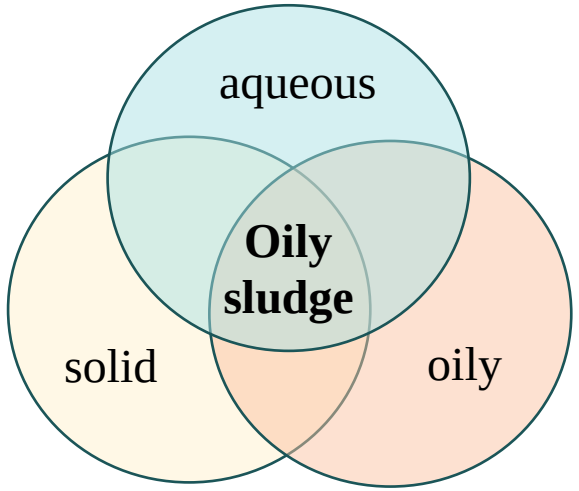
Environmental hazards

- Air, water and soil pollution
- Toxic composition

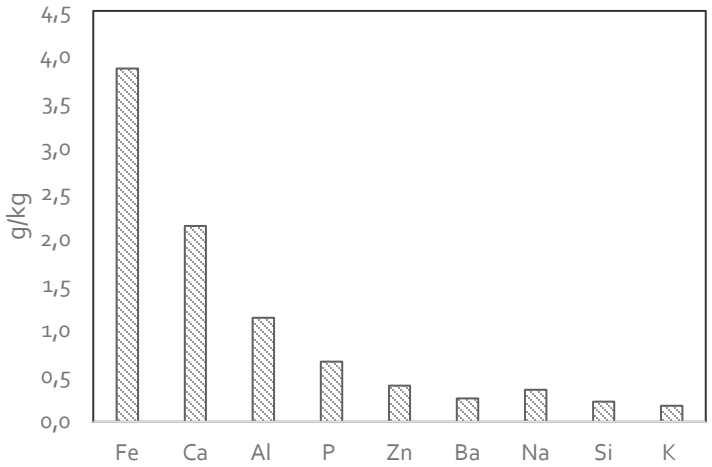
Conventional treatment

- Oil recovery
- Reduce water content
- High costs
- Neccesary adequate disposal
- No valorization

Oily sludge



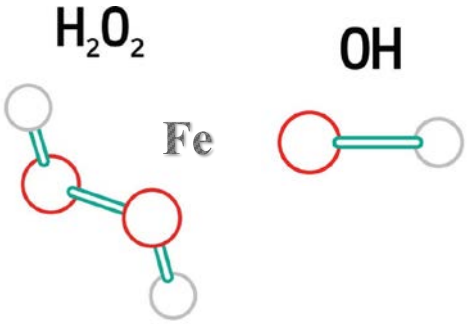
- Oily phase: PHCs (high C content)
- Aqueous phase: low C content and nutrients
- Solid phase: metals and organic material



Fenton oxidation pre-treatment

Advantages

- Removal of harnessing pollutants
- Low energy, time and operational requirements
- **Not neccesary iron catalyst → autocatalytic**



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

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$

$2\ H_2O_2 \rightarrow HO\bullet + HOO\bullet + H_2O$

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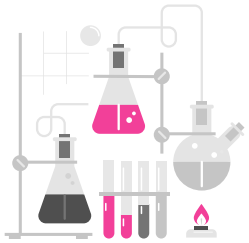
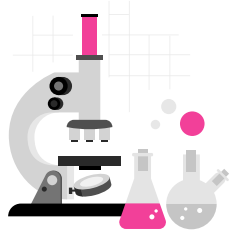
— Break down the stable oil-water-mud emulsion and improve the solid-liquid separation

