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Degradation of anionic surfactants using the reactor based on dielectric barrier discharge

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Abstract: Two anionic surfactants (sodium lauryl sulfate – SDS and sodium dodecylbenzenesulfonate – SDBS) were treated with dielectric barrier discharge. Loss of surfactant activity, decrease in chemical oxygen demand (*COD*) and total organic carbon (*TOC*) as well as lower toxicity of degradation products was determined. Effects of catalysts – hydrogen peroxide and iron (II), on the above mentioned parameters, were determined. Catalysts affected the degradation of SDBS, but in the case of SDS, catalysts had no effect on degradation. Both catalysts induced the decrease of *COD* and *TOC* values. Toxicity of the solutions after the plasma treatment was lower in all the systems tested.

Keywords: plasma treatment; sodium lauryl sulfate; sodium dodecylbenzenesulfonate; homogenous; catalysis.

INTRODUCTION

Surfactants are a diverse group of chemicals designed to have cleaning or solubilization properties. They generally consist of a polar group (either charged or uncharged) and a nonpolar hydrocarbon chain. They are widely used in household detergents, personal care products, textile industry, paint formulations, polymers, pesticide formulations, pharmaceuticals, mining (as flotation reagents), oil recovery and pulp and paper industries. After being used, surfactants are mainly discharged into the sewage treatment plants and subsequently dispersed in the environment through effluent discharge into surface waters and sludge disposal on lands. Surfactants are essentially non-toxic and harmless; however, recent stu-

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dies revealed that some of the synthetic surfactants and their degradation products could impose potential health and environmental risks. Environmental effects associated with the presence of synthetic surfactants in the aquatic environment are considered a serious problem because these compounds are often toxic to aquatic vertebrates and invertebrates, have a potential to disrupt their hormonal systems and thus alter the ecosystem.[1,2]

Sodium dodecylbenzenesulfonate (SDBS) and sodium lauryl sulfate (SDS) are anionic detergents (surfactants) used worldwide. Both compounds belong to the group of linear alkylbenzenesulfonates (LAS), synthetic anionic surfactants extensively used for more than 40 years. Commercially available products represent very complex mixtures containing homologues with alkyl chains ranging from 10 to 14 carbon units (C10–C14 LAS). Since the phenyl group could be attached to any internal carbon atom of the alkyl chain, each homologue contains 5–7 positional isomers.

The removal efficiency of anionic surfactants from water in traditional wastewater treatment plant has been reviewed.[3] Aerobic process is much more effective for anionic surfactants removal compared to the anaerobic process. In both processes, main problem is the concentration of anionic surfactants in the sewage sludge. In aerobically digested sludge, their concentration is found to be in the range of 100–500 mg kg^{-1} whereas anaerobically digested sludge contains an average of 1000–30000 mg kg^{-1} LAS dry wt. When sludge contains 40-60 mg kg^{-1} LAS dry wt., the surfactant can interfere with the reproduction and growth of the soil invertebrates and earthworms.[4]

For this reason, many investigations are exploring the advanced oxidation processes for degradation of surfactants. Advanced oxidation processes (AOP) are defined as the processes that generate hydroxyl radicals in sufficient amount for oxidizing the majority of complex chemicals present in the effluent.[5] Hydroxyl radicals are powerful oxidizing reagents with an oxidation potential that exhibit faster rates of oxidation reactions compared to conventional oxidants like hydrogen peroxide or $KMnO_4$.

Surfactants were in focus of many investigations that use AOPs for their degradations.[6,7] Some of them are ozonization, Fenton and Fenton-like processes, H_2O_2–UV and photocatalytic processes.[8–15]

