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Removal of Linear Alkylbenzenesulfonate by Fenton's Oxidants and Coagulation

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Abstract

본 연구는 폐수 중 함유된 고농도의 LAS를 제거하기 위해 $FeSO_4$를 이용한 응집, 펜톤산화, 펜톤 공정 전·후에 응집공정을 조합시킨 Coagu-oxidation 및 Fenton's Coagulation을 이용하여, 처리시 최적 조건을 도출하고, 효율적인 화학적 처리방법을 검토하기 위해 수행되었다. 연구로부터 얻어진 결론은 다음과 같다.

응집공정은 pH 8, 응집제의 주입량 200 mg/L인 조건에서, 펜톤산화는 pH 3, H_2O_2에 대한 Fe^{2+}의 비가 1:1인 조건에서 최적 효율을 보였다. Fenton's Coagulation 처리 시 LAS의 개환율은 높아졌고, 주입된 LAS농도의 73~96%가 제거되어 4가지 처리 방법 중 가장 좋은 처리효율을 보였다.

따라서, LAS의 생물학적 처리시 거품 및 부산물 생성 등에 의해 저해작용을 감안한다면, LAS가 다량으로 함유한 산업 폐수에서 화학적 처리방법의 도입이 적절할 것으로 생각되며, 이들 중 Fenton's Coagulation을 유용하게 적용될 수 있을 것으로 판단된다.

I. Introduction

Linear alkylbenzenesulfonates(LAS) is still representative globally because it has most widely been used in the manufacture of industrial cleansers as well as commercial detergents[1]. However, LAS which was substituted for ABS in behalf of the excellent biodegradation gave rise to rather more serious problems that LAS toxicity was 2-3 times higher than ABS toxicity and reached to the range of 0.1-8.2 mg/L as LC_{50} values in the aquatic ecosystem. Probably LAS is a unique chemical compound which occupies more than 3 % of ratio to BOD in mg/L[2,3].

Besides, as a serious problem, enormous foam can be generated even if LAS is dissolved in water at very low concentration such as 0.1-1.0 mg/L or blow[4]. Particularly foam which is generated in the aeration tanks causes some serious problems including very slow growth rate of microorganism and the obstruction of air transportation in biological treatment process, so it is difficult to expect the excellent removal efficiency of LAS itself by microorganism.

Therefore, it is required to use chemical treatment for the effective degradability of LAS in wastewater plant. Accordingly, this study was performed to evaluate the feasibility of Fenton's oxidation from the various operating processes using ferrous ion in the degradation of high concentration LAS.

II. Materials and Methods

1. Chemicals and Analytical Methods

Ferrous sulfate was used as a coagulant in ferrous coagulation as well as a catalyst in Fenton's oxidation and alum was used as a coagulant for comparison of coagulation treatment of LAS as shown in Table 1.

Major analytical items and methods are shown in Table 2. Among analytical methods, Concentration of LAS were determined by the MBAS method and spectrophotometrical method at 223 nm (UV_{223} method). The UV_{223} method in combination with the MBAS method is useful to measure concentration of LAS to its intermediates, sulfophenylalkanoates(SPAs) as shown in Fig. 1.[5,6]

However, in these experiments, UV_{223} reduction as LAS concentration in various operating processes using ferrous sulfate was mostly excluded by the interference of ferrous ion in the spectrophotometrical measurement.

2. Experimental methods

The applied concentrations of LAS were 100 mg/L in these experiments including coagulation and Fenton's oxidation, since it has been known

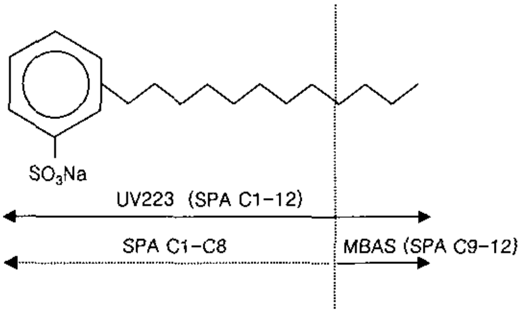

Fig. 1. Structure of LAS and SPAs by MBAS and UV_{223} method.

