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PRELIMINARY RESULTS IN OZONE/PERCARBONATE SLUDGE TREATMENT TO ENHANCE VOLATILE FATTY ACIDS GENERATION

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Introduction

Chemical oxidation with sodium percarbonate was studied before in order to enrich the sewage sludge in volatile fatty acids (VFAs), valuable compounds in other industries. But the weakness of the method consisted in desintegration of the organic polymers cell for which it was required a strong oxidant. It is supposed that the sludge oxidation can be improved if it is applied an innovative mix of advanced oxidation processes based on ozone and sodium percarbonate (SPC): either as two-steps process, especially as a pretreatment method to microbial fermentation or, less studied, as one-step process that could improve the VFAs production, alongside solubilizing the organic matter and accelerating sedimentation. The second process was exploratory analyzed in this work with the aim to evaluate the efficacy in VFAs generation from the biological waste sludge from the chocolate industry wastewater. The results were briefly interpreted through the prism of other physico-chemical indicators as the fluorescence intensity of solubilized organic matter.

Materials and methods

Residual sludge samples, with 1.2% dry mass, were collected from a wastewater station from the chocolate industry. All samples were centrifuged before at 10000 RPM, 4˚C for 10 minutes with Thermo Scientific MicroCL 17R. VFAs was identified and quantified from the acidified supernatant by gas chromatography with a flame ionisation detector, GC-FID 6890N, and separation on FFAP column, 30 m x 0.25 mm x 0.25 µm. Clariostar was used to investigate fluorescence spectra for solubilized organic matter in the range of 320-600 nm ex and 350-600 nm emmision. The Rigaku CG X-ray spectrofluorimeter and Thermo Scientific ICP-MS were used to achieve metallic characterisation of sludge and supernantant. The size of particles from supernatant and sludge were analysed with Malvern Mastersizer 2000.The oxidation experiments were realised at laboratory scale in a semicontinous batch that consisted in a glass reactor with 100 mL sludge in which were added different doses of sodium percarbonate (Na_2CO_3 x 1.5 H_2O_2) and ozone.

Results and conclusions

Sludge characterization. The volatile acids with highest concentration in fresh sludge was found to be acetic acid, butyric acid and propionic acid, which represents 31.2%, 20.7% and 19.7% from the VFAs total amount. The initial VFAs content of the sludge was determined to be as 1577 mg O_2/L which represents 8.15% of total chemical oxygen demand (COD), but due to microbial activity this concentration varied over time, even by preserving at low temperatures, 4˚C.

Critical operational parameters

The effectiveness of the oxidative method was assessed according to essential parameters such as ozone dose, percarbonate dose and molar ratio.

By applying the ozone dose for a range of concentrations of 0.029-0.49 g/g total solid suspension (TSS), the VFAs production was enhanced for the first 5-25 minutes oxidation to 124-138%. The concentration of carboxylic acids was observed to increase at ozone dose lower than 2.0 g O_3/g TSS, where 0.146g O_3/g TSS was determined to be the optimal ozone dose for this particular matrix.

Also, a similar effect was observed when percarbonate dose was added to ozone (O_3/SPC). While for SPC higher dose (2.82 g /g TSS) it had an inhibitory effect, a lower amount (0.21 g SPC/g TSS) increased specifically the acetic, butyric and hexanoic acids up to 106% after the first 15 minutes of oxidation, and isobutyric, isopentanoic and isohexanoic acids increased to 48.7% after 30 minutes. Nevertheless, the mineralization degree of O_3/SPC is slightly lower than ozonation with 1.6%. Compared with untreated sample, it was determined the formation of fluorescent compounds as UVC and VIS humic acids-*like* (significantly increased with 589% and 254%), UVA fulvic acids-*like* and amino acids as tryptophan.

After studying the other critical parameter, ozone / percarbonate ratio (0.043-2.45 g/g), it was revealed that for an amount of 0.2 g SPC /g TSS (ratio 0.6) the production of VFAs was stimulated with 36%, and the availability of Al, Ni and Pb in supernatant decreased, but the particle diameter doubled its size to 105 µm, most probable as a result of organics oxidative degradation and an *in situ* coagulation process.

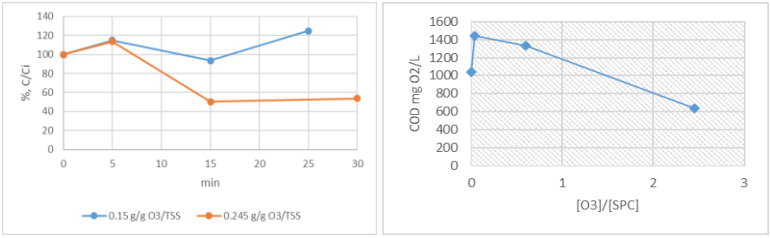

Fig.1. The percentage ratio of acetic acid during alkaline oxidation with ozone (left) and VFAs content for different O_3/SPC molar ratio after 60 minutes oxidation (right)

In summary, the preliminary results showed that a small amount of oxidants and a specific O_3/SPC ratio improved the content of VFAs after maximum 60 minutes of oxidation.

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