

## FENTON DEGRADATION OF LINEAR ALKYL BENZENE SULPHONATES (LAS)

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**Abstract.** Among Advanced Oxidation Processes (AOPs), Fenton's reagent has been efficiently used as a chemical process for wastewater treatment. Fenton's reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds. Fenton system consists of ferrous salts combined with hydrogen peroxide under acidic condition. The effect of Fenton degradation of linear alkylbenzene sulphonates (LAS) at different initial concentration ( $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L) was investigated. All experiments used a temperature of 30°C, stirring speed of 125 rpm, a reaction time of 90 min and initial pH of 3.0. It was found that 82%, 64% and 49% of TOC removals were achieved at  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L respectively. It was also found that the main degradation of LAS proceeds via reaction with OH<sup>•</sup> radicals. The addition of sodium benzoate, an OH<sup>•</sup> radical scavenger was inhibited and retarded the oxidation. For instance, 28 % and 82 % of TOC removals were achieved in the presence and absence of radical scavenger at LAS concentration of  $0.25 \times 10^{-3}$  mol/L.

*Key words:* AOPs, Fenton's reagent, Radical Scavenger, Wastewater, LAS

### 1.0 INTRODUCTION

Linear alkylbenzene sulphonate (LAS) was first commercialized in the early sixties as a replacement of the poorly biodegradable DBS (Dodecylbenzene Sulphonate-branched alkylbenzene sulphonate). 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 environment concern [1]. Linear alkylbenzene sulphonates (LAS) are anionic surfactants which were introduced in 1964 as the readily biodegradable replacement for highly branched tetrapropylbenzene sulphonate. LAS contain an aromatic ring sulphonated at the para position and attached to a linear alkyl chain at any position except the terminal ones.

The commercial product mainly consist of a complex mixture of various homologues and isomers, representing different alkylchain lengths (ranging from 10 to 14 carbon atoms) and aromatic ring positions along the linear alkyl chain [2]. In search of efficient destructive treatment technologies for LAS-containing effluents, several oxidation processes have been tested.

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Ozonation [3],[4], wet air oxidation [5],[6],[7],[8] and ultrasonic irradiation [9],[10] have been employed to treat LAS. In recent years, considerable interest has been shown in the application of Fenton's reagent for the treatment of hazardous contaminants in water.

Over the last 15 years, Fenton oxidation had been used in wastewater due to its ability to eliminate undesirable chemical compounds [11]. Fenton's reagent, a mixture of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup>, which can generate great amount of ·OH with powerful oxidizing ability, has been proposed for the degradation of some organic pollutants [12]. The Fenton system uses Fe<sup>2+</sup> to react with H<sub>2</sub>O<sub>2</sub>, producing OH· with powerful oxidizing abilities to degrade toxic organic contaminants [13]. Several research studies reported successful removal of a wide range of organic pollutants [11], [13-20]. Fenton process can be defined as the oxidation of organic compound in an aqueous solution by using Fenton reagent (ferrous ion and hydrogen peroxide). In Fenton system, interaction between H<sub>2</sub>O<sub>2</sub> and Fe (II) produces OH· radicals with powerful oxidizing abilities to degrade toxic organic contaminants [13]. In general the accepted mechanism of Fenton reaction to form hydroxyl radicals is as follows:



Fe(II) also regenerated through the reaction of Fe(III) with H<sub>2</sub>O<sub>2</sub> in the so-called Fenton-like-reaction



The OH· radicals formed through Equation (1) will then attack the organic substrates present in the wastewater. When large amounts of Fe<sup>2+</sup> are present either in Fenton reaction or Fenton-like-reaction system, the degradation of organic compounds are very fast because large amount of OH· radical are produced. In order to have additional data and information concerning the contribution of OH· radicals to the Fenton degradation of LAS, a series of Fenton experiment were made in the presence of a radical scavenger. Adding some species known as radical scavenger will suppress the organic oxidation [21-22]. This happened because the characteristic of antioxidant which attack the free radicals present in the solution.

