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Investigating the removal of linear alkyl benzene sulfonate from aqueous solution by ultraviolet irradiation and hydrogen peroxide process

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ABSTRACT

This study investigated the efficiency of ultraviolet radiation and hydrogen peroxide for the removal of linear alkylbenzene sulfonate (LAS) from aqueous solutions. Methylene blue active substances assay and spectrophotometry were used to determine the amount of anionic and residual surfactants. The effect of H_2O_2 concentration, initial concentration of surfactant, pH, and length of UV radiation were examined. The potential for use of UV/H_2O_2 to degrade LAS was analyzed statistically using multiple linear regression analysis. The results showed that after 20 min of contact time, ultraviolet radiation alone removed 38.44% of the LAS. The use of hydrogen peroxide alone for 10, 20, and 30 min showed no effect on the removal of LAS. The removal rates for the combination UV/H_2O_2 at 10, 20, and 30 min were 86.2, 90, and 96.5%, respectively. The results of this study showed that the use of ultraviolet radiation and hydrogen peroxide individually for degradation of anionic surfactant was not effective, but the combination of UV/H_2O_2 was effective for the removal of anionic detergents.

Keywords: Linear alkyl benzene sulfonate; Ultraviolet irradiation; Hydrogen peroxide; Aqueous solution

1. Introduction

During the past decade, large quantities of surfactants have entered the environment with an increased use of synthetic detergents in industrial and home applications [1,2]. Anionic surfactants are the most common detergents. The presence of sulfonate and phosphate groups in the structure of these detergents means that they produce negative ions during ionization [1,3]. Increased use of surfactants in various applications and the per capita increase in consumption have increased the percentage of these compounds in sewage. Advanced oxidation processes (AOP_S) are processes that use highly active radicals such as hydroxyl radicals ($HO^{\bullet}$) as oxidants [4] to remove the waste from water. In recent years, the use of AOP_S to eliminate trace pollutants has been a prevalent technology for water and wastewater treatment [5,6].

AOPs often use UV, UV/H_2O_2, UV/O_3, $UV/H_2O_2/O_3$, and $UV/H_2O_2/ZnO$. The homogeneous UV/H_2O_2 process is popular because it is relatively of

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low cost and simple to operate [1,7]. Hakim et al. [8] used UV/H_2O_2 for the removal of BTEX compounds from liquid solutions. Daneshvar et al. [9–11] and Movahedian and Rezaee [12] used this process to remove organic colors from industrial wastewater.

The most common mechanism for photolysis of hydrogen peroxide is the degradation of the O–O band by means of ultraviolet light to produce two hydroxyl radicals ($HO^{\cdot}$) [13]. The amount of photolysis of hydrogen peroxide is sensitive to pH and will increase under alkaline conditions, when the reactions occur in order. When the reactions occur in an environment containing organic pollutants, these radicals are produced and will decompose the pollutants [13,14]. The present study evaluated the efficiency of an AOP using UV/H_2O_2 to remove linear alkylbenzene sulfonate (LAS) from aqueous solution.

2. Materials and methods

Testing was done using concentrations of 10, 50, and 100-mg/l LAS anionic surfactant and 5, 10, 20, 40, 50, and 100-mg/l hydrogen peroxide. The process occurred under a 150-W mercury lamp with a wavelength of 254 nm for time periods of 10, 20, and 30 min. A total of 216 samples were tested and testing was done in duplicate.

The pilot used a stainless steel closed-bottom cylinder (Tehran Steel; Iran). A magnetic mixer was placed inside the cylinder for continuous mixing during irradiation. During operation, the temperature of heat generated by the UV lamp should be cooled constantly; for this purpose, the cylinder was placed into a 4-l cooling container to maintain the solution temperature at <30˚C for all experiments. To maintain a pH of 6, normal sulfuric acid solution (H_2SO_4) and sodium hydroxide (NaOH) were added as needed. A model E520 pH meter was used to measure pH.

