Effects of pilot-plant photochemical pre-treatment (UV/H_2O_2) on the biodegradability of aqueous linear alkylbenzene sulfonate (LAS)

Mehrab Mehrvar,[1,†] Gelareh Bankian Tabrizi,[1] and Nabil Abdel-Jabbar[2]

[1] *Department of Chemical Engineering, Ryerson University, 350 Victoria Street, Toronto, Ontario, Canada M5B 2K3*

[2] *Department of Chemical Engineering, Jordan University of Science and Technology, Irbid, Jordan 22110*

ABSTRACT. The effects of the photochemical pre-treatment by using a pilot-plant UV/H_2O_2 process on the biodegradability of aqueous linear alkylbenzene sulfonate (LAS) were studied. It was observed that the photochemical pre-treatment of the LAS solutions by UV-254/H_2O_2 increased the biodegradability of LAS solutions. Aqueous solutions with higher concentrations of LAS (> 100 mg/L) were non-biodegradable. The ratio of BOD_5/COD of the pre-treated LAS solutions was increased, indicating that the pre-treated LAS solutions were more biodegradable. This ratio was improved as the LAS solutions were more pre-treated. Also, the biodegradability factor for the pre-treated LAS solutions was increased as the time of the photochemical pre-treatment was increased.

1. INTRODUCTION

Linear alkylbenzene sulfonate (LAS) is the major anthropogenic source of organic compounds in primary sludge in municipal wastewater treatment plants. LAS has been identified with the concentrations of lower than μg/L in surface water supplies [1] and with the concentrations of 0.001–0.008 mg/L in drinking water in different countries [2]. It is also able to enhance the solubility of compounds in water, which are otherwise insoluble in other matrices; hence, it can reduce the resistance to mass transfer [3]. Due to its high water solubility, polarity, and the high mobility, LAS is a hazardous contaminant in ground and surface water supplies [4]. LAS and its intermediates are degradable in activated sludge system by consortia of aerobic microorganisms up to 99.5 and 99.1%, respectively [5, 6]. On the other hand, it has been reported that the intermediates produced by biological treatment are 10–100 times less toxic than the parent compounds [2]. LAS has also shown inhibitory effects on the anaerobic biological treatment [7, 8]. It has been reported that LAS with the concentrations of less than 10 mg/L is biodegradable under aerobic activated sludge treatment and its degradation follows Monod's equation over the ranges of 0.1–20 mg/L [9]. Moreover, it has been reported that the fate of LAS can follow first order kinetics for the similar ranges of concentrations [10]. However, the growth rate of microorganisms can be inhibited at the concentration of greater than 95 mg/L [2]. The minimum concentration of LAS which makes it toxic is not known [11]. Aqueous LAS degradation is also possible by different chemical processes [12]. Although advanced oxidation processes (AOPs) are promising alternatives to degrade solutions containing organic contaminants, the total mineralization through these processes is very expensive. On the other hand, biological treatment is relatively cheap and reliable process. However, the biological treatment is not applicable for non-biodegradable and bio-resistant compounds. Therefore, a combination of theses processes could be a cheaper and more efficient treatment option for wastewaters containing toxic and refractory organics [13].

[†]E-mail: mmehrvar@ryerson.ca

2. EXPERIMENTAL SET-UP AND PROCEDURES

Photochemical pre-treatment of LAS solutions was carried out in a pilot-plant cylindrical photoreactor using UV-254/H_2O_2. Sodium salt of dodecylbenzenesulfonic acid (Aldrich), a mixture of phenyl-substituted alkyl chain, was used in the experiments (Figure 1). The alkyl chain contains 12 carbons with the molecular weight of 348.48. The initial concentration of the LAS solutions in the photoreactor was 100 mg/L. The optimum concentration of H_2O_2 for the photolytic degradation of LAS was found 720 mg/L. Since H_2O_2 is a hydroxyl radical scavenger, the photochemical degradation of LAS decreased at higher concentrations of H_2O_2 beyond its optimum loading. The photochemical pre-treatment experiments were performed in a 76.6-L pilot-plant cylindrical re-circulating batch photoreactor, with the outside diameter of 32 cm and the nominal length of 102 cm as shown in Figure 2. Six low-pressure mercury UV lamps, with the maximum wavelength of 253.7 nm and 40 W each, were symmetrically immersed inside the photoreactor. A three-impeller mixer with adjustable speed of 44–208 rpm was inserted on the main axis of the cylindrical photoreactor. A centrifu-

