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Efficiency investigation of photo-Fenton process in removal of sodium dodecyl sulphate from aqueous solutions

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ABSTRACT

Surfactants are amphiphilic molecules with a hydrophilic head and hydrophobic tail which increase solubility of hydrophobic compounds. These materials can be harmful for human health and the environment. The aim of this study is to investigate efficiency of photo-Fenton process in removal of sodium dodecyl sulphate from aqueous solutions. An experimental study conducted in 2015 at Environmental Health Engineering Research Center, Kerman University of Medical Sciences, Kerman, Iran. Parameters which influence on removal; including: pH, concentration of H_2O_2 and Fe^{2+}, UV radiation, the initial concentration of sodium dodecyl sulphate and contact time were investigated. Experiments were also conducted under obtained optimal conditions on wastewater of soft drink in Kerman city. Sampling and experiments were done according to the Standard Methods for Examination of Water and Wastewater 20th edition. Optimum conditions were pH 3, H_2O_2 = 0.5 mmol, Fe^{2+} = 40 mg/L, UV-C = 45 watt, the initial concentration of sodium dodecyl sulphate = 25 mg/L and contact time = 30 min. Maximum removal were achieved as 94.36 and 71% for synthetic solutions and soft drink wastewater, respectively. Photo-Fenton process is an effective and high-efficiency method in removal of anionic surfactants from aqueous solutions. This method can remove sodium dodecyl sulphate from real sample of water with efficiency of 71% in 30 min.

Keywords: Photo-Fenton; Sodium dodecyl sulphate; Advanced oxidation; Anionic surfactant; Synthetic surfactant; Detergent; Water

1. Introduction

Surfactants are amphiphilic molecules consisting of a hydrophilic head and hydrophobic tail which increase solubility of hydrophobic compounds [1,2]. They are widely used in several industries such as food, textile, paints, pesticides, pharmaceutical, oil recovery, and paper [1,3,4]. One of their application in food industry is formation of inclusion complex with natural dextrin which induce changes in aggregation [5,6]. Surfactants, especially SDS have been studied for micellar systems. These systems due to their capability

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to solubilize water insoluble food flavoured agents such as benzyl acetate, 2-phenyl ethanol and geraniol have attracted remarkable industrial and food application [7,8]. Four groups of surfactants including cationic, anionic, amphoteric and non-ionic based on the ionic charge are distinguished. Anionic surfactants have negative charge which approximately constitute 90% of all ionic surfactants [1,3]. Sodium dodecyl sulphate is one of the anionic surfactants [1]. This surfactant is a representative of synthetic surfactants with a simple hydrocarbon chain that is widely used in chemical detergents [1]. Surfactants cause harmful effects on human, short and long term changes in ecosystem, foam formation in rivers and wastewater treatment plant effluent, abnormality in algal growth and formation of difficult–to-separate emulsion [1]. Different methods have been proposed for treatment, such as coagulation, microwave, oxidation with ozone and electrochemical processes [4,9–12]. Chemical oxidation processes have varieties and high efficiencies rather than mentioned methods [13]. In advanced oxidation process (AOP), highly reactive species are generated which are capable to oxidize organic compounds and degrade them to harmless materials and final products including water and CO_2 [14–16]. Fenton process is one of AOPs [16] that hydroxyl radicals are generated which are capable to oxidize most organic compounds [13,16–18].

In Fenton process as shown in Eq. (1), hydrogen peroxide decomposed into hydroxyl radicals by oxidation of ferrous into ferric ions [15,16].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$

Fenton process depends on some parameters such as sample properties, pH, iron and hydrogen peroxide concentrations and reaction time [15,16]. In photo-Fenton process Fenton reagent and UV radiation are applied. This process increases generation of hydroxyl radicals [3]. This increase attributed to photo reduction of Fe^{3+} into Fe^{2+} which increases generation of hydroxyl radicals and also photolysis of hydrogen peroxide which are shown in Eqs. (2) and (3) [3]:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (2)$$

$$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH \quad (3)$$

Another advantage of photo-Fenton rather than Fenton is reduction in the amount of produced sludge during the process [3,16]. Photo-Fenton process has many applications in removing of pollutants from aqueous solutions. Zarjam et al. investigated the removal of sodium dodecyl benzene sulphate from aqueous solutions by Fenton and photo-Fenton processes. Panizza et al. reported the removal of surfactant sodium dodecyl benzene sulphonate from aqueous solutions by electro Fenton. Amat et al. reported the removal of commercial surfactants by photo-Fenton process. Panizza et al. determined the synthetic dyes removal by electro Fenton.