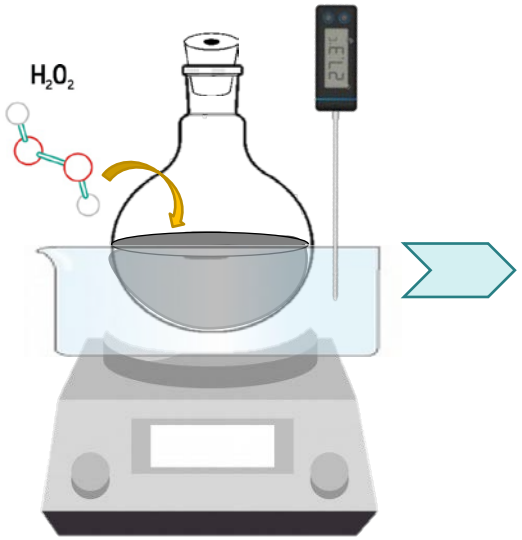
— Solubilise the oily sludge, decreasing its hydrocarbon content



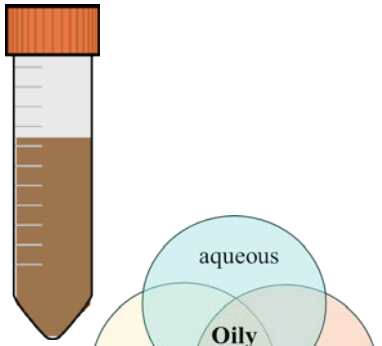
— Release of biodegradable organic matter into the aqueous phase



Autocatalytic Fenton experiments



Conditions
- 90, 45 and 20 g/l H_2O_2
- 25, 40, 60 and 80 ºC
- Reaction time: 2 hours
- Continuous stirring
- Not addition of catalyst
- pH ca. 7.5

