Degradation of surfactant SLS in water by singlet oxygen generated by the reaction between hydrogen peroxide and hypochlorite

Luiz Alberto Cesar Teixeira, Mariana de Faria Gardingo, Lidia Yokoyama and Fabiana Valeria da Fonseca Araujo

ABSTRACT

The synergistic aqueous combination of hydrogen peroxide and hypochlorite which results in the formation of the highly oxidizing intermediate species singlet oxygen ($^1$O$_2$) was effective in the degradation of the anionic surfactant sodium lauryl sulphate (SLS) in water. The process was effective in the near neutral pH range of 6–8, and up to initial SLS concentration values of 10 mg/L. For initial [SLS] = 5 or 10 mg/L, pH = 6–8, and excess molar ratio ([H$_2$O$_2$] + [NaClO])/[SLS] = 5:1 it was possible to achieve a final concentration of [SLS] < 0.5 mg/L (95% degradation) in t = 60 min at 25 °C in a batch reaction. By comparison, the same reaction with either of the separate oxidants (only H$_2$O$_2$ or only NaClO) at the same excess molar ratio oxidant/SLS of 5:1 gave a maximum of about 50% degradation of the SLS over the same 60 min reaction time. An empirical rate equation was derived: $-d[SLS]/dt = k[SLS]^{0.8}[H_2O_2]^{0.3} [NaClO]^{0.3}$, with $k = 4.8 (±1.0) × 10^{-1}$ L/mol s at 25 °C.

Key words | hydrogen peroxide, hypochlorite, singlet oxygen, SLS degradation

INTRODUCTION

Highly polluted water bodies in regions that lack adequate sanitation may contain surfactants in concentrations as high as 6 mg/L (Lin et al. 1999; Ying 2006; Mungray & Kumar 2008; Sánchez-Martín & Beltrán-Heredia 2010). The World Health Organization recommends a limit of 0.5 mg/L (WHO 2008) for these contaminants in drinking water. Surfactants such as sodium lauryl sulphate (SLS), which may be commonly present along with others in such waters, are difficult to remove in potable water treatment plants (WTP). Although that type of substance is biodegradable, a conventional in-plant pre-oxidation would require several hours of reaction time to be effective under typical oxidant doses of a few mg/L. Such long pre-oxidation times are not usually available in conventional WTPs.

One option for relatively fast and efficient surfactant degradation is the Fenton’s process (Lin et al. 1999; Sanz et al. 2005; Wang et al. 2008; Mousavi et al. 2009). It takes about 1 h in a batch reaction for virtually complete degradation of 10 mg/L surfactant in water, using H$_2$O$_2$ = 60 mg/L; [FeSO$_4$] = 90 mg/L; and pH = 3. It is a simple to operate process which only requires an open agitated tank or duct but, for the treatment of natural waters with pH in the range 6–9, the Fenton’s process requires lowering the pH of the water to the optimum pH range 3–4 for the oxidation step, and then back to neutral pH to be used, which adds operating cost to the oxidation step.

Ozone and advanced oxidation processes (AOPs) based on the activation of H$_2$O$_2$ with O$_3$ or UV are capable of promoting degradation of surfactants in water in near neutral pH (Adams & Kuzhikannil 2000; Kelsuke & El-Din 2004), but these require significant capital expenditure for equipment, which may not be feasible in the short term in developing regions.
Thus, in that context, there is interest in developing new processes for the degradation of surfactants (as well as other oxidizable contaminants) in water that might be of low cost, fast, and capable of operating at near neutral pH. Among the processes that are likely to offer those features are a class of AOPs based on controlled catalytical decomposition or oxidation of H2O2, leading to the generation of highly active oxygen species, like the singlet oxygen 1O2.

Thus, the present study has the objective of evaluating an AOP utilising the combination of hydrogen peroxide (H2O2) and hypochlorite (NaClO) as a system to generate singlet oxygen, and testing if this can be an efficient and fast method for the degradation of surfactant SLS in water.

