

## Applying moving bed biofilm reactor for removing linear alkylbenzene sulfonate using synthetic media

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### ABSTRACT

Detergents and problems of their attendance into water and wastewater cause varied difficulties such as producing foam, abnormality in the growth of algae, accumulation and dispersion in aqueous environments.

One of the reactors was designated with 30% of the media with the similar conditions exactly same as the other which had filling rate about 10 %, in order to compare both of them together. A standard method methylene blue active substance was used to measure anionic surfactant. The concentrations of linear alkylbenzene sulfonate which examined were 50, 100, 200, 300 and 400 mg/l in HRT 72, 24 and 8 hrs.

The removal percentage for both of reactors at the beginning of operating at 50 mg/l concentration of pollutant had a bit difference and with gradually increasing the pollutant concentration and decreasing Hydraulic retention time, the variation between the removal percentage of both reactors became significant as the reactor that had the filling rate about 30 %, showed better condition than the other reactor with 10 % filling rate. Ideal condition in this experiment was caught at hydraulic retention time about 72 hrs and 200 mg/l pollutants concentration with 99.2% removal by the reactor with 30% filling rate. While the ideal condition for the reactor with 10% filling rate with the same hydraulic retention time and 100 mg/l pollutants concentrations was obtained about 99.4% removal.

Regarding anionic surfactant standard in Iran which is 1.5 mg/l for surface water discharge, using this process is suitable for treating municipal wastewater and industrial wastewater which has a range of the pollutant between 100-200 mg/l. but for the industries that produce detergents products which make wastewater containing more than 200 mg/l surfactants, using secondary treatment process for achieving discharge standard is required.

**Key words:** Media, Biofilm, Moving bed, Methylene blue, Anionic surfactant

### INTRODUCTION

Making the point that detergents are used widely around the world for different household and industrial purposes [1], and by the negative effects of them such as foaming, eutrophication and their drawbacks for human, aquatic animals, water treatment plants and underground water caused researchers thought about solving the environmental problems of them [2]. Detergents consist of various components that among them surfactants have a major for reducing surface tension of water [1, 3]. They reduce the surface tension of water which can cause good penetrating into fabric tissue and also connecting the water droplets and dirt particles [4]. Surfactants are divided into four groups including anionic, cationic, nonionic and amphoteric [3, 4]. Anionic surfactants are the most popular between them. Anionic surfactants produce negative ions in water. In between anionic surfactants, linear alkylbenzene

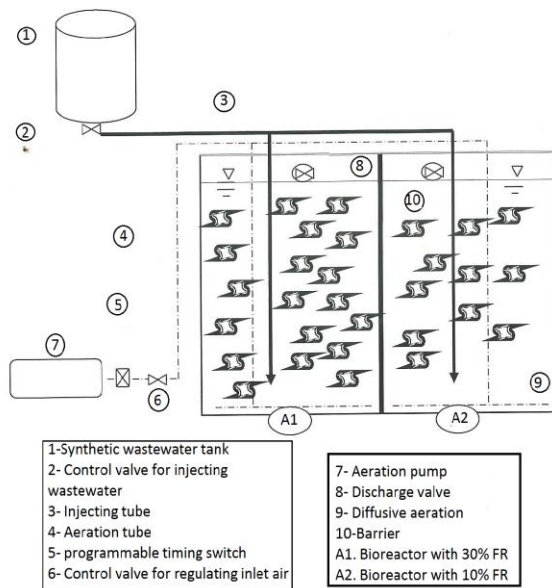
sulfonate (LAS) is under a production near two millions and half each year which totally includes 27 percent of constructed surfactants in Europe [5]. Their resistance habit against degradation, forced different attempts started for finding suitable treatment methods for them [6]. Different processes were applied by researchers to evaluate the degree of their degradation, for example coagulation, microwave irradiation, oxidation with ozone, photo catalytic degradation, and adsorption or fenton reagent and also electrochemical process were examined [6, 7]. Biological processes for many reasons are the vantage point in comparison with the other processes. There are easy for handling, low cost and also environmentally friendly processes. Among the biological processes, sequencing batch reactor (SBR) and activated sludge had efficient effect for removing anionic surfactants [8]. But moving bed biofilm reactor (MBBR) with its advantages such as low

