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Characterization and chemical stabilization of anaerobic digestate from municipal solid wastes

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Outline

1- Introduction

2- Methodologies

3- Results and discussion

3.1- Characterization of digestate

3.2- Chemical stabilization of digestate

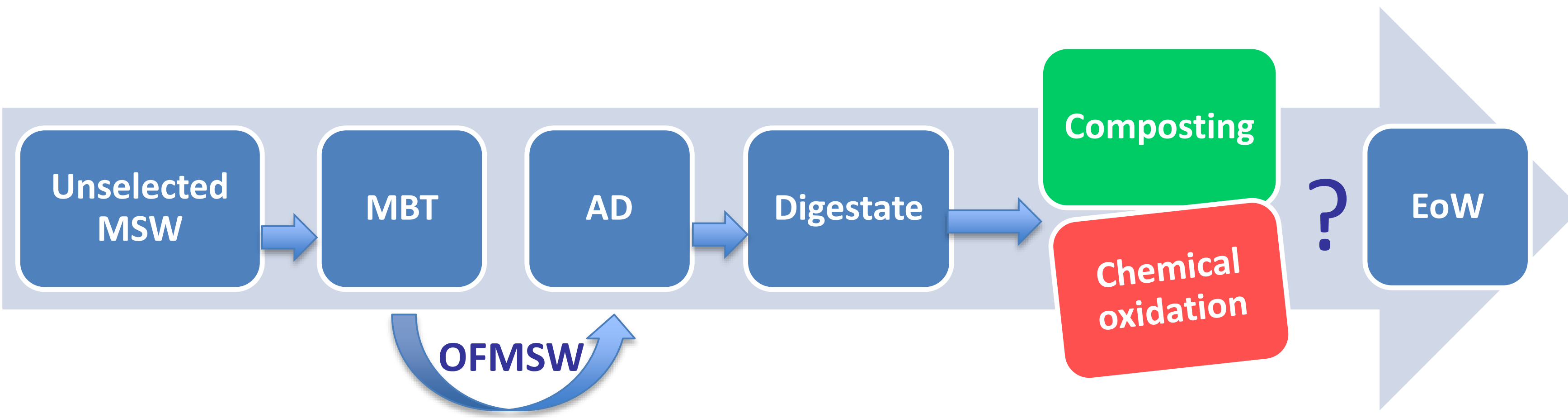
4- Conclusions

1- Introduction

- A significant fraction of unselected Municipal Solid Waste (**MSW**) is being directed to Mechanical Biological Treatment (**MTB**).

- Anaerobic digestion (**AD**) $\rightarrow$ controlled decomposition of biowaste under specific conditions (free O_2 is absent, T suitable for occurring mesophilic or thermophilic anaerobe bacteria), which convert the inputs to a CH_4-rich biogas and whole **digestate**, which can confer benefits to soils.

- Waste Framework Directive 2008/98/EC (WFD) $\rightarrow$ "**end-of-waste" (EoW**): no longer considered a waste, by ensuring that the material is not detrimental to human health or the environment.



OBJECTIVE: using the Fenton's process as a chemical approach to stabilize anaerobic digestate as an alternative to the traditional composting process.

1- Introduction

Figure 1 - MBT where Anaerobic Digestate was collected (centre region of Portugal)

1- Introduction

Composting

is the biological aerobic decomposition and stabilization of organic material under controlled conditions that allow for the development of an end product stable, free of pathogens and viable plant seeds, and can be applied to land beneficially. [Environmental Engineering, 5th ed., John Wiley& Sons, (2003)]

Substrates: OM, mo, H_2O

air — O_2

→ **Composting Process** →

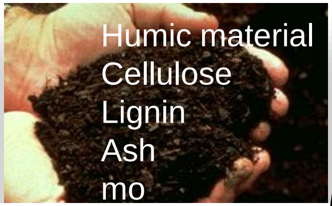
Compost: $OM_{resistant}$, mo

CO_2 (g)

H_2O (g)

NH_3 (g) +…

Heat

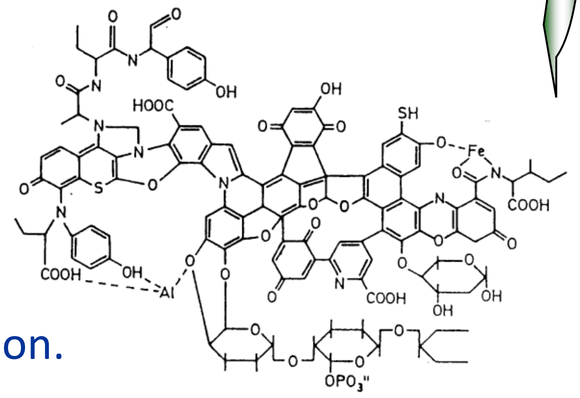


Proteins
Aminoacids
Lipids
Carbohydrates
Cellulose
Lignin
Ash
H_2O

Pathogens
Weed seeds
….

Main disadvantages:

- slow kinetic
- requiring some months of maturation.



1- Introduction

Chemical Oxidation: Fenton's Process

promotes the formation of the highly reactive hydroxyl radicals, according to Eq. (1), able to oxidize a wide range of compounds:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \qquad (1)$$

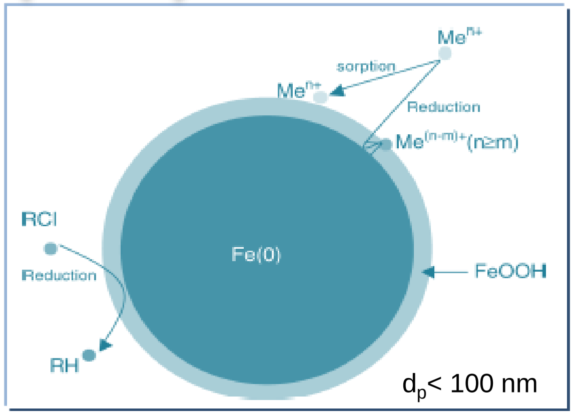
The main shortcoming: significant loads of iron containing sludge

