

Removal efficiency of anionic surfactants from water during UVC photolysis and advanced oxidation process in H₂O₂/UVC system

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Keywords: advanced oxidation process, anionic surfactants, ether carboxylic derivate, H₂O₂/UVC system, linear alkyl benzene sulfonate, UVC photolysis.

Abstract: Surfactants after their use are discharged into aquatic ecosystems. These compounds may be harmful to fauna and flora in surface waters or can be toxic for microorganisms of the activated sludge or biofilm in WWTP. In order to determine effectiveness of different advanced oxidation processes on the degradation of surfactants, in this study the degradation of anionic surfactants in aqueous solution using photolysis by 254 nm irradiation and by advanced oxidation process in a H₂O₂/UVC system was investigated. Two representatives of anionic surfactants, linear alkyl benzene sulphonate (LAS-R₁₁₋₁₄) and ether carboxylic derivate (EC-R₁₂₋₁₄E₁₀) were tested. The influence of pH, initial surfactant concentration and dose of hydrogen peroxide on the degradation was also studied. Results show outstanding effectiveness of the H₂O₂/UVC system in the removal of surfactant from aqueous solutions.

Introduction

Surfactants are a wide group of chemical compounds which have a large number of applications in household cleaning detergents, personal-care products, textiles, paints, polymers, pesticides, pharmaceuticals, mining, oil recovery, and the pulp and paper industries (Fernández-Serrano et al. 2014, Zgola-Grzeskowiak et al. 2015, Jurado et al. 2013). Moreover, biosurfactants such as saponin, tannin and rhamnolipids JBR 515 and 425 can be applied for heavy metals removal from immobilized activated sludge (Kuczajowska-Zadrożna et al. 2015). After their use, surfactant residues and their degradation products are discharged into aquatic ecosystems in treated or untreated wastewaters, and enter in various environmental compartments such as surface waters, sediments and biota (Ying 2006). Recent studies have demonstrated the persistence and accumulation of surfactants and their biodegradation products in the environment (Sanz et al. 2013, Cserháti et al. 2002, Petrovic et al. 2002, Robert-Peillard et al. 2015). Several of these compounds may be harmful to fauna and flora in surface waters. For example, surfactants may cause acute and chronic effects on sensitive organisms, such as crustaceans and fish (Roberts and Marshall 1995, Ferrara et al. 2005). Moreover, they affect the growth, motility and photosynthetic ability of algae (Rebello et al. 2014). The presence of high concentrations of surfactants in biologic stations of WWTP inhibits aerobic microorganisms, is toxic to anaerobic microorganisms, and

produces foams, which leads to the perturbation of treatment process (Aloui et al. 2009, Bozkurt and Sanin 2014).

According to the European Committee of Organic Surfactants and their Intermediates, the total quantity of surfactants excluding soap produced in Western Europe in 2013 was equal to 2.98 million tons (CESIO 2014). It is predicted that the surfactant market will grow with a compound annual growth rate (CAGR) of 6.19% until 2017 (Markets 2013). The universality of application of these compounds leads to their presence in water environment. The concentration of LAS-R₁₁₋₁₄ in raw sewage ranged from 1 to 15 mg dm⁻³ while in surface water LAS-R₁₁₋₁₄ were detected below 0.05 mg dm⁻³ (HERA 2013). However, the concentration of this compound in industrial wastewater as well as in laundry sewage was found to be about 200 mg dm⁻³ (Han 2013) and up to 1024 mg dm⁻³ (Braga 2011), respectively. Therefore, it is required finding the proper methods of their degradation.

Biodegradation is the cheapest method of the pollutants degradation (Chidambara and Quen 2005), however, in many cases surfactants solutions are toxic for microorganisms of the activated sludge or biofilm (Ledakowicz et al. 2005) causing strong inhibition on dehydrogenase activity of activated sludge biomass (Liwerska-Bizukoje and Bizukoje 2008). Furthermore, some surfactant molecules are not readily biodegradable and relatively high residuals as well partially degraded products are found in the treated effluents and receiving waters (Ying 2006). Therefore, a more efficient option for highly concentrated

surfactant effluents could be the coupling of advanced oxidation and the biological process that could reduce the final concentration of contaminant in the WWTP outlet (Sanz et al. 2013, Lechuga et al. 2014).

