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Feasibility of spent metalworking fluids as co-substrate for anaerobic co-digestion

Ivan Rodriguez-Verde [a], Leticia Regueiro [a], Rocio Pena [b], Juan A. Álvarez [b], Juan M. Lema [a], Marta Carballa [a,*]

[a] Department of Chemical Engineering, Institute of Technology, University of Santiago de Compostela, E- 15782 Santiago de Compostela, Spain
[b] AIMEN Technological Centre, C/Relva, 27A – Torneiros, E-36410, Porriño, Pontevedra, Spain

HIGHLIGHTS

- Spent metalworking fluids (SMWF) were co-digested with pig manure (PM).
- Biochemical methane potential of SMWF was very low (25%).
- Anaerobic co-digestion of SMWF and PM enhanced process efficiency (70%).
- *Pseudomonas* was corroborated as the main species during SMWF treatment.

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ABSTRACT

In this paper, anaerobic co-digestion of spent metalworking fluids (SMWF) and pig manure (PM) was evaluated. Three SMWF:PM ratios were tested in order to find the highest process efficiency. The best results (COD removal efficiencies of 74%) were achieved co-digesting a mixture with a SMWF:PM ratio of 1:99, w/w[1] (corresponding to 3.75 mL SMWF/$L_{reactor}$ week), which indicates that SMWF did not affect negatively PM degradation. Furthermore, two different weekly SMWF pulse-frequencies were performed (one reactor received 1 pulse of 3.75 mL/$L_{reactor}$ and the other 3 pulses of 1.25 mL/$L_{reactor}$) and no differences in COD removal efficiency were observed. Microbiology analysis confirmed that *Pseudomonas* was the predominant genus when treating anaerobically SMWF and the presence of a higher fraction of *Archaea* was indicative of good digester performance. This study confirms the feasibility of anaerobic co-digestion as an appropriate technology for treating and valorising SMWF.

1. Introduction

During machining processes, metal pieces need to be cooled and lubricated in order to achieve the desired result. These properties can be provided by metalworking fluids (MWF) or metal cutting fluids which are mixtures consisting of water (coolant properties), oil (lubricant properties) and several organic compounds as additives to provide mainly antioxidant and anticorrosive properties. MWF may also contain biocides in order to avoid the proliferation of microorganisms that could adversely affect its performance.

MWF are reused until their properties are not optimal anymore for the process and, at this time, they become a hazardous waste regarding international legislation (Directive 2008/98/EC). The residues are either called spent metalworking fluids (SMWF) or spent metal cutting fluids. Three types of treatment are usually considered: (a) physical methods (Burke, 1991; Chang et al., 2001; Gutiérrez et al., 2007; Hilal et al., 2004); (b) chemical methods (Burke, 1991; Kobya et al., 2008; Portela et al., 2003; Sánchez-Oneto et al., 2007); and (c) biological processes (Carvalhinha et al., 2010; Cheng et al., 2005; Jagadevan et al., 2013; Kim et al., 1992; Perez et al., 2006, 2007; Rodriguez-Verde et al., 2012; Van Der Gast et al., 2003). Nowadays, since non-oil based MWF with higher additive content are usually applied instead of oil-in-water emulsions (formulated with high oil concentration), biological treatments have had to face these changes which physico-chemical methods could not solve completely (Cheng et al., 2005).

Aerobic processes were thoroughly applied to treat SMWF (Cheng et al., 2005), but in general, they present some limitations, such as large energy costs due to the very high organic concentration present in SMWF. Anaerobic processes appear then as a suitable alternative for the treatment of this type of wastes with the additional advantage of energy production as biogas, although

* Corresponding author. Tel.: +34 881 816020; fax: +34 881 816702.
E-mail addresses: ivan.rodriguez@usc.es (I. Rodriguez-Verde), leticia.regueiro.abelleira@gmail.com (L. Regueiro), rpena@aimen.es (R. Pena), jaalvarez@aimen.es (J.A. Álvarez), juan.lema@usc.es (J.M. Lema), marta.carballa@usc.es (M. Carballa).

[1] w/w, wet weight basis.

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it should be considered that some compounds present in SMWF may become toxic, which may then deteriorate the process performance. The available literature on this topic is very scarce and most studies focused on the anaerobic treatment of wastewater streams containing SMWF, but not on SMWF itself. When treated in quite diluted concentrations (500 mg COD/L) in an anaerobic sequencing batch biofilm reactor in mesophilic range, organic matter removal efficiencies of up to 87% were attained, in terms of chemical oxygen demand (Carvalhinha et al., 2010). Operation at higher influent concentration (5,500 mg COD/L) was studied by Kim et al. (1992) resulting in a lower COD removal (65%) and showing a non-toxic effect on the microbial community. Similar elimination (70%) was obtained in thermophilic conditions with an influent concentration of approximately 2,000 mg COD/L (Perez et al., 2007), indicating that the increase of process temperature did not improve the performance.

All the afore-discussed studies treated diluted SMWF effluents, thus implying low quantities of SMWF and large volumes of dilution water. A similar but much more efficient approach can be the use of anaerobic co-digestion (ACo-D): one base substrate at high proportion and one or more co-substrates at lower fractions. Typical base substrates used in ACo-D are sewage sludge (Murto et al., 2004) or animal manure (Regueiro et al., 2012a); however, to the best of our knowledge, no studies focused on ACo-D of the latter substrates and SMWF are available in literature. Only Perez et al. (2006) studied the co-digestion of SMWF with wine distillery wastewater achieving a removal efficiency of 89%, although the biogas production rate was very low (0.006 $m^3/m^3_{digester}$ d).