sensitivity, achieving mixed liquor suspended solids (MLSS) up to 12000 mg/l easily, requiring very small area, without sludge recycle, high sludge age, and high expandability can be another alternative for treating anionic surfactants [9, 10]. This process works with media made of polyethylene which has got specific weight about 0.98 N/m<sup>3</sup> that is lighter than water which causes their submerging [11].

## MATERIALS AND METHODS

Synthetic wastewater was made ready by solving 100 g/l LAS purchased from Aldrich company with tab drinking water Every day. For keeping the ratio of COD/N/P about 100:5:1, nutrient solution which is necessary for the growth of microorganisms was prepared by combining nutrient solution and synthetic wastewater [10]. The components of nutrient were K<sub>2</sub>HPO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, NH<sub>4</sub>Cl, CaCO<sub>3</sub>, and NaHCO<sub>3</sub> with proportion about 5, 15, 120, 10 and 10 grams per liter of drinking water respectively [12]. The pH former adjusted to its neutral range and after that synthetic wastewater for microorganism applied.

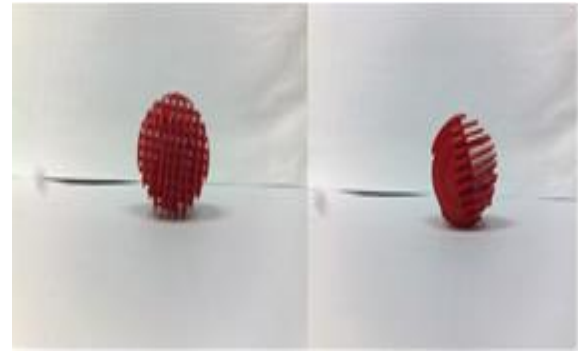
The schematic of the reactor was illustrated in Fig.1.



**Fig.1:** The schematic of the set up reactor in the experiment.

It consists of 4mm Plexiglas plate with dimension about 10×34×10 cm for each reactor which has a total useful volume of 3 liter and remaining supposed as free board, an air injection pump (HAILEA ACO-328 70 lit/min), an hour timer switch, and the other equipment. For feeding instead of applying pump in this experiment a gravitational feeding tank was used by arranging droplets which injected to the deepest point of the bioreactor. In order to achieve the correct range of droplets, before starting the process the feeding

tank accuracy for gravitational droplets effluent was checked. Near the line which the range of droplets started changing was marked. Then each time that the level of liquid was near to the line, the feeding tank was refilled. Media selected for the MBBR was manufactured by the Kavian company made of polyethylene which has the specific surface area of 775m<sup>2</sup>/m<sup>3</sup> with specific weight about 0.98 N/m<sup>3</sup> as shown in the Fig.2.



**Fig.2:** Two view of media with 775m<sup>2</sup>/m<sup>3</sup> specific surface which used in this experiment.

First of all the 1/3 of bioreactors was filled with the sludge which was procured from the return sludge of the wastewater treatment of a detergent company so media volume in the reactor was assigned about 30% and 10% for the both of the reactor's experimental volume and 2/3 of the bioreactor filled with the supernatant of a return sludge. As it could be clear two reactors were taken which were side by side with a sealed barrier that separated them from each other totally. In those we filled 30% and 10% media for reactors A1 and A2, respectively.

Room temperature was operative temperature for the both reactors. In order to keep dissolving oxygen at 2 mg/l, flow of aerating had been doing nearby 1.6 l/min. Firstly; the bioreactors were started for adaptation phase of microorganism acclimatization. During the adaptation phase the bioreactors operated as batch reactors which were aerated about 2hrs and settled down about 0.5h. Injecting of nutrient and pollutant as LAS source was done regularly. We began feeding the reactors from 5 mg/l until 45 mg/l by LAS. After reaching the bioreactors to our starting concentration for operation (50 mg), the bioreactors were shifted to continuous condition which nutrient and LAS as inlet were injected and aeration became lasting. Under the operation, Foam production has been hindered by using anti foam which was purchased from the BASF Company and it was used in 2-3 droplets for the volume of the reactor. Effluent valve was designed on the boundary line in between free space and wastewater surface of the each bioreactor.

