Original Article

Study of Electrochemical Process Effect on Detergent Removal from Polluted Water and Fish Bioassay Test of the Effluent

Davarkhah Rabbani[1], Gholam Reza Mostafaii[1], Vahid Eskandari[2], Rouhollah Dehghani[1], Fatemeh Atoof[3]

[1]Department of Environmental Health Engineering, Social Determinants of Health Research Centre, Health School, Kashan University of Medical Sciences, Departments of [2]Environmental Health Engineering and [3]Epidemiology and Biostatistics, Health School, Kashan University of Medical Sciences, Kashan, Iran

Abstract

Aims: Linear alkylbenzene sulfonate (LAS) is an anionic surfactant which is widely used in household and industrial detergents usage, and after use, it usually finds a way to the wastewater treatment systems. Conventional treatment is not recognized as an efficient method due to the long residence time and enlarged cost. Hence, advanced oxidation processes including electrochemical techniques are important. In this paper, electrochemical degradation of a synthetic solution of LAS with initial concentration 200 ppm has been investigated. **Methods**: The experiment was performed using eight stainless steel electrodes as cathode and anode with a monopolar arrangement. The effects of current intensity and density were studied as operational parameters on detergent removal efficiency. **Results**: The maximum removal efficiency 94% was achieved at current intensity equal to 300 mA and current density 6 mA/cm^2. The energy consumption was calculated 2.7 ± 0.1 WH/g. The bioassay test showed that only under optimum conditions, 80% of fish was survived until 4 days since the end of the process and the rest were died immediately. All ten fish leaved in unpolluted were survived until 4 days monitoring. **Conclusion**: The results showed that, by reducing the current density, removal efficiency increases it was true for all current intensities.

Keywords: Bioassay, detergent, surfactant, water pollutants

Introduction

Public and industrial wastewaters are a main reason of contamination of water resources. One of the major components forming the wastewater are detergents that a lot of damage caused to the environment by entrance into the water and soil.[1,2] One of the main constituents of detergents is surfactants. Surfactants are dual nature materials that owing to their chemical characters can weaken the water surface tension and to increase its cleaning effect.[3,4] They are composed of two parts of water solvable (hydrophilic) and water insolvable (hydrophobic).[5] Based on the character of the hydrophilic part, the surfactants can be classified in the form of cationic, anionic, nonionic, and amphoteric.[6,7] Anionic surfactants are the largest type of surfactants used in detergent formulation.[8] Linear alkylbenzene sulfonate (LAS) is the largest type of anionic surfactants.[9] LAS has used widely in household cleaners, health and cosmetics products, and other industries[10,11] and have highest utilization amount in the surfactant types as reported by CESIO institute.[12] Due to the high consumption of surfactants in various applications, their presence in wastewater have also increased, and after the use, they discharged into the wastewater system and from there, find their way to the treatment plants.[13,14] Thus, the surfactant concentration in municipal and industrial wastewater effluent can be very high. For example, LAS concentration in laundry wastewater was observed to several 100 mg/L.[15] To reduce the environmental impacts, surfactants, and particularly LAS, has been intensely studied and various physical, chemical, and biological methods have been used to remove it.[16] The general technologies such as ultra-filtration and ion exchange[17] and adsorption[18,19] have been studied for removing surfactants from wastewater. Over the years, conventional physicochemical and biological methods such as absorption, coagulation, and

Access this article online

Quick Response Code:

Website: http://iahs.kaums.ac.ir

DOI: 10.4103/iahs.iahs_10_17

Address for correspondence: Dr. Davarkhah Rabbani, Department of Environmental Health Engineering, Social Determinants of Health Research Centre, Health School, Kashan University of Medical Sciences, Kashan, Iran.
E-mail: davarrabbani@gmail.com

