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# Catalytic wet peroxide oxidation as a solution for the treatment of liquid effluents from mechanical biological treatment plants for municipal solid waste

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*A liquid effluent with high pollutant load was collected from a mechanical biological treatment plant for municipal solid waste and the ability to treat it by catalytic wet peroxide oxidation (CWPO) was assessed. Since catalyst design plays a crucial role in CWPO, a high performance hybrid magnetic graphitic nanocomposite (CoFe<sub>2</sub>O<sub>4</sub>/MGNC) – composed by a cobalt ferrite core and a graphitic shell – was developed and applied in the treatment process. CWPO was found to efficiently treat the effluent, in spite of its very high concentration of chlorides (3664 mg L<sup>-1</sup>) and bicarbonates (14350 mg L<sup>-1</sup>). In addition to the high catalytic performance of CoFe<sub>2</sub>O<sub>4</sub>/MGNC in a wide range of solution pH, its magnetic properties allow to implement magnetic separation systems for catalyst recovery after the CWPO stage. Current studies are focused on the effect of CWPO on the toxicity, biodegradability and microbial population of the effluent, as well as on the assessment of the CoFe<sub>2</sub>O<sub>4</sub>/MGNC catalyst stability in successive CWPO cycles.*

## 1. Scope

The organic fraction accounts for about 30 – 40 wt.% of the municipal solid waste (MSW) produced in Europe, corresponding to over 70 million tons per year<sup>1</sup>. Although landfilling is not sustainable, a significant portion of this biodegradable waste still ends up in a landfill<sup>1</sup>. Under the concept of hierarchical waste management, mechanical biological treatment (MBT) plants are already recognized as a solution to limit the environmental impact of direct landfill disposal (in compliance with the Council Directive 99/31/EC), while benefiting of resources (e.g. recyclables separated using mechanical means) and energy recovery (e.g. through biogas production from the organic fraction of the MSW)<sup>2</sup>. However, MBT plants generate a liquid stream with high pollutant load, mainly containing process waters collected from different operations: (i) anaerobic digestion (0.4 – 0.6 m<sup>3</sup> per ton of waste), (ii) leachate from intensive rotting, (iii) pressing water from digestate dewatering and (iv) condensates and/or scrubber water from the exhaust treatment<sup>3</sup>.

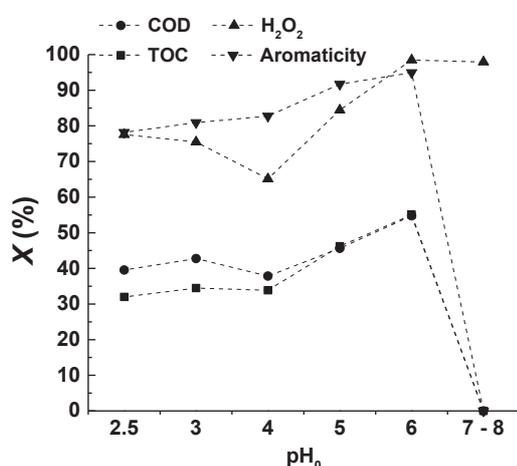
Taking into account the lack of studies on the treatment of this type of effluents with high pollutant load, an effluent sample was collected from a MBT plant located in the Northeast region of Portugal (currently processing 50000 tons of MSW per year). The ability of catalytic wet peroxide oxidation (CWPO) – a low cost advanced oxidation process – for the treatment of the collected effluent was evaluated under atmospheric pressure and mild temperature. Catalyst design plays a crucial role in CWPO, since this treatment technology relies on the catalytic decomposition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) via formation of hydroxyl radicals (HO<sup>•</sup>). Therefore, taking advantage on the knowledge acquired on previous works on the combination of active and magnetically separable iron-based materials with the easily tuned properties of carbon-based materials<sup>4</sup>, a novel high performance hybrid magnetic graphitic nanocomposite catalyst (CoFe<sub>2</sub>O<sub>4</sub>/MGNC) – composed by a cobalt ferrite core and a graphitic shell – was employed in this study.

## 2. Results and discussion

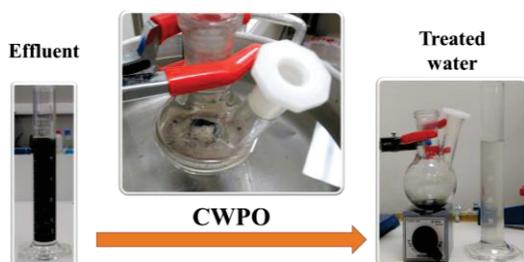
A high performance hybrid magnetic graphitic nanocomposite catalyst was prepared by inclusion of cobalt ferrite nanoparticles within a carbon shell, adapting the procedure described in a previous work<sup>5</sup>.

**Table 1.** Overall characterization of the liquid effluent from the MBT plant for MSW

Parameter	COD (mg L <sup>-1</sup> )	IC (mg L <sup>-1</sup> )	TOC (mg L <sup>-1</sup> )	Bicarbonates (mg L <sup>-1</sup> )	Chlorides (mg L <sup>-1</sup> )	pH at 25 °C	Conductivity (μS cm <sup>-1</sup> )	Iron (mg L <sup>-1</sup> )
Value	9206	2144	2046	14350	3664	8.2	23933	6.4



**Figure 1.** Chemical oxygen demand (COD), total organic carbon (TOC), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and aromaticity conversions obtained in CWPO runs performed during 24 h with CoFe<sub>2</sub>O<sub>4</sub>/MGNC (0.5 g L<sup>-1</sup>) and T = 80 °C.



**Figure 2.** Color removal during the CWPO run performed at pH 6 and in situ magnetic separation system employed for catalyst recovery after the reaction stage.

The resulting material (denoted as CoFe<sub>2</sub>O<sub>4</sub>/MGNC) was characterized in detail and then employed in the CWPO of the effluent from the MBT plant – whose overall characterization is given in Table 1. The CWPO experiments were performed at T = 80 °C, atmospheric pressure and with a low catalyst dosage (0.5 g L<sup>-1</sup>). The effect of the initial pH (pH<sub>0</sub>) was studied in the range 2.5 – 8 (cf. Figure 1). Due to several synergistic effects arising from the inclusion of magnetic materials within a carbon shell, the CoFe<sub>2</sub>O<sub>4</sub>/MGNC catalyst was effective for pH values in the range 2.5 – 6. Indeed, the maximum pollutant removal was obtained at pH 6. For pH above 6, the bicarbonates present in the effluent promote a readily and inefficient consumption of H<sub>2</sub>O<sub>2</sub>, thus inhibiting the treatment of the effluent by CWPO.

A glimpse on the color removal obtained at the optimum operating conditions is given in Figure 2. As also observed, the magnetic properties of the CoFe<sub>2</sub>O<sub>4</sub>/MGNC catalyst allow to implement magnetic separation systems for catalyst recovery at the end of the CWPO stage.

### 3. Conclusions

The ability of CWPO to efficiently treat a liquid effluent from a MBT plant for MSW was shown, in spite of its very high concentration of chlorides (3664 mg L<sup>-1</sup>) and bicarbonates (14350 mg L<sup>-1</sup>). In addition to the high catalytic performance of CoFe<sub>2</sub>O<sub>4</sub>/MGNC in a wide range of solution pH, its magnetic properties allow to implement magnetic separation systems for catalyst recovery after the CWPO stage.

Current studies are focused on the effect of CWPO on the toxicity, biodegradability and microbial population of the effluent. Additional studies to assess the stability of the CoFe<sub>2</sub>O<sub>4</sub>/MGNC catalyst are also envisaged.

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