Environmental Engineering and Management Journal

June 2019, Vol. 18, No. 6, 1245-1254
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

"Gheorghe Asachi" Technical University of Iasi, Romania

UV-H_2O_2 ADVANCED OXIDATION OF ANIONIC SURFACTANT: REACTION KINETICS, EFFECTS OF INTERFERING SUBSTANCES AND OPERATING CONDITIONS

Bijoli Mondal[1], Asok Adak[1*], Pallab Datta[2]

[1]Department of Civil Engineering, Indian Institute of Engineering Science and Technology,
Shibpur, Howrah 711103, India
[2]Center for Healthcare Science and Technology, Indian Institute of Engineering Science and Technology,
Shibpur, Howrah 711103, India

Abstract

This paper deals with the degradation kinetics of an anionic surfactant (sodium dodecyl sulfate, SDS) under UV and UV-H_2O_2 advanced oxidation process (AOP). Experiments were performed in a batch reactor which emits monochromatic light centered at 253.7 nm. The photon flux of the UV reactor was $1.9(\pm0.1)\times10^{-4}$ Einstein/L-min. Under direct UV, only 45% SDS degradation was observed at a fluence of 40.65 J/cm^2 for initial SDS concentration of 0.35 mM. The apparent fluence-based pseudo-first order rate constant was found to be $1.77(\pm0.24)\times10^{-5}$ cm^2/mJ. However, very fast degradation (almost 100%) was observed for UV-H_2O_2, process at a fluence of 0.45 J/cm^2. The apparent fluence-based rate constant in this case was found to be about 450 times higher than direct photolysis. Further, using a probe compound (para chlorobenzoic acid) competition kinetics study was performed to determine the second order hydroxyl radical rate constant for SDS. The rate constant thus obtained was $8.18\ (\pm0.26)\times10^{9}\ M^{-1}\ s^{-1}$. Effects of different operating parameters like H_2O_2 concentration, initial SDS concentration and water quality parameters, including pH (7 - 12), alkalinity (0 - 10 mM HCO_3^-) and nitrate concentration (0 - 1 mM as NO_3^-), were investigated. The observed rate constants were influenced by all the studied parameters and these parameters were optimized for field application. Degradation of SDS was also carried out in municipal wastewater. In conclusion, UV-H_2O_2 AOP is an efficient treatment method for SDS in environmental matrices.

Key words: direct photolysis, hydroxyl radical rate constant, scavenging effect, sodium dodecyl sulfate, wastewater

Received: May, 2017; Revised final: November, 2017; Accepted: January, 2018; Published in final edited form: June 2019

1. Introduction

Surfactants are long chain fatty acids with cleansing or solubilization properties. These contain both polar group (either charged or uncharged) and nonpolar hydrocarbon chain of 10 - 20 carbon atoms. There are four different types of surfactants such as anionic, cationic, non-ionic and amphoteric. The predominant classes of anionic surfactants are branched alkylbenzenesulfonate (ABS), linear alkylbenzenesulfonate (LAS) and linear alkyl sulfate. An example of linear alkyl sulfate is sodium dodecyl sulfate (SDS).

Surfactants are commonly used in various industries such as textile, fibre, dye, personal care product, paint, polymer, pharmaceutical, mining, and pulp-paper, along with being used for domestic activities (Kitinya et al., 2017; Rivera-Utrilla et al., 2012). After usage, surfactants are discharged into sewage treatment plants, creating beds of foam that appear near sewage outlets. Surfactants are harmful to fauna and flora in surface waters. For example, their

---

[*] Author to whom all correspondence should be addressed: e-mail: asok@civil.iiests.ac.in; Phone: +91-33-2668 4561 (extn. 713); Fax: +91-33-2668 2916

persistent presence in surface water even at toxic levels produces several pathological, physiological, and biochemical adverse effects on aquatic life. They cause break-down of chlorophyll–protein complex, cell death by damage to the cell membrane and delayed metabolism or growth rate (Onder et al., 2007). As per United States Environmental Protection Agency (USEPA), surfactants should not exceed an upper limit of 1.0 mg/L for class SW-1 waters (for salt pans, shell fishing, mariculture and Ecologically Sensitive Zone). Thus, the removal of surfactant is essential for the protection of water quality.

Surfactants-bearing wastewater can be treated by various physico-chemical methods like coagulation (Abbasi and Taheri, 2018; Beltran-Heredia et al., 2011; Bobirica et al., 2014; Mahmoud and Ahmed, 2014), adsorption (Kyzas et al., 2013; Raval and Desai, 2012; Yakout and Nayl, 2009), reverse osmosis (Kowalska, 2012; Zenouz, 2009), and chemical oxidation (Betianu et al., 2008; Lin et al., 1999; Orbeci et al., 2017). Each of these methods have certain advantages and disadvantages; whereas in general, treatment of wastewater with high surfactant concentration is difficult by any of the above methods. For example, reverse osmosis system is expensive to install and operate.

In coagulation process, large amounts of sludge are generated. While adsorption is widely used for removing organics from wastewater; this process results in only phase transfer of pollutants, instead of their elimination. The methods like coagulation, reverse osmosis and adsorption produces concentrated surfactant-bearing solutions which again requires treatment. On the other hand, biological process is eco-friendly as well as low cost treatment option particularly for low concentration of surfactants. For anionic surfactant removal, aerobic biological process is much more effective than anaerobic process but main problem is the high concentration of surfactants in wastewater particularly from industries. In aerobically digested sludge, their concentration is in the range of 100–500 mg/kg whereas anaerobically digested sludge contains an average of 1000–30000 mg LAS /kg sludge dry weight. When sludge contains 40-60 mg LAS /kg sludge dry weight, surfactants can affect the reproduction and growth of soil invertebrates and earthworms (Aonyas et al., 2016).

Due to this fact, many researchers have explored advanced oxidation processes (AOP) for degradation of surfactants. In AOPs non-selective hydroxyl radicals are generated which can oxidize organic contaminants to mineral end products. Furthermore, AOPs can be used as a pre-treatment for highly concentrated wastewater to increase the biodegradability of recalcitrant organics.

AOPs generally used to degrade various recalcitrant pollutants include photochemical process (Ghaderpoori and Dehghani, 2016; Olmez-Hanci et al., 2011; Paphane and Ramirez, 2013; Sanz et al., 2013), photocatalytic processes (TiO_2/UV) (Czech, 2012; Samadi et al., 2014; Shahbazi et al., 2014) and photo-Fenton processes (Chitra et al., 2014; Ono et al., 2012). However, the application of most of these processes remain limited due to high operational costs. Fenton process requires lower pH and continuous pH adjustment. Addition of iron in wastewater also creates problem of sludge disposal. In photocatalytic process, uniform UV irradiation is required. Therefore, to overcome such limitations of surfactant removal from wastewater, in the present study we propose to use a treatment of homogeneous UV-H_2O_2 AOP as a more efficient option to completely degrade one of the most widely used anionic surfactants - SDS. Previously, Sanz et al. (2013) have studied UV-H_2O_2 AOP for the pre-treatment of anionic surfactant (linear LAS) to enhance their biodegradability and temperature effect on the degradation of surfactant. However, detailed reaction kinetics or influence of different operating parameters for field application of degradation of anionic surfactant by UV-H_2O_2 AOP have not been yet reported. Hydroxyl radicals generated during a UV-H_2O_2 process are highly reactive to organic molecules (Zepp et al., 1992) and hence this process is expected to effectively degrade SDS.

