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High-rate anaerobic treatment of Fischer–Tropsch wastewater in a packed-bed biofilm reactor

Mauro Majone [a,*], *Federico Aulenta* [a], *Davide Dionisi* [a], *Ezio N. D'Addario* [b], *Rosa Sbardellati* [b], *David Bolzonella* [c], *Mario Beccari* [a]

[a] *Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy*
[b] *Eni S.p.A, Refining and Marketing Division, via E. Ramarini 32, 00016, Monterotondo, Italy*
[c] *Department of Science, Technology and Market of Wine, University of Verona, via della Pieve 70, 37020 San Floriano, Verona, Italy*

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ABSTRACT

This study investigates the anaerobic treatment of an industrial wastewater from a Fischer–Tropsch (FT) process in a continuous-flow packed-bed biofilm reactor operated under mesophilic conditions (35 °C). The considered synthetic wastewater has an overall chemical oxygen demand (COD) concentration of around 28 g/L, mainly due to alcohols. A gradual increase of the organic load rate (OLR), from 3.4 gCOD/L/d up to 20 gCOD/L/d, was adopted in order to overcome potential inhibitory effects due to long-chain alcohols (>C6). At the highest applied OLR (i.e., 20 gCOD/L/d) and a hydraulic retention time of 1.4 d, the COD removal was 96% with nearly complete conversion of the removed COD into methane. By considering a potential of 200 tCOD/d to be treated, this would correspond to a net production of electric energy of about 8×10^7 kWh/year.

During stable reactor operation, a COD balance and batch tests showed that about 80% of the converted COD was directly metabolized through H_2^- and acetate-releasing reactions, which proceeded in close syntrophic cooperation with hydrogenotrophic and acetoclastic methanogenesis (contributing to about 33% and 54% of overall methane production, respectively). Finally, energetic considerations indicated that propionic acid oxidation was the metabolic conversion step most dependent on the syntrophic partnership of hydrogenotrophic methanogens and accordingly the most susceptible to variations of the applied OLR or toxicity effects.

1. Introduction

The Fischer–Tropsch (FT) process converts a mixture of CO and H_2 (i.e., syngas), possibly derived from coal or methane, into a range of hydrocarbons. It can hence be considered as an alternative to crude oil for the production of both liquid fuels (gasoline and diesel) and chemicals (in particular, 1-alkenes). The wastewater generated in the FT process is typically characterized by a high COD content (up to 30 gCOD/L), mainly comprising of alcohols, monocarboxilic organic acids, and hydrocarbons (Du Preez et al., 1985; Nijs and Jacobs, 1981). Due to its high strength (up to 30 gCOD/L) and large amounts (around 300 m^3/h) being typically generated by FT industrial plants (i.e., around 200 tCOD/d), anaerobic digestion is typically regarded as an ideal treatment technology for this type of industrial wastewater. However, most of the COD (up to 85%) in FT wastewaters is typically due to alcohols of different chain lengths (from methanol to decanol) and literature data

* *Corresponding author*. Tel.: +39 06 49913646; fax: +39 06 490631.
E-mail address: Mauro.Majone@uniroma1.it (M. Majone).
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on anaerobic treatability of alcohol-containing wastewaters are scarce (Mijaylova-Nacheva et al., 2006). Moreover, most of published studies almost exclusively focused on the anaerobic fate of short-chain alcohols such ethanol or methanol (Castilla et al., 2005; Dufresne et al., 2001; Han et al., 2005; Jeison et al., 2009; Paulo et al., 2003; Ruiz et al., 2002). Among these studies, Han et al. (2005) investigated the UASB treatment of a wastewater mainly composed of volatile fatty acids and ethanol, obtaining high conversion into methane up to organic loading of 13 gCOD/L/d; with similar substrates, other researchers (O'Flaherty and Colleran, 1999; O'Flaherty et al., 1999) also obtained almost complete COD removal; C3 and C4 alcohols were successfully treated in an hybrid (fixed bed-suspended biomass) reactor (Henry et al., 1996). On the other hand, long-chain alcohols are much less studied and there are some evidences that they can inhibit microbial activity (Carlsen et al., 1991; Kabelitz et al., 2003).

A previous study by this research group (Dionisi et al., 2007) had investigated the anaerobic treatment of a FT wastewater by means of batch tests. It was shown that long-chain alcohols (from 6 to 10 C atoms) exerted a strong inhibitory effect on the activity of unacclimated anaerobic sludge, with both acidogenic and methanogenic population being adversely affected. However, acidogenic activity resumed after long adaptation (about 20 days), followed by methane formation which recovered as soon as long-chain alcohols were depleted. Conversely, hydrocarbons were neither inhibitory nor biodegraded under the tested experimental conditions.

