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Effect of inhibitory compounds on the two-phase anaerobic digestion performance of diluted wastewaters from the alimentary industry

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ABSTRACT

This paper deals with the quantitative measurement of the influence of different inhibitory compounds present in olive oil mill and winery industrial wastewaters on their anaerobic digestion treatment. Specifically, the physical separation of the two stages (acidogenic and methanogenic) that comprise the anaerobic digestion process, and the acclimation time of the microorganisms have been evaluated.

First, a series of experiments with glucose model solutions made clear that external pH control (>8) in methanogenic reactor is a key factor to guarantee suitable overall chemical oxygen demand (COD) removals and biogas production rates in a two-phase operation. Next, a response surface methodology (RSM) was applied to quantify the effect of olive oil, ethanol and phenol (in form of synthetic solutions simulating diluted real wastewaters) on the two above mentioned responses. According to the results of this method, inhibiting power of these compounds follows the order: ethanol > phenol ≫ olive oil.

Although the general trends observed in a two-stage anaerobic digestion process do not differ much from the ones obtained in a single-stage process, it should be emphasized the higher stability of the process, with yields >60% even in the presence of moderate concentrations of inhibiting compounds (0.25% w/w olive oil, 75 mg L^{-1} phenol and 125 mg L^{-1} ethanol).

1. Introduction

Anaerobic digestion is an attractive wastewater treatment process in which both pollution control and energy recovery can be achieved. Many agricultural and industrial wastes are ideal candidates for anaerobic digestion because they contain high levels of easily biodegradable materials. For example, in an earlier work we demonstrated that both olive mill and winery industrial wastewaters could be successfully treated by anaerobic digestion even in the presence of small amounts of inhibitory substances [1]. Nevertheless, other problems such as low methane yield and process instability are often encountered in anaerobic digestion, preventing this technique from being more widely applied [2].

A wide variety of inhibitory substances are the primary cause of anaerobic digester upset or failure. Considerable efforts have been made to identify the mechanism and the controlling factors of inhibition [3]. In spite of the numerous studies investigating heavy metal inhibition and toxicity in a single-phase anaerobic digestion process, less emphasis has been focused on the adverse effects that organic substances might cause. Moreover, a limited amount of literature exists describing the utilization of these substrates in methanogenic biofilm reactors. Organic compounds which have been reported to be toxic to the anaerobic processes include long chain fatty acids (LCFAs) [4], phenol and alkyl phenols [5,6], and alcohols [7,8].

For this reason, in a previous work [1] we investigated the effect of some above mentioned inhibitory compounds (olive oil, ethanol and phenol) on the single-phase anaerobic digestion performance of wastewaters from alimentary industry. The results showed that the addition of olive oil at moderate concentration (up to 0.5% w/w) did not change the chemical oxygen demand (COD) removal percentage and biogas production rate in comparison with that observed when feeding to the system a glucose model solution. However, low concentrations of ethanol or phenol (250 and 150 mg L^{-1}, respectively) almost completely inhibited the methanogenic phase. Moreover, a strong interaction between ethanol and phenol concentrations on COD removal was observed.

The results from this work suggested that the process efficiency could be improved in several ways such as: (1) enlarging the acclimation time of microorganisms to that compound being the source of carbon [9]; and (2) performing the acidogenesis and methanogenesis processes in two separate reactors [10].

Firstly, higher inhibitory compounds removal rates may be reached if microorganisms are acclimated to those compounds used as a source of carbon [9]. This acclimation should last 2 weeks at least, which was the exact length of experiments in our previous work [1]. For this reason, the length of experiments has been duplicated in the present work. In principle, this longer acclimation time for the anaerobic microorganisms should

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increase their tolerance to the toxicants shock and enhance the toxicant biodegradability [11].

The second suggestion is related to the use of two separate reactors for acidogenesis and methanogenesis processes, since the increase of volatile acids concentration leads to a decrease of pH of culture media, and consequently, methane production decreases. The separation improves stability of processes and sometimes overall BOD (biochemical oxygen demand) and COD removal efficiencies [10,12,13]. However, such a separation will not generally significantly accelerate or increase overall methane-production, although it can be of some advantage in making the process more resistant to shock loading [14]. Finally, it should be noticed that the acidogenic phase could also represent a significant loss of C (as CO_2 formed) fed to the methanogenic phase [15].

To sum up, the purpose of this research was the evaluation of the inhibitory effects of different compounds (olive oil, phenol and ethanol) on the anaerobic digestion of synthetic solutions and real industrial wastewaters from alimentary industries. The main novelties of this work in contrast to the previous work [1] is the separation of acidogenesis and methanogenesis processes in two different upflow packed-bed biodigesters, and the enlargement of the length of experiments (from 15 to 30 d) to provide a better acclimation of each type of microorganisms to the inhibiting compounds.

Previously to the two-phase anaerobic digestion experiments with synthetic solutions from alimentary industry, some preliminary experiments with glucose solutions were performed in order to establish the appropriate operating pH values in each reactor.

As in our previous study [1], a Response Surface Methodology (RSM) was applied to results in experiments with synthetic solutions to quantify the effect of each inhibiting compound on two different responses: % COD removal and biogas production rate. In this way, the results obtained for a two-phase anaerobic digestion process could be properly compared to those obtained for a single-phase system [1].

