

ANIONIC SURFACTANTS OXIDATION USING AOPs AND A NOVEL “IN-FOAM UV/AIR OXIDATION” PROCESS

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This paper presents some results of an experimental investigation of the possibility of using an “in-foam UV/air oxidation” process for the degradation of anionic surfactants. In this process, only the foam generated by bubbling air through the surfactant solution is exposed to the UV-C light, followed by recirculation to solution using a positive displacement pump.

The developed process, tested for sodium dodecylbenzenesulfonate and sodium dodecylsulfate 0.3-0.5 mM aqueous solutions seems to be promising, even compared with advanced oxidation processes such as UV/H₂O₂, depending on photosensitizer dose.

Based on the analysis presented in this article the “in-foam UV/air oxidation” process has surprisingly good performances related to both surfactant concentration (primary degradation) and chemical demand (mineralization), but is limited by the lowest useful foaming concentration. The foam acts as a support for photochemical reactions, as it concentrates the surfactant to a high area interface, where it is exposed to the UV light and oxygen. By contrast, when only the solution is exposed to UV light, the “in-solution UV/air oxidation” process, the efficiency is low and, as expected, higher for the UV-absorbing aromatic compound sodium dodecylbenzenesulfonate. The “in-foam UV/air oxidation” process can be used as a pretreatment before biological aerobic treatment of clear waste water containing surfactants and is also an interesting research alternative for the oxidation of other organic compounds. This process can be refined by adding photosensitizers.

Keywords: “in-foam UV/air oxidation”, surfactant, waste water, UV/H₂O₂

Introduction

The primary option for treating surfactant containing effluents is biological aerobic degradation. Biological aerobic degradation of surfactants for concentrated streams is difficult due to foaming, adverse effects on oxygen transfer and toxic effects. Various treatment methods, mainly based on oxidation/ advanced oxidation processes are tested [1,2].

This work aims to do a preliminary investigation of the possibility of an in-foam photodegradation process for the treatment of surfactant concentrated aqueous systems.

Research works show that linear alkylbenzenesulfonates and alkylsulfates are effectively degraded in oxidation and advanced oxidation process using various combinations of ozone, hydrogen peroxide, ultraviolet light irradiation, and iron salts. It was found that the biodegradability of these surfactants is improved after the treatment. Oxidation and advanced oxidation processes (AOPs) are studied for aqueous systems with low or high concentration. The removal efficiency of organic pollutants and the energy and reagents requirements are depending on the reaction conditions [3,5].

Other interesting converging works are focused to exploit the foam generated by surfactant – air systems as an adsorption/absorption media and as a support for photocatalysis [5,6]. As the foam seems to have interesting applications in an UV-assisted oxidation process, in the present work we try

an approach to a less studied UV oxidation, the *in-foam* oxidation process, possibly an alternative to already studied AOPs.

Experimental

The experimental set-up is shown in Fig. 1 and Fig. 2. The key component of the experimental setup is the photoreactor (800ml) which was operated with a 150W Heraeus TQ150 medium pressure mercury lamp (water cooled, by means of a quartz jacket). The UV naked lamp has a specific radiation power output of about 12 W for $\lambda = 200\text{-}300$ nm.

All experiments (excluding simple photolysis) were conducted with air sparging (UV/air system). The foam resulting due to air sparging was collected in a side column type foam buffer vessel and continuously pumped back to the photoreactor using a positive displacement pump – peristaltic. The photoreactor also had a magnetically driven stirrer. For the “*in-foam UV/air oxidation*” process, the start-up (filling) level was just below the UV lamp cooling jacket, in order to minimize the exposure to UV light of the bulk solution. In this process, only the foam generated by bubbling air through the surfactant solution is exposed to the UV-C light.

For the “*in-solution UV/air oxidation*”, the photoreactor was filled with surfactant solution, below the air-foam outlet. In this process, the solution is fully exposed to UV-C light and was used for UV/air systems (atmospheric oxygen as the oxidant) and also for the H₂O₂ assisted processes- in UV/H₂O₂/air systems.

