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Degradation of surfactants using dielectric barier discharge reactor

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Degradacija surfaktanata primenom reaktora sa dielektričnim barijernim pražnjenjem

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Abstract

Surfactants are a group of compounds, which are widely used in industrial, agricultural, and pharmaceutical markets in various products, including detergents, pesticides, petroleum products, cosmetics and pharmaceuticals. Surfactants and their degradation products are widely detected in domestic and industrial wastewater. Due to their significant effects on the aquatic environment, degradation of surfactants is subject of many research papers. In addition to the classical wastewater treatment a lot of research is addressed to the usage of advanced oxidation process for removal of various surfactants.

The aim of this study was to investigate using of non-thermal plasma (water falling film dielectric barrier discharge plasma reactor) for degradation of two anionic surfactants (sodium dodecyl sulfate - SDS and sodium dodecylbenezene sulfonate - DBS) and two nonionic surfactant (Triton X-100 and nonylphenol ethoxylate - NPE). Surfactants examined in this research are predominantly used in formulations of laundry detergents and for industrial cleaning application. The effects of two catalytic plasma systems,(iron (II) salt and hydrogen peroxide), were tested to improve the degradation of surfactants. Efficiency of degradation was determined by spectrophotometric determination of decrease of surfactants concentration. Decrease of chemical oxygen demand and total organic carbon were measured to determine degree of mineralization.

In cases of two nonionic surfactants and sodium dodecylbenzene sulpfonate catalytic systems exhibited significant improvements in degradation efficiency especially in beginning of treatment. In the case of sodium dodecyl sulphate catalysts have no effect on surfactant degradation. Mineralization of surfactants in all cases was significantly improved in presence of catalyst.

Toxicity test with *Artemia salina* (*A. salina*) test organisms showed that toxicity in all case were decreased after treatment of solutions in water falling film dielectric barrier discharge plasma reactor.

Key-words: surfactants, advanced oxidation process, non-thermal plasma, dielectric barrier discharge, homogenous catalysis, toxicity test

Izvod

Surfaktanti predstavljaju grupu jedinjenja koja se šitoko koristi u industriji, poljoprivredi i farmaceutskoj industriji u različitim proizvodima uključujući detergente, pesticide, proizvode petrohemijske industrije, kozmetičke proizvode i lekove. Surfaktanti i prozvodi njihove degradacije su vrlo često prisutni u kanalizacionim i industrijskim otpadnim vodama. Usled njihovog efekta na vodene organizme degradacija surfaktanata predstavlja značajnu oblast istraživanja. Pored klasičnih tretmana otpadnih voda istraživanja su usmerena i ka primeni unapređenih oksidacionih procesa za uklanjanje različitih surfaktanata iz otpadnih voda.

Predmet ovoga rada je ispitivanje mogućnosti primene netermalne plazme (korišćenjem reaktora sa dielektričnim barijernim pražnjenjem kroz tanak film vode) za degradaciju dva anjonska surfaktanta (natrijum-dodecil-sulfata i natrijum-dodecilbenzen-sulfonata) i dva nejonska surfaktanta (Triton X-100 i nonilfenol etoksilata). Ovi surfaktanti se koriste u formulacijama detergenata za pranje veša i u procesima industrijskog pranja. Pored toga ispitani su i efekti homogenih katalizatora (soli gvožđa (II) i vodonik-peroksida na poboljšanje efikasnosti degradacije. Efikasnost degradacije je praćena spektrofotometrijskim određivanjem smanjenja koncentracije surfaktanata. U cilju određivanja stepena mineralizacije odnosno potpune razgradnje organske supstance određeni su hemijska potrošnja kiseonika i ukupan organski ugljenik nakon tretmana.

U eksperimentima sa dva nejonska surfaktanta i natrijum-dodecilbenzen-sulfonata katalitički sistemi su pokazali značajan efekat u povećanju efikasnosti degradacije posebno pri nižim vrednsotima primenjene energije. U eksperimentu sa natrijum-dodecil-sulfatom katalizatori nisu pokazali uticaj na efikasnost degradacije. U svim eksperimentima katalizatori su pokazali značajan uticaj na mineralizaciju rastvora odnosno na razgradnju organske supstance.

