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Assessment of process control parameters in the biochemical methane potential of sunflower oil cake

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ABSTRACT

A laboratory-scale study was conducted on the batch anaerobic digestion of sunflower oil cake (SuOC), solid waste derived from the extraction process of sunflower oil. A multi-reactor system was used to compare methane production from this waste at inoculum to substrate ratios (ISRs) of 3.0, 2.0, 1.5, 1.0, 0.8 and 0.5 (expressed as volatile solids (VS) basis). The tests were carried out at mesophilic temperature (35 °C) and run against a control of inoculum without substrate. The results obtained in the biochemical methane potential (BMP) tests showed that the ultimate methane yield ($Y_{M,ult}$) decreased considerably from 227 ± 23 to 107 ± 11 ml CH_4 at standard temperature and pressure (STP) conditions $g^{-1}\,VS_{added}$ when the ISR decreased from 3.0 to 0.5, showing a clear influence of the ISR on the methane yield coefficient. The biodegradability (BD) of the waste also decreased from 86% to 41% when the ISR varied from 3.0 to 0.5. A net total ammonia nitrogen (TAN) yield of 39.2 mg N $g^{-1}\,VS_{added}$ was obtained, and this value was not influenced by the ISRs assayed, which demonstrated the appropriate operation of the hydrolytic–acidogenic stage of the overall digestion process. A clear imbalance of the methanogenic process was observed at the lowest ISRs studied (0.5 and 0.8) due to a considerable increase in CODs and TVFA in the digestates. The profile of VFA was also influenced by the ISR, typical of the proteinaceous substrates.

1. Introduction

In Spain large quantities of waste from the sunflower oil industry are generated from the industrial processing of sunflower seeds into edible oils. This produces an organic agricultural by-product called sunflower oil cake (SuOC). The SuOC is a part of whole sunflower seeds, which remains after the extraction of the oil by extraction processes. This by-product can be broken down into three main components: a proteinaceous fraction, a lignocellulosic fraction and a soluble fraction [1]. It is also edible and has a high nutritional value, especially due to its high protein content. It has been used as animal feed (for animals such as ruminants, poultry and fish), but its high lignocellulosic material content limits this use [2]. The SuOC has other biotechnological applications: production of enzyme alfa-amylase [3], mushroom production [4], production of the antibiotic cephamycin C [5,6] and anti-microbial clavulanic acid [7]. Moreover, some pyrolysis experiments were carried out to obtain oil that could be used as fuel [8]. More recently, SuOC was used as an excellent raw material for the manufacturing of agro-materials [9].

Anaerobic treatment processes are used widely for the biological degradation of concentrated organic wastes. However, some doubts have been cast on the anaerobic treatment efficiency and process reliability since many potential residues for bioconversion are relatively non-biodegradable and

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Nomenclature

BD	biodegradability (%)
BMP	biochemical methane potential
COD	chemical oxygen demand ($mg\,O_2\,l^{-1}$)
CODt	total chemical oxygen demand ($mg\,O_2\,l^{-1}$)
CODs	soluble chemical oxygen demand ($mg\,O_2\,l^{-1}$)
HAc	acetic acid ($mg\,l^{-1}$)
HBu	butyric acid ($mg\,l^{-1}$)
HPr	propionic acid ($mg\,l^{-1}$)
HVa	valeric acid ($mg\,l^{-1}$)
ISR	inoculum to substrate ratio
NDF	neutral detergent fiber (wt%)
$P_{M,cum}$	cumulative methane production ($ml\,CH_4$ STP)
$P_{M,ult}$	ultimate methane production ($ml\,CH_4$ STP)
SuOC	sunflower oil cake
STP	standard temperature and pressure
TA	total alkalinity ($mg\,CaCO_3\,l^{-1}$)
TAN	total ammonia nitrogen ($mg\,N\,l^{-1}$)
TKN	total Kjeldahl nitrogen ($mg\,N\,l^{-1}$)
TS	total solids ($mg\,l^{-1}$)
TVFA	total volatile fatty acids ($mg\,COD\,l^{-1}$)
VFA	volatile fatty acids ($mg\,l^{-1}$)
VS	volatile solids ($mg\,l^{-1}$)
wt	weight (%)
$Y_{M,cum}$	cumulative methane yield ($ml\,CH_4\,STP\,g^{-1}\,VS_{added}$)
$Y_{M,ult}$	ultimate methane yield ($ml\,CH_4\,STP\,g^{-1}\,VS_{added}$)