Plasma technology could be competitive towards AOPs. Plasma represents partially or fully ionized gas consisting of electrons, free radicals, ions and neutrals and it can be produced by a variety of electrical discharges. Non-thermal plasma does not express local thermodynamic equilibrium and therefore, offers high energy efficiency in plasma chemical reactions. Non-thermal plasma is obtained using less power (*e.g.*, corona discharge, dielectric barrier discharge, gliding arc discharge, glow discharge and spark discharge), which is characterized by an energetic electron temperature much higher than that of the bulk-gas molecules.[16] In such a plasma, the energetic electrons can collide with background molecules (N_2, O_2, H_2O, etc.), producing secondary electrons, photons, ions and radicals. Therefore, applications of the atmospheric pressure electrical plasma technologies for water treatment attract the increasing interest and emerge as technological opportunities.[16,17]

In the presented research, the degradation of two anionic surfactants, SDS and SDBS was studied using advanced oxidation process (AOP) in a non-thermal plasma reactor based on coaxial dielectric barrier discharge with water falling film (DBD).

EXPERIMENTAL

Materials

The surfactants, sodium lauryl sulfate and sodium dodecylbenzenesulfonate, were purchased from Sasol S.P.A (Italy) and used without further purification. Homogenous catalysts used in degradation reactions were hydrogen peroxide, H_2O_2, 30 % (Carlo Erba, Italy) and iron(II) sulfate heptahydrate (Merck, Germany). *Artemia salina* cysts were purchased from Dajana Pet (Czech Republic). Synthetic seawater was made by dissolving 100 g of sea salt (Reef Salt, Aqua Medic, Germany) in 3 L of deionized water. All other chemicals used were of analytical grade. Each surfactant solution was prepared by dissolving the corresponding surfactant in deionized water (conductivity between 1.0 and 1.5 μS cm^{-1}) at adequate amount to make 100.0 mg L^{-1} solution.

Instrument

Water falling DBD reactor used in this paper was a non-thermal plasma reactor operating at atmospheric pressure. Construction of the reactor was previously described.[18,19] Surfactant solutions were pumped to the top of the reactor through the inner tube by the peristaltic pump at 210 ml min^{-1} flow rate. The system was powered by the high-voltage transformer connected to the frequency inverter which enables the sinusoidal variations of voltage with a frequency of up to 500 Hz. Frequency of the reactor was set at 300 Hz – the optimal value previously optimized. The discharge was generated in a gaseous phase, between the glass and water layer, by applying the 17 kV voltage. The plug-in energy density of ~45 kJ L^{-1} was introduced into the solution with a single pass through the reactor. Applied energy density was increased by recirculating the solution up to the point when applied energy density reached a value of 450 kJ L^{-1}, *i.e.*, each solution was recirculated ten times. In each series of experiments, starting volume of the surfactant solution was 2 L. After each passing, 100 ml of solution was sampled.

Methods of analysis

Determination of surfactants was done by measuring the methylene blue index (MBAS).[20] MBAS represents the spectrophotometric method for determination of anionic surfactants by measuring the methylene blue index in a water environment. The efficiency of degradation is defined as a percentage of absorbance decrease for surfactant derivatives according to Eq. (1):

$$\text{Decolorization} = 100\frac{A_0 - A}{A_0} \tag{1}$$

where A_0 presents the absorbance at the wavelength which shows the maximum absorption of surfactant derivative (λ_{max}), while A presents the absorbance at λ_{max} of the surfactant derivatives after the plasma treatment. Spectrophotometric measurements were done by GBC Cintra 10 (GBC Scientific Equipment Pty Ltd., Australia) spectrometer with quartz cuvettes that have 1 cm long optical path, 5 min after the plasma treatment.

Chemical oxygen demand was determined according to the standard procedure after the tenth pass through the DBD. Total organic carbon (TOC) analysis was done in accordance with method ISO 8245:2007.[21]

For the toxicity screening test, the brine shrimp *Artemia salina* was used according to Vanhaecke and Persoone, and experiment was repeated three times.[22] Complete procedure of the test was described in our previously published work.[19]

RESULTS AND DISCUSSION

In this paper, degradation of the two anionic surfactants, SDS and SDBS, using the reactor based on water falling film utilizing method of dielectric barrier discharge was studied. The goal of the experimental part of the paper was to determine the efficiency of the DBD reactor and effects of the homogenous catalyst (Fe^{2+} and H_2O_2) on surfactant degradation, chemical oxygen demand (COD) and total organic carbon (TOC). After degradation process, sample toxicity was examined by *Artemia salina* test organisms.