With considering the importance of photo-Fenton process, the aim of this paper is efficiency investigation of photo-Fenton process in removal of sodium dodecyl sulphate from aqueous solutions.

2. Experiments

2.1. Materials and reagents

Structure of sodium dodecyl sulphate (SDS) is shown in Fig. 1 and was of analytical grade and purchased from Merck. All other chemicals, including sulphuric acid, sodium hydroxide, ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$), hydrogen peroxide (30% w/w) were also of analytical grade and purchased from Merck.

2.2. Analytical methods

The pH of solutions were measured by pH metre (model: HANNA). The amount of SDS in each sample were measured by spectrophotometer model Shimadzu (Japan) according to the methylene blue active substance (MBAS) analysis in standard methods for the examination of water and wastewater [19]. Magnetic stirrer (model: Fan Azmagostar) was used for stirring. Scale model Shimadzu-Libror was used to weigh chemicals.

2.3. Experimental procedure

An experimental study in 2015 at Environmental Health Engineering Research Centre of Kerman University of Medical Sciences was conducted. In order to evaluate of photo-Fenton process efficiency each parameter, including pH 3, 7, 10, contact time: 10, 20, 30, and 40 min, concentration of ferrus ion: 20, 40, 60, 80, 100, and 120 mg/L, concentration of hydrogen peroxide: 0.1, 0.3, and 0.5 mmol, the initial concentration of SDS: 25, 50, 75, and 100 mg/L, UV-C power: 15, 30, 45, and 60 watt was investigated. Experiments were carried out by changing each

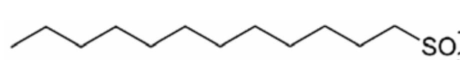

Fig. 1. Chemical structure of SDS [14].

parameters in different mentioned amounts while other parameters were fixed and in optimum amounts. All experiments were conducted in room temperature (25 ± 2). Experiments conducted three times in order to increase accuracy and reliability and then results expressed in average values.

2.4. Photo-Fenton degradation of surfactant

An experimental set-up that is shown in Fig. 2 was used in order to conduct photo-Fenton process. Designing was according to study of Ono et al. [20].

Photoreactor was put under hood for safety and filled with 1 l of sample. The initial pH adjusted by NaOH and H_2SO_4. Predetermined amount of iron salt was added to the sample and mixed well, then a given volume of hydrogen peroxide was added. The beginning time of reaction was the time at which UV lamps were turned on. At selected times, aliquots of samples by syringe were withdrawn and their adsorptions measured by UV spectrophotometer according to MTBA method (5540.C) in Standard Methods for Examination of Water and Wastewater.

3. Results and discussions

3.1. Effects of H_2O_2

The mean removal efficiency of SDS in the range of 0.1–0.7 mmol of hydrogen peroxide against reaction time is shown in Fig. 3.

Fig. 3 shows that with increasing of hydrogen peroxide from 0.1 to 0.5 mmol, the removal efficiency increases from 59.1 to 95%. In concentrations more than 0.5 mmol, the removal efficiency decrease. This figure also shows by increasing in contact time the removal efficiency increases. Increasing in removal efficiency up to a certain amount of hydrogen peroxide can be attributed to increase in generation of hydroxyl radicals [3,20–22]. Reduction in removal efficiency after that amount attributed to the scavenging effect of H_2O_2 and also its reaction with hydroxyl radicals and production of hydroproxyl radicals which are less effective and does not have any roles in degradation of organic compounds [3,22]. Sohrabi et al. reported that in their study with increase hydrogen peroxide from 0.1 to 0.2 mmol, the removal efficiency of Carmoisine dye increased but after increasing from 0.2 to 0.3 mmol, the removal efficiency decreased [21]. Bahmani et al. in their study showed that by increasing hydrogen peroxide from 0.73 to 2.9 mmol, removal efficiency of reactive blue fifth dye increased and in concentrations more than 2.9 mmol the removal efficiency decreased [22]. Khandelwal et al. found that by increasing in hydrogen peroxide around 1 ml the removal efficiency increased and in more concentrations the removal efficiency decreased [23]. The results of this paper are similar to the previous studies.