Chemical Oxidation: Fenton-like Process (nZVI)

$$Fe^{0} + 2H^{+} \rightarrow Fe^{2+} + H_2 \qquad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \qquad (3)$$

$$2Fe^{3+} + Fe^{0} \rightarrow 3Fe^{2+} \qquad (4)$$



The main advantages: recycling of ferric iron into ferrous species at the metal sheet surface

Chemical Oxidation: Fenton-like Process (nZVI)

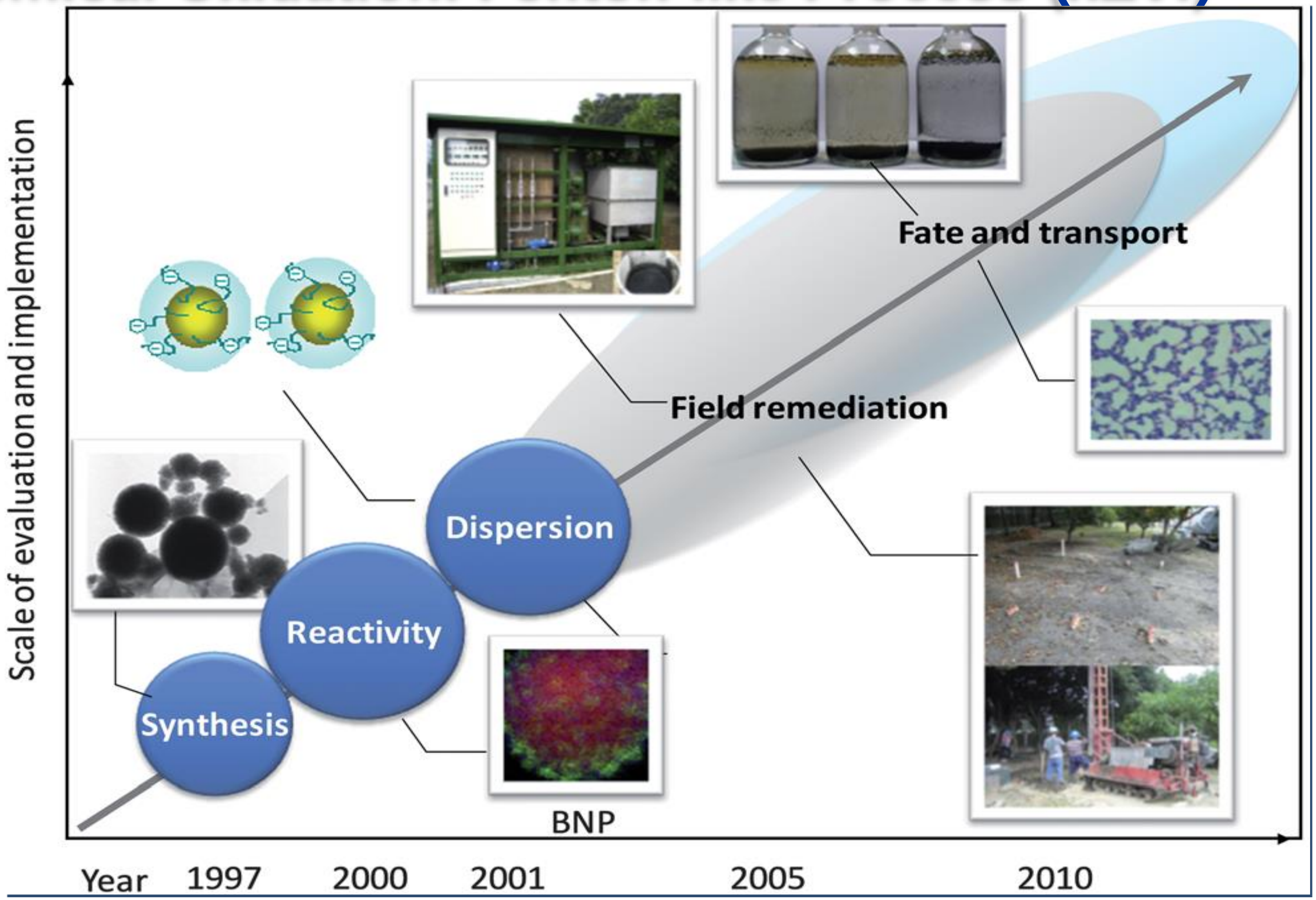


Figure - Developmental milestones of nZVI technology over the past 15 years

[Yan, W., Lien, H.-L., Koel, B.E., Zhangd, W.-X., Iron nanoparticles for environmental clean-up: recent developments and future outlook, Environ. Sci.: Processes Impacts, 15 (2013) 63-77.]

1- Introduction

General uses of nanoparticles of zero-valent iron (nZVI)

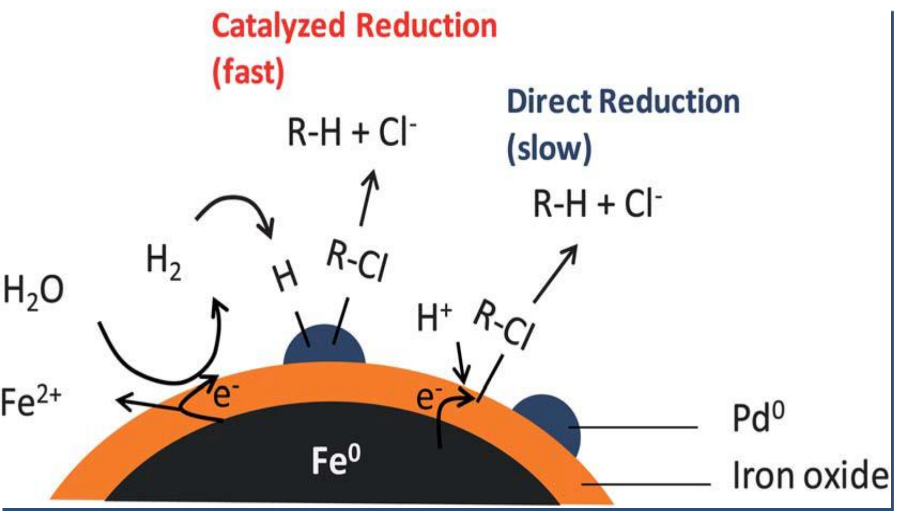


Fig. - Mechanisms of reductive dechlorination by monometallic nZVI and palladium-doped nZVI.

