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OPTIMIZING LINEAR ALKYL BENZENE SULFONATE REMOVAL USING FENTON OXIDATION PROCESS IN TAGUCHI METHOD

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Linear alkyl benzene sulfonate (LAS), which is the most common used anionic surfactant in detergents manufacturing, can discharge onto water resources through wastewater and causes change in taste and odor, disruption in water treatment processes, aquatics death, and oxygen transfer limitation. Accordingly, this article investigates to optimize LAS removal using Fenton oxidation process in Taguchi Method for the first time. LAS removal using Fenton oxidation was perused experimentally in a lab-scale reactor. In order to save relevant costs, 25 runs were qualified to specify the optimum conditions of Fenton oxidation using Taguchi method by Minitab 16 software. Sampling and testing procedures were executed based on the standard methods for the examination of water and wastewater. The optimum conditions included 900 mg/L hydrogen peroxide, 170 mg/L ferrous ion, pH of 4 and the reaction time of 20 min. Fenton oxidation, as a second order reaction with the rate coefficient of 0.0152 L/mg · min, provided 86.5% efficiency for LAS removal in the optimum conditions. Despite Fenton oxidation appeared as a high efficiency process in LAS removal, low removal efficiency of chemical oxygen demand corresponding with LAS affirmed its partial degradation.

Keywords: linear alkyl benzene sulfonate, detergent, Fenton oxidation, wastewater.

Introduction

Surface active agents, usually referred to as surfactants, are amphipathic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon chain containing $8 - 18$ carbon atoms, which is attached

to a polar hydrophilic portion. Hence, they are able to solve insoluble materials and are used as one of the main ingredients in the structure of detergents [1, 2]. So that, in 2006, the worldwide production of detergents has been announced over 12.5 million tonnes. Linear alkyl benzene sulfonate (LAS) anionic surfactant makes up approximately 5 − 30% by weight of various detergents because of its biodegradability [1, 3, 4].

Because surfactants produce stable foams at the surface of receiving waters in more than 1 mg/L [2], they can cause changes in taste and odor, disruptions in water treatment processes, aquatics death, and oxygen transfer limitation [1, 3 − 5].

In addition to domestic wastewater, the main sources of surfactants in water resources comprise wastewater resulting from industries producing detergents, cleaners, cosmetics, and textile, as well as cleaning operations in various industries [1 − 3]. LAS concentration in raw municipal wastewater ranges from 3 to 21 mg/L [5].

According to standards provided by the Iran department of environment, the maximum allowable concentration of detergent in the effluent for discharge to surface waters and absorbing wells or agricultural reuse is 1.5 and 0.5 mg/L, respectively [6].

So far, various approaches such as coagulation, floatation, biological processes, adsorption, membrane processes, ultrasonic irradiation and advanced oxidation have been studied to remove detergents from wastewaters [3 − 5, 7 − 14].

Oxidation processes have been investigated for the pre-treatment of refractory surfactants in the past decades. Results of these studies reveal that surfactants resistant to biological treatment are removed well by ozonation and photochemical methods [1, 3, 15 − 21].

Fenton is one of the oxidation processes in which ferrous ion as a catalyst reacts in an acidic condition with hydrogen peroxide as oxidizer and produces hydroxyl radical. This process has great potential for oxidation of refractory organic compounds due to producing highly active hydroxyl radicals [15,16,22]. Fenton oxidation is affordable while having optimal performance and easy operation in comparison with other advanced oxidation processes [8 − 11].

Lin S.H. et al. [9] showed that the efficiency of Fenton oxidation process in removing ABS and LAS enhances if it is integrated with the coagulation process.

Wang X.J. et al. [11] reduced LAS amount in detergent factory wastewater to less than 5 mg/L using pretreatment by Fenton oxidation and biological processes.

Mousavi S.A.R. et al. [8] acquired Fenton oxidation process efficiency about 86% to remove 470 mg/L LAS while the removal efficiency of chemical oxygen demand (COD) corresponding to LAS was obtained approximately 60%. The process included 750 mg/L hydrogen peroxide, 130 mg/L ferrous ion, pH about 3, and reaction time of 80 min.

Abdel-Rahman A.M. et al. [5] reported the LAS removal efficiency by wastewater stabilization ponds between 55 and 77% in various seasons.

