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Comparison of the removal efficiency of linear alkylbenzene sulfonate (LAS) by biological and integrated biochemical treatment

R. Saberi[a,*], A.H. Hassani[b], M.S. Abedi[b], A.T. Ardeshir[a], A. Mozaffari[c]

[a]*NSTRI, P.O. Box 11365-8486, Tehran, Iran, emails: rsaberi@aeoi.org.ir (R. Saberi), ali_ardeshiri@yhoo.com (A.T. Ardeshir)*
[b]*Environment and Energy Faculty, Science and Research Branch, Islamic Azad University, Tehran, Iran, emails: ahh1346@gmail.com (A.H. Hassani), M.S_Abedi@yahoo.com (M.S. Abedi)*
[c]*KNT University of Technology, Tehran, Iran, email: Mozaffari.Ali@hotmail.com*

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ABSTRACT

In this study, ozone as an advanced oxidation process was used to increase the efficiency of linear alkylbenzene sulfonate (LAS) detergent removal in the treatment of wastewater. The first part of this research contains the study of LAS removal from the wastewater by the Moving Bed Biofilm Reactors (MBBR) biological reactor. For this purpose, the LAS removal efficiency was determined at different levels of LAS (low, medium and high concentrations) for different hydraulic retention times. The results show that increasing the hydraulic retention time had a positive effect on the MBBR reactor, efficiency, but Increasing- LAS Concentration had negative impact on system performance and decreased LAS removal rate. The second part of this research contains a study on LAS removal from the wastewater by using a combination system of MBBR and post-ozonation process. The results show that this combination system can remove LAS completely at the low concentration of LAS and dramatically improving the removal efficiency of LAS in medium and high concentrations.

Keywords: Ozone; MBBR; LAS; Modeling; Advanced oxidation; Integrated process

1. Introduction

The purpose of this work is to evaluate a novel technology for the removal and degradation of linear alkylbenzene sulfonate (LAS) using a combination system of "Moving Bed Biofilm Reactors (MBBR)" and post-chemical oxidation process. Most of the previous works in this area has focused on the fixed bed reactors [1–4].

LAS is one of the major surfactant productions in the detergents and cleaners facilities. The presence of LAS causes a lot of serious problems in the treatment of wastewater, and at the high concentrations, they can hamper the processes of biological treatment. Some of their usage consequences are toxicity, production of eutrophication, destruction of ecosystems, water and soil contamination, effects of mutagenicity and xenobiotic, can decrease the oxygen level of the waters and so on [5–7]. There are lots of studies to address the development of an efficient and cost effective treatment for removal of LAS from the wastewater, such as physicochemical methods, which are effective but quiet expensive [8–13]. The positive points of the biological processes are cheaper and more environmental friendly alternative for the treatment of LAS [14,15].

Nowadays, MBBR was introduced and used as a new technology for treatment of the aqueous or polluted water in lots of countries in the world [16].

It is improved by experiences that the use of MBBR treatment alone is not sufficient to remove LAS effectively. Therefore, the use of additional specific step such as advanced oxidation or ozonation processes are highly recommended by the research institutes and treatment facilities to remove LAS sufficiently [17–21].

To use synergetic effectiveness of the two processes instead of separately or in sequence, a combination process of biological and chemical oxidation treatment should be considered [22–24].

*Corresponding author.

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The main purpose of this study is to use a combination system of MBBR reactor with post-oxidation process to remove LAS as high as possible in the wastewater especially in the entrance of low concentration of LAS to the system. Based on the results, it is necessary to mentioned that the preozonation process has negligible effect on the removal percentage of the LAS.

2. Materials and methods

2.1. Materials

All the used chemical agents (sulfuric acid (H_2SO_4), potassium dichromate ($K_2Cr_2O_7$), phenanthroline monohydrate ($C_{12}H_8N_2$), ferric sulfate ($FeSO_4$), FAS, KHP, mercury sulfate ($HgSO_4$), silver sulfate (Ag_2SO_4), sodium hydroxide (NaOH), sodium hydrogen phosphate (NaH_2PO_4), chloroform ($CHCl_3$), methylene blue ($C_{16}H_{18}N_3SCl$), phenolphthalein ($C_{20}H_{14}O_4$), ethanol (C_2H_6O), methanol (CH_4O), potassium iodide (KI), sodium thiosulfate ($Na_2S_2O_3$), potassium dihydrogen phosphate (Na_2HPO_4) and carbamide, LAS were in the condition of high purity analytical grade reagents supplied by Merck, and used without further purification in this study.