How to cite this article: Rabbani D, Mostafaii GR, Eskandari V, Dehghani R, Atoof F. Study of electrochemical process effect on detergent removal from polluted water and fish bioassay test of the effluent. Int Arch Health Sci 2017;4:53-7.

filtration have been used to remove various contaminants. Because these methods, especially for toxic contaminants including surfactants and high concentrations of contaminants, are not recognized very effective and moreover, are somewhat costly therefore, researches have continued to find new techniques.[20] Among these, new techniques are advanced oxidation processes (AOPs).[21] AOPs due to advantages such as high efficiency and versatility have been identified as promising alternatives. AOPs are based on the production of hydroxyl radicals, a strong oxidant.[22,23] AOPs were first introduced in the 1980s for water purification and later have been used for the treatment of various types of sewages because strong oxidants generated in this process can easily degrade organic pollutants.[24,25] Electrochemical methods are among of AOPs and have provided appropriate field in the environmental pollutants treatment.[26] The main advantage of this method is that it does not require chemical and electrical energy is only used to decompose pollutants.[27] In recent years, electrochemical methods such as electrooxidation, electrocoagulation, and electroflotation have attracted a lot of attention and widely been used for the treatment of sewage and water disinfection.[28] The widespread use of different types of surfactants and their entry into the environment, particularly aquatic environment, can have harmful effects on ecosystems and living organisms.[29,30] In the past years, the electrochemical removal of surfactants from wastewater has attracted many studies and various variables have been investigated to determine the effect of the electrochemical method including the type of electrode material, current intensity, current density, voltage, pH, solution flow rate, electrical conductivity, and electrical connection of electrodes. Among them, the parameters of current intensity and current densities are the easiest parameters for controlling the electrochemical process. Also, the electrode material plays a major role in determining the mechanism of elimination of the pollutants. The electrodes such as boron-doped diamond (BDD) are expensive.[5,31] Therefore, in this study, we tried to find the optimal conditions for LAS removal using these three variables (current density, current intensity, and electrode material). Stainless steel electrode has advantages such as cheapness, availability, and resistant to corrosion. The change in the immersion height of the electrode and the use of a relatively wide range of currents intensity are the new inventions of this study compared to the previous studies because they have fixed electrode height and examined the current density effect by change in current intensity. Hence, the way to further study in this area is still open.

To assess the toxicity effects of these pollutants on aquatic biota, physical and chemical tests alone are not enough and toxicity tests are necessary to assess the quality.[32] Toxicity tests usually are done on fish, daphnia, and algae. The purpose of this experiment was investigation of effect of electrochemical process on detergent removal from synthetic wastewater also, assessment of its effect on detergent detoxification by fish bioassay test.

Materials and Methods

Apparatus

The system consists of eight stainless steel electrodes as cathodes and anodes that are connected monopolar. This arrangement reduces the energy consumption of the system due to the parallelization of the electrodes. A 2 L beaker is also used as a reactor. A simple schematic of the system can be seen in Figure 1. A magnetic stirrer was also used to stir the solution during the test. The samples were prepared using tap water to provide solutes needed for electrical conductivity of the solution. The tap water had chemical composition as below:

Total hardness = 280 mg/L, Na = 130 mg/L, K = 5 mg/L, SO_4^{2-}=201 mg/L, Cl^-=191 mg/L.

The electrical conductivity of the solution was measured using a METROHM 644 conductometer. Chemical experiments and bioassay test were carried out at a constant laboratory temperature (about 20°C), which was determined using a glass mercury thermometer. Hence, there was no need to control the temperature during the experiment.

For the bioassay test, black molly fish was used. Suitable conditions for keeping this fish are temperature = 20°C–26°C, pH = 7.5–8, and DO = min 3 mg/L. The minimum dissolved oxygen in the samples that measured using an oxygen sensor (AL20OXi AQUALYTIC) was 4.8 mg/L. Hence, there was no need to aeration of samples during the test.