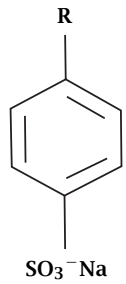

Figure 1. *Molecular structure of LAS.* R *represents the alkyl chain,* R = $(CH_2)_{11}CH_3$. *Molecular weight* = 348.48.

gal pump re-circulated the solution. The temperature of the system was controlled at 20 ± 0.01 °C by a water bath (Neslab, RTE Series). Before turning on the UV lamps, LAS was fed to the feed tank to make the proper initial concentration of the LAS. The liquid was then re-circulated for 1 h to make the LAS concentration homogeneous throughout the system prior to the start of the UV lamps. After this stabilization period, the reaction started by turning on all UV lamps. Three samples were taken periodically from the effluent of the photoreactor and analyzed immediately. The treated wastewater from this photoreactor was collected and used for the subsequent biological treatment. LAS concentrations were measured based on the transfer of methylene blue active substance (MBAS) from an aqueous solution into an immiscible phase containing anionic surfactant. This transfer was possible by ion pair formation of anionic surfactant and methylene blue. Excess methylene blue was extracted into chloroform and the blue color in the chloroform was read at 652 nm by a UV/Vis Spectrophotometer (Ultrospec 1100 *pro*, Biochrom Ltd.).

Chemical Oxygen Demand (COD) was determined by a powerful chemical oxidant, potassium dichromate in acidic solution. As the predicted COD for the sample solutions was above 50 mg/L and there were no suspended solids present in the sample solutions, the closed refluxed method (an economical technique) was chosen according to the Standard Methods to determine COD [14]. This technique is based on the oxidation of organics by a mixture of potassium dichromate and sulfuric acid. In the colorimetric method (closed reflux), oxygen consumption was measured against standards at 600 nm with the UV Spectrophotometer. The reagents were prepared in the vials (Bioscience, Inc.) in the range of 20–900 mg/L. The COD reactor (Bioscience, Inc.) was preheated to 150 ± 2 °C prior to preparing the vials.

Biochemical Oxygen Demand (BOD) was determined to monitor the effectiveness of photochemical pretreatment on the biodegradability of the LAS solutions. The low value of BOD either shows very clean water or a toxic wastewater which can inhibit microorganisms from growth. BOD_5 tests were performed according to the Standard Methods, Section 5210B [14].

To measure the Ultimate Biological Oxygen Demand (UBOD), the BOD bottles were placed in a shaker-incubator (New Brunswick Scientific Co., Inc.) at 20 °C for an extended period of time. The dissolved oxygen concentrations (DO) were measured initially and frequently to ensure that the level of DO (measured by YSI 58 Dissolved Oxygen Meter) was not low and anaerobic condition had not been occurred. If the level of the DO reached around 2 mg/L, the sample solution was aerated again. To measure the ultimate BOD, dissolved oxygen was measured frequently over a period of 30 to 60 days. When DO falls around 2 mg/L, a small amount of sample solution was transferred into a beaker and re-aerated with air. The new DO was also recorded. The total DO consumed was subtracted from the blank's DO uptake.

Removal of residual H_2O_2 is specifically important in the biological treatment step. The concentration of H_2O_2 was measured by DMP method (2,9-dimethyl-1,10-phenanthroline) and DPD method (N,N-diethyl-p-phenylenediamine). The detection limits for DMP and DPD methods were 3.4–170 and 0.1–40 mg/L, respectively. DPD method has DPD reagent tablets, which are commercially available with a colorimetric kit. It was used when lower concentration of H_2O_2 was expected. On the other hand, DMP method was used when precise determination was desirable and the H_2O_2 concentration was not expected to be very low. The DMP procedure is based on the reduction of copper(II) with H_2O_2 and production of a stable bright yellow complex of $Cu(DMP)_2^+$ with maximal absorbance at 454 nm [15].

