Comparison of Fenton and Photo-Fenton Processes for Removal of Linear Alkyle Benzene Sulfonate (Las) from Aqueous Solutions

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Abstract

The aim of our study was to investigate the effectiveness of Fenton and photo-Fenton processes for removing anionic surfactants from aqueous solutions. The study was conducted using 200 mgL^{-1} linear alkyl benzene Sulfonate (LAS) as a model of anionic surfactants. This study revealed that the mean removal efficiency of LAS in Fenton and photo-Fenton at 20 minutes reaction time at 100 mgL^{-1} constant concentration of hydrogen peroxide and 20 mgL^{-1} ferrous Iron were 20.16 and 22.47%, respectively. Meanwhile, LAS removal efficiency (at 80 minutes reaction time for constant concentration of 800 mgL^{-1} hydrogen peroxide and 120 mgL^{-1} ferrous ion) were 69.38 and 86.66%, respectively, which is consistent with the significant increase in the rate of LAS removal efficiency with reaction time ($P<0.05$). In conclusion, anionic surfactants removal was significantly correlated with reaction time by both methods, but showed less dependence on H_2O_2 and Fe^{2+} concentrations.

Keywords: anionic surfactants, detergent, Fenton process, photo–Fenton process

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Introduction

Surfactants are the main ingredients of synthetic detergents [1]. They are widely used in soap, toothpaste, cleaning detergents, and shampoo [2, 3]. They also have numerous industrial applications in cosmetic and medicinal products, textiles, foodstuffs, paper, oil recovery, paints, polymers, pesticides, and mining [2, 4].

According to their hydrophilic properties, surfactants are categorized into four classes (cationic, anionic, amphoteric, and non-ionic) [5, 6]. Ionic surfactants (anionic and cationic surfactants) constitute approximately two-thirds of all surfactants, and anionics constitute more than 90% of all Ionics [7]. One estimate of worldwide surfactant production is 13 million tons per year [8]. Also, statistics from the Council of European Surfactants Producers place the total quantity of surfactants (without soaps) consumed in Western Europe at more than 3 million tons [9].
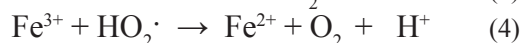
Surfactants can be partly biodegraded under aerobic conditions in wastewater, but they are rarely biodegraded under anaerobic conditions [7, 10-12]. Consequently, they are discharged to surface water and groundwater through household and industrial wastewaters [13]. They also cause foam in rivers and effluent treatment plants and reduce water quality, and also cause short- and long-term damage to the environment [14-16]. Surfactants are harmful for fish and human beings [14] – for instance LAS in low concentrations (i.e., 1 mgL^{-1} can poison aquatic organisms) [17]. LAS poisoning may increase proportionally to total carbon content of the alkyl chain [2]. It has been reported that LAS at concentrations of less than 10 mgL^{-1} is biodegradable under aerobic activated sludge treatment.

Mehrvar et al. reported that LAS biodegradability depends on its concentration. LAS solutions with 100 mgL^{-1} concentration are non-biodegradable and have inhibitory effects on microorganisms [12]. Therefore, due to their resistance against biodegradation, they can accumulate in aqueous environments and could threaten the health of aquatic organisms, animals, and human beings [8, 18]. The removal efficiency of surfactants from aqueous environments depends on the method of treatment employed [18]. Various procedures are employed for removing or destroying surfactants, including an anaerobic fluidized bed reactor (FBR) [19], chemical or electro-chemical oxidation, membrane technology, chemical precipitation, and photo catalytic degradation [6, 17, 20-22]. However, the limitations of biological procedures and difficulties in using other technologies (such as membranes) or adsorbing procedures challenge us to develop and employ new methodologies to deal with this issue [5]. Thus, advanced oxidation processes (AOPs) are recommended for pretreating wastewater or tertiary treatment when wastewater compounds have a high chemical stability and/or low biodegradability. AOPs come in numerous types, including oxidation with ozone [23], Fenton (Fe^{2+}/H_2O_2), electro-Fenton [24], photo-Fenton ($Fe^{2+}/H_2O_2/UV$), UV/H_2O_2, etc. [25-28].