The objective of this work was to evaluate the feasibility of anaerobic co-digestion of SMWF with pig manure (PM) in a lab-scale continuous stirred tank reactor (CSTR). Firstly, the physico-chemical characteristics of SMWF were determined as well as the biochemical methane potential (BMP), and later, the operational conditions enabling a stable continuous performance were established. Biomolecular techniques were applied in order to analyse the impact of SMWF on the microbial community structure of the anaerobic reactors.

2. Methods

2.1. Wastes and inoculum

PM was taken from a 3000-pig fattener farm and it was stored at 4 °C. Several batches of PM were used throughout the experimental period due to the impossibility of storage of the entire amount needed. SMWF were provided by AIMEN Technological Centre (Pontevedra, Spain) and they corresponded to the waste derived from the use of Quakercool 3604 metalworking fluid in several processes. Quakercool 3604 is a mineral oil aqueous solution with unspecified additives. MWF fabricants do usually not provide the precise composition of their products due to industrial secret matters. Only hazardous additives are specified but they were present in small quantities. Furthermore, MWF composition changes and some metal are dissolved during metalworking processes.

Both residues were characterised in terms of pH, total alkalinity (TA, g $CaCO_3$/L), total (TS, g TS/L) and volatile (VS, g VS/L) solids content, COD (g O_2/L), lipid content (g/L), total Kjeldahl nitrogen (TKN, g N-TKN/L) and ammonium (NH_4^+, g N-NH_4^+/L) concentration. In addition, total (TSS, g TSS/L) and volatile (VSS, g VSS/L) suspended solids, elementary analysis (C, H, N, O, S) and metals content (Fe, S, Ca, Mg, Al, K, Zn, Si, Mn, Cu, Ba, Ni, Cr, As, Sr, Nb, Co, Pb, Cd, Hg) were also determined in SMWF.

The inoculum used in both biochemical methane potential (BMP) tests and the anaerobic reactors was anaerobic granular biomass (20 g VSS/L) coming from an internal circulation reactor treating brewery wastewater.

2.2. Biochemical methane potential (BMP) tests

BMP tests were carried out in 500 mL bottles (375 mL of working volume) in triplicate following the protocol described by Álvarez et al. (2010). The bottles were filled with inoculum (5 g VSS/L), macro- and micro-nutrients solution, resazurin, L-cysteine and $NaHCO_3$ and pH was adjusted to 7 with NaOH or HCl. After the addition of the substrate, the liquid phase was bubbled with N_2 and the bottles were sealed with rubber stoppers and capped with plastic seals. After flushing the head space with N_2, the bottles were incubated in a shaker (120 rpm) at 37 °C.

2.2.1. BMP of SMWF

Three substrate-to-inoculum ratios (SIR, g COD/g VSS) were tested: 0.29, 0.62 and 0.97. In addition, one bottle (SIR: 0.32 g COD/g VSS) containing a volatile fatty acids (VFA) mixture (50% acetic acid, 25% propionic acid, 25% butyric acid; COD basis) as co-substrate (50% COD_{fed}), an abiotic (without inoculum) and a blank (without substrate) control were also included.

2.2.2. BMP of PM–SMWF mixtures

Five different mixtures (90:10, 75:25, 50:50, 25:75, 10:90; PM:SMWF, COD basis) were tested at a SIR ranging from 0.70 to 0.78 g COD/g VSS. An abiotic and a blank control were included as well.

Biogas production and composition were monitored over time. The evolution of methane production was fitted by the modified Gompertz Eq. (1) (Zwietering et al., 1990), where CH_4 (t) is the cumulative methane produced until time t (g COD–CH_4), P is the total methane produced (g COD–CH_4), F_{CH4} is the maximum methane flow rate (g COD–CH_4/d) and λ is the lag-phase (days).

$$CH_4(t) = P \cdot \exp\left\{-\exp\left(\frac{F_{CH_4} \cdot e}{P} \cdot (\lambda - t) + 1\right)\right\} \quad (1)$$

A liquid sample was taken on a weekly basis for COD and VFA analysis. At the end of the experiment, the bottles were opened and pH, residual COD and VFA were determined.

2.3. Anaerobic reactors

Two CSTR (IKA RW20, 80 rpm) made of glass with a working volume of 4 L were operated in mesophilic range (37 ± 1 °C). After inoculation (in-reactor concentration of 15 g VSS/L), the digesters were operated semi-continuously (once a day draw-off and feeding). Over the entire performance, the hydraulic retention time (HRT) was kept constant at 20 days. Temperature, pH, stirring speed and biogas flow were monitored on line. Other parameters (COD, ammonium and VFA) were measured off-line three times per week. Besides, biomass samples were taken from reactors in the most representative operational periods (days 150, 200 and 280) for microbiological analysis. Day 150 was chosen to study the differences between the reactor working with PM as a sole substrate and the one working with PM and SMWF in co-digestion. On day 200, the microbial response against VFA accumulation and high ammonium levels was evaluated. Finally, the differences between the two ways of feeding SMWF (1 or 3 pulses per week) were examined on day 280.

2.4. Operational strategy

The experiment comprised three periods, according to the feeding strategy applied.