Advanced oxidation processes (AOPs) have been extensively studied for the removal of recalcitrant xenobiotic compounds from water and wastewater (Luo et al. 2014). These processes have several advantages over conventional chemical oxidation using potassium permanganate or chlorine, for example higher oxidation potential and no production of potentially carcinogenic chlorinated by-products. Moreover, the oxidants used in AOPs are in situ generated and not persistent, so they do not affect the biological treatment processes (Ikehata and El-Din 2004). The anionic surfactant LAS-R₁₁₋₁₄ is relatively well degraded by some AOPs including ozonation, Fenton, photo-Fenton and H₂O₂/UV processes (Sanz et al. 2013, Pagano et al. 2008, Lechuga et al. 2014). In recent years, study on effective removal of LAS-R₁₁₋₁₄ and other important non-ionic surfactants is becoming more and more active topic. Some studies, such as this published by Sanz et al. (2013), demonstrated the influence of reaction temperature on the degradation of LAS using a H₂O₂/UV system. Pagano et al. (2008) studied the oxidation of alcohol ethoxylates and alkylphenol ethoxylates by Fenton and H₂O₂/UV processes, while Lechuga et al. (2014) indicated that the removal of LAS is increased by the consecutive use of ozonation and biodegradation. However, the degradation of new families of surfactants by AOPs, such as ether carboxylic derivatives remains unstudied.

In order to contribute to increasing the information concerning the effectiveness of different AOPs, the present investigation was specifically aimed at the degradation of two different anionic surfactants by direct photolysis and advanced oxidation in H₂O₂/UVC system. The influence of various parameters in the degradation (pH, initial surfactant concentration and dose of hydrogen peroxide) was also studied.

Methods

Two anionic surfactants were used in this study: linear alkyl benzene sulfonate (LAS-R₁₁₋₁₄), supplied by Petresa (Madrid, Spain), and ether carboxylic derivative (EC-R₁₂₋₁₄E₁₀) supplied by Kao Corporation S.A. (Tokyo, Japan). Table 1 shows the structure, the percentage of active matter and the critical micelle concentration (CMC) of the surfactants tested. The initial surfactants concentrations used ranged from 9.3 to 60.0 mg dm⁻³ and from 6.4 to 89.3 mg dm⁻³ for LAS-R₁₁₋₁₄ and EC-R₁₂₋₁₄E₁₀, respectively. These concentrations were chosen in order to study the degradation of surfactants above

and below the CMC. The used concentration of hydrogen peroxide (30%) (POCH, Poland) ranged from 1×10⁻² mol dm⁻³ to 1×10⁻¹ mol dm⁻³.

All the solutions used in the experiments were prepared in distilled water treated in Millipore Milli-Q Plus System and the pH of the solutions was adjusted by a phosphate buffer (H₃PO₄, KH₂PO₄, Na₂HPO₄, NaOH, all p.a., POCh, Poland) in the range from 2 to 12.

For both process: UVC photolysis and the H₂O₂/UVC system, low-pressure lamps (Luzchem) emitting mainly at the wavelength λ = 254 nm were applied. The tested solutions were irradiated in a merry-go-round device with quartz test tubes (volume: 10 cm³, average optical path length: 0.85 cm), placed between two exposure panels, each of them consisting of three 7.2 W lamps. The samples were irradiated for 120 min in the case of UVC photolysis and for 4 min when the H₂O₂/UV system was used. In the case of H₂O₂/UV system, degradation experiments were additionally performed in the presence of hydroxyl radicals scavenger. In these studies 1×10⁻¹ mol dm⁻³ tert-butanol (Fluka) was used. The experiments were performed at room temperature equal to 22°C.

The surfactant degradation was monitored by means of the residual-surfactant concentration over time using a colorimetric method in which the absorbance is directly proportional to the surfactant concentration. The method is based on the formation of the ionic-pair anionic surfactant-methylene blue (Jurado et al. 2006). For spectrophotometric measurements, 5×10⁻³ dm³ of sample placed in 1×10⁻² dm³ glass vials were made alkaline to pH 10.0 by adding 2×10⁻⁴ dm³ of 5×10⁻² mol dm⁻³ sodium tetraborate, pH 10.5, and then 10⁻⁴ dm³ of methylene blue 1 g dm⁻³ stabilized was added. Finally, 4×10⁻³ dm³ of chloroform was added and, after stirring and 5-min wait, the absorbance at 650 nm was measured. This method allows to measure the concentration of LAS-R₁₁₋₁₄ and EC-R₁₂₋₁₄E₁₀ with a limit of detection of 0.05 mg dm⁻³.

