EFFECT OF FENTON PROCESS (H\(_2\)O\(_2\) / Fe\(^{2+}\)) ON REMOVAL OF LINEAR ALKYLBENZENE SULFONATE USING CENTRAL COMPOSITE


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ABSTRACT
This study investigates the degradation of Linear Alkylbenzene Sulfonate (LAS) in aqueous solution using Fenton’s process in a batch reactor (at pH = 3 and 25°C). Experiments were carried out to survey the effects of the amounts of ferrous sulfate (FeSO\(_4 \cdot 7\)H\(_2\)O) and hydrogen peroxide (H\(_2\)O\(_2\)) on the LAS and COD removal. Central composite design and response surface methods were used to optimize the Fenton oxidation process through examination of three independent operating variables namely oxidant dose (H\(_2\)O\(_2\)), catalyst dose (Fe\(^{2+}\)) and reaction time., hydrogen peroxide dose ranging from 150 to 750 mg /L and Fe\(^{2+}\) concentration in the range of 10 –130 mg /L were selected to be examined at different reaction times between 20 and 80 minutes. Models were developed and results shows that the oxidation capacities of H\(_2\)O\(_2\)/Fe\(^{2+}\) were highly dependent on the concentration of H\(_2\)O\(_2\) and Fe\(^{2+}\). Satisfactory decay rates of LAS to lock up biodegradable concentration level were obtained, and in the case for oxidation of 200 mg /L LAS, the optimum values were achieved at 600 and 130 mg/L for H\(_2\)O\(_2\) and Fe\(^{2+}\), respectively.

Key words: Linear alkylbenzene sulphonate; Fenton process; hydroxyl radicals; Central Composite Design; Response Surface Methodology

INTRODUCTION
A group of organic chemicals are surfactants “surface-active agents” which are formulated with cleaning or solubilization properties (Eng et al., 2006; Mungray and Kumar, 2009). They are classified in four types: anionic, cationic, nonionic and amphoteric (Mungray and Kumar, 2009). The world surfactant production was 9.3 million tons in 1995, and it was applied in different fields such as textiles, fibers, food, paints, polymers, cosmetics, pharmaceuticals, microelectronic, mining, oil recovery, and pulp-paper industries (Aboulhassan 2006). Also, Erkuden Pérez-Carrera and coworkers (2010) reported, the consumption of surfactants in Europe was two million tons during the year 1999, as stated by the Council of European Surfactant Producers (CESIO) information.

Anionic surfactants, which are used in formulation of detergents are the most important group of surfactants (Aboulhassan 2006). Furthermore, among anionic surfactants, Linear Alkylbenzene Sulphonate (LAS) is used extensively in production of household and industrial detergents because of its greater cleansing properties and relatively
low cost (Garcia et al., 2005; Krogh et al., 2007; Mungray and Kumar, 2009). The molecule of LAS is made up by an alkyl chain with different length and SO$_3$Na group, and both are connected to a benzene ring which are hydrophobic and hydrophilic groups, respectively (Jensen, 1999). Surfactants can enter the environment through discharge of some wastewaters such as those from manufacturing toiletries and detergents (Papadopoulos, et al., 1997; Dehghani, et al., 2007), and raw sewage which contains about 1-15 mg/L of LAS (Tchobanoglous, et al., 2003).

Usage of sewage sludge for amendment of soil was reported as a way of LAS release to the environment (Carlsen et al., 2002). They can cause foams in rivers and effluent treatment plants. Moreover, these components have adverse impacts on human, plants and animals such as fish (Aboulhassan, 2006). Mungray and Kumar (2009) reported that 0.02 – 1.0 mg LAS /L in aquatic environment can cause harm in fish gills. Therefore, the allowable concentration of LAS were limited to 0.5 mg/L for drinking water and 1.0 mg/L for other objectives (Aboulhassan, 2006).

