The effect of trace elements on the performance efficiency of an anaerobic fixed film reactor treating a petrochemical effluent

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Abstract

The effect of trace elements on the anaerobic digestion of an effluent of Sasol – a coal to petroleum plant – was examined, using a downflow fixed film reactor. This effluent contained mainly monocarboxylic acids (6 700 mg/ℓ acetic acid) as well as small amounts of alcohols, ketones and hydrocarbons. The COD value was 12 800 mg/ℓ.

The addition of a first series of trace elements consisting of B, Ca, Mn, Zn, Mg, Co, Mo and Al, did not significantly affect the reactor efficiency. The application of a second series of trace elements, containing the above elements plus Si, Se, Ni and W, resulted in a marked increase in the reactor performance. The stimulatory effects observed were independent of sulphate.

Introduction

Anaerobic wastewater treatment is one of the major biological waste treatment processes and has been employed for many years in municipal sewage units. The process becomes attractive, especially when basic energy recovery and conservation are considered (Switzenbaum, 1983; Speece, 1983; Brune *et al.*, 1982).

As the anaerobic digestion of especially industrial wastewater becomes more popular, the lack of understanding of the fundamental process concepts becomes more pronounced. The intensive study of the microbiology and biochemistry involved, has helped to overcome many of the problems associated with methane production (Switzenbaum, 1983).

In recent years it has been shown that the methanogenic bacteria are representative of an unique phylogenetic and physiological group, namely the archaebacteria (Balch *et al.*, 1979). These organisms play a key role in the anaerobic digestion process. As a result of their slow growth rates and metabolic activity, they are regarded as the rate limiting factor in the process. Key nutritional factors, such as their requirement for trace elements, have recently been discovered. Certain trace elements (eg. Si, Se, Ni and W) are usually not required for normal bacterial growth or stimulation of growth. However, in studies on pure cultures of methanogens it has been shown that trace elements like F, Co, Mo, Na, Si, Se, Ni, W and Fe could, under certain conditions, stimulate methanogenesis or could be essential for their cell growth (Speece, 1983; Schönheit *et al.*, 1979; Perski *et al.*, 1981; Hoban and Van den Berg, 1979; Speece *et al.*, 1983). According to Switzenbaum (1983) this represents an important discovery, since the development of anaerobic wastewater treatment processes has been greatly delayed due to inadequate information on nutrient requirements.

While research in the field of methanogen biochemistry is progressing rapidly, little information is available regarding the effects of trace elements on the nett effectivity of anaerobic fixed film systems treating petrochemical effluents. The aim of this study was to determine whether higher kinetic rates could be accomplished by using trace element stimulation in the fixed film anaerobic treatment of a Sasol petrochemical effluent.

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Materials and methods

Reactor

Details of the downflow fixed film reactor used in this study are given in Figure 1. The reactor had a working volume of 3,5 litres and was operated at 35°C. Temperature and level controls, using temperature sensitive probes, were employed (Meyer *et al.*, 1983; Britz *et al.*, 1983). An inert cylindrical polyethylene bacterial carrier (length = 850 mm; ID = 50 mm; OD = 70 mm) was placed

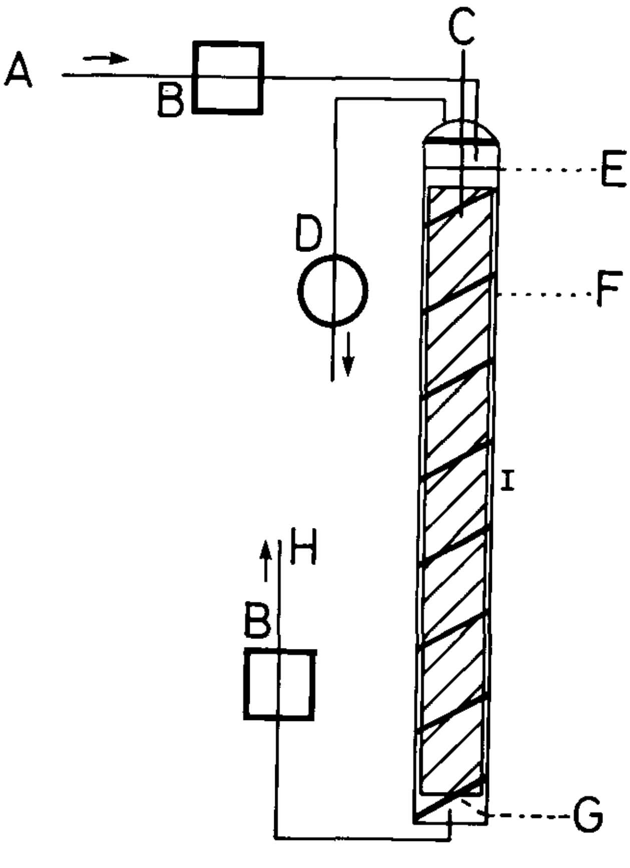

Figure 1
Diagram of the anaerobic downflow fixed film reactor (A – substrate feed; B – peristaltic pump; C – thermometer; D – gas collector; E – liquid level control; F – temperature sensor; G – heating tape with temperature control; H – reactor effluent; I – reactor column with bacterial carrier).