The initial reaction rates were calculated by differentiating exponential curve that fitted experimental points (C, t) at the correlation factor higher than 0.97.

Results and discussion

In the beginning, the possibility of surfactants degradation during exposure to UVC radiation was tested.

Fig. 1 presents absorption spectra of the tested substances at different pH and the emission spectrum of the UV lamps. LAS-R₁₁₋₁₄ molecules absorb radiation with maximum at 224 nm, while EC-R₁₂₋₁₄E₁₀ very poorly absorbs UVC radiation.

The investigated compounds were irradiated for 120 minutes and the influence of their initial concentration and

Table 1. Description of the surfactants used (R: alkyl-chain length, n: degree of ethoxylation, X=H⁺ or Na)

Surfactant	Linear alkyl benzene	Ether carboxylic derivative
Abbreviation	LAS-R ₁₁₋₁₄	EC-R ₁₂₋₁₄ E ₁₀
Structure	R-CH-(CH ₃)(C ₆ H ₄)-SO ₃ -Na ⁺	R-(CH ₂ -CH ₂ O) _n -O-CH ₂ -COO-X
% Active Matter	46.8 ^a	94.0 ^a
CMC, mg dm ⁻³	25.5 ^b	69.0 ^b

^a Supplied by the manufacturer

^b (Lechuga et al. 2013)

pH were studied. Fig. 2 shows changes of relative surfactant concentration versus radiation dose (E). The degradation of investigated compounds during photolysis by 254 nm irradiation occurs slowly and is a highly energy-consuming process. The use of radiation dose of 57.2 kJ m^{-2} results in about 10% reduction of initial surfactants concentration (Fig. 2). While, the UV disinfection dose usually applied for tap water treatment is equal to 0.4 kJ m^{-2} (Canonica et al. 2008), therefore it is not possible to remove these compounds during disinfection process.

In the case of $\text{EC-R}_{12-14}\text{E}_{10}$, the photolysis occurs the fastest in neutral pH (Fig. 3A), while the increase in alkalinity practically does not influence the reaction rate of LAS-R_{11-14} photolysis (Fig. 3A). An increase in the initial

concentration caused increase of $\text{EC-R}_{12-14}\text{E}_{10}$ reaction rate (Fig. 3B), and did not accelerate the LAS-R_{11-14} photodegradation (Fig. 3B).

The addition of hydrogen peroxide to the reaction solution resulted in a significant acceleration of degradation process (Fig. 2). A 10-fold lower radiation dose (5.72 kJ m^{-2}) than mentioned above for photolysis allows for 60% reduction of initial LAS-R_{11-14} concentration (Fig. 2A) and about 50% reduction of initial $\text{EC-R}_{12-14}\text{E}_{10}$ concentration (Fig. 2B). Pagano et al. (2008) also found high removal rates of surfactants: alcohol ethoxylates and alkylphenol ethoxylates using the $\text{H}_2\text{O}_2/\text{UV}$ process.

The degradation in the $\text{H}_2\text{O}_2/\text{UV}$ system requires establishing of an optimal hydrogen peroxide concentration,

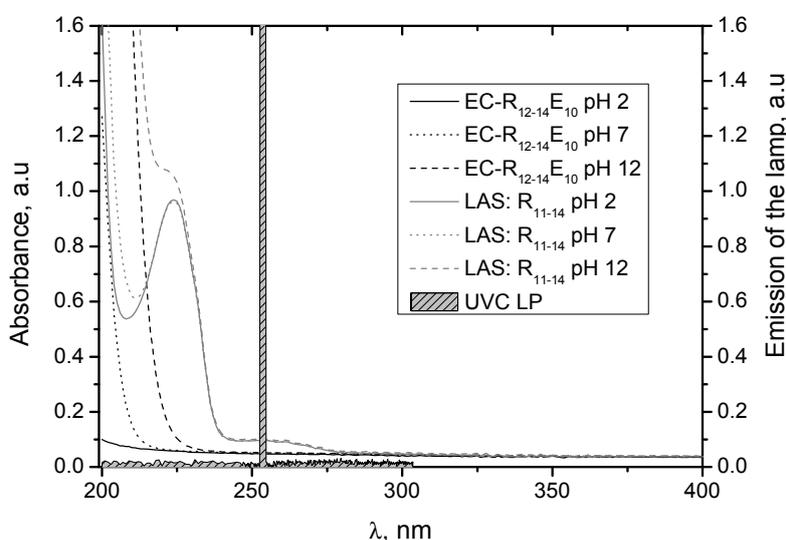


Fig. 1. Absorption spectra of LAS-R_{11-14} (A) ($C_0=45 \text{ mg dm}^{-3}$) and $\text{EC-R}_{12-14}\text{E}_{10}$ (B) ($C_0=26 \text{ mg dm}^{-3}$) at pH=2, 7 and 12, overlaid against emission spectra of UVC lamps used in experiments