Testovi ispitivanja toksičnosti sa *Artemia salina* organizmima su pokazali da je u svim eksperimentima toksičnost rastvora smanjena nakon tretmana u reaktoru sa dielektričnim barijernim pražnjenjem.

Ključne reči: surfaktanti, unapređeni oksidacioni procesi, netermalna plazma, dielektrično barijerno pražnjenje, homogena kataliza, test ispitivanja toksičnosti

Abbreviations

Abbreviation	Parameter
Advanced oxidation process	AOP
Alcohol ethoxylates	AE
Alcohol ether sulfates	AES
Alkylbenzene sulfonates	ABS
Alkylphenol ethoxylates	APE
Alkylphenoxy carboxylates	APEC
Alkylphenol polyethoxylate	APEO
Alkylpolyglucosides	APG
Alkyl sulfates	AS
Alkyl Amine oxides	AO
Artemia salina	*A. salina*
Atomic absorption spectrometry	AAS
The bioconcentration factors	BCF
Critical micelle concentration	CMC
Chemical oxygen demand	COD
Dielectric barrier discharge	DBD
Ethylene oxide	EO
The energy density	ED
Fatty acid alkanolamides	FAA
Mass spectrometry	MS
N-methylglucamides	NMG
nonylphenol	NP
Nonylphenol ethoxylate	NPE
Polyethylene glycol esters	PEG
Propylene oxide	PO
The sorbed surfactant concentration	S
The surfactant concentration in the solution	C
Secondary alkane sulfonates	SAS
Sodium dodecyl sulphate	SDS

Sodium dodecylbenzenesulfonate	SDBS
Sodium linear alkylbenzene sulphonate	LAS
Sulphophenyl Carboxylates	SPC
Surface discharge	SD
Triton X-100	TX-100
Total organic carbon	TOC
Ultraviolet	UV
Urban wastewater treatment plant	UWWTP
Vibrio fischeri	*V. fischeri*
Volume discharge	VD
Wastewater treatment plants	WWTP
Water falling film DBD reactor	WFF DBD

List of figures

27. Degradation scheme of TX-100 decomposition with non-catalytic and catalytic DBD treatments.
28. Mass spectrum of Triton X-100 molecules.
29. Mass spectrum of Triton X-100 solution after degradation in the non-catalytic DBD with introduced energy density of 180 kJ L^{-1}.
30. Mass spectrum of Triton X-100 solution after degradation in the Fe^{2+} DBD system with introduced energy of 180 kJ L^{-1}.
31. Mass spectrum of Triton X-100 solution after degradation in the H_2O_2 /DBD system with introduced energy of 180 kJ L^{-1}.
32. *Artemia salina* toxicity test results for Triton X-100 and NPE.
33. Mineralization efficiency after Triton x-100 degradation in the DBD reactor
34. Degradation efficiency of DBS and SDS with dielectric barrier discharge.
35. Changes of pH with introduced energy density.
36. DNPH derivative of formaldehyde.
37. Chromatograms and changes in intensity of DNPH derivatives of formaldehyde with number of passes.
38. Changes in concentrations of hydroxyl radical in distilled water with introduced energy density.
39. Reaction between ozone and indigo dye forming colorless products.
40. Changes of ozone concentration in distilled water with introduced energy density.
41. Degradation efficiency of DBS in DBD reactor.
42. Degradation efficiency of SDS in DBD reactor.
43. Toxicity of surfactant solutions before and after the plasma treatment (Number of replications: 3).
44. Mineralization efficiency of plasma treated solutions presented as percentage of decrease of COD value compared to solutions that didn’t undergo plasma treatment.
45. Mineralization efficiency of plasma treated solutions presented as percentage of decrease of TOC value compared to solutions that didn’t undergo plasma treatment.
signala na niskom oksidacionom potencijalu za dijagnostiku celijakije (*eng. coeliac disease*

List of tables

CONTENTS

1.General Introduction

1.1 Surfactants - General Introduction

Surfactants are a group of compounds, which are widely used in industrial, agricultural, and pharmaceutical markets in various products, including detergents, pesticides, petroleum products, cosmetics and pharmaceuticals. Surfactants have a broad spectrum of applications because of their amphiphilic nature: they consist of a polar head group and a nonpolar hydrocarbon tail and combine both hydrophobic and hydrophilic properties in one molecule [1].