Efficiency of degradation

Efficiency of degradation was monitored using MBAS test (λ_{max} = 650 nm) for both surfactants. After each passing through the DBD reactor, small aliquots of solutions were extracted and tested for surfactant activity. As shown in Fig. 1, in both cases loss of surfactant activity could be observed. Both surfactants have similar trends in degradation and after ten passes and introduced energy of 450 kJ L^{-1} degradation efficiencies were around 90 %.

Influence of homogenous catalysts

Usage of homogenous catalysts in chemical and technological processes is a lot simpler and demands fewer steps than the heterogeneous catalysis. Heterogeneous catalysts have to be removed from the system after the catalytic cycle. Homogenous catalysis is easier to perform, especially for industrial wastewater treatments because catalysts need not be removed from the system afterwards. A necessary condition that all the homogenous catalysts used in those treatments have to meet is that they are not toxic. Some of them, like H_2O_2, decompose over time. Other catalysts, *e.g.*, Fe^{2+}, Fe^{3+} are Mn^{2+} are easily deposited by changing the redox conditions in water and by adjusting the pH value.

Based on our previous investigation, we tested the influence of H_2O_2 and Fe^{2+} on degradation efficiency of SDS and SDBS in the DBD reactor.

As shown in Fig. 2, both catalysts have an influence on the degradation of sodium dodecylbenzenesulfonate. Hydrogen peroxide had a greater impact on the degradation efficiency than iron (II) as a catalyst. The increase was about 30 % for the first four passes, while other passes showed an increase of about 10 %. In the case of iron (II), increase was around 10 % for all the passes. For both catalysts, final degradation (after ten passes through reactor) increased for approximately 10 %.

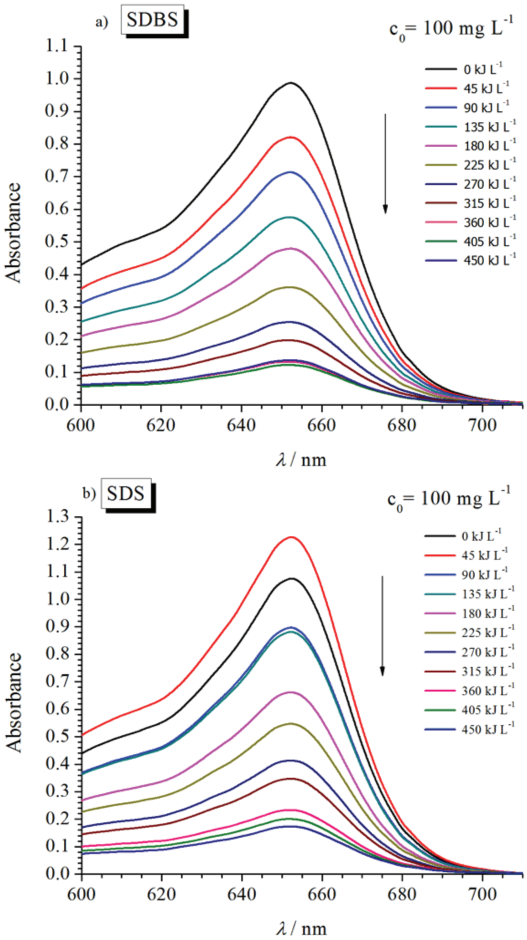

Fig. 1. Visible absorption spectrum of derivatized surfactants during degradation process: a) SDBS, b) SDS; (initial concentration of surfactants 100 mg L^{-1}, pH value native, 24 h after the plasma treatment, without homogenous catalysts).

Increased efficiency of degradation in systems that contain H_2O_2 could be explained based on peroxone process, where in the reaction of ozone and hydrogen peroxide hydroxyl radical was generated Eq. (2):[23]

$$H_2O_2 + 2O_3 \rightarrow 2^{\bullet}OH + 3O_2 \quad (2)$$

During discharge, UV light was generated, so another way of hydroxyl radical generation is decomposition of hydrogen peroxide under UV radiation, Eq. (3):

$$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH \tag{3}$$

The hydroxyl radical is a strong oxidant species that could attack aromatic ring and/or aliphatic part of a molecule.

