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ORIGINAL ARTICLE

Oxidation of Sodium Dodecylbenzenesulfonate with Chrysotile: On-line Monitoring by Membrane Introduction Mass Spectrometry

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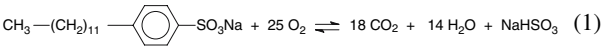
Abstract Chrysotile was tested for anionic surfactant (SDBS) removal from aqueous solutions. Results showed that the reduction was due to a catalytic process onto the chrysotile surface, which is formed of hydroxyl groups. Trap and release membrane introduction mass spectrometry using a modified direct insertion membrane probe (DIMP-T&R-MIMS) was used to monitor on-line SDBS oxidation by air in an aqueous alkaline media containing chrysotile. It was possible to estimate the amount of CO_2 formed in SDBS catalyzed reaction through quantification of CO_2 formed by the hydrolysis of $MgCO_3$. A mass balance for the SDBS reaction is proposed. DIMP-T&R-MIMS monitoring identified no VOCs or SVOCs as degradation intermediates, but CO_2 was detected to account for SDBS degradation. Hence, simple chrysotile adsorption is excluded as a main process of SDBS consumption, and a "SDBS in-CO_2 out" mechanism on the chrysotile surface accounts for the experimental observations.

Keywords Surfactant degradation · SDBS · Oxidation · CO_2 determination · Online monitoring · Membrane probe

Introduction

Sodium dodecylbenzenesulfonate (SDBS), a common and efficient surfactant, is used extensively in many human activities: in domestic, industrial, commercial and agricultural applications. Because of this widespread use in domestic and industrial detergents, SDBS is a common water pollutant [1]. Its biodegradation by molecular oxygen (Eq. 1) proceeds via *w*-oxidation and subsequent *b*-oxidation, and by ring opening, which is the slowest and rate determining step taking up to 15 days to proceed [2].



(1)

To speed SBDS degradation, a variety of advanced oxidative processes have been tested, and evidence has been provided that chrysotile also acts as a catalyst for this reaction [3]. Chrysotile is a hydrated magnesium silicate of the serpentine group of minerals whose chemical composition may be given stoichiometrically as $Mg_3Si_2O_5(OH)_4$. Its major use is in cement composites, but new applications have explored its action as an efficient catalyst or catalyst support [4–6].

Experiments have been carried out with SDBS aqueous solutions above the critical micelle concentration (CMC) in the presence of chrysotile fibres and it was observed that SDBS consumption is up to 20% after 2 h, and as much as 70% after 24 h [3].

Nevertheless, this relatively fast consumption could either involve chrysotile-catalyzed oxidation or simple SDBS adsorption onto chrysotile surface. A rapid, direct, sensitive and ideally on-line technique for analysis of organics in water would therefore be ideal for monitoring the aqueous SDBS oxidation and to prove the SDBS consumption/degradation process.

Membrane introduction mass spectrometry (MIMS) [7–9], particularly the trap and release technique (T&R-MIMS) [10, 11], is highly suitable for the combined monitoring of both volatile organic compounds (VOC) and

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semi-VOC (SVOC) in aqueous solutions. T&R-MIMS benefits both from the rapid and selective transport of VOCs through a hydrophobic silicone membrane directly into a mass spectrometer, and of the pre-concentration in the membrane of the SVOC and their further fast and efficient thermal desorption. From chemical to biochemical and on to physiological monitoring, MIMS has found widespread use [12–19], its many advantages include simplicity, speed, high sensitivity and selectivity, accuracy, nearly real-time, on-line and in situ monitoring.

A fully-integrated MIMS system had previously been developed using a direct introduction membrane probe (DIMP) in the trap and release mode for combined VOC and semi-VOC analysis [20]. In this study, the DIMP/T&R-MIMS system is used to monitor chrysotile-assisted degradation of SDBS to discern between chrysotile action as either a simple adsorbent or as a degradation catalyst (or both), and an attempt to identify possible VOC or semi-VOC intermediates and CO_2, the final oxidation product.

Experimental

Reagents

SDBS was obtained from Gessy Lever do Brasil (97.8% m/m) and chrysotile 5R (surface area of 12.6 $m^2\ g^{-1}$) was supplied by SAMA Mineração de Amianto Ltda. (Cana Brava-GO Mine). Prior to use, the chrysotile was washed, sieved (250 mesh) and dried, as described elsewhere [21].