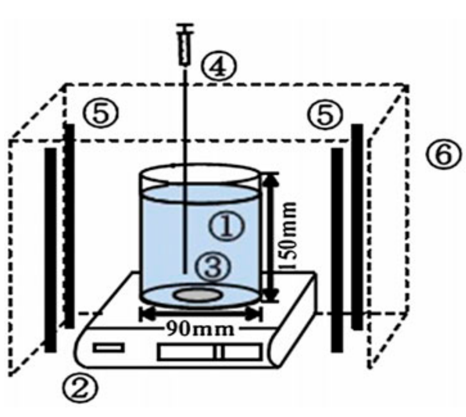

Fig. 2. Set-up for experiments.
Notes: (1) Photoreactor, (2) Magnetic stirrer, (3) Stirring bar, (4) Sampling syringe, (5) UV lamps, (6) Saftey hood.

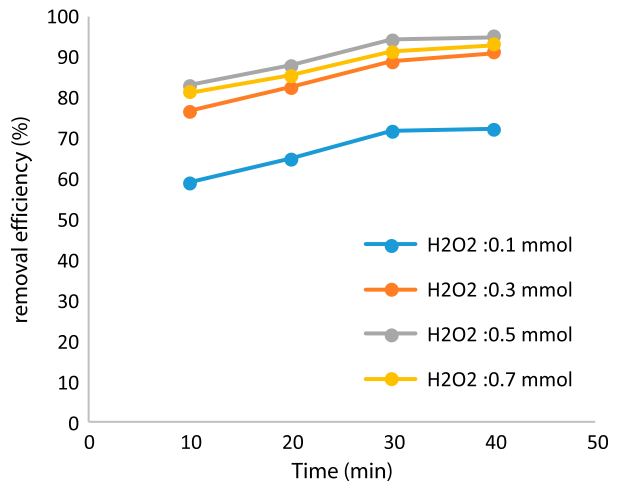

Fig. 3. The mean removal of SDS regarding to the concentration of hydrogen peroxide in pH 3, reaction time: 10–40 min, Fe^{2+}: 40 mg/L, UV power: 45 watt, the initial concentration of SDS: 25 mg/L.

3.2. Effects of Fe^{2+}

The mean removal efficiency of SDS in the range of 20 to 120 mg/L of Fe^{2+} against reaction time is shown in Fig. 4.

Fig. 4 shows that by increasing in Fe^{2+} concentration from 20 to 40 mg/L, the removal efficiency increases from 54.2 to 96%, but more increases in Fe^{2+}concentration from 40 to 120 mg/L, the removal efficiency decreases. This figure also shows by Increasing in reaction time removal efficiency increases.

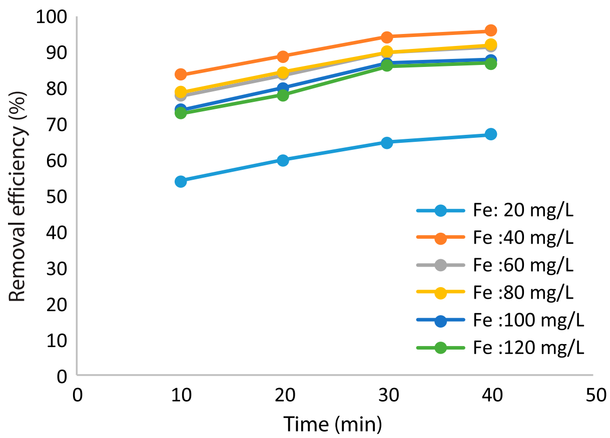

Fig. 4. The mean removal of SDS in reaction time 10–40 min regarding to the concentration of Fe^{2+} in pH 3, H_2O_2 = 0.5 mmol, UV power: 45 watt, the initial concentration of SDS: 25 mg/L.