2.2. Analytical methods

pH of the solution was measured with an Orion 420A pH-meter. LAS was determined using a Varian Cary-100 spectrophotometer. Dissolved Oxygen was determined with Crison DO-meter. The DO was measured by a membrane covered amperometric electrode. Ozone was generated from ARDA (COG-1A) ozone generator. 7F-3 oxygen maker was used for production of oxygen. Etatron DS (DL2MA) peristaltic pump was used for injection. HAILEA ACO-328 air compressor was used for production of the air.

2.3. Experimental methods

Study on LAS removal is divided into two parts, biological MBBR process for the primary removal of LAS and post-ozonation process for supplementary treatment of residual LAS. LAS was determined using an HP-1090 chromatograph and a well validated specific HPLC method.

2.4. Wastewater

The sugar-manufacturing synthetic wastewater, used in this study, consisted of beet sugar molasses with tap water and some added materials resulting in a ratio of COD/N/P = 100/5/1. The initial quality parameter is mentioned in Table 1 and was preserved at 22°C till used. The laboratory Regent (LR) grade chemicals were used in the experiments and analytical grade (AR) chemicals were used for analysis. These LR and AR grade chemicals were obtained from Merck chemical Ltd. The wastewater was at various COD concentrations in the range between 978 and 2,615 mg COD l^{-1}. Each gram of molasses used for preparing synthetic wastewater has a COD concentration equal to 978 mg L^{-1} (Table 1).

Table 1
Composition of sugar-manufacturing synthetic wastewater (100 ppm)

Chemical	Amount
pH	7.2 ± 0.1
Electrical conductivity mS m^{-1}	1.57
TOC mg L^{-1}	29 ± 6
Color U	2.6
T-N mg L^{-1}	1.1 ± 0.24
NH_4-N mg L^{-1}	0.19 ± 0.045
NO_2-N mg L^{-1}	0.00
PO_4-P mg L^{-1}	1.41 ± 0.55
F^- mg L^{-1}	0.12 ± 0.002
Cl^- mg L^{-1}	3.75 ± 0.7
SO_4^{2-} mg L^{-1}	3.53 ± 0.67
Na^+ mg L^{-1}	1.95 ± 0.24
K^+ mg L^{-1}	5.82 ± 1.1
Mg^{2+} mg L^{-1}	0.33 ± 0.75
Ca^{2+} mg L^{-1}	0.64 ± 0.082
COD mg L^{-1}	978 ± 195

2.5. Biological MBBR process for the removal of LAS

The type of the biological reactor is MBBR and the reactor specifications are illustrated in Table 2. Fig. 1 shows the schematic view of this reactor.

The type of used pumices in this study is Kaldnes K1. The Kaldnes plastic particles from Norway (Kaldnes K1) were used in this research. The diameter and the length of these particles are 7 and 10 mm, respectively. Due to its microscopic structure, it has a relatively high special surface area.

Kaldnes has also been tested and used in various environmental applications mainly as an adsorbent, and also for filtration media.

About 50% of MBBR reactor volume was filled with Kaldnes K1. Nominal diameter (mm), length (mm), density (lg m^{-3}) and specific surface area (m^2 m^{-3}) of Kaldnes K1 are: 9.1, 7.2, 150 and 500 sequentially. This reactor operated in upward mode by using a peristaltic pump with flow rate of 70 l h^{-1} to feed wastewater from the bottom. An air compressor in liquid phase over the bed provides dissolved oxygen to biomass through continuous recycle with 60 l h^{-1} rate that also assured the substrate distribution. The reactor was kept in a controlled temperature chamber with the temperature limit of 24°C–27°C. During the period of test operation, LAS, pH and DO concentration were measured at the influent and effluent from the MBBR. Analytical procedures followed in this research for LAS, pH and DO determinations were those outlined in standard methods for examination of water and wastewater [25].