LAS is biodegradable under aerobic conditions (Carlsen et al., 2002). However, researchers have shown that the conventional method using aerobic bacteria are suitable for treating only slightly contaminated waters containing maximum 50 mg (LAS)/L (Mantzavinos et al., 2001). The reason of such failure was low degradation kinetics and foam production (Aboulhassan, 2006). Among the various treatment methods, electrocoagulation and advance oxidation processes (AOPs) are known as proper techniques to remove and degrade toxic aqueous pollutants or these processes are applicable to improve the biodegradability of the organic materials existing in the wastewater (Luis and Varona 2003; Mahvi et al., 2007; Bazrafshan et al., 2007). Within the last two decades, researchers have focused on the use of chemical pretreatment methods to increase the rate of biodegradation of resistant compounds (Mantzavinos et al., 2001). Among the AOPs, Fenton process because of high oxidation power, rapid oxidation kinetics, being relatively cheap with easy operation and maintenance is used for treating various industrial wastewaters, which contain toxic and biologically refractory organic substances such as pesticides, aromatic amines and phenols (Sun et al. 2007; Tang and Tassos, 1997).

This process, which was revealed about 100 years ago (Neyens and Baeyens, 2003), generates hydroxyl radicals (‘OH) which is highly oxidative. The hydroxyl radical attacks the organic pollutants and degrades them (Neyens and Baeyens, 2003; Tang and Tassos, 1997). Literature shows that Fenton’s reagent (FR) has been utilized to treat inorganic and organic components in synthetic or real aqueous solutions such as LAS, atrazine, phenol, trihalomethanes, industrial wastewater (Chan and Chu, 2003; Gallard and De Laat, 2000; Grymonpré et al., 2001; Lin et al., 1999; Tang and Tassos, 1997).

The present work was undertaken to develop experimental tests employing Fenton oxidation process in treating LAS in synthetic solution and evaluate a model that provides optimum concentration of catalyst (FeSO$_4$), oxidant (H$_2$O$_2$) and oxidation time to reduce LAS concentration and to confine biodegradable concentration and The optimization of the operating conditions for Fenton process will be beneficial.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables on the response (Mason, 2003; Draper and Smith, 1998). In current researches, the Central Composite design (CCD) and response surface methodology (RSM) techniques have been applied for optimization and modeling of chemical and biological processes such as advance treatment of olive oil processing wastewater using Fenton with hydrogen peroxide (Ahmadi et al., 2005), coagulation–flocculation treatment of leachate using poly-aluminum chloride (PACl) and alum (Ghafari et al., 2009). Nitrate remediation in a novel upflow bio-electrochemical reactor (Ghafari et al., 2009). Therefore, in this study central composite design and response surface methodology were employed in order to examine different concentrations of H$_2$O$_2$, FeSO$_4$ and oxidation time and considering interactive effects of these three main parameters.
MATERIALS AND METHODS

Chemicals and wastewater
All reagents used in this work were analytical reagent grade. Synthetic solution of LAS was prepared from the commercial product with the formula C_{18}H_{29}NaSO_{3} (88%) supplied by ACORS ORGANIC. Ferrous sulfate (FeSO_{4}.7H_{2}O, 99.5%) and hydrogen peroxide (H_{2}O_{2}, 35% w/w) were supplied by Merck Company, Germany. A 50% NaOH stock solution was used to prepare its one molar solution, which is used to stop Fenton reaction at the prescribed reaction times. A 50% H_{2}SO_{4} solution was used to prepare its one molar solution, which is used to adjust pH at 3. All solutions of LAS, H_{2}O_{2}, FeSO_{4}.7H_{2}O, H_{2}SO_{4} and NaOH were made fresh before performing experiments to avoid any contamination during storage. Deionized water was used for dilution and preparation of solutions.

Experimental method
A series of batch tests were employed to examine degradation at the synthetic wastewater under different concentrations of H_{2}O_{2} and ferrous sulfate. All experiments were carried out at the environmental temperature using five series of Pyrex glass (volume=1.5L) as batch reactor, which was equipped with a variable mixer. Each flasks was designed at a specific concentration of Fenton reagent at different reaction times. The flaxes were filled to the capacity of 1L by stock LAS solution with initial concentration equal to 200 mg/L. Then pH of the solution was adjusted to 3. Furthermore, the hydrogen peroxide was as a variable at the arranged concentrations of 150, 300, 450, 600 and 750 mg/L. The concentrations of Fe^{2+} (as catalysts) as 10, 40, 70, 100 and 130 mg/L were tested in this study.

