Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2017.20866

77 (2017) 206–214
May

Combined Fenton-like oxidation and aerobic MBBR biological processes for treatment of the wastewater of detergent industries

Kamran Taghavi[a], Alireza Pendashteh[b], Saeed Pourkarim Mozhdehi[a,*]

[a]*Department of Environmental Health Engineering, School of Health, Guilan University of Medical Sciences, Rasht, Iran, Tel. +981334569165/+989391316372; email: saeedpoorkareem@yahoo.com (S.P. Mozhdehi), Tel. +989113321633; email: kam2000ir@yahoo.com (K. Taghavi)*
[b]*Environmental Science Department, Faculty of Natural Resources, University of Guilan, Rasht, Iran, Tel. +989111329011; email: arpendashteh@guilan.ac.ir (A. Pendashteh)*

Received 26 April 2016; Accepted 26 April 2017

ABSTRACT

Surfactant is one of the most important compounds widely used in the formulation and structure of detergents all over the world. In this study, we investigated the combined Fenton-like oxidation and aerobic moving bed biofilm reactor (MBBR) biological processes for treatment of the wastewater of detergent industries. The average chemical oxygen demand (COD) and linear alkylbenzene sulfonate (LAS) in the raw wastewater were 24,039 and 210 mg/L, respectively. The maximum removal efficiencies of the pretreatment and Fenton-like oxidation process for COD and LAS were 95% and 90%, respectively, and the effluent concentrations of COD and LAS were about 1,250 and 100 mg/L, respectively. For MBBR process, in reactor 1 (with lower LAS concentrations) with 36 h hydraulic retention time (HRT), the maximum removal efficiencies were found to be 94.20% and 99.99% for the influent COD and LAS, respectively ($R^2 = 0.93$ and $p < 0.05$ and $R^2 = 0.92$ and $p < 0.05$). Also, for reactor 2 (with higher LAS concentrations), in the same condition with 36 h HRT, the maximum removal efficiencies were 93.41% and 95% for the influent COD and LAS, respectively ($R^2 = 0.92$ and $p < 0.05$ and $R^2 = 0.84$ and $p < 0.05$). This investigation shows that Fenton-like oxidation process, in combination with MBBR process, can provide the local effluent discharge standard for detergent industries.

Keywords: Detergent; Linear alkylbenzene sulfonate; Fenton-like oxidation; MBBR process; Industrial wastewater

1. Introduction

Surfactant is one of the most important compounds widely used in the world in the formulation and structure of detergents [1]. This compound has two poles. One pole is hydrophilic (alkyl chain), and the other one is hydrophobic (sodium sulfate; Fig. 1) [2,3]. Surfactants are divided into four categories, namely anionic, cationic, nonionic and amphoteric [3–5]. Anionic and nonionic surfactants are two major categories of synthetic detergents [1,6]. Detergent industries are the main source of the discharge of wastewater into the environment, and a large amount of their pollution load is related to washing devices [2]. The release of such wastewater into the aquatic environment can have an adverse impact on aquatic life [7,8]. Anionic surfactants have a lower biological biodegradability and also have a very low cellular adsorption ratio compared with other typical compounds [9,10]. The resistance of some of the compounds to the biological degradation is due to the existence of three or four carbon chains in their structures [11]. These three and four carbon chains prevent bacterial enzyme from having an impact on the sensitive areas of such compounds [2,12]. Furthermore, these compounds in concentrations of 20–50 mg/L were limiter for the growth of the microorganism and could have an intense effect on the cell membrane and their permeability properties in the adsorption of organic compounds [4,9].

* Corresponding author.

1944-3994/1944-3986 © 2017 Desalination Publications. All rights reserved.

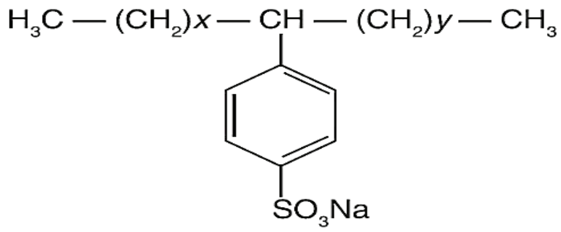

Fig. 1. Chemical structure of linear alkylbenzene sulfonate (LAS).

The pretreatment methods for the treatment of such wastewater include coagulation–flocculation, adsorption, chemical oxidation, electrochemical oxidation, membrane technology and among other things [2,4,6,13–15]. Therefore, for the treatment of such wastewater a suitable, inexpensive, simple and efficient method should be used [9]. Oxidation technologies may be used either for the complete mineralization or partial oxidation of pollutants to carbon dioxide, water and/or intermediate compounds [16]. In general, a chemical oxidation method or complete mineralization of pollutants might be very expensive since a number of highly oxidized end-products are formed, which tend to be resistant to total oxidation [14,16]. To convert initially biorecalcitrant organics into more readily biodegradable intermediates and also for the biological oxidation of these intermediates, we need to use a chemical oxidation pretreatment step instead of complete oxidation through chemical methods [17–19]. For instance, organic macromolecules may be too large to permeate cell walls, which can affect the oxidation of these organic compounds by microorganisms. With chemical oxidation, these macromolecules might break into smaller intermediate compounds (e.g., short-chain organic acids) that can permeate the cell and may be more readily biodegradable than the original molecules [16,17–21].

Fenton oxidation is a proven and effective technology for the degradation of a large number of hazardous organic pollutants [22]. The mixture of ferrous iron and hydrogen peroxide (Fenton's reagent) at low enough pH results in the formation of a strong oxidizing agent (hydroxyl radicals) that destroys organic compounds in a short time [23]. Besides Fenton process, Fenton-like reactions, in which ferric ions or other transition metal ion are utilized, have been effective in organic components degradation in wastewater [24]. Jiang et al. [25] studied the effects of various parameters such as H_2O_2 concentration, iron dosage and pH, on the phenol degradation in Fenton and Fenton-like reactions. The results of their study demonstrated that although the reaction mechanisms and effects of parameters were different, the overall degree of phenol degradation at optimal conditions was the same in the two reactions.

Fenton degradation of anionic surfactant linear alkylbenzene sulfonates (LASs) and the optimization of the operating parameters have been reported previously [26]. The results showed that the degradation capacity of the Fenton's reagent was highly dependent on the concentration of H_2O_2 and Fe^{2+}. The optimum $FeSO_4/H_2O_2$ ratio obtained was higher than 1 and the optimum pH was around 3. Under the optimum conditions, the LAS surfactant removal was over 95%. The Fenton-like agent, $Fe(0)/H_2O_2$, has been used to degrade anionic surfactant, and sodium dodecylbenzene sulfonate (SDBS). Approximately, 90% of SDBS degradation efficiency was accomplished at a pH range of 3.0–6.5 [27].