Radical scavenger (antioxidant) is a substance that prevents the oxidation. OH· radicals that were produced in Fenton reaction degraded and break the molecules of organic compound into smaller intermediate compound that can be degraded easily than the original molecules. The presence of radical scavenger such as sodium benzoate added into the process will inhibit the degradation of organic substrates. This is due to the radical scavenger scavenged free radicals, attacked and converted them to other products before free radicals can attack the compound. The interaction between radical scavenger and hydroxyl radical caused reduction of free radical amount in solution.

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 Fenton reaction at different initial concentrations. The effect of sodium benzoate (a radical scavenger) on Fenton degradation of LAS will also be studied.

## 2.0 MATERIALS AND METHODS

### 2.1 Materials

The specific LAS compound studied, sodium dodecylbenzene sulphonate ( $C_{12}H_{25}C_6H_4SO_3Na$ ), sodium benzoate ( $C_7H_5NaO_2$ ), ferrous sulfate and hydrogen peroxide (30% extra pure) were purchased from Scharlau Chemical S. A., Spain. Sodium perchlorate and acetonitrile for HPLC analysis were purchased from Merck. Fenton experiments (with and without the presence of radical scavenger) were performed with three different initial LAS concentrations,  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L, and the pH of 3.0. This resulted in an initial TOC of  $\approx 20$ , 50 and 100 mg/L respectively. The TOC results were not very much different from the theoretical TOC values from each concentration in that the theoretical TOC values for  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L were  $\approx 22$ , 54 and 108 mg/L respectively.

### 2.2 Fenton Experiments

Aqueous solution of the LAS substrate were prepared (at concentrations of  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L) and subjected to Fenton experiments. Fenton degradation of LAS was carried out continuously while being stirred at 150 rpm and at  $30^\circ C$  for 90 minutes. In a typical Fenton experiment, 2000 mL of the LAS solution was loaded into the glass reaction vessel and mixed with 0.01 mol/L of  $FeSO_4 \cdot 7 H_2O$ . Initial pH was adjusted to 3.0 with the addition of 0.1 mol/L of  $H_2SO_4$  solutions. After pH adjustment, 5 mL of 0.1 mol/L hydrogen peroxide ( $H_2O_2$ ) was added to the mixing of SDBS and Fe(II) solution to start the experiment. For Fenton experiments in the presence of radical scavenger, the above steps were repeated; however 40 mL of 0.5 mol/L of sodium benzoate was added before  $H_2O_2$  samples were taken from the vessel at the end of each experiment (after 1, 2, 5, 10, 20, 30, 45, 60 and 90 min) for analysis with respect to total organic carbon (TOC) and High Performance Liquid Chromatograph (HPLC) analysis.

### 2.3 High Performance Liquid Chromatography (HPLC) Analysis

High performance liquid chromatography (HPLC) was used for the determination of LAS concentrations during Fenton degradation. This analysis was done by comparing the residual LAS during Fenton experiments with external standards which were prepared with known concentration ( $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L) of LAS substrate. The residual LAS after Fenton experiments were determined by reverse phase high performance liquid chromatography (HPLC) on Water 600 Controller with absorbance detector (Water Model 486) and UV detector at wavelength of 230 nm using column 18 (3.9mm x 150mm). A specially developed gradient method utilizing an acetonitrile-water-sodium perchlorate mobile phase was used to elute and separate the LAS and its reaction products. Two mobile phases were used: solution A containing 70% acetonitrile (Merck), deionised water and 0.15M sodium perchlorate (merck); and solution

B containing 0.15M sodium perchlorate in deionised water. Mobile phase A was injected between two consecutive HPLC runs to ensure no residuals from the previous run were carried out over to the next run as well as to wash sample needles and sample loop. Both the standards and the samples were periodically run in duplicate to test the reproducibility of the measurements which was within  $\pm 5\%$  difference.

