Decomposition of sodium dodecylbenzene sulfonate surfactant by Electro/Fe$^{2+}$-activated Persulfate process from aqueous solutions

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Abstract

The decomposition of sodium dodecylbenzene sulfonate (SDBS), which is a dangerous and anionic surfactant, was investigated by the electro/Fe$^{2+}$/persulfate process from aqueous solutions. The activation of persulfate anion and production of active radicals were performed by means of heat, UV and iron ions (released from iron electrodes). The finding illustrated that the pH value of the solution, initial concentration of persulfate anion, the amount of input voltage and iron dosage were entirely effective in SDBS removal. Nearly 100% of SDBS was removed under the optimum conditions: pH 3, voltage 10 V, anion persulfate concentration 25 mM/L, iron ion dosage 0.25 g/L and reaction time 25 min. Furthermore, the application of the persulfate anion process in concert with the electrochemical process, in order to generate electrical iron and persulfate activation, had a better performance compared to separate methods.

Keywords: Electro/Fe$^{2+}$-activated persulfate decomposition, sodium dodecylbenzene sulfonate, Active radicals

1. Introduction

Surfactants are divided into four groups: anionic, cationic, nonionic and amphoteric. Anionic surfactants are widely used; linear alkylbenzene sulfonates (LAS), from this group, were introduced in 1964 as easily biodegradable alternatives to highly branched tetrapropylbenzene (Manousaki et al., 2004) and are solely produced approximately 2.5 tonnes yearly. Sodium dodecylbenzene sulfonate (SDBS), a representative LAS molecule, (Manousaki et al., 2004) is being used largely because it lacks benzene ring in its structure (Otero et al., 2012). SDBS, which is an anionic surfactant, has various applications in industry: stabilization of colloids, washing of metals, production of cleaners and flotation of minerals. Moreover, it is known as persistent organic pollutants (POPs) (Zhang et al., 2012). Common methods for surfactant removal from aqueous environments are as follows: chemical and electrochemical oxidation, membrane processes, precipitation, photocatalytic degradation, adsorption and biological measures (Tran et al., 2009), some of which are expensive and the other have low performance efficiency. For example, recycling of SDBS from absorbents is very difficult even though adsorption is regarded as an inexpensive method (Zhang et al., 2012). Of course, activated sludge can effectively treat surfactants from wastewaters; however, under anaerobic conditions the amount of surfactant increases dramatically in the effluent (Tran et al., 2009; Méndez-Díaz et al., 2010). Advanced oxidation processes (AOPs) are novel methods for removing organic matters from water solutions by generating oxidizing radicals (Matilainen and Sillanpää, 2010). From frequently used in situ chemical oxidation, persulfate has been more taken into account because of its powerful oxidation–reduction potential (EO=2.01 V). It is a rather stable oxidant in water; however, it can be activated by UV, heat, base, or transition metals to create a stronger oxidant, sulfate radical (SO$_4^{2-}$, EO=2.6 V); following reactions (1 and 2) take place in the application of persulfate (Wang et al., 2013; Zhou et al., 2013):

$$\text{S}_2\text{O}_8^{2-} + \text{heat or UV} \rightarrow 2\text{SO}_4^{2-}$$  \hspace{1cm} (1)

$$\text{M}^{(n+1)+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-} + \text{M}^{n+}$$  \hspace{1cm} (2)

This oxidant has been used for treating several pollutants like ethyl carbonate (Gu et al., 2013), chlorophenol (Sohrabi et al., 2013), bisphenol A (Jiang et al., 2013) and so forth. As mentioned above, one of the ways to active persulfate is using metal ions such as iron and cobalt. Recently, great attention has been taken to iron because it is nontoxic, cheap and effective. Reactions 3-5, which happen in the presence of iron, are as follows (Ahmad et al., 2013):

$$\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-}$$  \hspace{1cm} (3)

$$\text{Fe}^{2+} + \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-}$$  \hspace{1cm} (4)


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SO₄²⁻ + Fe²⁺ → Fe³⁺ + SO₄²⁻ \hspace{1cm} (5)

The activation of persulfate by Fe (II) has two main problems: first, by adding Fe (II) to the reactor, the reactions occur effectively during a few minutes and then Fe (II) changes into Fe (III) which stops the efficiency, second, Fe (II) acts as sulfate radical scavenger and according to the following reaction (6) creates other species of sulfate which have lower oxidation power (Jiang et al., 2013).