A few studies have reported directly the biological treatment of real surfactant wastewater because of its toxicity, low degradability and scum problems. For example, Duarte et al. [1] used a horizontal anaerobic immobilized biomass reactor for the treatment of LAS, Delforno et al. [3] used expanded granular sludge bed reactors for the treatment of anionic surfactants and Okada et al. [5] used upflow anaerobic sludge blanket reactor for the removal of LAS [5].

Biological processes are a cost-effective alternative for the treatment of wastewater [28]. One of the best processes for organic carbon and nutrient removal in municipal wastewater plants is the biological processes based on suspended biomass. But some problems such as sludge settleability, the need for large reactors, biomass recycling and settling tanks make operation of the process difficult [29]. The utilization of biofilm processes can be an acceptable method for the treatment of wastewater without some of the problems of activated sludge processes [30].

There are several advantages to the utilization of moving bed biofilm reactors (MBBRs) in comparison with suspended biomass processes such as higher biomass concentration, high organic loading rate (OLR), high endurance to loading impact, lower hydraulic retention time (HRT), higher sludge age, no sludge bulking problem and relatively small area requirement [31]. This system is a combination of suspended biomass and biofilm processes and carrier inside the biological reactor as a media for the biofilm growth. This process has been proven to be a very simple and efficient technology in wastewater treatment [25]. The microbial carrier is one of the important elements in the MBBR process, which has a high specific area, porosity, permanence and surface roughness. The growth of microorganisms on the carriers to form a biofilm can increase the efficiency of the process [32].

Several studies have been conducted by MBBR processes in combination with other wastewater treatment methods. For example, Shin et al. [33] studied a combined process consisting of an MBBR reactor and chemical coagulation for textile wastewater treatment. Also, Chen et al. [34] utilized moving-bed biofilm reactor combined with Fenton–coagulation pretreatment for the treatment of pesticide wastewater.

On the basis of the abovementioned properties and low degradability of detergent wastewater, in this study, Fenton process was specifically chosen as a pretreatment method for detergent wastewater. It was expected that by oxidation, we can improve biodegradability and also reduced the COD by oxidation plus coagulation at the same time [34,35]. Finally, the pretreated detergent wastewater was further treated by MBBR.

2. Materials and methods

Because of the low degradability and difficulties in treating of detergent wastewater by using only biological processes, we used a process consisting of pretreatment using coagulation/flocculation, Fenton-like oxidation followed by MBBR process.

2.1. Coagulation/flocculation pretreatment processes

The pretreatment of detergent wastewater sample by coagulation/flocculation process was examined through a jar test apparatus. In this study, $FeCl_3$ was used as the coagulant. The jar tests were run at 180 rpm for 1 min, 30 rpm for 20 min and settling for 120 min. The dose of $FeCl_3$ was varied in the range between 500 and 3,000 mg/L [6]. Samples of the clarified wastewater were taken for determining the effectiveness of the method for the surfactant and COD removal.

2.2. Fenton-like oxidation process

Fenton-like oxidation was carried out in a batch mode, and to conduct the experiments, a 500-mL jar was used. The temperature of the reaction was 25°C ± 1°C for all Fenton-like experiments. For the adjustment of pH, NaOH and HCl were used. At the beginning of the reaction, pH was adjusted, then ferric chloride ($FeCl_3.6H_2O$) was added to the reaction and after 1 min hydrogen peroxide, H_2O_2 30% (w/w), was then added. After the end of the reaction and slightly before adding NaOH, the calcium hydroxide ($Ca(OH)_2$) was added, and for about 1 min, the aqueous solution was stirred rapidly. Then, 5 M NaOH solution was added in order to adjust the pH to 7–8, and a small amount of the polyelectrolyte solution was added for suitable flocculation. After 1 h, sedimentation of the flocs, the supernatant COD and LAS were measured.

2.3. Moving bed biofilm reactor design

The experiments were based on an arrangement with two reactors running in parallel, approximately with a volume of 6.5 L (Fig. 2). Both reactors were operated in the same operation conditions (e.g., mixed liquor suspended solids [MLSS], temperature and C/N/P). Then, in these conditions, in order to compare the two reactors, the influent with different loading rate was injected. Dissolved oxygen (DO), pH and temperature were monitored daily using portable devices during the experiments. The reactor filling ratio in this study was considered 50%. The characteristics of the media used in the reactor are shown in Table 1. After this period, raw wastewater was injected into the reactors with COD and LAS concentrations of 400 ± 50 and 20 ± 2 mg/L, respectively, for 30 d for the adaptation of the microbial consortium with the wastewater and the formation of an appropriate layer on the surface of the media. The pH value of the injected feeding was kept at 6.5–8. To provide the microbial growth of the values of the nutrient, the ratio of C/N/P was close to about 100/5/1, and the nutrient solution was mixed with the injected wastewater into the reactor [36,37]. The concentrations of nutrient (KH_2PO_4, NH_4Cl and $NaHCO_3$) for providing phosphate, nitrogen and inorganic carbon source were about 197, 910 and 1,500 mg/L, respectively [36].

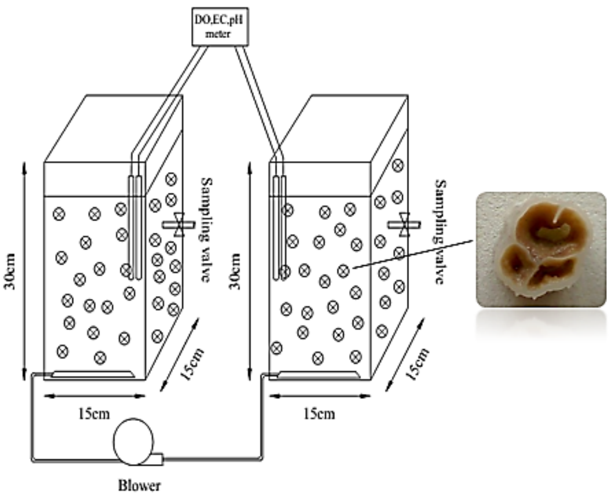

Fig. 2. Schematic of MBBR reactor.

