Characterization and chemical stabilization of digestate from municipal solid wastes

D.V. Lopes[1], L.G. Cruz[1], R.C. Martins[1], L.M. Gando-Ferreira[1], C.M. Dias-Ferreira[2], M.J. Quina[1] and R.M. Quinta-Ferreira[1]

[1]CIEPQPF- Centro de Investigação em Engenharia dos Processos Químicos e Produtos da Floresta, GERST – Group on Environment, Reaction, Separation and Thermodynamics, Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima, 3030-790 Coimbra, Portugal
[2]CERNAS – Research Centre for Natural Resources, Environment and Society, Campus da Escola Superior Agrária de Coimbra, Bencanta, 3040-316 Coimbra, Portugal
Presenting author email: guida@eq.uc.pt

Landfills are no longer a viable option for organic wastes disposal due to the high production of leachates associated alongside with odors and gases formation. Composting arose as a green alternative for avoiding this problem, and it may lead to the production of a stable final product which can be used as a soil conditioner. However, besides the fact that the compost needs several months of maturation before its use, some organic wastes may contain bio-refractory and toxic compounds that will jeopardize microorganisms action. In the other hand, others may not have a proper degree of stability.

Fenton's process is one of the most used advanced oxidation processes (AOPs) in the last decades to treat industrial wastewaters due to its simplicity and low cost maintenance, because it works at ambient temperature and pressure. This oxidation is based on adding a strong oxidant, hydrogen peroxide, H_2O_2, which in an acidic medium with an iron catalyst (Fe^{2+}), promotes the production of hydroxyl radicals, HO•, leading to the mineralization of organic matter, i.e., the production of CO_2 and H_2O (Neyens and Baeyens, 2003). In the last years, few studies were found in literature for Fenton's peroxidation in a solid matrix. Neyens *et al.* (2003) performed a pilot-scale Fenton treatment with sewage sludge, Buyukkamaci (2004) studied the dewatering capacity of biological sludge when treated with the Fenton's oxidation and Hu *et al.* (2010) analyzed semi-solid Fenton process in a swine farming sludge. However, in these works it was not quantified the organic matter after the chemical treatment nor the degree of stabilization of the compost. Moreover, iron nanoparticles have been extensively studied for water depuration, as well as soil contamination with organic and inorganic pollutants.

In this context, the aim of the present research and its main innovative approach consists in using the Fenton's process as a chemical approach to stabilize organic wastes as an alternative to the traditional composting process. For this purpose, a sample of digestate resultant from the anaerobic digestion of the organic fraction of municipal solid wastes (OFMSW) was taken from a mechanical-biological treatment (MBT) plant in the center of Portugal. In the MBT station, the digestate produced undergoes composting but the compost produced has some difficulties in its application also due to the lack on legislation. Nevertheless, one of the possibilities may be to use the compost as a soil amendment. With this investigation, it is expected to determine if the composting process performed at the MBT plant can be replaced or if the Fenton's process could be integrated with composting. In a second phase of the research, iron nanoparticles previously synthesized with $NaBH_4$ according to the methodology used by Wang and Zhang (1997) were considered as an iron catalyst for the Fenton's process. Thus, the efficiency of both processes (with and without iron catalyst) may be compared.

The digestate sample was extensively characterized in terms of moisture (M), total solids (TS), volatile solids (VS), total dissolved solids (TDS) and chemical oxygen demand (COD) according to Standard Methods (Greenberg *et al.*, 2005). Dissolved organic carbon (DOC), pH and electric conductivity (EC) were estimated in a liquid-solid ratio of 10 (L/S = 10). The phytotoxicity of the sample was determined by the germination index (GI) with *Lepidium sativum* seeds. The bulk density (BD) was estimated by the test methods of the examination of composting and compost (TMECC). The water holding capacity (WHC) was evaluated by relating the mass saturated with the dried mass of the sample. Total Kjeldahl nitrogen (TKN) was measured with *Velp Scientifica* equipment by the digestion of samples, distillation and titration with HCl. The C/N ratio was assessed by elemental analysis, and atomic absorption spectroscopy was used to determine metals after acid digestion with *aqua regia*. To measure the degree of stability of the digestate, the oxygen uptake rate (OUR) was determined in duplicate for 4 days, in a respirometric installation, at 37 ºC. Temperature and oxygen concentration were followed during the experiments, with *Redlion* and *XLlogger* software, respectively. Nanoparticles were characterized regarding their morphology and particle size distribution by transmission electron microscopy (TEM), as well as their specific surface area by nitrogen gas absorption (BET). The nanoparticles showed to be spherical, but strongly aggregated in chain-like structures, with 51.9± 33.2 nm of particle size. A specific surface area of 46.9 m^2/g was obtained by BET.