Fenton and photo-Fenton reactions are AOPs where oxidant species are generated from hydrogen peroxide and Fe^{2+}/Fe^{3+} as a catalyst [29]. In a Fenton reaction ferrous salts react with hydrogen peroxide and generate the hydroxyl radicals according to (1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + HO^- \quad (1)$$
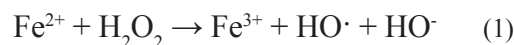
Then Fe^{3+} can be reduced by reaction with H_2O_2 to form ferrous ion again with an additional amount of hydroxyl radicals. This second process is called a "Fenton-like process." It is slower than the Fenton reaction and allows Fe^{2+} regeneration to appear as a catalyst according to (2-4):

$$Fe^{3+} + H_2O_2 \leftrightarrow FeOOH^{2+} + H^+ \quad (2)$$

$$FeOOH^{2+} \rightarrow HO\cdot_2 + Fe^{2+} \quad (3)$$

$$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

The rate of contaminant degradation can be considerably increased due to photochemical reaction in the photo-Fenton process. In this case, the regeneration of Fe^{2+}, with additional production of Hydroxyl radicals, is followed by the photo reduction process according to (5-6).

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+ \quad (5)$$

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + HO\cdot \; \lambda < 410 \text{ nm} \quad (6)$$
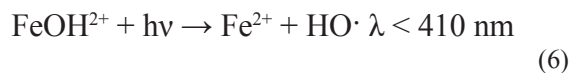
Although several studies have been conducted on the treatment of surfactant wastewater using various methods such as combined Fenton oxidation and aerobic biological, ultrasonic, simultaneous use of ozone and powdered activated carbon, nano flocculation, photo catalysis, iron species as heterogeneous catalysts, UV/H_2O_2 chemical oxidation, Fenton-like reaction over zerovalent iron-based catalyst, and bioremediation [30-37].

Moreover, literature shows that Fenton has been utilized to treat azo dyes, phenols, nitrobenzene, COD, herbicides, and Di-(2-Ethylhexyl) phthalate (DEHP), as well as to reduce linear alkylbenzene sulfonate (LAS) in wastewater [38-43]. The photo-Fenton process also has been utilized to treat inorganic and organic components in synthetic or real aqueous solutions such as LAS, COD, Metoprolol, TOC, and pesticides [39, 42, 44-47].

Abu Hassan et al. showed that the initial concentration of LAS increases its degradation [48]. Also, Ono et al. on non-ionic surfactant degradation with anionic and cationic surfactant compound performed by photo-Fenton process found that UV light is effective in forming OH radical, resulting in accelerating the photo-Fenton reaction [49].

Based on literature review, other research has not compared the Fenton and photo-Fenton processes for removal of LAS. Thus the main objective of our study was to compare their efficiency for removal of LAS

from synthetic wastewater under similar conditions and investigate the effects of iron concentration, H_2O_2 dose, and reaction time on LAS removal.

Materials and Methods

Chemicals

The surfactant used in this study contained 88% sodium dodecylbenzenesulfonate (LAS) provided by ACROS ORGANIC. SDBS was used as anionic surfactant (family: LAS) for performing experiments. Other chemicals such as H_2SO_4, $FeSO_4$_$7H_2O$, NaOH, hydrogen peroxide (30% v: v solution), $CHCl_3$, $NaH_2PO_4.H_2O$, and methylene blue were supplied by Merck Co.

Experimental Setup

Fenton Process

Experiments were performed at room temperature in a 2 L glass cylindrical reactor that was protected from incident light by aluminum foil. The reactor was equipped with a magnetic stirrer to completely mix the reagents (H_2O_2 and Fe^{2+} ion).

Photo-Fenton Process

As shown in Fig. 1, the photo-Fenton process was carried out in a 2 L glass reactor equipped with an external light irradiation-type photo reactor. The photo reactor was mounted on a magnetic stirrer and complete mixing of the reagents (H_2O_2 and Fe^{2+} ion) was achieved by magnetic stirring. The UV light irradiation sources were four 15-Watt UV-C lamps (Osram G15T8) having peak radiation at 254 nm wavelength. The distance between the photo reactor surface and the lamps (which were parallel to the photo reactor axis) was 3 cm.