2.6. Start-up period

To start up the MBBR, sludge sample from the convectional domestic sewage treatment plant was used. A combination of milk (40%) and glucose (60%) was used to provide the carbon source. At the first step the amount of COD was adjusted to 250 mg L^{-1}. After reaching to high efficiency (more than 97%), the amount of COD increased gradually to 350 mg L^{-1}. After 8 d, the system converted from batch mode to continuous state. 15 d after the change of regime to continuous system, now the MBBR is ready to work properly by formation of biofilm on Kaldnes plastic particles. The COD concentration in MBBR feed gradually increased from 350 to 1,000 mg L^{-1} during 80 days. After this time and also to ensure efficiency of 80%, LAS concentration of 5 mg L^{-1} was injected into the system. Then the concentration of LAS gradually increased to 1,000 mg L^{-1}.

2.7. Biological MBBR process with chemical post-ozonation process for the removal of LAS

This part of the study has been performed after reaching to the steady state condition of the MBBR reactor. To increase the efficiency of MBBR reactor operation, the post-ozonation process used for synergetic removal of LAS from the effluent in an optimal time and neutral pH conditions. Fig. 2. shows the process which are used at this stage.

Table 2
MBBR reactor specification

Material	Plexiglas
Wall thickness (mm)	5
Internal cross section (cm)	24 × 25
External cross section (cm)	25 × 26
Total height (cm)	60
Effective height (cm)	50
Total volume	36
Effective volume	30

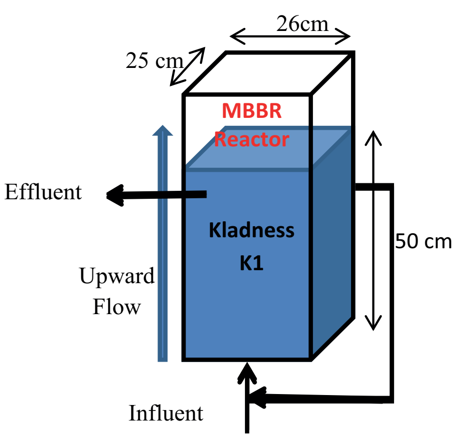

Fig. 1. Schematic view of MBBR reactor.

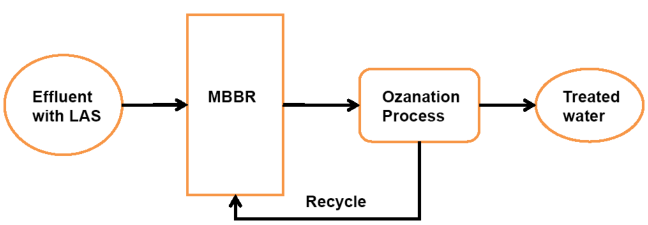

Fig. 2. Schematic view of MBBR + post-ozonation process.

3. Results

3.1. Low concentration of LAS: 5–50 mg L^{-1}

The effects of time on the removal of LAS in low concentrations (5–50 mg L^{-1}) for both cases are shown in Figs. 3–5. As seen in Fig. 3, at LAS concentrations of 5–10 mg L^{-1}, the combination of MBBR reactor and ozonation system were

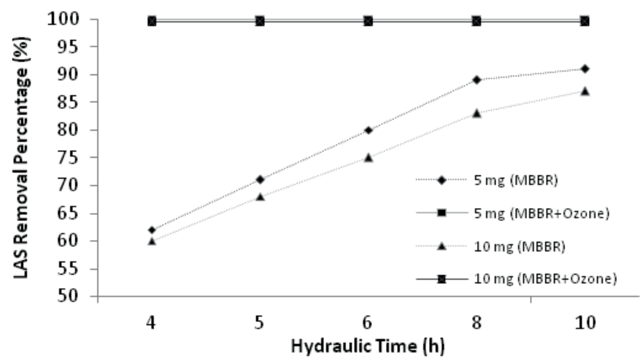

Fig. 3. Effect of hydraulic retention time in low concentrations of LAS (5 and 10 mg).

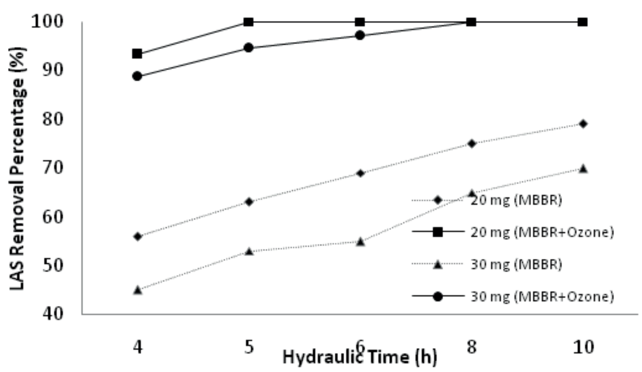

Fig. 4. Effect of hydraulic retention time in low concentrations of LAS (20 and 30 mg).

