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# Influence of the cleaning additives on the methane production from brewery effluents

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## HIGHLIGHTS

- Toxicity caused by fatty acids esters or ethoxilated alcohols on UASB anaerobic digestion was studied.
- Toxicity towards the UASB granular sludge was higher than towards normalized organisms *Vibrio fischeri*.
- Fatty acids esters were more toxic towards UASB granules than ethoxilated alcohols.

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## ABSTRACT

Batch and continuous anaerobic tests were used to study the effect of cleaning additives on the methane production from brewery effluents. The detergents studied were based on fatty acids esters or on ethoxilated alcohols and presented $EC_{50}$ values in *Vibrio Fischeri* of 4.3 and 14.1 g/L respectively. However, these detergents were toxic to the granular sludge even at lower concentrations indicating that some of the microorganisms presented in the granular sludge were more sensitive than the *Vibrio Fischeri*. Comparing batch and continuous tests, it was observed that under continuous conditions the toxicity was lower than under batch conditions, indicating the capability of the microorganisms to get acclimatised, in the long term, to the surfactants. In the case of the detergent based on ethoxilated alcohols, the microorganisms were capable to acclimatise even at concentrations of 1000 mg/L, however in the case of the detergents based on fatty acids esters, concentrations higher than 500 mg/L caused toxicity. This toxic effect reduced the methane production significantly, reducing the energy recovery from the wastewater to about a 35% of the original value. From the results it was concluded that the detergents based on ethoxilated alcohols were more adequate than the detergent based on fatty acids esters because of its toxic effect towards granular sludge.



## 1. Introduction

The Anaerobic Digestion (AD) process is very widespread to treat different kinds of high loaded industrial wastewaters because it presents a number of advantages. The main advantages are the biogas generation, the low biomass production and the low overall cost [1]. In the AD process, a complex consortium of bacteria converts the contained organic substrates into more stabilized ones under anaerobic conditions.

Breweries consume significant amounts of water, being therefore, a large producer of wastewater. Due to the high organic load and biodegradability of the effluents generated in breweries, these industrial wastewaters are usually anaerobically digested. The brewery wastewaters mainly consist of organic substrates generated in the main process production of the industry. In addition, wastewaters also come from clean-in-place (CIP) methods for decontaminating equipment and from lubricant procedures carried out [2]. Anaerobic digestion usually enables industries to comply with the stringent standards for treated brewery wastewater imposed by law, obtaining energy as interesting by-product. However, the presence of additives used for CIP activities, e.g. surfactants, could modify the performance of the bioprocess, reducing the effluent quality and the viability of the energy obtention [3].

Cleaning additives are formulations of different chemical compounds presenting cleaning and solubilisation properties. These formulations are composed of surfactants and secondary components. Surfactants are organic compounds with a lipophilic portion and a hydrophyilic one. There are several classifications for

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surfactants, the most common is based on their dissociation in water: anionic, non-ionic, cationic and amphoteric.

Anionic surfactants are the most commonly used, and account for about 50% of the world production [4]. Non-anionic surfactants are the second most used with the 45% of the overall industrial production. Cationic surfactants are less used since are more expensive than anionic. Consequently, cationic surfactants are only used when there is no cheaper substitute. Finally, amphoteric surfactants are generally quite expensive, and therefore their use is limited to very special applications, in which their low toxicity is of primary importance [5].

In the brewery industry, the most used surfactants are the non-ionic. Two of the most important non-ionic surfactants are ethoxylated alkylphenols and ethoxylated alcohols. Ethoxylated alkylphenols were the first non-ionic surfactants widely used but, because of their low biodegradability and because they may generate by-products like alkylphenols and aldehydes that are more toxic than the starting molecules, they are been replaced by easily biodegradable surfactants. The new generations of non-ionic surfactants displacing the ethoxylated alkylphenols are the ethoxilated alcohols and the fatty acid esters.

The selection of an inadequate surfactant in the brewery industry could disturb the stability of the bacteria groups involved in the anaerobic degradation of the organic substrates, such as an impairment of biological function or an adverse effect (not necessarily lethal) on biological metabolism, inhibitory and toxic effects, respectively, leading to short and long-term effects [6]. Because of the effects exposed above, in recent years, there has been an increasing interest in the study of the toxicity and inhibitory effect caused by the new generation of surfactants.