The absorbance of solutions was measured by a spectrophotometer (DR/2010; HACH Co.).

pH was measured by a pH meter model 262 TS technology and current intensity by a digital multimeter model ECS820B SOAR respectively.

Experimental procedure

- Step a: At first, 2 L tap water was taken from urban network, and with the addition of LAS, the synthetic wastewater with certain concentration (200 mg/L) was prepared. The polluted water was poured in an

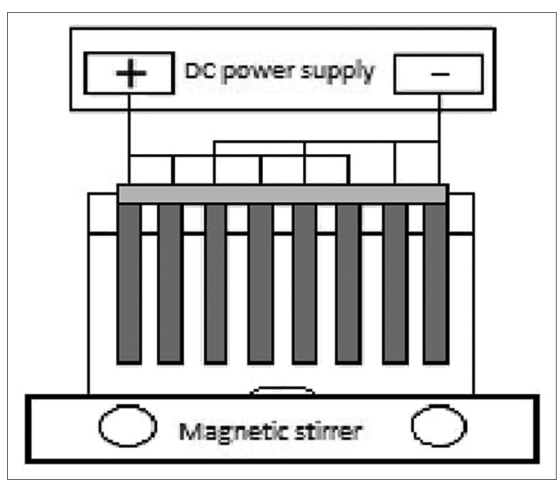

Figure 1: Schematic of experimental set-up

electrolytic cell (a 2 L beaker) and using stainless steel electrodes (15 cm length, 3 cm width, and 1 mm thickness) electrochemical process was applied on it. In this run, 3 cm height of electrodes was submerged in the solution. The electrochemical process was done without, any changes in pH (about 7–8), temperature (about 20°C) and electroconductivity (2200 µs/cm), it was done by the aforementioned electrodes at the current intensity of 200 mA for 1 h. Then, a sample was taken to determine the concentration of LAS residue. The LAS residue was measured using methylene blue active substance on the basis of the 5540°C method in the 22nd edition of standard methods for the examination of water and wastewater book. Finally, transferring the rest of cell content to another vessel, a total of 10 fish were leaved in it. The experiments were repeated four times for good accuracy.

- Step b: Such as step a but with current intensity of 200, 300, 400, 500, 600, 700, 800, and 900 mA, the experiments were done
- Step c: At this stage, the submerged height of electrodes was increased to 6 cm and the steps a and b were repeated
- Step d: This stage is similar to the step c with the exception of 9 cm submerged electrodes height.

The energy consumption was calculated by the following formula for each run.

$$\text{Required energy} = \frac{U.I.t}{(C_0 - C).V}$$

Which, U is voltage, I is current intensity, t is period of process time, V is volume of sample, C_0 is initial concentration of LAS, and C is final concentration of LAS.

Black molly fish (*Poecilia sphenops*) was applied to the bioassay test on treated and untreated synthetic wastewater samples. Ten fish 5 ± 1 cm length, 2 ± 1 g weight were leaved in each of them. The fish survival status was monitored up to 96 h. The number of dead and live fish at the end of each 24 h was recorded. Findings were analyzed by Chi-square and ANOVA test by SPSS statistical software version 16.

Results

In this study, the effect of electrochemical process to remove LAS from synthetic wastewater was investigated and bioassay test was used for its detoxification confirmation.

Table 1 shows the remained LAS concentrations besides, energy consumptions according to electrical current intensity and electrode immersion heights. It is noticeable that the initial concentration in all runs was 200 mgL^{-1}. It can be concluded that the optimum electrical current and electrode height are 300 mAmp and 9 cm, respectively. In this condition, the energy consumption was calculated 2.7 WH/g removed LAS.

In Figure 2, the LAS removal efficiency in terms of current intensity for different electrode submersion heights has been shown. As can be seen with increasing height of electrode immersion, LAS removal efficiency was increased. Obviously, the optimum current intensity and electrode height were 300 mA and 9 cm, respectively. In this condition, the maximum removal efficiency of LAS was 94%, which the LAS concentration was reduced from 200 to 12 mg/L.