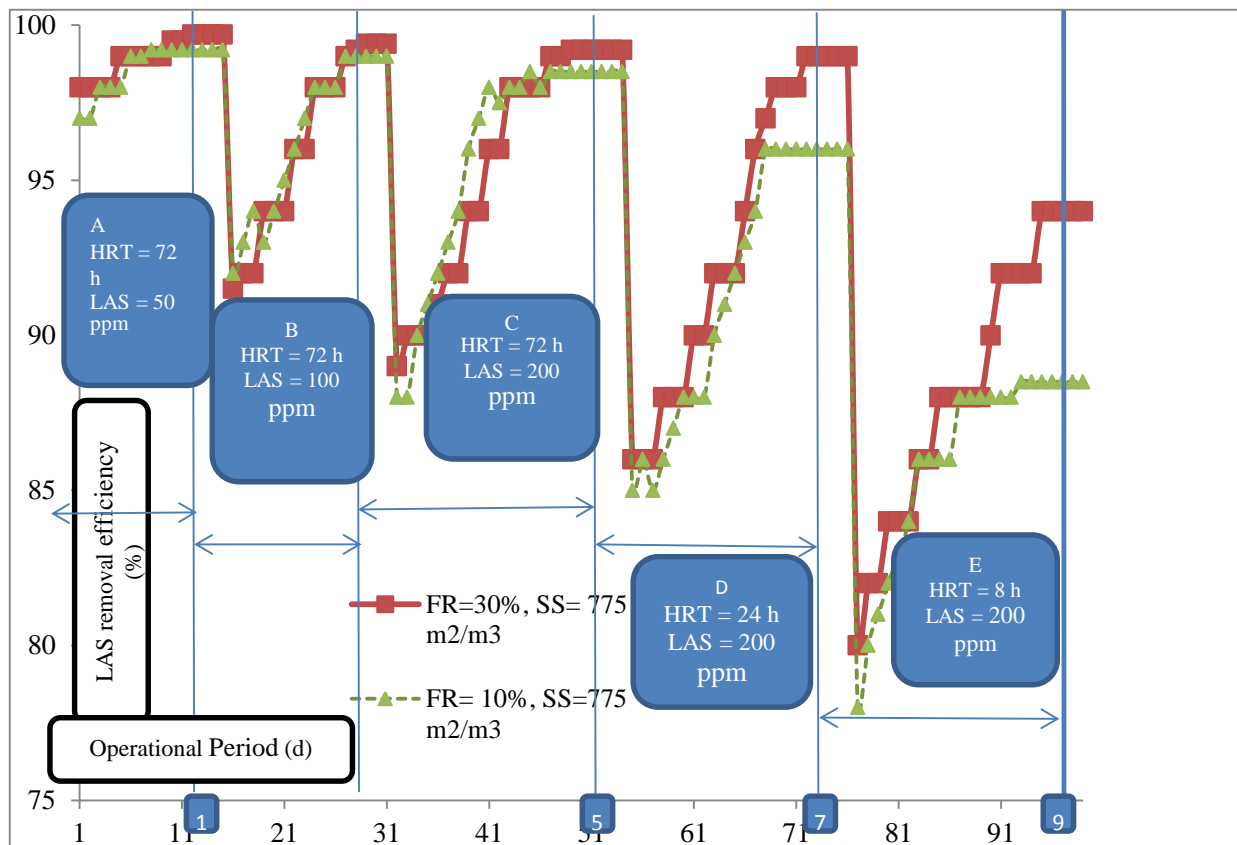
Operation condition has been conducted in two situations. Different concentrations and constant hydraulic retention time (HRT) was one of the

