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Extraction of Humic substances from residual mixed Municipal Solid Waste

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Background

Humic substances are present in all organic ecosystems, i.e. oceans, rivers, lakes and top soils due to biodegradation of dead organic matter

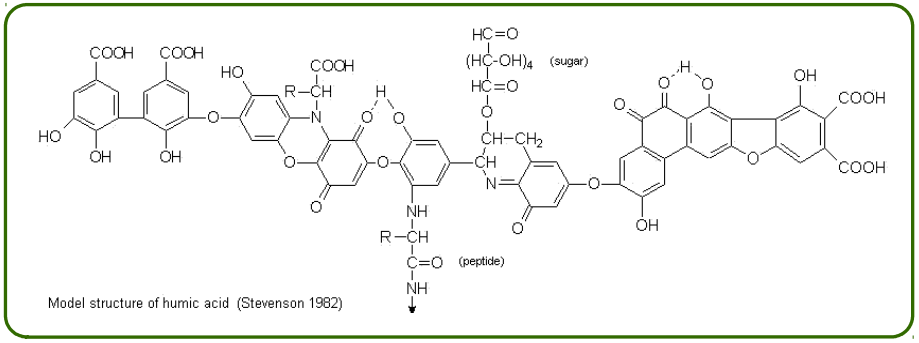
HUMIC SUBSTANCES

- *Humic Acids* : Soluble in alkaline solutions
- *Fulvic Acids* : Soluble in both acidic and alkaline solutions
- *Humin* : Insoluble in either alkaline or acidic conditions

Humic Acids (HA) are a mixture of weak aliphatic and aromatic organic acids characterized by large amounts of carboxylic and phenolic groups

These compound can act as:

- Chelating agents
- Ion-exchangers
- Surfactants



Model structure of humic acid (Stevenson 1982)

Background

Based on the ***Circular economy*** concept, several works performed so far demonstrated the possibility of using ***Humic Substances extracted from organic waste*** (as the ***compost***) for various purposes :

- formulation of detergents
- textile dyeing baths
- soil fertilizers and plant bio-stimulants for agriculture
- dispersants and binding agents for ceramics manufacture
- auxiliaries for soil/water remediation and enhanced oil recovery
- nanostructured materials for chemical and biochemical catalysis

Others waste materials, as the residual mixed wastes from Mechanical-Biological Treatment (***MBT waste***), could be adopted for the extraction of these substances

Background

Aim

- Evaluation of the viability of extracting humic substances from **MBT wastes**
- Assessment of the operating parameters that allow to enhance the performance of the process

Experimental activities

- Material: Residual mixed wastes from Mechanical-Biological Treatment collected in a plant near Rome
- Extraction of humic substances from MBT wastes by **changing the operating parameters**
    - Waste particle dimension
    - S/L ratio
    - Extract concentration
    - Extraction time
- Extraction of humic substances from MBT wastes that underwent a further **maturation phase**

Methods: Humic substances Extraction

Mechanical-Biological Treated Waste
(solid)

↓

ALKALINE EXTRACTION
(NaOH, 65°C)

↓

CENTRIFUGATION

HU

Humin
(solid residue)

Soluble Bio-Organic substances
(liquid extracted)

SBO

↓

Acidification
(pH < 2)

FA

Fulvic Acid
(soluble at any pH)

Humic Acid
(insoluble at pH <2)

HA

Methods: Humic substances Extraction

Operating Conditions

Test **T1:** Standard procedure commonly used for extracting organic matter from soil:

- 500 ml of NaOH (0.1 M)
- 50g of MBT Waste
- T = 65°
- Time = 4h

Effect of the variation of the operating conditions (tests **T2**, **T3**, **T4** and **T5**)

