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Accurate assessment of the biodegradation of cationic surfactants in activated sludge reactors (OECD TG 303A)

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ABSTRACT

The continuous-fed activated sludge test (OECD TG 303A) was used to predict the removal of cationic surfactants from wastewater in activated sludge plants. However, a method to differentiate between adsorption and biodegradation is not provided in these guidelines. Assessment of removal by biodegradation was possible with analysis of the surfactant present in mixed liquid suspended solids in combination with a simple equation. This equation was derived from the mass balance of the activated sludge unit in steady state. The removal by biodegradation of decylamine, tetradecylamine, octadecylamine, dioctadecylmethylamine and dioctadecyldimethylammonium chloride that have different capacities to adsorb was $>99.9\%$, $>99.9\%$, 98.2%, 94.2%, and 69.0%, respectively. The total removal of all five cationic surfactants from the influent was $\geq 98.8\%$. The removal of octadecylamine spiked at different influent concentrations indicated first order kinetics.

1. Introduction

Cationic surfactants combine hydrophobic and hydrophilic properties in one molecule. The hydrophobic part consists of alkyl chains ranging from C8 to C22 originating from both natural and synthetic sources. The hydrophilic part of cationic surfactants carries a positive charge, which is usually associated with a nitrogen atom contained in an amine or quaternary ammonium group. Quaternary ammonium compounds are permanently charged, independent of the pH of the solution. Primary, secondary and tertiary amines are considered quasi-cationic, because the nitrogen atom usually is protonated under acidic conditions (Visek, 2003). Use of cationic surfactants is based on the following properties: surface activity, adsorption onto negatively charged solids, biocidal activity and their reaction with anionics. Because of these properties cationic surfactants are used in a number of applications such as fabric softeners, disinfectant, demulsifiers and emulsifiers. Due to these uses cationic surfactants end up in wastewater and are subsequently treated in biological wastewater treatment plants. Information on the fate of cationic surfactants in biological treatment plants is of greatest importance to assess their environmental risks.

The main processes determining the fate of organic substances in biological treatment systems are (a)biotic degradation, adsorption and volatilization. The fate of cationic surfactants will be primarily determined by biodegradation and adsorption because losses due to volatilization are not expected to occur (Ginkel, 1995). Adsorption and biodegradability are most often determined separately in batch experiments. The most important parameter for the evaluation of the adsorption is the sorption coefficient (K_d). The K_d normalized to the organic carbon content of the sorbent (K_{oc}) is regularly used for comparison of the adsorption potential of chemicals. Cationic surfactants with one to two alkyl chains of ≥ 2 carbons atoms are rapidly biodegraded (Ginkel and Kolvenbach, 1991; Ginkel et al., 2003; Ginkel, 2004; Qin et al., 2005). These cationic surfactants with the exception of dialkyldimethylammonium compounds with alkyl chain lengths of >12 carbon atoms are even classified as readily biodegradable (Ginkel, 2004). The extent of biodegradation and adsorption in activated sludge systems is subsequently evaluated through modeling using the data obtained in batch experiments (Struijs et al., 1991; Cowan et al., 1993; Wierich and Gerike, 1981). This approach, however, ignores mutual influences of biodegradation and adsorption and is consequently almost certainly inaccurate to fully assess biodegradation.

In the continuous-fed activated sludge (CAS) test (OECD TG

Abbreviations: CAS, continuously-fed activated sludge; OECD TG 303A, organization for economic co-operation and development test guideline 303A; MLSS, mixed liquid suspended solids; SPME, solid-phase microextraction; K_d, sorption coefficient; K_{oc}, organic carbon–water partition coefficient; K_{ow}, octanol–water partition coefficient; HRT, hydraulic retention time; SRT, sludge retention time; SS, suspended solids; NPOC, non purgeable organic carbon; COD, chemical oxygen demand; ASE, accelerated solvent extraction; LC–MS/MS, liquid chromatography–mass spectrometry; m/z, mass-to-charge ratio

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303A) simulating activated sludge treatment, adsorption and biodegradation can be concomitantly assessed. The main operating parameters of CAS units i.e. hydraulic retention time (HRT) and sludge retention time (SRT) are strictly maintained (OECD, 2001a). This test does assess biodegradation and adsorption in a continuously operated system although a method to differentiate between removal by biodegradation and adsorption is not provided.

In this paper a simple expression was derived which allows clear distinction between removal by biodegradation and adsorption of cationic surfactants in a CAS test operated under steady state conditions. Concentrations of five cationic surfactants with varying capacities to adsorb were determined in the influent, effluent and mixed liquid suspended solids (MLSS, activated sludge). The analysis allowed determination of the biodegradation of these cationic surfactants in continuously operated biological treatment systems.

2. Materials and methods

2.1. Chemicals

Decylamine (95%), tetradecylamine (95%), octadecylamine (≥ 99%), dioctadecylmethylamine (≥ 99%), dioctadecyldimethylammonium chloride (≥ 97%), were obtained from Sigma Aldrich (Zwijndrecht, The Netherlands). Chemical structures of these cationic surfactants are presented in Fig. 1. Stock solutions/suspensions of these surfactants were prepared using deionized water from a water purification system. Tween 80 used as emulsifier, silica gel (Davisil grade 636, pore size 60 Å, 35–60 mesh, ≥ 99%) used in the extraction procedure and all other chemicals used (reagent grade) were purchased from Sigma Aldrich.

