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Fate and effect of quaternary ammonium compounds on a mixed methanogenic culture

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ABSTRACT

The potential inhibitory effect of four quaternary ammonium compounds (QACs) and Vigilquat®, a commercial sanitizer which is a mixture of the four QACs, was investigated at concentrations up to 100 mg/L using a mixed, mesophilic (35 °C) methanogenic culture. Dextrin and peptone were used as the carbon and energy sources. A batch assay conducted at a range of QAC concentrations showed that QACs were inhibitory to methanogens at and above 25 mg/L. Methanogenesis was more susceptible to QAC inhibition than acidogenesis. Adsorption of QACs on biomass was successfully simulated with the Freundlich isotherm equation. The inhibitory effect of Vigilquat® on the mixed methanogenic culture was also investigated in a batch reactor fed with dextrin and peptone. Methanogens were inhibited when the total QAC concentration reached 30 mg/L and volatile fatty acids (VFAs) accumulated. However, methane production recovered in 57 days of incubation, and all VFAs were consumed, suggesting that a prolonged incubation period is necessary for the methanogens to overcome the transient inhibition at a relatively low QAC concentration. None of the QACs tested in this study was biodegraded under methanogenic conditions.

1. Introduction

Quaternary ammonium compounds (QACs) are organic compounds that contain four functional groups attached covalently to a positively charged central nitrogen atom (R_4N^+). These functional groups (R) include at least one long chain alkyl group and the rest are either methyl or benzyl groups. QACs are extensively used in domestic and industrial applications as surfactants, emulsifiers, fabric softeners, disinfectants and corrosion inhibitors (Garcia et al., 1999; Patrauchan and Oriel, 2003).

Most uses of QACs lead to their release into wastewater treatment systems or the environment. QACs are persistent in the environment (Neu, 1996) and toxic to aquatic life (Kummerer et al., 1997; Nalecz-Jawecki et al., 2003). The fate of QACs in aerobic biological treatment systems has been widely studied. QAC biodegradability, ranging from 0% to 100%, has been reported in activated sludge systems; however, the extent of biodegradation varies depending on the QAC concentration, structure, microbial acclimation and presence of QAC resistant/degrading microorganisms. Certain microorganisms that are resistant to QACs and capable of QAC degradation have been isolated (van Ginkel et al., 1992; Nishihara et al., 2000; Al-Ahmad et al., 2000; Patrauchan and Oriel, 2003). However, because QACs have high affinity to adsorb onto (bio)solids, adsorption outcompetes biodegradation and therefore, QACs are transferred to anaerobic digesters as part of the waste activated sludge (Boethling, 1994). It was reported that QAC concentrations may reach 4–50 mg/L in anaerobic digesters of sewage treatment plants (ECTOC, 1993; Garcia et al., 1999). QAC concentrations may exceed these levels in biological treatment systems of

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industrial facilities, such as food processing, that extensively use QACs. Under anaerobic conditions, there is no evidence of mineralization of QACs that contain alkyl or benzyl groups (Battersby and Wilson, 1989; Federle and Schwab, 1992; Garcia et al., 1999, 2000), most likely because of the highly reduced nature of these substituent groups. Moreover, QACs are inhibitory to anaerobic microbial processes such as methanogenesis (Battersby and Wilson, 1989; Garcia et al., 1999, 2000). In spite of the fact that the presence of QACs in anaerobic treatment systems is inevitable, their fate and effect under anaerobic conditions have not been studied extensively. In addition, information on the effect of QACs on specific physiological groups participating in the complex anaerobic digestion process is presently lacking.

The objectives of this research were to: (a) evaluate the potential inhibitory effect of selected QACs on acidogenesis and methanogenesis in a mixed, mesophilic (35 °C) methanogenic culture; and (b) quantify the fate and phase distribution of the selected QACs in the same culture. Assays were conducted using serum bottles (batch) and a fed-batch reactor at a range of QAC concentrations.