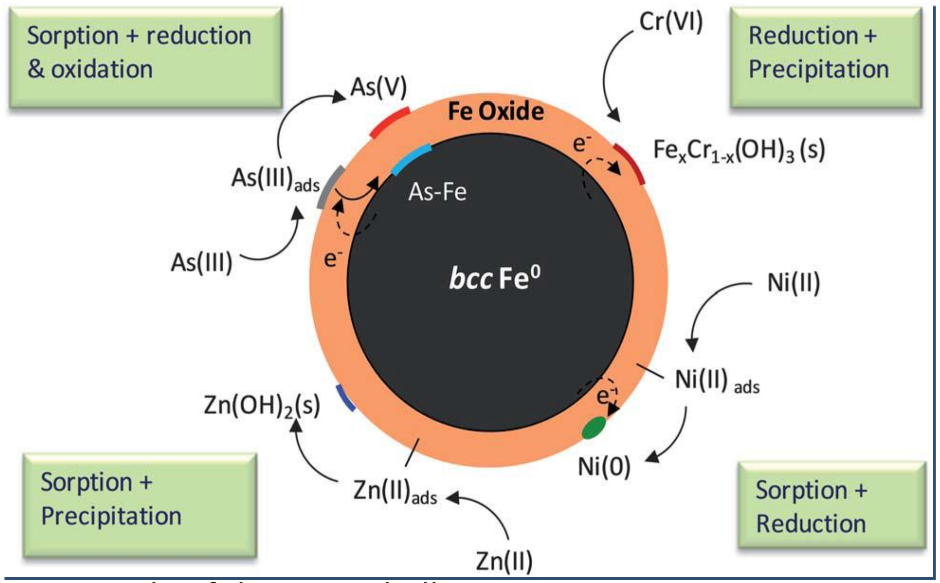


Fig. - Role of the core–shell structure in contaminant sequestration.

[Yan, W., Lien, H.-L., Koel, B.E., Zhangd, W.-X., Environ. Sci.: Processes Impacts, 15 (2013) 63-77.]

Chemical Oxidation: Fenton-like Process (nZVI)

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$$

2- Methodologies

Characterization of anaerobic digestate

- ✓ moisture (H) and total solids (TS)
- ✓ volatile solids (VS)
- ✓ total dissolved solids (TDS)

according to the Standard Methods

- ✓ chemical oxygen demand (COD)
- ✓ dissolved organic carbon (DOC)
- ✓ pH and electric conductivity (EC)

liquid-solid ratio of 10 (L/S = 10

- ✓ bulk density (BD) → test methods for examination of composting (TMECC)
- ✓ water holding capacity (WHC) → relating saturated mass with dried mass of the sample
- ✓ total Kjeldahl nitrogen (TKN) → *Velp Scientifica* equipment (digestion, distillation, titration)
- ✓ C/N ratio
- ✓ C, H, N, S

Elemental analysis

- ✓ heavy metals (Pb, Cu, Zn, …, Fe) → FAAS after acid digestion with *aqua regia*
- ✓ phytotoxicity → germination index (GI) with *Lepidium sativum* seeds
- ✓ oxygen uptake rate (OUR) → 4 days, in a respirometric installation, at 37 ºC

Characterization of nZVI (nano zero-valent iron)

- ✓ morphology
- ✓ particle size distribution

TEM

- ✓ specific surface → nitrogen gas absorption (BET), Micromeritics ASAP 2000
- ✓ …

2- Methodologies

nZVI synthesis

Two approaches :
top-down or bottom-up

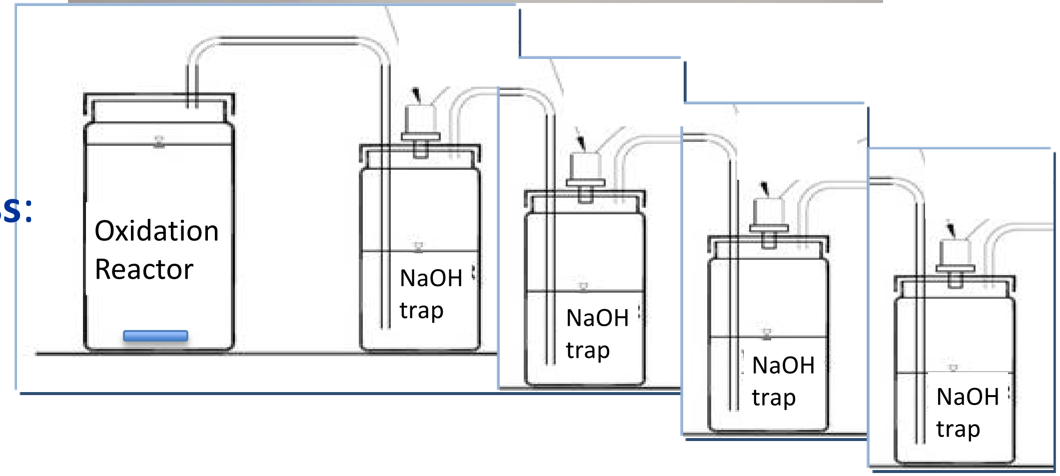
Aqueous reduction of iron salts [Wang C.-B., Zhang W.-X. Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs. Environmental Science & Technology. 31 (1997) 2154–2156]:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4\,Fe^0\downarrow + 3H_2BO_3^- + 12H^+ + 6H_2$$

- 1.6 M $NaBH_4$ added to 1.0 M $FeCl_3{\cdot}6H_2O$ at 6.8 mL/min through a peristaltic pump
- stirring at 200 rpm with a mechanical device, aqueous solution at room temperature
- caution due to the hydrogen gas production
- washing and filtration of nZVI particles
- preservation of nZVI particles in ethanol

Chemical Oxidation: Fenton's and Fenton-like Process

Experimental trials:
- batch reactor of 500 mL, under stirring;
- mass of digestate of 22 g (dry basis);
- Liquid-solid ratio (L/S) = 5;
- reaction time is about 15 min;
- CO_2 released was captured in 4 gas scrubbers placed in series;
- The scrubbers were partially filled with NaOH, and titrated with HCl.