The objective of this study is to evaluate the effectiveness of UV/H_2O_2 AOP for degradation of anionic surfactant SDS in wastewater at different operating conditions. In particular, the specific aims of this study are as follows: (1) to determine fluence-based reaction rate constants for the process; (2) to optimize H_2O_2 concentration; (3) to determine second order hydroxyl radical rate constant with SDS; (4) to identify influence of initial SDS concentration and (5) to examine the effects of water quality parameters, namely pH, alkalinity, nitrate concentration, and wastewater matrix on SDS degradation.

The goal of the work is to degrade concentrated surfactant solutions generated from industrial sources or from waste streams emanating from adsorption, coagulation-flocculation, and/or reverse osmosis treatment systems to a point where biological processes can treat the transformation products.

2. Material and methods

2.1. Materials

Acridine orange II (ACO) (MP Biomedical, France), glacial acetic acid and sodium dodecyl sulfate (SDS), toluene and H_2O_2 (Merck, India), were used as received. All other chemicals used in this study were of high purity and used without further purification.

2.2. UV Reactor

All experiments were conducted using batch UV reactor (M/s. Lab Tree, India) system which emits monochromatic light cantered at 253.7 nm. The UV reactor comprises of eight U.V. bulbs, fitted in a heavy metal enclosure with a highly polished stainless-steel reflector. The schematic diagram of the reactor is shown in Fig. 1.

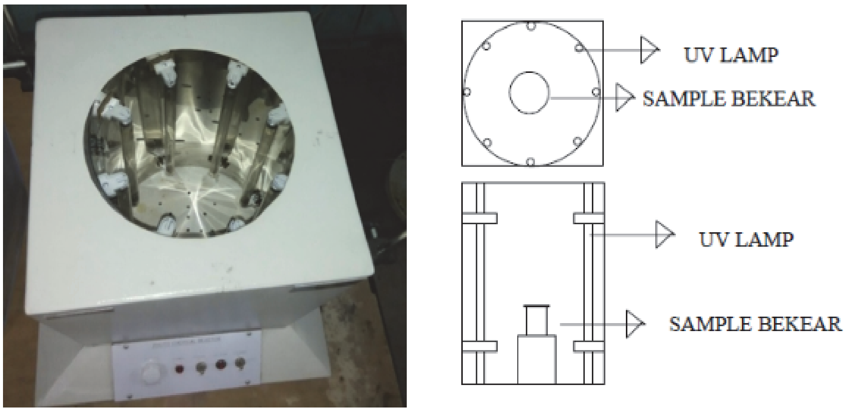

Fig. 1. Top view and schematic diagram of the UV Reactor

The UV photon flux was measured and monitored throughout the experiments by using potassium ferrioxalate actinometry (Hatchard and Parker, 1956). The photon flux and fluence of the UV reactor was 1.9(±0.1)×10^{-4} Einstein/L-min and 113(±5.7) mJ/cm^2-min, respectively.

2.3. Analytical methods

Anionic surfactant was determined using a simple, rapid and reliable spectrophotometric method (Adak et al., 2005). Acridine orange (ACO) was used as ion pairing agent with anionic surfactant. 10 mL of anionic surfactant solution (concentration in the range of 3.5×10^{-4} to 2.1×10^{-2} mM of SDS) was taken into a 25 mL separating funnel. Then, 100 μL glacial acetic acid and ACO (5 x10^{-3} M) were added; followed by addition of 5 mL toluene. The mixture was shaken for 1 min, and then it was allowed to separate the phases. The aqueous layer was discarded and the toluene layer was collected in cuvette. The absorbance of the toluene layer was measurement at 467 nm. The limit of detection of this spectrophotometric method is 1.4×10^{-3} mM (Adak et al., 2005).

2.4. Degradation studies of anionic surfactants

Direct photolysis and UV-H_2O_2 AOP experiments were performed in a batch reactor as mentioned in the previous section. The experiments were carried out with 100 mL of anionic surfactant (0.35 mM of SDS)-bearing synthetic wastewater and 10 mM phosphate buffer at 27(±2)°C. Such concentration of anionic surfactant is usually selected in earlier research for investigating removal of surfactants from wastewater (Ghaderpoori and Dehghani, 2016; Ríos et al., 2017). The samples for direct photolysis were exposed for 6 h. Samples were taken at every 30 min intervals and analysed for remaining SDS concentration. The integrated mass balance equation for direct photolysis of SDS is given in Eq. (1).

$$ln\frac{[SDS]}{[SDS]_0} = -k'_{app}H' \qquad (1)$$

In the above equation, *[SDS]* is SDS concentration at any time *t*; *$[SDS]_o$* is initial SDS concentration; k'_{app} is apparent fluence-based pseudo-first order rate constant (cm^2/mJ) and H' is the fluence corresponding to time *t* (mJ/cm^2). The fluence based rate constant will be required to select UV dose for real field application. For UV-H_2O_2 AOP, different peroxide concentration (0.125, 0.25, 0.5, 1, 2, 5, and 7.5, mol of H_2O_2/mol of SDS) were investigated to identify the concentration for maximum degradation of surfactant. The pH of the solution was kept at 7±(0.1) using 10 mM phosphate buffer. Samples were taken at regular intervals from 0 to 10 min of irradiation.

The experimental results were analyzed by above kinetic model (Eq. 1). Furthermore, influence of initial SDS concentration in the range of 0.35 – 3.5 mM (100 - 1000 mg/L) were studied. A competition kinetic study was performed to determine the second order hydroxyl radical rate constant with SDS. Para chlorobenzoic acid (pCBA) was used as a reference compound for this experiment. Under direct photolysis of pCBA, the apparent fluence-based pseudo-first order rate constant was found to be 8.0×10^{-05} cm^2/mJ. Second order hydroxyl radical rate constant for transformation of pCBA reported in literature is 5.8×10^9 $M^{-1}s^{-1}$ (Buxton et al., 1988). The ratio of surfactant to pCBA was taken as 1 mol pCBA/ mol SDS. The peroxide concentration was kept at 1 mol H_2O_2/mol of SDS.