On the basis of such preliminary investigations, the present study aimed to investigate the feasibility of continuous anaerobic treatment of a synthetic FT wastewater in a packed-bed bioreactor. In order to prevent inhibition from long-chain alcohols, the reactor was started up with a low organic load, consisting of a modified feed deprived of long-chain alcohols. Subsequently, the organic load and long-chain alcohol concentration were progressively increased (up to 20 gCOD/L/d), while monitoring reactor performance in terms of COD removal, methane production, and effluent concentration of major components.

2. Materials and methods

2.1. *The Fischer–Tropsch wastewater*

Based on a typical composition of aqueous waste streams generated from the liquefaction of hydrocarbons with the Fischer–Tropsch process, a synthetic wastewater was prepared. The main components were alcohols (84.9% of overall COD), acids (10.7%) and hydrocarbons (4.5%). The synthetic wastewater was prepared in a mineral medium containing NH_4Cl (0.95 g/L), $MgCl_2 \cdot 6H_2O$ (0.1 g/L), $CaCl_2 \cdot 2H_2O$ (0.05 g/L), K_2HPO_4 (0.70 g/L), $NaHCO_3$ (8.4 g/L), resazurine (0.1% w/v, 1 mL/L), and metal solution (10 mL/L). The latter contained: $FeSO_4 \cdot 7H_2O$ (0.55 g/L), $MnSO_4 \cdot H_2O$ (0.086 g/L), $CoCl_2 \cdot 2H_2O$ (0.17 g/L), $ZnSO_4 \cdot 7H_2O$ (0.21 g/L), $NiCl_2 \cdot 6H_2O$ (0.02 g/L), $NaMoO_4 \cdot 2H_2O$ (0.01 g/L), H_3BO_3 (0.019 g/L), and nitriltriacetic acid (4.5 g/L). The complete composition of synthetic wastewater in terms of COD is reported in Table 1.

2.2. *The packed-bed anaerobic reactor*

The anaerobic reactor consisted of a 2 L Perspex column. The packed-bed consisted of Anox-Kaldnes AB (Lund, SE) KMT-k1 supports (height: 7 mm, diameter: 8 mm, specific surface 690 m^2/m^3, void fraction: 0.75), which filled the lower part of the column. The packed-bed occupied a volume of approximately 1 L. In the upper part of the reactor (above the packed-bed), a free volume (approx. 1 L) was left to facilitate effluent clarification and gas separation. The liquid effluent was continuously recirculated, in an upflow mode, at 35 mL/min through an internal heat exchanger, in order to maintain the desired temperature (35 °C) and a high degree of axial mixing. Along its length, the column was equipped with sampling ports. However, due to the high recirculation ratio adopted, no concentration profiles were typically observed along the flow path (data not shown) and the reactor was regarded as completely mixed. The volume of produced biogas was continuously recorded by using a Milligascounter® (Ritter, Bochum, DE).

Table 1 – Composition of the synthetic Fischer–Tropsch wastewater.

Compounds		C atoms	mg/L	mgCOD/L	% of COD
Short-chain Alcohols (SCA)	Methanol	1	2379	3568	12.7
	Ethanol	2	2523	5265	18.7
	Propanol	3	2303	5527	19.7
	Butanol	4	1720	4463	15.9
	Pentanol	5	993	2708	9.6
Total SCA				21 531	76.7
Long-chain Alcohols (LCA)	Hexanol	6	480	1355	4.8
	Heptanol	7	205	594	2.1
	Octanol	8	80	236	0.8
	Nonanol	9	28	84	0.3
	Decanol	10	9	27	0.1
Total LCA				2296	8.2
Volatile Fatty Acids (VFA)	Acetic	2	1009	1076	3.8
	Propanoic	3	691	1046	3.7
	Butanoic	4	344	625	2.2
	Pentanoic	5	99	202	0.7
	Hexanoic	6	24	53	0.2
Total VFA				3002	10.7
Hydrocarbons (HCH)	Pentane	5	68	250	0.9
	Hexane	6	25	90	0.3
	Heptane	7	6	20	0.1
	Pentene	5	204	545	1.9
	Hexene	6	75	199	0.7
	Heptene	7	16.7	44	0.2
	Acetone	3	50	107	0.4
Total HCH				1255	4.5
Total COD				28 084	100