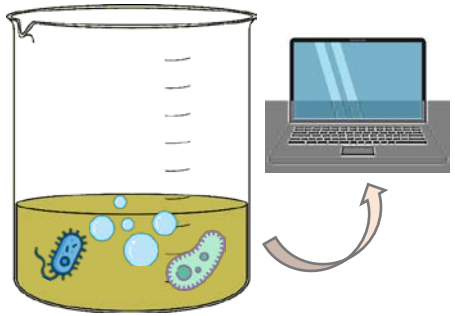


Fractional characterization
- Aqueous phase
- Oily phase
- Solid phase

Oily and solid phase

Specific characterization
- GCMS
- TPHs
- CST

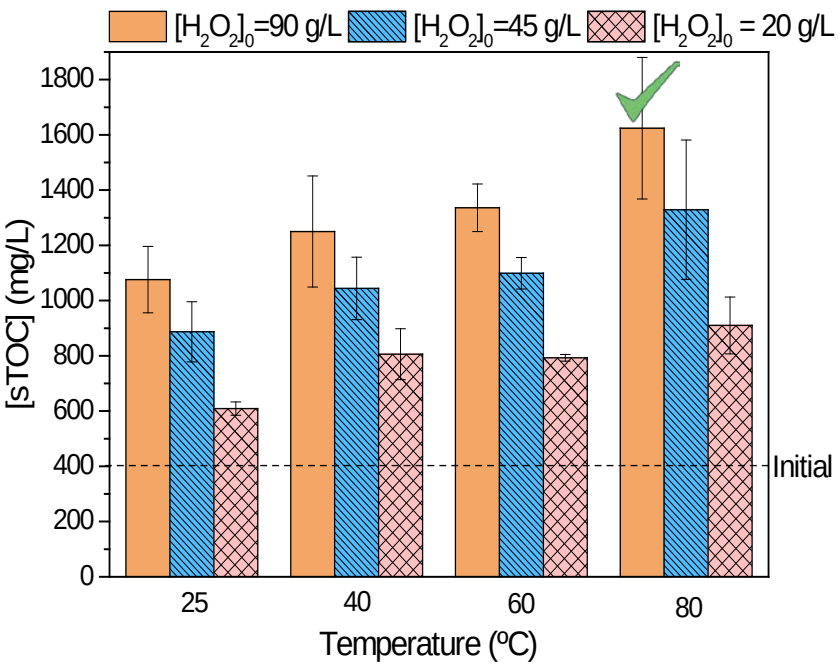
Aqueous phase

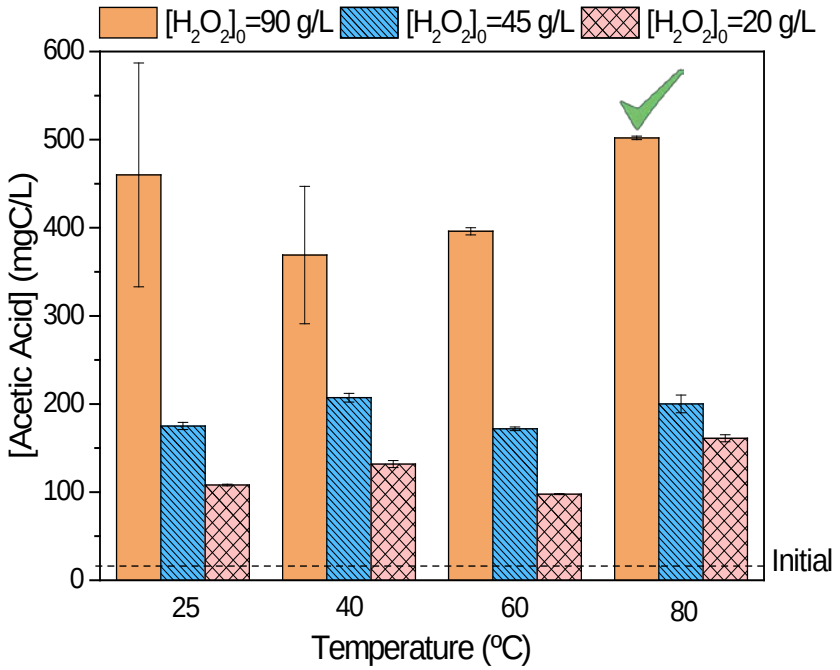


Rapid biodegradability assay (Respirometry tests)
- Aerobic sewage sludge
- 25 ºC and pH ca. 7
- Oxygen control
- Continuous stirring

Results autocatalytic Fenton experiments

— Aqueous phase





$[H_2O_2]$ = 90 g/L		
	TKN (mg/L)	**P (mg/L)**
Initial	69 ± 41	0.7 ± 0.2
25 ºC	248 ± 39	11 ± 1
40 ºC	240 ± 58	11 ± 1
60 ºC	250 ± 51	7 ± 1
80 ºC	297 ± 55	8 ± 1

It is obtained an aqueous phase with higher soluble C content (sTOC)

30% of total sTOC corresponds to acetic acid

Total soluble P and TKN concentrations increased for highest $[H_2O_2]$

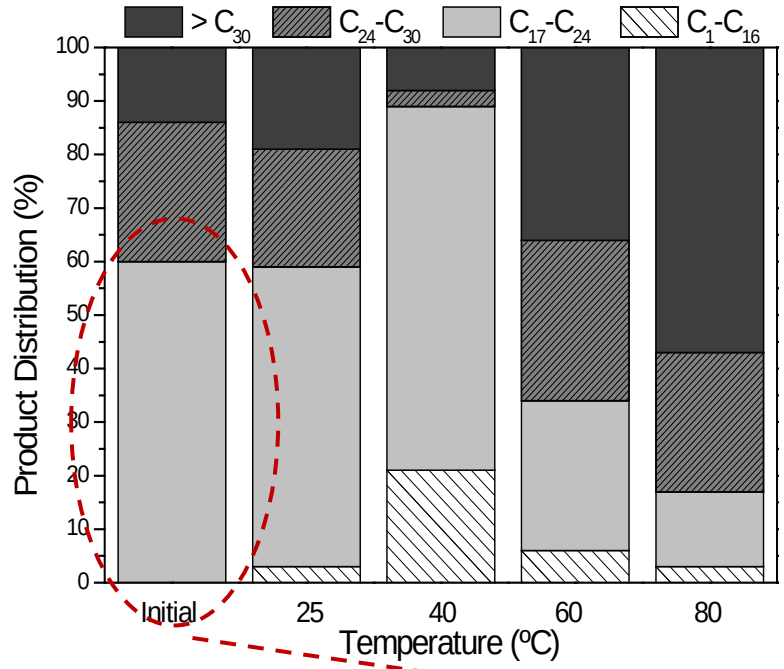
Results autocatalytic Fenton experiments