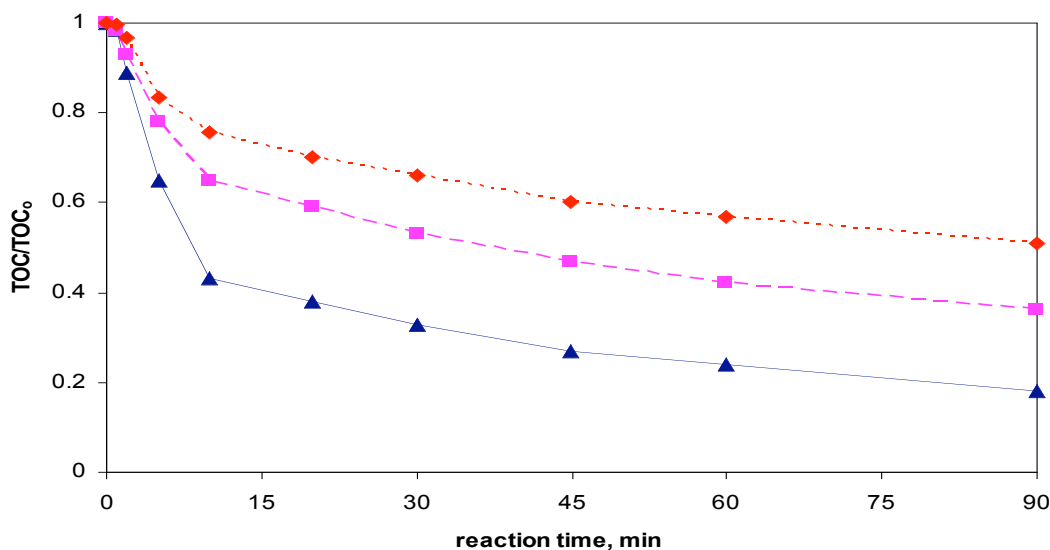
## 2.4 Total Organic Carbon (TOC)

TOC is defined as the total amount of organically bound carbon in a sample. TOC was assessed so as to determine the organic carbon that had been fully oxidized to  $\text{CO}_2$ . TOC was measured with a Shimadzu TOC- $V_E$  Analyser which is based on combustion and subsequent nondispersive infrared (NDIR) gas analysis. Total organic (TC) was firstly measured and then the inorganic carbon (IC) was measured. TOC was determined by subtracting IC from TC. The uncertainty in assays, quoted as the deviation of three separate measurements, was never larger than 1% for the range of TOC concentration.

## 3.0 RESULTS AND DISCUSSION

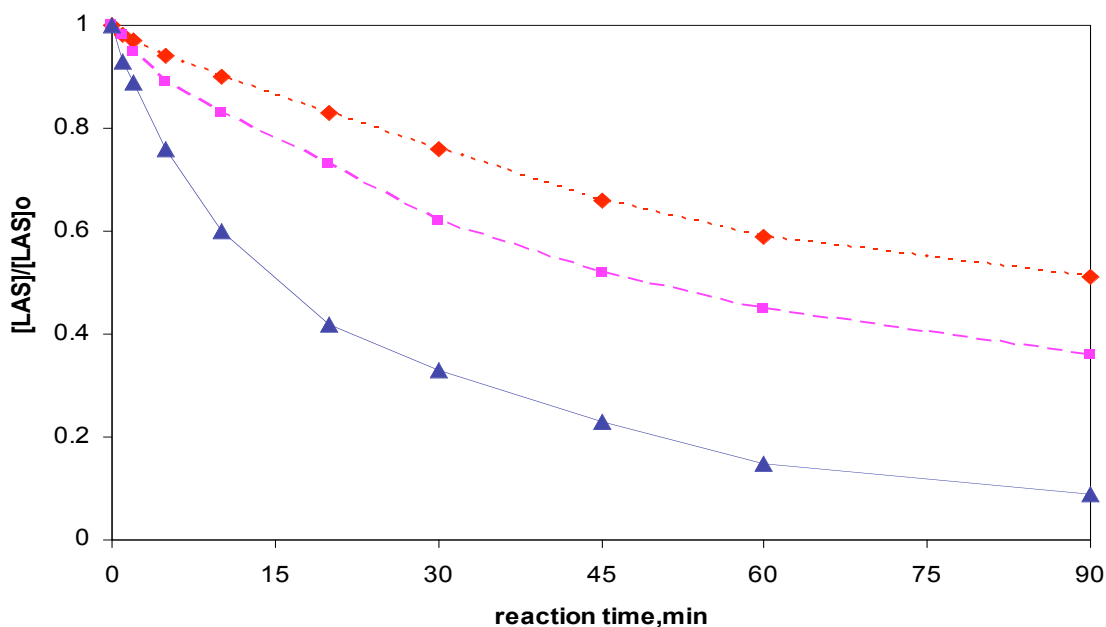
### 3.1 Effect of Initial LAS Concentration on the Fenton Degradation of LAS

