ULTRASONIC IRRADIATION OF THE REMOVAL OF LINEAR ALKYL BENZENE SULPHONATES (LAS) FROM WASTEWATER

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Abstract. The effect of low frequency (20 kHz) ultrasonic irradiation on the removal of sodium Linear Alkylbenzene Sulphonates (LAS) from aqueous solutions has been investigated. Sonication of three different initial concentrations of LAS, 500 µmol/l, 750 µmol/l and 1000 µmol/l, were performed. All experiments used a temperature of 30°C, frequency of 20 kHz, power of 125 W, a batch time of 120 min and the pH was left uncontrolled. It was found that the main degradation of LAS at micromolar concentrations proceeded via a reaction with OH• radicals. The initial degradation rate increased with an increase in the surfactant concentration over the whole concentration range studied. The sonolysis of LAS showed a strong inhibition of H2O2 production at a higher concentration. Sonication of LAS in the presence of Br– suggested that OH• radicals induced degradation pathways was the dominating sonochemical degradation mechanism.

Keywords: Surfactants, ultrasonic, wastewater, total organic carbon (TOC)

1.0 INTRODUCTION

Linear alkylbenzene sulphonate (LAS) was first commercialised in the early sixties as a replacement of the poorly biodegradable dodecylbenzene sulphonate-branched
alkylbenzene sulphonate (DBS). LAS is a major anionic surfactant used in industrial detergents and the production of household products throughout the world because of its effectiveness. Its presence in wastewaters may cause environmental concern [1]. The widespread and relatively large usage of LAS (1.5 - 2.0 million ton/year worldwide and 300,000 ton/yr within EU) has led to extensive research in determining acceptable levels of use and release of LAS, and the environmental impact of this surfactant [2]. The synthetic commercial alkylbenzene sulphonate is one of the most thoroughly investigated with respect to biodegradability.

In recent years, considerable interest has been shown in the application of ultrasonic as a destructive process for the treatment of hazardous contaminants in water. The study of sonication as a promising wastewater treatment method has increasingly become an important topic of research. The chemical effect of ultrasonic on chemical reaction was first reported in 1927 by Richards and Loomis [3]. Ultrasonic is the name given to sound waves having frequencies higher than those to which the human ear can respond (i.e. >16 kHz) [4]. Ultrasonic radiation is essentially sound waves which have passed through a system via ultrasonic devices such as an ultrasonic beaker system, ultrasonic horn system, ultrasonic probe system etc.

Ultrasonic irradiation of aqueous solutions in the range of 20 - 1000 kHz induces acoustic cavitation, which can be defined as the cyclic formation, growth and subsequent collapse of micro-bubbles or cavities occurring in extremely small intervals of time and releasing large quantities of energy over a small location. Thus, cavitation serves as a mean of concentrating the diffused energy of ultrasonic into micro-reactors. Several recent studies report successful removal of a wide range of organic pollutants from dilute aqueous solutions (i.e. up to few mg/L) [5]; nonetheless, little attention has been paid on the application of ultrasonic to degrade surfactants, and in particular, LAS.

In our previous study, we have employed ultrasonic irradiation to treat phenol, 2-chlorophenol and 3,4-dichlorophenol from aqueous solutions [6]. Phenolic compounds (at an initial concentration of 0.1 g/l) are only partially removed by ultrasonic irradiation with 2-chlorophenol being more susceptible to degradation than phenol and 3,4-dichlorophenol. However, the presence of Fe ²⁺ ions at concentrations as low as about 10⁻³ g/l generally increases the rate of the uncatalysed sonolytic degradation. This is attributed to iron being capable of readily decomposing hydrogen peroxide in a Fenton-like process to form reactive hydroxyl radicals as well as being an effective oxidation catalyst.