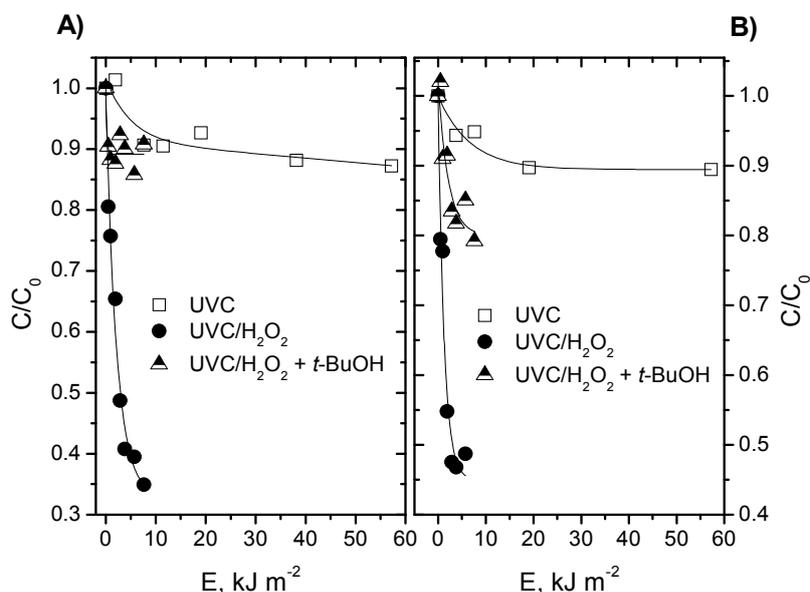


Fig. 2. Changes of relative LAS-R_{11-14} (A) ($C_0=45 \text{ mg dm}^{-3}$, $C_{\text{H}_2\text{O}_2}=3 \times 10^{-2} \text{ mol dm}^{-3}$, $C_{\text{t-BuOH}}=1 \times 10^{-1} \text{ mol dm}^{-3}$, pH=7, $E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$) and $\text{EC-R}_{12-14}\text{E}_{10}$ (B) ($C_0=26 \text{ mg dm}^{-3}$, $C_{\text{H}_2\text{O}_2}=3 \times 10^{-2} \text{ mol dm}^{-3}$, $C_{\text{t-BuOH}}=1 \times 10^{-1} \text{ mol dm}^{-3}$, pH=7, $E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$) concentration during the photolysis and advanced oxidation

i.e. when the H_2O_2 photolysis produces plenty of $\bullet\text{OH}$ radicals and their consumption by hydrogen peroxide is negligible. The highest reaction rate of the surfactants degradation was attained at H_2O_2 concentration of $3 \times 10^{-2} \text{ mol dm}^{-3}$, as shown in Fig. 4. This optimal H_2O_2 concentration was chosen to evaluate the influence of other parameters on the advanced oxidation of the investigated surfactants in $\text{H}_2\text{O}_2/\text{UV}$ system.

The results of advanced oxidation in $\text{H}_2\text{O}_2/\text{UV}$ system at various pH of reaction solutions are presented in Fig. 5. In the case of LAS-R_{11-14} the process occurs with a similar efficiency at neutral and acidic conditions (Fig. 5A), whereas for $\text{EC-R}_{12-14}\text{E}_{10}$ it is the most effective at pH 7 (Fig. 5B). In alkaline solutions degradation of investigated compounds

was strongly inhibited, which is mainly connected with the hydrogen peroxide dissociation (1) ($\text{pK}_a=11.6$ (Hoigne 1998)). The anions formed in this reaction have a much higher molar absorption coefficient in comparison to hydrogen peroxide ($\epsilon_{254\text{nm}}=240 \text{ M}^{-1}\text{cm}^{-1}$ (Legrini et al. 1993), $\epsilon_{254\text{nm}}=18.6 \text{ M}^{-1}\text{cm}^{-1}$ (Nicole et al. 1990)), and can react both with H_2O_2 (2) and $\bullet\text{OH}$ (3) radicals leading to reduction of $\bullet\text{OH}$ radicals concentration in the reaction mixture.