Figure 3 shows the LAS removal efficiency versus current density; it can be concluded that the best efficiency is obtainable in 6 mA/cm^2.

ANOVA test on chemical results to compare optimal conditions with other conditions showed a significant difference between them ($P < 0.05$).

To assess the electrolysis detoxification of LAS biological test carried out on samples using molly fish (*P. sphenops*). Ten fish were leaved in each 2 L beaker full of the treated solution than the fish vital status every hour up to 96 h from the beginning. In parallel, this test was done on contaminated water without electrochemical process and raw water as control groups. All fish leaved in uncontaminated water survived for 4 days while all in untreated contaminated samples died in early minutes. Only under the optimum electrochemical process condition, eight fish were survived until 4 days since the end of the process [Figure 4] and the statistical analysis showed a meaningful difference between optimum condition and the others for fish survival ($P < 0.05$).

Discussion

The aim of this article was investigation of effect of electrochemical process on LAS removal from synthetic wastewater and fish bioassay test to assessment of the process capability for detoxification of detergent. A review of several studies on the removal of LAS from real and synthetic effluents shows that with increasing the current density, the LAS removal efficiency was increased. For example, Koparal *et al*.[1] showed that, in the range of 10–15 mA/cm^2, a uniform increase in the efficiency of LAS removal was observed. Similar results were obtained in the study of Lissens *et al*.,[31] Kong *et al*.,[33] and Önder *et al*.[26] These researchers used BDD, Ti, and cast iron electrodes in their tests, respectively. However, the Panizza *et al*.[5] showed that, at a current density of 25–75 mA/cm^2, the removal efficiency decreased by increasing the current density, which is more consistent with our results. Therefore, it can be concluded that, at lower current densities, the higher removal efficiency and at the higher current densities, the lower removal efficiency are achieved. Hence, there is an optimal current density, in which the removal efficiency can be the highest. Of course, according to the study of Önder *et al*.,[26] the type of electrode also plays an important role in this current density position as with low oxygen evolution potential electrodes, lower current density is preferred and with high oxygen evolution potential electrodes, higher current density is more important. The reason for reducing the removal efficiency in the 300–700 mA range is due to the side reactions in the reactor that compete with LAS removal reaction. The most important of these reactions is the release of oxygen in the anode based on the following reaction:

Table 1: Remained linear alkyl benzene sulfonate and energy consumption in different electrical current intensities and electrode immersion heights

Electrode height (cm)	Current (mA)							
	200 (*n*=4)	300 (*n*=4)	400 (*n*=4)	500 (*n*=4)	600 (*n*=4)	700 (*n*=4)	800 (*n*=4)	900 (*n*=4)
3 (cm)								
Remained LAS (mg/L)	87±1	67±6	70±2	75±1	80±2	83±4	82±2	69±6
Energy consumption	3.5±0.3	5.2±0.4	7.7±0.4	12.5±0.5	17.8±1	22.3±1.1	28.1±1	30.5±1.2
6 (cm)								
Remained LAS (mg/L)	84±3	36±4	47±3	66±2	71±3	79±3	68±4	54±4
Energy consumption	2.9±0.2	3.8±0.2	6.0±0.4	8.8±0.7	10.9±0.8	15.4±0.8	16.4±0.9	18.2±0.9
9 (cm)								
Remained LAS (mg/L)	85±4	12±5	36±2	43±1	56±7	72±3	59±3	33±3
Energy consumption	2.9±0.2	2.7±0.1	4.4±0.3	5.9±0.4	8.3±0.5	12.6±0.8	13.4±0.8	13.3±0.8