Standard S/L Ratio Conctact Time

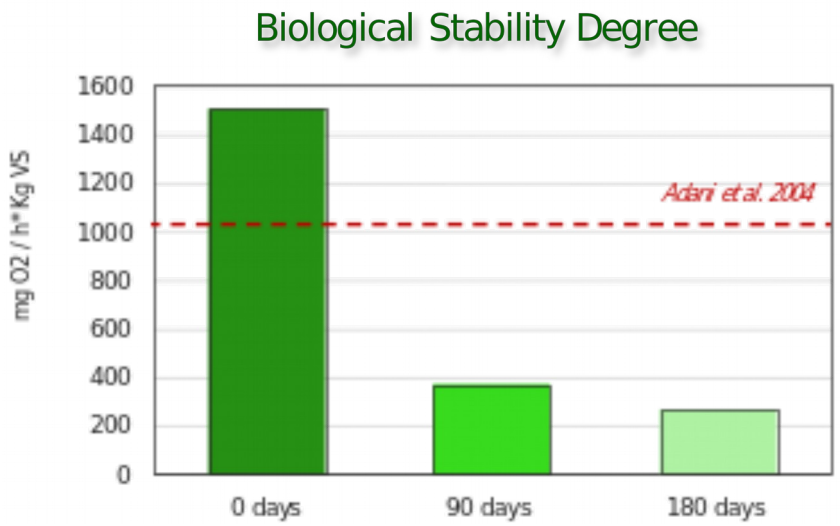
Grinding NaOH

	T1	T2	T3	T4	T5
Pre-Treatment	No	Yes	No	No	No
S/L Ratio [mg/l]	1:10	1:10	1:5	1:10	1:10
NaOH Molarity [M]	0.1	0.1	0.1	0.25	0.1
Extraction time [h]	4	4	4	4	24

Material

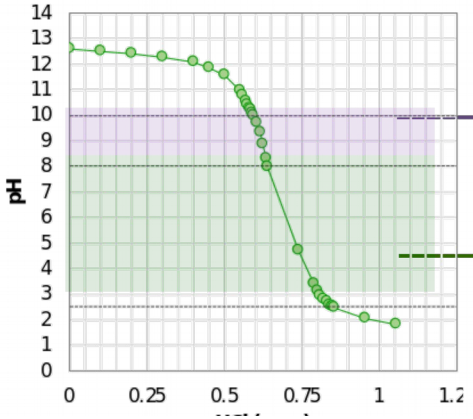
All the extraction (**T1**, **T2**, **T3**, **T4** and **T5**) were performed using 3 MBT samples:

- After treatment (no maturation)
- 90 days of maturation
- 180 days of maturation



Analysis

- *Amounts of extracted HA*
- *Functional groups quantification* by HCl titration (HA)



Phenolic range (10<pH<8) → Only 50% of the phenolic group dissociated from pH 10 to pH 8

Carboxylic range (8<pH<2.5) → All the Carboxylic group dissociated from pH 8 to pH 2.5

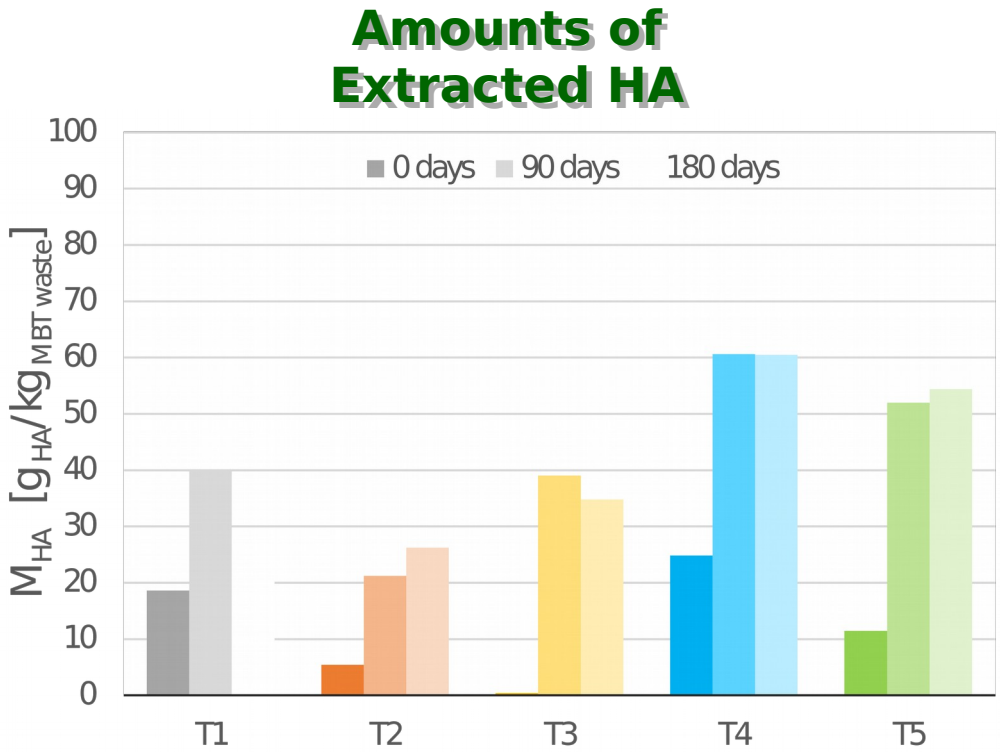
- *Optical Properties* by Spectrophotometric analyses