operation conditions and the other situation was under the condition of HRTs variation and constant concentration. We applied LAS concentrations as pollutant: 50, 100, 200, 300 and 400 mg/l, respectively with HRTs about 8, 24, and 72hrs. In order to achieve steady- state situation the reactors were kept protracting. Remaining at constant removal percentages represents that steady-state situation was obtained (with standard deviation about 3%) [13]. The degree of LAS mineralization was measured by COD method [14]. Reaching each steady-state took a period about 21-25d. LAS and COD analyzed daily for each reactor. Filtration of samples was done by using 0.42  $\mu\text{m}$  whatman paper filters prior to analysis for limiting particles. LAS removal was measured by Scanning Spectrophotometer PHILIPS Pu 8750 UV/VIS, in the wave length 652 nm through the methylene blue active substance (MBAS) method that has been described in standard methods [15]. All materials for MBAS experiment such as sulfuric acid, chloroform, methylene blue and other required materials were purchased from the Merck Company. COD during the experiment was measured according to the standard methods [15].

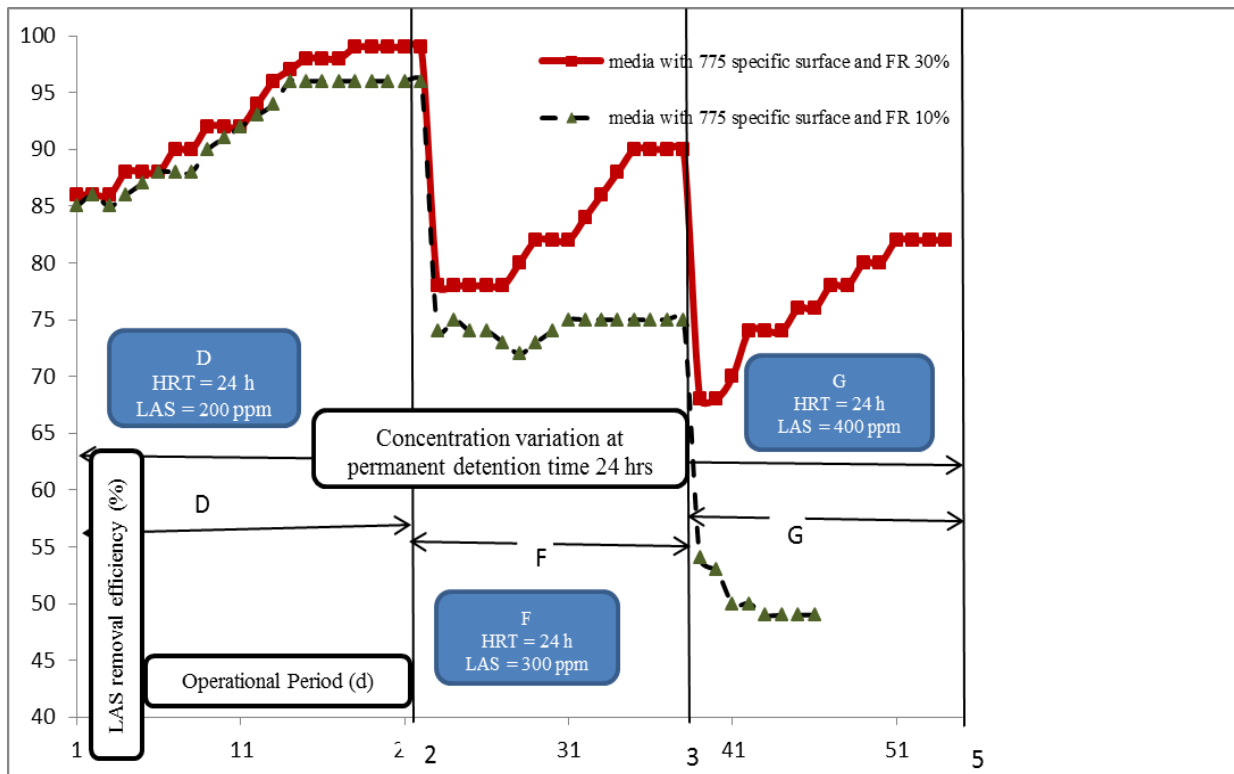
Like what is written in the standard methods, MLSS was determined to estimate the suspended biomass into the reactors [15]. The pH of influent and synthetic wastewater by using a sensitive electrode (Jenway 3505) was evaluated. The biofilm growth visualization for depicting biofilm morphology was investigated by the scanning electron microscope (SEM Hitachi S4160). Before SEM analysis, media samples were taken from the bioreactor and dried at room temperature for 16hrs [12].