Experimental trials with the Fenton reaction were conducted in batch mode with a 500 mL reactor of three entrances, under stirring, in which the CO_2 released from the oxidation process was captured in 4 gas scrubbers placed in series. The scrubbers were partially filled with NaOH, which was used to estimate the CO_2

amount by titration with HCl. The optimization of the Fenton's process was performed by using different concentrations of H_2O_2 (33% w/v), which where injected into the reactor, at pH 3 and 5, with a mass of waste of 22.3 g (dry basis) and a liquid-solid ratio (L/S) of 5.

Some of the main parameters studied are described in Table 1. The results showed that the digestate from the MBT plant is phytotoxic (30 < GI (%) < 60), according to Zucconi *et al.* (1981) classification. Around 7,8 mg Fe/kg of waste are present in the sample, which means that for the Fenton's process it could not be necessary to add the iron salt catalyst, decreasing the costs of the chemical treatment proposed. Comparing the OUR values to the ones obtained by Barrena *et al.* (2011), the digestate shows low biodegradability (OUR < 2 mg O_2 g^{-1} VS h^{-1}). 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 seemed to be promising, although still requiring further studies. Namely, OUR tests are still being performed at the chemical treated digestate, with the optimum conditions of Fenton's process, to ascertain the degree of stabilization of the waste and to compare it with the composting process performed at the MBT plant. Also Fenton's peroxidation with iron nanoparticles will need deepen analysis for comparison of efficiencies.

Table 1. Physico-chemical characterization of the digestate.

Parameters	Value	Parameters	Value	Parameters	Value
M (%)	70.3±0.5	BD (kg/m^3)	1076.4±30.3	Ni (mg/kg)	22.7±3.0
TS (%)	29.8±0.5	WHC (%)	75.39±0.3	Fe (mg/kg)	7811.3±104.7
VS (% ST)	57.3±0.9	TKN (% ST)	8.95±0.6	N (%)	2.0
TDS (% ST)	3.2±0.1	C/N ratio	15.0	C (%)	29.7
COD (mg O_2/L)	2199±11.7	Pb (mg/kg)	101.2±2.5	H (%)	3.8
DOC (ppm)	330.1	Cu (mg/kg)	109.6±1.2	S (%)	< LD
pH	8.4±0.001	Zn (mg/kg)	351.9±33.3	OUR_{max} (mg O_2 g^{-1} VS h^{-1})	1.0±0.6
EC (mS/cm)	8.4±0.006	Cd (mg/kg)	3.1±2.3	OUR_{24h} (mg O_2 g^{-1} VS h^{-1})	0.8±0.7
GI (%)	37.4	Cr (mg/kg)	26.5±1.3	-	-

Acknowledgements

This work is funded by the European Regional Development Fund (ERDF) through COMPETE – Operational Programme for Competitiveness Factors (OPCF), and by Portuguese National funds through the FCT – Fundação para a Ciência e a Tecnologia, under the Project PTDC/AGR AAM/101643/2008 NanoDC.
R.C. Martins gratefully acknowledges the FCT for the financial support under the Post-Doc grant (SFRH/BPD/ 72200 / 2010).

References

Barrena, R., Gea, T., Ponsá, S., Ruggieri, L., Artola, A., Font, A., Sánchez, A. (2011). Categorizing raw organic material biodegradability via respiration activity measurement: A review. Compost Science & Utilization 19, 105 – 113.

Buyukkamaci, N. (2004). Biological sludge conditioning by Fenton's reagent. Process Biochemistry 39, 1503–1506.

Greenberg, A., Clesceri, L., Eaton, A. (1985). Standard methods for the examination of water and wastewater. American Public Health Association: Washington DC.

Neyens, E., Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials 98, 33-50.

Hu, L.-F., Long, Y.-Y., Feng, H.-J., Yao, J. Fang, C.-R., Shen, D.-S. (2010). A New Hazardous Solid Waste Detoxication Method: Semi-solid Fenton Process (SSFP). Water Air Soil Pollut, 212:3–12.

US Department of Agriculture and US Composting Council. (2001). Test Methods for the Examination of Composting and Compost. Edaphos International, Houston.

Wang, C.-B., Zhang, W.-X. (1997). Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. Environtal Science Technology 31, 2154-2156.

Zucconi, F., Peram, A., Forte, M., De Bertolidi, M. (1981). Evaluating toxicity of immature compost. BioCycle 2254-56.