Most interesting wavelength:
- λ=280nm
- λ=465nm
- λ=665nm

→
- Aromaticity, Molecular Weight
- E_4/E_6
- Δ logK

- *Humic substances polymerization* by Elemental analyses (MBT waste, HA and FA)
  - Total Organic Carbon (TOC)
  - CHNS-O analysis

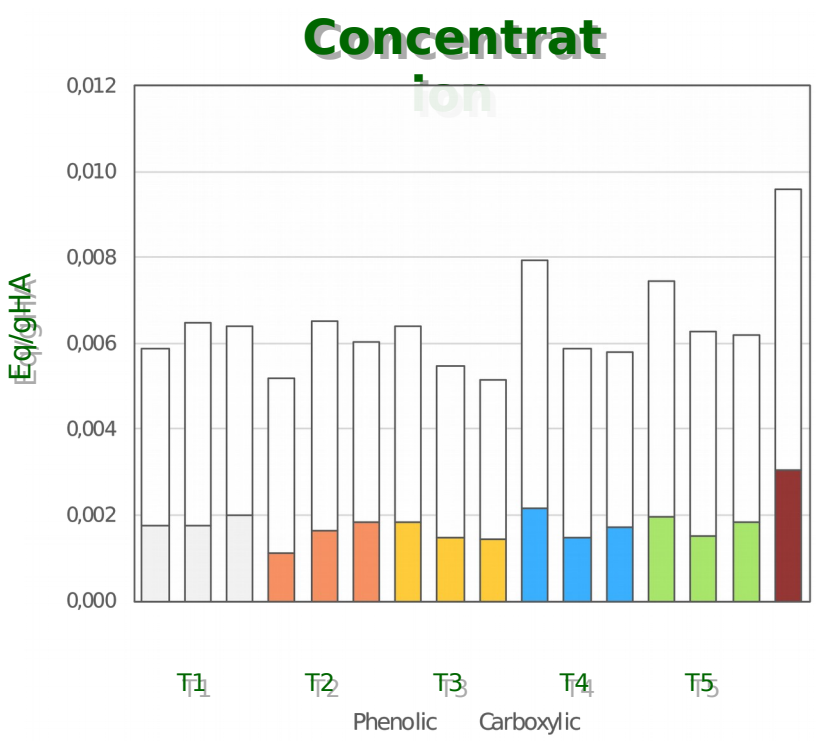
Results: Amounts of Extracted Humic Acids