## RESULTS

Performance of MBBR in biodegradation of LAS was examined at the entrance of LAS concentrations about 50, 100, 200, 300 and 400 mg/l and 72, 24 and 8 hrs HRTs. Figs.3 and 4 depicts the results of LAS biodegradation and removal in the MBBR under the explained conditions. For assessing mineralization of LAS, reduction of COD equals to LAS and organic loading rate was studied in this experiment intermittently.



**Fig.3:** Time course results of biodegradation and LAS removal in the MBBR with permanent HRT at 72 hrs at LAS concentration increasing from 50 to 200 mg/l in zones A-C, and LAS concentration permanent at 200 mg/l and HRT decreasing from 72hrs to 8hrs in zones C-E.



**Fig.4:** Time course results of biodegradation and LAS removal in the MBBR with permanent HRT at 24hrs at LAS concentration increasing from 200 to 400 mg/l in zones D, F and G.

As can be seen in zones A, B and C Fig.3, the average of steady-state removal percentage of LAS at 72 hrs HRT for 30% filling rate (FR) reactor were 99.7 %, 99.4% and 99.2% respectively, for 50, 100, and 200 mg/l LAS inlet concentrations, which COD removal percentage equals to LAS was about near them with  $\pm 0.25\%$  variations. In comparison with 10% FR reactor, LAS removal percentages were approximately 99.2%, 99% and 98.5% respectively, for 50, 100 and 200 mg/l LAS inlet concentrations. But gradually the removal efficiency in both reactors went up till they achieved steady-state.

After that HRT was decreased again from 24 hrs to 8 hrs (by increasing droplets from 1 milliliter per 29 sec to 1 milliliter per 10 sec). zone E of Fig.3, in this conditions again decrease in LAS removal efficiency for both reactors to percentages below 81% and 80% was seen respectively. However, in both reactors slowly increasing LAS removal was obtained until we caught the point of steady-state condition. HRT was altered from 72 hrs to 24 hrs and 8 hrs respectively with 200 mg/l LAS permanent concentration. Under this situation for 30% FR reactor, the mean percent of steady-state removal of LAS at the HRTs of 24 hrs and 8 hrs was 99% and 94%, respectively. In comparison with 10% FR reactor, removal percentages of LAS at the HRT of 24 hrs and 8 hrs were 96% and 88.5% respectively, which in both bioreactors; COD removal percentage was in variation about  $\pm 0.5\%$  in comparison with LAS removal