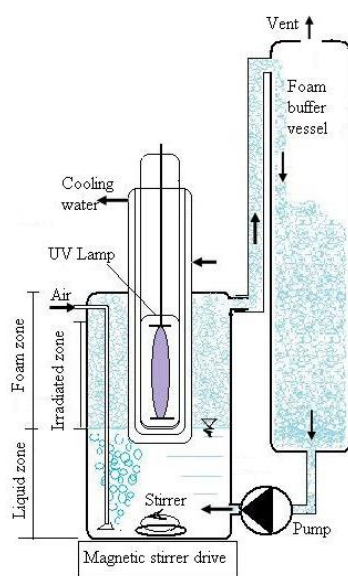


Fig. 1- The experimental setup for the UV „in-foam” oxidation process

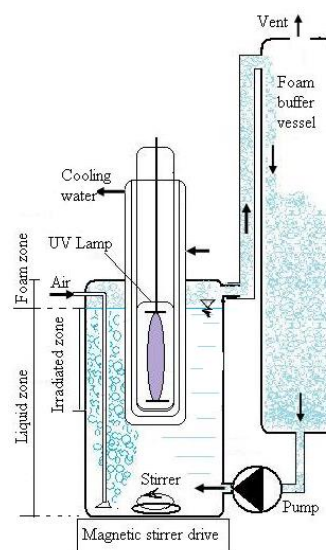


Fig. 2- The experimental setup for the UV „in-solution” oxidation process

The foam volume in the buffer vessel was kept low by varying the pump flow rate (the volume of foam outside the photoreactor was negligible).

Sodium dodecylbenzenesulfonate (Fluka 80%) –SDBS and sodium dodecylsulfate (Merck 99%) –SDS were used without further purification for the preparation of synthetic solutions.

Anionic surfactants concentration was measured by the standard methylene blue method.

Mineralization was evaluated by measuring the chemical oxygen demand (COD).

Results and Discussions

The sodium dodecylbenzenesulfonate for the *in-solution* oxidation in UV/air system (fig.3-4) is slow, with an initial rate of 0.76 mg/L/min, slightly higher if compared with the direct photolysis of the SDBS solution (with an initial reaction rate of 0.61 mg/L/min). Due to

the photolysis, the surfactant primary degradation is noticeable (activity for the methylene blue and also the foaming capacity of the solution is decreasing). During direct photolysis, but also during the *in-solution* oxidation process, oxidation is not important, as it is indicated by the residual oxygen demand, even for long process time, extended to approx. 3h).

The primary degradation of SDBS using the *in-foam* process (fig. 3 and 4) has a significant higher rate (initially 2mg/L/min) and a degradation yield of about 85% is obtained in 1.5 h. The process could not be continued to a higher extent as the foaming capacity of the solution had become too low. For the *in-foam* process, the primary degradation of surfactant is accompanied by the oxidation of the reaction by-products: the degree of mineralization was 73% for a 1.5 h reaction time. Such a high mineralization degree can be sustained by a high rate oxidation in the foam phase and also by the capacity of byproducts of being transferred by surfactant to foam phase.

The *in-foam* oxidation process rate, related both to the surfactant concentration in solution and to the remanent COD was compared with the results obtained for the UV/H₂O₂/air system, and it was found that the results are similar to those obtained for low hydrogen peroxide doses (even with a rough correction for a volume difference of 35%). For the primary degradation, the UV/H₂O₂/air system is more efficient, but it was noted a higher efficiency for the *in-foam* oxidation process in relation with the mineralization degree. This cannot be easily explained and can be related including to the impurities in the SDBS used for the experiments. For the UV/H₂O₂/air systems, r represents the initial molar ratio H₂O₂ to surfactant divided by the stoichiometric ratio required by direct H₂O₂ oxidation.

As indicated by the fig. 5 and 6, the degradation and oxidation in the *in-foam* and *in-solution* processes applied for the sodium dodecylsulfate (SDS) are similar to those for SDBS: the primary degradation of SDS is much faster for the *in-foam* process. Also, it can be seen the main difference between the two processes – the mineralization of organic load is very low (negligible) for the *in-solution* process. Compared to the UV/H₂O₂ systems, the *in-foam* photooxidation process of SDS is slower for all H₂O₂ initial concentrations, if reported to the surfactant remanent concentration, but it can be seen on the graph (fig.5 and 6) that the process is clearly distinct. Interesting, the mineralization degree for the *in-foam* process is closer to those obtained for UV/H₂O₂ system with the lowest H₂O₂ concentration ($r=0.2$).

It is confirmed that the foam acts as a support for photochemical reactions, as it concentrates the surfactant to a high area interface, where it is exposed to the UV light and oxygen confined within the foam.

Conclusions

Carefully designed systems can handle surfactant-air bubbling systems in respect to foam generation and irradiation. The photodegradation of surfactants in an UV/air system is the result of few processes: direct photolysis, oxidation with molecular species such as O₂ or O₃ formed *in-situ* and oxidation with radicalic species resulted from photolysis of ozone, depending on UV light used.

The oxidation process of surfactants in UV/air system in which the foam is collected outside photoreactor and repumped to liquid phase can employed without foam in the irradiated zone (*in-solution* process) or with exposing foam in irradiated zone (*in-foam* process).