The effects of pH (5 - 12) and other interfering substances such as bicarbonate and nitrate on SDS transformation were also studied. In addition, SDS degradation experiments were conducted in the municipal wastewater collected from IIEST Shibpur campus. In all cases, the SDS concentration was 0.35 mM (100 mg/L) and peroxide concentration was 1 mol H_2O_2/mol SDS. Raw wastewater was collected from municipal sewer having five-day biochemical oxygen demand (BOD_5) of 200 mg/L, chemical oxygen demand (COD) of 848 mg/L, total solids of 1334 mg/L, fixed solids of 950 mg/L and dissolved solids of 384 mg/L. The AS concentration in raw wastewater was found to be 6.3×10^{-3} mM (as SDS). It was filtered using a commercial filter paper and followed by Whatman 42 filter paper. The filtrate was used to prepare 0.35 mM SDS spiked sample.

The biodegradability of intermediate products was examined for transformation of SDS, spiked in distilled water by UV-H_2O_2 treatment. The BOD_5 and COD of the degraded samples were measured, and the BOD_5/COD ratio was used to describe changes in biodegradability. Results are reported as mean ± SD for N = 3 unless otherwise stated. Origin Pro8 software was used for analysis of variance (ANOVA) of the experimental data. Significant difference was asserted at 95% confidence interval ($p < 0.05$).

3. Result and discussions

3.1. Effect of UV irradiation on SDS removal

SDS solution (0.35 mM) was subjected to UV radiation at 253.7 nm for different time periods up to 6 h at pH 7±(0.1). Fig. 2 indicates that maximum degradation obtained at 6 h irradiation was not more than 45%, showing low efficiency of direct photolysis of SDS as also reported previously (Adak et al., 2014). The transformation of SDS followed the pseudo first order kinetic model. The time-based rate constant was $2.20(\pm 0.27)\times 10^{-3}$ min^{-1} and the fluence based rate constant was found to be $1.77(\pm 0.23)\times 10^{-5}$ cm^2/mJ.

In addition, quantum yields were also calculated for the degradation of SDS by UV irradiation. Quantum yield is useful for determination of the photolytic efficiency and it is defined as the moles of a compound transformed per mole of photons absorbed by the compound (Bolton and Stefan, 2002). Apparent fluence-based pseudo-first order rate constant was used to calculate the apparent quantum yield (Eq. 2).

$$k'_{p,app} = \frac{\Phi_{253.7,app}\varepsilon_{253.7,app} \ln 10}{U_{253.7}} \qquad (2)$$

In Eq. 2, $k'_{\mathrm{p,app}}$ is the experimentally determined apparent fluence-based pseudo-first order photolysis rate constant (cm^2 mJ^{-1}), $\Phi_{253.7,app}$ is the apparent quantum yield at 253.7 nm (mol $Einstein^{-1}$), $\varepsilon_{253.7,app}$ is the apparent molar absorptivity at 253.7 nm (M^{-1} cm^{-1}), and $U_{253.7}$ is the molar photon energy at 253.7 nm (4.72×10^5 J $Einstein^{-1}$). The quantum yield for degradation of SDS was found to be 0.385(±0.034) mol $Einstein^{-1}$. It is to note that UV absorbance at 254 nm of SDS solution (0.35 mM) and its degraded samples was very low (<0.010 cm^{-1}). Comparable quantum yields of 0.582 mol $Einstein^{-1}$ and 1.344 mol $Einstein^{-1}$ for cetyltrimethylammonium bromide and LAS respectively have been reported in previous studies (Acharya and Rebery, 2009; Sanz et al., 2003).

3.2. Removal of SDS in presence of only H_2O_2

Solution with initial SDS concentration of 0.35 mM and H_2O_2 concentration of 1 mol of H_2O_2/ mol of SDS was kept in dark to observe the effect of only H_2O_2 on SDS degradation. Samples were withdrawn at different time intervals and analysed. No significant SDS degradation was observed upto a period of 30 days. This is because hydroxyl radicals were not formed without UV radiation (Adak et al., 2014).

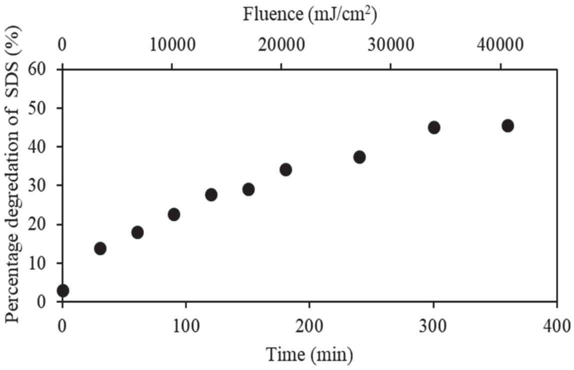

Fig. 2. Degradation of SDS spiked in distilled water at UV 253.7 nm at pH 7.0(±0.1)

3.3. Effect of UV-H_2O_2 on SDS removal

To examine the effect of UV-H_2O_2 AOP, SDS solution having initial concentration of 0.35 mM and pH of 7(±0.1) was treated with H_2O_2 and irradiated with UV. Samples were withdrawn at specified time intervals and analyzed for kinetic model. It was observed that almost 100% degradation of SDS was achieved within 4 min (Fig. 3). The contribution of hydroxyl radicals to the total degradation of SDS was found to be about 100%. Kinetic analysis showed that degradation followed the pseudo-first order kinetic model. Time- and fluence-based rate constants were found to be 0.9130(±0.18) min^{-1} and $8.10(\pm 1.6)\times 10^{-3}$ cm^2/mJ respectively. Rate constants found in this case were ~ 460 times higher compared to those calculated from SDS degradation through direct photolysis. The COD removal corresponding to 4 min of UV irradiation was found to be ~21%. This is comparable to the degradation of alkyl-dimethylbenzyl ammonium chlorides by UV-H_2O_2 process (Adams and Kuzhikannil, 2000). This study also reported that UV-H_2O_2 pre-treatment increased the efficiency of biodegradation of the surfactant upto 90%.

At a disinfection-level UV dose of 40-190 mJ/cm^2, negligible (< 0.16%) transformation is expected for SDS. However, the same fluence with a ratio of 1 mol H_2O_2/mol SDS yields transformation efficiencies of 9% and 43% for 40 and 190 mJ/cm^2 respectively. UV doses typically employed in advanced oxidation are 540–2000 mJ/cm^2 (Baeza and Knappe, 2011; Keen et al., 2012). Increasing the fluence to 450 mJ/cm^2 and employing 1 mol H_2O_2/mol SDS allowed greater than 98% transformation of SDS.

To investigate effect of H_2O_2 concentration in UV-H_2O_2, 0.35 mM SDS solution was degraded with the fluence of 0.45 J/cm^2 keeping the pH constant at 7(±0.1) and varying the peroxide concentration as follows: 0.125, 0.25, 0.5, 1, 2, 5 and 7.5, mol H_2O_2/ mol SDS.