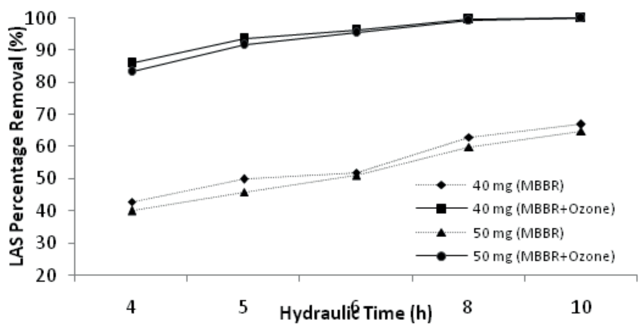

Fig. 5. Effect of hydraulic retention time in low concentrations of LAS (40 and 50 mg).

able to remove almost the LAS completely. However, the LAS removal percentage by MBBR reactor alone is about 60% to 90%.

At concentrations of 20 and 30 mg L^{-1}, based on Fig. 4, integrated system of MBBR reactor and ozonation system were removed about 90% to 100% of the LAS, but the removal efficiency of LAS from effluent by the MBBR reactor alone was about 44% to 80%.

By increasing the LAS concentrations to 40 and 50 mg L^{-1}, the removal efficiency of MBBR reactor with ozonation system was about 83% to 100%, while the efficiency of MBBR reactor was 40% to 65% separately.

It is demonstrated that, the best hydraulic time for removal of low concentration of LAS was 10 h and by increasing the concentration of LAS, the LAS removal percentage will be decreased, especially in the case which only MBBR reactor is used. The combined system of MBBR reactor with ozonation system could remove almost all of the LAS from the effluent stream at 5 to 50 mg L^{-1} of LAS concentrations.

3.2. Medium concentration of LAS: 75–200 mg L^{-1}

Fig. 6 shows the effect of time on the removal of LAS in medium concentrations (75–100 mg L^{-1}). As seen in this figure, generally, time increasing lead to increase in the LAS removal efficiency at all levels. At 75 mg concentration, the maximum and minimum removal percentage of LAS by combination of MBBR reactor and ozonation system are 76.4% and 97.6%, respectively, in different retention times. These numbers were 36.1% and 63.6%, respectively, for MBBR reactor alone.

With increasing concentration of LAS from 150 to 200 mg L^{-1}, the removal efficiency of MBBR reactor with ozonation system was between 65% to 90.9%, while the efficiency of MBBR reactor was 32% to 61.1% separately (Fig. 7).

It is demonstrated that, the best hydraulic time for removal of medium concentration of LAS from effluent stream, was 10 h and with increasing the concentration of the LAS, the LAS removal percentage will be decreased, especially in the case in which only MBBR is used.

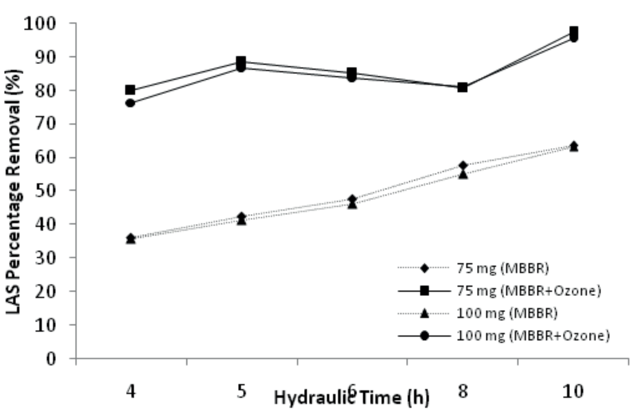

Fig. 6. Effect of hydraulic retention time in medium concentrations of LAS (75 and 100 mg).

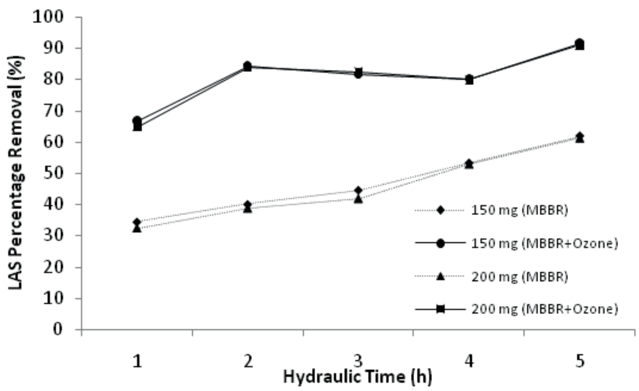

Fig. 7. Effect of hydraulic retention time in medium concentrations of LAS (150 and 200 mg).