Methyl blue active substances (MBAS) assay was carried out to determine the amount of anionic surfactant. The color intensity in the isolated samples was measured using a spectrophotometer at 652 nm. Hydrogen peroxide (H_2O_2) (Merck; Germany) with a purity of 30% was used; a molar solution of sodium thiosulfate ($Na_2S_2O_3$) was used to neutralize the remaining hydrogen peroxide at the end of the reaction [14]. Calibration curves were developed to measure the removal of LAS as follows:

(1) Fill the reactor with LAS solution,
(2) Turn on pump to begin mixing,
(3) Sample solution in reactor to determine initial concentration of detergent,
(4) Add H_2O_2 at a specified amount and turn on UV lamp,
(5) Sample solution at specified intervals and measure residual H_2O_2 by titration,
(6) Deactivate residual H_2O_2 in harvested samples using $Na_2S_2O_3$.

3. Results and discussion

3.1. Effect of UV exposure alone for removal of LAS

A 50-mg/l concentration of detergent was prepared and subjected to UV radiation to investigate the effect of UV radiation for removal of LAS. A sample of solution was taken before the lamps were switched on. Sampling was done at specific time intervals and the residual detergent present was measured using a spectrophotometer. The results indicated that UV radiation caused a little degradation of LAS. The removal efficiency after 20 min at a solution pH of 8 for 50 mg/l detergent was 38.44%. It is evident that ultraviolet radiation alone produced these results and shows that UV radiation alone is not useful to degrade the LAS. These results are in accordance with the results of other studies [12].

3.2. Effect of H_2O_2 alone for the removal of LAS

To determine the effect of H_2O_2 alone on the removal of LAS, a solution of 50-mg/l detergent was prepared and exposed to H_2O_2. The H_2O_2 concentration was 40 mg/l. Samples were taken at different time intervals and the amount of residual detergent was measured using a spectrophotometer. The results showed that H_2O_2 had no effect on LAS removal at 10, 20, and 30 min. The reason for the lack of effect can be assumed to be that $HO^{\cdot}$ was unable to form without the presence of UV radiation [12].

3.3. Effect of combined UV/H_2O_2 for the removal of LAS

To evaluate the effect of combined UV/H_2O_2, it was tested using 50-mg/l anionic detergent solution with a pH of 8 prepared with an optimal concentration of H_2O_2 (40 mg/l). This solution was exposed to UV radiation and sampling was carried out at specified time intervals and the residual detergent was measured using a spectrophotometer. The results for UV/H_2O_2 efficiency are shown in Fig. 1. The efficiency for the removal of LAS of the combined process at 10, 20, and 30 min was 86.2, 90, and 96.5%, respectively. It was concluded from previous testing that UV radiation for 20 min was 38.44%. As seen, the combined

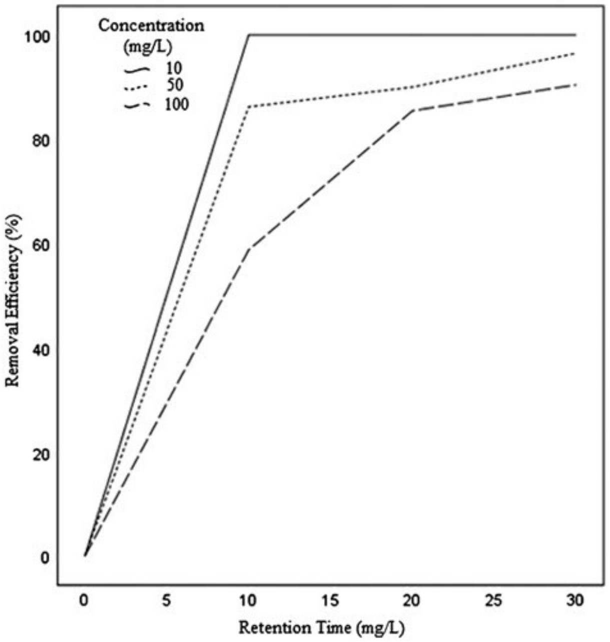

Fig. 1. Combined effect of UV/H_2O_2 for the removal of LAS (50 mg/l initial concentration; 40 mg/l H_2O_2; pH 8).