$[H_2O_2]$ = 90 g/L

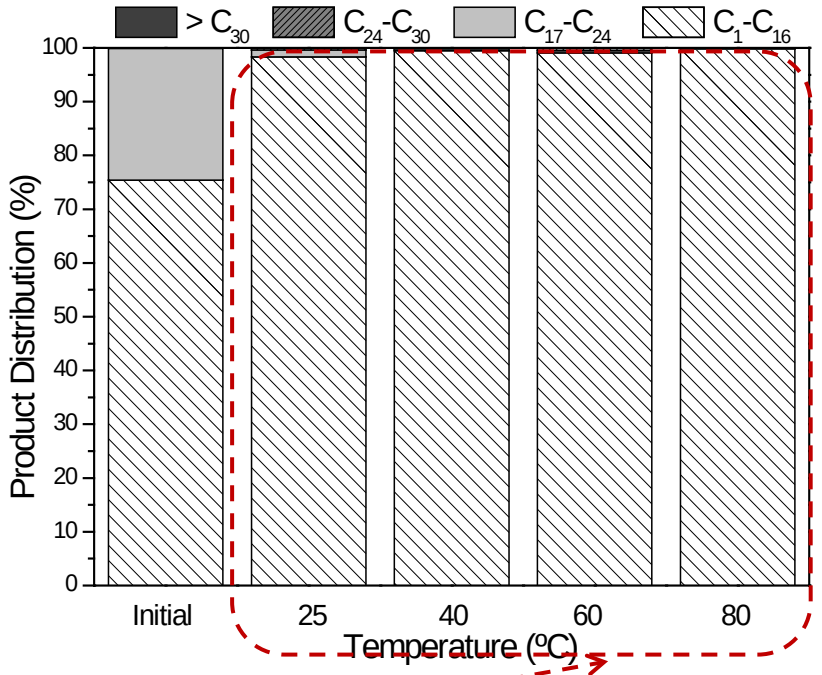
Solubilization of C content into aqueous phase correspond with degradation of PHC presents at untreated oily phase

The C content correspond also with other organic acids and short carbon chain hydrocarbons, with higher concentration at higher T and $[H_2O_2]$