Optimization of the Fenton's like process:
- pH adjusted to 3 (H_2SO_4 (3 M));
- concentration of H_2O_2 (33% w/v),
- concentration of nZVI

2- Methodologies

Characterization and chemical stabilization of digestate from municipal solid wastes

Chemical Oxidation: Fenton's and Fenton-like Process

How to measure efficiency?

of chemical oxidation and stability (biological)

CO_2 released

VS in the solid

TOC in the solid

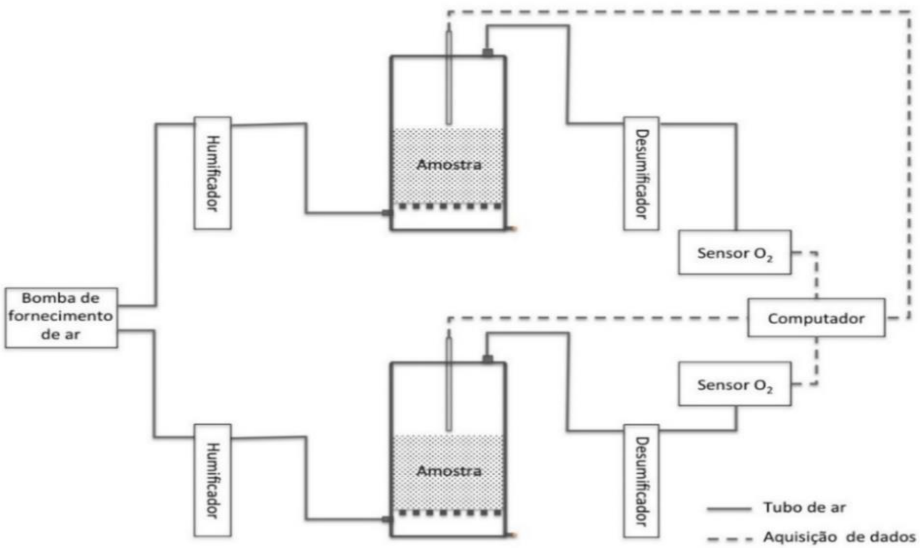
Respirometry (O_2 consumed)

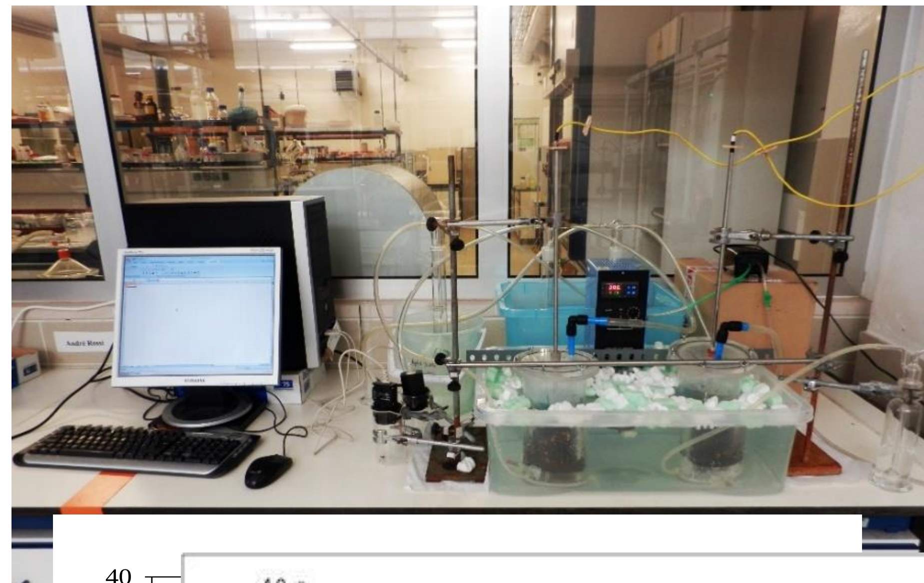
Biodegradability (based on lignin content)

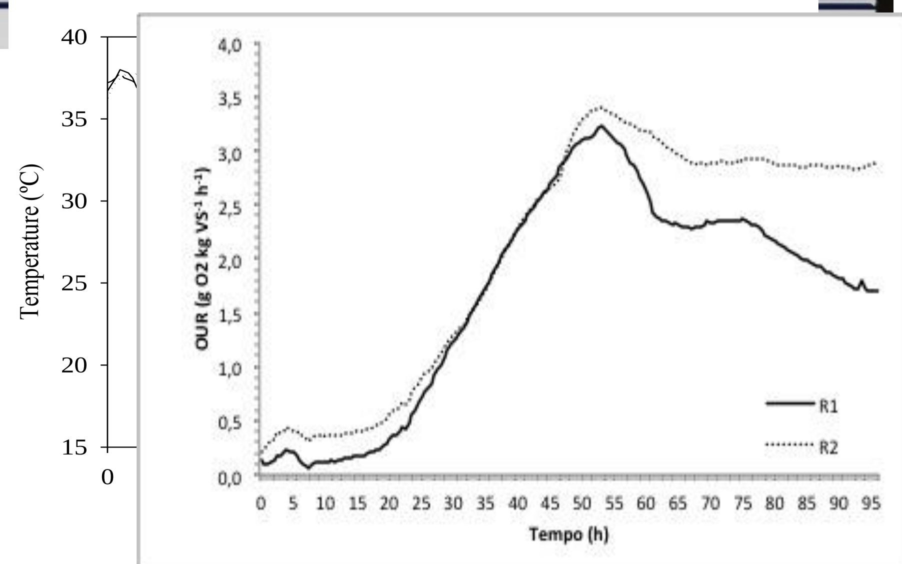
FTIR

2- Methodologies

Respiration tests:







Oxygen Uptake rate

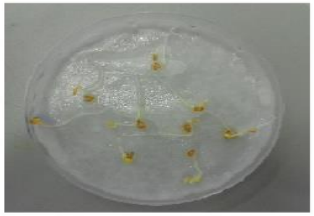
$$OUR\ (\mathrm{g}\ O_2\ \mathrm{kg}\ VS^{-1}h^{-1} = \frac{F(O_{2\ in} - O_{2\ out})}{M \times 100} \times \frac{P \times 32 \times 60}{R \times T \times ST \times VS}$$