3. RESULTS AND DISCUSSIONS

3.1. Impact of catalase on the analysis of H_2O_2.

Since the presence of H_2O_2, due to the photochemical pre-treatment, interferes with the BOD tests and inhibits the growth of microorganisms, catalase was used to eliminate the H_2O_2 present in the system for subsequent biological treatment. To investigate the impact of the addition of insufficient or excessive amounts of catalase on the analysis of H_2O_2 and BOD_5 tests, different concentrations of catalase were examined. To decompose 60 mg/L of H_2O_2, 0.1 mg of catalase was added to 100 mL of sample without stirring for 100 min [16]. The concentration of H_2O_2 was then measured by DPD method and it was observed that its concentration was close to zero. Insufficient or excessive amounts of catalase were added to six samples of H_2O_2 with the volume of 100 mL each. Sodium acetate was chosen as a standard to compare the impact of catalase on the chosen tests. BOD_5 test was chosen as a reference test. Six different samples containing different concentrations

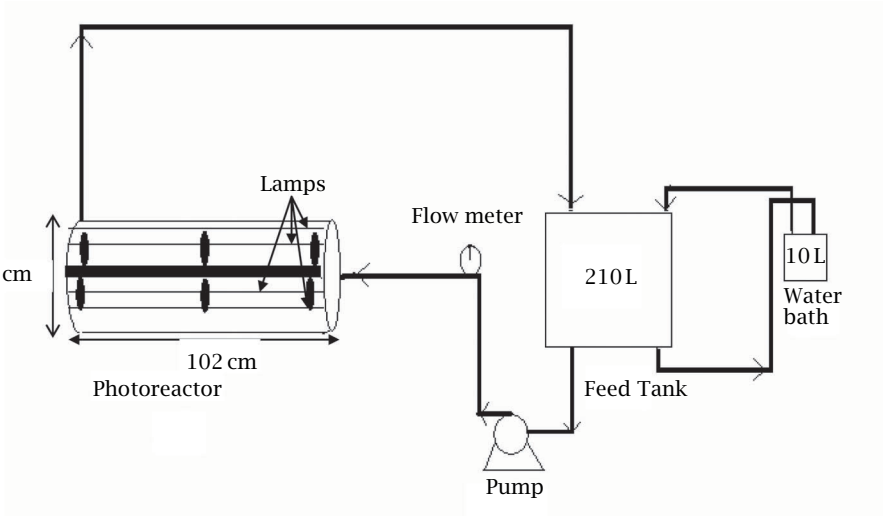

Figure 2. *Schematic diagram of the pilot-plant photochemical reactor set-up.*

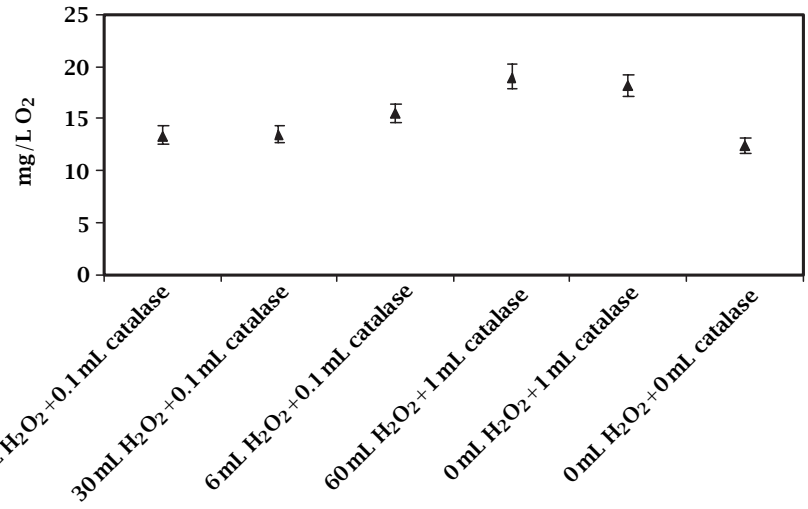

Figure 3. *The impact of the addition of insufficient or excessive amount of catalase on BOD_5 test for different concentrations of catalase. The error bars are the standard deviations of triplicates of each sample.*

of catalase were prepared. Samples 1–5 contained 0, 0.05, 0.1, 0.5, and 1 mg of catalase, respectively. The mentioned masses of catalase were dissolved in 100 mL of H_2O_2 solution with initial concentration of H_2O_2 equal to 60 mg/L. Sample 6 was 1 mg catalase with no H_2O_2 in it. Sample 7 was just sodium acetate with the concentration of 30 mg/L. Thirty mL of sodium acetate were added to 7 BOD bottles, and 25 mL of samples 1–6 were added to just 6 of those bottles. The rest of the bottles were filled with appropriate amount of seed solution and diluted water. The sealed bottles were kept in incubator at 20 °C for 5 days. It was expected that if the H_2O_2 was reduced by proper amount of catalase, the BOD_5 for the solutions should be around the BOD_5 for sodium acetate solution alone. Figure 3 depicts that when the concentration of catalase was lower than that of its optimum level, there are still some H_2O_2 present in solution. Therefore, residual H_2O_2 produce a toxic effect and reduce the consumption of oxygen, and BOD_5 cannot reach to its true value which is equal to the BOD_5 of sodium acetate alone. Moreover, excessive amount of catalase can increase the consumption of oxygen in the test. Dissolved oxygen (DO) concentration was more than saturation level when catalase was in excess. However, DO was dramatically decreased after 5 days of incubation. Therefore, the concentration of catalase should be around its optimum value, which is 0.1 mg of catalase per 100 mL of sample containing 60 mg/L H_2O_2, to eliminate 60 mg/L of H_2O_2 effectively.