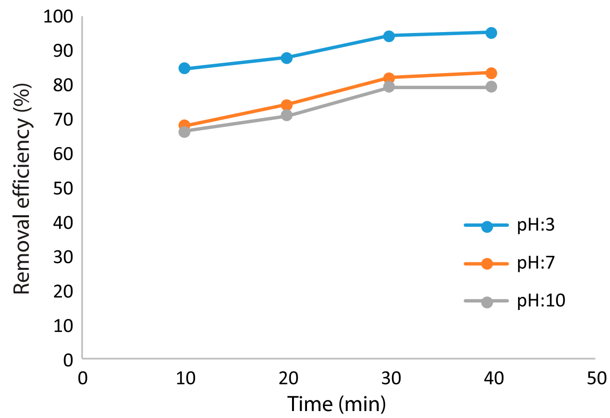

Fig. 5. The mean removal of SDS in reaction time 10–40 min regarding to pH in Fe^{2+} = 40 mg/L, H_2O_2 = 0.5 mmol, UV power: 45 watt, the initial concentration of SDS: 25 mg/L.

Fe^{2+} is another important parameters in photo-Fenton process [16]. Fe^{2+} plays the role of starter and catalyser in this process [16,22].

Increasing in removal efficiency in first stage can be attributed to the improving of photo-Fenton process and generation of hydroxyl radicals [24]. Decreasing in the removal efficiency in second stage when upraised the Fe^{2+} from 40 to 120 mg/L, is due to the scavenging effect which causes hydroxyl radicals convert into hydroxide ions according to Eq. (4):

$$^{\cdot}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (4)$$

Zarjam et al. in their study found that by increasing the concentration of Fe^{2+} up to 80 mg/L, 43.2% in removal efficiency achieved [3]. Hameed BH et al. found by increasing in Fe^{2+} up to 0.1 mmol, the removal efficiency of Malchite green increased [25]. Daud et al. reported by increasing in Fe^{2+} concentration from 0.010 mmol to 0.1 mmol mg/L the removal efficiency of SBDN increased, but more increases in Fe^{2+} concentrations, the removal efficiency did not show significant enhancement [26].

3.3. Effects of pH

The mean removal efficiency of SDS in pH 3–10 against reaction time is shown in Fig. 5.

Fig. 5 shows that by increasing in pH from 3 to 10 the removal efficiency decreases from 95.3 to 66.3%, also increasing in reaction time causes more removal efficiency.

Fenton process deeply depends on pH. It can be attributed to the presentation of iron and hydrogen peroxide species. According to the previous studies, optimum pH for Fenton process regardless to the targeted substance is around 3 [16]. In pH more than 3, due to existence of comparatively inactive iron oxohydroxides and precipitation of iron ions as iron hydroxide the removal efficiency decreases [16,21]. In addition, hydrogen peroxide is unstable in this condition and fewer hydroxyl radicals are generated which causes lower efficiency [16,21,24]. Sohrabi et al. in their study by increasing pH more than 3.5 reported the removal efficiency of Carmoisine dye decreased [21]. El Hadad et al. in their study by increasing pH from 3 to 7 showed that the removal efficiency decreased around 40% [24].

3.4. Effects of UV-C radiation

The mean removal of SDS in different UV radiation against reaction is shown in Fig. 6.

Fig. 6 shows by increasing UV radiation from 15 to 60 watt the removal efficiency increases from 64.5 to 96% and also by increasing in reaction time the removal efficiency increases. Increasing in UV radiation more than 45 watt has a negligible effect.

The high efficiency in SDS removal by increasing radiation attributed to the increase in reduction of ferric ions [20]. Zarjam et al. in their study by increasing UV radiation achieved the same results [3].

3.5. Effect of the initial concentration of SDS

The mean removal of SDS in different initial concentrations from 25 to 100 mg/L of SDS against reaction time is shown in Fig. 7.