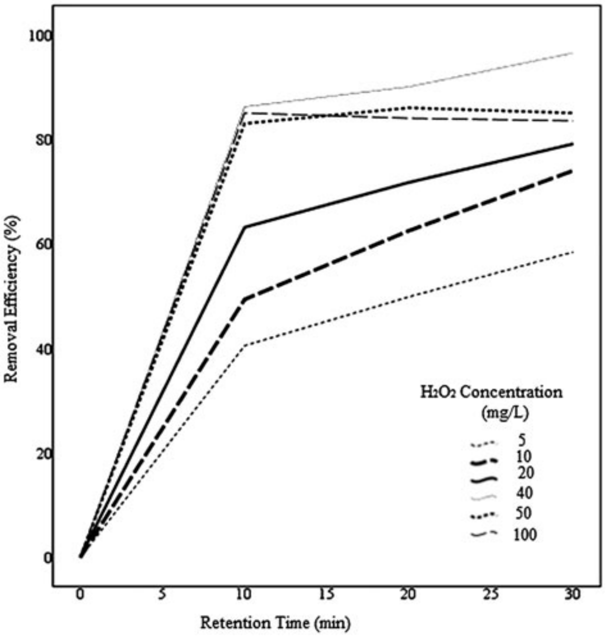

Fig. 2. Effect of H_2O_2 concentration on removal of LAS from 50-mg/l anionic detergent at pH 8.

UV/H_2O_2 process was effective for the removal of 90% anionic detergent during the same time interval. The results of this study coincide with those of Adams and Kuzhikannil [15] who also achieved high efficiency for pollutant removal.

3.4. Effect of H_2O_2 concentration in UV/H_2O_2 for removal of LAS

To evaluate the effect of the concentration of hydrogen peroxide in the combined UV/H_2O_2, 50 mg/l anionic detergent solution was prepared at pH 8. H_2O_2 in concentrations of 5, 10, 20, 40, 50, and 100 mg/l was added to the detergent solution, which was then exposed to UV radiation. Samples were taken from the solution at specified time intervals and the residual detergent concentration was measured using a spectrophotometer.

Fig. 2 shows the performance at different concentrations of H_2O_2. As seen, as the amount of H_2O_2 increased (5–40 mg/l), removal of LAS from the anionic detergent increased. The increase in H_2O_2 had no effect after at 40–100 mg/l. The main reason for this phenomenon is recombination of hydroxyl radicals at this stage. As its concentration increased past a certain point, H_2O_2 rejoined the hydroxyl radicals, which eliminated them from the solution [9–13]. The optimal concentration of H_2O_2 in these experiments was 40 mg/l. Arslan-Alaton and Erdinc [16] found that the optimal concentration of H_2O_2 to remove anionic surfactant was 1,000 mg/l. The reason for the large difference in concentration can be attributed to factors such as detergent type, duration, and type of radiation from the ultraviolet lamps [16].

3.5. Effect of initial concentration of detergent on UV/H_2O_2 removal of LAS

To evaluate the effect of initial concentration of detergent on removal using UV/H_2O_2, solutions of anionic detergent were tested at concentrations of 10, 50, and 100 mg/l with a pH of 8 using the optimal concentration of 40 mg/l H_2O_2 and different exposure intervals. Samples were taken from the solution at specified intervals and the amount of residual detergent was measured using a spectrophotometer.

The efficiency of the process for different concentrations of anionic detergent is shown in Fig. 1. As seen, process efficiency at low concentrations decreased considerably as the concentration of detergent increased. Multiple linear regression analysis shows that increasing the concentration of anionic surfactant decreased the removal efficiency to $B = -0.144$ (Table 1). This means that increasing the anionic surfactant concentration decreased the removal efficiency of UV/H_2O_2, and there was a significant relationship between surfactant concentration and removal rate ($p < 0.001$). Movahedian and Rezaee [12] also reported

Table 1
Results of multiple linear regression analysis

Coefficients[a]

Model		Unstandardized coefficients		Standardized coefficients		
		B	Std. Error	Beta	*t*	Sig.
1	(Constant)	0.363	0.101		3.595	0.001
	pH	−0.019	0.036	−0.031	−0.524	0.602
	Concentrate	−0.144	0.023	−0.379	−6.394	0.0001
	Dose	0.073	0.036	0.120	2.032	0.045
	H_2O_2	0.277	0.022	0.734	12.392	0.0001
	Time	0.090	0.022	0.239	4.047	0.0001

[a] Dependent variable: efficiency.

that the removal rate decreased as the initial concentration of pollutant increased.