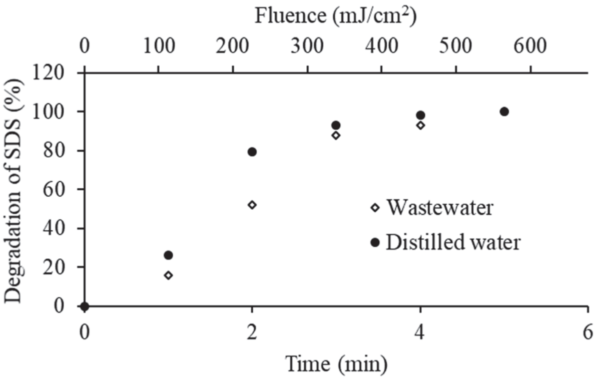

Fig. 3. Degradation of SDS (0.35 mM) spiked in distilled water and wastewater by UV-H_2O_2 process with $[H_2O_2]/[SDS] = 1$ at pH 7.0(±0.1)

Fig. 4 shows the fluence-based SDS degradation rate constants at different H_2O_2 concentration. The fluence-based rate constants significantly increase with the increase of H_2O_2 concentration when the H_2O_2 concentration is below 1 mol H_2O_2/ mol SDS. When the H_2O_2 concentration is over 1 mol H_2O_2/ mol SDS, the fluence based rate constant showed significant decrease as H_2O_2 concentration was increased.

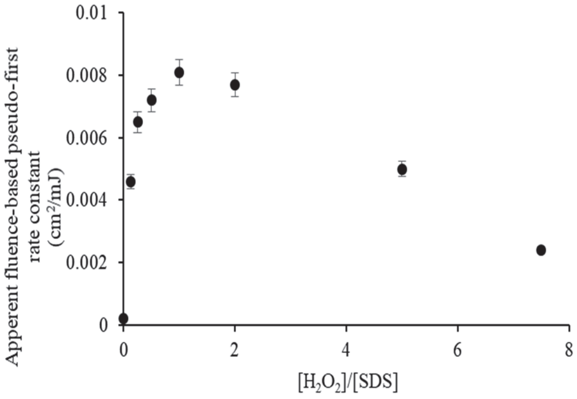

Fig. 4. Effect of concentration of H_2O_2 on SDS (0.35 mM) degradation rate constant at pH 7.0(±0.1) ($p = 1.01\times10^{-5}$ for groups $[H_2O_2]/[SDS] = 0$ to 7.5 and $p = 0.048$ for groups $[H_2O_2]/[SDS] = 1$ to 2)

At higher peroxide concentration, additional H_2O_2 did not increase appreciably the degradation efficiency. This may be due to hydroxyl radicals reacting with excess H_2O_2 rather than SDS molecules. The reaction between hydroxyl radical and H_2O_2 produces hydroperoxyl radicals which are less reactive compared to the hydroxyl radicals (Adak et al., 2014; Lopez et al., 2003; Ríos et al., 2017). Furthermore, the steady state hydroxyl radical concentration was determined to be $5.7(\pm0.2)\times10^{-11}$, $8.2(\pm0.3)\times10^{-11}$, $9.9(\pm0.3)\times10^{-11}$, $11.5(\pm0.6)\times10^{-11}$, $10.6(\pm0.4)\times10^{-11}$, $5.9(\pm0.2)\times10^{-11}$ and $2.6(\pm0.1)\times10^{-11}$ M at 0.125, 0.25, 0.5, 1, 2, 5, and 7.5 mol H_2O_2/mol SDS respectively. Thus, optimum H_2O_2 concentration in this case might be selected as 1 mol H_2O_2/ mol SDS.

3.4. Effect of initial SDS concentration

To observe the effect of initial SDS concentration on UV-H_2O_2 degradation process, SDS solution (0.35-3.5 mM concentration range at pH 7.0(±0.1)) were irradiated with a peroxide concentration of 1 mol H_2O_2/ mol SDS. The efficiency of the process for different concentrations of SDS is shown in Fig. 5. The SDS degradation significantly decreased with increasing initial concentration. Ríos et al. (2017) also reported that removal efficiency decreased with increased anionic surfactants concentration. Almost 100% degradation of SDS with an initial concentration of 0.35 mM was obtained with a UV fluence of 450 mJ/cm^2, whereas, the degradation efficiencies were found to be only 75%, 43% and 11% for initial SDS concentration of 0.7, 1.75 and 3.5 mM respectively for the same fluence dose (Fig. 5). These results are in accordance with the results of other studies like microcystin – LR and diethanolamine (DEA), using UV-H_2O_2 AOP (He et al., 2011; Madihah et al., 2015). The molar absorptivity of SDS and H_2O_2 are 11.53 and 19.6 $M^{-1}cm^{-1}$ respectively. Thus, it is expected that the production of hydroxyl radical will not be sufficient at higher SDS concentration. However, when SDS concentration is high, the concentration of H_2O_2 is also high which may scavenge the hydroxyl radical. Thus, the rate constant decreased with increasing SDS concentration.

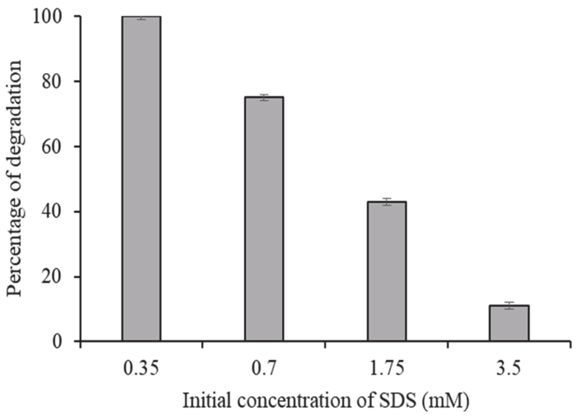

Fig. 5. Influence of SDS initial concentration on its degradation with $[H_2O_2]/[SDS] = 1$ at pH 7.0(±0.1) ($p = 2.07\times10^{-10}$ for SDS concentration range of 0.35 to 3.5 mM)

3.5. Competition kinetic study for determining second order hydroxyl radical rate constants with SDS

Competition kinetic experiments were performed to determine second order hydroxyl radical rate constant of SDS. Here, pCBA was used as a hydroxyl radical reference compound. In the absence of H_2O_2, surfactant and pCBA showed fractional transformation by UV light at 253.7 nm. The corresponding pseudo-first order rate constants for UV irradiation were added in the competition kinetics relationship. The integrated form of the mass balance on SDS in the batch reactor can be written as shown in Eq. (3).

$$-ln\frac{[SDS]}{[SDS]_0} = {}^{\circ}k'_{p,{}^{\circ}SDS}\,{}^{\circ}H' + k''_{OH\cdot,SDS}\int_0^t [OH\cdot]dt \quad (3)$$