Table 1. Major chemicals used in these experiments

Item	Chemical
Surfactant	Linear Alkylbenzenesulfonates(LAS)
Oxidants	Hydrogen peroxide
Coagulants	Ferrous sulfate, Alum
Catalyst	Ferrous sulfate
pH Adjuster	0.01 N phosphoric acid, 0.01 N caustic soda solution
Quenching Agents	1 % $Na_2S_2O_3$ solution

Table 2. Major analytical items and methods

Item	Analytical Method
pH	Corning pH/ion analyzer 350
SPAs	UV-Visible spectrophotometer (shimadzu UV 1601, λ ; 223nm)
MBAS	UV-Visible spectrophotometer (shimadzu UV 1601, λ ; 650nm)
Oxidants	Hach DPD kit, Hach DR/2000
Ferrous ion	Hach DR/2000, Fe Aquaquant E, Merck

that relatively high concentration of surfactants are usually dissolved in industrial wastewater.[7)]

1) Removal of LAS by Coagulation

The jar tester which was shown in Fig. 2 was employed by 10 minutes of rapid mixing at 100 rpm. After 30 minutes of slow mixing at 40 rpm, then the mixed samples were allowed to stand for 30 minutes. pH of samples were adjusted to certain values that are required. Prior to analysis of samples, 0.1 ℓ supernatants of samples were collected and filtered by 0.45 μm filter papers.

2) Removal of LAS by Various Processes using Ferrous sulfate.

The fenton's coagulation in this study intented to represent the effects of Fenton's oxidation and sequent ferrous coagulation. The Fenton's oxidation, where hydrogen peroxide and ferrous sulfate was doesed as oxidant and catalyst respectively at pH 3~3.5 of sample by a rapid agitating of 100 rpm. Then, ferrous coagulation was introduced sequently, where pH was readjusted to 8.0 in order to form $Fe(OH)_3$.

Reversely, as ferrous coagu-oxidation process, after ferrous coagulation is conducted first at pH 8 of sample and then remained ferrous sulfate could be used as a catalyst of Fenton's oxidation by addition of hydrogen peroxide at pH readjustment of 3-4.

In these experiments, the comparison of LAS removal efficiencies in every process using ferrous ion, namely, ferrous coagulation, Fenton's oxidation, fenton's coagulation and ferrous coagu-oxidation was performed when the concentration of ferrous sulfate increased from 0 to 300 mg/L at intervals of 50 mg/L in the presence of 200 mg/L hydrogen peroxide. Also, the optimum ratio of H_2O_2 to $FeSO_4$ was determined for the most effective removal of LAS when hydrogen peroxide dosage increased from 0 to 300 mg/L at constant intervals of 50 mg/L.

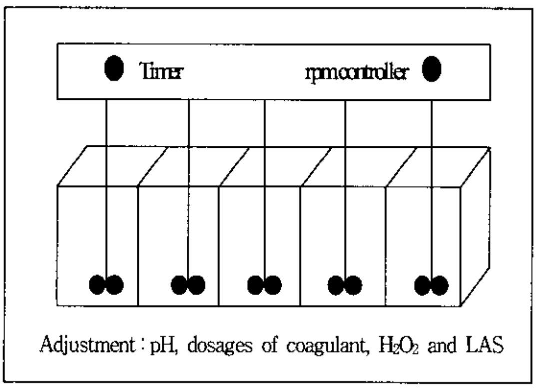

Fig. 2. Apparatus for reaction of LAS by Coagulation and Fenton's oxidation.

Ⅲ. Results and Discussion

1. Effect of pH in Coagulation and Fenton's oxidation of LAS

Fig. 3 shows the effect of pH on the LAS

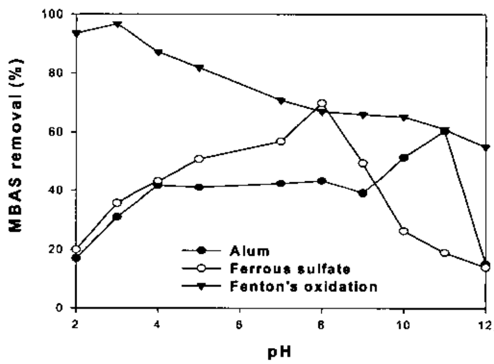

Fig. 3. Effect of pH on MBAS removal by coagulation and Fenton's oxidation.
Alum coagulation : LAS ; 100 mg/L, alum ; 200 mg/L
Ferrous coagulation : LAS ; 100 mg/L, $FeSO_4$, ; 200 mg/L
Fenton's oxidation : LAS ; 100 mg/L, $FeSO_4$, H_2O_2 ; 200 mg/L

removal in coagulation and Fenton's oxidation ata pH range of 2-12 when concentration of ferrous sulfate, Alum and hydrogen peroxide were 200 mg/L, respectively.

