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Anaerobic treatment of p-acetamidobenzene sulfonyl chloride (p-ASC)-containing wastewater in the presence or absence of ethanol in a UASB reactor

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ABSTRACT

A lab-scale UASB reactor was operated for the treatment of p-acetamidobenzene sulfonyl chloride (p-ASC)-containing wastewater with and without ethanol for 210 days. The influence of the organic loading rate on the performance of reactor by step-decreasing HRT reduction/step-increasing the concentration of p-ASC was evaluated. Almost complete degradation of 50 mg/l p-ASC and COD removal efficiency (79.5%) was noticed with a COD removal of 79.5% at HRT of 0.5 day or longer and an applied p-ASC loading rate below 120 mg/l/day. No inhibition to the performance of this reactor was observed even at a p-ASC concentration up to 1000 mg/l. Of interest that despite the absence of sulfate in the feed, a certain quantity of sulfate and sulfide was simultaneously generated in the effluent. The trial result in the absence of ethanol demonstrated that p-ASC could be used as the sole source of carbon and energy. Clone libraries for the archaeal and bacterial communities were constructed for a biomass sample taken on day 190. The majority of bacterial clones were represented by *Proteobacteria*, followed by *Thermotogae*, *Bacteroidetes* and *Firmicutes*. Bacterial groups within the phyla *Clostridia* might be responsible for the desulfonation of p-ASC.

Introduction

Aromatic sulfonates include a wide range of chemicals and are extensively applied as important industrial chemicals, especially in the dye and pharmaceutical industries. The presence of a sulfonated group makes these compounds highly water-soluble (Tan et al., 2005), which results in the generation of large volumes of high strength industrial waste streams (Zerbinati et al., 1997). The dominant approach to remove organic matter from high strength industrial wastewater is anaerobic digestion due to the low energy input required, the sludge yield and the production of biogas as clean fuel. Two sulfonated azo dyes (Acid Orange 7 and Direct Red 254) have been observed to be effectively degraded in a methanogenic UASB reactor (Brás et al., 2005). However, it has taken time to understand the anaerobic treatability of linear alkylbenzene sulfonate (LAS), which historically had been considered to severely impede methane production and persist during anaerobic treatment. It was reported by Prats et al. (1997) that LAS can be anaerobically degraded in the presence of various electron donors. Until now, the treatability of the aromatic sulfonates-containing wastewater under anaerobic conditions could only be elucidated through experimental approaches.

p-Acetamidobenzene sulfonyl chloride (p-ASC), is a derivative of sulfonated aromatic amines as shown in Fig. 1. It has been applied as an intermediate in the synthesis of p-aminobenzene sulfonamide (sulfanilamide, SN), one of the most frequently used sulfonamide type antibacterial medicines (Tan et al., 2011). Since the synthesis operations in pharmaceutical manufacturing industries usually generate larger volumes of wastewater (Chelliapan et al.,

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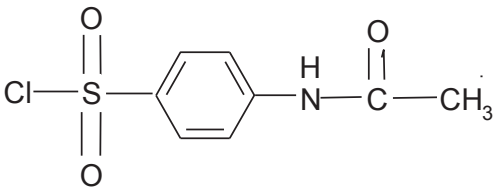

Fig. 1. Chemical structure of p-acetamidobenzene sulfonyl chloride (p-ASC).

2011), it is vital that wastewater containing p-ASC and other organic compounds is treated both effectively and economically during the SN production process. The reduction of azo dyes results in the formation of aromatic amines that mostly cannot be metabolized anaerobically. The exception of a few examples bearing hydroxyl and carboxyl groups can be fully degraded under methanogenic conditions (Razo-Flores et al., 1996). The conclusion can be also confirmed in an earlier study, which show that sulfonated aromatic amines are not readily degraded (Lange et al., 1995b). Tan et al. (2005) investigated the biodegradation of ten sulfonated aromatic amines including 2,4-diaminobenzenesulfonic acid, 1-aminonaphthalene-4-sulfonic acid, etc. in both aerobic and anaerobic conditions. None of the sulfonated aromatic amines tested were degraded anaerobically, while aerobic degradation was only observed with the inoculum sources that were historically polluted with sulfonated aromatic amines. To the best of our knowledge, almost no literature has been published so far on anaerobic degradation of p-ASC. In this study, a USAB reactor was established to treat p-ASC-containing wastewater under different conditions for a period of 210 days. The performance of the reactor was evaluated by following the changes of the p-ASC, COD and volatile organic acid concentrations in the effluent and the methane production rate. At the same time, clone libraries for the archaeal and bacterial communities were constructed for a biomass sample taken on day 190 to analyze the microbial population possibly involved in p-ASC degradation. The study could provide useful information for the treatment of wastewater containing p-ASC or similar compounds.