In Eq. (3), *[SDS]* is the concentration of SDS at time t, $k'_{p,SDS}$ is the fluence-based pseudo-first order rate constant for SDS, $[OH\cdot]$ is the hydroxyl radical concentration, and $k''_{OH\cdot,SDS}$ is the second order rate constant for transformation of SDS by hydroxyl radicals. Transformation of a pCBA can be described by a similar relationship (Eq. 4).

$$-ln\frac{[pCBA]}{[pCBA]_0} = {}^{\circ}k'_{p,{}^{\circ}pCBA}\,{}^{\circ}H' + k''_{OH\cdot,pCBA}\int_0^t [OH\cdot]dt \quad (4)$$

Assuming pCBA and the surfactant experience the same hydroxyl radical exposure (i.e., $\int_0^t [HO\cdot]\,dt$), Eq. (5) can be used to determine $k''_{OH\cdot,SDS}$.

$$ln\frac{[SDS]}{[SDS]_0}.+{}^{\circ}k'_{p,{}^{\circ}SDS}\cdot = \left[ln\frac{[pCBA]}{[pCBA]_0}\circ+{}^{\circ}k'_{p,pCBA}\,{}^{\circ}H'\right]\frac{k''_{OH\cdot,SDS}}{k''_{OH\cdot,pCBA}}\cdot \quad (5)$$

Therefore, from the slope of a plot of

$$ln\frac{[SDS\ ]}{[SDS\ ]_0}.+{}^{\circ}k'_{p,{}^{\circ}SDS}\cdot \text{ vs. } \left[ln\frac{[pCBA]}{[pCBA]_0}\circ+{}^{\circ}k'_{p,pCBA}\,{}^{\circ}H'\right]\frac{k''_{OH\cdot,SDS}}{k''_{OH\cdot,pCBA}}\cdot;$$

$k''_{OH.,SDS}$ can be directly determined as mentioned in Fig. 6. The second order hydroxyl radical rate constants with SDS was found to be 8.18(±0.26)×10^9 M^{-1} s^{-1}. The second order hydroxyl radical rate constants with sodium dodecylbenzenesulfonate has been reported as 1.6(±0.1)×10^{10} M^{-1} s^{-1} (Ikehata and El-din, 2004).

3.6. Effect of solution pH on SDS degradation by UV-H_2O_2

As the pH of wastewater coming from different industries like textile, dye varies greatly, the effect of this parameter on UV-H_2O_2 process was studied. The experiments were conducted at different pH in the range of 5-12 with initial SDS concentration of 0.35 mM and a peroxide concentration of 1 mol H_2O_2/mol SDS. The pH of the solution was maintained by 10 mM phosphate buffer. It was observed that degradation of SDS was effective near pH 5-8 with no significant difference in this range (Fig. 7). Increase in pH beyond 10 resulted in a significant decrease in apparent fluence based rate constant as well as removal efficiency.

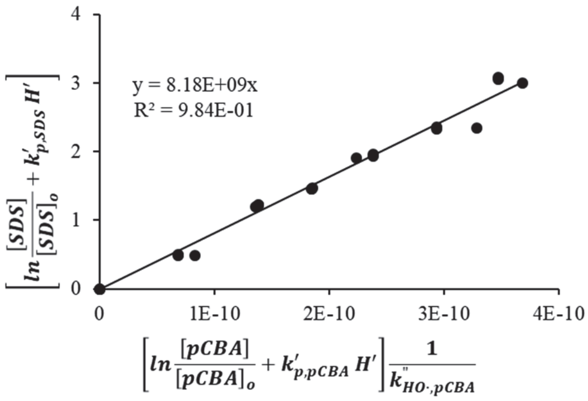

Fig. 6. Determination of the second order rate constant for SDS (0.35 mM) transformation by hydroxyl radicals using competition kinetic study at pH 7.0(±0.1)

At higher pH, H_2O_2 (pKa =11.8) is ionized to hydroperoxide (HO_2^-) (molar absorptivity at 254 nm =240 M^{-1} cm^{-1}) ion having a much higher molar absoptivity than hydrogen peroxide (molar absorptivity at 254 nm = 18.6 $M^{-1}cm^{-1}$) and can react both with hydrogen peroxide and hydroxyl radicals leading to reduction of hydroxyl radicals (Ríos et al., 2017). This resulted in lower rate constant at higher pH. Moreover, the steady state concentration of hydroxyl radical was determined to be 11.1(±0.4)×10^{-11}, 10.5(±0.3)×10^{-11}, 11.4(±0.4)×10^{-11}, 9.1(±0.3)×10^{-11}, 9.0(±0.3)×10^{-11}, 7.6(±0.2)×10^{-11}, 5.0(±0.1)×10^{-11} and 4.17(±0.4)×10^{-11} M for pH 5, 6, 7, 8, 9, 10, 11 and 12 respectively.

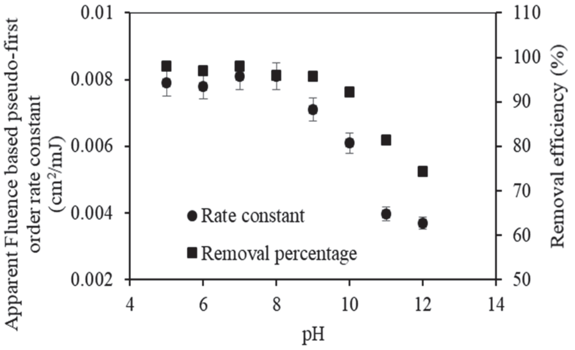

Fig. 7. Effect of solution pH on removal efficiency for a fluence of 450 mJ/cm² with the corresponding apparent fluence-based pseudo-first order rate constant for SDS degradation by UV - H_2O_2 process with [H_2O_2]/[SDS] = 1 (p = 0.9907 for pH range 5 to 8 and p = 0.000241 for pH range 8 to 12)

3.7. Effect of bicarbonate

The effect of bicarbonate concentration (0-10 mM) on SDS degradation was investigated for solutions containing 0.35 mM of SDS with a peroxide concentration of 1 mol H_2O_2/mol SDS at pH of 7(±0.1). The second order hydroxyl radical rate constant for bicarbonate was reported to be 8.5×10^6 M^{-1} s^{-1} (Buxton et al., 1988). This reaction rate is much slower than hydroxyl radical reaction with SDS, for which a rate constant of 8.18×10^{9} M^{-1} s^{-1} was determined. The apparent fluence-based rate constant showed significant decrease with increasing bicarbonate concentration (Fig. 8). The fraction of hydroxyl radicals that reacts with bicarbonate compared to all other species is expressed by Eq. (6) (adapted from Adak et al., 2014).