Generation of singlet oxygen and its use as an AOP for water and effluent treatment

Singlet oxygen, represented as 1O2, is an excited form of molecular dioxygen which includes two different metastable electronic configurations (Kearns 1971). Similarly to the HO• free radical, singlet oxygen is an excited species with a very high capacity for capturing electrons from substances it may collide with in an aqueous solution, or otherwise decay to its fundamental state, in the course of its very short life.

The idea of researching the use of an AOP based on the generation of singlet oxygen derived from the knowledge acquired from scientific investigations on the reaction between hydrogen peroxide and hypochlorite (Khan & Kasha 1965). The final product of the reaction is oxygen in the fundamental state, derived from a singlet oxygen intermediate, which is a strong oxidant with standard reduction potential E°(O2) = 1.52 V, in the half-cell 1O2 + 4 H+ + 4 e− = 2 H2O, calculated using data from Koppenol et al. (2010). According to Held et al. (1978) and to Evans & Upton (1985), the reaction of H2O2 with OCl− leads to 100% yield of 1O2.

Similar to the hydroxyl radical, singlet oxygen has a very short half-life of milliseconds (Merkel & Kearns 1972; Anastasio 2001). It is during this very short life time before decaying to the fundamental state that the singlet oxygen intermediate has the chance of colliding with a contaminant species, capturing electrons from it and transforming it into a potentially less toxic compound.

There is very little information on the kinetics of 1O2 generation by the reaction between H2O2 and Cl2 (hydrolyzed to the conjugated pair HClO/ClO− (pKa = 7.5)). The main reference, which did not foresee the generation of the intermediate 1O2, is the paper by Connick (1947). The following mechanism was proposed for diluted solutions of hypochlorous acid (less than 10−4 mol/L of HClO):

\[
\text{HOCI} = \text{H}^+ + \text{ClO}^−
\]  
(1)

\[
\text{ClO}^− + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}^− + \text{O}_2
\]  
(2)

with \(k = 1.7 \times 10^5\) L/mol min at 25 °C.

Held et al. (1978) developed rate laws in a later investigation: \(d[O_2]/dt = k_2[HClO][H^+][Cl]\) for an acidic medium and \(d[O_2]/dt = k_3[H_2O_2][OCl]\) for the alkaline pathway.

Another more recent study with a focus on the use of hydrogen peroxide for the dechlorination of seawater discharged from desalination (El Din & Mohammed 1998) indicated that the kinetics of the reaction between H2O2 and ClO− follows a second order mechanism with a rate equation \(d[O_2]/dt = k[H_2O_2][ClO]\). The determined \(k\) values were in the range \(k = 4.5–8.2\) L/mol s at 25 °C, but no consideration was made on the formation of the 1O2 intermediate.

METHODS

The effect of oxidation conditions (using H2O2 only; NaClO only; and H2O2 + NaClO in equimolar amounts) on the kinetics of SLS degradation were investigated covering a realistic composition range of surface water heavily contaminated with SLS, where the initial concentration of SLS surfactant was 5 or 10 mg/L and pH 6–8.

Experiments were carried out in a batch reaction in a 1 L glass beaker with mechanical stirring, using 500 mL of distilled water doped with SLS made up to the set initial concentration. Temperature of the laboratory was 25 ± 1 °C. Initial pH was adjusted by addition of either NaOH or H2SO4. SLS as 99.5% minimum pure compound C12H25SO4Na, NaOH, and H2SO4 were supplied by Vetec (Brazil). NaClO (10% weight) was supplied by...
Panamericana (Brazil) and H$_2$O$_2$ (50% weight) by Peróxidos do Brasil. pH was monitored by a glass electrode/pH meter. SLS solutions were made up for each run with concentrations set to nominal levels of 5 and 10 mg/L.