3- Results & discussion

3.1- Characterization of digestate

Parameters	Value	Parameters	Value	Parameters	Value
H (%)	70.3±0.5	BD (kg/m^3)	1076±30	Cr (mg/kg)	26.5±1.3
TS (%)	29.8±0.5	WHC (%)	75.39±0.3	Ni (mg/kg)	22.7±3.0
VS (% ST)	57.3±0.9	TKN (% ST)	8.95±0.6	Fe (mg/kg)	7811.3±104.7
TDS (% ST)	3.2±0.1	C/N ratio	15.0	N (%)	2.0
COD (mg O_2/L)	2199±11.7	C_{org} (%)*	27.4	C (%)	29.7
DOC (mg/L)	330.1	Pb (mg/kg)	101.2±2.5	H (%)	3.8
pH	8.4±0.001	Cu (mg/kg)	109.6±1.2	S (%)	< LD
EC (mS/cm)	8.4±0.006	Zn (mg/kg)	351.9±33.3	OUR_{max} (mg O_2 g^{-1} VS h^{-1})	3.86±0.6
GI (%)	37.4	Cd (mg/kg)	3.1±2.3	OUR_{24h} (mg O_2 g^{-1} VS h^{-1})	3.48±0.7

C_{org}	%
VS/1.8	26.1
Elemental analysis	29.7
TOC in solids*	27.4



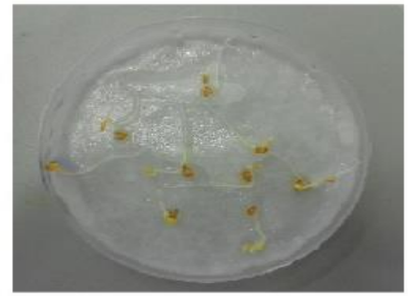

3- Results & discussion

3.1- Characterization of digestate

Germination Index with *Lepidium sativum* seeds

$$GI\ (\%) = \frac{RSG\ (\%).\,RRG\ (\%)}{100}$$

$$RSG\ (\%) = \frac{N_{SG,T}}{N_{SG,B}} \times 100 \qquad RRG\ (\%) = \frac{L_{R,T}}{L_{R,B}} \times 100$$



GI =37.4 %

Phytotoxic
(30 < GI (%) < 60)

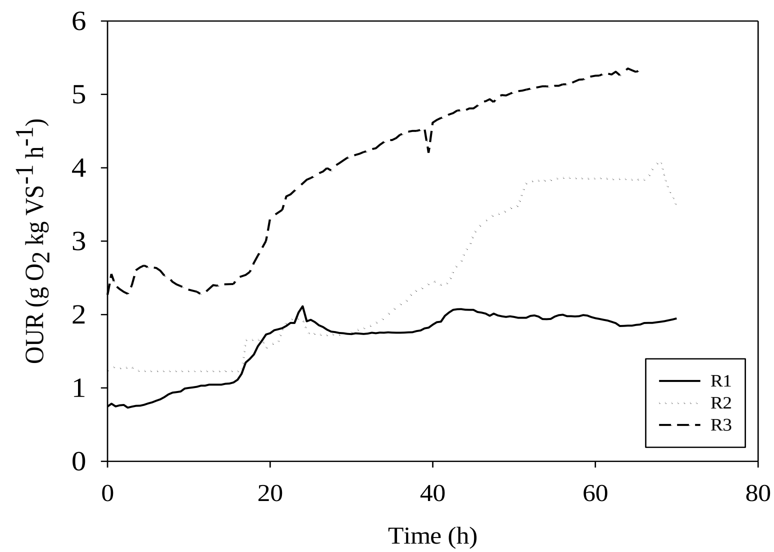
Oxygen uptake rate (OUR)

$$OUR\ (\mathrm{g}\ O_2\ \mathrm{kg}\ VS^{-1}h^{-1}) = \frac{F(O_{2\,in} - O_{2\,out})}{M \times 100} \times \frac{P \times 32 \times 60}{R \times T \times ST \times VS}$$

OUR_{max} (mg O_2 g^{-1} VS h^{-1})	3.86
OUR_{24h} (mg O_2 g^{-1} VS h^{-1})	3.48

Moderate biodegradability

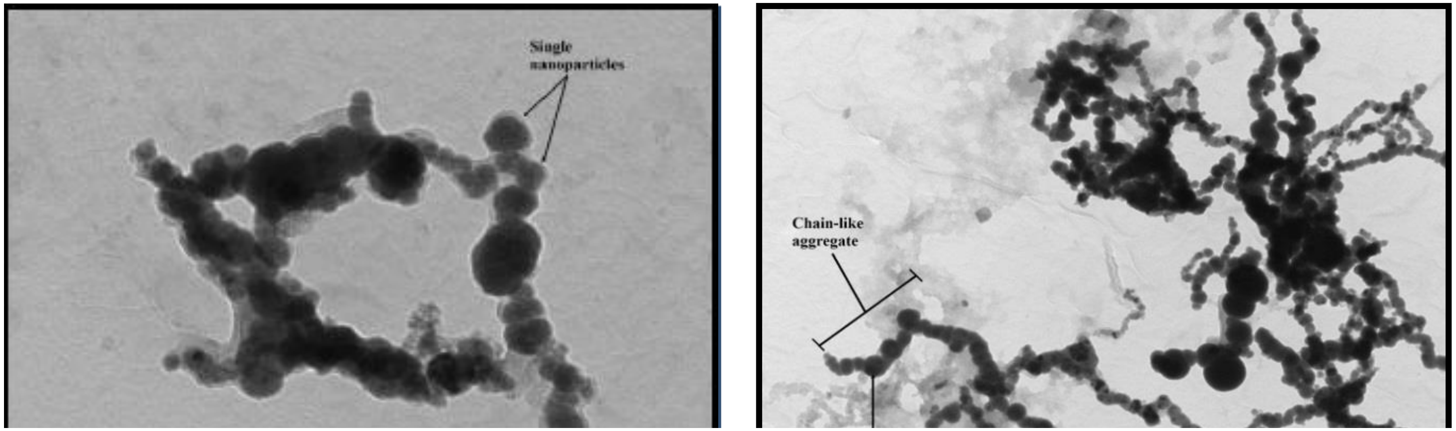
(2<OUR < 5 mg O_2 g^{-1} VS h^{-1})