3.6. Effect of pH on LAS removal using UV/H_2O_2

To evaluate the effect of pH on removal of LAS using UV/H_2O_2, a 50-mg/l detergent solution was prepared and the optimal concentration of 40-mg/l H_2O_2 was tested at different pH values. Samples were taken from the solution at specified time intervals and the amount of residual detergent was measured using a spectrophotometer. The amount of residual detergent by pH level is shown in Fig. 3. As seen, removal of LAS under alkaline conditions (50-mg/l detergent; 40 mg/l H_2O_2) was more efficient than under acidic conditions. The residual detergent at 20 min under alkaline pH was 9.42 mg/l, showing a removal efficiency of about 90%. The residual detergent at 20 min under acid pH was 20 mg/l for a removal efficiency of about 80%. These results show that the optimal pH for the removal of anionic surfactant using UV/H_2O_2 is alkaline.

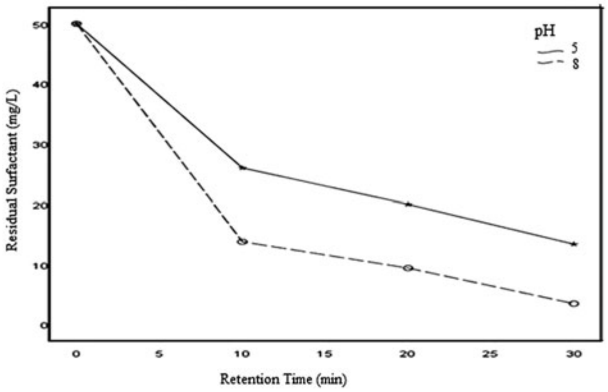

Fig. 3. Effect of pH on residual surfactant concentration (50-mg/l detergent; 40-mg/l H_2O_2).

Multiple linear regression analysis was used to test the effect of pH on the LAS removal rate of UV/H_2O_2. Table 1 indicates that as pH increased, removal efficiency increased to $B = 0.019$; the per-unit increase in pH (from 5 to 8) increased the removal rate by 0.019 units. Although there was an increase in the removal rate with an increase in pH, it was not significant ($p < 0.602$). Previous studies have shown a significant increase in processing the efficiency with an increase in pH [16–18].

The results show that exposure to UV radiation alone had little effect on the anionic detergent. It was also shown that H_2O_2 alone also had no effect on LAS removal. The results obtained from this research indicate that UV/H_2O_2 is an useful and effective method for water and wastewater purification of LAS. Table 1 shows the lack of significance between pH and removal rate. Arslan-Alaton and Erdinc [16] found that a range of 5–9 for pH made the H_2O_2 more stable so that more free radicals ($HO^{\cdot}$, $HO_2^{\cdot}$) form with ultraviolet photolysis. Their study tested this range for pH to remove the surfactant and produced results similar to those from the present study, as shown in Fig. 1. In the present study, the highest removal efficiency was obtained at pH 7–9; the results of Arsalan-Alaton and Erdine [15,16] confirmed these findings.

The removal of anionic surfactants by UV/H_2O_2 requires the optimal values for concentration of H_2O_2, initial concentration of LAS, pH, and duration of exposure. These conditions were determined to be 40-mg/l H_2O_2, alkaline pH, and low concentrations of anionic detergent. Testing showed that, of all these variables, H_2O_2 concentration had the greatest and pH had the least effect on the efficiency of the UV/H_2O_2 process.

4. Conclusion

The results of this research indicate that a combination UV/H_2O_2 process was effective for the removal of LAS. Separate testing of the effects of UV radiation and H_2O_2 showed that they had little effect on the removal of LAS. Of the AOP_S, the combination of UV/H_2O_2 is relatively of low cost and has been used extensively for the removal of various pollutants from water and wastewater in recent years. The main advantages of UV/H_2O_2 are no production of sludge, ease of operation, it can be carried out at air temperature, and oxygen formed during the process aids the biological degradation process if used as a pretreatment.

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