Each run started (at time zero) by the addition of a calculated amount of the first oxidant (H$_2$O$_2$) to the SLS aqueous solution, which had previously been adjusted for pH, with vigorous stirring. A calculated amount of the second oxidant (NaClO) was added some 4 to 6 s later. The run was carried out for a total of 60 min, and samples were withdrawn at 20, 40 and 60 min for immediate SLS determination with a Merck Spectraquant kit (number 114697) based on the Standard Methods routine number 5540-D (AWWA/APHA/WPCF 1998), also known as the ‘Methylene Blue Active Substances’ routine, using a Merck Nova 60 spectrophotometer.

For each experiment, oxidant doses were defined by the excess oxidant to SLS molar ratio, meaning that an excess molar ratio of oxidant/SLS $= 1$ corresponded to the stoichiometric requirement of oxidant to satisfy the complete mineralization of SLS reaction (i.e. an excess H$_2$O$_2$/SLS molar ratio $= 1$ means 36 moles of H$_2$O$_2$ added to react with 1 mole of SLS), in any of the likely complete oxidation reactions (3), (4) or (5):

$$C_{12}H_{25}SO_4Na + 36H_2O_2 \rightarrow 12CO_2 + 48H_2O + Na^+ + H^+ + SO_4^{2-}$$ (3)

$$C_{12}H_{25}SO_4Na + 36ClO^- \rightarrow 12CO_2 + 12H_2O + Na^+ + H^+ + SO_4^{2-} + 36Cl^-$$ (4)

$$C_{12}H_{25}SO_4Na + 18^1O_2 \rightarrow 12CO_2 + 12H_2O + Na^+ + H^+ + SO_4^{2-}$$ (5)

### RESULTS AND DISCUSSION

#### Preliminary experiments

Preliminary runs conducted at pH 7 and initial [SLS] = 10 mg/L, and reported in Table 1, were carried out to evaluate the performance of each separate oxidant on the rate of SLS degradation. Initial rates were calculated as the difference between [SLS] values at zero and 20 min, divided by 20, with the results given in mg/L min.

It can be seen that either oxidant applied separately, even at the fairly high value of excess oxidant/SLS molar ratio $= 5$ perform slowly. In any of the runs, degradation did not exceed 50% in 60 min of reaction time.

Having confirmed the slow performance of both oxidants applied separately, tests were continued on the capability of singlet oxygen (generated by reaction of peroxide and hypochlorite) to significantly enhance the oxidative degradation of SLS in water. This was carried out using a factorial design with an initial range of variables given in Table 2. Additional experiments were later performed at pH 8 and at excess (H$_2$O$_2$ + NaClO)/SLS molar ratio levels of 1, 2 and 10, to further widen the range of the investigated variables.

Results of kinetic runs are presented in Table 3. Interpretation of the effects of each investigated variable are also given. Duplication of four runs in preliminary experiments not reported here allowed estimation of the maximum observed experimental error in the initial SLS degradation rate to be $\pm 0.03$ mg/L min. It was observed that in all runs pH remained constant ($\pm 0.1$) during the course of the reaction. This indicates that degradation of the surfactant function would have occurred without leading to mineralization, as it would be expected from reactions (3) to (5). Factorial design codes shown in Table 3, and statistical
analysis of main effects and factor interactions presented in Table 4, were carried out according to Box et al. (1978).

**Statistical analysis of the effects and interactions of investigated variables**

As the results of the preliminary runs showed that H$_2$O$_2$ promotes SLS degradation faster than NaClO does, when added as separate oxidants, the statistical analysis of the effect of the control variables on the initial rate of SLS degradation was studied based on the comparison of the action of $^1$O$_2$ generated by H$_2$O$_2$ + NaClO versus the direct H$_2$O$_2$ oxidation, for equal values of excess molar ratios of oxidant/SLS = 5, according to the stoichiometry of reactions (5) and (3).