2.2. Activated sludge and domestic sewage

Secondary activated sludge and primary settled sewage were collected weekly from a municipal wastewater treatment plant Nieuwgraaf in Duiven, The Netherlands. This treatment plant consists of mechanical and biological stages, including a nitrification and denitrification step, for the treatment of predominantly domestic wastewater. The plant operates with an HRT of 0.5–1 day and SRT of 20–30 days. The approximate concentrations of chemical oxygen demand (COD), kjeldahl-nitrogen and total phosphorous in the primarily settled sewage are 0.6 g/L, 0.05 g/L and 7 mg/L, respectively. The primary settled sewage was buffered with $NaHCO_3$ (0.1 g/L) and stored at − 20 °C until required. Secondary activated sludge was stored in a conical flask at room temperature under continuous stirring for one week at the most.

2.3. Operation of CAS units

The CAS tests were performed according to OECD test guidelines using reactors constructed of glass (OECD, 2001a; Swisher, 1987). The units consisted of an aeration vessel capable of holding 0.35 L from which the liquor was passed continuously to a settler of 0.2 L (Fig. 2). A test unit, dosed with domestic wastewater supplemented with a cationic surfactant, was always operated in combination with a control unit fed with domestic wastewater only. The units were started with secondary activated sludge at a concentration of 3 g/L dry weight. Aeration and mixing was achieved by operating an air-lift through a capillary on the bottom. A sludge retention time of 10 days was achieved by the daily removal of 35 mL of MLSS from the aeration vessel. An activated sludge concentration between 2 and 3 g/L dry weight was maintained through addition of secondary activated sludge collected. Domestic sewage in a container kept at 4 ± 1 °C was fed at a rate of 1.4 L/day resulting in a HRT of 6 h. Both units were preconditioned for one week. After this period ≥ 90% removal of non purgeable organic carbon (NPOC) from the domestic wastewater was found in both units. Subsequently, wastage of the sludge was started and cationic surfactants were dosed directly to the aeration vessel of the CAS reactor using a syringe pump. Decylamine was dosed using an aqueous solution whereas the poorly water-soluble cationic surfactants were added as suspension prepared with Tween 80 (1:1 w/w). The content of the syringe was continuously agitated with a small magnetic stirrer bar inside the syringe to prevent precipitation of suspended particles. Dioctadecyldimethylammonium chloride was dosed to the reactor at a nominal influent concentration of 10 mg/L. The other surfactants were added to the units at 50 mg/L. Octadecylamine was also tested at influent concentrations of 5 and 0.5 mg/L.

2.4. Analytical methods

Dry weight concentrations of the MLSS were determined by filtering activated sludge over preweighed 12 μm cellulose nitrate filter. Cellulose nitrate filters with 0.45 μm pore size were used to determine the dry weight concentration of suspended solids (SS) present in the effluent. Filters were dried for 1.5 h at 104 °C and weighed after cooling. Dissolved oxygen concentrations, temperature and pH in the CAS units were determined with an electrochemical oxygen sensor, a thermo couple connected to a data logger and a pH meter, respectively. Prior to analysis suspended solids were removed from influent and effluent samples by filtration using 8 μm cellulose nitrate filters. NPOC concentrations were determined in effluent samples of the control and test unit sampled between day 40 and 60 upon introduction of the surfactant. The units were at steady state during the whole sampling period. NPOC analyses were performed using a total organic carbon analyser which uses a catalytic combustion followed by infrared detection of the produced carbon dioxide (Shimadzu Corporation, ‘s-Hertogenbosch, The Netherlands). Ammonium, nitrite, and COD concentrations were analyzed spectrophotometrically in influent and effluent samples of the control CAS units using standard test kits with colorimetric methods (Hach Lange, Düsseldorf, Germany). Ammonium, nitrite and COD were measured after 14 and 60 days following the introduction of the surfactant.

Cationic surfactant concentrations in the MLSS and effluent of the CAS units were determined in samples taken during a two weeks period at steady state conditions of the CAS units. Samples were preserved upon sampling by addition of H_2SO_4 to give a pH of approximately 2. Acidified effluent sampled over a period of 24-h (1 L) was filtered using 8 μm cellulose nitrate filters prior to dilution with leaching solution. The leaching solution consisted of 100 g/L $MgCl_2 \cdot 6H_2O$ in methanol:2-propanol (50:50 v/v). Activated sludge samples (10 mL) were centrifuged for 10 min at 1500 RCF. Supernatant of the samples was diluted with leaching solution. $MgCl_2 \cdot 6H_2O$ (1 g) and sillica gel (2 g) was added to the sludge residue in the centrifuge tube. After thorough mixing, the content of the centrifuge tube was transferred into an 11 mL stainless steel accelerated solvent extraction (ASE) cell. This cell was placed in a Dionex ASE200 and the test substance was extracted from the sludge residue using methanol:2-propanol (50:50 v/v) as eluent. The following extraction program was used: preheat 5 min; heat 6 min; static 5 min; flush 50 vol%; purge 90 s; cycles 3; pressure 1500 psi; temp 125 °C. Extract of the ASE cell was collected and brought up to volume using leaching solution. The centrifuge tube used to mix the activated sludge with the $MgCl_2 \cdot 6H_2O$ and silica gel was rinsed with leaching solution. Dilutions in leaching solution of effluent samples, supernatant and extracts of the activated sludge samples, and the rinsing fluid were