2. Materials and methods

2.1. Quaternary ammonium compounds (QACs)

Vigilquat® (VQ) and its four active quaternary ammonium ingredients were used in this study. VQ (Alec C. Fergusson, Inc., Frazer, PA, USA) is comprised of four QACs and ethanol as follows (molecular formula, % w/v): *N*-alkyl (C_{12}–C_{16}) *N*,*N*-dimethyl *N*-benzyl ammonium chloride ($C_{21-25}H_{38-46}NCl$, 3%), didecyl dimethyl ammonium chloride ($C_{22}H_{48}NCl$, 1.35%), dioctyl dimethyl ammonium chloride ($C_{18}H_{40}NCl$, 0.9%), octyl decyl dimethyl ammonium chloride ($C_{20}H_{44}NCl$, 2.25%) and ethanol (C_2H_5OH, 1.5%). Octyl decyl dimethyl ammonium chloride was supplied as a mixture of octyl decyl (40%), dioctyl (16%) and didecyl (24%) dimethyl ammonium chlorides. The individual QACs had a purity of between 50% and 80%. Stock solutions (10,000 mg/L) of each individual QAC were prepared based on the active ingredient purity and concentration. Individual QACs are hereafter abbreviated based on their functional groups (R_1 and R_2)(e.g., didecyl dimethyl ammonium chloride is referred to as didecyl). The chemical oxygen demand (COD) of each of the QACs in 200 mg QAC/L solution was as follows (in mg COD/L): alkyl benzyl, 629.5±27.1; didecyl, 622.2±23.5; dioctyl, 609.8±19.1; and octyl decyl, 603.1±6.4.

2.2. Mixed methanogenic culture

A mixed, methanogenic culture, developed with inoculum obtained from a mesophilic, municipal anaerobic digester and maintained fed-batch with a 35-d solids retention time at 35 °C was used as seed in all assays reported here. The culture was fed with 8 g/L dextrin and 4 g/L peptone (in the feed) and anaerobic culture media as reported by Beydilli and Pavlostathis (2005) and amended with 0.5 g/L $Na_2S \cdot 9H_2O$ and 3.5 g/L $NaHCO_3$. The culture was fed twice a week corresponding to an average organic loading rate of 0.34 g COD/L-day. The steady-state gas-phase methane and carbon dioxide concentration of this culture was 60.7±0.5% and 39.2±0.4% (mean±standard deviation), respectively. The steady-state total (TS) and volatile solids (VS) concentration of this culture was 6.9±0.3 and 2.2±0.1 g/L (mean±standard deviation), respectively.

2.3. Batch inhibition assay

A batch assay was performed to investigate the potential inhibitory effect of VQ, alkyl benzyl, didecyl, dioctyl and octyl decyl on the mixed methanogenic culture. The assay was conducted in 160-mL serum bottles (100 mL liquid volume) sealed with rubber stoppers and aluminum crimps and flushed with helium gas for 15 min before any liquid addition. An aliquot of 80 mL of mixed liquor from the mixed methanogenic culture taken at the end of a 7-day feeding cycle was anaerobically transferred to each serum bottle along with 15 mL of culture media. A dextrin/peptone solution (D/P), which served as carbon/energy source, and QACs at desired concentrations were added and the total liquid volume was adjusted to 100 mL with deionized water (DI). The D/P COD in the bottles was 1200 mg/L. The first culture series included six bottles that were amended with VQ resulting in total QAC concentrations of 10, 15, 25, 37.5, 50 and 100 mg/L. The other four culture series were prepared with alkyl benzyl, didecyl, dioctyl or octyl decyl, respectively. Each culture series had five bottles that were amended with individual QACs resulting in total QAC concentrations of 10, 25, 50, 75 and 100 mg/L. The QAC concentrations were selected according to literature reports, which state that QAC concentrations in anaerobic digesters may range from 4 to 10.5 mg/g-dry solids (ECTOC, 1993; Garcia et al., 1999). For our culture, which had 6.12±0.02 g TS/L, this range corresponds to QAC concentrations from 25 to 65 mg/L. Based on the expectation that QACs will favor solids, their concentration range was increased to 100 mg/L. Two additional culture series were prepared: seed blank and reference which consisted of only seed, culture media and DI water, and seed, culture media, DI water and D/P (1200 mg COD/L), respectively. Each culture series, including blank and reference, was prepared in triplicate. The initial pH in all culture series was 7.1±0.1. All culture series were incubated in the dark at 35 °C and the bottles were agitated daily by hand. Throughout the incubation period, the total gas volume produced and its methane and carbon dioxide content were measured. At the end of the incubation period, the pH, volatile fatty acids (VFAs) concentrations, as well as the total and liquid phase QAC concentrations were measured. The total amount of methane and VFAs produced in each culture series throughout the incubation period was expressed in COD units. The COD processed as methane or VFAs was normalized relative to the total COD processed in the reference series and used to evaluate the inhibition of methanogenesis and acidogenesis in the culture series amended with QACs.

2.4. QAC phase distribution test

The phase distribution of QACs in the mixed methanogenic culture was evaluated at the end of the batch inhibition assay.