

DOI: <http://doi.org/10.21698/simi.2024.ab06>

## CHALLENGES IN APPLYING HYBRID OXIDATION WITH OZONE AND SPC TO RESIDUAL SLUDGE TO GENERATE VOLATILE FATTY ACIDS

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**Keywords:** *advanced chemical oxidation, humin, residual sludge, volatile fatty acids*

### **Introduction**

The chemical oxidation of residual sludge from wastewater treatment plants is a less studied topic reported to the recovery of economically significance compounds as volatile fatty acids (VFAs).

The proposed hybrid treatment with O<sub>3</sub> and sodium percarbonate (SPC) should oxidizes synergistically the organic matter, possibly through the generation of oxygenated reactive species. But the sludge matrix is complex and unstable, so chemical oxidation processes are limited by reaction competition, compound diffusion, and mass transfer. Furthermore, side effects of oxidation such as loss of sludge content due to foaming or VFA removal by ozone purge rate or oxidation are challenging. The aim of this study particularly resides to identify the optimal oxidation conditions to improve VFAs generation from waste sludge.

### **Materials and methods**

For these tests it was collected samples of residual wastewater activated sludge, with 0.9-2.3% solid content, from chocolate industry wastewater treatment station. The samples treatment consisted in 10 minutes' centrifugation at 10000 RPM, 4°C (Thermo Scientific MicroCL 17R) and stabilisation with formic acid. The VFAs were determined by gas chromatography (GC-FID 6890N) equipped with FFAP column (30x0.25x0.25). The fluorescence spectra of soluble matter (excitation/emission 200-700 nm) were investigated with microplate reader Clariostar (BMG Labtech) and Lumina (Thermo Scientific). This exploratory research was achieved at a laboratory scale, in a semicontinuous instalation, where the reactor with sludge and different doses of sodium percarbonate (Na<sub>2</sub>CO<sub>3</sub> x 1.5 H<sub>2</sub>O<sub>2</sub>) was purged with 5% ozone.

### **Results and conclusions**

The main technological parameters were assessed in this study. It was found that concentration as 0.2 g SPC/g TS show a reasonable impact in sludge treatment by increasing with 60.7% the acetic acid (AA) concentration in 60 min reaction time. Also, by treating the sludge with O<sub>3</sub>/SPC at ozone dose of 0.12 and 0.18 g O<sub>3</sub>/g TS, the VFAs concentration successfully increased up to 206% (hexanoic acid) in 15 minutes. But the main problem that arose was foaming due to strong oxidants (ozone

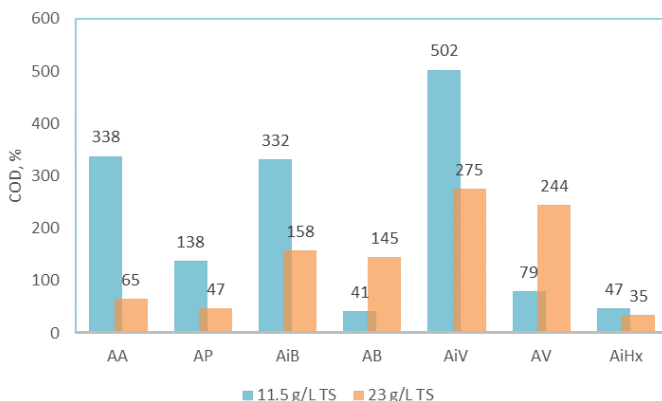
dose) and alkaline media that increase or influence the superficial tension at the surface of gas bubble.

For this reason, dimethyl siloxane (DMT) was chose as antifoam agent. Unfortunately, foam control induces a significant decrease in VFAs generation. In order to settle this challenge, several solutions were applied as NaCl treatment, an increase time response to oxidation and addition of an another oxidation step.

The salt impact consisted in a strong synergic effect with the SPC, especially for the generation of acetic acid, propionic acid and valeric acid, and a linear correlation between NaCl and concentrations of butyric acid, isovalerianic acid and valeric acid after 60-minute time reaction.

However, the addition of ozone releaves an enhance in oxidation efficiency than in VFAs formation even after 24 h of sedimentation. Only the second oxidation step with  $O_3$  or SPC appears to induce the expected outcomes, as an increase of 502% of isovalerianic acid and 337.5% of acetic acid in the first 48h (Figure 1).

The proposed  $O_3$ /SPC oxidation technique deals especially with the competitiveness of organic matter against oxidants, as being observed that solubilisation of humins and proteins, and hydroxilation occurs in high-solids sludges while oxidation and VFAs generation appears in low contents solids.



**Figure 1.** VFAs generation percentage expressed as chemical oxygen demand (COD) for sludge solid content of 11.5 and 23 g/L, after 2-step chemical oxidation with  $O_3$ /SPC

### Acknowledgement

This study was funded by the Ministry of Research, Innovation, and Digitalization of Romania by "Nucleu" Programme, contract no. 3N/2022, Project PN 23 22 03 01.