Experimental Procedure

The laboratory unit was filled separately with 1 L of synthetic wastewater. The initial concentration of the LAS solutions in units was 200 mgL^{-1}. Since optimum pH of about 3 had been observed by the previous researchers for the Fenton and photo-Fenton processes, the pH of the solution was maintained constant at pH 3.0 by the addition of NaOH or HCl. For runs using the Fenton and the photo-Fenton processes, a given weight of iron salt was added. The iron salt was mixed very well with the wastewater before the addition of a given volume of hydrogen peroxide. For the photo-Fenton process, the time at which the ultraviolet lamp was turned on was considered time zero, or the beginning of the experiment, which was taking place simultaneously with the addition of hydrogen peroxide. At selected time intervals, supernatants of the solution were withdrawn and the reaction stopped by the addition of aqueous NaOH (final pH of ca. 12) to precipitate iron oxides.

Analytical Determinations

The pH of the solution was measured using a TS-TECHNOLOGY PH262 pH meter. LAS was measured
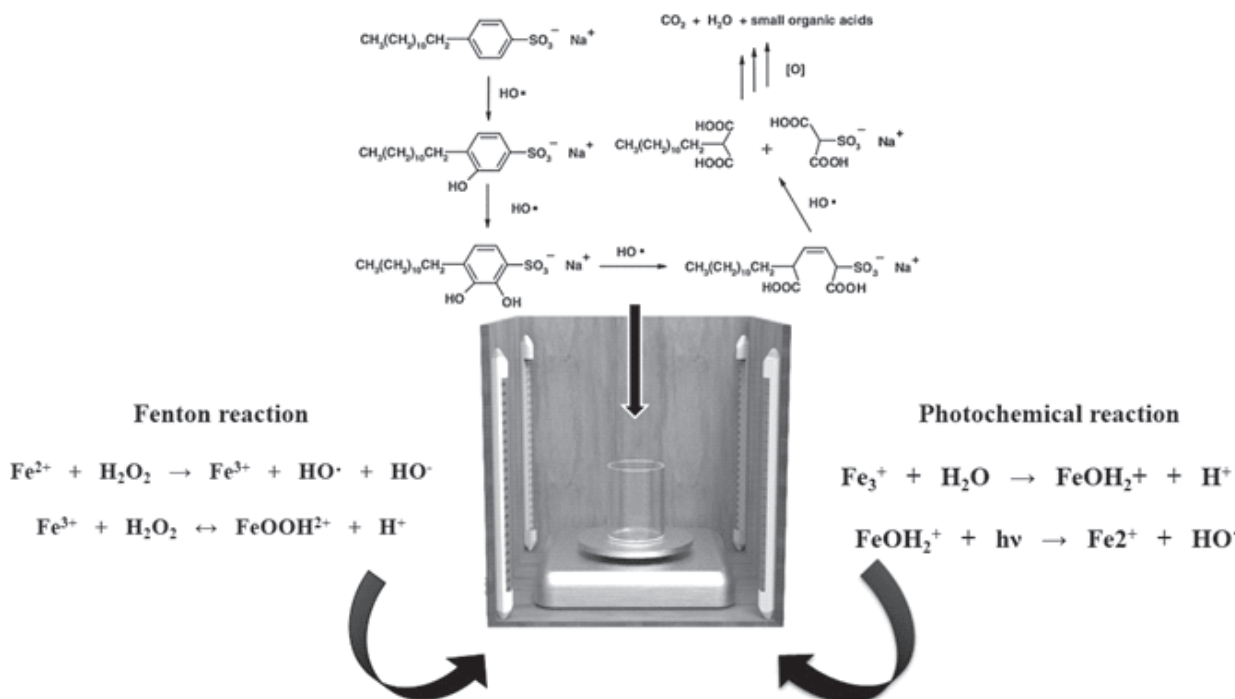

Fig.1. Schematic of pilot-plant of photo-Fenton reactor in our study.