Optimum pH for LAS removal by Alum, ferrous sulfate and Fenton's oxidation were 11, 8 and 3 respectively, where the removal efficiencies of MBAS were 60.5%, 69.8% and 96.8%.

These results show that the optimum pH for LAS removal by Alum is very different from pH which is 5-6 in coagulation of humic matter by Alum. However optimum pH of Fenton's oxidation and ferrous coagulation in LAS removal are similar with references reported.

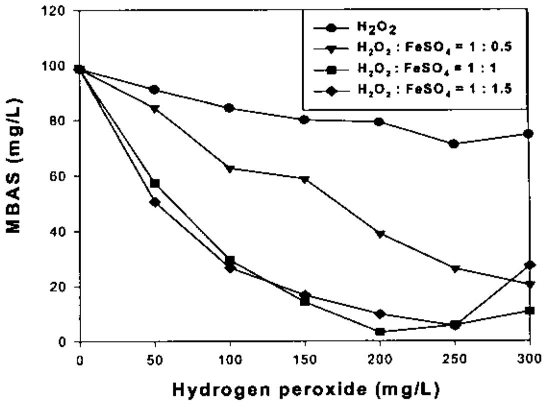

Fig. 4. Change of MBAS concentration by H_2O_2/$FeSO_4$ ratio variation.(pH ; 3, LAS ; 100 mg/L)

2. Ratio of H_2O_2 to $FeSO_4$ in Fenton's oxidation of LAS

It is needed to maintain the possibly large ratio of H_2O_2 to Fe^{2+} and small ratio of Fe^{2+} to substrates in Fenton's oxidation since the excess dosage of ferrous ion brings about the adversely low treatment efficiency[8,9].

When the hydrogen peroxide increased from 0 mg/L to 300 mg/L at intervals of 50 mg/L at pH 3, the LAS concentrations remained depending on ratio of H_2O_2 to $FeSO_4$ were very different as shown in Table 3 and Fig. 4.

As hydrogen peroxide increased from 0 mg/L to 200 mg/L at overall range of Fenton's oxidation, the removal efficiencies of LAS increased obviously. However the hydrogen peroxide more than 250 mg/L brought about rather lower treatment efficiency.

The results indicates that the optimum ratio of H_2O_2 to $FeSO_4$ for LAS removal in Fenton's oxidation is 1 : 1 when concentration of hydrogen peroxide is 200 mg/L. The removal efficiency of LAS can reach to around 96.9 % at this condition.

3. Comparison of Various Operating Processes Using Ferrous Sulfate

The Fenton's coagulation in this study intented to represent the effects of Fenton's oxidation and sequent ferrous coagulation by variation of pH. The Fenton's oxidation, where hydrogen peroxide and ferrous sulfate was doesed as oxidant and catalyst respectively at pH 3~3.5 of sample by a rapid agitating of 100 rpm. Then, ferrous coagulation was introduced to use remained ferrous sulfate sequently, where pH was readjusted to 8.0 in order to form $Fe(OH)_3$.

In reverse, as ferrous coagu-oxidation process, after ferrous coagulation is conducted by pH adjustment of 8 first and then the remained ferrous sulfate could be used as catalyst of Fenton's oxidation by addition of hydrogen peroxide after pH of sample was readjusted to 3~3.5.

The comparison of ferrous coagulation, ferrous coagu-oxidation, Fenton's oxidation and fenton's coagulation was performed in LAS removal of high concentration when the concentration of

Table 3. LAS concentration remained depending on ratio of H_2O_2 to $FeSO_4$ in Fenton's oxidation

$H_2O_2 : FeSO_4$	H_2O_2 (mg/L)						
	0	50	100	150	200	250	300
1 : 0	98.58	91.19	84.40	80.00	79.17	71.05	74.58
1 : 0.5	98.58	84.51	62.68	58.77	38.95	26.27	20.27
1 : 1	98.58	57.30	22.50	14.20	3.14	5.67	10.68
1 : 1.5	98.58	50.57	26.65	16.75	9.67	5.45	27.35

ferrous sulfate increased from 0 to 300mg/L at intervals of 50mg/L in the presence of 200mg/L of hydrogen peroxide.

As shown in Fig. 5, the average removal efficiency of LAS in whole concentration of ferrous sulfate was 24.3%, 55.9%, 75.9% and 81.0% respectively. Particularly, when concentration of ferrous sulfate was 200mg/L, the LAS removal efficiency by fenton's coagulation reached to 98.2%.

