Effects of advanced ultraviolet/H$_2$O$_2$ treatment on oxidation of linear alkylbenzene sulfonate in detergent wastewater

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Received 24 October 2022; Accepted 5 March 2023

**Abstract**

In developing countries with inadequate municipal sewage systems, untreated domestic wastewater is discharged into the environment; this worsens environmental pollution. Detergents in domestic wastewater are difficult to manage. Here, we investigated the effects of the ultraviolet/H$_2$O$_2$ advanced oxidation process on the degradation of linear alkylbenzene sulfonate (LAS) (a very persistent chemical in detergents). The advanced oxidation process degraded LAS in pure water, powder, liquid, and cream detergents; the degradation rates were 3.426, 3.896, 2.504, and 0.913 cm$^2$/J, respectively, indicating that degradation efficiency greatly varied according to detergent ingredients. Both the extent of ultraviolet absorbance and the concentrations of radical scavengers influenced degradation efficiency. In addition, changes in solution properties before and after attainment of the critical micelle concentration affected degradation.

**Keywords:** Linear alkylbenzene sulfonate; UV/H$_2$O$_2$; Critical micelle concentration

1. Introduction

Domestic wastewater management is challenging because of the need for environmental sustainability in the 21st century. Water pollution from untreated graywater creates health hazards; it affects both the natural environment and the tourism industry. Although appropriate graywater treatment is important worldwide, the practices and technologies remain inadequate, particularly in developing countries where infrastructures and public services are stressed by rapid population influxes and urbanization [1]. Often, untreated graywater is discharged into rivers [2].

Linear alkylbenzene sulfonate (LAS) is a surfactant; 80% of all LAS is used in household laundry detergents, while the remaining 20% is used in industrial materials [3]. Compared with conventional alkyl benzene sulfonate, LAS is more biodegradable and exhibits less foaming [4,5]; however, LAS remains problematic from both environmental and public health perspectives. Under aerobic conditions, microbial degradation of LAS commences at the methyl moiety at the end of the alkyl group; this is followed by oxidative shortening of the alkyl group and cleavage of the benzene ring to water, carbon dioxide, and sulfate ions [6]. Oxidative shortening of the alkyl group and cleavage of the benzene ring require distinct enzyme systems; complete microbial degradation of LAS is slow [7]. LAS biodegradability is low under hypoxic conditions, which leads to LAS persistence [8,9]. LAS toxicity has been investigated using *Daphnia magna* (a crustacean), the fathead minnow, and the medaka (a fish); the lethal concentration 50% (LC$_{50}$) has been employed as an indicator. In *D. magna*, the 24-h LC$_{50}$ values were 53.1, 15.8, 10.7, 2.7, and 1.2 mg/L for C$_{10}$, C$_{11}$, C$_{12}$, and C$_{13}$ LAS, respectively [6]. Verge et al. [10] reported similar values at a water hardness of 200 mg/L CaCO$_3$; the LC$_{50}$...
values were 13.9, 8.1, and 1.22 mg/L for \( \text{C}_{12}, \text{C}_{13}, \text{and} \ \text{C}_{14} \) LAS, respectively. In the fathead minnow, the values were 48.0, 17.0, 4.7, and 0.6 mg/L, respectively, for \( \text{C}_{12} - \text{C}_{14} \) LAS; in the medaka, the figures were 76, 7.6, and 1.45 mg/L for \( \text{C}_{12}, \text{C}_{13}, \text{and} \ \text{C}_{14} \) LAS, respectively [6]. Thus, LAS becomes more toxic as the chain length of the alkyl group increases.

Surfactants (e.g., LAS) are degraded by advanced oxidation treatments that feature hydroxyl radicals (‘OH) [11–17]. In our previous article [13], effect of \( \text{H}_2\text{O}_2 \) concentration and initial concentration of LAS was investigated over degradation of the pure LAS solution. However, in actual environment, LAS itself is contained in detergents of various forms: liquid, powder, and cream. Degradation of LAS is primarily regulated by reaction of ‘OH, how ever, minimal information is available about its reaction in actual detergent, which have a lot of ingredients to have complex water matrices. When ultraviolet (UV) light acts on hydrogen peroxide to produce radical scavengers, treatment efficiency is principally affected by UV transmittance and the radical level. Therefore, the present study focused on the effects of UV absorbance and radical scavengers on the LAS degradation efficiencies in detergents with additional discussion about pH.