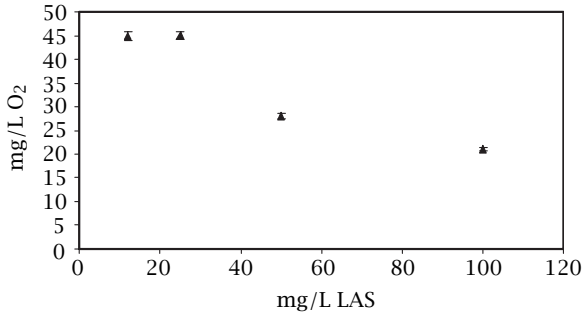

Figure 4. *BOD_5 test results for different concentrations of untreated LAS. The error bars are the standard deviations of triplicates of samples.*

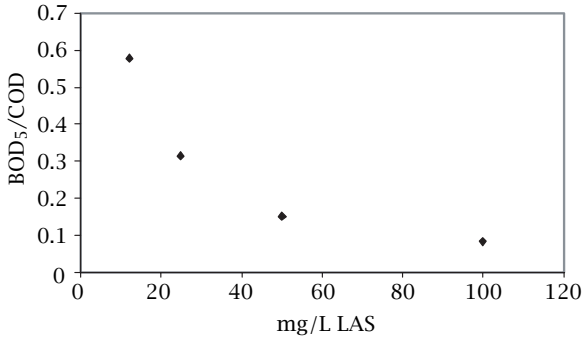

Figure 5. *Ratio of BOD_5/COD for different concentrations of untreated LAS.*

3.2. Effects of photochemical pre-treatment on the biodegradability of LAS. The biodegradability of four different concentrations of untreated LAS was examined (12, 25, 50, and 100 mg/L LAS). The BOD_5 tests for all solutions were performed. Residual H_2O_2 was eliminated prior to each test as outlined in previous section. As Figure 4 shows, by increasing the concentration of LAS, the consumption of O_2 was decreased by about 50% by increasing the concentration of LAS from 25 mg/L to 100 mg/L. It is obvious that this decrease was not due to the decrease of organics in solutions, however, the microorganisms in the activated sludge could not grow and use oxygen by increasing the LAS concentration. Therefore, LAS has inhibitory effect on microorganisms as its concentration increases. Moreover, the ratio of BOD_5/COD is often used to express the biodegradability of wastewater. Values of BOD_5/COD less than 0.4 suggest that the wastewater is difficult for biodegradation. Figure 5 shows the ratio of BOD_5/COD for LAS at 100 mg/L is about 0.1, suggesting that LAS is recalcitrant at higher concentrations and it is resistant to conventional biological treatments. These results were in accordance with other studies that the growth rate of mixed culture of microorganisms can be inhibited by LAS at the concentration of 95 mg/L [2, 17].

As Figure 6 depicts, the ratio of C/C_o (concentration of LAS at time t/initial concentration of LAS) was decreased up to 92% during 90 minutes of photolytic reaction. However, this decrease was sharp during the initial period of the reaction. After 15 minutes, C/C_o decreased and an opposite trend was observed for the ratio of BOD_5/COD. This suggests that as the concentration of LAS decreased, LAS with lower concentrations and its intermediates were more biodegradable than the parent compound. After 90 minutes, the BOD_5/COD was 0.4, suggesting that although the untreated LAS was recalcitrant to microorganisms, LAS with lower concentration and its intermediates were biodegradable under conventional biological treatment.

3.3. Biodegradability of pre-treated LAS solutions based on ultimate BOD (UBOD). The conventional BOD tests were also carried out for the following LAS solutions:

(1) Untreated LAS solution with an initial concentration of 100 mg/L,

(2) Photo-chemically pre-treated LAS solution by UV and optimum concentration of H_2O_2 (720 mg/L) after 15 minutes of pre-treatment, and

(3) Photo-chemically pre-treated LAS solution by UV and optimum concentration of H_2O_2 (720 mg/L) after 1.5 h of pre-treatment.