Analytical methods
The LAS concentration (using Perkin Elmer Lambda 25 UV/Vis Spectrophotometer at652 nm) and chemical oxygen demand (COD ) were determined according to Standard methods (APHA., 1998); hydrogen peroxide was measured by iodometric titration and pH was adjusted with a Meter Lab E520 pH Meter which was calibrated with acidic standard buffers.

Experimental design and data analysis
For statistical design of experiments and data analysis the Design-Expert (version 8.0) software was used. The CCD technique and response surface methodology were used to study the effects of the Fenton’s oxidation on the removal of LAS. Also, the three operating variables: H_{2}O_{2} and Fe^{2+} concentrations and HRT were optimized.
by this software. The literature review and preliminary study were the basis for determining the ranges of different variables. As shown in Table 1 a CCD was used with 8 factorial points, 6 axial points and center point with 6 additional experimental trials as the replication of this point.

The term of coded value was used to present the independent variables at 3 levels consist \(-1\) (minimum), 0 (central), and \(+1\) (maximum). The Design Expert software was used to analyze the results by analysis of variance (ANOVA) for graphical analysis of data to achieve the
interaction between the variables and responses. The accuracy of the polynomial model was explicated by the coefficient of determination (R^2). Also model terms were selected or rejected based on the P value with 95% confidence level. Surface plot (three-dimensional) and respective contour plots (two-dimensional) were provided for LAS and COD removal rate based on the effects of H_2O_2 and Fe^{2+} doses in the actual values at different reaction times. The complete set of experimental conditions and results are shown in Table 1.
RESULTS
The results of central composite design for studying of three experimental variables; \( \text{H}_2\text{O}_2 \), \( \text{Fe}^{2+} \) doses, reaction times and the achieved LAS degradation rates, COD % removal and \( \text{H}_2\text{O}_2 \) % residual are summarized in Table 1. Fig. 1 declares the percentage of \( \text{H}_2\text{O}_2 \) residual in different reaction times between 7 to 85 percent. Response contour (a) and response surface plot (b) for removal rate of LAS at reaction time of 80 min for different dose of \( \text{H}_2\text{O}_2 \) and \( \text{Fe}^{2+} \) are shown in Fig. 2. Figs. 3 and 4 show the effect of \( \text{H}_2\text{O}_2 \) and \( \text{Fe} \) (II) dosage on LAS removal efficiency. Figs. 5 and 6 reveal that the reduction of COD is not the same as LAS degradation in different concentrations of Fenton reagent. The ANOVA results for all responses are summarized in Table 2 that confirms significant results.

DISCUSSION
Effective parameters in Fenton process

The synthetic wastewater containing 200 mg/L LAS with initial COD = 457mg/L under and Fenton oxidation was obtained the results are given in Table 1. One of the noted points in

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Table 1: The results of central composite design for studying of three experimental variables; \( \text{H}_2\text{O}_2 \), \( \text{Fe}^{2+} \) doses, reaction time and the achieved LAS degradation rates, COD % removal and \( \text{H}_2\text{O}_2 \) % residual