For more detailed comparison, the ratio of LAS concentration removed to ferrous sulfate concentration dosed in various processes is shown in Table 4. At ferrous sulfate of 150 mg/L, the ratio of LAS concentration removed per ferrous sulfate concentration dosed was 0.20 in ferrous coagulation, 0.31 in ferrous coagu-oxidation, 0.54 in Fenton's oxidation and 0.61 in Fenton's coagulation respectively.

In comparison of ferrous coagulation and fenton's coagulation, the ratio of LAS concentration removed to ferrous sulfate concentration dosed in Fenton's coagulation was 3.05 times larger than that in ferrous coagulation.

These results indicate that fenton's coagulation is far better than ferrous coagulation, ferrous coagu-oxidation and Fenton's oxidation in the removal efficiency of LAS and the performance of fenton's coagulation is mainly governed by Fenton's oxidation than ferrous coagulation.

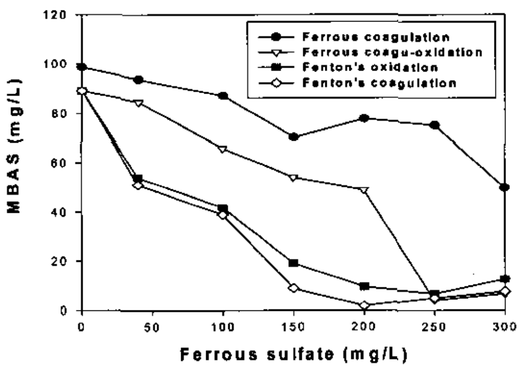

Fig. 5. Comparison of various processes using ferrous ion.
LAS ; 100 mg/L
H_2O_2 ; 200 mg/L
pH ; Ferrous coagulation(8), Fenton's oxidation(3)
Fenton's coagulation(3→8), Ferrous coagu-oxidation(8→3)

Table 4. LAS concentration removed per mg/L of $FeSO_4$ concentration dosed in various processes($FeSO_4$; 150mg/L, H_2O_2 ; 200mg/L, LAS ; 100mg/L)

Processes	(mg/L) LAS removed/ (mg/L) $FeSO_4$ dosed
Ferrous coagulation	0.20
Ferrous coagu-oxidation	0.31
Fenton's oxidation	0.54
Fenton's coagulation	0.61

4. Comparison of Coagulation and Fenton's coagulation in LAS Removal

As LAS concentration increased from 50mg/L to 500mg/L at their own optimum conditions, basic tendencies on the degradation of MBAS and UV_{223} by coagulation and Fenton's oxidation were more or less similar as shown in Fig. 6.

However, the removal efficiencies of MBAS was a little large than that of UV_{223} in whole concentration of LAS.

The removal efficiency of LAS decreased gradually as LAS concentration increased. Especially, LAS was very difficult to be treated with any processes when LAS concentration was higher than 400 mg/L.

Fenton's coagulation was far better than any other process in the removal efficiency of LAS when LAS concentration was less than 400 mg/L. Among coagulation treatments, ferrous coagulation by ferrous sulfate was slightly better than alum coagulation in the LAS removal efficiency at a whole range of LAS concentration.

Also, Figure 7 shows the comparison of the distribution ratio depending on number of carbons in alkyl groups from MBAS and UV_{223} removal of 100mg/L LAS by coagulation and fenton's coagulation. Since LAS was relatively resistant to alum and ferrous sulfate in LAS removal by coagulation, cleavage ratios of benzene rings were not more than 51% and 53%. However the cleavage rate of aromatic ring by fenton's coagulation was far better than coagulation with alum and ferrous sulfate because it showed 92 % of cleavage rate.

These results indicate that fenton's coagulation is the best chemical treatment to degrade LAS and its intermediates suchlike SPAs since it can amputate the aromatic rings effectively.

CONCLUSION

This study was performed to evaluate the feasibility of Fenton's oxidation among the various operating processes using ferrous ion in the degradation of high concentration LAS.