The statistical design of experiments is an interesting technique for chemical and biochemical research to study the empirical relationships, in terms of a mathematical model, between one or more measured responses and a number of variables or factors. They have been successfully used for a long time [16] and permit expression of the response as a polynomial model.

Response Surface Methodology (RSM) usually consists of 5 steps: (1) defining the independent input variables and desired responses with the design constraints while adopting experimental design, (2) performing the regression analysis with the quadratic model of response surface, (3) calculating the statistical analysis of variance (ANOVA) for the independent input variables and to find which parameter significantly affects the desired response, (4) obtaining the optimal influencing parameters with the design constrains and, (5) conducting a confirmation experiment to verify the optimal parameters.

Finally, anaerobic digestion experiments on real industrial effluents from olive oil and winery industries were performed to confirm the results from the simplified study with synthetic solutions of similar composition in COD content, total and volatile suspended solids (TSS and VSS), alkalinity, volatile acidity and pH value.

2. Materials and methods

2.1. Microbial culture

Anaerobic sludge from an anaerobic digester in the Urban Reclamation Station of Toledo (Spain) was used as a source of microorganisms for the laboratory scale attached growth anaerobic digester. This reclamation station treats urban wastewaters ($20{,}000\ m^3\ d^{-1}$), with average BOD_5 and TSS 214 and 437 $mg\ L^{-1}$, respectively, being the average yields in the removal of these two parameters 88% and 93%, respectively. Anaerobic digester treats 120–180 m^3 sludge daily, with an average removal of VSS around 50%. The influent sludge has a pH value of 5.5–6.0, whereas the effluent sludge has a pH value of 6.8–7.2.

2.2. Wastewater composition

The anaerobic sludge was fed into a lab-scale digester with a model wastewater (composition in parentheses) prepared with chemicals of analytical grade and purchased from Panreac (Spain): D(+) glucose ($C_6H_{12}O_6$) ($8\ g\ L^{-1}$), $(NH_4)HCO_3$ ($0.4\ g\ L^{-1}$), KH_2PO_4 ($0.4\ g\ L^{-1}$), $NaHCO_3$ ($0.4\ g\ L^{-1}$), $MgSO_4{\cdot}7H_2O$ ($5\ mg\ L^{-1}$), $FeCl_3$ ($5\ mg\ L^{-1}$), $CaCl_2$ ($5\ mg\ L^{-1}$), KCl ($5\ mg\ L^{-1}$), $CoCl_2$ ($1\ mg\ L^{-1}$) and $NiCl_2$ ($1\ mg\ L^{-1}$). The formulation of model feed wastewater was supplemented with olive oil (acidity 4°, Koipe, Spain), phenol (98% v/v, Panreac, Spain), and/or ethanol (96% v/v, Panreac, Spain) in some experiments.

For analytical measurement, sulfuric acid 0.2 N (Panreac), sodium hydroxide 0.1 N (Panreac), and commercial kits for COD measurement (Hach, Germany) were used.

2.3. Experimental set-up

Anaerobic digestion experiments were performed in two in-series commercial small-scale upflow packed-bed anaerobic digesters (model W8, Armfield Ltd., UK), each one with 5 L volume (Fig. 1). The only difference in contrast to this previous research is that the effluent from the acid-phase reactor was sent to an intermediate reservoir to collect the necessary quantity of liquid to be continuously pumped to the methanogenic-phase reactor. This reservoir was also used to properly modify the pH value of the influent to the second reactor, so the pH value in methanogenic stage is fully controlled. This pH value was previously determined by means of preliminary experiments with the model effluent.

2.4. Previous experiments

Apart from the operation with two in-series reactors, other main difference with respect to previous studies [1] consists of the enlargement of experiment length until 30 d, both for synthetic and real wastewaters. After this time, biogas production rate and all effluent parameters (pH, TSS, VSS, alkalinity, volatile acidity, and COD) had reached stationary values.

The reactor was started up at the beginning of each experiment. Firstly, a determined volume of sludge (1 L) was added to each

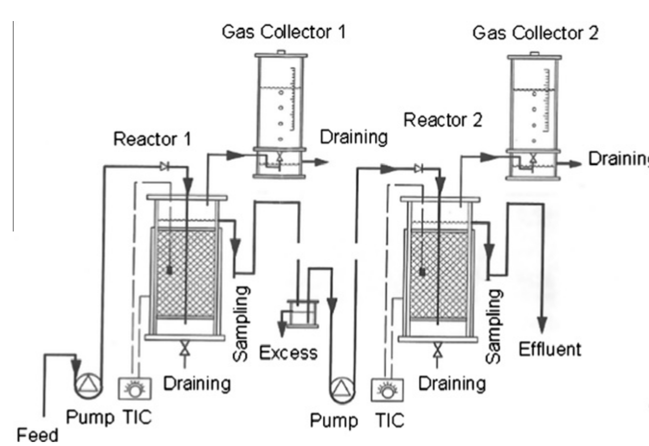

Fig. 1. Experimental set-up (source: Armfield Ltd., UK).