$$f_{HO\cdot,HCO_3^-} = \frac{k''_{HO\cdot,HCO_3^-}\left[HCO_3^-\right]}{k''_{HO\cdot,SDS}\left[SDS\right]+k''_{HO\cdot,HCO_3^-}\left[HCO_3^-\right]+\sum_{i=1}^{n}k''_{HO\cdot,S_i}\left[S_i\right]} \qquad (6)$$

where, $[S_i]$ *is* concentration of other hydroxyl radical scavengers like carbonate, phosphate, and hydrogen peroxide; $k''_{HO\cdot,S_i}$ is the second order hydroxyl radical rate constant of scavengers; $k''_{HO\cdot,HCO_3^-}$ is the second order hydroxyl radical rate constant of carbonate and $k''_{HO\cdot,SDS}$ is the second order hydroxyl radical rate constant of SDS. The fraction of hydroxyl radicals consumed by bicarbonate was calculated to be 3.0×10^{-3}, 7.4×10^{-3}, 14.7×10^{-3}, and 28.9×10^{-3} for bicarbonate concentrations of 1, 2.5, 5, and 10 mM, respectively. Hydroxyl radical scavenging by bicarbonate resulted in a lower fraction of hydroxyl radicals reacting with SDS (*i.e.*, $f_{HO\bullet SDS}$ =0.99, 0.98, 0.97, and 0.96) respectively. The hydroxyl radical demand of hydrogen peroxide and phosphate was about 3.20% and 0.22% respectively. These findings indicate that alkalinity differences in surfactant contaminated water may impact the observed reaction kinetics in UV-H_2O_2 systems; furthermore, these findings also suggest that real water matrices containing high concentrations of dissolved organic matter may further determine surfactant treatment efficiency through hydroxyl radical scavenging.

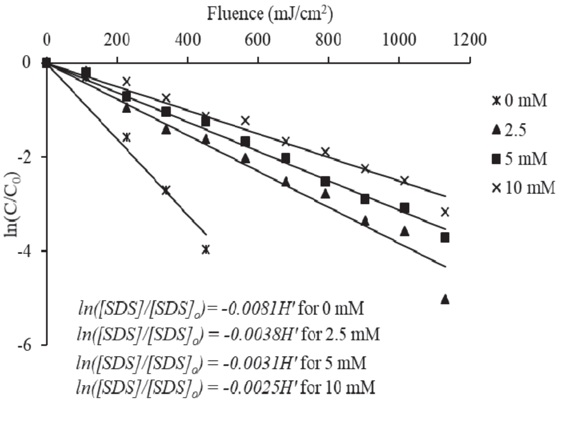

Fig. 8. Effect of alkalinity (expressed as HCO_3^- concentration) on SDS degradation process having initial concentration of 0.35 mM with $[H_2O_2]/[SDS]=1$ and pH 7.0(±0.1) ($p = 0.000145$ between 0 and 10 mM bicarbonate and $p = 0.016$ between 2.5 and 10 mM bicarbonate)

3.8. Effect of nitrate concentration

Generally, surface water and wastewater contain high concentrations of nitrate. The effect of nitrate (0-1 mM) on SDS photodegradation was studied. In these experiments, initial SDS concentration was taken as 0.35 mM. The peroxide concentration and pH were 1 mol H_2O_2/mol for SDS and 7 respectively. Experimental data were analyzed using a first order kinetic model and apparent fluence-based pseudo-first order rate constants were calculated (Fig. 9). The observed rate constant decreased linearly with significant difference between studied groups for nitrate concentrations of 0 to 1 mM due to scavenging of hydroxyl radicals by nitrate ($k''_{HO\cdot,NO_3^-} = 9.7\times10^{9}$ M^{-1} s^{-1} (Buxton et al., 1988)). The fractions of hydroxyl radicals consumed by nitrate were calculated to be 0.46, 0.63, 0.72 and 0.77 for nitrate concentrations of 0.25, 0.50, 0.75 and 1.0 mM, respectively. Hydroxyl radical scavenging by nitrate, therefore, resulted in a lower fraction of hydroxyl radicals reacting with SDS (*i.e.*, $f_{HO\bullet,SDS} = 0.54$, 0.37, 0.28, and 0.23 respectively). The hydroxyl radical demand of hydrogen peroxide for these experiments was approximately 3%. The effect of nitrate was found to be more pronounced compared to alkalinity of water sample.

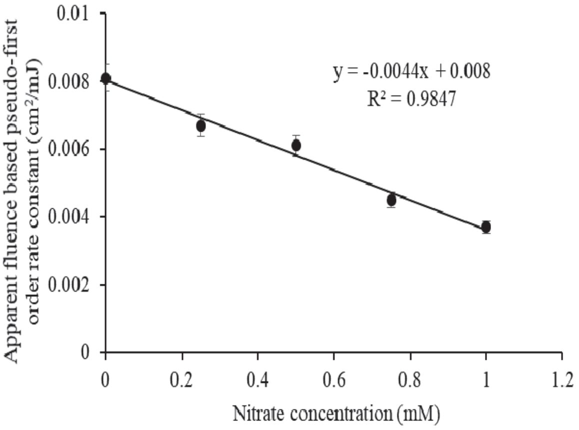

Fig. 9. Effect of nitrate on SDS degradation in the UV-H_2O_2 process having initial SDS concentration of 0.35 mM with $[H_2O_2]/[SDS]=1$ and pH 7.0(±0.1) ($p = 0.0067$ for 0 to 1 mM nitrate concentration)

3.9. Effect of municipal wastewater on surfactant degradation

SDS solution having initial concentration of 0.35 mM was prepared with filtered municipal wastewater having BOD_5 of 200 mg/L, COD of 848 mg/L, total solids of 1334 mg/L, fixed solids of 950 mg/L and dissolved solids of 384 mg/L. The $[H_2O_2]/[SDS]$ was 1 and the pH was 7.1(±0.1). It was observed that after addition of SDS in filtered wastewater the COD value increased to 1100 mg/L. This indicated that the contribution of COD for 0.35 mM of SDS is approximately 252 mg/L. The degradation of SDS in this case was found to be less compared to distilled water spiked samples (Fig. 3). For example, the degradation of SDS at 2 min were found to be 73(±6.2) and 49(±4.8)% for distilled water spiked and wastewater spiked samples respectively ($p = 0.006$). The fluence- and time-based rate constants for this case were found to be 5.5×10^{-3} cm^2/mJ and 0.6189 min^{-1} respectively. These values were ~1.4 times lower compared to the rate constant found in case of distilled water spiked samples at pH 7(±0.1). The UV absorbance of wastewater at 253.7 nm was determined to be 0.629 cm^{-1}. This high absorbance significantly hinders photolysis of H_2O_2. Furthermore, slower kinetics in wastewater matrix can be attributed to the scavenging of hydroxyl radicals by dissolved organic matter (as represented by COD) present in wastewater matrix. Thus, the results are in consonance with other documented results (Cater et al., 2000; Wang et al., 2006; Westerhoff et al., 1999).