— Oily phase

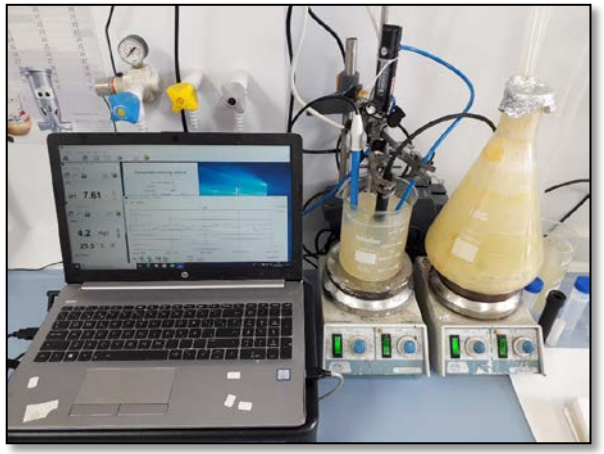


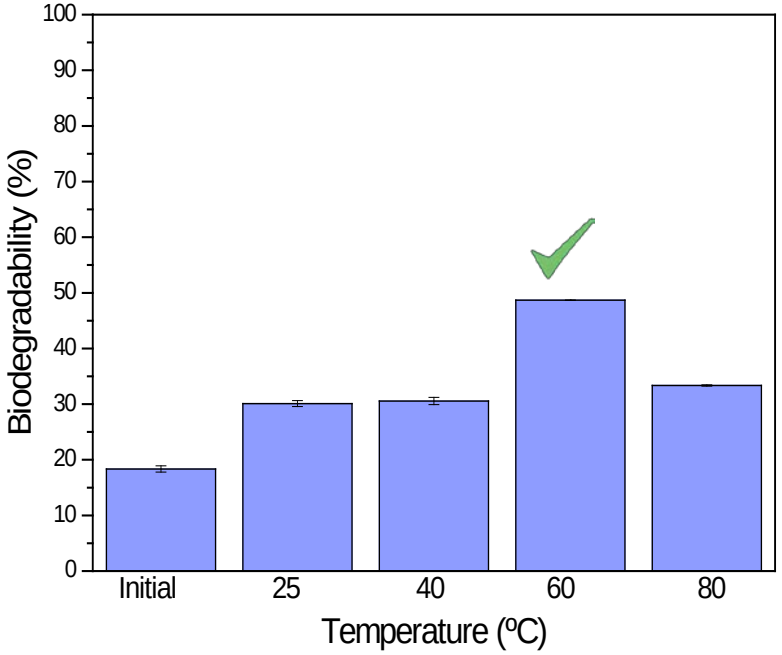
— Aqueous phase

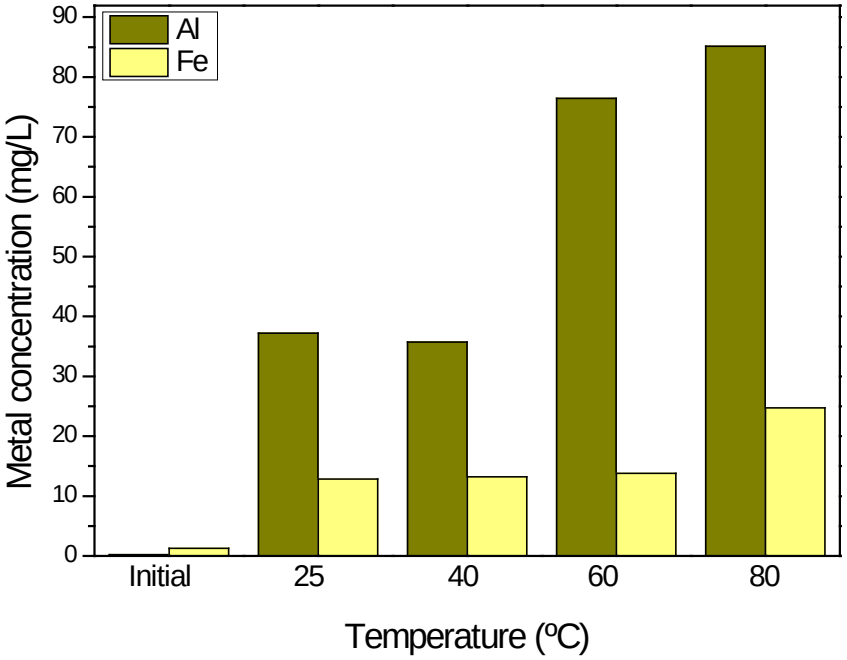


	Initial	25 ºC	40 ºC	60 ºC	80 ºC
TPHs (wt. %)	30 ± 5	11 ± 1	10 ± 1	10 ±1	11 ±1

Results of rapid biodegradability assay (Respirometry tests)







Fenton process improve the biodegradability, increasing short-chain carboxylic acids coming from the oxidative degradation of hydrocarbons

At 80 º C a decrease on the biodegradability was evidenced which could be attributed to the presence of recalcitrant components, and also to a higher concentration of Al and Fe.