Table 1
The characteristics of media used in this study

Parameter	Amount
Kind of media	High-density polyethylene
Media shape	Cylindrical with a cross in the middle
External diameter	10 mm
Height	7 mm
Effective surface of media	857 mm^2
Specific surface area	517 m^2/m^3
Specific gravity	0.96 g/cm^3

2.4. Analytical methods

In this study, different amounts of LAS were added to wastewater synthetically. For this purpose, LAS (CAS No. 25155-30-0, technical grade) and other materials were purchased from Aldrich (Merck KGaA, Germany). The amounts of anionic surfactant, COD and BOD_5 in each sample, were determined according to the standard methods for the examination of water and wastewater [38]. The biofilm activity was determined by specific oxygen uptake rate (OUR) method [34]. The DO, temperature and pH were monitored using a portable device (Aqualytic AL15) and the intervals of pH were set up by adding 0.1 N of NaOH and HCl. The biofilm growth was visualized to show the biofilm morphology, using the scanning electron microscope (SEM; Hitachi S-4200 FE). The media samples before the SEM analysis were taken from the bioreactors and dried at room temperature for 24 h. Biofilm thickness was measured by light microscopy (Eclipse E100-LED) to determine the biofilm thickness of the media samples that were removed from the reactors. After sampling, the media were dried and then the biofilm thickness profile along the length of each media was determined. Each media was cut into two 1-cm long sections. To determine the average biofilm thickness (L_f), the thresholded images were quantified [39–41].

3. Results and discussion

3.1. Effect of pretreatment (coagulation)

In this study, we investigated the application of Fenton-like process in combination with the aerobic MBBR method for the treatment of wastewater of detergent industries. The required wastewater was supplied from the effluent wastewater of Ivan detergent factory (Table 2). The effluent wastewater of this factory is discharged into the environment without any treatment. The characteristics of the effluent wastewater are shown in Table 1. Based on the sampling carried out, the average values of the COD and LAS of the raw wastewater used in the study were 24,039 and 210 mg/L, respectively.

In this study, the $FeCl_3$ were used as the coagulant. The changes in the removal efficiency of COD and LAS with three different concentrations (210, 500 and 1,000 mg/L), along with the change of FeCl dosage, are shown in Fig. 3. As shown in this figure, the optimum dose of coagulant was found to be 2,500 mg/L, and in this dose, the best removal efficiencies of COD and LAS (210, 500 and 1,000 mg/L) were 65% (9,270 mg/L) and 78% (46 mg/L), 58% (212 mg/L) and 49.5% (495 mg/L), respectively. In order to supply enough alkalinity and also for adjusting the reaction of the pH to the best condition of coagulant performance, calcium hydroxide ($Ca(OH)_2$), with the approximate dose of 3,500 mg/L, was used. At the end of the reaction and after the sedimentation of the flocks, the supernatant pH was 11. This pH in the most of the investigations was reported as the optimum pH for the coagulation of such wastewater [4,6,10].

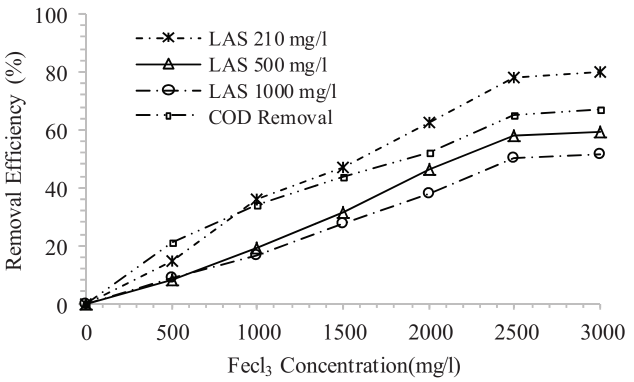

Fig. 3. COD and LAS effluent changes with change of coagulant dose.

Table 2
The characteristics of the effluent wastewater of Ivan detergent factory

COD (mg/L)	24,039 ± 150
BOD_5 (mg/L)	4,550 ± 25
Total suspended solids (mg/L)	108.4 ± 5
LAS (mg/L)	210 ± 10
O&G (mg/L)	195.8 ± 5
pH	7.3 ± 0.3
Total phosphorus (mg/L)	26.3 ± 1
Total nitrogen (mg/L)	12.7 ± 0.7

3.2. Optimum condition of Fenton-like oxidation process

For the study of Fenton-like process efficiency in wastewater treatment, a series of experiments were conducted to examine the reaction parameters. In Table 3, the complete results of this investigation have been shown. Because of the complete removal of the residual LAS with a concentration of 45 mg/L after a Fenton-like process, these results have not been included in the table.

Figs. 4 and 5 show the removal efficiency of COD and LAS in different conditions of Fenton-like oxidation process. In Fig. 4, the removal efficiency of COD and LAS was

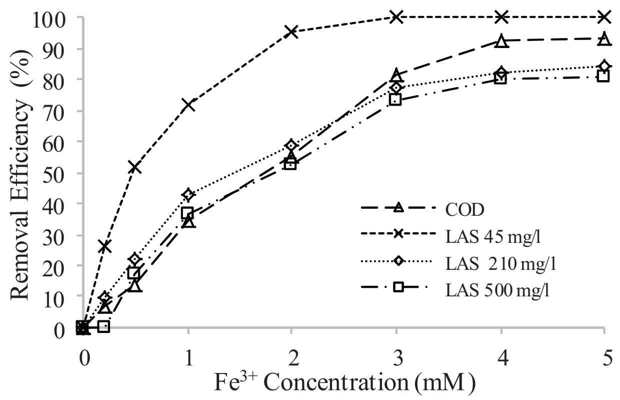

Fig. 4. Effect of Fe^{3+} dosage on the removal of COD and LAS (H_2O_2 = 25 mM, pH = 4, time = 60 min).

Table 3
The result of the pretreatment (coagulation), Fenton-like oxidation and anaerobic biological treatment process

Pretreatment (coagulation)		Fenton-like oxidation		Biological treatment		
COD (mg/L)	LAS (mg/L)	COD (mg/L)	LAS (mg/L)	HRT (h)	COD (mg/L)	LAS (mg/L)
				–	–	–
8,910 ± 500	46 ± 20	1,050 ± 100	<1.5	–	–	–
				–	–	–
				8	737 ± 10	8 ± 1
9,080 ± 500	210 ± 20	1,250 ± 100	45 ± 3	20	328 ± 7	<1.5
				36	73 ± 5	<1.5
				8	736 ± 10	64 ± 2
9,250 ± 500	490 ± 20	1,300 ± 100	100 ± 5	20	340 ± 8	37 ± 2
				36	88 ± 5	5 ± 1

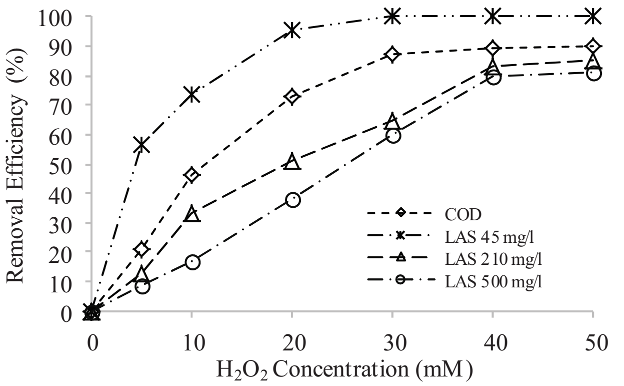

Fig. 5. Effect of H_2O_2 dosage on the removal of COD and LAS (Fe^{3+} = 4.1 mM, pH = 4, time = 60 min).