inside the reactor giving a surface area (cm^2) to liquid volume (cm^3) ratio of about 1. The substrate was continuously introduced at the top of the reactor at the required rate and the effluent was removed from the bottom. Gas exited at the top of the reactor and volumes were determined by means of a brine displacement system. Initially the reactor was filled with sludge from a local municipal anaerobic digester and was intermittently fed with an acetate-propionate solution (4 000 mg/ℓ) to promote the growth of methanogenic bacteria. The initial hydraulic retention time (HRT) was 20 days whereafter the loading rate was increased stepwise in response to the efficiency of substrate removal. After 30 days the acetate-propionate solution was replaced with the petrochemical wastewater. The flow rate was increased until an HRT of 3 days was obtained and steady state conditions persisted. Steady state conditions were assumed when the variation in gas production and volatile fatty acid removal was less than 10% during a period of five volume turnovers.

The hydraulic retention time and organic loading rate was kept constant at 3 days and 4,26 kg COD/m^3.d respectively throughout the study period. The study was conducted over a period of 195 days and was divided into two phases of 60 and 135 days respectively, according to the type of trace elements supplemented. Since the lack of trace elements in a substrate results in improper methane production (Speece, 1983) the first phase of the study, where trace element solution I was added, was considered as a control.

TABLE 1
COMPOSITION OF THE TWO TRACE ELEMENT SERIES USED, GIVEN AS TRACE ELEMENT (g) PER LITRE OF SUBSTRATE FED.

Trace element	Series I (Day 1 to 60)	Series II (Day 60 to 195)
B (as H_3BO_3)	$1{,}244 \times 10^{-5}$	$1{,}244 \times 10^{-5}$
Ca (as $CaCl_2$)	0,036	0,036
Mn (as $MnSO_4.5H_2O$)	$2{,}41 \times 10^{-4}$	$2{,}41 \times 10^{-4}$
Zn (as $ZnCl_2$)	$2{,}015 \times 10^{-4}$	$2{,}015 \times 10^{-4}$
Mg (as $MgCl_2.6H_2O$)	0,024	0,024
Co (as $CoCl_2$)	$0{,}91 \times 10^{-4}$	$0{,}91 \times 10^{-4}$
Mo (as MoO_3)	$6{,}6 \times 10^{-5}$	$6{,}6 \times 10^{-5}$
Al (as $AlCl_3$)	$8{,}1 \times 10^{-5}$	$8{,}1 \times 10^{-5}$
Se (as H_2SeO)	–	$9{,}2 \times 10^{-5}$
Si (as SiO_2)	–	$3{,}5 \times 10^{-6}$
W (as $Na_2WO_4.2H_2O$)	–	$1{,}67 \times 10^{-6}$
Ni (as $NiCl_2$)	–	6×10^{-6}

Petrochemical wastewater composition

The petrochemical wastewater was obtained from the Sasol I plant as effluent generated during the Sasol coal gasification process. The petrochemical wastewater used in this study had a COD value of 12 800 mg/ℓ and a total volatile fatty acid concentration of 9 355 mg/ℓ. The fatty acids consisted of acetic (72%), propionic (14%), iso-butyric (2%), n-butyric (8%), iso-valeric (1%) and n-valeric acid (3%). The wastewater also contained small amounts of phenols, alcohols, ketones and emulsified oils. After addition of KH_2PO_4 (500 mg/ℓ) and urea (500 mg/ℓ), neutralization to pH 6 (6M NaOH), boiling and subsequent filtering, the effluent was found to contain less than 0,1 mg/ℓ of Mg, Fe, Zn, Mn, Cr. The presence of other trace metals (Cu, Mo, Cd, Pb, Ni, Se, W) could not be detected. The effluent contained less than 1 mg/ℓ of $SO_4^{=}$.

Trace elements

Series I and II trace element solutions (Table 1) were added continuously with the use of a peristaltic pump independent of the substrate pump. Nitrilotriacetic acid was used as chelating agent (0,1% m/v) during the preparation of trace element stock solutions. Double glass distilled water was used throughout the study. The concentrations of the different trace elements were based on the concentrations used by Hungate and Stack, (1982), Belayev *et al.* (1983), Touzel and Albagnac (1983) and Brune *et al.* (1982).