Table 1. The mean and standard deviation of remaining anionic surfactant (LAS) according to various parameters in Fenton and photo-Fenton processes.

P value	Photo-Fenton X±S.D	Fenton X±S.D	Method	Variable
0.136	148.37±28.45	155.64±24.5	100	
0.121	130.28±43.72	141.57±34.88	300	
0.065	122.14±46.03	136.55±38.2	600	H_2O_2(mg/l)
0.042	113.61±51.8	131.25±41.6	800	
0.001	128.59±44.97	141.25±36.31	total	
0.059	143.22±33.32	153.7±26.43	20	
0.016	131.72±42.31	147.96±29.24	50	
0.125	122.52±47.48	134.85±39.67	80	Fe^{2+}(mg/l)
0.182	116.94±54.34	128.5±42.47	120	
0.001	128.59±44.97	141.25±36.31	total	
_	200	200	0	
0.000	135.4±14.53	145.47±10.63	20	
0.001	122.25±18.7	134.32±14.59	40	
0.000	103.28±22.14	18/120±69/19	60	Time(min)
0.000	82.05±32.75	106.29±26.42	80	
0.001	128.59±44.97	141.25±36.31	total	

using methylene blue active substance (MBAS) on the basis of the 5540.C method in the Standard Methods book (Carlos et al., 2008). The experiments were based on the transfer of MBAS from an aqueous solution into an immiscible phase containing anionic surfactant. This transfer was possible by ion pair formation when methylene blue, a cationic dye, reacts with anionic surfactants. The MBAS method comprises three successive extractions from aqueous medium containing excess methylene blue into chloroform ($CHCl_3$), followed by an aqueous backwash and measurement of the blue
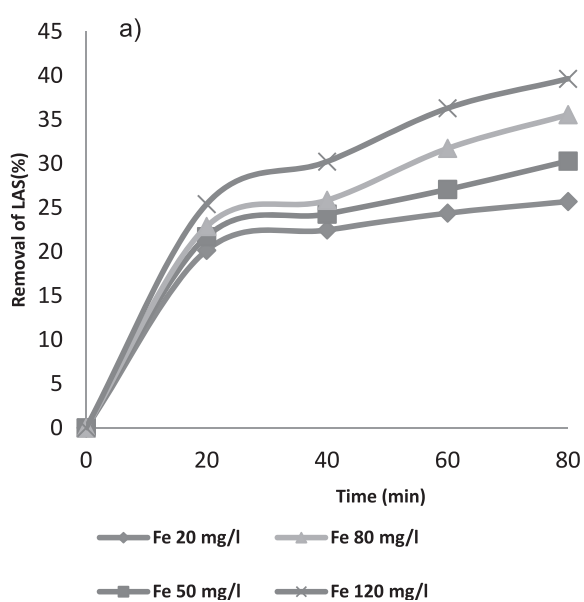

Fig. 2a). Effect of reaction time on Fenton process for the degradation LAS (conditions: initial LAS degradation, 200 mgL⁻¹; initial PH, 3; H_2O_2 concentration; 100 mgL⁻¹).
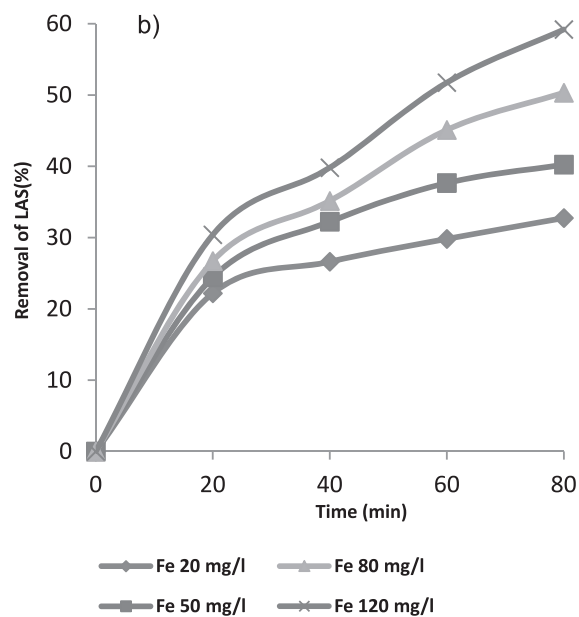
Fig. 2b). Effect of reaction time on Fenton process for the degradation LAS (conditions: initial LAS degradation, 200 mgL⁻¹; initial PH, 3; H_2O_2 concentration; 300 mgL⁻¹).

color in the CHCl$_3$ by spectrophotometer at 652 nm. Excess methylene blue was read by an HACH-DR 2010 spectrophotometer.