LAS: Linear alkyl benzene sulfonate

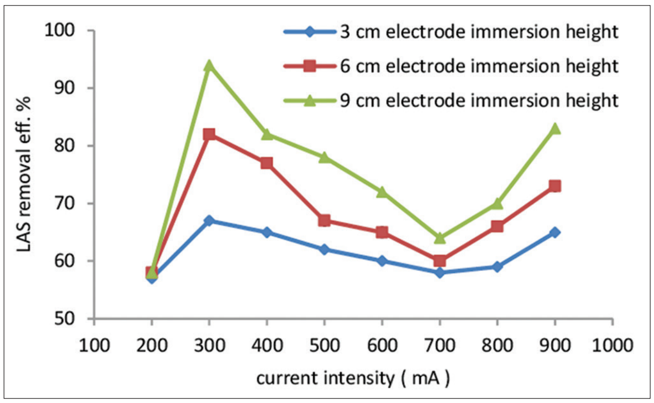

Figure 2: The linear alkylbenzene sulfonate removal efficiency in terms of current intensity for different electrode submersion heights

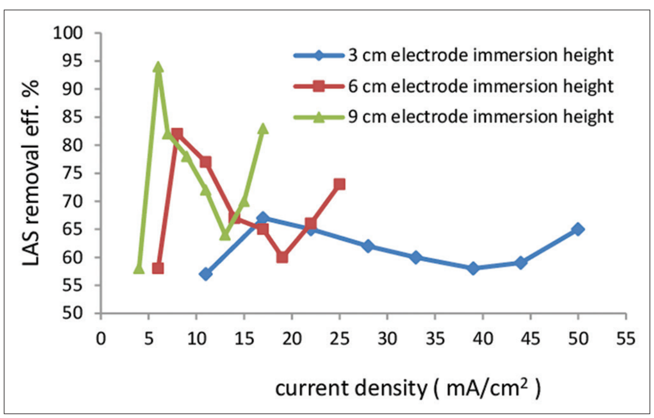

Figure 3: The linear alkylbenzene sulfonate removal efficiency versus current density

$$2H_2O \leftrightarrows O_2 + 4H^+ + 4e^-$$

Furthermore, due to the presence of oxidable anions such as chloride in solution (following reaction), the removal efficiency increases in high current intensities as shown in Figure 2 at current intensities higher than 700 mA. Because the molecule of chlorine is a strong oxidizing agent in the chemical oxidation of LAS.

$$2Cl^- \leftrightarrows Cl_2 + 2e^-$$

We applied bioassay test for assessment of the effectiveness of electrochemical process on LAS detoxification. Results showed all fish leaved in uncontaminated water survived for 4 days whereas all in untreated contaminated samples died in early minutes that is due to the high toxicity of LAS for fishes at concentrations higher than 12 ppm.

Only under optimum conditions, 80% of fish was survived until 4 days since the end of the process. From the standpoint of bioassay test, the difference between optimum and the other conditions was significant, so it can be concluded that the electrochemical process under optimum condition has a good capability to reduce the LAS toxicity as well as detergent removal.

Conclusion

From the results of this experiment, it can be deduced that both the surface area of the electrode and the current intensity are effective in determining the removal efficiency. Therefore, based on the findings of optimal conditions, the design of large-scale batch electrochemical reactors is easy. Because the use of expensive electrodes such as BDD in the large scale is not economical and due to the ease and simplicity of the reactor used in the test, the importance of this study is further enhanced. The results of this study can solve the environmental problems of plants such as detergent manufacturers, laundries, and carwashes that are exposed to high concentrations of surfactants in their wastewater. The authors recommend that the effect of the surface area of the electrode and the current intensities above 1000 mA that are not addressed in this study be examined in more detail.

Acknowledgment

The authors are grateful to the deputy of research and technology of Kashan University of medical sciences for financial support. We are also thank full from Ali Azari, PhD student of environmental health engineering, school of public health, Tehran University of medical sciences, for his considerable help in review of this paper.