3.10. Biodegradability

Due to the high operating costs of AOPs, application of short-term AOP followed by biological treatment is preferred for recalcitrant pollutants like SDS. Thus, it is required to examine the biodegradability of the SDS transformation products. Biodegradability can be represented by the ratio of biochemical oxygen demand (BOD_5) to chemical oxygen demand (COD). Fig. 10 shows the BOD_5/COD of UV-H_2O_2 treated effluents at different time. It was observed that BOD_5/COD increased significantly with time. In particular, 0.35 mM SDS solutions were treated by UV-H_2O_2 for 2, 4, 6, and 8 min. Residual H_2O_2 in the treated samples was quenched by catalase before measurement of BOD_5 and COD. The initial BOD_5/COD ratio for 0.35 mM of SDS solution was found to be 0.12 (±0.02), indicating that SDS is not biodegradable. BOD_5/COD fraction increased from 0.12 to 0.6 fraction within 8 min of degradation for 0.35 mM of SDS. Further, it is to note that initial BOD_5 and COD were determined to be 30 and 255 mg/L respectively.

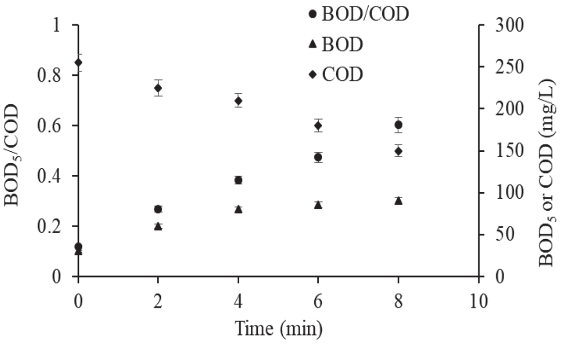

Fig. 10. Increase in biodegradability for UV-H_2O_2 degraded 0.35 mM SDS at $[H_2O_2]/[SDS] = 1$ at pH 7.0(±0.1) ($p = 1.23\times10^{-12}$ for 0 to 8 min)

4. Conclusions

In summary, disinfection-level UV treatment at 253.7 nm transforms a nominal fraction (< 0.16%) of SDS in water and indicates the need for higher fluence to attain significant transformation efficiencies. For the UV-H_2O_2 process, 100% transformation of SDS was achieved with a fluence of 450 mJ/cm^2 and peroxide concentration of 1 mol H_2O_2/mol SDS.

The rate constants for UV irradiation at 253.7 nm and transformation by hydroxyl radicals are comparable to other systems; however, pH, alkalinity, and nitrate concentrations may affect surfactant transformation. The pH in the range of 5-8 demonstrated no significant effect on SDS transformation; whereas the degradation rate constant decreased in the range 8-12. The transformation of SDS was adversely affected with increase in nitrate concentration in the range of 0 to 1 mM. Though low alkalinity (up to 2.5 mM of HCO_3^-) demonstrated no significant effect on SDS transformation, bicarbonate concentration of 10 mM, resulted in near 50% decrease in rate constant. The second order hydroxyl radical rate constant for SDS was found to be $8.18(\pm0.26)\times10^9$ M^{-1} s^{-1}. Municipal wastewater matrix showed more adverse effect on SDS degradation compared to distilled water spiked samples.

The biodegradability of SDS as well as intermediate products was significantly increased after oxidation. Corresponding BOD_5 was increased from 30 mg/L (0 min) to 90 mg/L (30 min). Thus, it is concluded that UV-H_2O_2 AOP provides an efficient and quick transformation of anionic surfactant and is proposed for treatment of concentrated surfactant solutions generated from industrial sources or from waste streams emanating from adsorption, coagulation-flocculation, and/or reverse osmosis treatment systems.

Acknowledgements

Bijoli Mondal acknowledges the institute scholarship support received from Ministry of Human Resources and Development, Govt. of India.

References

Abbasi M., Taheri A., (2018), Treatment of synthetic oily wastewaters by coagulation - MF hybrid process using mullite - alumina ceramic membranes, *Environmental Engineering and Management Journal*, **17**, 551-559.

Acharya S., Rebery B., (2009), Fluorescence spectrometric study of eosin yellow dye – surfactant interactions, *Arabian Journal of Chemistry*, **2**, 7-12.

Adak A., Pal A., Bandyopadhyay M., (2005), Spectrophotometric determination of anionic surfactants in wastewater using acridine orange*, Indian Journal of Chemical Technology*, **12**, 145-148.

Adak A., Mangalgiri K.P., Lee J., Blaney L., (2014), UV irradiation and UV-H_2O_2 advanced oxidation of the roxarsone and nitarsone organoarsenicals, *Water Research*, **70**, 74-85.

Adams C.D., Kuzhikannil J.J., (2000), Effects of UV/H_2O_2 preoxidation on the aerobic biodegredability of quaternary amine surfactants, *Water Research*, **34**, 668-672.

Aonyas M.M., Dojcinovic B.P., Dolic S.D., Obradovic B.M., Manojlovic D.D., Markovic M.D., Roglic G.M., (2016), Degradation of anionic surfactants using the reactor based on dielectric barrier discharge, *Journal of the Serbian Chemical Society*, **81**, 1097-1107.

Baeza C., Knappe D.R.U., (2011), Transformation kinetics of biochemically active compounds in low-pressure UV Photolysis and UV/H_2O_2 advanced oxidation processes, *Water Research*, **45**, 4531-4543.

Beltran-Heredia J., Sanchez-Martin J., Barrado-Moreno M., (2011), Removal of anionic surfactants in aqueous solutions with Moringa Oleifera seed extract coagulant, *Sustainability*, DOI: 10.3390/wsf-00628.

Betianu C., Caliman F.A., Gavrilescu M., Cretescu I., Cojocaru C., Poulios I., (2008), Response surface methodology applied for Orange II photocatalytic degradation in TiO2 aqueous suspensions, *Journal of Chemical Technology and Biotecchnology*, **83**, 1454-1465.

Bobirica C., Dabija G., Bobirica L., Mihai M., Costache C., (2014), Performance evaluation of anionic polymer-cationic surfactant complex coagulants in water treatment, *Environmental Engineering and Management Journal*, **13**, 2045-2050.

Bolton J.R., Stefan M.I., (2002), Fundamental photochemical approach to the concepts of fluence (UV dose) and electrical energy efficiency in photochemical degradation reactions, *Research on Chemical Intermediates*, **28**, 857-870.

Buxton G.V, Greenstock C.L., Helman W.P., Ross A.B., (1988), Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O) in aqueous solution, *Journal of Physical and Chemical Reference Data*, **17**, 513-886.

Cater S.R., Stefan M.I. Bolton J.R., Safarzadeh-Amiri A., (2000), UV/H_2O_2 treatment of methyl tert-butyl ether in contaminated waters, *Environmental Science & Technology*, **34**, 659-662.

Chitra S., Paramasivan K., Shanmugamani A. G., Rao S. V. S., Paul B, (2014), Advanced oxidation processes for the treatment of surfactant wastes, *Journal of Chemical Engineering and Chemistry Research*, **1**, 163-173.