Statistical Methods

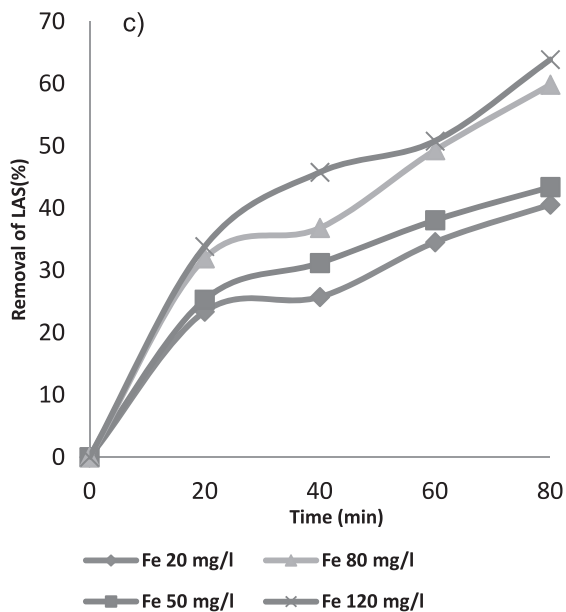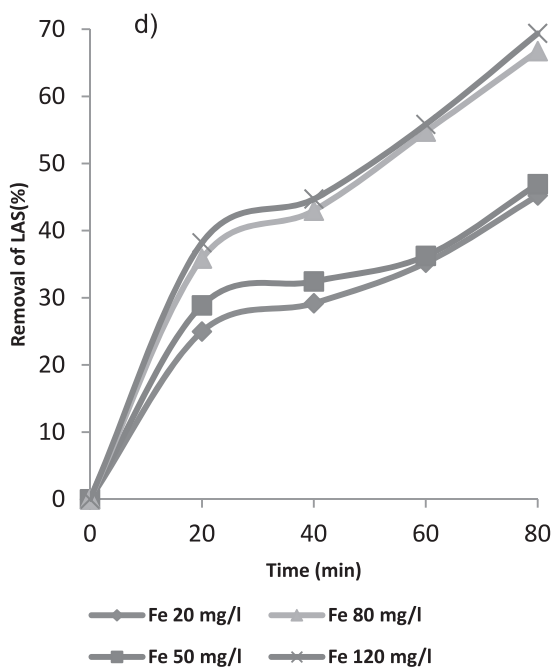After collecting data concerning mean and standard deviation, the eliminated LAS according to reaction time

Fig. 2c). Effect of reaction time on Fenton process for the degradation LAS (conditions: initial LAS degradation, 200 mgL^{-1}; initial PH, 3; H$_2$O$_2$ concentration; 600 mgL^{-1}).

Fig. 2d). Effect of reaction time on Fenton process for the degradation CLAS (conditions: initial LAS degradation, 200 mgL^{-1}; initial PH, 3; H$_2$O$_2$ concentration; 800 mgL^{-1}).

variables, Fe^{2+} ion and H$_2$O$_2$ concentrations were measured. The process capacity of Fenton and photo-Fenton in biodegrading LAS was measured by the presence of changeable concentrations of H$_2$O$_2$ and Fe^{2+} using two-way ANOVA, and reaction time using repeated measurement analysis. Then the post-hoc Tukey test was used.

Results

Table 1 shows the results of the mean and standard deviation of remaining anionic surfactant based on reaction time, concentration of hydrogen peroxide, and concentration of Fe^{2+} for both Fenton and photo-Fenton processes. As shown in this table, it is obvious that minimum and maximum remaining concentrations of LAS occur at 80 and 20 Minutes reaction time, respectively (without consideration of the blank sample).