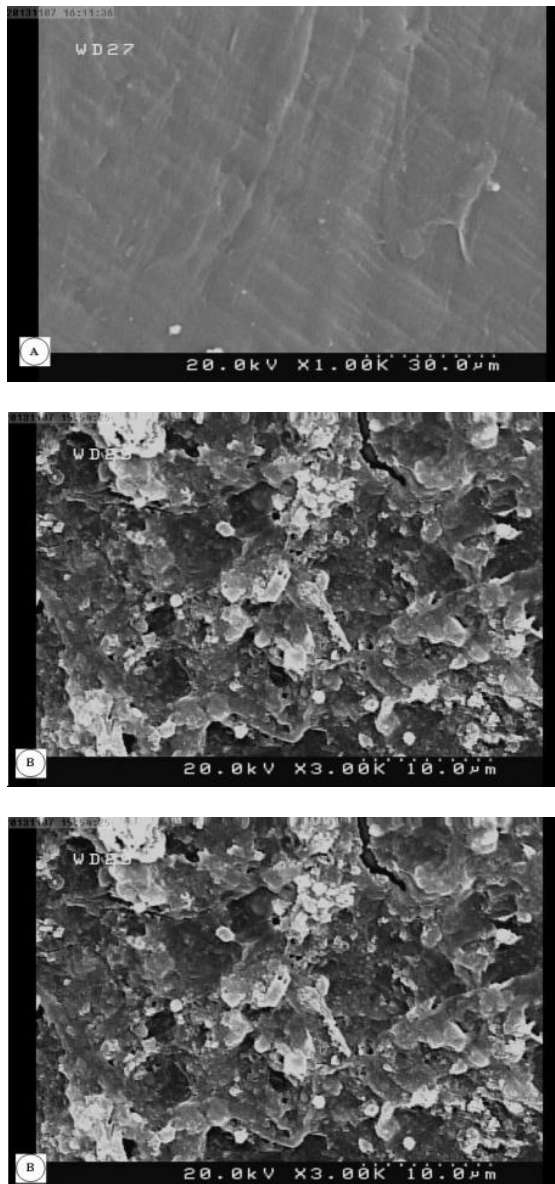
percentage, in order to find mineralization. In HRT of 24 hrs and 8hrs, the standard of discharging in surface water was not obtained by the both reactors, although the removal percentage was desirable. During the condition of 8hrs of HRT variation (zone E) 10% FR reactor did not catch desirable removal percentages. It attributes again to biofilm on the media which puts a significant effect on the efficiency of the removal percentages [17]. We continued applying equally reactors to obtain capacity of them for LAS removal efficiency. For the aim that we obtained discharge standard in HRT of 24 hrs for 200 mg/l LAS concentration, the reactors were applied in the same HRT of 24 hrs with concentration variations of 300 and 400 mg/l. Zone F and G Fig.4, the removal percentages were decreased after increasing concentration from 200 to 300 mg/l and HRT from 8 hrs to 24 hrs. The average steady-state removal percentage of LAS at HRT 24 hrs for 300 mg/l inlet concentration was in both reactors 90% and 75% respectively. The both reactors were gone on HRT of 24 hrs at inlet LAS concentration of 400 mg/l up to the mean percent of steady-state removal obtained 82% and 42%. At zone F and G Fig.4, COD removal percentage equals to LAS removal was about in  $\pm 1.5\%$  variation in comparison with LAS removal percentage.

MLSS of primary sludge that procured from the return sludge line of a wastewater treatment was measured 2056 mg/l. at the end of the operation the reactors MLSS was measured and data were

obtained 1192 mg/l for 30% FR reactor and 3236 mg/l for 10% FR reactor which says that the difference between them has changed to biofilms on the media (carriers).

During the operation, in order to avoid foaming, we used anti foam because we wanted to reduce effect of COD removal by foaming especially in high levels of LAS concentrations Such as concentrations about 100 mg/l and higher. A few anti foam was employed in the experiment was about 5-6 droplets for each reactor at most.

The visualization of the biofilm surface morphology on the media was done by SEM micrographs (shown in Fig.5).



**Fig.5:** Morphology of the biofilm surface formation on media was visualized with SEM micrographs. Photo A shows clean media without attached growth compared with photos B and C which show media surface with attached growth by 3000 and 10000 zoom, respectively