Rodriguez et al. [14] established a model to express degradation kinetics for application of ozone into LAS degradation. Another study by Sanz et al. [15] revealed importance of pH and molar ratio of \( \text{H}_2\text{O}_2 \) over LAS. The initial LAS concentration may also be important [16]. When LAS solutions of 10, 50, and 100 mg/L were tested, the 10 mg/L preparation exhibited optimal degradation. Rios et al. [17] found that the critical micelle concentration (CMC) also played an important role in LAS degradation. At LAS concentrations above the CMC (25.5 mg/L), the degradation rate first plateaued and then decreased. At LAS concentrations below the CMC, degradation slowed because the surfactant molecules were primarily located at the water/air interface, thus reducing accessibility. The CMC depends on the type of surfactant; mixtures of certain surfactants yield CMCs lower than the CMCs of the individual surfactants [18,19]. The addition of inorganic salts to aqueous solutions of anionic surfactants can significantly affect the CMCs [20,21]. Such methods of CMC reduction are used in many detergents to increase cleaning power. The CMCs of surfactants above greatly differ from the CMCs of those surfactants combined with detergents. Similarly, there is variation in the LAS concentration that is optimally degraded by the advanced oxidation process. Therefore, we investigated the CMCs of both LAS alone and detergents containing LASs; we also explored differences in degradation before and after CMCs had been reached. We applied the UV/\( \text{H}_2\text{O}_2 \) process to three brands of household laundry detergents that contained LAS. We employed a collimated UV beam to explore the effects of UV absorbance, radical scavenger concentration, and the CMC.

2. Materials and methods

2.1. UV irradiation

The light source was a 254-nm UV lamp (Panasonic, 20 W). A 500 mL glass beaker served as the reaction vessel; the contents were gently stirred with a magnetic stirrer, as shown in Fig. 1. The UV fluence rates were measured via iodide/iodate actinometry [22]; they were 0.216, 0.276, and 0.234 mW/cm² for the left, center, and right depending on a position of the beaker placed.

2.2. Reagents

We used three laundry detergents (a powder, a liquid, and a cream) that contained LAS; we also used sodium dodecylbenzenesulfonate (Sigma-Aldrich). Samples were UV-irradiated in the presence of 4.1 mM \( \text{H}_2\text{O}_2 \). The initial LAS concentrations were 6–150 mg/L (five steps).

2.3. LAS quantitation

LAS molecules were separated according to carbon number (\( \text{C}_{12} - \text{C}_{14} \)) via ultra-performance liquid chromatography (Acquity UPLC H-Class; Waters) on an Acquity UPLC BEH C8 column at 40°C. LASs were detected by fluorescence (excitation wavelength 221 nm and emission wavelength 284 nm); 10-μL volumes of catalase (from bovine liver, Sigma-Aldrich) solution were then added to quench the reactions.

2.4. Other parameters

Absorbances at 254 nm were obtained using a spectrophotometer (V-670 Japan Spectrophotometer) (irradiation time 0 min). A quartz vial (10 mm × 10 mm × 45 mm) was used to obtain all measurements in triplicate; the data were then averaged. Ultrapure water was employed for zero-point adjustment; it also served as a blank. FWA-1 and FWA-5 (typical fluorescent brightening agents of laundry detergents) served as (possible) radical scavengers. Those brightening agents are normally contained in commercial detergents, which may hamper degradation efficiency of LAS by UV/\( \text{H}_2\text{O}_2 \) process. Therefore, in this study we investigated the impact of FWA-1 and FWA-5, for the purpose of practical applications. As a structure, FWA-1 and FWA-5 contain carbon double bonds and benzene rings [23,24]. Because ‘OH moieties preferentially attack high-electron density regions of molecules, these substances presumably serve as radical scavengers [25]. FWA was added at 0, 0.01, 0.05, 0.1, and 0.72 mg/L to an aqueous solution of 12 mg/L.
dodecylbenzenesulfonic acid with 4.1 mM H$_2$O$_2$; each solution was subjected to the UV/H$_2$O$_2$ process. Changes in FWA fluorescence and FWA denaturation were explored using a three-dimensional fluorescence spectrophotometer (FP-8200, Japan Spectroscopy) [emission wavelength (Em) = 280–550 nm, excitation wavelength (Ex) = 220–450 nm]; the bandwidth and data-reading intervals were all 5 nm.