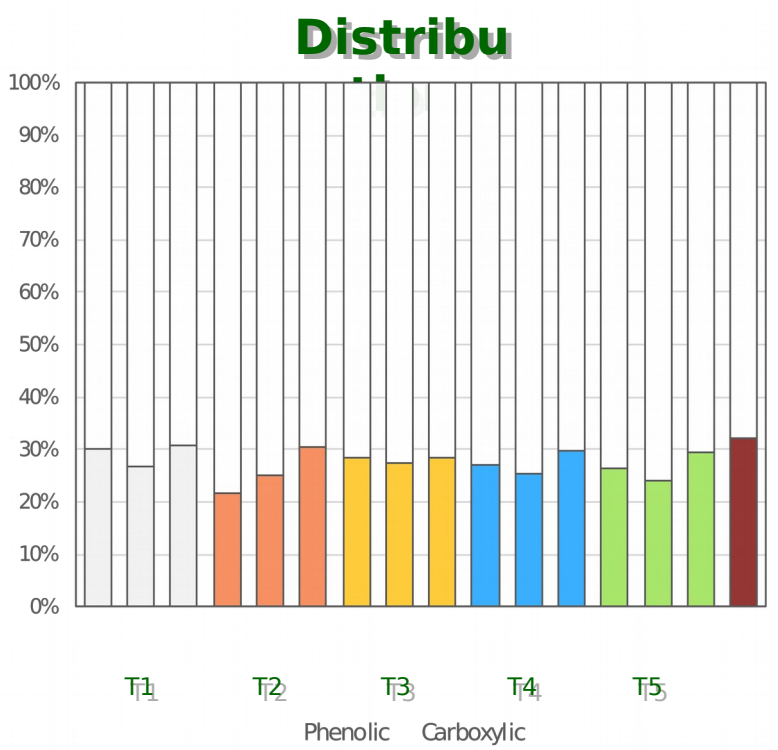


- 0.4 – 25 g/kg of HA extracted from the MBT waste before the maturation phase
- 21 – 60 g/kg of HA extracted from the MBT waste that underwent at least 90 days of further maturation
- In tests T4 and T5 higher amount of HA were extracted

T1	T2	T3	T4	T5
Reference	Ground	S/L Ratio	NaOH molarity	Time

Results: Functional groups quantification

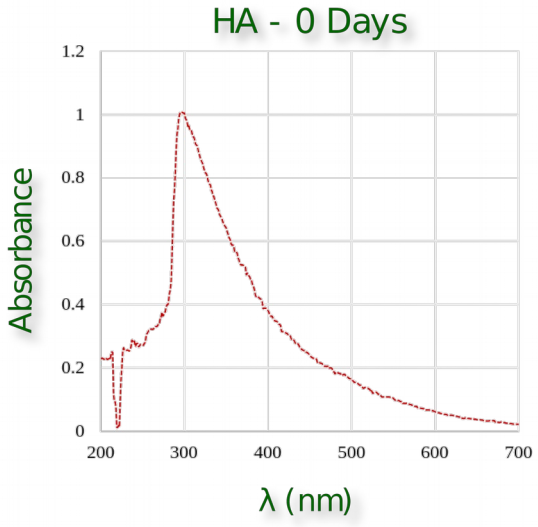


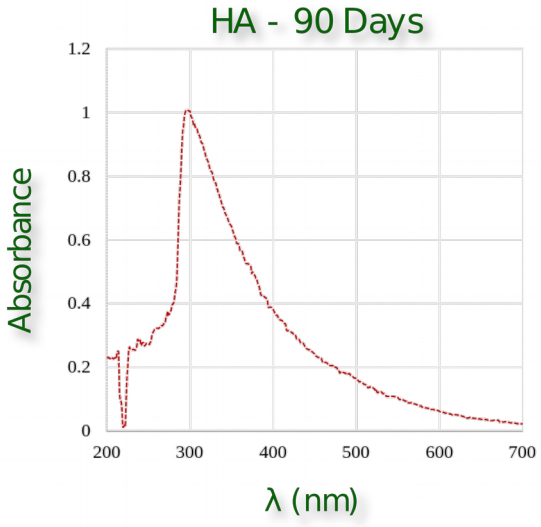


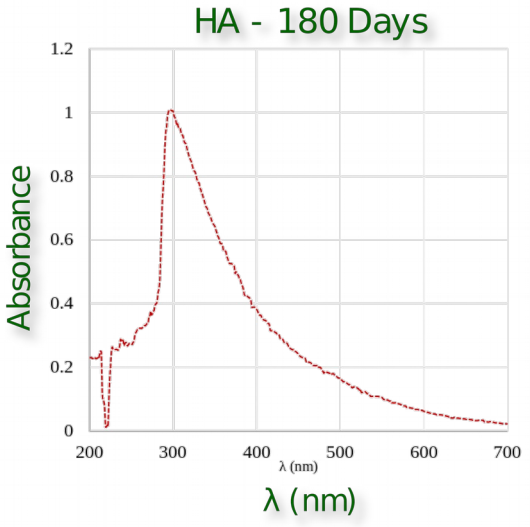
- The amounts of functional groups generally decreased with the maturation
- The distribution of the functional groups in the extracted HA proved to be similar to the one of commercial HA (30% Phenolic and 70% Carboxylic groups)
- Functional groups resulted slightly less then the one extracted from commercial HA (*red column*)
- Slightly higher amounts of functional groups for tests T4 e T5

