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# OZONE TREATMENT APPLIED TO WINERY WASTEWATER: FOCUS ON RECALCITRANT ORGANIC MATTER EVALUATION AND REMOVAL

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## Introduction

In wine production, several wastewaters are generated with different type of pollution and concentration ranges. The winery effluents are characterized by high COD concentrations, around 10 kg COD/m<sup>3</sup> with high degradable matter content close to 90%, making it suitable for biological treatments such as aerobic and anaerobic processes (Bolzonella, D. 2013). The remaining COD after biological treatment is usually low but the biodegradability is also very low. The wastewater from washing pesticides machines, in individual or collective platform has a lower COD concentration but the fraction of recalcitrant organic matter is high, making difficult the application of a biological system for its treatment (Massot, A. 2012). Few techniques are allowed by the French laws to treat this kind of wastewater, most of them are based on physical systems such as concentration (Ministère de l'Agriculture et de la Pêche 2006). Finally, the wastewater from municipal wastewater treatment plant, in the context of water scarcity, can be used for vineyard irrigation if suitable treatment is applied in order to ensure pollution and sanitation performances (Ministère des Affaires Sociales et de la Santé 2014). For all these wastewaters, ozone treatment is a potential technique that can achieve the required objectives: disinfection, pesticides removal and conversion of recalcitrant organic matter into biodegradable one. Brown melanoïdin compounds, known as Maillard Reaction Products (MRP), are known to be recalcitrant compounds frequently found in agro-food effluent and in digestate (Battimelli, A. 2009). Based on oxidation reactions, ozonation is able to break membrane cells, mineralize organic molecules into CO<sub>2</sub> and to produce shorter oxidized molecules that can be further biodegraded. This study gives an overview on the potentiality of ozone application to the winery wastewater with an emphasis on the conversion of recalcitrant COD into biodegradable effluent. This article describes the methodology for the recalcitrance estimation by the original use of the melanoïdins as a synthetic model compound.

## Methodology

Three samples were studied in order to represent the winery effluents. The first one called vinasse is the effluent from an industrial distillery located in Narbonne, the second one, called digestate, is the effluent from a pilot scale anaerobic reactor treating the sample vinasse. The last sample is a synthetic solution containing recalcitrant organic compounds, the melanoïdins. The characteristics of the wastewaters are shown in table 1. Ozone treatment was performed in semi-batch conditions at lab scale, as described in previous

study (Battimelli, A. 2010). All analyses were performed in triplicate following standardized methods.

Table 1: Physicochemical characteristics of the samples

Parameters	Vinasse	Digestate	Melanoïdins	Units
SCOD	4.74	1.7	2.29	g/L
pH	4.0	7.0	6.83	-
Aromatics (A 254 nm)	8.6	6.74	2.29	a.u.
TOC	0.97	0.55	0.42	g/L
IC	< 20	238	< 20	mg/L
Color (A 475 nm)	1.74	3.95	0.32	a.u.

## Results and discussion

Before ozone treatment, the BOD of the samples was estimated after 5 days for the easily degradable fraction and after 21 days for the ultimate biodegradability quantification. Recalcitrant fractions of the COD were 18%, 12% and 88% for the vinasse, the digestate and the melanoïdins respectively. Only the digestate and the melanoïdins were oxidized, in same ozonation conditions. At the highest treatment time, the chemical treatment led to a decrease of the COD, 61% and 58% for the digestate and the melanoïdins respectively, indicating also different reaction kinetics. The biodegradability ratio after ozonation were modified, 72% and 33% for the digestate and the melanoïdins respectively. In the case of melanoïdins the biodegradability increased since for the digestate characterized by a high initial biodegradability, the biodegradable fraction decreased. These results confirm the interest of ozone treatment for the removal of recalcitrant compound: the chemical oxidation should only be applied to a wastewater with a biodegradable fraction as low as possible, in order to limit the ozone consumption. Ozone treatment is confirmed to be a suitable technique for the treatment of winery wastewater. Several potential applications are linked to different objectives in relation to the wastewater origin: the removal of pesticides in diluted flows, the disinfection of water in the case of reuse or conversion of recalcitrant organic matter accumulated after biological treatment. In this last case, the ozone dosage should be minimized in an optimized combination of ozone/biological reactors.

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