Fenton degradation of three different initial concentrations of LAS,  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L, were performed. To quantify the overall Fenton degradation of LAS, the percentage of TOC removal of the solutions was measured as a function of time. Figure 1 shows the normalized TOC removal during Fenton degradation of LAS at different initial concentrations. As seen, the TOC removal increases with decreasing initial concentrations of LAS. For instance,  $0.1 \times 10^{-3}$  mol/L resulted in almost 82% TOC removal after 90 min of Fenton degradation, and 64% and 49% TOC removals were achieved at  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L respectively after 90 min of Fenton degradation.



**Figure 1** Normalised TOC-time profiles during Fenton degradation of LAS as a function of concentration. -▲-  $0.1 \times 10^{-3}$  mol/L, -■-  $0.25 \times 10^{-3}$  mol/L, -◆-  $0.5 \times 10^{-3}$  mol/L

Figure 2 shows the LAS degradation profiles with time for different initial concentrations of  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L. As shown, the LAS degradation increases with decreasing initial concentrations of LAS. For instance,  $0.1 \times 10^{-3}$  mol/L resulted in almost 91% LAS removal after 90 min of Fenton degradation, and 64% and 49% LAS removals were achieved at  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L respectively after 90 min of Fenton degradation. Ashokkumar *et al.* reported that the degradation of LAS increases with a decrease in the LAS concentration. They also added that the increasing of LAS degradation closely related to the LAS molecules that are readily to be attacked by  $\text{OH}^\bullet$  radicals. The reaction between LAS and  $\text{OH}^\bullet$  radicals can be explained using Eq. (8). From this equation it can be concluded that the LAS degradation increases with a decrease in the initial LAS concentrations. This is consistent with the results of Manouski *et al.* where they found that the anionic surfactant degradation increases with a decrease in the initial surfactant concentrations.

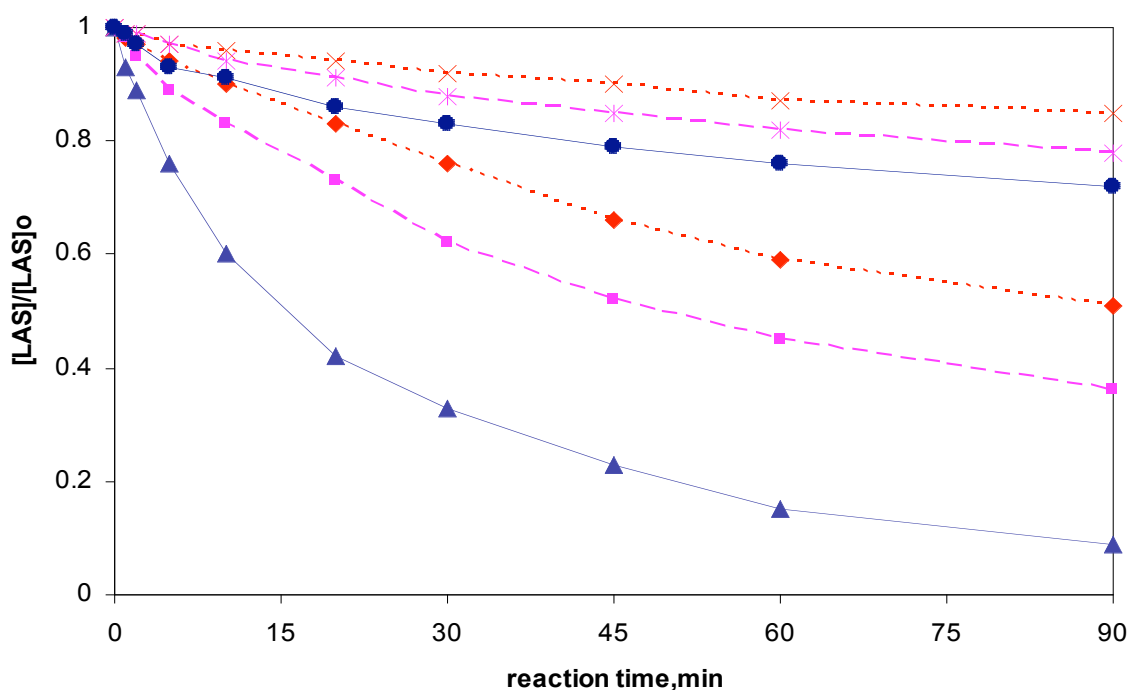


**Figure 2** Normalised LAS concentration-time profiles during Fenton degradation of LAS as a function of concentration. -▲-  $0.1 \times 10^{-3}$  mol/L, -■-  $0.25 \times 10^{-3}$  mol/L, -◆-  $0.5 \times 10^{-3}$  mol/L