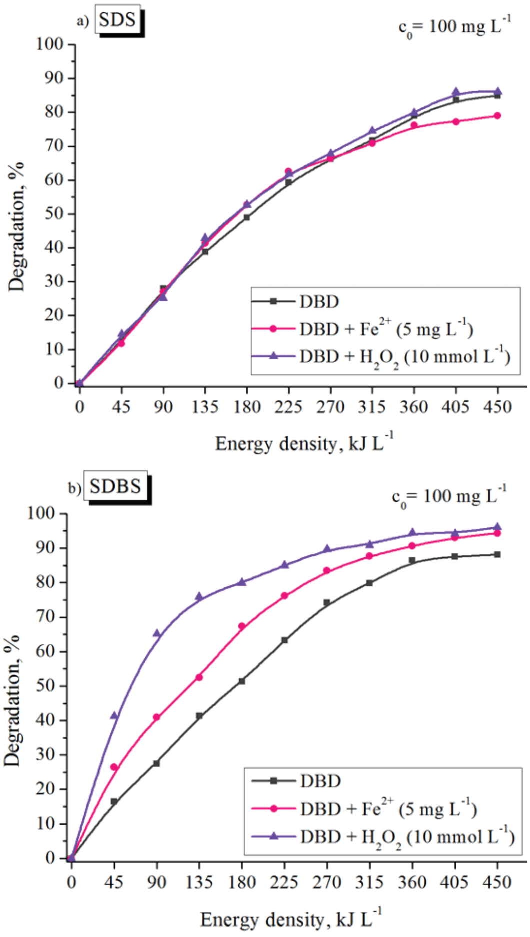

Fig.2. Degradation efficiency of anionic surfactants in the DBD reactor and the influence of homogenous catalysts at degradation efficiency: a) SDS and b) SDBS.

Increased efficiency of degradation in the systems that contain Fe^{2+} could be explained by Fenton's reaction and reaction of Fe^{2+} with ozone. It is well known that DBD reactor produces H_2O_2 based on Eq. (4) and Eq. (5):[24]

$$2H_2O + e^- \rightarrow H_2O_2 + H_2 + e^- \tag{4}$$

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2 \tag{5}$$

Adding Fe^{2+} into the solution to be treated in DBD reactor increases the oxidation power by triggering the reaction with generated H_2O_2. The reaction between Fe^{2+} and H_2O_2 is known as Fenton's reaction that generates ${}^{\bullet}OH$ based on Eq. (6):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \quad (6)$$

Another way of the hydroxyl radical formation is through the reaction of ozone with Fe^{2+} based on Eq. (7) and Eq. (8):[25]

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \quad (7)$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \quad (8)$$

In the case of sodium lauryl sulfate, catalysts had no effect on surfactant degradation. This is to the contrary of the previous results for ozonization of SDS where adding hydrogen peroxide influenced SDS degradation.[26] However, the most significant difference between those results and our work is pH. After first passing through the DBD reactor, pH decreased from starting pH 7 to 3.5 in the case of SDS. After five passages, pH decreased to 2.6. Similar results were obtained in the case of catalyzed reaction. At pH 2.6, SDS underwent fast hydrolysis to sulfuric acid and dodecanol.[27] Conditions during plasma treatment (local high concentration of hydrogen ion and local increase of temperature) could significantly increase hydrolysis of SDS at higher pH.

Chemical oxygen demand

The *COD* value of initial solutions (0 kJ L^{-1}) for the two surfactants and the solutions after the plasma treatment (450 kJ L^{-1}) was determined. Values of *COD* are presented in Fig. 3. In the case of SDS, we obtained a higher degree of *COD* removal using DBD treatment. This can be explained by the fact that higher alcohols have higher values of reaction rate constant than DBS.[28] Catalyst influenced *COD* removal and better results were obtained using hydrogen peroxide as catalyst. In the case of SDS, we obtained 38 % of *COD* removal. Better results in *COD* removal for SDS than SDBS, could also be explained by the resistance of aromatic nuclei to oxidation.