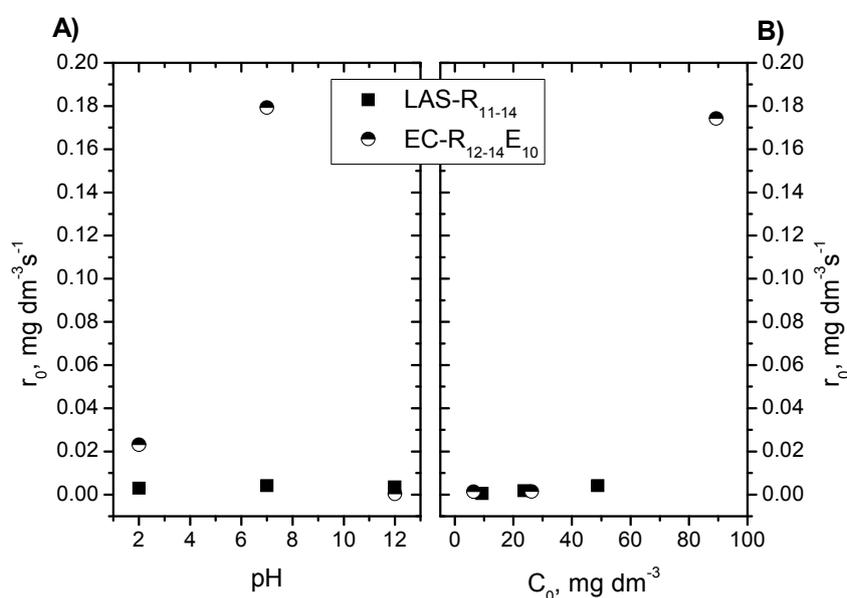
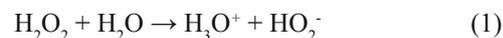


Fig. 3. Influence of pH (A) (LAS-R_{11-14} : $C_0=46 \text{ mg dm}^{-3}$, $E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$; $\text{EC-R}_{12-14}\text{E}_{10}$: $C_0=30 \text{ mg dm}^{-3}$, $E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$) and initial surfactant concentration (B) ($E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$, $\text{pH}=7$) on initial reaction rate

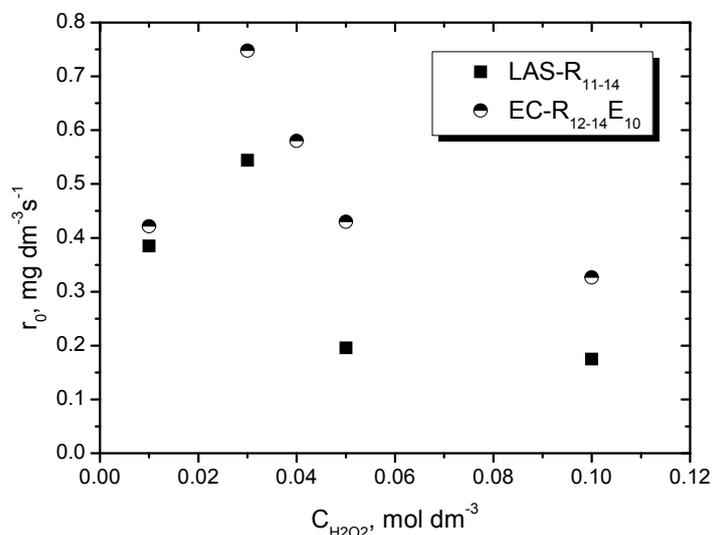


Fig. 4. Dependence of initial reaction rate on hydrogen peroxide concentration (LAS-R_{11-14} : $C_0=50 \text{ mg dm}^{-3}$, $\text{pH}=7$, $E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$; $\text{EC-R}_{12-14}\text{E}_{10}$: $C_0=40 \text{ mg dm}^{-3}$, $\text{pH}=7$, $E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$)

The surfactant degradation at four different initial concentrations was studied (Fig. 6). In the case of LAS-R₁₁₋₁₄, there is an optimal concentration (26 mg dm⁻³) above which degradation process slowed down (Fig. 6A), what can be explained by the advantage of this compounds over H₂O₂ in the competition of photons and domination of direct photolysis of LAS-R₁₁₋₁₄. CMC of LAS-R₁₁₋₁₄ is equal to 25.5 mg dm⁻³ (Table 1) and the optimal concentration coincides with this value, i.e. when the solubilization of the surfactant molecules takes place in micelles. However, at concentrations above the CMC the degradation does not occur faster, and the percentage of degradation is lower (Fig. 6A). In addition, this process slowed down when the LAS-R₁₁₋₁₄ concentration was below CMC due

to the fact that the molecules of surfactants were mainly in the water-air interface and access to them was more difficult.