The removal percentage of LAS for the Fenton process, with constant concentration of 100 mgL^{-1} hydrogen peroxide and 20 mgL^{-1} Fe^{2+} based on reaction time of 20 minutes, is shown in Figs 2(a, b, c, d), where the minimum removal was 20.16%, whereas in constant concentration of 800 mgL^{-1} hydrogen peroxide and 120 mgL^{-1} Fe^{2+} with reaction time at 80 minutes it was 69.38%, which shows the maximum removal percentage.

Also, on the photo-Fenton process Figs 3(a, b, c, d), the removal percentage of LAS with constant concentration of 100 mgL^{-1} hydrogen peroxide and 20 mgL^{-1} Fe^{2+} based on reaction time of 20 minutes was 22.47%, which shows the least removal percentage, whereas in constant concentration of 800 mgL^{-1} hydrogen peroxide and 120 mgL^{-1} Fe^{2+} with reaction time at 80 minutes it was 86.66%, which shows the highest removal percentage. In both photo-Fenton and Fenton processes, the removal rate of LAS increased with increasing concentrations of H$_2$O$_2$ and the Fe^{2+} ion, and reaction time.

As shown in Table 2, the effects of reaction time by itself and other counter-effects are significantly meaningful (P value<0.05), but counter-effects of time, the process, Fe^{2+} concentration, and H$_2$O$_2$ concentration were not significantly meaningful (P value = 0.308).

Discussion

Previous studies have shown that Fenton efficiency depends on sample characteristics, PH, Fe^{2+} concentration, H$_2$O$_2$ dose, and reaction time. In our study, sample concentration and PH were constant, but Fe^{2+} concentration and H$_2$O$_2$ dose varied.

The Effect of Hydrogen Peroxide

Regarding Figs 2(a, b, c, d) and 3(a, b, c, d), it is indicated that with increasing the initial concentration of hydrogen peroxide, LAS removal and degradation rates mount. For example, the removal rate in a constant concentration of photo-Fenton process with 80 mgL^{-1} Fe^{2+}

Table 2. References of differences of LAS removal by using repeated measurements model on the presence of time factor and its mutual effect on the presence of other factors.

Source	Type III sum of squares	Df	Mean square	F	P $_{value}$
Time	29149.2	1.15	25385.07	1637.67	0.000
Time* method	715.83	1.15	623.39	40.218	0.000
Time * H$_2$O$_2$ dose	2148.28	3.445	623.62	40.232	0.000
Time * Fe^{2+} dose	1259.47	3.445	365.61	23.587	0.000
Time*method*H$_2$O$_2$ dose	179.31	3.445	52.05	3.358	0.018
Time*method*Fe^{2+} dose	170.42	3.445	49.47	3.192	0.023
Time*H$_2$O$_2$ dose*Fe^{2+} dose	380.45	10.335	36.81	2.375	0.016
Time*method*H$_2$O$_2$ dose*Fe^{2+} dose	191.19	10.335	18.5	1.194	0.308

and 60 minutes and in 100, 300, 600, and 800 mgL^{-1} of H$_2$O$_2$ is 36.08, 50.41, 56.79, and 63.36%, respectively, which is likely due to the rate of OH radical production. According to previous studies, increasing the initial concentration of H$_2$O$_2$ increases the rate of OH radical production. Previous studies also have found that increasing OH radical production is done due to certain concentrations of H$_2$O$_2$, and if H$_2$O$_2$ is added to the process it causes limitation and removal of the procedure [50-53].

The Effect of Fe^{2+} Concentration

The obtained results from Figs 2(a, b, c, d) and 3(a, b, c, d) indicate that increasing the Fe^{2+} concentration causes the LAS removal and degradation rates to increase and, therefore, the rate of OH radical increases, too. For instance, in the Fenton process for constant concentration

of 600 mgL^{-1} H$_2$O$_2$ and 80 minutes, the removal rate of Fe^{2+} concentration for 20, 50, 80, and 120 mgL^{-1} was 40.59, 43.4, 59.85, and 63.88%, respectively, which is consistent with our previous study [53-55].