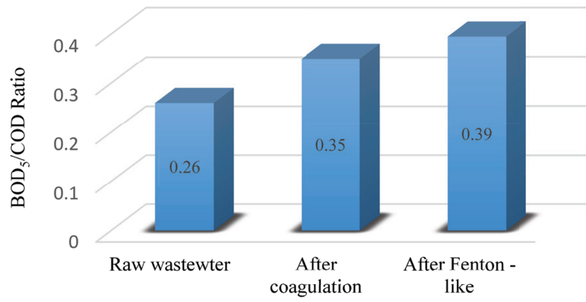

Fig. 6. The BOD_5/COD ratio after the end of the any process.

investigated with different concentrations of Fe^{3+} ion. If the solution's pH is too high, the iron precipitates in the form of $Fe(OH)_3$, which catalytically decomposes the H_2O_2 into molecular oxygen, without forming hydroxyl radicals. Hence, we kept the initial pH unchanged (3.5–4.5) for all the subsequent tests. As shown in this figure, an increase in the concentration of Fe^{3+}, causes an increase in the removal of COD and LAS. At the initial concentration of Fe^{3+} (0.2–5 mM) with 25 mM H_2O_2, the maximum removals of COD and LAS (45, 210 and 500 mg/L) were found to be 92.89%, 99.99%, 81.99% and 80.4%, respectively. The results show that with an increase in Fe^{3+} ions, the removal efficiency improves [9]. This phenomenon shows the importance of Fe^{3+} ions in the Fenton-like process [42]. According to reaction (3)–(5), a low Fe(III) dose would lead to a low concentration of $[Fe^{III}OOH]^{2+}$ complex. When the Fe(III) dose increases, the formation of the complex improves as well, consequently, the formation of Fe(II) and $OH^{\bullet}$ also accelerates [25]. Furthermore, in the higher concentrations of Fe(III) ions, this may be considered a useful method for the removal of pollutants because of the post-coagulation process [42,25].

The corresponding mechanism of Fenton-like oxidation is as follows:

$$Fe^{3+} + H_2O_2 \leftrightarrow \left[Fe^{III}OOH\right]^{2+} + H^+ \leftrightarrow Fe^{2+} + HOO^o + H^+ \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + 2OH^o \quad (2)$$

$$\begin{aligned} Fe^{3+} + H_2O_2 + OH^o &\rightarrow Fe^{3+} + HOO^o + H_2O \\ &\rightarrow Fe^{2+} + H^+ + H_2O + O_2 \end{aligned} \quad (3)$$

However, an excessive rise in Fe^{3+} ions causes a higher cost of reagent, needs further treatment to remove residual ferric iron, causes more sludge to be produced and its disposal cost is higher [43]. Therefore, the optimum amount of Fe^{3+} ion was considered 4.1 mM.

In Fig. 5, the effect of changes in H_2O_2 dosage has been shown. The Fe^{3+} dosage and the time of reaction were 4.1 mM and 60 min, respectively. As shown, in the figure, as a result of an increase in the concentration of H_2O_2, the removal efficiency improved and COD and LAS (45, 210 and 500 mg/L) residuals in the supernatant were found to be 1,023, <1.5, 31 and 94 mg/L, respectively. The increase in the removal rate as a result of an increase in H_2O_2 is due to the increment in the OH^o radicals [44]. By increasing the H_2O_2 concentration, the H_2O_2 decomposition rises until an optimal H_2O_2 concentration is achieved. When the H_2O_2 concentration exceeds the optimal concentration, the decomposition of H_2O_2 decreases as a result of the scavenging effect and regeneration of H_2O_2 according to the following reactions: [25]

$$H_2O_2 + OH^o \rightarrow H_2O + HO_2^{\ o},\ K = 2.7 \times 10^7\ M^{-1}s^{-1} \quad (4)$$

$$H_2O_2 + OH^o \rightarrow HOO^o + H_2O \quad (5)$$

$$HOO^o + HOO^o \rightarrow H_2O_2 + O_2 \quad (6)$$

$$OH^o + OH^o \rightarrow H_2O_2 \quad (7)$$

Due to the decomposition of H_2O_2 and generation of hydrogen gas, the application of H_2O_2 more than the optimal value can cause flotation of generated iron sludge. In addition, if there is residual hydrogen peroxide in the system, the results will be an increase in COD. 1 mg/L residual H_2O_2 produces about 0.27 mg/L of COD [26,45]. Therefore, the optimum value of H_2O_2 was considered 35 mM.

At the end of the chemical pretreatment, the BOD_5/COD ratio of this wastewater was increased from 0.18 to 0.39, which was suitable for the use of MBBR process (Fig. 6).

3.3. Biological degradation after Fenton-like oxidation process

The efficiency of two MBBR reactors in removal of LAS and COD was investigated with the COD influent approximate of 1,200 ± 100 mg/L and with two LAS concentrations of 45 and 100 mg/L in the 8, 20 and 36 h HRT.

3.4. Biofilm mass measurement

The mass of the attached-growth biofilm in MBBR was measured after separating the media from the reactor (15 pieces), and the media biomass was weighted after drying.

The total mass of the attached-growth biofilm in MBBR was calculated as follows:

$$\text{Attached} - \text{growth biofilm mass (mg)} = = \frac{n}{15} \times \left(m_1 - m_2\right) \quad (8)$$

where m_1 and m_2 are the mass of the media with biofilm and the clean media (mg), respectively, and n is the total number of the media in each MBBR [36].

In Fig. 7, the growth of biofilm on the surface of media in reactor 2 has been shown. As can be seen in this figure, increasing the operation time causes an increase in the thickness of biofilm on the surface of the media. A decrease in the thickness of the biofilm on the media at higher HRT and in different times of operation may be attributed to the deficiency of enough substrate and DO in the inner layers and the dominance of anaerobic conditions in the biofilm, or the mixing intensity that leads to the gradual sloughing of biofilm [37,46]. In a steady state, the biofilm thickness is dependent on the comprehensive effects of biofilm growth rate, mechanical shearing, and its subsequent detachment [47].

The performance of the MBBR process depends on the provided media percentage in the reactor and the OLR [48,49]. To move the media freely, the media filling fraction (percentage of reactor volume occupied by carriers in the empty tank) normally varies from 50% to 70% [50]. It has also been experienced that a higher filling percentage causes a decrease in the mixing efficiency [48,51]. In this investigation, the filling ratio was considered 50%.