### 3.2 Effect of Radical Scavenger on Fenton Degradation of LAS

It has been discussed previously that  $\text{OH}^\bullet$  radicals play a major role for the Fenton degradation of LAS. 82%, 64% and 49% TOC removals were achieved at  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L, respectively after 90 min of Fenton degradation in the absence of sodium benzoate. In order to determine the significant contribution of  $\text{OH}^\bullet$  radicals to the degradation of LAS, a series of Fenton degradation experiments were made in the presence of radical scavenger, sodium benzoate. The presence of radical scavenger as

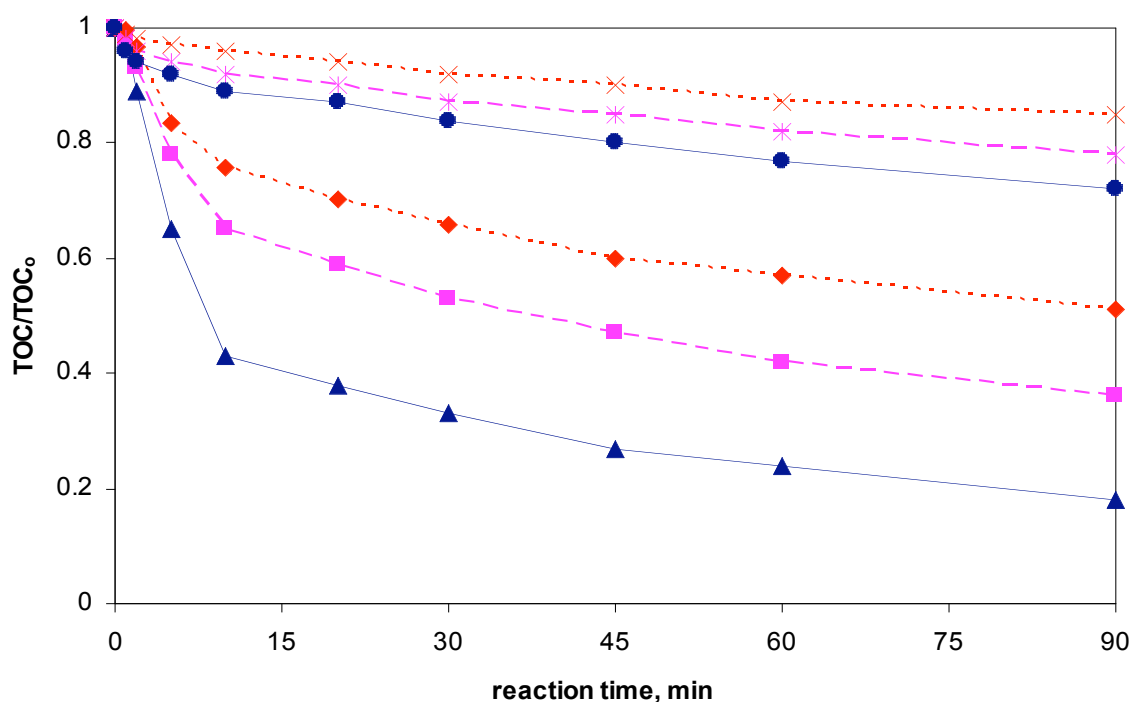
sodium benzoate added into the process will inhibit the degradation of organic substrates. Figure 3 shows the LAS degradation profiles with time for different initial concentrations of  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L in the absence and presence of the sodium benzoate. It can be seen that the degradation of LAS was inhibited in the presence of sodium benzoate. The degradation was quenched by the addition of sodium benzoate. As clearly seen, the addition of sodium benzoate at a concentration of  $0.5 \times 10^{-3}$  mol/L resulted in a small amount of LAS degraded compared to that in the absence of sodium benzoate suggesting that  $\text{OH}^\bullet$  radicals play a vital role in Fenton degradation of LAS. For instance, 28%, 22% and 15% LAS removals were achieved at  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L respectively after 90 min of Fenton degradation in the presence of sodium benzoate whereby 91%, 64% and 49% LAS removals were achieved at  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L respectively after 90 min of Fenton degradation in the absence of sodium benzoate.