Although some studies have been conducted concerning the efficiency of Fenton oxidation for treatment of industrial wastewaters, Taguchi method has not yet been used for determining the optimal conditions of this process to remove the anionic detergents. Therefore, this article investigates optimizing LAS removal using Fenton oxidation process in Taguchi method for the first time in order to reduce costs.

Experimental

Fenton oxidation was performed experimentally in a lab-scale 500 ml batch reactor. In order to provide the study objectives, residual LAS and COD concentrations as dependent variables were analyzed versus operational parameters such as initial concentration of LAS (8 − 40 mg/L), initial COD (100 − 700 mg/L), hydrogen peroxide (80 − 1200 mg/L), ferrous ion (30 − 170 mg/L), pH (4 to 8) and time reaction (20 to 60 min) as independent variables. The range of investigated parameters has been chosen based on the characteristic of municipal wastewater and the experiences obtained from the previous studies concerning Fenton oxidation.

Synthetic solutions were prepared by LAS ("Acros Organic", USA), $C_{18}H_{29}NaO_3S$. Sampling and testing procedures were accomplished using the standard methods for the examination of water and wastewater. LAS was examined using 5540 C standard method [23, 24] in which methylene blue active substances (MBAS) bring about the transfer of methylene blue, a cationic dye, from an aqueous solution into an immiscible organic liquid upon equilibration. The intensity of the resulting blue color in the organic phase is a measure of MBAS. It comprises three successive extractions from acid aqueous medium containing excess methylene blue into chloroform ($CHCl_3$), followed by an aqueous backwash and measurement of the blue color in the $CHCl_3$ by spectrophotometry at 652 nm.

COD experiments or oxygen consumed for oxidation of LAS were analyzed by closed reflux-colorimetric method, 5220 D standard method [23, 25, 26].

In this approach, a sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$) as an oxidant. This results in the change of chromium from the hexavalent (VI) state to the trivalent (III) state. $Cr_2O_7^{2-}$ and Cr^{3+} are colored and absorb strongly 420 and 600 nm spectrums, respectively [23].

Hydrogen peroxide interferes in COD amount and increases illusively it. To thwart the intervention of hydrogen peroxide, before measuring COD, samples' pH was adjusted within the range of $7 - 8$ [27].

In order to save costs, experiments were qualified by the Taguchi method [28] using Minitab 16 software. In this software, pH, initial LAS concentration, Fe^{2+} and H_2O_2 concentrations, and the reaction time were selected in five levels. Therefore, 25 specific runs were examined according to Table 1.

Table 1. LAS and COD removal efficiency by Fenton oxidation

| pH | H_2O_2 | Fe^{2+} | Time, min | LAS mg/L | | COD, mg/L | | LAS | COD |
	mg/L			Initial	Effluent	Initial	Effluent	rem. %	
4	80	30	20	8	2.5	124.95	102.06	68.75	18.32
4	300	80	30	10	2.9	193.62	106.64	71.00	42.86
4	600	120	40	15	2.4	296.62	156.42	84.00	47.27
4	900	140	50	25	2.8	405.35	250.84	88.80	38.12
4	1200	170	60	40	3.4	482.60	165.00	91.50	65.81
5	80	80	40	25	4.4	139.25	90.61	82.40	34.13
5	300	120	50	40	6.9	282.31	187.89	82.75	33.44
5	600	140	60	8	3.3	305.20	189.17	58.75	40.31
5	900	170	20	10	2.3	382.46	279.45	77.00	26.93
5	1200	30	30	15	7.6	534.10	173.59	49.33	67.5
6	80	120	60	10	4.6	107.88	62.00	54.00	42.47
6	300	140	20	15	4.1	230.81	139.35	82.67	39.67
6	600	170	30	25	4.8	368.15	242.26	80.80	34.20
6	900	30	60	40	6.0	519.79	465.43	85.00	10.46
6	1200	80	20	8	3.3	671.44	399.62	58.75	40.48
7	80	140	30	40	19.2	156.42	93.47	52.00	40.24
7	300	170	40	8	4.2	222.23	107.178	47.50	51.5
7	600	30	50	10	7.0	376.73	310.93	30.00	17.47
7	900	80	60	15	3.1	419.65	245.12	33.79	41.59
7	1200	120	20	25	5.1	491.18	362.43	79.60	26.21
8	80	170	50	15	5.8	222.23	367.87	61.33	24.46
8	300	30	60	25	11.2	296.62	222.23	55.20	25.08

Table 1 (Cont.)

