An Investigation of Ultrasonic Degradation of Linear Alkyl Benzene Sulfonic Acid in Aqueous Solution

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ABSTRACT

Surfactants used with several purposes have serious effects on biological life sustainability in aquatic environment. Linear Alkyl Benzene Sulfonic Acid (LABSA), which is a raw material in the manufacture of detergents and one of preferable anionic surfactants, is used as a model pollutant in this study. The degradation of LABSA by sonication process in aqueous solutions was investigated. Detergent concentration was evaluated to determine the efficiency of treatment process. The experimental conditions applied in ultrasonic irradiation were pH (4-8), reaction time (30-150 min) and initial LABSA concentration (8-20 mg/L). The effect of different types of oxidants on the progress of the reaction was also studied. Under the experimental conditions, pH of 4 and 10 mg/L initial concentration of LABSA, 44% detergent removal was obtained in 75 min of reaction time. In further study, by addition of K2S2O8 as an oxidant, the removal efficiency was reached at 76% for 150 min of reaction time and original pH value of solution, 5.2.

Keywords: Detergent raw material, LABSA, Ultrasonic treatment.

INTRODUCTION

Surfactants are large organic molecules that are slightly soluble in water and cause foaming in wastewater treatment plants and in the surface waters. Surfactants are composed most commonly of strongly hydrophobic group combined with a strongly hydrophilic group. (Metcalf&Eddy, 2014).

There are various severe effect of detergents on receiving bodies due to foam formation, oxygen consumption by biological degradation, eutrophication and toxic effects on aquatic biota and drinking water (Balcioğlu, 2014).

Many of the detergents used in the domestic and industrial laundry operations contain 5-30% of anionic-based surfactants such as sodium dodecyl sulphate...
and linear alkyl benzene sulphonate (Chitra et al., 2014). Linear Alkyl Benzene Sulfonic Acid (LABSA) nowadays is one of the preferable anionic surfactants as a raw material in the manufacture of detergents.

Sonication has been used as an advanced oxidation process (AOP) in wastewater treatment. Advanced oxidation processes are based on the formation of hydroxyl radicals with a high electrochemical oxidation potential. Hydroxyl radicals are not selective and react with all organic substances. CO₂ and H₂O were formed as the end product by the hydroxyl radicals (Martinez et al., 2003; Çatalkaya et al., 2004).

Ultrasonic irradiation produces cavitation bubbles in a liquid. The chemical and mechanical effects of ultrasonic waves are caused by the cavitation bubbles. Cavitation is known as the formation of micro bubbles in a very limited time range of milliseconds, growth and dissolution that is released large amounts of energy. In this process, energy and a pressure higher than 1000 atm are generated. This energy heats up the zone of bubbles and causes to chemical reactions. The main principle of ultrasound process is to use this high heat (energy) formed (Gogate and Pandit, 2004).

The high temperature produced during bubble collapse decomposes water into extremely reactive hydrogen atoms (H⁺), and hydroxyl radicals (•OH). These radicals recombine to form hydrogen peroxide and molecular hydrogen in the cooling phase. A summary of chemical reactions taking place during sonolysis of water is given in the following (Savun-Hekimoğlu and İnce, 2017):

\[
\begin{align*}
\text{H}_2\text{O}(+) & \rightarrow \text{OH}• + \text{H}• & \text{(1)} \\
\text{OH}• + \text{OH}• & \rightarrow \text{H}_2\text{O}_2 & \text{(2)} \\
\text{OH}• + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{O}_2\text{H}• & \text{(3)}
\end{align*}
\]

There are many studies in the literature about the degradation of surfactants such as adsorption (Akmil et al., 2004), UV/O₃/H₂O₂ process (Zanganeh et al., 2014), electrochemical oxidation (Koparal et al., 2006), photochemical treatment (Tabrizi and Mehrvar, 2006), sonochemical treatment (Dehghani et al., 2010), photodegradation and ozonation (Fernández et al., 2004), anaerobic degradation (Carosia et al., 2014; Duarte et al., 2010).

The aim of the present study was to evaluate the effect of ultrasonic irradiation on the degradation of LABSA for different initially LABSA concentrations, pH and irradiation time. The efficiency of sonication process was assessed in term of detergent removal. The study also aimed determining that the effects of different oxidants (H₂O₂ and K₂S₂O₈) on the removal efficiency.