## DISCUSSION

The results of present study were showed that it can be possible to meet standard of LAS removal for discharging in surface water (1.5 mg/l) by MBBR and 30% FR reactor under the condition of defined inlet concentrations and HRT (Fig. 3) but by using a same reactor with 10% FR under the similar conditions, standard of LAS outlet for discharging into the surface water was not achieved for 200 mg/l LAS concentrations at 72 hrs HRT. It proves that biomass attached as biofilm on the media surfaces plays an important role in biodegradation of LAS [10]. However, when shifting the operation from the 72 hrs HRT to 24 hrs (by increasing droplets from 1 milliliter per 88 sec to 1 milliliter per 29 sec as we know that each 15-16 droplets equals 1 milliliter) zone D of Fig.3, degradation levels and COD removal of LAS fell suddenly to percentages below 80%, for both reactors. The abrupt decreases in LAS removal efficiency of HRT decrease can be assumed to the prohibitory impact of LAS on metabolism occurs in microbial as a consequence of an increased volumetric loading rate in the bioreactor [16]. Biofilm growth on the media surface is linked to the characteristics of the media and connected hydrodynamic situation [18].

The SEM micrograph Fig.5, depicts that clear media surface was flat, but because of the biofilm shaping on their surface, they became uneven. Sclerotic and homologous biofilm form on the media can be related to the power of rigidity originated from media circulating in the bioreactor [19] sclerotic and homologous biofilm that causes enhancement of substrate rates and passage of oxygen and reducing the biofilm spread ambit and accelerate bio chemical reactions. It has been caused from the biological degradation promoted rate [20].

Take the point that around the concentrations more than 200 mg/l the MBBR reactors did not achieve Iran discharge standard for surface water, we can say that for high level of LAS concentrations beings in wastewater in order to obtain standard of discharge, using auxiliary treatment after MBBR reactor would be urgent. For treating urban wastewater which has got at most 5 mg/l detergents, biological process perfectly removes them and it doesn't make any differences between MBBR process or other bioreactors such as activated sludge or sequencing biological batch reactor (SBBR). In order to treat wastewater containing linear alkylbenzene sulfonate in the range of 50-200 mg/l using MBBR process suggested because of its strong points which were described prior and its capability for treating linear alkylbenzene sulfonate in those ranges [14].

Removal percentage of this experiment up to 200 mg/l concentration at HRT about 24 hrs was 99% which was more than other processes such as

Electro-Fenton that removed 50 mg/l concentration of anionic surfactant [16], and activated sludge process that had 99% removal effectiveness for only 5 mg/l detergent in wastewater [14, 18].

Appearing foam in aerobic processes from anionic surfactants is a major problem especially when dosages of them are high. In that case there can be two suggestions; firstly we can use anti foam substances and secondly is raising MLSS in the bioreactor because by rising MLSS the production of foam declines noticeably [19, 20].

Taking care of the age of media more than 20 years, and reducing electrical energy which is applied in other processes for returning sludge, this process can be called as a sufficient one for treating wastewater containing detergent. Also biological processes are more environmentally friendly whereas in those has not been put chemical materials, and more flexible and comfortable handling for operating them; price of electrical facilities, expert workers and extra money will decrease in this process.

## CONCLUSION

In order to treat linear alkylbenzene sulfonate MBBR process was established and conducted in this experiment. Two different situations of FR – 30% FR for one reactor and 10% FR for another – was investigated during the same operational condition for the both for assessing the efficiency of FR for removing the anionic surfactants. The MBBR process with 30% FR showed better effectiveness than the one with 10% of FR in degradation and mineralization of anionic surfactants. In conclusion, the MBBR process with 30% FR by 775m<sup>2</sup>/m<sup>3</sup> nominates as a sufficient, easy operating and appropriate bioprocess alternative for treating pollutants.

## LIST OF ABBREVIATION USED

LAS: Linear Alkylbenzene Sulfonate  
 SBR: Sequencing Batch Reactor  
 MBBR: Moving Bed Biofilm Reactor  
 MLSS: Mixed Liquor Suspended Solids  
 HRT: Hydraulic Retention Time  
 MBAS: Methylene Blue Active Substances  
 SEM: Scanning Electron Microscope  
 FR: Filling Rate  
 SBBR: Sequencing Biological Batch Reactor

## COMPETING INTERESTS

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## AUTHORS CONTRIBUTION

Dr. Seyed Bagher Mortazavi and Dr. Ahmad Jonidi Jafari help to prepare the original idea and edited the manuscript.

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