Oxidation Reaction

Experiments were performed with 0.250 L SDBS aqueous solution (3.0 mmol L^{-1}) and 4.0 g chrysotile in a 1.0-L beaker, at room temperature (25 ± 2 °C), in open vials. Aeration was performed using a mechanical bubbler, with a synthetic air (O_2 plus N_2 99.997%) flow of 40 mL s^{-1}. The SDBS consumption was followed using a Hewlett-Packard UV–vis Diode Array Spectrophotometer 8452 Å, through the 224 nm absorption band.

The reaction was carried out up to 2 h, as it was previously observed [3] that after this time there was no further consumption of the surfactant.

MIMS on-line monitoring was performed with the reaction vessel opened to air. Pumping was provided by an eight-roll peristaltic pump with a flow of 3 mL min^{-1}. The solution pH was adjusted to 13 (using NaOH solution) prior to air oxidation to trap CO_2 as carbonate. After 2 h, the solutions were acidified to pH 2 with an aqueous 6 mol L^{-1} HCl solution.

MIMS Monitoring

The DIMP/T&R-MIMS system used is described in detail elsewhere [20].

The system differs from the original T&R-MIMS system since it uses a direct introduction membrane probe (DIMP) to place a capillary membrane loop inside the ion source block exactly between two parallel filaments. The versatile DIMP/T&R-MIMS system can be operated in the standard MIMS mode for VOC detection during the trapping period of T&R-MIMS analysis while the system allows faster and more uniform heating of the membrane loop during the T&R-MIMS thermal desorption period needed for SVOC analysis. Therefore, SVOC sensitivity is improved and memory effects are minimized. MS analysis was performed using 70 eV electron ionization and a high transmission Extrel (Pittsburgh, PA) quadrupole mass spectrometer.

Continuous VOC monitoring and SVOC membrane trapping was performed during 2 h of aeration of the alkaline aqueous medium. The medium was then acidified to pH 2 while continuing to pump the aqueous solution through the system for 20 min so that possible VOC degradation intermediates ionized in the alkaline medium would permeate the membrane, now in its molecular form (due to the low pH), and be detected. This also concentrated the SVOC intermediates inside the membrane. A 2 min air plug was then introduced and pumped through the lines for the MS analysis of SVOCS. When it reached the membrane, heating by the filament rapidly raises the temperature to more than 250 °C, so that pre-concentrated SVOCs would be thermally released to the gas phase for MS analysis.

Results and Discussion

Full Mass Spectra

Operation of the T&R-MIMS system, either for VOC or SVOC analysis, detected no such intermediates in the chrysotile-catalyzed SBDS degradation (results not shown). Only CO_2, the final degradation product, was detected after the 2-h air bubbling and acidification of the medium.

Formation of CO_2

The SDBS oxidation reaction is carried out with air, which is bubbled through the alkaline SDBS-chrysotile aqueous solution. Therefore, the CO_2 released after acidification could come either from the air, by its adsorption as carbonate by the alkaline solution, or from chrysotile, or even from SDBS oxidation.

MIMS-monitoring of CO_2 as a function of oxidation time was then performed, using selected ion monitoring (SIM) of the *m*/*z* 44 ion. It was already known that SDBS aqueous solutions in contact with chrysotile fibres showed a concentration reduction up to 53% after 4 h of exposure [3]. Further adsorption/desorption experiments showed that with air bubbling, only 6% of the surfactant is recovered after successive washing steps in water.

A normal degradation experiment was performed and CO_2 was detected both during the 2 h of air bubbling and after acidification (Fig. 1, curve a). In the first control experiment, the same experimental conditions were used except that no SDBS was added; hence the medium contained just alkaline water and chrysotile. Figure 1 (curve b) shows that no CO_2 was released during the 2 h of air bubbling; when the medium was acidified, CO_2 was then released, but its evolution was near 50% lower than that observed when SDBS was added.

In a second control experiment, only alkaline water was used and after 2 h of synthetic air bubbling the solution was acidified. An irrelevant, nearly undetectable amount of CO_2 was released. In a third control experiment performed with air bubbling through a sodium dodecylbenzenesulfonate alkaline aqueous solution with no chrysotile, the amount CO_2 released was also nearly undetectable.

Clearly, therefore, CO_2 evolution occurred owing exclusively to the chrysotile-catalyzed oxidation of SDBS.

CO_2 Quantitation

An analytical curve was plotted to quantify the CO_2 released during the 2 h chrysotile-catalyzed oxidation of SDBS. Solutions were used with different concentrations of $MgCO_3$ (0–0.4 g L^{-1}), which were subsequently acidified with HCl 1% (pH 2.5) to allow the formation of CO_2 and consequently its permeation through the membrane.