In the degradation process of EC-R₁₂₋₁₄E₁₀, increase of initial concentration leads to the acceleration of reaction efficiency and reducing the energy input (Fig. 6B). During advanced oxidation of EC-R₁₂₋₁₄E₁₀, 40% reduction of the initial concentration equal to 7.5 mg dm⁻³ was achieved by using radiation dose of 3.81 kJ m⁻². About 6-fold higher initial concentration of these compounds results in 4-fold decreases of radiation dose which is needed to achieve the above degradation degree (Fig. 6B). The influence of CMC on advanced oxidation of EC-R₁₂₋₁₄E₁₀, cannot be studied because its initial concentration was below CMC in all cases.

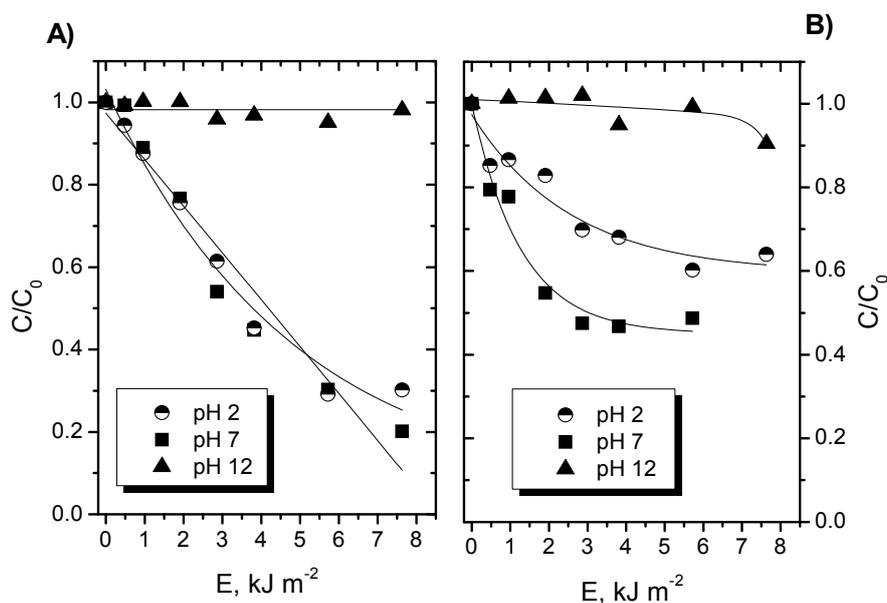


Fig. 5. Changes of relative LAS-R₁₁₋₁₄ (A) ($C_0=54 \text{ mg dm}^{-3}$, $C_{\text{H}_2\text{O}_2}=3 \times 10^{-2} \text{ mol dm}^{-3}$, $E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$) and EC-R₁₂₋₁₄E₁₀ (B) ($C_0=26 \text{ mg dm}^{-3}$, $C_{\text{H}_2\text{O}_2}=3 \times 10^{-2} \text{ mol dm}^{-3}$, $E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$) concentration during advanced oxidation in various pH values