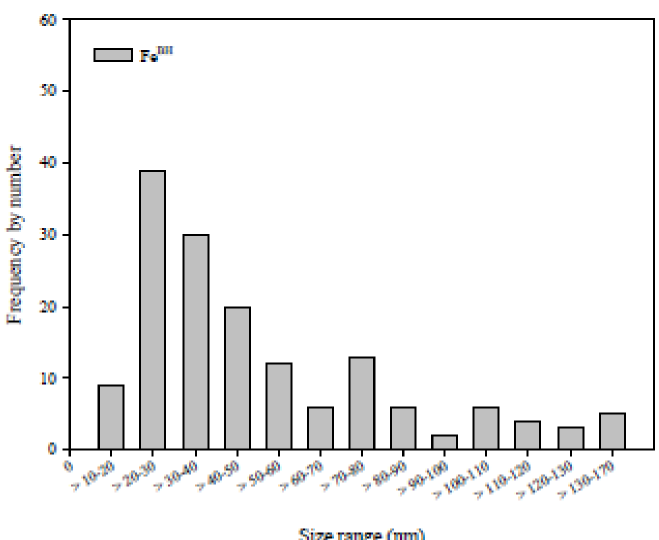


Barrena et al (2011), Compost Science & Utilization, (2011), Vol. 19, No. 2,105-113

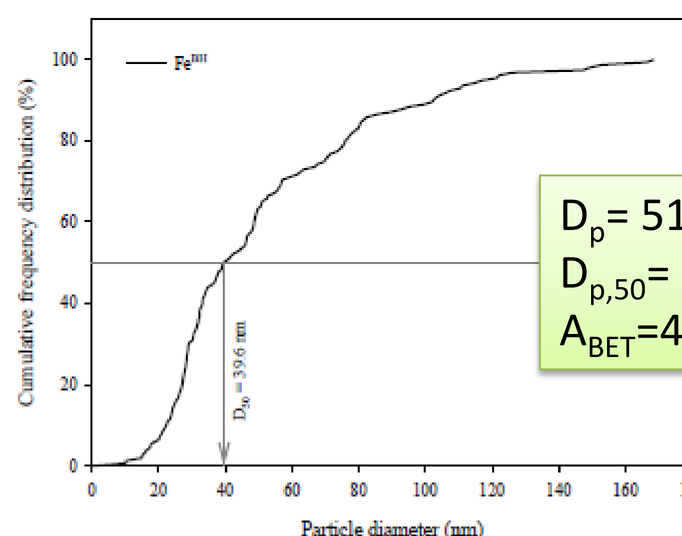
3.1- Characterization of nZVI

TEM image of Fe^{BH}





a)



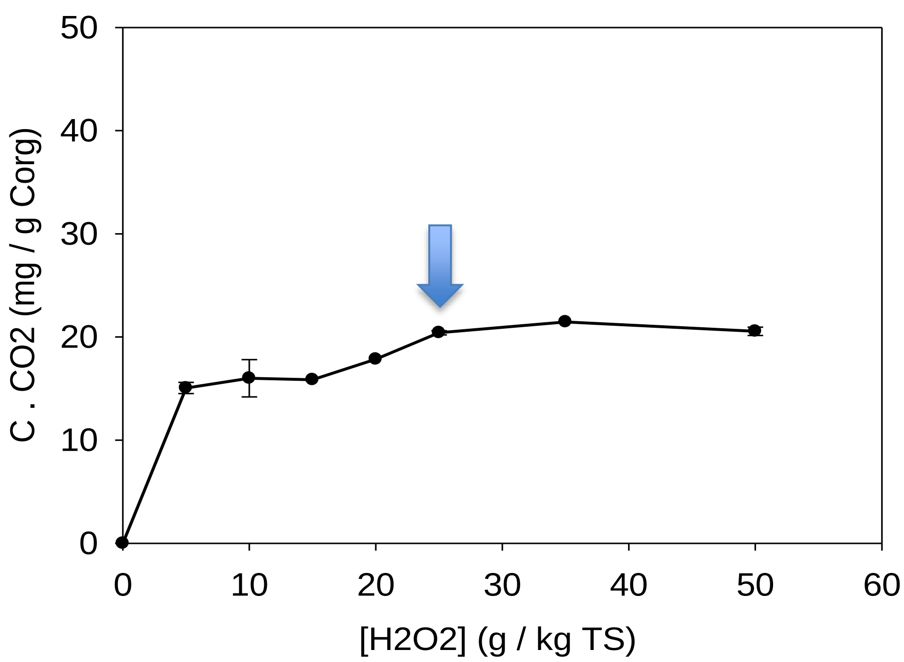
b)

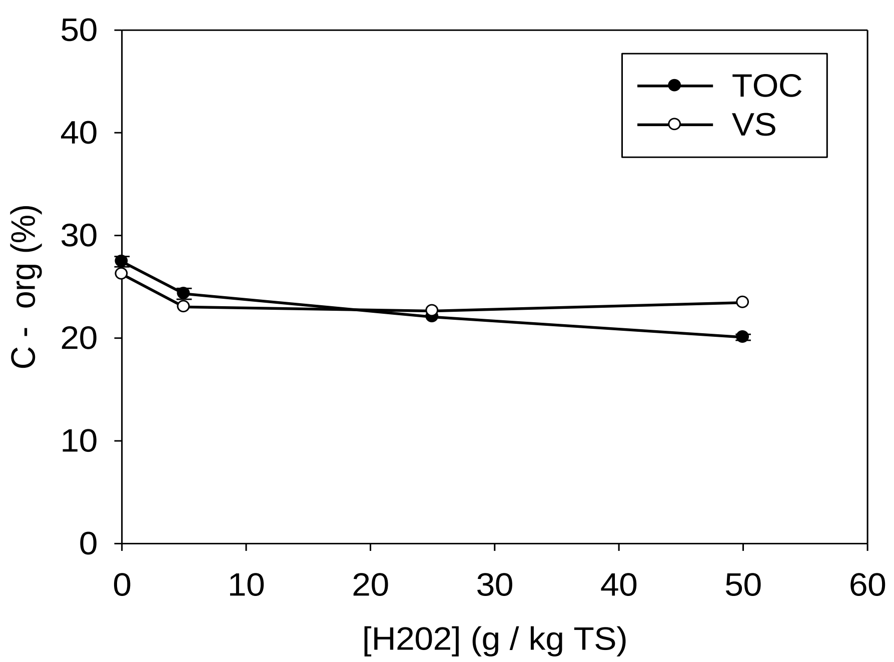
D_p= 51.9 ± 33.2 nm
$D_{p,50}$= 39.6 nm
A_{BET}=46.94 m^2/g