The analysis of variance of the effect of the variables studied and their interaction was carried out according to Yates algorithm, as described by Box et al. (1978). The following variables were found to be statistically significant compared to the estimate of error:

<table>
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<tr>
<th>Exp.</th>
<th>Initial pH</th>
<th>H$_2$O$_2$/SLS</th>
<th>NaClO/SLS</th>
<th>[SLS] (mg/L) at sampling times 0; 20; 40; 60 min</th>
<th>Removal yield of SLS at 60 min (%)</th>
<th>Initial rate mg/L min</th>
<th>Factorial design code</th>
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Table 2 | Experimental design matrix – control variables and its ranges

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<th>High level</th>
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<td>pH</td>
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<td>Excess oxidant/SLS molar ratio</td>
<td>5 H$_2$O$_2$ to 1 SLS or (2.5 H$_2$O$_2$ + 2.5 NaClO) to 1 SLS or</td>
<td></td>
</tr>
<tr>
<td>Excess oxidant/SLS molar ratio</td>
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<td></td>
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<tr>
<td>Excess $^1$O$_2$/SLS molar ratio</td>
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<td>5.0</td>
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Table 3 | Results of kinetic runs

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[SLS] and [1O2]/SLS excess molar ratio generated by H2O2 + NaClO. The effect of pH was not found to be significant in the range of pH 6–7, as it was found to be comparable to the estimate of error of ±0.03 mg/L min.

The only factor interaction found to be significant was between (1O2/SLS) and initial [SLS]. This was interpreted as the effect of the two separate significant variables (factors) not being linearly additive. This result might be expected for a kinetic description of a chemical reaction which, if it were to be a simple irreversible reaction, would follow a non-linear rate law of the kind: \(-d[SLS]/dt = k[SLS][1O2]\), as opposed to an additive equation such as, for example, \(-d[SLS]/dt = k_1[SLS] + k_2[1O2]\).

Synergistic effect of combining peroxide and hypochlorite on SLS degradation

The comparisons within runs carried out at pH 6 and at pH 7 – the latter shown in Figure 1 – in which the decay of [SLS] over time is observed, demonstrate the increase obtained by the combination of 2.5 excess moles of H2O2 with 2.5 excess moles of NaClO, for the degradation of each 1 mol of SLS. The observed initial rate from the combined oxidants is much higher than the individual rates of degradation by 5 excess moles of each oxidant separately. These observations may be interpreted in light of the knowledge of the generation of 1O2 through the peroxide + hypochlorite reaction, as a validation of the hypothesis that 1O2 is generated in the process and is capable of inactivating the surfactant function of SLS molecules, at a rate significantly higher than equal molar doses of peroxide or hypochlorite added separately.
which in turn induces a corresponding increase in the rate of attack on the SLS molecules.

The same set of runs were used for the calculation of the apparent order of reaction (a) with respect to $[^1O_2]$ generated by $\text{H}_2\text{O}_2 + \text{NaClO}$. The ratio of $\log(-d[SLS]/dt)/\log[^1O_2]$ gave the average value of $a = 0.3$ for a suggested empirical relation of the type $-d[SLS]/dt = k[^1O_2]^a$.

**Effect of initial [SLS]**

The comparison of the initial rate of SLS degradation by $[^1O_2]$ at the two nominal levels of SLS concentration (5 and 10 mg/L) in four pairs of runs (exps 9 and 10, 11 and 14, 17 and 18, 15 and 19, in Table 3) shows that an increase in the [SLS] causes a corresponding increase in the SLS degradation rate, according to an empirical relation of the type $-d[SLS]/dt = k[SLS]^b$.

Using the rates from the same pairs of runs to calculate the apparent order of reaction (b) with respect to [SLS] using the log($-d[SLS]/dt$)/log[SLS] procedure, gave an average value of $b = 0.8$ (average value of the apparent order of each of the four pairs of runs at pH values 6, 7 and 8 (runs 9 and 10 $b = 0.63$, runs 11 and 14 $b = 1.01$, runs 17 and 18 $b = 0.93$, and runs 15 and 19 $b = 0.69$).

**Effect of pH**

Although the statistical analysis of the effect of pH indicated this to be non-significant compared to the error value in the pH interval 6–7, the results of further runs done at pH 7.5 and 8 suggest that the maximum rate is obtained within the range of pH 7–7.5, as reported in Table 3.