2.5. CMC measurement

CMCs were measured by determining changes in the absorption maxima of UV-absorbing organic compounds in a surfactant solution [26,27]. When an organic compound (I) is added to an aqueous surfactant solution at a high concentration (i.e., at or above the CMC), I is dissolved in the aqueous solution by the surfactant micelles; the maximum absorption wavelength ($\lambda_{\text{max}}$) approaches the value observed during dissolution in organic solvents. However, at low concentrations (i.e., below the CMC), I is in the aqueous phase and $\lambda_{\text{max}}$ approaches the value observed in water. The curve of the relationship between $\lambda_{\text{max}}$ and the surfactant concentration shows that $\lambda_{\text{max}}$ decreases as the surfactant concentration approaches the CMC; it then increases rapidly when the CMC is exceeded. We used N,N-diethylaniline (DEA) (Aldrich, USA) as the organic compound (I); the $\lambda_{\text{max}}$ values of DEA in the organic solvent and water were measured, and the relationship between the detergent concentration and $\lambda_{\text{max}}$ was plotted to obtain the detergent CMC. In a test water sample, an excessive DEA concentration causes the absorbance of the entire solution to increase; this hinders the acquisition of an accurate spectrum. Therefore, the DEA concentration was maintained at 0.5 mL/L. To stabilize the peak wavelength, DEA was added after the preparation of a solution at the required concentration; all samples were incubated at room temperature for 15 min before measurements. Absorption spectra were recorded (using a spectrophotometer) from 190 to 400 nm (in the UV region). A quartz vial (10 mm × 10 mm × 45 mm) was used to obtain all measurements; ultrapure water was employed for zero-point adjustment and served as a blank. The CMC was the inflection point of the graph obtained through division of the measured $\lambda_{\text{max}}$ by the LAS concentration. All $\lambda_{\text{max}}$ values were in the range of 240–280 nm, where DEA exhibits absorbance.

3. Results and discussion

3.1. UV absorbance

LAS degradation was examined in three detergents that contained LAS, as well as an LAS reagent. Fig. 2 shows the LAS concentrations as a function of UV fluence; LAS degradation differed among detergents. As an overall trend, the result is consistent with a previous research [17] showing one tenth of degradation about 1,000 mJ/cm$^2$. Assuming a pseudo-first-order reaction, the degradation rates of the LAS reagent, as well as LAS in the powder, liquid, and cream detergents (initial LAS concentrations 12 mg/L), were 3.426, 3.896, 2.504, and 0.913 cm$^2$/mJ, respectively. Thus, LAS degradation was less effective in liquid and cream detergents than in pure LAS. The absorbances at 254 nm of detergents with the same initial LAS concentrations were 0.110, 0.121, 0.113, and 0.186 cm$^{-1}$, indicating that the absorbance of the cream detergent was higher than the absorbances of the other detergents; this finding implied that UV absorbance affects the rate of LAS degradation. Comparison of the powder and liquid detergents revealed that the degradation rate was lower for the liquid detergent, while the absorbance was higher for the powder detergent—these findings contrasted with the results described above. The discrepancies may reflect the effects of radical scavengers.

3.2. pH

Effect of pH was described in Fig. 3 as a function of pH against degradation rate. In a previous research by Sanz et al. [15] suggests complicated effect of pH on degradation of LAS by UV/H$_2$O$_2$ system. Briefly degradation was maximum at pH 7, followed by pH 5, 3, and 2.2. However, in our study, there seemed no clear effect of pH on degradation of LAS as in Fig. 3. Different trend between our study and a previous study [15] might be due to difference in range in degradation. Overall, there is no clear effect was observed by pH, we proceeded to additional investigations.

3.3. Radical scavengers

The degradation rates of various detergents (and a LAS solution) in the presence of FWA-1 and FWA-5 were examined at an initial LAS concentration of 12 mg/L. Fig. 4 shows the LAS concentration as a function of UV fluence. The degradation rates decreased as the concentrations of the optical brighteners increased. The respective rates of LAS...
degradation at FWA concentrations of 0.01, 0.05, 0.1, and 0.72 mg/L were 3.091, 2.464, 2.842, and 1.990 cm²/J for FWA-1; they were 3.116, 2.622, 3.262, and 2.453 cm²/J for FWA-5. The respective absorbances at 254 nm were 0.114, 0.113, 0.113, and 0.138 cm⁻¹ for FWA-1; they were 0.11, 0.115, 0.112, and 0.142 cm⁻¹ for FWA-5. With the exception of the LAS concentration of 0.72 mg/L, no significant differences were observed between the reagent LAS and the other samples.