The involvement of mainly OH⁺ radicals during sonication of surfactant has been proved [7-10]. Yim et al. [10] studied the sonolysis of several surfactants. They expected that the degradation of surfactants by ultrasonic irradiation should mainly due to the hydroxyl radical attack on the alkyl chain. They also added that the degradation of surfactant by ultrasonic irradiation involves 2 distinct pathways, the oxidation by OH⁺ radicals and pyrolytic reaction. Therefore, it can be concluded that two reaction
mechanisms have mainly been proposed to explain the results. The first mechanism is the generation of OH\textsuperscript{•} radicals in the cavitation bubbles, which subsequently oxidise the organic compounds. The second mechanism is pyrolysis in the cavitation bubbles. There have been several studies dealing with the reaction of OH\textsuperscript{•} radicals with surfactants [7-9, 11]. They stated that OH\textsuperscript{•} radicals react with the surfactant molecules to initiate the degradation process. Previous studies [12-17] also indicate that if the solute being degraded is a volatile compound then pyrolysis within the bubble may occur. Since LAS is an ionic surfactant of negligible volatility, direct pyrolysis of LAS can be expected to be insignificant. To the best of our knowledge, only two papers discussed the sonication of LAS [7, 10]. The aim of this work is to study the treatment of synthetic aqueous solutions containing a commercial LAS, namely sodium dodecylbenzene sulphonate (SDBS), by means of ultrasonic irradiation. The effect of low frequency (20 kHz) ultrasonic irradiation on the removal of sodium linear alkylbenzene sulphonates (LAS) from aqueous solutions at three different concentrations (500 µmol/l, 750 µmol/l and 1000 µmol/l) has been investigated. Additionally, the main reaction pathway of the degradation of LAS by ultrasonic was determined via ultrasonic irradiation in the presence of radical scavenger.

2.0 EXPERIMENTAL

2.1 Ultrasonic Experiments

Aqueous solutions of the LAS substrate were prepared (at concentrations of 500 µmol/l, 750 µmol/l and 1000 µmol/l) and subjected to sonication treatment. This resulted in an initial TOC of ≈100, 148 and 199 mgL\textsuperscript{−1} respectively. Ultrasonic irradiation of the LAS solution was carried out continuously with an Ultrason 250 (Labplant, UK) horn-type sonicator capable of operating either continuously, or in a pulse mode at a fixed frequency of 20 kHz and a maximum electric power output of 250 W. All experiments used a temperature of 30°C, frequency of 20 kHz, and electric power output of 125 W, a batch time of 120 min and the pH was left uncontrolled. Reactions were performed in a 0.12 L glass reaction vessel which was immersed in a temperature-controlled water bath to offset the heat dissipated during sonication, and the liquid bulk temperature was kept constant at 30°C. During sonication, the concentration of LAS was measured at 5, 10, 20, 30, 45, 60, 90 and 120 mins with respect to the liquid phase total organic carbon content (TOC), Methylene-Blue-Active-Substance (MBAS) and \( \text{H}_2\text{O}_2 \) generation analysis.

2.2 Analysis of TOC

Total organic carbon (TOC) was measured with a Shimadzu 5050 TOC Analyser whose operation is based on combustion/non-dispersive infrared (NDIR) gas analysis.
Total carbon was measured first, followed by inorganic carbon and TOC was determined by subtracting inorganic from total carbon. The uncertainty in this assay, quoted as the standard deviation of three separate measurements, was never larger than 1% for the range of TOC concentrations under consideration.

### 2.3 Methylene-Blue-Active-Substance (MBAS)

The MBAS method is useful for estimating the anionic surfactant content of waters and wastewaters. The LAS concentration was determined by the MBAS method [18]. The measurement was based on the formation of a blue salt or ion pair when methylene blue, a cationic dye, reacts with anionic surfactants such as LAS. MBAS bring about the transfer of methylene blue from an aqueous solution into an immiscible organic liquid upon equilibration. The intensity of the resulting blue colour in the organic phase is a measure of the concentration of LAS.