Fe²⁺ + SO₄²⁻ → Fe³⁺ + SO₄²⁻ \hspace{1cm} (6)

However, by using electricity little amount of Fe (II), it can be entered the reactor and Fe (III) is continuously reduced to Fe (II) on the cathode; also, on the anode, hydroxyl radical can be produced which can be used as a powerful oxidant (Rahmani et al., 2015; Godini et al., 2013).

The main objective of this study was to investigate the effectiveness of the Electro/Fe²⁺/Persulfate (EFPS) process activated by iron electrodes in order to remove SDBS from aqueous media. Furthermore, the effects of operating parameters of pH, voltage, persulfate concentration, and dye initial concentration were studied.

2. Materials and methods

2.1. Materials

All chemicals: SDBS powder (purity 80%) (Table 1.), NaOH (C.A.S. number: 1310-73-2 purity 95%), H₂SO₄ (C.A.S. number: 7664-93-9 purity 98%), Na₂SO₄ C.A.S. number: 7757-82-6 purity 99%, K₂S₂O₇ C.A.S. number: 7727-21-1, purity 95%), detergent reagent and toluene were of the highest commercially available quality and purchased from Sigma-Aldrich and Merck (Germany).

Table 1. General characteristics of sodium dodecylbenzene sulfonate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical structure</td>
<td></td>
</tr>
<tr>
<td>CAS Number</td>
<td>25155-30-0</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C₁₃H₂₉NaO₅S</td>
</tr>
<tr>
<td>Molar mass</td>
<td>348.48 g mol⁻¹</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>20%</td>
</tr>
</tbody>
</table>

2.2. Apparatus and procedure

A schematic diagram of the reactor used in this study has been shown in figure 1. A reactor (effective volume: 1000 ml) was used to conduct batch experiments. Four iron electrodes (two as anode and two as cathode) with same dimensions (2×20×200 mm) were arranged on a set of parallel plates at a distance of 2.0 cm.

Before each run, a stock solution of SDBS (1 g/L) was freshly prepared with deionized water. Furthermore, required contents of persulfate anion (10-100 mM/L) were provided to add the reactor manually. A pH-meter (Sension 378 – Hach comp. USA) was used to adjust the pH values by sulfuric acid or sodium hydroxide. An electronic magnetic stirrer (LTE Scientific, Greenfield, Oldham, England) was employed to agitate the solution during the runs at about 150 rpm. Adjustment of voltage ranged from 1 to 10 V was performed. Before analyzing and preparing the samples, they were centrifuged at 2500 rpm in order to eliminate possible adverse effects of the formed sludge on results.

Figure 1. A schematic diagram of the used pilot including four main parts: (1) DC power supply, (2) reaction cell, (3) electrodes and (4) magnet

2.3. Analytical methods

The detection of SDBS was conducted according to Standard Methods: method 5540 C (Association 1994). NaOH and H₂SO₄ (1N) were used to adjust pH. In order to improve the ionic property of solutions, Na₂SO₄ (fixed at 0.5 g/L) was used for all experiments. From SDBS, the stock solution was prepared (1g/1000 ml), and from which serial dilutions were made to obtain 100 to 1000 mg/L dilutions. In addition, required contents of persulfate anion (10 to 100 mM/L) were added to the reactor manually. Different concentrations of SDBS were taken before and after each run; then, after dilution 300 ml of the solution was taken and 10 ml of sulfate buffer was added to it; next, the obtained solution was shaken for 5 min and then a reagent was added to it. At this stage, 30 ml of toluene was added and the solution was shaken for 1 min. Finally, this solution was kept stable for 30 min to separate two phases; the residual SDBS content in the solution (mg/L) was measured by means of a spectrophotometer (HACH DR-5000, USA) at λmax = 597 nm.

3. Results and discussion

3.1. Effect of initial pH
So as to study the effect of pH value on the removal efficiency, values of 3, 6, 7, 9 and 11 were adjusted under the following conditions: initial concentration of SDBS = 100 mg/L, persulfate anion concentration = 25 mM/L, input voltage = 10 V (in the range of 1-1.5 amper) and electrolyte concentration = 0.5 mg/L. The obtained findings showed that this parameter was entirely effective on the removal efficiency (Figure 2a). As can be seen, the highest amount of SDBS removal was for pH value of 3, in which after 30 min 96.6% of this substance was removed. In the case of other pH values, a dramatic decline was seen in the efficiency. Therefore, the pH value of 3 was selected as the optimum value. Figure 2b illustrates the changes of pH during the process; as can be seen, the most amounts of pH changes occurred in 5 min. In general, it can be said that the process experienced a downward trend in pH value.