In this context, the objective of this work was to study the biodegradability and the toxicity of two commercial cleaning additives as well as the shock and continuous loads effects caused on the methane generation from brewery wastewaters. The commercial cleaning additives studied were similar except for the presence/absence of an ethoxylated linear alcohol and a fatty acid ester. Batch and continuous experiments were carried out, which enabled to determine the maximum cleaning additive concentration on the wastewater that does not affect significantly the process.

## 2. Materials and methods

### 2.1. Anaerobic granules

The anaerobic granular sludge used in this work was kindly provided by a brewery located at Castilla-La Mancha (Spain). It had been cultivated in a 1260 $m^3$ Upflow Anaerobic Sludge Blanket (UASB) reactor treating the wastewater from the brewery at 32 °C. The granules were of a regular, spherical shape and a brown-green colour. The volatile suspended solids concentration of the sludge was 68.5 g/L.

Before the experiments, the granular sludge was washed with demineralised water under anaerobic conditions in an upflow column. The flow rate applied in the column was selected such as to allow the granules to stay in the column, while dispersed material was washed out. Biogranules were used for the shock and continuous loading test on surfactants toxicity as well as for the determination of the biodegradable fraction of the surfactants. The operating conditions in the UASB reactor and the characteristics of the granular sludge are presented in Table 1.

**Table 1**
UASB operational conditions and characteristics of the granular sludge.

| UASB operating conditions | | Granular sludge | |
|---|---|---|---|
| Parameter | Mean value | Parameter | Mean value |
| Influent flow rate ($m^3$/h) | 150 | Surface area ($mm^2$) | 4.4 |
| Loading rate (kg COD/$m^3$ d) | 11 | Diameter (mm) | 1.2 |
| Upflow velocity (m/h) | 0.75 | Density (g/L) | 5.7 |
| pH | 7.2 | TS/VS ratio | 1.36 |

### 2.2. Wastewater

#### 2.2.1. Brewery wastewater

The brewery wastewater used in this work was synthesized by mixing demineralised wastewater and beer, the main contributions to the brewery wastewaters [7]. The final COD of the mixture was set to 4000 mg COD/L, because this is the average COD concentration of the wastewater generated in the brewery. This synthetic wastewater was supplemented with 3 g/L of sodium hydrogen carbonate ($NaHCO_3$) and 1 g/L of ammonium hydrogen carbonate ($NH_4HCO_3$) to provide alkalinity, buffering capacity and nutrient in the feed.

#### 2.2.2. Surfactants

To study the effect of the surfactants on the anaerobic digestion of the brewery wastewater, two commercial mixtures of chemical products were added to the brewery wastewater. Because of privacy policy of the company commercialising these cleaning additives, the commercial mixtures of chemical products used will be called from now onwards Types A and B. The only difference between both cleaning additives was the presence of fatty acid esters (5–15%) in Type A and the presence of linear alcohol ethoxilate (5–15%) in Type B.

### 2.3. Experimental setup and operation

#### 2.3.1. Toxicity bioassays

Toxicity tests were performed to determine the toxicity of both detergents, Types A and B. The toxicity test was based on the inhibition effect over the bioluminescence of luminescent bacteria *Vibrio Fischeri* [8]. That marine bacteria naturally emits light, the light production is directly proportional to the metabolic status of the cell, and any inhibition of cellular activity is reflected in a decrease in bioluminescence. The decreasing of light is measured with a photomultiplier in a luminometer. In literature, it has been described that this luminescence inhibition test can be accurately correlated with other standard acute toxicity assays [9]. The determination of toxicity was performed using Junior LB 9505 from Berthold Technologies (Bad Wildbad, Germany). The percent of inhibition (%I) can be determined by comparing the response given by a saline control solution to that corresponding to the sample. Therefore, bioluminescence inhibition was calculated as:

$$\%I = \left[1 - \left(\frac{\text{Dilution light}}{\text{Control light}}\right)\right] \cdot 100$$

Measuring the inhibition for a range of concentrations, the toxicity can be expressed as effective concentrations (ECs) causing a defined response.

#### 2.3.2. Biodegradable fraction and shock load test

The biodegradability of the cleaning additives by the granular sludge was assessed by the determination of the Specific Methanogenic Activities (SMA) test assays [10–12] with each cleaning additive as the sole substrate, ranging its concentration from 400 to 1000 mg/L. These biodegradability tests were carried out at 35 °C using anaerobic batch reactors equipped with a manometric sensor that measured the pressure generated by the biogas during the reaction. In each experiment, granular sludge was mixed with only