### 2.4 Determination of $\text{H}_2\text{O}_2$ Concentration

Hydrogen peroxide was determined by using the Titanium Spectrophotometric Method. The formation of hydrogen peroxide was determined by the reaction with titanyl sulphate in acid solution and measurement of the absorbance of the resultant yellow complex [19] at 410 nm with UV spectrophotometry.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Effect of the Initial Solute Concentration on the Sonochemical Degradation of LAS

Figure 1 shows the normalised TOC removal during the sonication of LAS at different initial concentrations. As seen, the TOC removal decreases with increasing initial concentrations of LAS. For instance, 500 $\mu$mol/l resulted in almost 26% TOC removal after 120 min of sonication, and 24% and 23% TOC removals were achieved at 750 $\mu$mol/l and 1000 $\mu$mol/l respectively after 120 min of sonication.

Figure 2 shows the amount of LAS degraded with sonication time for different initial concentrations during sonochemical degradation of LAS at 20 kHz, 125 W, 30°C and initial concentrations of 500 $\mu$mol/l, 750 $\mu$mol/l and 1000 $\mu$mol/l. It can be observed that the degradation rate ($d[\text{LAS}]/dt$) increases with an increase in the initial LAS concentration. However, for any specific initial LAS concentration, the degradation rate decreases with increasing sonication time. In Figure 3, the initial rates of the degradation of LAS were calculated as a function of initial concentrations within the first 30 min. The results reveal that the initial rate of degradation increases with increasing concentrations of LAS. This is in agreement with the findings by Yim et al. [10] and Ashokkumar et al. [7]. Yim et al. [10] who studied the sonochemical
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Ultrasonic irradiation of the removal of linear alkylbenzene degradation of LAS at 200 kHz under argon atmosphere reported that initial (i.e. within the first 10 min) rates increased with increasing concentrations (up to 0 ~1740 mg/l). In further studies, Ashokkumar et al. [7] reported that the initial degradation rate (i.e. within the first 15 min) increases with an increase in the initial

![Figure 1](image1.png)

**Figure 1** Normalised TOC-time profiles during the sonication of LAS as a function of concentration at 20 kHz, 125 W and temperature of 30°C

![Figure 2](image2.png)

**Figure 2** LAS degraded at different initial concentrations during the sonication of LAS at 20 kHz, 125 W and temperature of 30°C
LAS concentration. They also added that the increasing rate of degradation of LAS correlated closely with the decrease in the air/water surface tension of the surfactant solutions. From the data shown in Figure 3, initial (i.e. within the first 30 min) LAS degradation rates can be computed; the rates are about 6.1, 8.4 and 9.3 µmol/min/l at 500 µmol/l, 750 µmol/l and 1000 µmol/l of initial concentrations respectively.

To explain the data shown in Figures 2 and 3, i.e. the increase in the rate of LAS degradation with an increase in the initial surfactant concentrations, the reaction between the surfactant with OH• radicals needs to be considered in detail as shown below.

\[
\text{LAS} + \text{OH}^\bullet \rightarrow \text{PRODUCTS} \tag{1}
\]

Equation (1) indicates that the reaction rate is dependent on the concentrations of both LAS and OH• radicals. For a given sonication power, it can be expected that the rate of OH• radicals generated is constant [7]. However, an increase in the concentration of LAS would increase the probability of \( \text{OH}^\bullet \) radicals attack on LAS molecules leading to an increase in the degradation rate. Ashokkumar et al. [7] stated that in the absence of any solute, \( \text{OH}^\bullet \) radicals that escape into the bulk solution form hydrogen peroxide through Equation (2):

\[
\text{OH}^\bullet + \text{OH}^\bullet \rightarrow \text{H}_2\text{O}_2 \tag{2}
\]