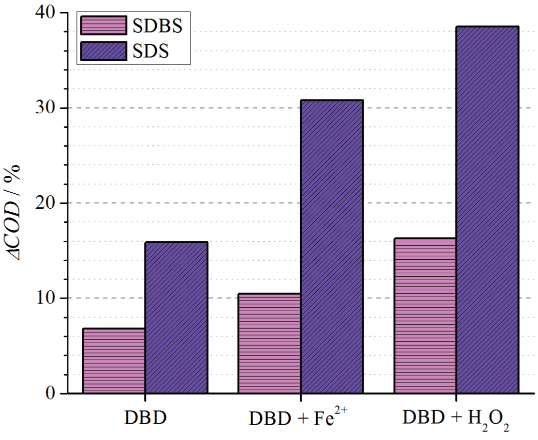

Fig. 3. Mineralization efficiency of plasma treated solutions presented as percentage decrease of *COD* value compared to the solutions that did not undergo plasma treatment.

Total organic carbon

Total organic carbon represents the amount of organic carbon present in the sample. It is often used as an indicator of water quality and it is a non-specific parameter, *i.e.*, it cannot be used for identification of organic substances present, but only for a determination of their amount. Results obtained for two samples of surfactants, shown in Fig. 4, before and after the plasma treatment showed the decrease of TOC value for all the systems tested. Better mineralization of SDS is achieved for the system where Fe^{2+} was used as a homogenous catalyst. That could be explained by the fact that iron as a catalyst favored degradation of oxalic acid (intermediate in alcohol oxidation).[29] The iron has low influence on mineralization of DBS. On the other hand, hydrogen peroxide has greater influence on DBS mineralization. In the case of hydrogen peroxide, dominant mechanism of degradation is through hydroxyl radical that has no influence on oxalic acid mineralization.[30]

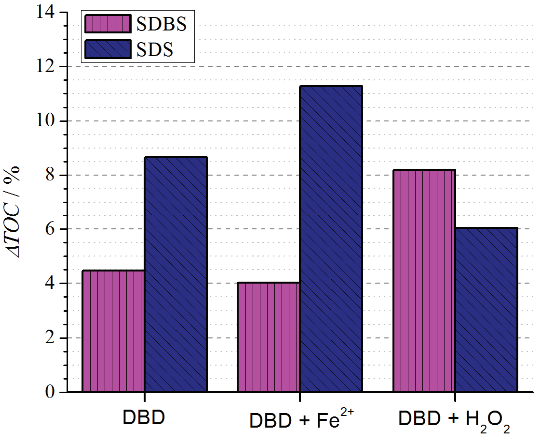

Fig. 4. Mineralization efficiency of plasma treated solutions presented as percentage decrease of TOC value compared to the solutions that did not undergo plasma treatment.

Toxicity tests

Toxicity of anionic surfactants, SDS and SDBS, was tested using *Artemia salina* organism and given as a percentage value of *Artemia salina* mortality (Fig. 5). As observed in Fig. 5, the toxicity of the plasma treated samples significantly decreased for all the systems tested. According to the literature, the value of LC_{50} for SDS in the case of *A. salina* was 41.04 (35.9–49.6) mg L^{-1} and for SDBS the LC_{50} value was 40.4 (38.7–48.5) mg L^{-1}.[31] The toxicity effect (%) of the initial solutions for both surfactants, samples diluted (1:1), was higher in comparison to the treated solutions of SDS and SDBS in all the systems (DBD, DBD + Fe^{2+} and DBD + H_2O_2). Treated solution of SDBS in the non-catalytic DBD system, as well as the catalytic DBD + Fe^{2+} system, generated a negative effect in the range of test validity criteria (≤10 %). The system with hydrogen peroxide as a catalyst

(DBD + H_2O_2) had slightly higher toxicity effect, however the mortality was under 20 % (Fig. 5a). In the case of SDS, solution treated in the non-catalytic DBD system and the catalytic DBD + Fe^{2+} system, induced lower toxicity in comparison to the catalytic system with hydrogen peroxide (DBD + H_2O_2) (Fig. 5b). Therefore, the most efficient reduction in mortality was achieved in the system where Fe^{2+} was used as a catalyst (DBD + Fe^{2+}).