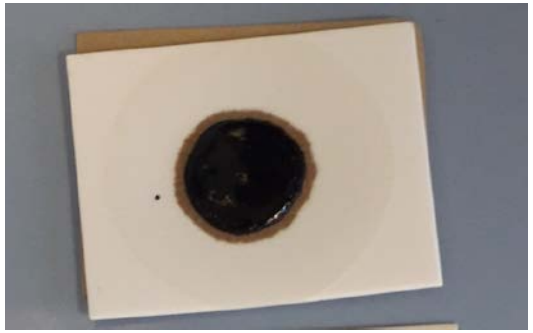
Untreated oily sludge

Treated oily sludge

Fenton pre-treatment was able to break down the stable oil-water emulsion and improve the solid-liquid separation.

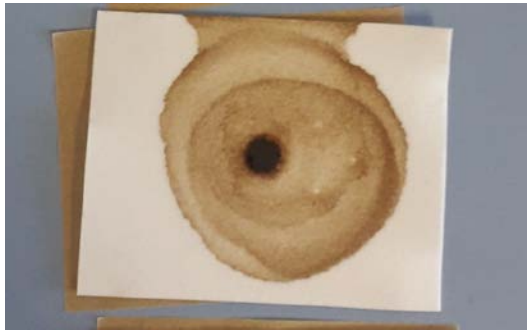
Further, CST showed a significant decrease 88% of the initial untreated sludge.

Untreated oily sludge



CST = 181s

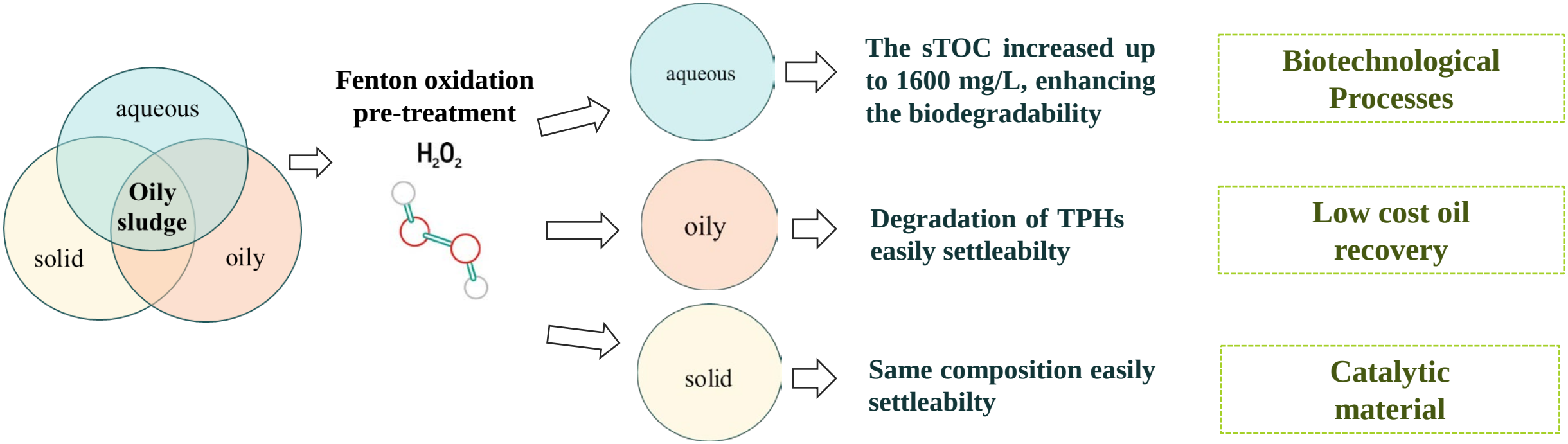
Treated oily sludge



CST = 21s

CONCLUSIONS

The present study demonstrates the technical feasibility of the Fenton oxidation for the treatment of an oily sludge, thereby providing an alternative option for sustainable management of this hazardous waste.



THANK YOU FOR YOUR ATTENTION

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