To support this explanation, Figure 4 shows the production of \( \text{H}_2\text{O}_2 \) as a function of time. Figure 4 shows the amount of \( \text{H}_2\text{O}_2 \) produced for the sonolysis of deionised
It can be seen that the sonolysis of LAS at three different initial concentrations shows a strong inhibition of H$_2$O$_2$ production compared to the sonolysis of deionised water. Additionally, the amount of H$_2$O$_2$ production increases with decreasing LAS concentration. This is an expected result as by increasing the concentration of LAS, the probability of OH$^\cdot$ radicals attack on LAS molecules increases and this leads to the inhibitory of H$_2$O$_2$ production at higher LAS concentration. Furthermore, with increasing sonication time, the H$_2$O$_2$ production tends to level off. This result could be explained due to the competition between the reactions of radical-radical recombination and the reaction of the radical with LAS molecules, as shown in Equations (1) and (2).

Another possible explanation for the observation shown in Figure 3 may be the fact that increasing the concentration of surfactants in the solution reduces the surface tension of the liquid, thus reducing the cavitation threshold for bubble generation and consequently increasing the amount of formed radicals [5]. Ashokkumar et al. [7] quantify the amount of hydrogen peroxide produced in the absence and presence of sodium dodecylbenzene sulphonate (SDBS) at micromolar concentrations by using its reaction with iodide. The amount of OH$^\cdot$ radicals was calculated by the difference in H$_2$O$_2$ produced between the pure water and the surfactant solutions in 15 min of sonication. They found that the efficacy of OH$^\cdot$ radicals scavenging increases with increasing SDBS concentration.

**Figure 4** H$_2$O$_2$ production versus time during the sonication of LAS at three different initial concentrations at 20 kHz, 125 W and temperature of 30°C.
3.2 Sonochemical Degradation of LAS in the Presence of Radical Scavenger

In addition to the compounds that are degraded by OH• radicals through cavitation and bubble collapse, pyrolysis can also be an important pathway for the destruction of compounds in aqueous solutions. Several studies have shown that oxidative pyrolysis in the gas phase of the collapsing cavitational bubble plays a significant role in solute decomposition [14, 15, 20]. Furthermore, there have been several studies dealing with the reaction of OH• radicals with solution solutes [5, 7, 11, 21, 22]. In general, when aqueous solutions are subjected to ultrasonic irradiation, chemical reactivity is believed to be initiated by the formation of “hot spots” and H• and OH• radicals. Previous studies [9, 15, 23] also indicate that if the solute being degraded is a volatile compound, then pyrolysis within the bubble is significant. Additionally, Ashokkumar et al. [7] hypothesized that for the sonication of LAS, the initial reaction pathway is OH• radical attack on the surfactant molecules leading to the formation of primary intermediates. In addition to this, the primary reaction products are also susceptible to further radical attack leading to both water-soluble organic products, such as acetic and propionic acids, and volatile organics (e.g. high molecular weight alkanes from the breakdown of the LAS) that are pyrolyzed within the cavitation bubbles (as shown in Figure 5).

Since LAS is an ionic surfactant of negligible volatility, direct pyrolysis of LAS within the bubble could be expected to be insignificant. In order to have additional

![Figure 5](image-url)  
**Figure 5** Reaction pathways involved in the sonochemical degradation of LAS in aqueous solutions at 20 kHz, 125 W and temperature of 30°C [7]
data and information concerning the contribution of pyrolysis to the degradation of LAS, a series of sonication experiments were made in the presence of a radical scavenger, Bromide (Br\textsuperscript{−}), where 300 µmol/l of Br\textsuperscript{−} was added at the beginning of each experiment. Potassium Bromide, a non-volatile strong electrolyte that can readily oxidised by free radicals, is a known scavenger for the interfacial region of the cavitation bubble and possibly for the bulk liquid region [24]. Arslan and Ferry [25] used 300 µmol/l of Br\textsuperscript{−} to study the effect of OH\textsuperscript{•} radical scavengers on the oxidation of acid dye Orange II. They found that at 300 µmol/l of Br\textsuperscript{−} it was enough for Br\textsuperscript{−} to scavenge the OH\textsuperscript{•} radicals. In the case where the degradation of LAS is inhibited by the presence of Br\textsuperscript{−}, one might conclude that OH\textsuperscript{•} radicals reaction play a significant role for the degradation of LAS.