A minimum of three replicate experiments were performed and the measured intensity of the *m*/*z* 44 ion was then plotted against theoretical CO_2 mols owing to carbonate evolution in acid media from $MgCO_3$ (calculated from the hydrolysis reaction). The resulting analytical curve (Fig. 2) showed the good performance of the T&R-MIMS system and the CO_2 values obtained allowed a mass balance calculation for the SDBS reaction.

UV–vis Analysis

After 2 h of oxidation, a sample of the reaction media was analyzed by UV–vis spectrometry. The absorbance peak at 224 nm, characteristic of SDBS, was reduced by 20% of its initial value.

Since 0.78 mmol of SDBS were used initially (3.0 mmol L^{-1}, 0.250 L), it was expected that 0.16 mmol of SDBS had therefore been consumed (20%). From the reaction stoichiometry (Eq. 1), the complete oxidation of 0.16 mmol of SDBS should produce 2.8 mmol of CO_2.

For these calculations the values for O_2 were not used, once it was saturated in the medium as the reaction was performed in open air.

The CO_2 SIM peak obtained after acidification (Fig. 1, curve b) and after deduction of the CO_2 formed from chrysotile as measured in the control experiment equates to 1.0 mmol, which correspond to 36% of the expected amount of CO_2 (2.8 mmol). Since a considerable amount of CO_2 is released during the 2 h degradation experiment (Fig. 1, curve a), it is possible to conclude that most of the consumed SDBS is mineralized to CO_2. The difference in the mass balance might also be attributed to the fact that

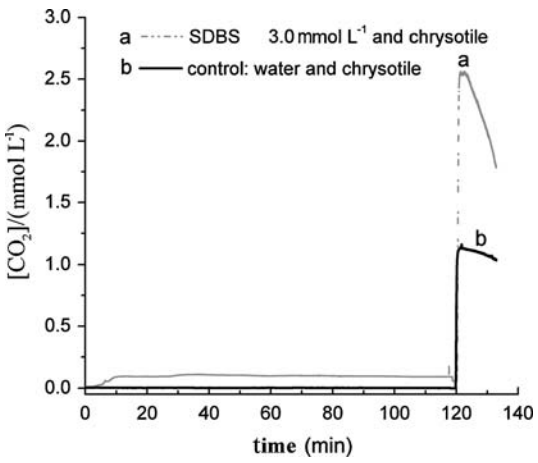

Fig. 1 SIM of CO_2 (*m*/*z* 44) released as a function of time of reaction for: *a* aeration of an aqueous alkaline solution (pH 13) of SDBS plus chrysotile, and *b* aeration of alkaline water (pH 13) plus chrysotile The medium was acidified after 2 h of contact External aeration was supplied during the 2 h period in both cases

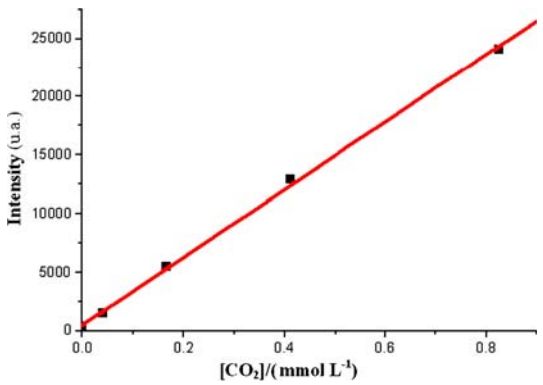

Fig. 2 Analytical curve obtained by the acidification of different concentrations of $MgCO_3$ solutions SIM was obtained under the same experimental conditions described in the experimental section for the SDBS reaction

the experiments were performed in open vials, what might led to losses of the formed product.

In a previous work, Hidaka et al. [2] observed that only 32% of the expected amount of CO_2 was released, for the TiO_2-photocatalytic degradation of SDBS. The 70% difference was assigned to possible formation of intermediate degradation products such as aldehydes and peroxides. In the chrysotile-catalyzed degradation herein investigated, the combined VOC and SVOC analysis performed by the highly sensitive DIMP-T&R-MIMS system was unable to detect any product with such characteristics, except the final mineralization product: CO_2. It can be assumed that if aldehydes and peroxides are involved as degradation intermediates, they may remain adsorbed and rapidly decomposed on the chrysotile surface, a process that would hinder their identification. Hence, only the final CO_2 degradation product would be released from the chrysotile catalyst surface.

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