in addition contain materials that are toxic to methanogenic micro-organisms. The biochemical methane potential (BMP) assay was developed as a standardized method to determine the ultimate biodegradability (BD) and associated methane yield during the anaerobic methanogenic fermentation of organic substrates. While the standardization of suitable aerobic test methods has already reached an advanced stage, there is no international standard anaerobic test method. One of the first and most referenced BMP methods was carried out by Owen et al. [10], but there was no clear description of all the parameters affecting the determination appeared. Some years later, Hashimoto [11] studied the influence of inoculum to substrate ratio (ISR) and fermentation time in the BMP test of wheat straw (*Triticum aestivum*), using 20 different ISRs that ranged from 10.91 to 0.03. Tong et al. [12] studied the methane fermentation of seven lignocellulosic materials with a few modifications to Owen's work. The main purpose of the study was to predict the BD, based solely on the lignin content of the materials. Although no clear ISRs were described in the article, they appeared to range between 1 and 2. Later, Turick et al. [13] studied the BMP of 32 woody biomass species and clones, concentrating on species of *Salix* (willow) and *Populus* (Poplar), using the Owen's system, at a fixed ISR of 2.0, based on the maximum methane production-rate constant obtained, but no justification of this fact was shown in the mentioned study. Owens and Chynoweth [14] carried out the BMP of municipal solid waste components with ISRs of between 3 and 4.

Finally, Chynoweth et al. [15] studied some factors that influenced the batch assay: inoculum source, inoculum to feed ratio and particle size. The ISR used was established again at 2.0 based only on the kinetic constants obtained.

Although some of the earlier work was carried out a few years ago, some more recent BMP studies still do not clearly describe the ISRs assayed [16]. These ISRs used were lower than 2.0 [17–19] and even the methane yields were compared at different ISRs [20].

The purpose of the study was to evaluate the BMP of SuOC, focusing on the influence of ISRs and the explanation of the results obtained based on the evolution and variation of chemical control parameters of the process with digestion time.

2. Materials and experimental methods

2.1. Substrate

The characteristics of SuOC are largely determined by the oil extraction process from which they are derived. Variations occur due to differences in seed, the number of hulls removed in processing and the processing method itself (mechanical or solvent extraction). SuOC usually contains 28–40% crude protein and 15–25% crude fibre [21].

The SuOC sample used in this study was taken from a sunflower oil factory located near Seville (Spain). Prior to using the substrate, it was sieved to give a fraction with a particle size lower than 2 mm, taking into account that more than 90% of the total particles of the SuOC had this size. The composition of the SuOC used in this study is detailed in Table 1.

Table 1 – Composition of the sunflower oil cake used

Dry matter (wt% as received)	92 (1)
Moisture (wt% as received)	8.0 (0.5)
Volatile solids (wt% dry basis)	93.4 (1.9)
Ash (wt% dry basis)	6.6 (0.1)
Chemical oxygen demand ($g\,O_2$/g dry basis)	1.08 (0.04)
Neutral detergent fibre (wt% dry basis)	48.4 (2.4)
Acid detergent fibre (wt% dry basis)	35.0 (1.8)
Lignin (wt% dry basis)	13.0 (0.6)
Total protein (wt% dry basis)	31.4 (1.6)
Fat (wt% dry basis)	1.7 (0.1)
Soluble sugars (wt% dry basis)	2.0 (0.1)
Polyphenols (wt% dry basis)	0.70 (0.03)
Carbon (wt% dry ash free basis)	43.6 (0.3)
Hydrogen (wt% dry ash free basis)	6.2 (0.1)
Nitrogen (wt% dry ash free basis)	4.6 (0.6)
Oxygen (wt% dry ash free basis)[a]	45.6 (0.5)

Mean values are averages of three determinations, with standard deviation in brackets.
[a] By difference.