8	600	80	20	40	17.1	299.48	247.98	57.25	17.20
8	900	120	30	8	3.8	282.31	202.20	52.50	28.38
8	1200	140	40	10	4.8	496.90	419.68	52.00	15.55

The signal to noise ratio as an optimal condition index was applied based on following equation [28] to determine the effect of independent variables and eventually to introduce the optimal conditions and prioritizing them in LAS removal:

$$\frac{S}{N} = -10 \left(\log \sum \frac{\frac{1}{(y^2_i)}}{n} \right),$$

where n is the number of tests and y_i is the response value measured for each test (percent of LAS removal); in this formula, the bigger S/N ratio the better condition [28].

The Kruskal-Wallis nonparametric one-way analysis of variance was applied using SPSS 16 software for comparing the results of Fenton oxidation runs in LAS removal.

Results and discussion

To achieve optimal conditions of Fenton oxidation process, LAS removal efficiency was determined at 25 runs specified using Taguchi method that corresponding results are presented in Table 1.

The amount of S/N ratio for factors affecting LAS removal is shown in Fig. 1. According to the principals of Taguchi method, the highest S/N ratio indicates the optimal level of each factor. Accordingly, the optimal conditions to remove 25 mg/L LAS using Fenton oxidation include pH of 4, 900 mg/L hydrogen peroxide, 170 mg/L ferrous ion and time of 20 min. The average LAS removal efficiency reached 86.5% upon laboratory results in optimal conditions; however, the removal efficiency of COD corresponding to LAS was 30%. On this basis, COD corresponding to LAS was decreased from 350 to 245 mg/L by Fenton oxidation in the optimal conditions.
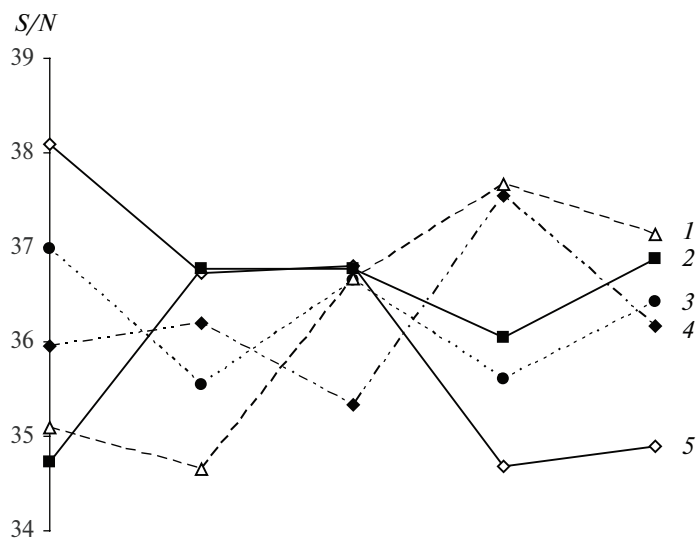
Fig. 1. S/N ratio versus levels of parameters affecting LAS removal: 1 − initial LAS concentration (8; 10; 15; 25; 50 mg/L); 2 − ferrous ion (30, 80, 120, 140, 170 mg/L); 3 − time (20 − 60 min); 4 − hydrogen peroxide (80; 300; 600; 900; 1200 mg/L); 5 − pH (4 − 8).

After conducting experiments according to Taguchi method, in addition to determine the optimal value of parameter affecting LAS removal, the importance of independent variables was prioritized to introduce optimal conditions in accordance with Table 2. In this table, Δ is the difference between the maximum and minimum values of S/N ratio, and the paramount parameter in LAS removal entails the Δ_{max}.

The Kruskal-Wallis nonparametric one-way analysis of variance test demonstrated the significant difference within 25 runs efficiencies on LAS removal by Fenton oxidation ($p < 0.05$).

The study of residual LAS concentration, logarithmic concentration and inverse concentration versus time in the optimal conditions based on the Fig. 2 indicated that Fenton oxidation for LAS removal is a second order reaction with the rate coefficient of 0.0152 L/mg · min.