Thus Fe^{2+} increases oxidation rate by producing OH radicals (OH$^•$) according to (1).

On the other hand, a high dose of Fe^{2+} is not practically advised, but a low dosage is advised in industrial applications since its highly used dosage demands higher costs and later treatment may be needed. It also causes more sludge which, in turn, increases removal costs [51, 55].

Although we could mount oxidation rates by increasing Fe^{2+} in our study, it has been proven in some studies that a higher dosage of Fe^{2+} can cause OH radicals (OH$^•$) recombination. In this case, Fe^{2+} reacts as a scavenger [51, 52, 54, 55].
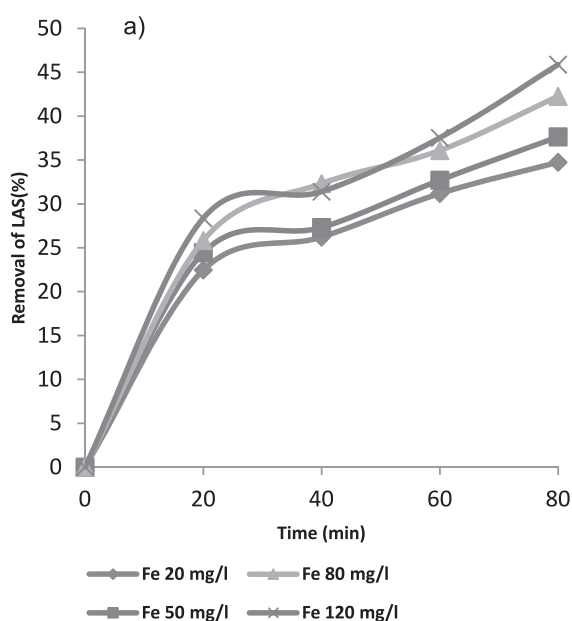

Fig. 3a). Effect of reaction time on photo-Fenton process for the degradation LAS (conditions: initial LAS degradation, 200 mgL^{-1}; initial PH, 3; H$_2$O$_2$ concentration; 100mgL^{-1}).
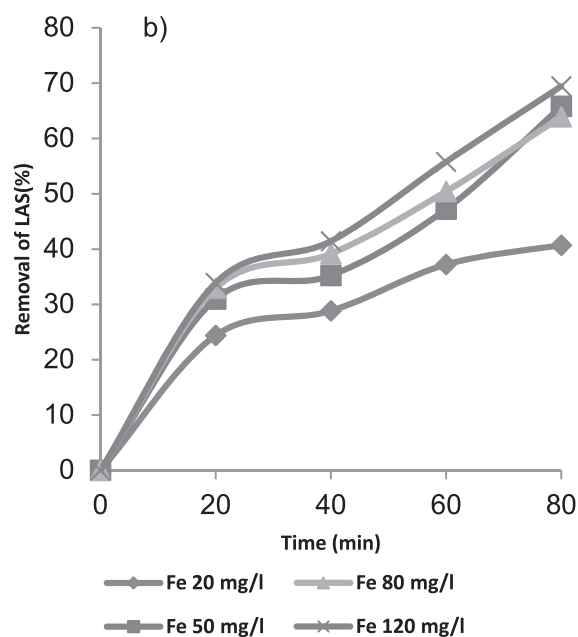

Fig. 3b). Effect of reaction time on photo-Fenton process for the degradation LAS (conditions: initial LAS degradation, 200 mgL^{-1}; initial PH, 3; H$_2$O$_2$ concentration; 300mgL^{-1}).

In addition, overtly increasing Fe^{2+} in the photo-Fenton process causes the brown turbidity to be darker, which prevents the observation of the UV light that is needed for photolysis and recombination of OH radicals. In this case, Fe^{2+} reacts with OH radicals as a scavenger [55].