T1	T2	T3	T4	T5
Reference	Ground	S/L Ratio	NaOH molarity	Time

Results: Spectrophotometric analyses







- Peak of absorbance near λ=280nm
- Lower absorbance than the *commercial HA*
- Higher absorbances for increasing maturation times

T1	T2	T3	T4	T5
Reference	Ground	S/L Ratio	NaOH molarity	Time

Results: Aromatic content

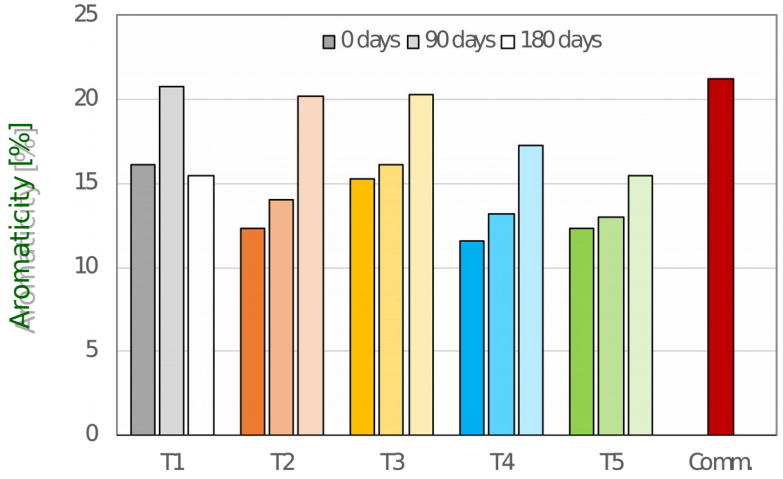
Correlation was observed between the molar absorptivity at 280 nm of the Humic Substances (*Chin et al. '94, Peuravuori et al. '97*) and their aromaticity/molecular weight

A = Absorption [adim]
C = Organic Carbon [mol_{Corg}/l]
b = Optical path [cm]
ε = Absorptivity [l/mol_{Corg} *cm]

$$\varepsilon = A / (C \cdot b)$$

Aromaticity [%]:
0.050*ε + 6.740 *(Chin et al. '94)*

Molecular Weight [g/mol]:
3.990*ε + 490 *(Chin et al. '94)*



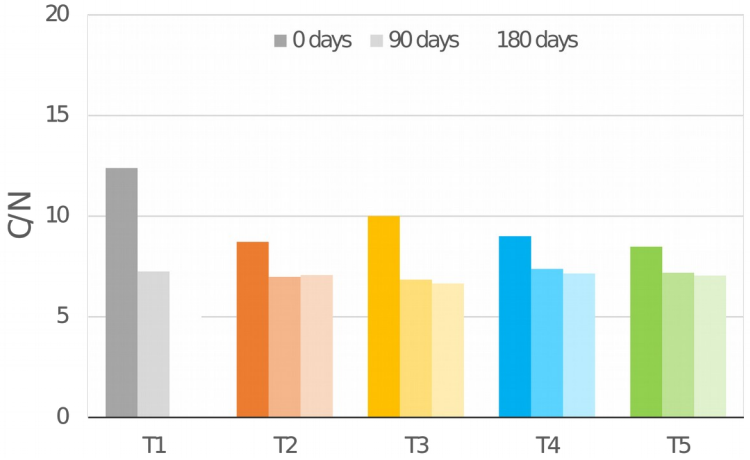
- Aromaticity increased with the maturation
- After 180 days of maturation the aromatic content resulted comparable with *commercial HA*
- *Molecular Weight* from 900÷1200 [g/mol] to 1200÷1600 [g/mol] after maturation