3.2- Chemical stabilization of digestate

Effect of hydrogen peroxide concentration in the Fenton's process

(pH_i=3; without addition of Fe; L/S=5; t=15 min)





3- Results & discussion

3.2- Chemical stabilization of digestate

Effect of hydrogen peroxide concentration in the Fenton's process

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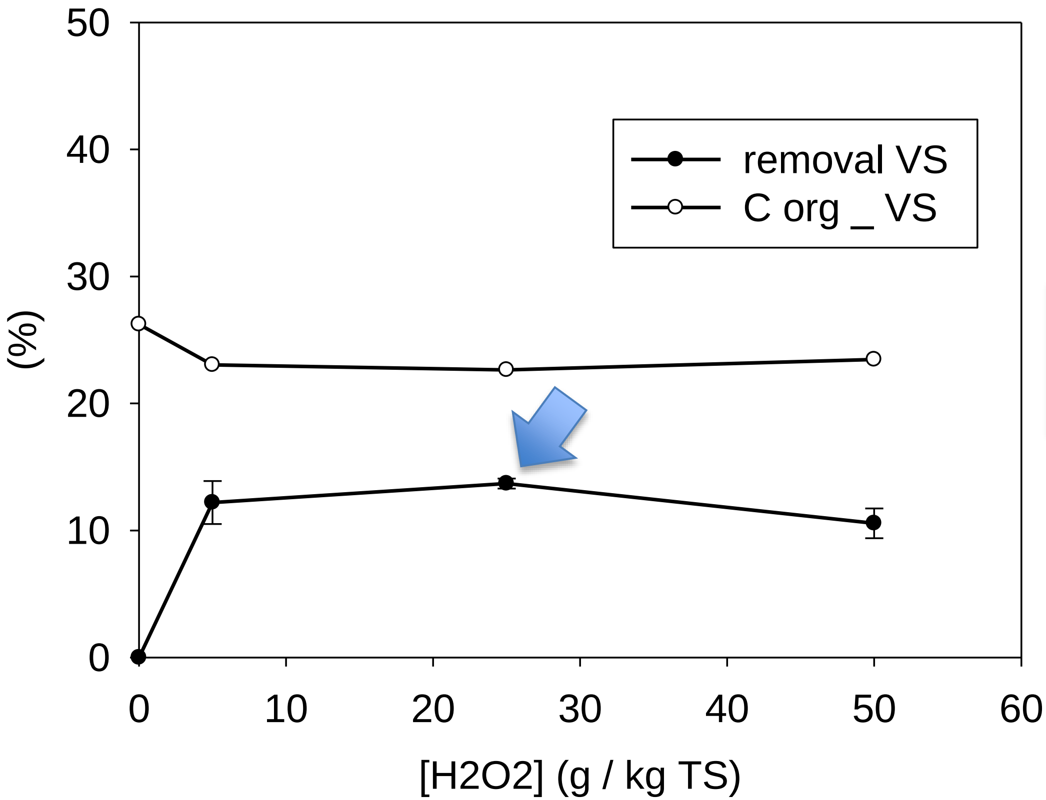


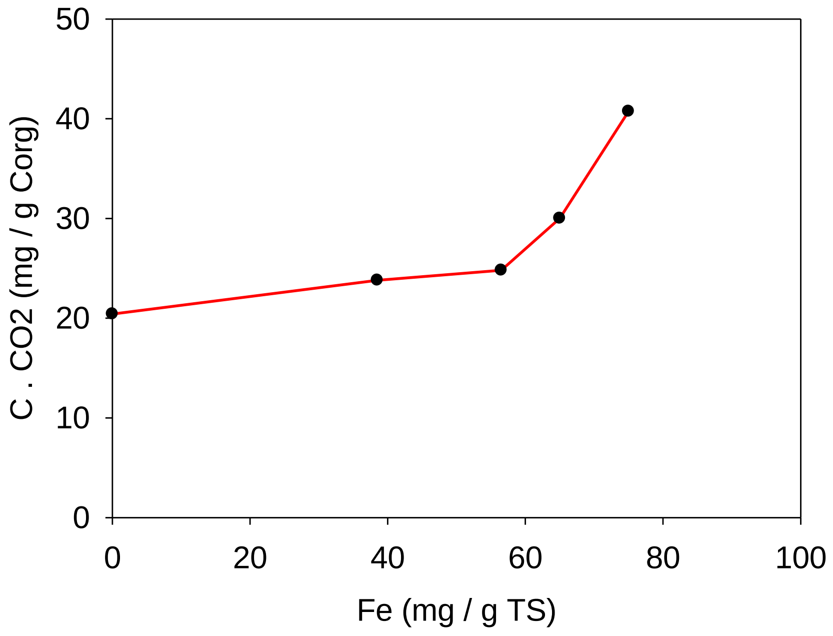
High H_2O_2 could lead to the scavenger effect