The photodegradation of alkylsulfonate and alkylsulfate in UV/air system ($\lambda < 254\text{nm}$) have interesting results: both the *in-solution* and *in-foam* processes can attain the primary degradation of surfactants but with much higher rates for the *in-foam* process. Further degradation / oxidation of the reaction intermediates – mineralization does not occur in the *in-solution* process. Mineralization has surprisingly high rates for the *in-foam* process which have efficiencies comparable with the photoassisted UV/H₂O₂ process for low H₂O₂ initial concentrations.

The *in-foam* process has a major drawback as it is limited by the lowest concentration of surfactant for which enough foam can be produced. Adding of photosensitizers as ozone or hydrogen peroxide for the *in-foam* process can be of interest for further research for aqueous systems containing surfactants alone or with other organic pollutants.

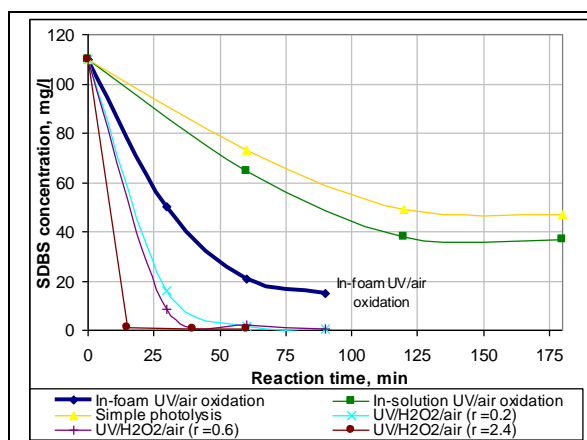


Fig. 3 SDS concentration vs. reaction time

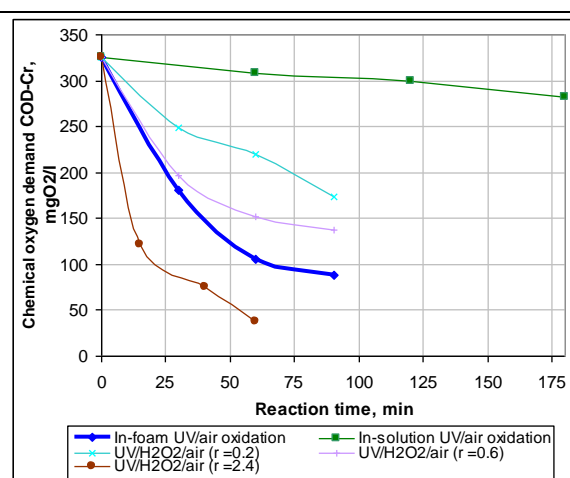


Fig. 4 Chemical oxygen demand evolution during SDS photooxidation

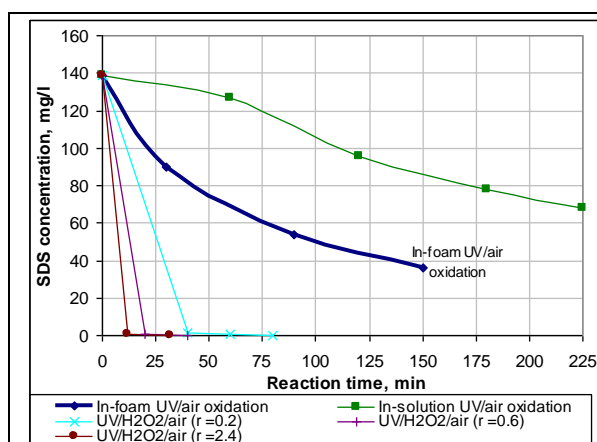


Fig. 5 SDS concentration vs. reaction time

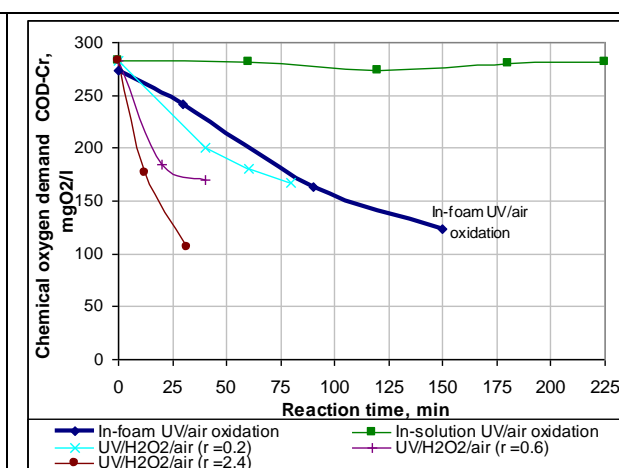


Fig. 6 Chemical oxygen demand evolution during SDS photooxidation

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