T1	T2	T3	T4	T5
Reference	Ground	S/L Ratio	NaOH molarity	Time

Results: Elemental Analysis of Humic Acids

		C [%]	H [%]	N [%]	O [%]
T1	0	43.80	6.11	4.12	6.13
T1	90	36.44	4.38	5.87	8.54
T1	180	38.18	4.54	6.25	8.40
T2	0	48.02	5.95	6.42	8.78
T2	90	41.17	4.91	6.88	9.39
T2	180	41.31	5.05	6.82	8.82
T3	0	44.18	5.67	5.15	6.84
T3	90	32.93	4.08	5.62	8.28
T3	180	38.19	4.77	6.70	9.04
T4	0	47.89	5.99	6.21	7.50
T4	90	38.66	4.67	6.11	8.11
T4	180	38.15	4.63	6.23	8.29
T5	0	45.40	5.62	6.25	8.71
T5	90	39.46	4.77	6.41	9.48
T5	180	39.53	4.72	6.55	8.70

C/N atomic ratio
(biological stability)



C/N atomic ratio decreased for increasing maturation times

Based on the elemental composition of the extracted Humic Acids, the following parameters were estimated:

H/C atomic ratio

$$\frac{\text{H [atomic \%]}}{\text{C [atomic \%]}}$$

(Niemiałkowska-butrym et al., 2012)

Humification Index

$$HI\ (\%) = \frac{C_{HA}}{C_{organic}} \cdot 100$$

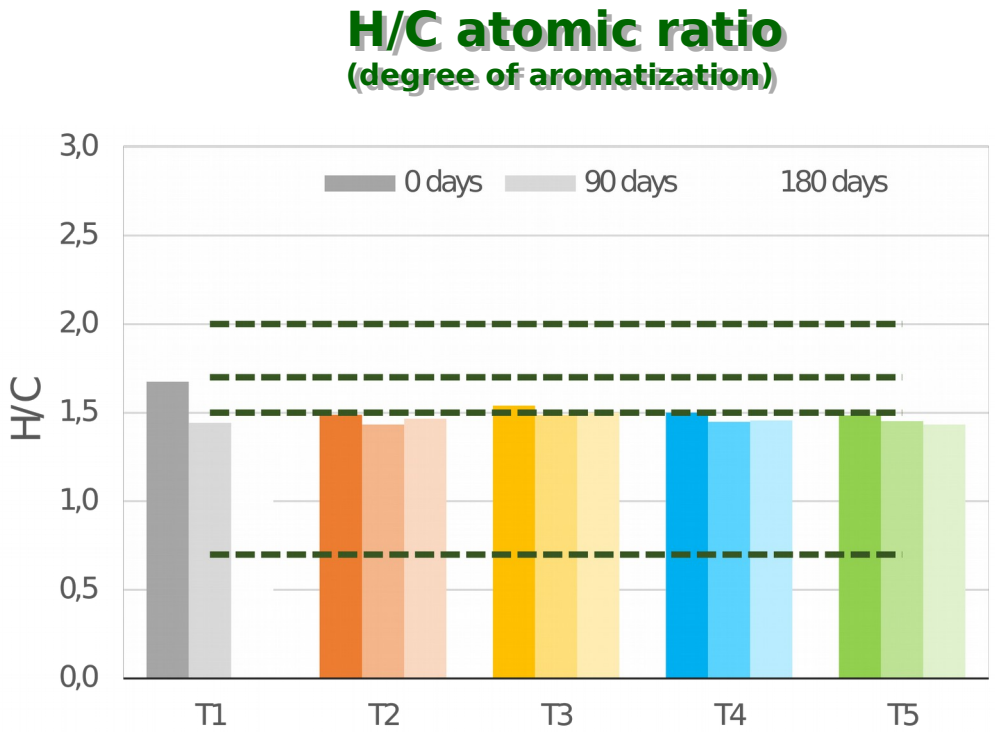
Polimerization Rate

$$\frac{C_{HA}}{C_{FA}}$$

(Bustamante et al., 2012)