In Fig. 8, the changes in OUR during the operation time of MBBR reactors (reactor 2) have been shown. OUR is one of the important parameters in the aeration biological systems, which shows how active the microorganisms present in the aeration tank, and these microorganisms consume and break down organic matter input to the system in the presence of oxygen [46]. With an increase in solids retention time in the system, because of the increase in the aging of bacteria consortium (nonactive population) and death (declining phase) of active bacteria, the oxygen consumption rate and the subsequent OUR (mg O_2/g mixed liquor volatile suspended solids h) both decrease [51]. Thus, in the first 5 d of the operation, its amount was about 11, but with an increase in SRT and at the end of the operation period, it decreased to about 2. It should be noted that in all circumstances, the amount of DO in the system was maintained at about 2.5–3 mg/L. Furthermore, in high media volumes, such as 40%–50%, the collision between the media particles became more intense and the biofilms became thinner, which interfered with the oxygen and substrate diffusion in the biofilms, and therefore, the biofilm activities decreased [34]. In addition, the decline in HRT and periodic changes in the biofilm thickness causes exposure of microorganisms with higher load of pollutants and increase of oxygen and substrate diffusion limitation in the biofilms, so the biofilm activities decreased [34,51].

3.5. SEM characterization of bacteria

In order to imagine the attached biofilm on the surface of media in both reactors, SEM images of clean and biofilm-attached media were prepared. As shown in Fig. 9(a), the surface of the clean carrier was naked. Gradually, with the operation of the reactor, the thickness of the biofilm on the carrier increased. At the end of the experiment, the structure of the biofilm was partly bushy (Figs. 9(b) and (c)).

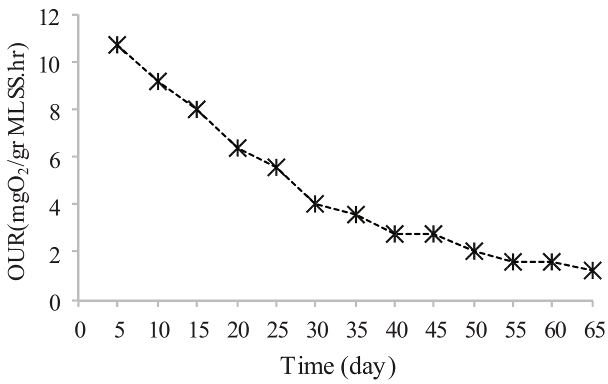

Fig. 8. OUR changes in the operation time of MBBR reactor (reactor 2).

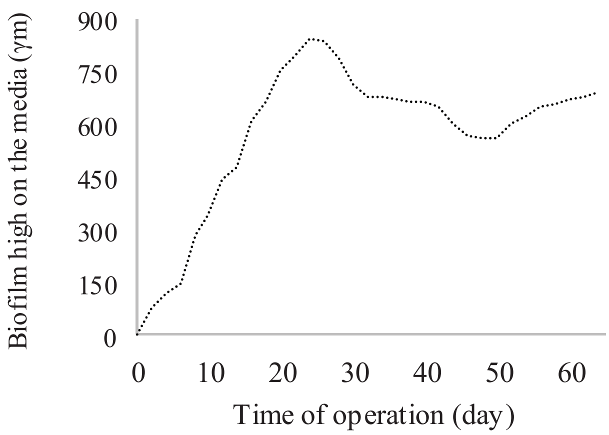

Fig. 7. Biofilm thickness in the MBBR reactor (reactor 2).

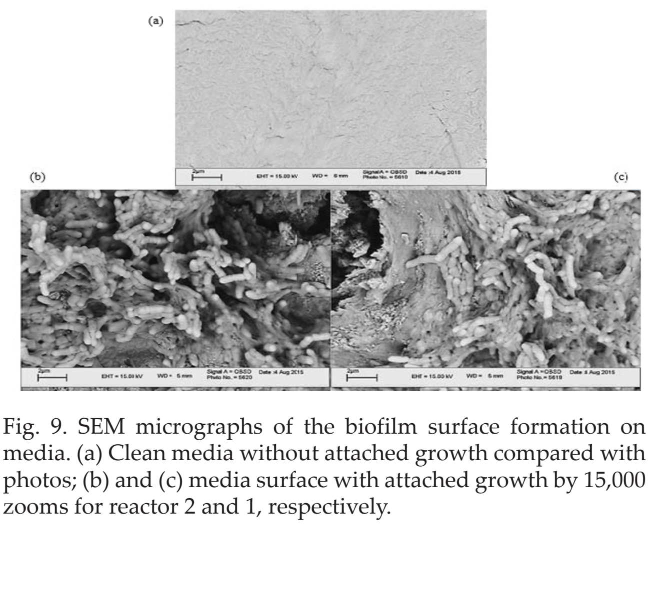

Fig. 9. SEM micrographs of the biofilm surface formation on media. (a) Clean media without attached growth compared with photos; (b) and (c) media surface with attached growth by 15,000 zooms for reactor 2 and 1, respectively.

As shown in Figs. 9(b) and (c) for reactor 1 and 2, respectively, the main community of aerobic bacteria in both reactors was more than bacilli and less than cocci. The aerobic bacilli were the long types. However, the long bacilli and cocci were the main types of the degradation of LAS [1,52].

3.6. COD and LAS removal in MBBR process

The results of LAS and COD biodegradation and the removal efficiency in both MBBR reactors have been shown in Figs. 10 and 11. As can be seen in Fig. 10 in 36 h HRT for reactor 1 and 2, the average removal of LAS with a concentration of 45 and 100 mg/L with 50% filling ratio were found to be 99.99% and 95%, respectively. For 20 and 8 h HRT, the average percentage removal of LAS (45 and 100 mg/L) were 98.88%, 62.31%, 82.23% and 36%, respectively. The efficiency of the two MBBR systems for COD removal has been shown in Fig. 11. In reactor 1 (with lower LAS concentration), the maximum removals of COD after 36, 20 and 8 h HRT were found to be 94.2%, 73.69% and 41% respectively. Also, for reactor 2 (with higher LAS concentration), the maximum removal efficiencies were 93.41%, 72.74% and 41.11% in 36, 20 and 8 h HRT, respectively. The correlation between the removal of COD and LAS and the amount of attached biomass on the media in the reactor 1 were $R^2 = 0.92$ and $p < 0.05$ and $R^2 = 0.84$ and $p < 0.05$, respectively.

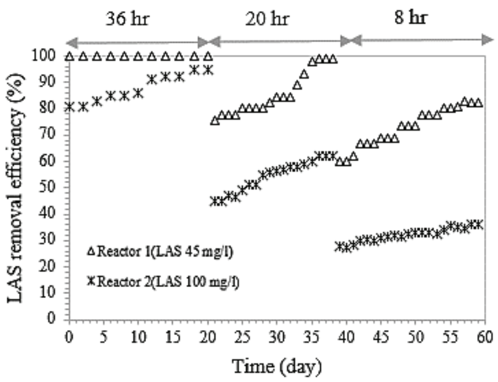

Fig. 10. LAS removal efficiency in the aerobic MBBR systems with two concentration of LAS (45 and 100 mg/L) at different hydraulic retention time (HRT).