**Figure 3** Normalised LAS concentration-time profiles at different initial concentrations during Fenton degradation of LAS in the absence and presence of sodium benzoate. -▲-  $C_{\text{LAS}} = 0.1 \times 10^{-3}$  mol/L,  $C_{\text{benzoate}} = 0$  mol/L, -■-  $C_{\text{LAS}} = 0.25 \times 10^{-3}$  mol/L,  $C_{\text{bromoide}} = 0$  mol/L, -◆-  $C_{\text{LAS}} = 0.5 \times 10^{-3}$  mol/L,  $C_{\text{bromoide}} = 0$  mol/L, -●-  $C_{\text{LAS}} = 0.1 \times 10^{-3}$  mol/L,  $C_{\text{bromoide}} = 0.5$  mol/L, -\*-\*  $C_{\text{LAS}} = 0.25 \times 10^{-3}$  mol/L,  $C_{\text{bromoide}} = 0.5$  mol/L, -x-  $C_{\text{LAS}} = 0.5 \times 10^{-3}$  mol/L,  $C_{\text{bromoide}} = 0.5$  mol/L

To determine the overall degradation of LAS, Figure 4 shows the TOC removals with and without the presence of sodium benzoate. From Figure 4 it can be seen that the degradation of LAS was inhibited in the presence of radical scavenger. The degradation was quenched by the addition of sodium benzoate. For instance, 28 %, 22 % and 15 % of

TOC removals were achieved at  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L respectively after 90 min of Fenton degradation in the presence of sodium benzoate and 82%, 64% and 49% TOC removals were achieved at  $0.1 \times 10^{-3}$  mol/L,  $0.25 \times 10^{-3}$  mol/L and  $0.5 \times 10^{-3}$  mol/L respectively after 90 min of Fenton degradation in the absence of sodium benzoate. From Figures 3 and 4, it can be suggested that the degradation of LAS was inhibited in the presence of radical scavenger, suggesting  $\text{OH}^\bullet$  radical induced degradation pathway is the dominating Fenton degradation mechanism of LAS.



**Figure 4** Normalised TOC-time profiles at different initial concentrations during Fenton degradation of LAS in the absence and presence of sodium benzoate. -▲-  $C_{\text{LAS}} = 0.1 \times 10^{-3}$  mol/L,  $C_{\text{benzoate}} = 0$  mol/L, -■-  $C_{\text{LAS}} = 0.25 \times 10^{-3}$  mol/L,  $C_{\text{benzoate}} = 0$  mol/L, -◆-  $C_{\text{LAS}} = 0.5 \times 10^{-3}$  mol/L,  $C_{\text{benzoate}} = 0$  mol/L, -●-  $C_{\text{LAS}} = 0.1 \times 10^{-3}$  mol/L,  $C_{\text{benzoate}} = 0.5$  mol/L, -\*-\*  $C_{\text{LAS}} = 0.25 \times 10^{-3}$  mol/L,  $C_{\text{benzoate}} = 0.5$  mol/L, -x-  $C_{\text{LAS}} = 0.5 \times 10^{-3}$  mol/L,  $C_{\text{benzoate}} = 0.5$  mol/L

#### 4.0 CONCLUSION

It can be summarized that Fenton degradation of LAS increases with decreasing initial concentrations. The TOC removals were increased as the initial concentration of LAS increased. The Fenton degradation of LAS was inhibited in the presence of sodium benzoate. Fenton degradation of LAS in the presence of radical scavenger suggests that  $\text{OH}^\bullet$  radical induced degradation pathway is the dominating Fenton degradation mechanism of LAS. This was clearly seen from the effect of sodium benzoate to the total degradation (i.e. TOC results) as well as the LAS degradation profiles.

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