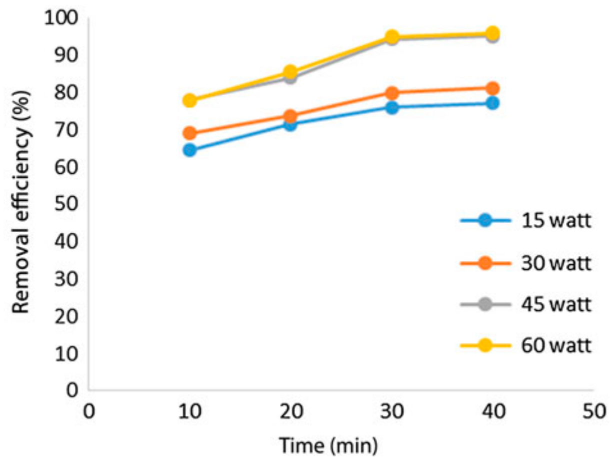

Fig. 6. the mean removal of SDS in reaction time 10–40 min regarding to UV radiation in Fe^{2+} = 40 mg/L, H_2O_2 = 0.5 mmol, pH 3, the initial concentration of SDS: 25 mg/L.

Fig. 7 shows by increasing in the initial concentration of SDS, the removal efficiency decreases from 94.8 to 38%. This figure also shows by increasing in reaction time the removal efficiency increases. The initial concentration is another important parameters in photo-Fenton process [21]. By increasing the initial concentration of SDS, the removal efficiency decreased [20]. This reduction attributed to the fixed amount of iron and hydrogen peroxide concentrations and being not enough in order to removing SDS [20]. In addition, by increasing in SDS concentration, a large amount of the radiation absorbed by SDS instead of hydrogen peroxide [21]. Sohrabi et al. in their study reported by increasing Carmoisine dye concentration from 20 to 30 mg/L, the removal efficiency decreased

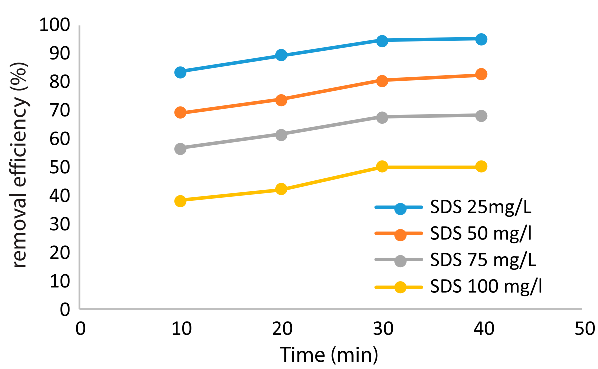

Fig. 7. The mean removal of SDS in reaction time 10–40 min regarding to the initial concentration of SDS in Fe^{2+} = 40 mg/L, UV: 45 watt, H_2O_2 = 0.5 mmol, pH 3, the initial concentration of SDS: 25 mg/L.

Table 1
Chemical and physical characteristics of soft drink wastewater

Parameters	Amount
BOD	540 mg/L
COD	1,400 mg/L
TSS	255 mg/L
pH	6

[21]. Mansourian et al. reported decrease in removal efficiency by increasing dye concentration from 10 to 500 mg/L [27].

After consideration the reaction time in all examined parameters, we observed that by increasing in reaction time the removal efficiency increased, but in all cases there were small differences between values at reaction times of 30 and 40 min, so the reaction time of 30 min was determined as optimum reaction time. After determination of optimum conditions on synthetic sample, experiments also were conducted in obtained optimum conditions on real wastewater of soft drink in Kerman city, south east part of Iran. Physical and chemical characteristic of the real wastewater were measured which are shown in Table 1. Removal efficiency in optimum conditions; including pH 3, contact time: 30 min, UV radiation: 45 watt, Fe^{2+}: 40 mg/L, H_2O_2: 0.5 mmol, the initial concentration of SDS: 25 mg/L were 94.36 and 71% for synthetic and real wastewater, respectively.

4. Conclusion

The removal of sodium dodecyl sulphate (SDS) from aqueous solutions using photo-Fenton process was studied. It was found that the solution pH, the concentrations of Fe^{2+} and H_2O_2, the initial surfactant concentration, the UV radiation and time are the main factors which have strong influences on removal of SDS by photo-Fenton process. The optimal operation parameters for photo-Fenton process of SDS were Fe^{2+} = 40 mg, H_2O_2 = 0.5 mmol, UV-C radiation = 45 watt, pH 3 for 25 mg/L SDS after 30 min. Under this condition 71% removal of SDS in 30 min from real wastewater was achieved. Thus, photo-Fenton process is a suitable and effective way for removal of SDS from aqueous solutions.

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