Figure 7 illustrates the BOD results for these three solutions in a 30-day period. With high concentration of LAS in the untreated sample solution, oxygen consumption was only 5.2 mg/L during 30 days, indicating that LAS had little biodegradability or was toxic to the microorganisms. The consumption of oxygen during 30 days for the second sample solution was 38 mg/L, which was eight times more than that of the first one. This consumption was still less than that of the third sample (57 mg/L O_2). Therefore, the pre-treated LAS solutions were more biodegradable than that of untreated LAS solutions. As the photochemical reaction progressed, the biodegradability of the LAS solution was increased. Ultimate BOD may be estimated by using the following equation:

$$\mathrm{BOD}_t = \mathrm{UBOD}(1 - e^{-kt}) \tag{1}$$

In which BOD_t, k, t, and UBOD are the amount of BOD at time t, reaction rate constant, reaction duration, and the ultimate BOD, respectively. Plotting the BOD versus time for those sample solutions indicated that the removal of LAS followed first order model (eq. (1)). Table 1 shows the constant parameters for eq. (1). As Table 1 shows, the sample solution with 1.5 h of photolytic pre-treatment had the fastest reaction rate ($k = 0.2839$ day^{-1}). Therefore, it would be biodegraded twice faster

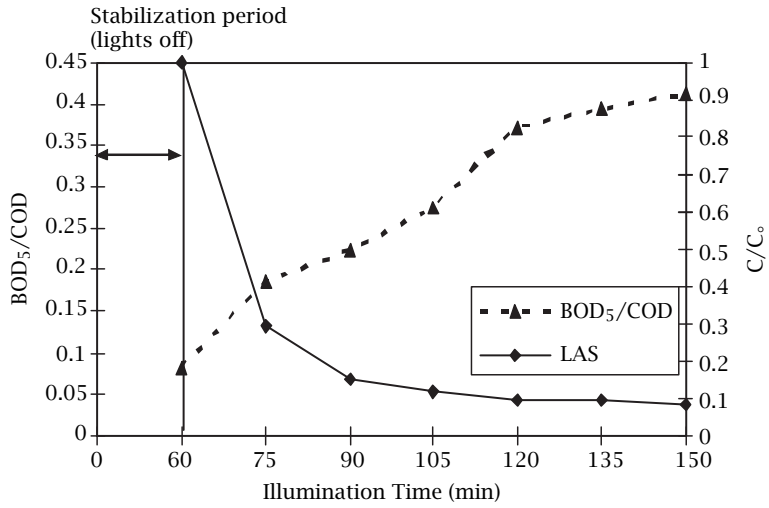

Figure 6. *Effects of photochemical pre-treatment of LAS using UV*-254 *and* 720 mg/L *of* H_2O_2 *on its biodegradability. Flow rate* = 8 LPM, *Mixing* = 183 rpm, C_{LAS} = 100 mg/L.

Table 1. *Parameters in BOD model based on eq.* (1) *for three sample solutions.*

PROCESS	**UBOD (mg/L O_2)**	k **(day^{-1})**
Untreated LAS with initial concentration of 100 mg/L LAS	5.2	0.1771
Pre-treated LAS solution after 15 min	38	0.2538
Pre-treated LAS solution after 1.5 h	60	0.2839

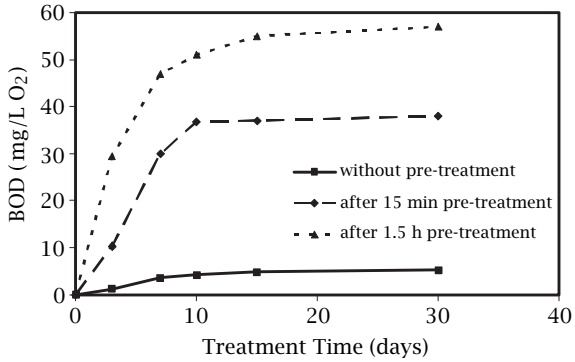

Figure 7. *BOD tests for three sample solutions in a* 30*-day treatment period for the following conditions* (1) *Untreated LAS solution with the concentration of* 100 mg/L, (2) *Pre-treated LAS solution after* 15 min *by a pilot-plant photoreactor using UV*-254 *and optimum concentration of* H_2O_2 (720 mg/L), (3) *Pre-treated LAS solution after* 1.5 h *by a pilot-plant photoreactor using UV*-254 *and optimum concentration of* H_2O_2 (720 mg/L).

than the untreated sample solution with initial concentration of 100 mg/L of LAS.