T1	T2	T3	T4	T5
Reference	Ground	S/L Ratio	NaOH molarity	Time

Results: Elemental Analysis of Humic Acids



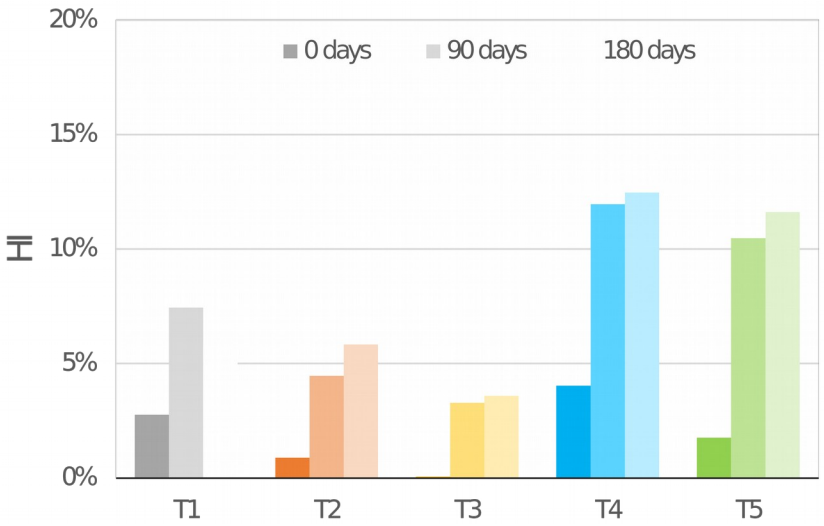
H/C atomic ratio is inversely proportional to the aromaticity of compounds:

- **H/C of 1.5 to 1.7** correspond to alicyclic hydrocarbons
- **H/C of 0.7-1.5** correspond to aromatic systems related with aliphatic chains composed of up to 10 carbon atoms

T1	T2	T3	T4	T5
Reference	Ground	S/L Ratio	NaOH molarity	Time

Results: Elemental Analysis of Humic Acids

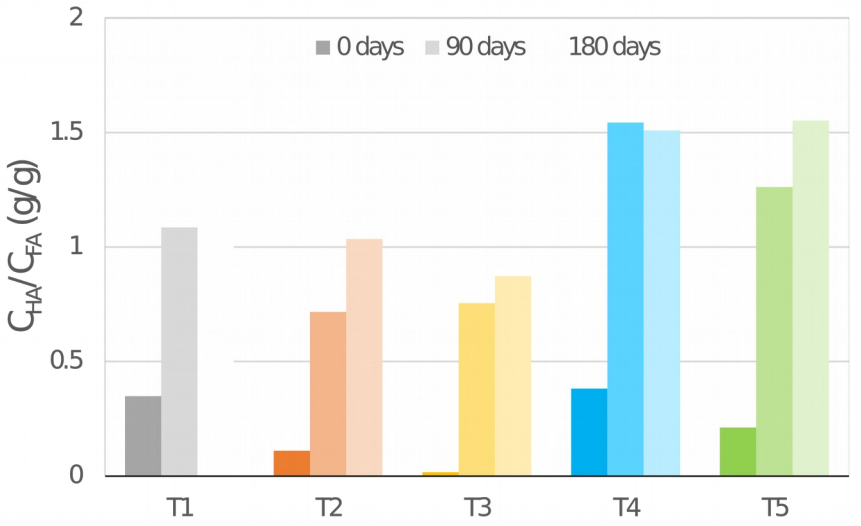
Humification Index



$$HI\,(\%) = \frac{C_{HA}}{C_{organic}} \cdot 100$$

- HI increased for increasing maturation times
- Higher HI values for tests T4 e T5

Polimerization Rate



$$\frac{C_{HA}}{C_{FA}}$$

- **Polymerization rate** grew with the maturation (humic structure more branched)
- Higher Polymerization rate for tests T4 e T5

T1	T2	T3	T4	T5
Reference	Ground	S/L Ratio	NaOH molarity	Time

Conclusions

- The viability of extracting Humic substances from MBT Waste was assessed evaluating the effects of the applied operating conditions and of the material maturation

- An increase in the concentration of NaOH and in the extraction time proved to be beneficial for :
  - Growing the amounts of both extracted Humic Acids and Fulvic Acids
  - Slightly increasing the amounts of functional groups
  - Enhancing the Humification Index and Polymerization Rate of the humic acids

- The application of a further maturation phase (at least 90 days) to the MBT waste proved to enhance the chemical properties and the amount of extracted humic substances

- In view of the reuse of the extracted substances their environmental behaviour needs to be investigated

Thanks for your attention!

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