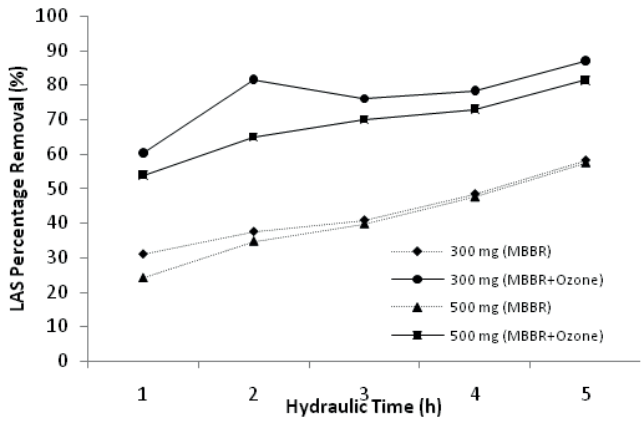

Fig. 8. Effect of hydraulic retention time in high concentrations of LAS (300 and 500 mg).

3.3. High concentration of LAS: 300–1,000 mg L^{-1}

Fig. 8 is drawn to determine the effect of time on the removal of LAS in high concentrations (300–500 mg L^{-1}). As seen in this figure, as the time increase, the LAS removal efficiency will increase at all levels. The removal efficiency of MBBR reactor with ozonation system was between 53% and 87%, while the efficiency of MBBR reactor was 24% to 58% (Fig. 8).

With increasing the LAS concentrations to 750 and 1,000 mg L^{-1}, the removal efficiency of MBBR reactor with ozonation system will be about 38.9% to 81.8%, while the efficiency of MBBR reactor was 19.5% to 57% separately.

It is demonstrated that, for the case of high concentration of LAS and 10-h hydraulic retention time, the maximum removal percentage of LAS was approximately 82% for 750–1,000 mg L^{-1} concentration and the minimum value was approximately 40% for 1,000 mg L^{-1} concentration (Fig. 9).

4. Conclusion

The amount of LAS input concentration directly affects the removal efficiency of LAS from the effluent. An increase in LAS input concentration could result to decrease in effi-

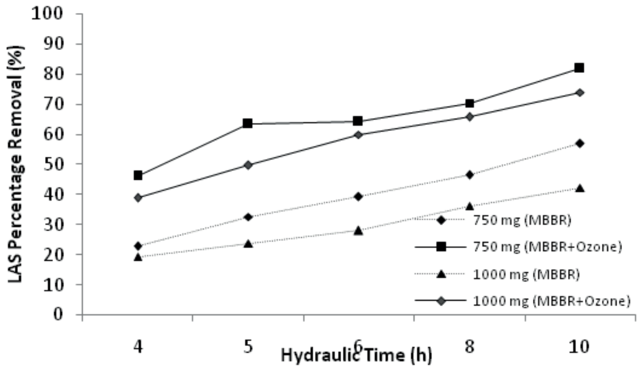

Fig. 9. Effect of hydraulic retention time in high concentrations of LAS (750 and 1,000 mg).

ciency of the LAS removal by the MBBR reactor because of the limited ability of biological systems.

The use of a combined system of MBBR reactor and post-ozonation process, dramatically improves the efficiency of the LAS removal, especially in the range of low LAS input dose (5–50 mg L^{-1}).

In the medium range of LAS input concentration (75–200 mg L^{-1}), the removal efficiency decreased due to limitation on the biological growth initiated by the entered LAS. So that by increasing the concentration of input LAS, the organic input load will be increased. This requires increasing the microbial load of the system, in order to use input LAS as a carbon source.

By using the post-ozonation process, the LAS can be removed properly by the combined system (MBBR reactor and post-ozonation process). The higher LAS concentration (300–1,000 mg L^{-1}) resulted in a steep decline in LAS removal efficiency and this is due to the inhibitory effect of LAS on biological activity. This combined system can remove the LAS completely in low ranges and dramatically increase the removal efficiency at the other concentrations.

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