Materials and methods

Experiment set-up

The UASB reactor was made of a plexiglass cylinder with an internal diameter of 100 mm and a working volume of 6 l, as shown in Fig. 2. The reactor was water-jacketed to keep a constant temperature at 37 ± 2 °C. The produced gas was sequentially absorbed by a 3 N NaOH solution and soda lime pellets to remove H_2S and CO_2, respectively, and then recorded by a wet gas meter.

Reactor operation

The mesophilic UASB reactor was inoculated with 3 l granule sludge partly from a UASB reactor treating pharmaceutical wastewater containing p-ASC for one year and partly from a full-scale UASB reactor treating food manufacturing wastewater. The initial sludge concentration was 46.5 g VSS/l. Synthetic wastewater consisting varying concentrations of p-ASC with and without ethanol was prepared and fed into the reactor at different stages over a period of 200 days, as detailed in Table 1. The initial OLR (organic loading rate) was 1.0 g COD/l/day, corresponding to an initial hydraulic retention time (HRT) of 3.5 days. Then the OLR was elevated to around 24.0 g COD/l/day by shortening HRT stepwise in Stage I. Thereafter, in Period II, the OLR was decreased backward to 7.0 g COD/l/day (HRT 0.5 day) to investigate the recovery ability of the reactor. The impacts of p-ASC to anaerobic treatment were evaluated by increasing p-ASC concentration in Stage III. Finally the reactor was operated without ethanol in Stage IV.

Analytical methods

The chemical oxygen demand (COD), pH, soluble sulfide, volatile fatty acids (VFA) and volatile suspended solids (VSS) were determined according to the standard analytical procedures published by the APHA (1998). Prior to COD measurement, the solution was aerated to oxidize S^{2-} to S deposit in order to prevent the interference by sulfide (Sun and Guan, 2009). The sulfide concentration in the effluent was measured using iodometric method, while the

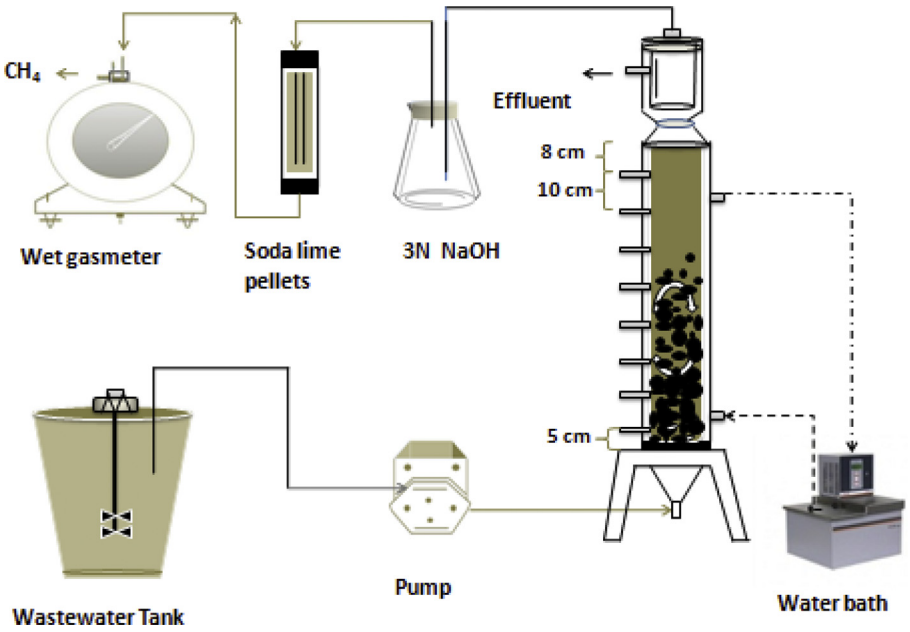

Fig. 2. Schematic diagram of the UASB set-up.