It is assumed that the ultimate BOD of an industrial wastewater sample solution is $0.92\times(COD)_d$, where $(COD)_d$ is the biodegradable portion of total COD of the sample solution [18]. Moreover, total soluble COD may be calculated as the sum of biodegradable and non-biodegradable COD. Therefore, the portion of non-biodegradable COD for the above sample solutions may be determined easily. It was observed that as the photolytic reaction of LAS proceeded, the portion of non-biodegradable COD was decreased. The non-biodegradable COD for the sample solutions after 1.5 h of photolytic pre-treatment with UV-254/H_2O_2 was 55% of total COD, while this value for the untreated LAS solution was 93%. Consequently, half of the total COD in the sample with 1.5 h pre-treatment was biodegradable, whereas almost all of the total COD in the untreated sample was non-biodegradable COD. Therefore, if LAS with photolytic pre-treatment is treated further by the biological treatment, all of the organics cannot be removed due to the presence of some non-biodegradable intermediates in the effluent of the photochemical pre-treatment. This portion of non-biodegradable COD can be corresponded to the primary photolytic degradation of LAS oxidizing alkyl chain and resulting sulfophenyl(di)carboxylates. It has also been reported that sulfophenyl(di)carboxylates are refractory to biodegradation [11]. Consequently, as the photolytic reaction proceeded, the biodegradable portion of COD was produced through the cleavage of the phenyl ring and removing sulfonate group.

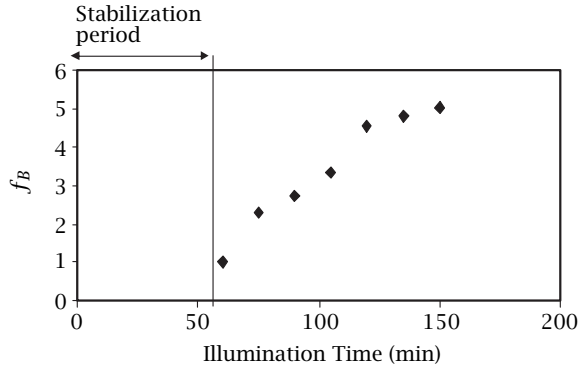

Figure 8. *Biodegradability factor for the pre-treated LAS solutions using UV*-254 *and* 720 mg/L H_2O_2.

Relative changes in the biodegradability of wastewater samples during the photochemical oxidation can be also expressed in terms of biodegradability factor, f_B, as follows [19]:

$$f_B = \frac{\mathrm{BOD}_{5,t}(\mathrm{COD}_t)^{-1}}{\mathrm{BOD}_{5,0}(\mathrm{COD}_0)^{-1}} \tag{2}$$

where f_B, COD_0, COD_t, $\mathrm{BOD}_{5,t}$, and $\mathrm{BOD}_{5,0}$ are biodegradability factor, initial COD, COD at time t, 5-day BOD at time t, and 5-day BOD at time zero, respectively. As Figure 8 illustrates, the biodegradability factor for the pre-treated LAS was increased as the time proceeded. Therefore, it was concluded that pre-treatment of LAS was toward the increasing of its biodegradability. Biodegradability factor was increased sharply during the first hour and later gradually. This is also in accordance with the $\mathrm{BOD}_5/\mathrm{COD}$ ratio, as this ratio follows the same pattern.

4. CONCLUSIONS

It was observed that the biodegradability of LAS highly depends on its concentration. LAS solutions with the concentration of 100 mg/L were non-biodegradable and had inhibitory effects on microorganisms. It was observed that as the concentration of LAS solutions increased, their biodegradability was decreased. The ratio of $\mathrm{BOD}_5/\mathrm{COD}$ of the LAS solutions was decreased as the concentration of the LAS in the solution increased. It was observed that this ratio was less than 0.3 for solutions with concentration of LAS greater than 25 mg/L. This indicates that the solutions with concentrations of higher than 25 mg/L LAS were non-biodegradable. Finally, the biodegradability factor for pre-treated LAS solutions was increased with the increase of pre-treatment time, indicating that pre-treated LAS solutions was more biodegradable than that of untreated solutions.

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