Analyses

The chemical oxygen demand (COD) was determined according to Standard Methods (American Public Health Association, 1976). The volatile fatty acid (FVA) and gas composition were determined gas chromatographically, as previously described by De Haast *et al.* (1983). The amount of gas produced was measured using a brine displacement system and corrected for standard temperature and pressure (STP).

Results and discussion

The effect of the two trace element solutions on the effectivity of the fixed film anaerobic reactor, treating the petrochemical wastewater, is given in Table 2. With the addition of trace element solution I, a COD removal of 69% and total VFA removal of 72,2% was found. The supplementation of trace element series II resulted in a pronounced improvement in the process effectivity. After 10 days (day 70) an increase in COD and volatile fatty acids removal of 6,5% and 10,8% respectively, was obtained. The efficiency of the reactor improved relatively quickly during the first 10 days after the addition of trace element series II, but more gradually thereafter.

Sixty days (day 120) after the first addition of trace element series II, a slight decrease in operational efficiency was observed. This decrease in efficiency could possibly be ascribed to trace metal accumulation, and subsequently the addition of trace elements was stopped. After 6 days (2xHRT) the COD reduction began to increase again. A further nine days later the reactor once more reached maximum effectivity. This was 75 days after the first addition of trace elements series II (Table 2). These steady state conditions persisted for another 60 days of continuous operation, while addition of trace elements during this period was reduced to a third of the initial dosage.

It can be seen from Table 2 that the acetic acid removal, at day 135, had increased by 29,3% in respect to the value at day 60. This suggests a specific stimulatory effect of these elements on the methanogenic bacteria. The aceticlastic methanogens are the only organisms known to catabolize acetate anaerobically in the absence of light or exogenous electron acceptors such as sulphate (Bryant, 1979). It was also evident that an additional 58ℓ of methane (STP) was obtained from each kg of COD removed.

This improvement is in accordance with the statement made by Switzenbaum (1983) that higher kinetic rates could be achieved by using nickel stimulation. Speece *et al.* (1983) showed that the addition of nickel to acetate utilizing methanogens resulted in the highest methane production rates recorded in the

TABLE 2
THE INFLUENCE OF THE ADDITION OF TWO TRACE ELEMENT SOLUTIONS ON THE REACTOR EFFICIENCY AT DIFFERENT STAGES.

Parameter	Trace element Series I (Day 1 to 60)* (SI)	Trace element Series II (Day 60 to 195) (Day 70) (SII.1)	Trace element Series II (Day 60 to 195) (Day 130 to 135) (SII.2)	Maximum improvement (SII.2 – SI)
COD removal	69%	75,5%	93,5%	24,5%
Acetic acid removal	66%	78,8%	95,3%	29,3%
TVFA removal	72,2%	83,07%	94,6%	22,4%
Gas production (STP)	0,88 m^3/m^3.d	1,078 m^3/m^3.d	1,36 m^3/m^3.d	0,48 m^3/m^3.d
Gas yield (STP)	0,296 m^3/kg COD removed	0,355 m^3/kg COD removed	0,341 m^3/kg COD removed	0,045 m^3/kg COD removed
Methane content of biogas	84,6%	89%	91%	6,4%
Methane yield (STP)	0,252 m^3CH_4/kg COD removed	0,298 m^3CH_4/kg COD removed	0,310 m^3CH_4/kg COD removed	0,058 m^3CH_4/kg COD removed

*Data was obtained during the last 10 days.

literature. This is in accord with the discovery that methanogens contain high concentrations of factor F430 which has been shown to be a nickel tetrapyrole (Diekert *et al.*, 1980; Diekert *et al.*, 1981). Scherer and Sahm (1981) found that selenium in a concentration of 10^{-7} M stimulated the growth of an aceticlastic methanogen. Selenium has also been found to be a component of one of the formate dehydrogenases of *Methanococcus vannielii,* while tungsten has been reported (Jones and Stadtman, 1977) to be an essential trace element for the optimum growth of *Methanococcus vannielii.*

Most of the research up to date on the effect of trace element stimulation was carried out on pure or enriched methanogenic cultures. The results obtained from this study show that higher kinetic rates in a fixed film reactor are possible using controlled trace element stimulation. The improvement in the effectivity of the anaerobic fixed film reactor used in this study can certainly be ascribed to the beneficial addition of Si, Se, W, and Ni and their effect especially on the methanogenic population.

Although the requirement for certain trace elements contributes to the stringent growth requirements of the methanogenic bacteria, stimulation in the order of magnitude observed in this experiment cannot be ignored. More in-depth research still needs to be done in order to determine the overall contribution of each trace element, either singly or in combination, to anaerobic digestion systems.

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