<table>
<thead>
<tr>
<th>No</th>
<th>Factor A: ( \text{H}_2\text{O}_2 ) concentration</th>
<th>Factor B: ( \text{Fe}^{2+} ) concentration</th>
<th>Factor C: Time</th>
<th>LAS removal (%)</th>
<th>COD removal (%)</th>
<th>( \text{H}_2\text{O}_2 ) removal (%)</th>
</tr>
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<tr>
<td>1</td>
<td>(0) 450 (0) 70 (0) 50</td>
<td>45.52</td>
<td>23</td>
<td>43</td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>(-1) 150 (-1) 10 (-1) 20</td>
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<td>1.9</td>
<td>64</td>
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<td></td>
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<tr>
<td>3</td>
<td>(0) 450 (+1) 130 (0) 50</td>
<td>61</td>
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<td>32.5</td>
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<td></td>
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<tr>
<td>4</td>
<td>(0) 450 (0) 70 (0) 50</td>
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<td>23</td>
<td>43</td>
<td></td>
<td></td>
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<tr>
<td>5</td>
<td>(+1) 750 (-1) 10 (-1) 20</td>
<td>24</td>
<td>14.6</td>
<td>85</td>
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<td></td>
</tr>
<tr>
<td>6</td>
<td>(+1) 750 (-1) 10 (+1) 80</td>
<td>31.8</td>
<td>19.5</td>
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<tr>
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<td></td>
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<tr>
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</tr>
<tr>
<td>11</td>
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<td>51.7</td>
<td>27.2</td>
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<td>7.9</td>
<td>28</td>
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<tr>
<td>13</td>
<td>(0) 450 (0) 70 (-1) 20</td>
<td>30.9</td>
<td>15.4</td>
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<td>58.2</td>
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<td>45.52</td>
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<tr>
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<td>(0) 450 (0) 70 (0) 50</td>
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<td>23</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>(+1) 750 (+1) 130 (-1) 20</td>
<td>60</td>
<td>41.6</td>
<td>59</td>
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</table>
Fenton process is the unconsumed value of H₂O₂ after reaction time. Because, the residual H₂O₂ that was mentioned in Table 1 can interfere with measured COD (Lin et al. 1999). 1 mg/L residual H₂O₂ produces about 0.27 mg/L COD (Lin and Lo 1997). Therefore, during the experiments after the reaction time residual H₂O₂ was measured in all test runs, and was amended the value of COD. On bases of Table 1 the high percentage of H₂O₂ residual (85%) was measured in lower reaction time with high concentration of catalyst and peroxide. The response contour (a) and response surface plot (b) in Fig. 1 for a dose of Fe (II)=70 mg/L shows that in low dose of peroxide(150 mg/L) with increase of reaction times, residual of H₂O₂ decreased, and with increase of H₂O₂ dosage in constant reaction time, concentration of residual H₂O₂ increased in solution. Lin and Lo (1997) confirmed that when H₂O₂ unused in solution the time is considered as end of reaction time. The results show that after 120 minutes reaction time degradation did not improve and after this reaction time H₂O₂ remained in solution (Lin and Lo 1997). Other important parameters in both Fig. 3 and 4 are the amounts of H₂O₂ and Fe (II), which with increase concentration of them efficiency of process improved. In case of LAS, the enhancement of oxidation was observed with increased of both catalyst and oxidant, but the COD removal in Table 1 and Fig. 5 and 6 was not same as LAS degradation because, the LAS molecules degrade to intermediate materials due to transform of materials by Fenton process (Neyens and Baeyens 2003). The COD removal was 60% at high reaction time with 130 mg/L ferrous ion.

**Optimization process**

The degradation of solution containing LAS in initial pH=3, under Fenton process was investigated to obtain optimum oxidant concentration, catalyst dose and reaction time. On the basis of results in Table 1 that was obtained from different conditions of three variables (dosage of H₂O₂ and Fe (II), and reaction time) the concentration of LAS and COD decreased. Also another response, residual of peroxide was concerned in all tests.