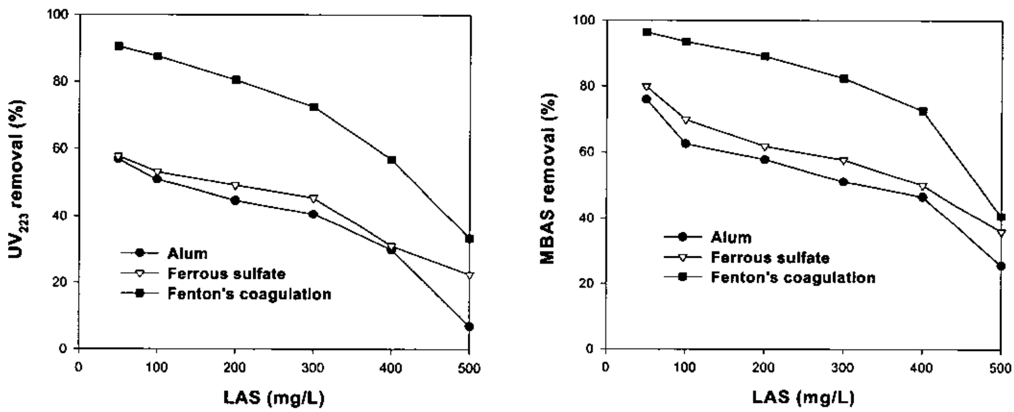

Fig. 6. Comparison of LAS removal efficiency by treatment methods in optimum conditions.
Alum coagulation ; pH 11, alum(300mg/L)
Ferrous coagulation ; pH 8, ferrous sulfate(200mg/L)
Fenton's coagulation ; pH 3, H_2O_2(200mg/L), ferrous sulfate(200mg/L)

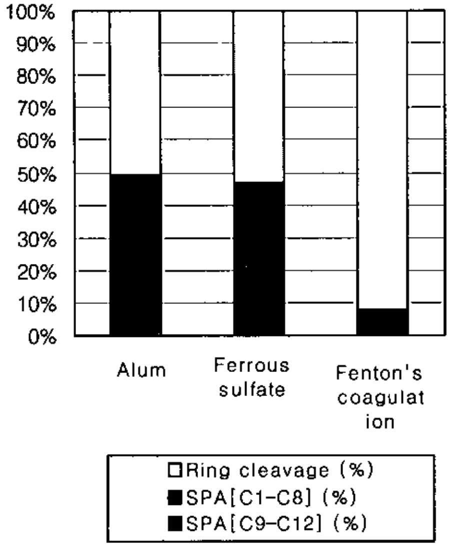

Fig. 7. Occupation of LAS and SPAs in LAS removal of 100 mg/L by coagulation and fenton's coagulation under their own optimum conditions
Alum coagulation ; pH 11, alum(300mg/L)
Ferrous coagulation ; pH 8, ferrous sulfate (200mg/L)
Fenton's coagulation ; pH 3, H_2O_2(200 mg/L), ferrous sulfate(200mg/L)

Especially, fenton's coagulation intented to represent Fenton's oxidation and sequent ferrous coagulation by readjustment of pH. Reversely, as ferrous coagu-oxidation process, after ferrous coagulation is conducted first at pH 8 of sample and then the remained ferrous sulfate could be used as a catalyst of Fenton's oxidation by addition of hydrogen peroxide at pH readjustment of 3-4.

1) The optimum pH for LAS removal in Fenton's oxidation was 3, where the removal efficiency of LAS was 96.8%. However, the removal efficiency of LAS decreased with higher pH. The optimum ratio of H_2O_2 to $FeSO_4$ for LAS removal was 1 : 1 when concentration of hydrogen peroxide concentration was 200mg/L.
2) The ratio of LAS concentration removed to dosage of 150mg/L ferrous sulfate in various processes was 0.20 in ferrous coagulation, 0.31 in ferrous coagu-oxidation, 0.54 in Fenton's oxidation and 0.61 in fenton's coagulation. Also, the ratio of LAS concentration removed to ferrous sulfate in fenton's coagulation was 3.05 times larger than that in ferrous coagulation. Therefor, fenton's coagulation was better than any other process including ferrous coagulation, ferrous coagu-oxidation and Fenton's oxidation in LAS removal from high concentrated solution. However, the performance of fenton's coagulation is mainly governed by Fenton's oxidation than coagulation by remained ferrous sulfate.
3) The cleavage rate of aromatic ring by fenton's coagulation was far better than coagulation with alum and ferrous sulfate because it showed about 92 % of cleavage rate. These results indicate that fenton's coagulation is the best chemical treatment to degrade LAS and its intermediates suchlike SPAs since it can amputate the aromatic rings effectively.
Among coagulation treatments, ferrous coagulation with ferrous sulfate was slightly better than alum coagulation in the efficiency of LAS removal at a whole range of LAS concentration.

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