The pH of solution affects both the valence of iron in solution and persulfate anions reactions with pollutants (Rastogi et al., 2009). Under acidic conditions, most iron ions existing in the process of electrosulfate are two-valent that result in a significant increase in efficiency by raising two-valent iron to three-valent iron ratio. Furthermore, at pH values above 4, solubility of ferric ions in solution decreased and these ions changed to colloidal form leading to a decrease in efficiency based on reaction 7 (Masomboon et al., 2010; Xu and Li, 2010).

Fe²⁺ + H₂O → FeOH⁺ + H⁺ (7)

When pH exceeded 9, (FeOH⁺, Fe(OH)₃⁺, Fe(OH)₄⁺ and Fe₂(OH)₆⁺) were formed which can active marginally persulfate anions (Zhou et al., 2013). Activation of persulfate anion can be done by ferric ions which results in sulfate radical; the production of this radical can be fluctuated via pH value and the hydroxyl radicals can be generated. That what radical is dominant in solution was entirely dependent upon pH value. At different pH values, different radicals were dominant as follows: sulfate radicals at pH values below 7, particularly from 3 to 5 (reactions 3-4), both radicals at pH values between 7 and 9 (reaction 6), hydroxyl radicals at very alkaline conditions (pH values above 12) (reaction 7).

S₂O₅²⁻ + 2e⁻ → 2SO₄²⁻, E° = 2/01 V (8)

SO₄²⁻ + e⁻ → SO₄²⁻, E° = 2/6 V (9)

Since at alkaline conditions the oxidation potential of hydroxyl radical decreased sharply, the efficiency of the process declined even when this radical was dominant. In addition to this, the stability of sulfate radical was higher than that of hydroxyl radical in aqueous solution (Romero et al., 2010) (reactions 8-9). Also, at high pHs, radicals of sulfate and hydroxyl had scavenging reaction together (reaction 12) which as a result decreases the efficiency (Kusic et al., 2011; Wang et al., 2014).

SO₄²⁻ + H₂O ↔ OH⁻ + H⁺ + SO₄²⁻ (10)

SO₄²⁻ + OH⁻ → OH⁺ + SO₄²⁻ (11)

SO₄²⁻ + OH⁺ → H⁺ + SO₄²⁻ + 0.5O₂ (12)

In this study, it was found that pH changed over the process. The activation of persulfate anion through ferric ions can finally produce sulfate radical under acidic conditions which can decrease pH value of the oxidation system. Based on reactions 7 and 8, sulfate radical tends to transform to hydrogen ions and consumes hydroxyl ions, which consequently decreases the pH of solution. Moreover, hydrogen ions were generated through chain reactions of separation HSO₄⁻ in water; all these reactions (10-12) decrease pH (Zhou et al., 2013; Lin et al., 2013).

SO₄²⁻ + OH⁻ → HSO₄⁻ + 0.5O₂ (13)

S₂O₅²⁻ + H₂O → 2HSO₄⁻ + 0.5O₂ (14)

HSO₄⁻ → H⁺ + SO₄²⁻ (15)

A comparative study by Khan et al. (2013) studied atrazine oxidation by UV/H₂O₂/Fe²⁺, UV/S₂O₅²⁻/Fe²⁺ and UV/H₂O₂/Fe²⁺ and they found that UV/S₂O₅²⁻/Fe²⁺ (at pH value of 3) was the best measure. Accordingly; another study concluded that pH 3 was the best value for the S₂O₅²⁻/Fe²⁺ process to decompose carbamazepine and they reported that pH value declined over the process (Rao et al. 2014). Furthermore, a study by Romero and et al., (2010) dealt with diuron removal by means of S₂O₅²⁻ activated by Fe²⁺ at three pH values: 3, 5 and 8; they reported that the
efficiency decreased by increasing pH and it went down during the process.