Financial support and sponsorship

This work was supported by Kashan University of Medical Sciences in Kashan. This paper is extracted from the results

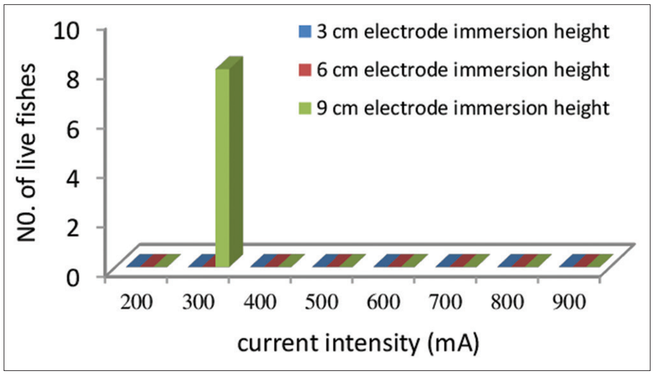

Figure 4: Number of live fishes in different current intensity

of research project No. 9522, which was conducted at Kashan University of medical sciences.

Conflicts of interest

There are no conflicts of interest.

References

1. Koparal AS, Önder E, Öütveren ÜB. Removal of linear alkylbenzene sulfonate from a model solution by continuous electrochemical oxidation. Desalination 2006;197:262-72.
2. Ruman M, Olkowska E, Drąg-Śmigalska M, Jankowski G, Polkowska Ż. Surfactants in Klodnica river (Katowice, Poland). Part I. Linear alkylbenzene sulphonates (LAS). Ecol Chem Eng S 2017;24:53-63.
3. Ciorba GA, Radovan C, Vlaicu I, Pitulice L. Correlation between organic component and electrode material: Consequences on removal of surfactants from wastewater. Electrochim Acta 2000;46:297-303.
4. Möbius D, Miller R, Fainerman V. Surfactants: Chemistry, Interfacial Properties, Applications. Amsterdam: Elsevier; 2001.
5. Panizza M, Delucchi M, Cerisola G. Electrochemical degradation of anionic surfactants. J Appl Electrochem 2005;35:357-61.
6. Andrade MV, Sakamoto IK, de Oliveira Paranhos AG, Silva EL, Varesche MB. Bioremoval of surfactant from laundry wastewater in optimized condition by anoxic reactors. Water Air Soil Pollut 2017;228:165.
7. Miranzadeh MB, Zarjam R, Dehghani R, Haghighi M, Badi HZ, Marzaleh MA, *et al*. Comparison of fenton and photo-fenton processes for removal of linear alkyle benzene sulfonate (Las) from aqueous solutions. Pol J Environ Stud 2016;25:1639-47.
8. Samadi MT, Dorraji MS, Atashi Z, Rahmani AR. Photo catalytic removal of sodium dodecyl sulfate from aquatic solutions with prepared ZnO nanocrystals and UV irradiation. Avicenna J Environment Health Eng 2014;1:e166.
9. Heibati B, Ghoochani M, Albadarin AB, Mesdaghinia A, Makhlouf AS, Asif M, *et al*. Removal of linear alkyl benzene sulfonate from aqueous solutions by functionalized multi-walled carbon nanotubes. J Mol Liq 2016;213:339-44.
10. Guan Z, Tang XY, Nishimura T, Huang YM, Reid BJ. Adsorption of linear alkylbenzene sulfonates on carboxyl modified multi-walled carbon nanotubes. J Hazard Mater 2017;322:205-14.
11. Tadros TF. Applied Surfactants: Principles and Applications. Strauss GmbH, Mörlenbach: John Wiley & Sons; 2006.
12. Camacho-Muñoz D, Martín J, Santos JL, Aparicio I, Alonso E. Occurrence of surfactants in wastewater: Hourly and seasonal variations in urban and industrial wastewaters from seville (Southern spain). Sci Total Environ 2014;468-469:977-84.
13. Ghaderpoori M, Dehghani MH. Investigating the removal of linear alkyl benzene sulfonate from aqueous solution by ultraviolet irradiation and hydrogen peroxide process. Desalination Water Treat 2016;57:15208-12.
14. Temmink H, Klapwijk B. Fate of linear alkylbenzene sulfonate (LAS) in activated sludge plants. Water Res 2004;38:903-12.