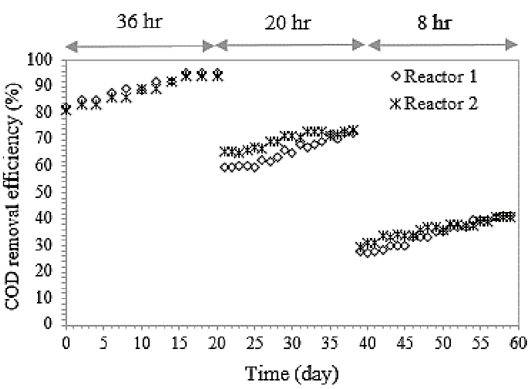

Fig. 11. COD removal efficiency in the two aerobic MBBR systems with different hydraulic retention time (HRT).

After decreasing HRT from 36 to 20 h, the removal efficiency of LAS and COD in both reactors decreased and reached 75.55% and 65.3% for reactor 1, and 45.21% and 59.48% for reactor 2, respectively. For reactor 2 the correlations between the removal of COD and LAS were $R^2 = 0.93$ and $p < 0.05$ and $R^2 = 0.92$ and $p < 0.05$, respectively.

In both MBBR reactors, there was a gradual increase in LAS and COD removal until the end of the stationary condition. As already shown, by decreasing the HRT from 36 to 20 and 8 h, neither of the MBBR systems was able to bring effluent into the surface water discharging standard. These characteristics belong to the attached biofilm media, which have a significant effect on the removal efficiency [37,53]. The primary MLSS of sludge that was injected into the MBBR reactors was about 4,500 mg/L. At the end of the operation period, the MLSS of both reactors decreased to about 1,520 mg/L. The sludge yields for both MBBRs were between 0.018 and 0.192 g total suspended solids/g COD. The lower sludge yields may be related to their infinite SRT and the existence of the media in the MBBR process [32,54].

It proves that the attached biofilm on the carrier plays a significant role in the biodegradation of COD and LAS. There might be two reasons for this phenomenon. First, because of the biofilm structure, MBBR could be more resistant to the inhibitory effects of the toxic contaminant impact load. In comparison with the suspended activated sludge, the biofilm structure increased mass transfer resistance to toxic substances in order to be diffused into the deeper biofilm layer. So, this configuration could decrease the inhibitory effect of toxic substances on the bacteria [54,55]. Second, after a good adaptation of biofilm to LAS, the LAS can be used as a good carbon source by microorganisms [56,57].

Biofilm development on the surface of the media is related to the characteristics of the media and hydrodynamic condition [37,58,59]. The removal efficiency of this investigation up to 100 mg/L LAS and COD about 1,200 mg/L at 36 h HRT was 95%, which was more than from other studies such as combined Fenton oxidation and aerobic biological processes which removed 40 mg/L of LAS [9], electro-Fenton degradation of anionic surfactants with LAS concentration of 50 mg/L [60] and activated sludge process with 99% removal efficiency for only 5 mg/L concentration of surfactant [37,58].

In one study, about 50 sites of the municipal wastewater treatment were investigated. This study included 15 activated sludge systems, 12 trickling filters, 6 oxidation ditches, 8 lagoons and 9 rotating biological contactor and treatment facilities in USA. Influent concentrations of LAS for all treatment plants showed a normal distribution with a mean of 5 mg/L. The average concentration of the effluent LAS ranged from 0.04 mg/L for activated sludge plants to about 1 mg/L for trickling filter plants. A range of removal rates over 99% for activated sludge process and an average of 77% for trickling filter plants were observed. The average removal of LAS in other treatment plant types ranged from 96% to 98% [61].

4. Conclusion

Pretreatment of detergent wastewater with coagulation in combination with Fenton-like oxidation process can increase the BOD_5/COD ratio in order to use biological processes.

Fenton-like oxidation process is a practical treatment for the wastewater that contains surfactants. They are able to eliminate a large amount of COD and LAS. The optimum amount of catalyzer (Fe^{3+}) and oxidant (H_2O_2), pH and time of reaction for the Fenton-like oxidation process were 4.1 and 35 mM, and 4 and 60 min, respectively. In the MBBR process, the removal efficiencies of reactor 1 were 94.20% and 99.99% for COD (1,200 mg/L) and LAS (45 mg/L) in the 36 h HRT, respectively. Also for reactor 2, the removal efficiency was found to be 93.41% and 95% for COD (1,200 mg/L) and LAS (100 mg/L) in the 36 h HRT, respectively. This result demonstrates that the aerobic MBBR process in combination with the Fe^{3+}/H_2O_2 process was quite efficient for the treatment of the wastewater of detergent industries.

Acknowledgments

This research was supported by the "Institute for Environmental Research", "School of Health, Guilan University of Medical Sciences, Rasht, Iran" and "Ivan Factory".

References

[1] I.C.S. Duarte, L.L. Oliveira, N.K. Saavedra, F. Fantinatti-Garboggini, C.B.A. Menezes, V.M. Oliveira, M.B.A. Varesche, Treatment of linear alkylbenzene sulfonate in a horizontal anaerobic immobilized biomass reactor, Bioresour. Technol., 101 (2010) 606–612.

[2] E.R. Bandala, M.A. Pelaez, M.J. Salgado, L. Torres, Degradation of sodium dodecyl sulphate in water using solar driven Fenton-like advanced oxidation processes, J. Hazard. Mater., 151 (2008) 578–584.

[3] T.P. Delforno, A.G.L. Moura, D.Y. Okada, M.B.A. Varesche, Effect of biomass adaptation to the degradation of anionic surfactants in laundry wastewater using EGSB reactors, Bioresour. Technol., 154 (2014) 114–121.

[4] F. Aloui, S. Kchaou, S. Sayadi, Physicochemical treatments of anionic surfactants wastewater: effect on aerobic biodegradability, J. Hazard. Mater., 164 (2009) 353–359.

[5] D.Y. Okada, T.P. Delforno, C. Etchebehere, M.B. Varesche, Evaluation of the microbial community of upflow anaerobic sludge blanket reactors used for the removal and degradation of linear alkylbenzene sulfonate by pyrosequencing, Int. Biodeterior. Biodegrad., 96 (2014) 63–70.

[6] A. Ayguna, T. Yilmazb, Improvement of coagulation-flocculation process for treatment of detergent wastewaters using coagulant aids, Int. J. Chem. Environ. Eng., 1 (2010) 97–101.

[7] U. Merrettig-Bruns, E. Jelen, Anaerobic biodegradation of detergent surfactants, Materials, 2 (2009) 181–206.