**MATERIAL AND METHODS**

**Materials**

LABSA (C₁₈H₂₉SO₂OH) was supplied from a detergent factory. Hydrogen peroxide (H₂O₂; 30 % w/w, Merck) and potassium persulfate (K₂S₂O₈, Merck) were used as an oxidant. The pH of the solution was adjusted using 1N NaOH /
H₂SO₄. All chemicals were of analytical grade and used in experiments without any further purification.

**Ultrasound System (US)**

Sonochemical oxidation experiments were performed with the probe type ultrasonic device (BANDELIN-SONOPULS HD 3400 model), at a maximum power of 400 W. The US probe which has got 25 mm diameter, 130 mm length, 82 µm amplitude and 20 kHz frequency is a titanium probe. The capacity of the reaction vessel is 100-2500 mL. The probe was immersed in the solution just 3 cm above from reactor bottom. Keeping the temperature constant (25 ± 2 °C) is provided by cooling water during the experiment. In addition, the system is built into the cabine partly preventive to the noise. Experiments were conducted at 60 % of amplitude and in pulse off application.

**Analysis**

The methylene blue active substances (MBAS) test is used to determine the presence of surfactants in water and wastewater for anionic surfactants (APHA, 2005). The determination of surfactants is accomplished by measuring the color change in in a standard solution of methylene blue dye. The intensity of the blue colored complex is measured colorimetrically at 652 nm using a spectrophotometer (HACH-LANGE Dr 5000). A digital pH-meter (HACH, HQd) was also used for pH measurement.

**RESULTS AND DISCUSSION**

In this study, degradation of LABSA was investigated by processes of US, US/H₂O₂ and US/S₂O₈⁻². Sonochemical experiments were run with 1L of LABSA solution which has different initial concentrations. Initially, the efficiency of the US process was investigated on detergent removal at different pHs in during a 75 min reaction time for 8, 10, 14 and 20 mg/L of initial concentrations of LABSA (Figure 1-4).
Figure 1. Efficiency of sonication process at 8 mg/L of LABSA concentration under different pH.

Figure 2. Efficiency of sonication process at 10 mg/L of LABSA concentration under different pH.
According to the Figures, the best removal efficiencies were achieved at pH 4 for all different initial concentrations of LABSA. 44% of removal efficiency was obtained at pH 4 for 10 mg/L of initial LABSA concentration. If the initial concentration of LABSA was over 10 mg/L, the removal efficiency of detergent was decreased. The optimum conditions were selected as 10 mg/L of initial LABSA concentration and pH4 for further steps of study. Under these experimental conditions, the effect of reaction time was determined (Figure 5).
According to Figure 5, the removal efficiency increased with increasing time.

In the second step, the effect of oxidants on the performance of process was examined at pH 5.20 which was the original pH of solution. 10 mM of $\text{H}_2\text{O}_2$ and $\text{S}_2\text{O}_8^{-2}$ were used as an oxidant. The effects of oxidants on the process were shown in Table 1.

Table 1. The effects of oxidants on the removal efficiency (%)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$\text{H}_2\text{O}_2$</th>
<th>$\text{S}_2\text{O}_8^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>46</td>
<td>60</td>
</tr>
<tr>
<td>120</td>
<td>55</td>
<td>69</td>
</tr>
<tr>
<td>150</td>
<td>63</td>
<td>76</td>
</tr>
<tr>
<td>175</td>
<td>49</td>
<td>73</td>
</tr>
</tbody>
</table>

According to the Table 1, using the $\text{S}_2\text{O}_8^{-2}$ as an oxidant was reached the removal efficiency up to 76 %. Over 150 minutes of the reaction time, it was observed that the removal efficiency decreased.

CONCLUSION

In this study, degradation of linear alkyl benzene sulfonic acid by sonication process was investigated. The efficiency of process was evaluated on the basis of detergent removal. Sonochemical experiments were run with probe type ultrasonic device at various initial LABSA concentrations and pH values. For
all different initial LABSA concentrations, the maximum removals of detergent were achieved at pH 4. The efficiency of detergent removal was obtained as 44% for 10 mg/L of initial LABSA concentration. When the S\textsubscript{2}O\textsubscript{8}\textsuperscript{-2} was used as an oxidant, the removal efficiency was found as 76% under the experimental conditions of pH 5.2 and reaction time of 150 min.
References


