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## CATALYTIC ACTIVITY OF A HIGH-CONTENT METAL SLUDGE IN PERCARBONATE-ADVANCED OXIDATION PROCESS

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### **Introduction**

The availability of the transition metals is a concern due to limited resources, while waste with different metal content constantly increased. The metallic sludge waste (MSW) is a high-content metals residue resulted in the treatment of galvanic wastewater. It was suggested that the high content of MSW in transitional and alkali metals (Ni, 39.6%; Na, 7.56%; Cu, 9.56%; Fe, 5.06% and Cr, 4.69%) could have a catalytic effect in the oxidation of organic matters from water, comparable to the conventional metal oxides catalysts often used in tertiary treatment.

Preliminary, its catalytic activity in advanced oxidation processes has been assessed for systems as percarbonate advanced oxidation process (AOP) (known also as modified Fenton-*like*), applied for the removal of organic compounds from water. Percarbonate system recently gain visibility in treating wastewater due to its organic removal performance compared to Fenton-*like* systems, with the worth of high H<sub>2</sub>O<sub>2</sub> content. The catalytic efficiency of MSW was evaluated by quantifying the removal of dissolved organic carbon and by highlighting the generation of reactive oxygen species (ROS) in solution and on the catalyst surface. A known refractory compound was studied, the disodium salt of terephthalic acid.

### **Materials and methods**

The MSW was finely ground and then calcined at 550°C for 4h. The metal content of this material was analysed by X-ray fluorescence (EDXRF, Rigaku). As reference materials, copper and nickel oxides were prepared by precipitation from the metal chloride precursor solutions in alkaline medium, followed by calcination at 550 °C and 950 °C, respectively. Percarbonate advanced oxidation processes involve the use of sodium percarbonate with 20-30% H<sub>2</sub>O<sub>2</sub> as the oxidant agent (Sigma Aldrich). Multi N/C 3100 analyzer (AnalytikJena) was operated for the quantification of organic and inorganic total carbon from water. To reveal the hydroxyl radical generation, disodium terephthalic acid (TA) (Acros Organic) was used and the generated hydroxyterephthalic acid (OH-TA) was analysed by spectrofluorometry (Thermo Scientific, Lumina). The ROS onto the solid surfaces were quantified as reactive oxygen by iodometric method. The dissolved metals fraction was quantified

by inductively coupled plasma-optical emission spectrometry (ICP-EOS, Perkin Elmer).

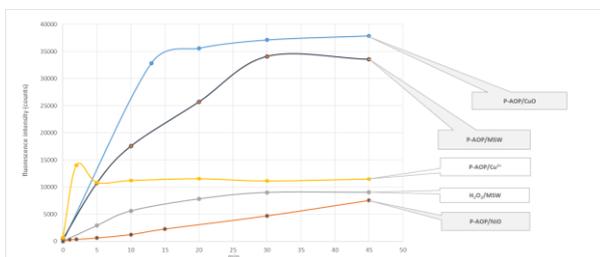
### Results and conclusions

The achieved results show that P-AOP/MSW exhibits a similar trend in mineralisation of TA compared to the other materials. After 120 min oxidation of 0.05 mM disodium terephthalate, the total dissolved organic carbon (TOC) is removed in the order: CuO > sludge > NiO. Varying the molar ratio by the increase of TA concentration, the mineralisation was negatively affected. The total inorganic carbon content determined for solution indicates a surplus of carbon.

For a brief assessment of MSW characteristics, the generation of HO $\cdot$  was highlighted by assessing the OH-TA intensity, the main byproduct reaction between TA and HO $\cdot$  ( $k = 4.4e+9 \text{ M}^{-1}\text{s}^{-1}$ ). MSW shows different behavior of HO $\cdot$  radicals rate generation, where, compared to the synthesised CuO catalyst, the results obtained in the modified Fenton-like process were similar, but higher than for NiO (Figure 1). The impact of possible solubilisation of Cu $^{2+}$  from sludge or CuO consists in generating of 41.8% HO $\cdot$  (3mM Cu $^{2+}$  or 24% Cu from CuO), or 14.1% HO $\cdot$  (0.09 mM Cu $^{2+}$  or 5.4% from MWS).

The selected materials show oxidant activity to KI which are related to surface oxidizing active centers (ROS), expressed as O $^*$ . The difference quantified for the catalysts in oxidant conditions was considered to be correlated to ROS. After 60 min reaction, the quantified ROS increase by 0.84 mg O $^*/\text{kg}$  sludge in percarbonate oxidant medium, while only H $_2\text{O}_2$  addition does not influence the initial concentration of 1.0 mg O $^*/\text{kg}$  sludge. Moreover, the ROS surface center where quantified in this order: CuO > sludge > NiO (1.88 mg O $^*/\text{kg}$  CuO, 0.84 mg O $^*/\text{kg}$  sludge, 0.065 mg O $^*/\text{kg}$  NiO).

The tested material meets several criteria for catalytic behavior in advanced oxidation processes comparable to NiO and CuO but additional tests should be performed to assess its stability and efficiency repeatability in oxidant systems and to identify its toxicity to aquatic organisms.



**Fig. 1** Emission intensity of OH-TA for P-AOPs and H $_2\text{O}_2$  systems, with 1000 mg/L solid material, 2.4 mM TA and 15 mM H $_2\text{O}_2$  at pH 9.

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