[8] L.L. de Oliveira, R.B. Costa, D.Y. Okada, D.V. Vich, I.C.S. Duarte, E.L. Silva, M.B.A. Varesche, Anaerobic degradation of linear alkylbenzene sulfonate (LAS) in fluidized bed reactor by microbial consortia in different support materials, Bioresour. Technol., 101 (2010) 5112–5122.

[9] X.J. Wang, Y. Song, J.S. Mai, Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulfate, J. Hazard. Mater., 160 (2008) 344–348.

[10] S. Jangkorn, S. Kuhakaew, S. Theantanoo, H. Klinla-Or, T. Sriwiriyarat, Evaluation of reusing alum sludge for the coagulation of industrial wastewater containing mixed anionic surfactants, J. Environ. Sci., 23 (2011) 587–594.

[11] M.A. Aboulhassan, S. Souabi, A. Yaacoubi, M. Baudu, Removal of surfactant from industrial wastewaters by coagulation flocculation process, Int. J. Environ. Sci. Technol., 3 (2006) 327–332.

[12] J. Gaca, M. Kowalska, M. Mróz, The effect of chloride ions on alkylbenzenesulfonate degradation in the Fenton reagent, Pol. J. Environ. Stud., 14 (2005) 23–27.

[13] A. Karci, I.A. Alaton, M. Bekbölet, Advanced oxidation of a nonionic surfactant: examination of the degradation products – acute toxicity relationship, Sigma, 31 (2013) 508–516.

[14] I. Arslan-Alaton, E.U. Cokgor, B. Koban, Integrated photochemical and biological treatment of a commercial textile surfactant: process optimization, process kinetics and COD fractionation, J. Hazard. Mater., 146 (2007) 453–458.

[15] A. Dhouib, N. Hdiji, I. Hassaïri, S. Sayadi, Large scale application of membrane bioreactor technology for the treatment and reuse of an anionic surfactant wastewater, Process Biochem., 40 (2005) 2715–2720.

[16] R.C. Martins, A.F. Rossi, R.M. Quinta-Ferreira, Fenton's oxidation process for phenolic wastewater remediation and biodegradability enhancement, J. Hazard. Mater., 180 (2010) 716–721.

[17] M. Lu, Z. Zhang, W. Qiao, X. Wei, Y. Guan, Q. Ma, Y. Guan, Remediation of petroleum-contaminated soil after composting by sequential treatment with Fenton-like oxidation and biodegradation, Bioresour. Technol., 101 (2010) 2106–2113.

[18] A.R. Rahmani, M. Zarrabi, M.R. Samarghandi, A. Afkhami, H.R. Ghaffari, Degradation of azo dye Reactive Black 5 and Acid Orange 7 by Fenton-like mechanism, Iran. J. Chem. Eng., 7 (2010) 87–94.

[19] M. Lua, Z. Zhang, W. Qiao, Y. Guan, M. Xiao, C. Peng, Removal of residual contaminants in petroleum-contaminated soil by Fenton-like oxidation, J. Hazard. Mater., 179 (2010) 604–611.

[20] A.M. Amat, A. Arques, M.A. Miranda, S. Seguí, Photo-Fenton reaction for the abatement of commercial surfactants in a solar pilot plant, Sol. Energy, 77 (2004) 559–566.

[21] J. Liang, S. Komarov, N. Hayashi, E. Kasai, Improvement in sonochemical degradation of 4-chlorophenol by combined use of Fenton-like reagent, Ultrason. Sonochem., 14 (2007) 201–207.

[22] H.J. Fan, S.T. Huang, W.H. Chung, J.L. Jan, W.Y. Lin, C.C. Chen, Degradation pathways of crystal violet by Fenton and Fenton-like systems: condition optimization and intermediate separation and identification, J. Hazard. Mater., 171 (2009) 1032–1044.

[23] M.A. Zazouli, Z. Yousefi, A. Eslami, M.B. Ardebilian, Municipal solid waste landfill leachate treatment by Fenton, photo-Fenton and Fenton-like processes: effect of some variables, Iran. J. Environ. Health Sci. Eng., 9 (2012) 1.

[24] Z.M. Abou-Gamra, Kinetic and thermodynamic study for Fenton-like oxidation of amaranth red dye, Adv. Chem. Eng. Sci., 4 (2014) 285.

[25] C. Jiang, S. Pang, F. Ouyang, J. Ma, J. Jiang, A new insight into Fenton and Fenton-like processes for water treatment, J. Hazard. Mater., 174 (2010) 813–817.

[26] S.A. Mousavi, A. Mahvi, S. Nasseri, S. Ghaffari, Effect of Fenton process (H_2O_2/Fe^{2+}) on removal of linear alkylbenzene sulfonate (LAS) using centeral composite design and response surface methodology, J. Environ. Health Sci. Eng., 8 (2011) 111–116.

[27] S.N. Zhu, C. Wang, A.C. Yip, D.C. Tsang, Highly effective degradation of sodium dodecylbenzene sulphonate and synthetic greywater by Fenton-like reaction over zerovalent iron-based catalyst, Environ. Technol., 36 (2015) 1423–1432.

[28] X.J. Wang, S.Q. Xia, L. Chen, J.F. Zhao, N.J. Renault, J.M. Chovelon, Nutrients removal from municipal wastewater by chemical precipitation in a moving bed biofilm reactor, Process Biochem., 41 (2006) 824–828.

[29] M. Kermani, B. Bina, H. Movahedian, M.M. Amin, M. Nikaein, Application of moving bed biofilm process for biological organics and nutrients removal from municipal wastewater, Am. J. Environ. Sci., 4 (2008) 675.

[30] S. Chen, D. Sun, J.S. Chung, Simultaneous removal of COD and ammonium from landfill leachate using an anaerobic–aerobic moving-bed biofilm reactor system, Waste Manage., 28 (2008) 339–346.

[31] J.C. Leyva-Díaz, K. Calderón, F.A. Rodríguez, J. González-López, E. Hontoria, J.M. Poyatos, Comparative kinetic study between moving bed biofilm reactor-membrane bioreactor and membrane bioreactor systems and their influence on organic matter and nutrients removal, Biochem. Eng. J., 77 (2013) 28–40.