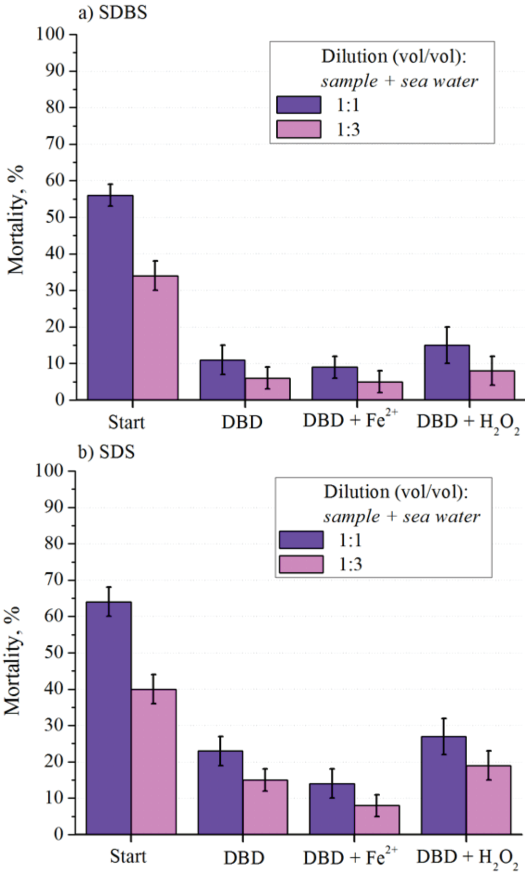

Fig. 5. Toxicity of surfactant solutions before and after the plasma treatment (number of replications: 3): a) SDBS and b) SDS.

CONCLUSION

The efficiency of degradation of the two anionic surfactants, sodium lauryl sulfate and sodium dodecylbenzenesulfonate, in the non-thermal coaxial plasma reactor with coaxial water falling film was studied. Influence of homogenous catalysts, H_2O_2 and Fe^{2+}, on the degradation efficiency was investigated. Based on the results, presence of catalyst affected the degradation of SDBS. In the case of SDS, catalyst had no effect on degradation. However, in both cases catalyst affected *COD* and *TOC* decrease. Hydrogen peroxide showed better results in

COD decrease for the treatment of both surfactants, while iron salts performed better in *TOC* decrease after the SDS treatment. Toxicology tests, done with *Artemia salina* test organisms, showed that the toxicity of solution decreased after the plasma treatment in all the systems tested.

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ИЗВОД

РАЗГРАДЊА АНЈОНСКИХ ПОВРШИНСКИ АКТИВНИХ СУПСТАНЦИ ПОМОЋУ РЕАКТОРА НА БАЗИ ДИЕЛЕКТРИЧНОГ БАРИЈЕРНОГ ПРАЖЊЕЊА

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Раствори два анјонска сурфактанта (натријум-лаурилсулфат – SDS и натријум-додецилбензенсулфонат – SDBS) третирани су у реактору који се базира на диелектричном баријерном пражњењу. Испитани су губитак активности сурфактаната, смањење вредности хемијске потрошње кисеоника и укупног органског угљеника. Испитан је и ефекат катализатора – водоник-пероксида и гвожђа(II), на ефикасност деградације и поменуте параметре. Катализатори утичу на деградацију натријум-додецилбензенсулфоната, док на деградацију натријум-лаурилсулфата немају утицај. Међутим, оба катализатора утичу на смањење вредности укупног органског угљеника и хемијске потрошње кисеоника. Токсичност раствора после третмана плазмом је нижа у испитаним системима.

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