Although the maximum LAS removal efficiency of Fenton oxidation, 91%, was achieved by 1200 mg/L hydrogen peroxide, 170 mg/L ferrous ion, pH of 4 and the time of 60 min based on Table 1; the optimal conditions was introduced by Minitab 16 software in view of LAS removal efficiency and chemical requirements at 900 mg/L hydrogen peroxide, ferrous ion 170 mg/L, pH of 4, and 20 min according to Fig.1 and Table 2.

a

LAS, mg/L

$y = -0.3475x + 17.661$
$R^2 = 0.6414$

b

ln LAS

$y = 0.0275x + 1.6881$
$R^2 = 0.2871$

c
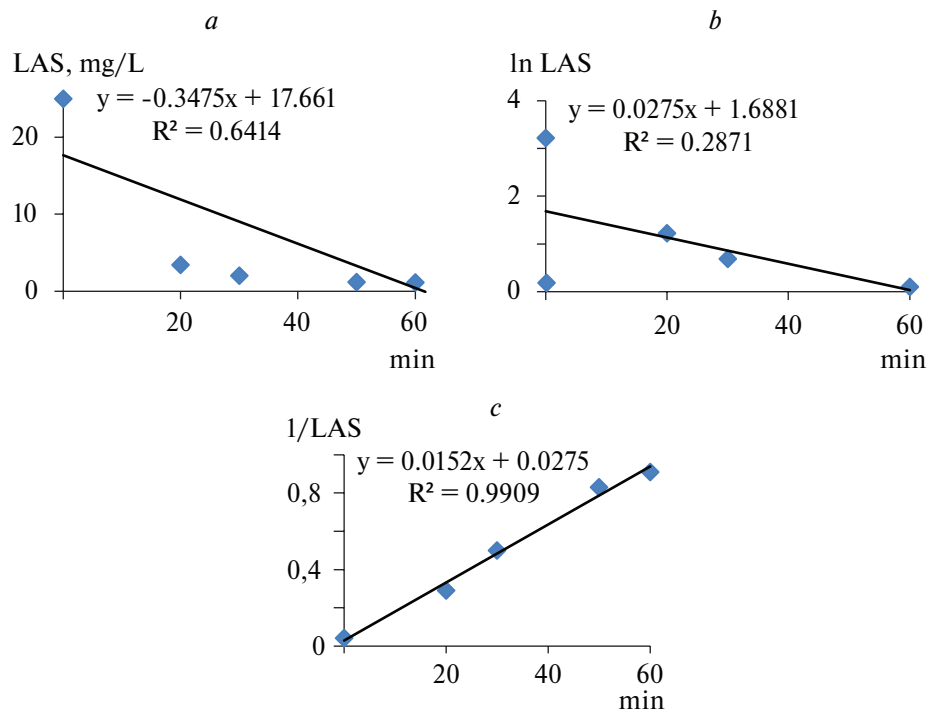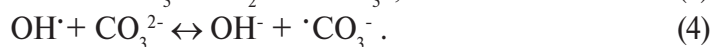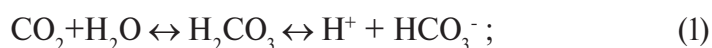
1/LAS

$y = 0.0152x + 0.0275$
$R^2 = 0.9909$

Fig. 2. Reaction order of Fenton oxidation: variation of residual LAS concentration (a), logarithmic concentration (b) and inverse concentration (c) versus time in the optimal conditions.

*Table 2. The priority of independent variables to introduce optimal conditions*

Level	S/N				
	pH	H_2O_2	Fe^{2+}	Time	LAS
1	38.09	35.96	34.72	36.98	35.09
2	36.73	36.20	36.77	35.55	34.65
3	36.80	35.34	36.78	36.65	36.66
4	34.68	37.54	36.04	35.6	37.66
5	34.89	36.16	36.88	36.42	37.13
Δ	3.41	2.19	2.16	1.42	3.01

The required time for Fenton oxidation depends on the catalyst, oxidant, and pollutant concentrations according to the results in Table 1; however, no significant difference in LAS removal efficiency was observed by increasing time in the optimal conditions ($p < 0.05$) with regard to Fig. 2, *a* which is consistent with Mohd Ariffin A.H. et al. findings [10].