Czech B., (2012), Advanced photooxidation of surfactants in wastewater, *Chemik*, **66**, 1314–1325.

Ghaderpoori M., Dehghani M. H., (2016), Investigating the removal of linear alkyl benzene sulfonate from aqueous solution by ultraviolet irradiation and hydrogen peroxide process, *Desalination and Water Treatment*, **57**, 15208-15212.

Hatchard C.G., Parker C.A., (1956), A new sensitive chemical actinometer. II. potassium ferrioxalate as a standard chemical actinometer, *Proceedings of the Royal Society A*, **235**, 518-536.

He X., Pelaez M., Westrick J.A., Shea K.E.O., Hiskia A., Triantis T., Kaloudis T., (2011), Efficient removal of microcystin-LR by UV-C/H_2O_2 in synthetic and natural water samples, *Water Research*, **46**, 1501-1510.

Ikehata K., El-din M.G., (2004), Degradation of recalcitrant surfactants in wastewater by ozonation and advanced oxidation processes: a review, *Ozone: Science & Engineering*, **26**, 327-343.

Keen O.S., Love, N.G., Linden K.G., (2012), The role of effluent nitrate in trace organic chemical oxidation during UV disinfection, *Water Research*, **46**, 5224-5234.

Kitinya J., Onyango M., Ochieng A., (2017), Removal of multilan red and multi-active blue dyes from aqueous solution by adsorption and oxidation techniques: equilibrium, kinetics and thermodynamic studies, *Environmental Engineering and Management Journal*, **16,** 2731-2743.

Kowalska I., (2012), Separation of anionic surfactants in a sequential ultrafiltration – ion exchange purification system, *Polish Journal of Environmental Studies*, **21**, 677-684.

Kyzas G.Z., Peleka E.N., Deliyanni E.A., (2013), Nanocrystalline akaganeite as adsorbent for surfactant removal from aqueous solutions, *Materials*, **6**, 184-197.

Lin S.H., Lin C. M., Leu H.G., (1999), Operating characteristics and kinetics studies of surfactant wastewater treatment by fenton oxidation, *Water Research*, **33**, 1735-1741.

Lopez A., Bozzi A., Mascolo G., Kiwi J., (2003), Kinetic investigation on UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution, *Journal of Photochemistry and Photobiology A: Chemistry*, **156**, 121-126.

Madihah N., Yaser B., Chemat F., Rashid T., Thanabalan M., (2015), Degradation of aqueous diethanolamine (DEA) solutions using UV/H $_2O_2$ process, *Chemical Engineering Transactions*, **43**, 1-6.

Mahmoud S.S., Ahmed M.M., (2014), Removal of surfactants in wastewater electrocoagulation method using iron electrodes, *Physical Sciences Research International*, **2**, 28-34.

Olmez-Hanci T., Arslan-Alaton I. Basar G., (2011), Multivariate analysis of anionic, cationic and nonionic textile surfactant degradation with the H_2O_2/UV-C process by using the capabilities of response surface methodology, *Journal of Hazardous Materials*, **185**, 193-203.

Onder E., Koparal A.S., Ogutveren U.B., (2007), An alternative method for the removal of surfactants from water: electrochemical coagulation, *Separation and Purification Technology*, **52**, 527-532.

Ono E., Tokumura M., Kawase Y., (2012), Photo-Fenton degradation of non-ionic surfactant and its mixture with cationic or anionic surfactant, *Journal of Environmental Science and Health, Part A*, **47**, 1087-1095.

Orbeci C., Stanescu R., Negoescu D., Parvulescu V., (2017), Synthesis, characterization and functionalization of MCM-41 for the removal of organic compounds from wastewaters, *Environmental Engineering and Management Journal*, **16**, 553-560.

Paphane B.D., Ramirez L.L.Z., (2013), Chemical pre-treatment of anionic surfactants contaminated waste water at Enaspol A. S. using H_2O_2/UV light waste water pre-treatment method, *Journal of Environmental & Analytical Toxicology*, **3**, 3-6.

Raval V.P., Desai H.H., (2012), Removal of anionic surfactant sodium dodecyl sulphate (SDS) from aqueous solution by using alumina, *Journal of Environmental Research and Development*, **7**, 851-862.

Ríos F., Olak-Kucharczyk M., Gmurek M., Ledakowicz S., (2017), Removal efficiency of anionic surfactants from water during UVC photolysis and advanced oxidation process in H_2O_2/UVC system, *Archives of Environmental Protection*, **43**, 20-26.

Rivera-Utrilla J., Bautista-Toledo M.I., Sanchez-Polo M., Mendez-Diaz J.D., (2012), Removal of surfactant dodecylbenzenesulfonate by consecutive use of ozonation and biodegradation, *Engineering in Life Sciences*, **12**, 113-116.

Samadi T.M., Dorraji S.S.M., Atashi Z., Rahmani A.R., (2014), Photo catalytic removal of sodium dodecyl sulfate from aquatic solutions with prepared ZnO nanocrystals and UV irradiation, *Avicenna Journal of Environmental Health Engineering*, **1**, 217-225.

Sanz J., Lombraæa J.I., de Luis A., (2003), Ultraviolet-H_2O_2 oxidation of surfactants, *Environmental Chemistry Letters*, **1**, 32-37.

Sanz J., Lombrana J.I., de Luis A., (2013), Temperature-assisted UV/H_2O_2 oxidation of concentrated linear alkylbenzene sulphonate (LAS) solutions, *Chemical Engineering Journal*, **215**-**216**, 533-541.

Shahbazi A., Gonzalez-olmos R., Kopinke F., Zarabadi-poor P., Georgi A., (2014), Natural and synthetic zeolites in adsorption / oxidation processes to remove surfactant molecules from water, *Separation and Purification Technology*, **127**, 1-9.

Wang G.S., Liao C.H., Chen H.W., Yang H.C., (2006), Characteristics of natural organic matter degradation in water by UV/H_2O_2 treatment, *Environmental Technology*, **27**, 277-287.

Westerhoff P., Aiken G., Amy G., Debroux J., (1999), Relationships between the structure of natural organic matter and its reactivity towards molecular ozone and hydroxyl radicals, *Water Rese*arch, **33**, 2265-2276.

Yakout S.M., Nayl A.A., (2009), Removal of cationic surfactant (CTAB) from aqueous solution on to activated carbon obtained from corncob, *Carbon - Science and Technology*, **2**, 107-116.

Zenouz M.B., (2009), Desalination water with surfactant a new method with clear vision, *Nature and Science*, **7**, 86-90.

Zepp R.G., Faust B.C., Hoign J., (1992), Hydroxyl radical formation in aqueous reactions (pH 3–8) of iron(II) with hydrogen peroxide: the photo- Fenton reaction, *Environmental Science & Technology*, **26**, 313-319.