15. Gao Q, Chen W, Chen Y, Werner D, Cornelissen G, Xing B, *et al.* Surfactant removal with multiwalled carbon nanotubes. Water Res 2016;106:531-8.
16. Delforno TP, Okada DY, Faria CV, Varesche MB. Evaluation of anionic surfactant removal in anaerobic reactor with fe(III) supplementation. J Environ Manage 2016;183:687-93.
17. Kowalska I. Surfactant removal from water solutions by means of ultrafiltration and ion-exchange. Desalination 2008;221:351-7.
18. Nayak AK, Pal A. Performance evaluation of surfactant removal by adsorption technique and its comparative studies with other existing treatment processes: A short review. J Indian Chem Soc 2016;93:837-42.
19. Putra IM, Widhiantara IG. Adsorption of linear alkylbenzene sulfonate (LAS) on eggshell powder. Nat B 2015;3:143-9.
20. Swaminathan M, Manickavachagam M, Sillanpaa M. Advanced oxidation processes for wastewater treatment 2013. Int J Photoenergy 2014;2014:2.
21. Aonyas MM, Dojčinović BP, Dolić SD, Obradović BM, Manojlović DD, Marković MD, *et al*. Degradation of anionic surfactants using the reactor based on dielectric barrier discharge. J Serb Chem Soc 2016;81:1097-107.
22. Feng Y, Yang L, Liu J, Logan BE. Electrochemical technologies for wastewater treatment and resource reclamation. Environment Sci Water Res Technol 2016;2:800-31.
23. Zanta CL, Friedrich LC, Machulek A Jr., Higa KM, Quina FH. Surfactant degradation by a catechol-driven fenton reaction. J Hazard Mater 2010;178:258-63.
24. Boczkaj G, Fernandes A. Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review. Chem Eng J 2017;350:608-33.
25. Deng Y, Zhao R. Advanced oxidation processes (AOPs) in wastewater treatment. Curr Pollut Rep 2015;1:167-76.
26. Önder E, Koparal AS, Öğütveren ÜB. An alternative method for the removal of surfactants from water: Electrochemical coagulation. Sep Purif Technol 2007;52:527-32.
27. Comninellis C, Kapalka A, Malato S, Parsons SA, Poulios I, Mantzavinos D. Advanced oxidation processes for water treatment: Advances and trends for R and D. J Chem Technol Biotechnol 2008;83:769-76.
28. Särkkä H, Bhatnagar A, Sillanpää M. Recent developments of electro-oxidation in water treatment – A review. J Electroanalytical Chem 2015;754:46-56.
29. Ivanković T, Hrenović J. Surfactants in the environment. Arh Hig Rada Toksikol 2010;61:95-109.
30. Olkowska E, Ruman M, Polkowska Z. Occurrence of surface active agents in the environment. J Anal Methods Chem 2014;2014:769708.
31. Lissens G, Pieters J, Verhaege M, Pinoy L, Verstraete W. Electrochemical degradation of surfactants by intermediates of water discharge at carbon-based electrodes. Electrochim Acta 2003;48:1655-63.
32. Brandes R, Newton B, Owens M, Southerland E. Technical Support Document for Water Quality-Based Toxics Control. Washington, DC, (USA): Environmental Protection Agency, Office of Water Enforcement and Permits; 1985.
33. Kong W, Wang B, Ma H, Gu L. Electrochemical treatment of anionic surfactants in synthetic wastewater with three-dimensional electrodes. J Hazard Mater 2006;137:1532-7.