In Fenton oxidation process, organic carbon is transformed into inorganic carbon such as carbon dioxide. In longer reaction times, carbon dioxide will be transformed into bicarbonate and carbonate according to reactions (1) and (2). These intermediate products act as a scavenger of the hydroxyl radical according to reactions (3) and (4). Hence, they can reduce LAS oxidation by consuming hydroxyl radical [29]:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- ; \qquad (1)$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} ; \qquad (2)$$
$$OH^{\cdot} + HCO_3^- \leftrightarrow H_2O + {\cdot}CO_3^- ; \qquad (3)$$
$$OH^{\cdot} + CO_3^{2-} \leftrightarrow OH^- + {\cdot}CO_3^- . \qquad (4)$$

According to Table 1, Fe^{2+}/H_2O_2 ratio is considered as one of the factors affecting the efficiency of Fenton process in removing LAS. In optimal conditions, Fe^{2+}/H_2O_2 ratio of 0.08 was introduced by Minitab 16 software for the removal of LAS. In various studies, depending on the type of pollutant, this ratio has been announced between 0.04 and 0.12. Based on reaction (5), Fe^{2+} alongside H_2O_2 in an appropriate molar ratio increases the production of hydroxyl radical and decreases the pollutants. However, the increase in molar ratio of Fe^{2+}/H_2O_2 and the excessive presence of ferrous ions decreases the efficiency of Fenton oxidation through the unnecessary consumption of hydroxyl radical according to reaction (6) [29, 30]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^- ; \qquad (5)$$
$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^- . \qquad (6)$$
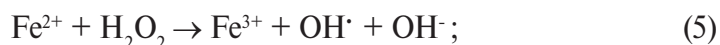
Since ferrous ion is more soluble in a pH of about 3 to 4, the production of hydroxyl radical will increase by the reaction between ferrous ion and hydrogen peroxide in an acidic pH. On the other hand, alkaline pH will lead to the formation of the Ferric hydrate and the rapid decomposition of H_2O_2 to oxygen and water, thus limiting the production of OH* radical [8, 10, 31]. Therefore, the efficiency of Fenton oxidation process in removing LAS increases in an acidic pH. The results presented in Table 1 completely correspond with this analytical description. After LAS oxidation, pH is reduced due to the production of organic acids [8].

Ahmadi M. et al. [30] obtained the maximum removal of sodium dodecylbenzene sulfonate using Fenton oxidation in pH of 3.77 that it is near to our results.

Lin S.H. et al. [9] introduced the appropriate conditions of Fenton oxidation process at 90 mg/L ferrous ion, 60 mg/L hydrogen peroxide, the time of 50 min, and initial pH of 3. Under these conditions, LAS and ABS removal efficiencies were reported 93.21 and 93.4% in the absence of coagulation and 98.4 and 99.5% in the presence of coagulation, respectively. This study proved the positive effect of coagulation for improving LAS removal efficiency, which is justifiable with detergents adsorption on chemical flocs.

Wang X.J. et al. [11] decreased LAS of the detergent factory wastewater from 490 to 23 mg/L through Fenton oxidation (120 mg/L hydrogen peroxide, 600 mg/L ferrous ion, pH of 8 and the reaction time of 40 min), and then detracted it to less than 5 mg/L using biological treatment. The alkaline pH has been used to provide sweep coagulation mechanism and removing flocs in the biological reactor.

Findings of the current study, while being consistent with the similar studies, indicate that LAS removal by Fenton oxidation, as a second order reaction, has apparently high efficiency. However, the low COD removal efficiency corresponding to LAS indicates its incomplete decomposition. So that none of the 25 runs presented in Table 1, even including low initial LAS levels, acquired the allowable COD in the effluent. On this basis, it is necessary to identify LAS byproducts resulting from Fenton oxidation using special studies. It is obvious that the evaluation of LAS removal by Fenton oxidation will not be correct without attention to COD removal rates. Unfortunately, this issue has been overlooked in most studies.

Conclusions

Although Fenton oxidation appears as a high efficiency process in LAS removal, low efficiency of COD corresponding with LAS indicates its incomplete degradation by this process.

Acknowledgments

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