The Effect of Reaction Time

As illustrated in Figs 2(a, b, c, d) and 3(a, b, c, d), with increasing reaction time the percentage of degradation

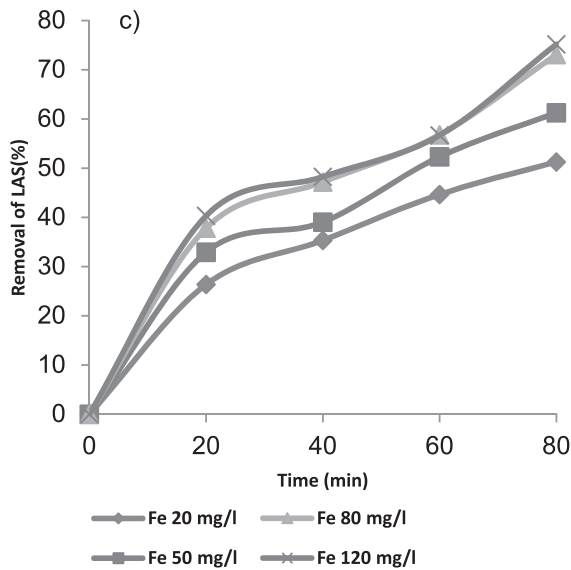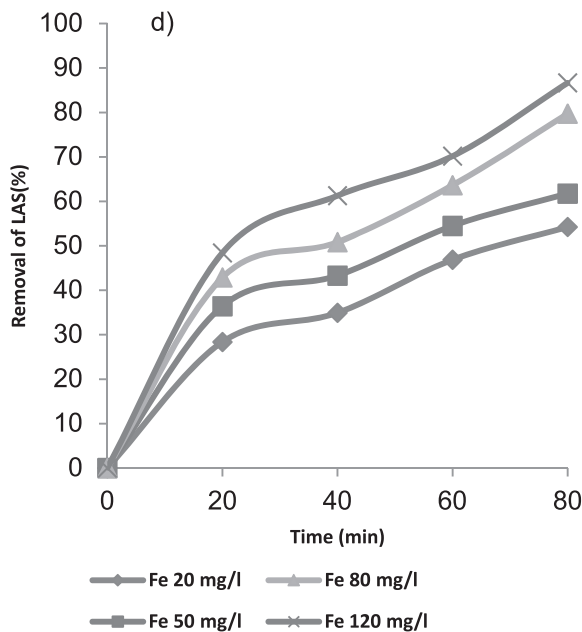

Fig. 3c). Effect of reaction time on photo-Fenton process for the degradation LAS (conditions: initial LAS degradation, 200 mgL⁻¹; initial PH, 3; H_2O_2 concentration; 600mgL⁻¹).

and removal of LAS in the Fenton process mounts and the removal rate at 20, 40, 60, and 80 minutes reaches 38.2, 44.72, 55.83, and 69.38%, respectively, but in photo-Fenton to 48.41, 61.28, 70.17, and 86.66%, respectively.

In fact, photo-Fenton process efficiency is observed more than for Fenton, which is due to UV radiation accelerating the formation of hydroxyl (OH) radicals as well as faster removal of LAS.

Also, our study found that the total squared errors for the time factor by themselves are 29,149, whereas the explained squared errors by other factors and time factor are too small. So the time factor has the most effect regarding contract time with H_2O_2 concentration of (2,148.28), then the most effect relates to contract time with Fe^{2+} concentration (1,259). Of course the contract effects of all factors mentioned relate to surfactant removal, which was significantly meaningful except the interaction of four factor effects (Time*method*H_2O_2 dose*Fe^{2+} dose) (P value<0.05).

Conclusions

This study confirms that both Fenton and photo-Fenton processes are efficient methods for the treatment of wastewaters with high anionic surfactant concentration prior to discharge to the environment. Our study also reveals that LAS removal efficiency for photo-Fenton is higher than for the Fenton process and the anionic surfactant removal in both methods are highly dependent on reaction time. The correlation between anionic surfactant removal and H_2O_2 and Fe^{2+} concentration was less significant.

Fig. 3d). Effect of reaction time on photo-Fenton process for the degradation LAS (conditions: initial LAS degradation, 200 mgL⁻¹; initial PH, 3; H_2O_2 concentration; 800mgL⁻¹).

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