Figure 6 shows the amount of LAS degraded with sonication time for different initial concentrations during sonochemical degradation of LAS at 20 kHz, 125 W and temperature of 30\textdegree C in the absence and presence of Br\textsuperscript{−}. As clearly seen, the addition of Br\textsuperscript{−} at a concentration of 300 µmol/l resulted in a small amount of LAS degraded compared to that in the absence of Br\textsuperscript{−}, suggesting that during LAS degradation, OH\textsuperscript{•} radicals are involved.

**Figure 6** LAS degraded at different initial concentrations during the sonication of LAS in the absence and presence of Br\textsuperscript{−} at 20 kHz, 125 W and temperature of 30\textdegree C
degradation, OH radicals reaction occurs. Additionally, Figure 7 shows the amount of H$_2$O$_2$ produced during sonochemical degradation of LAS in the absence and presence of Br$. It can be seen that the amount of H$_2$O$_2$ produced during sonochemical degradation of LAS in the presence of Br is lesser compared to that in the absence of Br$. From Figures 6 and 7, it can be suggested that most of OH radicals are scavenged by Br and OH radicals that are available or diffuse to react with Br, react with LAS or recombined to produce H$_2$O$_2$.

Furthermore, to quantify the overall degradation of LAS, Figure 8 shows the TOC removal with and without the presence of Br$. From Figure 8, it can be seen that the degradation of LAS was inhibited in the presence of Br$. The degradation was quenched by the addition of Br$. For instance, 8%, 7% and 6% of TOC removals were achieved at 500 µmol/l, 750 µmol/l and 1000 µmol/l respectively in the presence of Br$, after 120 min of sonication, while 26%, 24% and 23% of TOC removals were achieved at 500 µmol/l, 750 µmol/l and 1000 µmol/l respectively in the absence of Br$, after 120 min of sonication. From Figures 6, 7 and 8, it can be suggested that the
degradation of LAS was inhibited in the presence of Br\(^-\), suggesting that an OH\(^+\) radical induced degradation pathway is the dominating sonochemical degradation mechanism of LAS.

4.0 CONCLUSIONS

It can be summarised that the main degradation of LAS at micromolar concentrations proceeds via a reaction with OH\(^+\) radicals and since LAS is an ionic surfactant of negligible volatility, direct pyrolysis of LAS can be expected to be insignificant. The TOC removals were decreased as the initial concentration of LAS increased. The initial degradation rate increases with an increase in the surfactant concentration over the whole concentration range studied. This could be explained due to the fact that an increase in the concentration of LAS would increase the probability of OH\(^+\) radicals attack on LAS molecules leading to an increase in the degradation rate. Another possible explanation may be the fact that increasing the concentration of surfactants in the solution reduces the surface tension of the liquid, thus reducing the cavitation threshold for bubble generation and consequently increasing the amount
of formed radicals [5]. The sonolysis of LAS shows a strong inhibition of H₂O₂ production at higher concentrations as by increasing the concentration of LAS, the probability of OH⁻ radicals attack on LAS molecules increases and this leads to the inhibitory of H₂O₂ production. Sonication of LAS in the presence of Br⁻ suggests that OH⁻ radicals induced degradation pathway is the dominating sonochemical degradation mechanism. This was clearly seen from the effect of Br⁻ on the total degradation (i.e. TOC removals).

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NOMENCLATURES

µmol/l  concentration in micromole per liter.
LAS  linear alkylbenzene sulphonates.
OH⁻  hydroxyl radicals.
TOC  total organic carbon.
H₂O₂  hydrogen peroxide.

REFERENCES