[32] Q. Feng, Y. Wang, T. Wang, H. Zheng, L. Chu, C. Zhang, H. Chen, X. Kong, X.H. Xing, Effects of packing rates of cubic-shaped polyurethane foam carriers on the microbial community and the removal of organics and nitrogen in moving bed biofilm reactors, Bioresour. Technol., 117 (2012) 201–207.
[33] D.H. Shin, W.S. Shin, Y.H. Kim, M.H. Han, S.J. Choi, Application of a combined process of moving-bed biofilm reactor (MBBR) and chemical coagulation for dyeing wastewater treatment, Water Sci. Technol., 54 (2006) 181–189.
[34] S. Chen, D. Sun, J.S. Chung, Treatment of pesticide wastewater by moving-bed biofilm reactor combined with Fenton-coagulation pretreatment, J. Hazard. Mater., 144 (2007) 577–584.
[35] M. Lapertot, C. Pulgarín, P. Fernández-Ibáñez, M.I. Maldonado, L. Pérez-Estrada, I. Oller, W. Gernjak, S. Malato, Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton, Water Res., 40 (2006) 1086–1094.
[36] E.H. Koupaie, M.A. Moghaddam, S.H. Hashemi, Post-treatment of anaerobically degraded azo dye Acid Red 18 using aerobic moving bed biofilm process: enhanced removal of aromatic amines, J. Hazard. Mater., 195 (2011) 147–154.
[37] J. Mollaei, S.B. Mortazavi, A.J. Jafari, Applying moving bed biofilm reactor for removing linear alkylbenzene sulfonate using synthetic media, Iran. J. Health Saf. Environ., 2 (2015) 204–210.
[38] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, D.C., USA, 2000.
[39] M. Lemos, S. Wang, A. Ali, M. Simões, D.I. Wilson, A fluid dynamic gauging device for measuring biofilm thickness on cylindrical surfaces, Biochem. Eng. J., 106 (2016) 48–60.
[40] J.M. Connolly, B. Jackson, A.P. Rothman, I. Klapper, R. Gerlach, Estimation of a biofilm-specific reaction rate: kinetics of bacterial urea hydrolysis in a biofilm, npj Biofilms Microbiomes, 1 (2015) 15014.
[41] R. Bakke, P.Q. Olsson, Biofilm thickness measurements by light microscopy, J. Microbiol. Methods, 5 (1986) 93–98.
[42] L.M. Nieto, G. Hodaifa, S. Rodríguez, J.A. Giménez, J. Ochando, Degradation of organic matter in olive-oil mill wastewater through homogeneous Fenton-like reaction, Chem. Eng. J., 173 (2011) 503–510.
[43] K. Cui, H. Yi, Z.J. Zhou, Q.F. Zhuo, Y.X. Bing, Q.W. Guo, Z.C. Xu, Fenton oxidation kinetics and intermediates of nonylphenol ethoxylates, Environ. Eng. Sci., 31 (2014) 217–224.
[44] I. Kıran, N. Bektaş, H. Cengiz Yatmaz, M. Tekbaş, Photocatalytic Fenton oxidation of sodium dodecyl sulfate solution using iron-modified zeolite catalyst, Desalin. Wat. Treat. 51 (2013) 5768–5775.
[45] Y. Deng, J.D. Englehardt, Treatment of landfill leachate by the Fenton process, Water Res., 40 (2006) 3683–3694.
[46] Z. Dong, M. Lu, W. Huang, X. Xu, Treatment of oilfield wastewater in moving bed biofilm reactors using a novel suspended ceramic biocarrier, J. Hazard. Mater., 196 (2011) 123–130.
[47] S. Zhang, Y. Wang, W. He, M. Wu, M. Xing, J. Yang, N. Gao, D. Yin, Responses of biofilm characteristics to variations in temperatureand NH_4^+-N loading in a moving-bed biofilm reactor treating micro-polluted raw water, Bioresour. Technol., 131 (2013) 365–373.
[48] J.S. Weiss, M. Alvarez, C.C. Tang, R.W. Horvath, J.F.Stahl, Evaluation of moving bed biofilm reactor technology for enhancing nitrogen removal in a stabilization pond treatment plant, Proc. Water Environ. Fed., 14 (2005) 2085–2102.
[49] Y.G. Maksimova, Microbial biofilms in biotechnological processes, Appl. Biochem. Microbiol., 50 (2014) 750–760.
[50] H. Ødegaard, The Moving Bed Biofilm Reactor, Water Environmental Engineering and Reuse of Water, Hokkaido Press, Norway, 1999, pp. 205–305.
[51] A. Barwal, R. Chaudhary, To study the performance of biocarriers in moving bed biofilm reactor (MBBR) technology and kinetics of biofilm for retrofitting the existing aerobic treatment systems: a review, Rev. Environ. Sci. Biotechnol., 13 (2014) 285–299.
[52] M.F. Carosia, D.Y. Okada, I.K. Sakamoto, E.L. Silva, M.B.A. Varesche, Microbial characterization and degradation of linear alkylbenzene sulfonate in an anaerobic reactor treating wastewater containing soap powder, Bioresour. Technol., 167 (2014) 316–323.
[53] H. Fernandes, M.K. Jungles, H. Hoffmann, R.V. Antonio, R.H.Costa, Full-scale sequencing batch reactor (SBR) for domestic wastewater: performance and diversity of microbial communities, Bioresour. Technol., 132 (2013) 262–268.
[54] N. Chowdhury, G. Nakhla, J. Zhu, M. Islam, Pilot-scale experience with biological nutrient removal and biomass yield reduction in a liquid-solid circulating fluidized bed bioreactor, Water Environ. Res., 82 (2010) 772–781.
[55] E.G. Lauchnor, T.S. Radniecki, L. Semprini, Inhibition and gene expression of *Nitrosomonas europaea* biofilms exposed to phenol and toluene, Biotechnol. Bioeng., 108 (2011) 750–757.
[56] Y.M. Kim, D. Park, D.S. Lee, J.M. Park, Inhibitory effects of toxic compounds on nitrification process for cokes wastewater treatment, J. Hazard. Mater., 152 (2008) 915–921.
[57] Q. Gu, T. Sun, G. Wu, M. Li, W. Qiu, Influence of carrier filling ratio on the performance of moving bed biofilm reactor in treating coking wastewater, Bioresour. Technol., 166 (2014) 72–78.
[58] C. Pizzaro, A. Donoso-Brave, D. Jeison, G. Ruiz-Filippi, R. Chamy, Biofilm formation for organic matter and sulphate removal in gas-lift reactors, Electron. J. Biotechnol., 14 (2011) 235–239.
[59] S. Wäsche, H. Horn, D.C. Hempel, Influence of growth conditions on biofilm development and mass transfer at the bulk/biofilm interface, Water Res., 36 (2002) 4775–4784.
[60] M. Panizzaa, A. Barbucci, M. Delucchi, M.P. Carpanese, A. Giuliano, M. Cataldo-Hernández, G. Cerisola, Electro-Fenton degradation of anionic surfactants, Sep. Purif. Technol., 118 (2013) 394–398.
[61] A.K. Mungray, P. Kumar, Fate of linear alkylbenzene sulfonates in the environment: a review, Int. Biodeterior. Biodegrad., 63 (2009) 981–987.