The fluorescence intensity of each sample before and after treatment was observed using an excitation emission matrix. FWA-1 and FWA-5 exhibited maximum fluorescence intensities (fluorescence peaks) at [Em, Ex] = [440, 360] and [Em, Ex] = [430, 350], respectively. Table 1 lists the fluorescence peaks before and after treatment. FWA-1 reduced the intensity by an average of 29%, but a peak remained after treatment. Although FWA-1 scavenges •OH, the process is inefficient. In contrast, FWA-5 significantly reduced the fluorescence intensity (by > 90%) at all concentrations tested, indicated that FWA-5 efficiently scavenges •OH. The fluorescence wavelengths revealed powder and liquid detergent peaks at [Em, Ex] = [430, 350], similar to the wavelengths of FWA-5; in particular, the liquid detergent exhibited high fluorescence intensity. Such high fluorescence (despite treatment) may reflect a high concentration of FWA-5. Thus, FWA scavenges •OH and competes with LAS in terms of degradation.

3.4. Critical micelle concentration

Changes in DEA λ_max values were measured according to detergent concentration. The λ_max values at each concentration (minus the λ_max of the aqueous phase) are shown in Fig. 5. The λ_max values of all detergents exhibited sharp increases of 3–4 nm above a certain concentration. The CMCs

Table 1
Change in fluorescence intensity before and after UV/H₂O₂ treatment [intensity]

<table>
<thead>
<tr>
<th>Detergent</th>
<th>FWA-1 (Em 440, Ex 360)</th>
<th>0.01 mg</th>
<th>0.05 mg</th>
<th>0.1 mg</th>
<th>0.72 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>20</td>
<td>98</td>
<td>224</td>
<td>1,806</td>
<td></td>
</tr>
<tr>
<td>120 min</td>
<td>17</td>
<td>63</td>
<td>170</td>
<td>1,120</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Detergent</th>
<th>FWA-5 (Em 430, Ex 350)</th>
<th>0.01 mg</th>
<th>0.05 mg</th>
<th>0.1 mg</th>
<th>0.72 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>518</td>
<td>2,580</td>
<td>5,134</td>
<td>&gt;10,000</td>
<td></td>
</tr>
<tr>
<td>120 min</td>
<td>7</td>
<td>14</td>
<td>8</td>
<td>27</td>
<td></td>
</tr>
</tbody>
</table>
developed immediately prior to the increases; for the reagent LAS and the powder detergent, \( \lambda_{\text{max}} \) increases occurred between LAS concentrations of 50 and 75 mg/L. In contrast, for the liquid and cream detergents, \( \lambda_{\text{max}} \) increases occurred between LAS concentrations of 25 and 50 mg/L, indicating that their CMCs were lower than the CMC of the reagent LAS. When they are combined, certain surfactants reduce both the surface tension and the CMC. The liquid detergent contains both LAS and alkyl ether surfactants; the alkyl ether surfactants may have reduced the CMC. The addition of inorganic salts to solutions with surfactants also triggers rapid CMC reductions; the solutions become milky.

The manufacturer indicates that the cream detergent contains both sodium carbonate and sodium sulfate, which may have reduced the CMC and enhanced the absorbance.

To examine the effects of CMC and LAS concentration on degradation, the rate of change in degradation according to the initial LAS concentration was determined using Eq. (1).

\[
\frac{\Delta \kappa}{\Delta C} = \frac{\ln \left( \frac{\kappa_j}{\kappa_i} \right)}{\Delta C}
\]

where \( \Delta \kappa \) : change in degradation rate constant (cm\(^2\)/J) and \( \Delta C \) : amount of change in initial LAS concentration (mg/L).

4. Conclusions

We explored UV/H\(_2\)O\(_2\)-mediated LAS degradation in three household laundry detergents. LAS degradation was less effective in liquid and cream detergents than in reagent LAS. The high concentrations of radical scavengers (i.e., fluorescent brighteners) in the liquid detergent and the high absorbance of the cream detergent led to reduced LAS degradation. LAS degradation was significantly lower prior to attainment of the CMC. Therefore, efficient degradation can be obtained by using an LAS concentration below the CMC.

Acknowledgements

This study was partially-supported by the Obayashi Foundation.

References


