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## SODIUM PERCARBONATE ENHANCED OZONATION PROCESS FOR 2,4 DICHLOROPHENOXYACETIC ACID REMOVAL

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### **Introduction**

Advanced oxidation processes of wastewater with peroxone ( $O_3/H_2O_2$ ) is known to be a viable solution in treatment methods due to its synergistic effect in generation of hydroxyl radical and other reactive oxygenated species. Newer studies point out that using sodium percarbonate (SP) as a solid  $H_2O_2$  carrier significantly reduces the input costs of the oxidation method while having the same effectiveness as  $H_2O_2$  applied in solution. However, the  $O_3/SPC$  mechanism is not fully elucidated and is contradictory since apparently the presence of carbonate and bicarbonate does not inhibit hydroxyl radical activity. The molar ratio between oxidants represents also an important key issue in controlling the organics mineralisation. The oxidant system was tested for the degradation of a model refractory compound, 2,4-dichlorophenoxyacetic acid (2,4 D). It was investigated the influence of a metallic oxides material obtained from sludge waste (MSW) on hybrid oxidant system.

### **Materials and methods**

The ozonation tests were done in a semi-batch system which defines a closed reactor with a continuous purge of ozonated air (C-Lasky ozone generator) in the 2,4 D solution (Acros Organic, analytical purity). Sodium percarbonate (Sigma Aldrich), which consists in 20-30%  $H_2O_2$  in  $Na_2CO_3$ , was added as an additional source of oxidizing agent. The metallic sludge waste (MSW) used as a catalyst was pretreated by grounding and calcination.

2,4 D was quantified by GC-ECD technique, after derivatization with methanol in acidic conditions (5%  $H_2SO_4$ , J.T. Baker). The organic and inorganic total carbon from water were determined by Multi N/C 3100 analyzer (AnalytikJena). Residual ozone was calculated by the classic volumetric technique with KI. The efficiency of the method was assessed by the apparent kinetic rate constant ( $k_{app}$ ) which is calculated from the half-life time for pseudo-first order rate law of 2,4 D degradation.

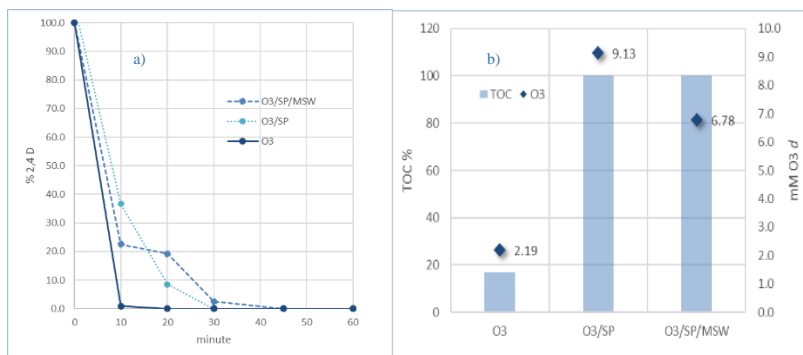
### **Results and conclusions**

In this study were tested different ozonated systems:  $O_3$  (pH 9), ozonation with sodium percarbonate ( $O_3/SP$ ) and catalytic ozonation with sodium percarbonate ( $O_3/SP/MSW$ ). The performance of the oxidation processes was assessed with

respect to targeted pollutant removal, to the degree of mineralisation and ozone demand. 2,4 D was completely degraded for all tested AOP systems. It was evaluated:

- the effect of sodium percarbonate addition in  $O_3$  system which was an increase of TOC mineralisation from 17% to 100% for the same amount of time (60 min). The reason could be the synergistically effect between the ozone and  $H_2O_2$  from sodium percarbonate.
- the effect of catalyst addition to  $O_3$ /SP system was:
- an acceleration of 2,4 D degradation rate ( $k_{app} = 8.68 \text{ s}^{-1}$  than  $6.43 \text{ s}^{-1}$ ) for the first 10 minutes (Figure 1a),
- a decrease of reacted ozone by 25.7% compared to  $O_3$ /SPC (Figure 1b) which indicates the participation of MSW active sites centres in  $H_2O_2$  decomposition.

It was observed that the dose of ozone decomposition is highly dependent on peroxide initial dose, which correspond to a molar ratio of 1:1, where  $H_2O_2$  from SP was applied as 7.5-15 mM and  $O_3 > H_2O_2$ . These results need further studies to clarify the model reaction of ozone decomposition. Also, the findings demonstrate that the ozone/percarbonate system is an effective process and requires onward advanced research to be applied as a treatment step in water/wastewater treatment plants.



**Fig. 1.** Graphic representation of a) 2,4 D time-removal and b) mineralisation degree (TOC%) and ozone demand for TOC removal ( $O_3 \text{ diff}$ ) after 60 min reaction in  $O_3$ ,  $O_3$ /SP and  $O_3$ /SP/MSW systems.