**Table 2:** ANOVA results for the equations of the Design Expert 6.0.6 for studied responses

<table>
<thead>
<tr>
<th>Response</th>
<th>Transformation</th>
<th>Final equations with significant terms of coded factors</th>
<th>Probability</th>
<th>R²</th>
<th>Adj. R²</th>
<th>Adeq. Precision</th>
<th>SD</th>
<th>CV</th>
<th>PRESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD removal</td>
<td>-</td>
<td>+23.03+10.48 * A+11.39 * B+4.80 * C+4.52 * A * B+0.85 * C+1.80 * B * C+3.43 * A²-0.71 * B²+1.76 * C²</td>
<td>&lt;0.0001</td>
<td>0.9916</td>
<td>0.9840</td>
<td>48.548</td>
<td>1.55</td>
<td>6.77</td>
<td>345.48</td>
</tr>
<tr>
<td>LAS removal</td>
<td>-</td>
<td>-19.33664+0.095807 * A-3.21843E-003 * B+0.65861 * C+3.37500E-004 * A²+2.44444E-004 * B * C+1.27778E-003</td>
<td>&lt;0.0001</td>
<td>0.9840</td>
<td>0.9697</td>
<td>33.668</td>
<td>3.31</td>
<td>8.25</td>
<td>1324.49</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>-</td>
<td>+43.29+8.20 * A-11.10 * B-18.80 * C+1.00 * A * B+1.75 * A * C+2.25 * B * C-2.73 * A²+2.27 * B²+0.27 * C²</td>
<td>&lt; 0.0001</td>
<td>0.9942</td>
<td>0.9890</td>
<td>59.919</td>
<td>1.80</td>
<td>4.16</td>
<td>440.02</td>
</tr>
</tbody>
</table>

A: first variable, H₂O₂; B: second variable; Fe; C: Time; R²: determination coefficient, Adj. R²: adjusted R²; Adeq. precision: Adequate precision; SD: standard deviation, CV: coefficient of variation, PRESS: predicted residual error sum of squares
run. The range of $\text{H}_2\text{O}_2$ dose (150-750) was concerned for obtaining the limit of detergent concentration for interring conventional biological treatment (50mg/L) (Mantzavinos et al. 2001). Also, the Fe (II) with range (10-130) as catalyst was used to activate peroxide as (HO*) in acidic condition according to the overall reaction equation (1) (Chan and Chu, 2003).

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^{-} + \text{HO}^0 \quad (1)
\]

Another parameter is time reaction that was selected to cover the range of (20-80) on the basis of preliminary study as least time to start LAS degradation in this study. Fig. 2a and 2b demonstrates degradation of LAS as a response surface plot for relative runs. The best LAS removal was observed in reaction time 80 minutes and $\text{H}_2\text{O}_2$ and Fe (II) dosage 600 and 130 mg/L, respectively. The result obtained in Figures 3 and 4 show reaction time is important parameter in Fenton process. Because, the efficiency of FR was increased with increase of time at low dose of oxidant and catalyst. Also, in least reaction time of 20 minutes, still peroxide exists in solution. Therefore, increase of reaction time decreases the FR cost, but the extra $\text{H}_2\text{O}_2$ dose by dissociation into oxygen and water can supply oxygen to microorganisms in biological treatment facilities, it can also control the undesirable biofilm growth as a disinfecting agent (Neyens and Baeyens 2003).

Central composite design
In this study, the experimental design was used to get optimum significant reaction conditions that was confirmed by other researchers as a sui Table method because the chemical treatment system has intricacy, different variables and relativity to each other, and the optimization of them with CCD than the methods as “one at a time” would be able to be defined (Ostra et al. 2007). In case of LAS removal by FR on the basis of the result in Table 2, to fit the experimental data, RSM and CCD a second order polynomial model was used. The residual $\text{H}_2\text{O}_2$, LAS and COD removal in terms of response was represented as function of the operating variables for Fenton oxidation process $\text{H}_2\text{O}_2$ (A), Fe$^{2+}$ (B), reaction time (C) and the two-level interaction (AB) or (BC) of the variables are the significant model terms for both conditions. The results were completely analyzed using analysis of variance (ANOVA) by Design Expert software. Three-dimensional plots and their respective contour plots were obtained based on the effect of the levels of the two factors. From these three-dimensional plots, the simultaneous interaction of the two factors on the responses was studied. The ANOVA results for all responses are summarized in Table 2. The model terms in the equations are after the elimination of insignificant variables and their interactions. Based on statistical analysis, the models were highly significant with very low probability values (<0.0001). It is noted in Table 2 that the model terms of independent variables were significant at confidence level. The square of correlation coefficient for each response was computed as the coefficient of determination ($R^2$). Model terms were selected or rejected based on the P value with 95% confidence level. The figure represents high significant regression at 95% confidence level. Simultaneously, low values of the coefficient of variation (CV) indicated good precision and reliability of the experiments.

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