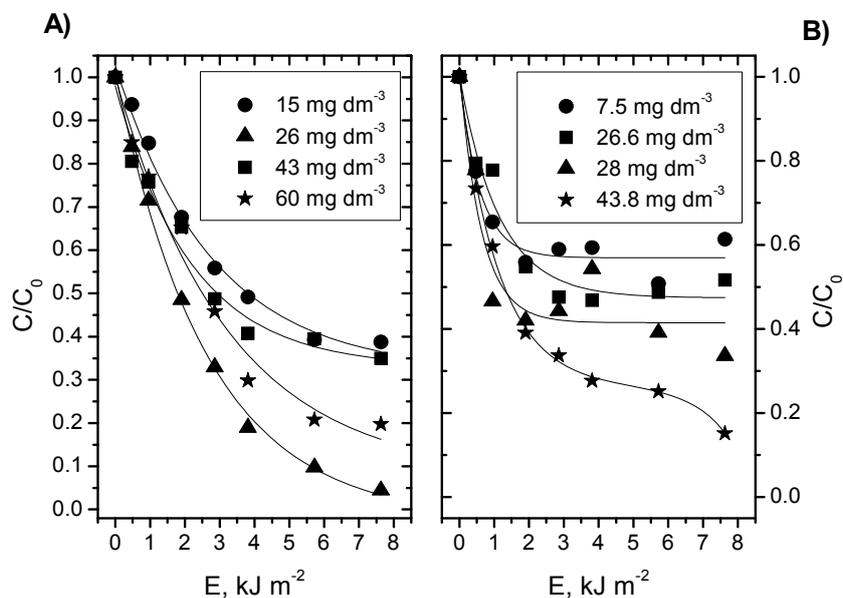


Fig. 6. Changes of relative LAS-R₁₁₋₁₄ (A) ($C_{\text{H}_2\text{O}_2}=3 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{pH}=7$, $E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$) and EC-R₁₂₋₁₄E₁₀ (B) ($C_{\text{H}_2\text{O}_2}=3 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{pH}=7$, $E_0=10.6 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$) concentration during advanced oxidation for various initial concentration of surfactant

In addition, surfactant degradation was studied in the presence of hydroxyl radical scavengers (Fig. 2). The influence of tert-butanol on the reaction run was investigated. For both surfactants, the reaction is not inhibited to the direct photolysis level, what may suggest that an additional reaction (“third pathway”) occurs. Similar situation was observed during butylparaben (Błędzka et al. 2010) and fluorene (Ledakowicz et al. 1999) degradation in H₂O₂/UV system.

Conclusions

The studies performed on degradation of two surfactants: linear alkyl benzene sulphonate and ether carboxylic derivate exposed to UVC irradiation in aqueous solutions with and without addition of hydrogen peroxide enable us to draw the following conclusions.

The photolysis of EC-R₁₂₋₁₄E₁₀ occurs the fastest in neutral pH, while the increase in alkalinity practically does not influence reaction rate of LAS-R₁₁₋₁₄ photolysis.

An increase in the initial concentration of surfactants caused increase of photolysis rate.

Advanced oxidation of EC-R₁₂₋₁₄E₁₀ is the most effective at pH 7, whereas for LAS-R₁₁₋₁₄ it occurs with a similar efficiency at neutral and acidic conditions. However, for both investigated compounds this process was strongly inhibited in alkaline solutions.

The highest degradation rate of surfactants in H₂O₂/UV system was attained at H₂O₂ concentration of 3×10⁻² mol dm⁻³.

Increase of EC-R₁₂₋₁₄E₁₀ initial concentration leads to the acceleration of advanced oxidation, while in the case of LAS-R₁₁₋₁₄, there is an optimal concentration above which degradation process slowed down.

Advanced oxidation process in a H₂O₂/UV system represents an effective method to degrade surfactants. This technique has advantages over using photolysis alone: degradation is a faster and less energy-consuming process.

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Efektywność usuwania surfaktantów anionowych z wody przy zastosowaniu promieniowania UVC i zaawansowanego utleniania w układzie H_2O_2/UV

Streszczenie: Surfaktanty, podobnie jak większość tego typu substancji chemicznych, po wykorzystaniu trafiają do środowiska wodnego. Związki te mogą stwarzać zagrożenie dla flory i fauny zasiedlającej wody powierzchniowej, jak również mogą działać toksycznie na mikroorganizmy znajdujące się w osadzie czynnym w oczyszczalniach ścieków.

W niniejszej pracy przedstawiono wyniki badań degradacji wybranych surfaktantów anionowych w środowisku wodnym przy zastosowaniu promieniowania UVC i zaawansowanego utleniania w układzie H_2O_2/UV . Zbadano wpływ następujących parametrów reakcyjnych: odczyn środowiska reakcyjnego, początkowego stężenia obiektów badań i nadtlenu wodoru na szybkość degradacji surfaktantów. Uzyskane w toku prac badawczych wyniki potwierdzają wysoką skuteczność zaawansowanego utleniania w układzie H_2O_2/UV w usuwaniu badanych surfaktantów ze środowiska wodnego, które jest procesem znacznie efektywniejszym w porównaniu do procesu fotolizy.