3.2. Effect of voltage

In order to investigate the effect of voltage, the experiments were carried out under conditions as follows: initial SDBS concentration = 100 mg/L, persulfate anion concentration = 25 mM/L and electrolyte concentration = 0.5 mg/L (with voltage ranging from 2.5 to 10 V). Figure 3 shows how the efficiency changes at different voltages. As can be seen, by increasing voltage SDBS, the removal efficiency increased and reached 96.6% at voltage of 10 V. An increase in voltage led to an increase in removal efficiency owing to oxidants production increase (Rahmani et al., 2016). Voltage increase results in the release of iron ions from the surface of the sacrificed anode and also reactions 2-5, the activation of persulfate is performed via iron ion. Therefore, the more iron ions are released, the more oxidants (SO$_4^{2-}$) are generated, which, in turn, leads to an increase in efficiency.

![Figure 3. Effect of voltage on the process of electro-persulfate (SDBS concentration: 100 mg/L, S$_2$O$_8^{2-}$ concentration: 25 mM/L, Na$_2$SO$_4$ concentration: 0.5 g/L, pH: 3)](image)

3.3. Effect of Fe$^{2+}$ concentration

A range of 0.05-0.5 mg/L of Fe$^{2+}$ was employed to study the effect of this parameter on the efficiency under conditions as follows: initial SDBS concentration = 100 mg/L, persulfate anion concentration = 25 mM/L, electrolyte concentration = 0.5 mg/L, input voltage = 10 and pH = 3. As can be seen from Figure 4, Fe (II) increased the efficiency dramatically. At concentration of 0.25 mg/L, 95.17% of SDBS was removed in 25 min.

By increasing the amount of Fe (II), the removal efficiency went up, but there was a downward trend in the concentrations over 0.25 mg/L. Therefore, this value (0.25 mg/L) was selected as optimum concentration. Of course, at concentrations of two-valent iron higher than the optimum value not only the efficiency decreased but also an increase in sludge production happened. The efficiency can also decrease through reaction between sulfate radicals and two-valent iron ions (reaction 18) (Ji et al., 2014; Rodriguez et al., 2014).

SO$_4^{2-}$ + Fe$^{2+}$ → SO$_2^{2-}$ + Fe$^{3+}$

(16)

Fe$^{3+}$ + e$^-$ → Fe$^{2+}$

(19)

After activation of persulfate anion by means of ferric, iron is oxidized and Fe$^{3+}$ ions are formed; thus, because of the lack of main activation, huge amount of two-valent iron is needed, which results in an increase in sludge production as well as costs. Employing the persulfate process in concert with the electrochemical method (iron electrodes) can lessen the cost of operation; in this case, iron is continuously generated through the iron anode and then it is oxidized to Fe$^{3+}$ converted to Fe$^{2+}$ on the surface of the cathode. This generation has the best efficiency under

![Figure 4. Effect of two-valent iron on the process of electro-persulfate (SDBS concentration: 100 mg/L, S$_2$O$_8^{2-}$ concentration: 25 mM/L, Na$_2$SO$_4$ concentration: 0.5 g/L, pH: 3, voltage: 10 V)](image)

In regard to the effect of persulfate anion concentration, it can be pointed that when concentration increased by the optimum amount it could be effective, but in the case of values exceeding that they had lower efficiency because according to reaction 19 it resulted in persulfate radical consumption (Liang et al., 2007).

S$_2$O$_8^{2-}$ + SO$_4^{2-}$ → S$_2$O$_4^{2-}$ + SO$_4^{2-}$

(17)

Therefore, in this study, the content of 25 mM/L was selected as the optimum amount. Most studies, in which the oxidation of organic pollutants have been investigated, have reported that an increase in concentration declines the efficiency; a few reasons have been suggested for this: a decrease in the ratio of produced radical to pollutant concentration and an increase in intermediates tending to consume the radicals (Wu et al., 2012). Besides, two-valent iron ions at the beginning of the process cause rapid oxidation in the reactor. The upside of adding two-valent iron is having lower time reaction and higher efficiency. Wang and Chu, (2011) claimed that two-valent iron could raise significantly the efficiency of the Electro-Fe(II)/Oxone process. Since in persulfate process iron anodes were the only source of ferric to active persulfate anions in reactor and detection of the amount of released iron on the surface of anode (Gu et al., 2013) and Fe$^{2+}$ recreation via continuous regeneration of Fe$^{3+}$ on the surface of cathode (reaction 17) were controlled by applied voltage to the electric cell (Lin et al., 2013; Wu et al., 2012).