A pH effect was likely to exist over the wider pH range 6–8, as a point of inflection of the distribution between the conjugated species HClO/ClO$^-$/C$^0$ occurs at pH 7.5. In support of this hypothesis, earlier studies of the kinetics of $[^1O_2]$ generation by $\text{H}_2\text{O}_2 + \text{NaClO}$ carried out by Held et al. (1978), derived one rate law for the reaction between $\text{H}_2\text{O}_2$ and hypochlorous acid as $d[\text{O}_2]/dt = k_2[\text{HOCl}][\text{H}^+][\text{Cl}^-]$ for pH $< 7.5$ and a different rate law for pH $> 7.5$ involving the hypochlorite ion, as $d[\text{O}_2]/dt = k_3[H_2\text{O}_2][\text{OCI}^-]$.

**Simple mechanistic considerations**

It may be concluded that the SLS oxidative degradation reaction proceeds according to main reactions (6) and (7) below:

\[
\text{H}_2\text{O}_2 + \text{ClO}^- \rightarrow \text{H}_2\text{O} + \text{H}^+ + \text{Cl}^- + ^1\text{O}_2 \quad (6)
\]

and

\[
^{1}\text{O}_2 + \text{SLS} \rightarrow \text{degradation products} \quad (7)
\]

where the SLS degradation reaction (7) probably follows a multistep complex mechanism.

In addition to the above reactions (6) and (7), the following other two parallel reactions (8) and (9) take place, although to a lesser extent, in the course of the process.

Hydrogen peroxide direct degradation of SLS and hypochlorite direct degradation of SLS:

\[
\text{H}_2\text{O}_2 + \text{SLS} \rightarrow \text{degradation products} \quad (8)
\]

and

\[
\text{ClO}^- + \text{SLS} \rightarrow \text{degradation products} \quad (9)
\]

To add to the complexity of the scenario of the SLS degradation process by $[^1O_2]$, self-decomposition reactions of $\text{H}_2\text{O}_2$ and ClO$^-$ into oxygen also take place and interfere with the overall kinetics.

All these reactions combined certainly result in a complex system whose detailed investigation was beyond the scope of the present work. Nevertheless, for practical purposes, it is reasonable to derive a purely empirical rate equation which may approximately describe the investigated process as:

\[
d[SLS]/dt = k[SLS]^{0.8}[(\text{H}_2\text{O}_2 + \text{NaClO})]^{0.3} \quad (10)
\]

And, the rate constant calculated as the average of the $k$ values of each kinetic run reported in Table 2 is $k = 4.8 \times 10^{-1}$ L/mol s, at 25 °C.
The potential generation of organochloride byproducts was not part of the scope of this study. Nonetheless, a study by Eichhorn et al. (2002) on the behaviour of anionic surfactants subjected to chlorination during drinking water production indicates that chlorinated surfactants do not seem to be generated.

CONCLUSIONS

The advanced oxidation process driven by the aqueous reaction of hydrogen peroxide + sodium hypochlorite generating singlet oxygen was effective for the degradation of sodium laurel sulphate (SLS) in water, as the generated $^1$O$_2$ was seen to act significantly faster compared to H$_2$O$_2$ and ClO$^-$ when separately used at the same molar doses (excess molar ratio of oxidant/SLS).

The process was effective in the near neutral pH range of 6–8, and up to initial SLS concentration values of 10 mg/L.

In conditions of initial [SLS] of 5 or 10 mg/L, pH = 6–8, and excess molar ratio ([H$_2$O$_2$] + [NaClO])/[SLS] = 5, it was possible to achieve a final concentration of [SLS] < 0.5 mg/L (95% degradation) at $t$ = 60 min at 25 °C, in a batch reaction. By comparison, the same reaction with either of the separate oxidants (only H$_2$O$_2$ or only NaClO), at the same excess molar ratio oxidant/SLS of 5:1 gave a maximum of about 50% degradation of the SLS over the same 60 min reaction time.

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REFERENCES


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