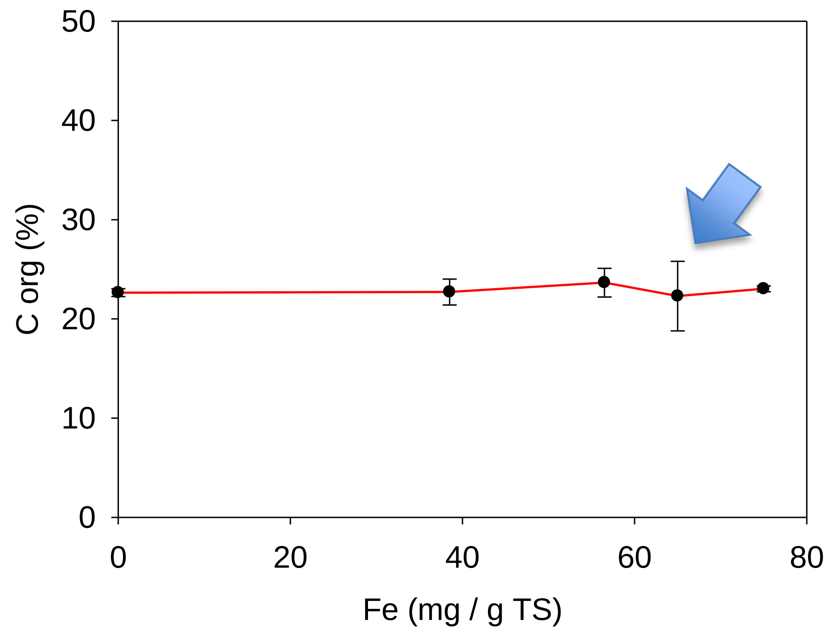
$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H^{+}$$

3- Results & discussion

3.2- Chemical stabilization of digestate

Effect of nZVI (pH_i=3; [H2O2] = 25 g/kg TS; L/S=5; t=15 min)





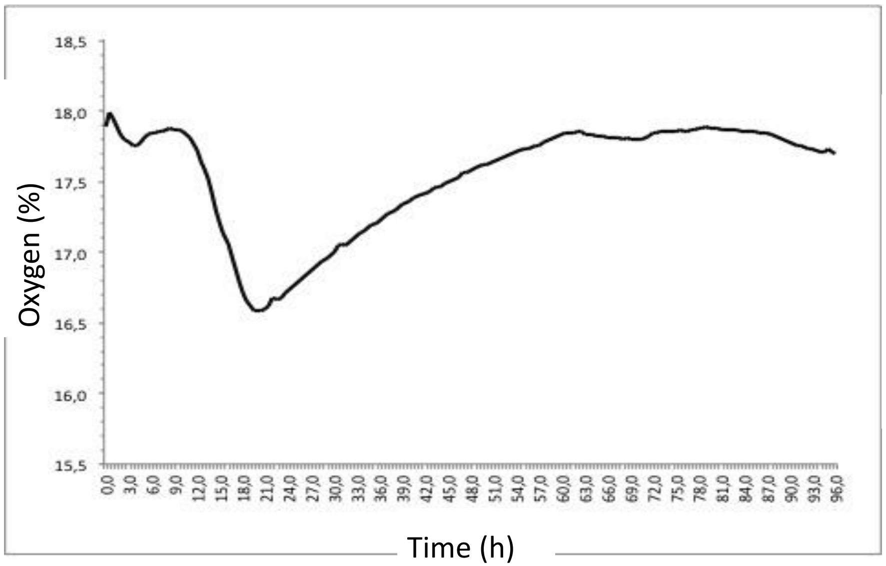
But high amount of Fe could lead to the scavenger effect

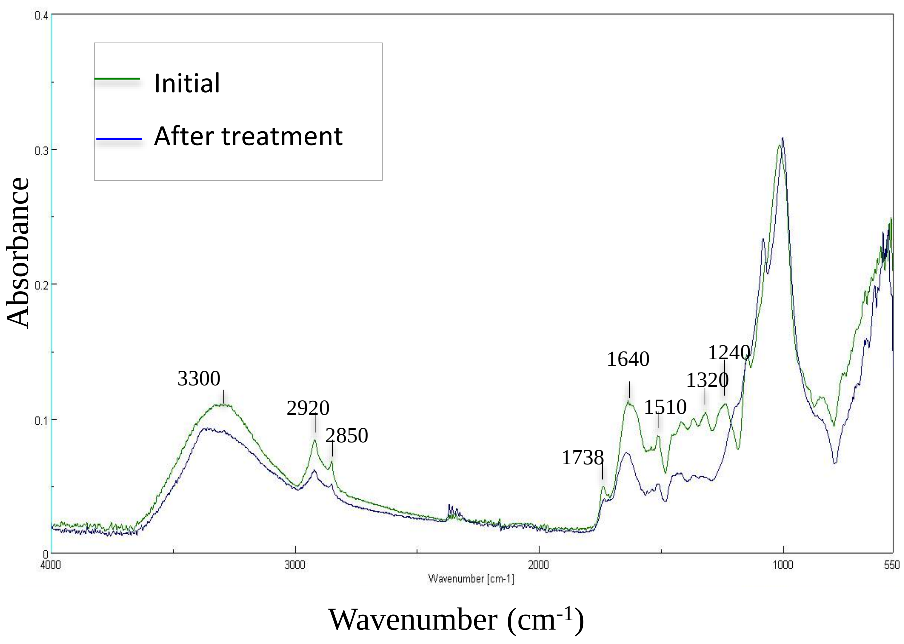
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+}$$

3.2- Chemical stabilization of digestate:

Studies in progress:

- -optimization of Fenton's Like with nZVI;
- - respirometry;
- - FTIR and biodegradability





4- Conclusions

- The digestate from the MBT plant is phytotoxic (30 < GI (%) < 60) and shows moderate biodegradability (OUR < 2 mg O_2 g^{-1} VS h^{-1}).

- Digestate has 7,8 g Fe/kg, which is positive for the Fenton's process;

- Adding nZVI could improve the Fenton's like process, but studies need deepen analysis;

- The Fenton's peroxidation revealed that at pH 3, with 25 g H_2O_2/kg of waste, the maximum of CO_2 release was attained.

- The results seem to be promising, although still requiring further studies:
  - OUR tests are still being performed at the chemical treated digestate;
  - Biodegradability (lignin content)
  - FTIR

Acknowledgments

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