Fe → Fe$^{2+}$ + 2e$^-$

(18)

Fe$^{3+}$ + e$^-$ → Fe$^{2+}$

(19)
DECOMPOSITION OF SODIUM DODECYLBENZENE SULFONATE SURFACTANT

Acidic conditions (Lin et al., 2014). Wang and Chu, (2011) used Electro-Fe(II)/Oxone to degrade 2,4,5-trichlorophenoxyacetic acid by using iron sheet as the sacrificial anode; in this process, sulfate radical was produced after activation.

3.4. Effect of persulfate concentration

Under conditions of initial SDBS (100 mg/L), voltage (10 V), electrolyte (0.5 mg/L) and the optimized amounts of pH = 3 and Fe(II) = 0.25 mg/L, the effect of persulfate concentration changing from 10 to 100 mM/L was investigated (Figure 5). As can be seen, the efficiency increased until the amount of 25 mM/L of persulfate anion and then it decreased. It should be pointed out that this variable had a significant effect in removal efficiency because at the optimum value (25 mM/L) the removal efficiency reached approximately 100%.

Figure 5. Effect of persulfate anion on the process of electro-persulfate (SDBS concentration: 100 mg/L, Na₂SO₄ concentration: 0.5 g/L, pH: 3, voltage: 10 V)

3.5. Effect of SDBS concentration

At this stage, all conditions were adjusted at optimum values and concentrations of SDBS ranged between 100 and 1000 mg/L.

Figure 6. Effect of initial concentration of SDBS on the process of electro-persulfate (S₂O₈²⁻ concentration: 25 mM/L, Na₂SO₄ concentration: 0.5 g/L, pH: 3, voltage: 10 V)

The removal efficiency decreased with the increase of SDBS and it declined from 100 to 21% when the content increased from 100 to 1000 mg/L in 60 min. This is because of a decrease in the oxidant/SDBS ratio. That is, the oxidant agents are consumed owing to the increase of SDBS content. In this case, all SDBS molecules cannot be degraded. Thus, higher concentrations of iron and persulfate are needed to raise SDBS degradation.

3.6. Synergistic effect of different conditions:

In order to investigate synergistic effect, samples were prepared separately to measure the effectiveness of pH, electrolyte concentration, persulfate, persulfate in conjunction with electrolyte, electrochemical process, the electrochemical process in conjunction with electrolyte, the electropersulfate process without electrolyte, electro/Fe²⁺/Persulfate process, Fe (II), and Fe (II) in the presence of persulfate (Figure 7).

Figure 7. Synergistic effect of pH, electrolyte concentration, persulfate, persulfate in conjunction with electrolyte, electrochemical process, the electrochemical process in conjunction with electrolyte, the electropersulfate process without electrolyte, electro/Fe²⁺/Persulfate process, Fe (II), and Fe (II) in the presence of persulfate.

The findings showed that the electro/Fe²⁺/Persulfate process could remove approximately 100% of SDBS. In general, it can be resulted that a process such as Fe (II) did not have high efficiency, but when it was combined with other processes, a dramatic increase was seen in efficiency. As can be seen in Figure 8, the reaction of SDBS decomposition through Electro/Fe²⁺-activated persulfate process follows a first-order reaction ($R^2=0.996$). It was found that the amount of SDBS removal is entirely dependent upon operating parameters as a 99.9% efficiency was attained at the optimum values.

Figure 8. First-order kinetic analysis for SDBS removal (S₂O₈²⁻ concentration: 25 mM/L, Na₂SO₄ concentration: 0.5 g/L, pH: 3, voltage: 10 V).

4. Conclusion
The results of this study showed that the efficiency of the electro/Fe$^{2+}$/Persulfate process for SDBS removal decreased when there was an increase in pH value; there was not a same pattern for anion persulfate concentration because the efficiency went up at the concentrations from 0 to 25 mM/L of this anion, but it decreased when the concentrations were between 25 and 100. Furthermore, the findings showed that the pH parameter was effective over the process. The bottom line is that the application of the electrochemical process in concert with the anion persulfate process, which can generate electrical iron activating persulfate, had higher ability to remove SDS in comparison with single processes.

References