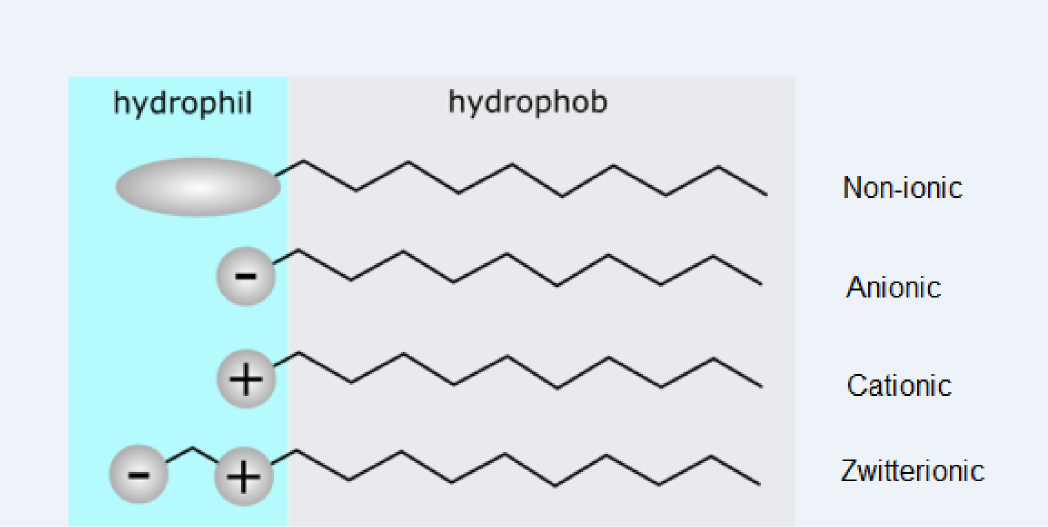


Figure 1. The four main different types of surfactants.

At low concentrations they accumulate at interfaces and surfaces thus reducing interface and surface tensions. When adding surfactants to a solution they will enrich at interfaces and because of their dual hydrophilic and hydrophobic nature they will lower the free energy (surface tension). At the interface, the hydrophilic part of the surfactant orients itself towards the aqueous phase and the hydrophobic parts orient itself away from the aqueous phase into the second phase [2]. When the interfaces and surfaces are fully occupied and the concentration of the surfactants in the water exceeds its solubility, several of their molecules form aggregates called micelles with the hydrophobic moieties of the molecules directed to the center (Figure 2). The concentration at which micelle formation begins is called Critical Micelle Concentration (CMC) [1].

The CMC of a surfactant is dependent on the hydrophilic head and the hydrophobic tail. More hydrophilic heads will result in a higher CMC value, conversely the presence of more hydrophobic surfactant will result in a lower CMC value.

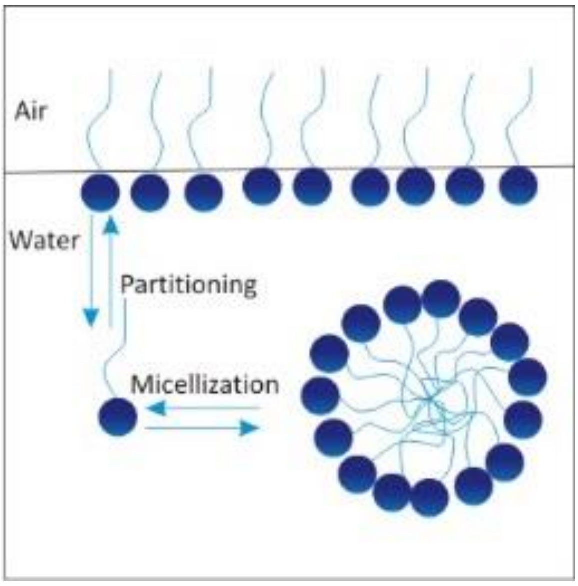


Figure 2. Partitioning of surfactants between air and water and micellization.

The total quantity of surfactants (without soaps) consumed in Western Europe in 2002 was more than 2.5 Mt, 49.5% of which were non-ionic, 38.5% ionic, 9% cationic and 3% amphoteric, according to Statistics of the European Committee of Surfactants and their Organic Intermediates (CESIO) [3,4]. A trend in the surfactant production in Western Europe during last decade is presented on the Figure 3.

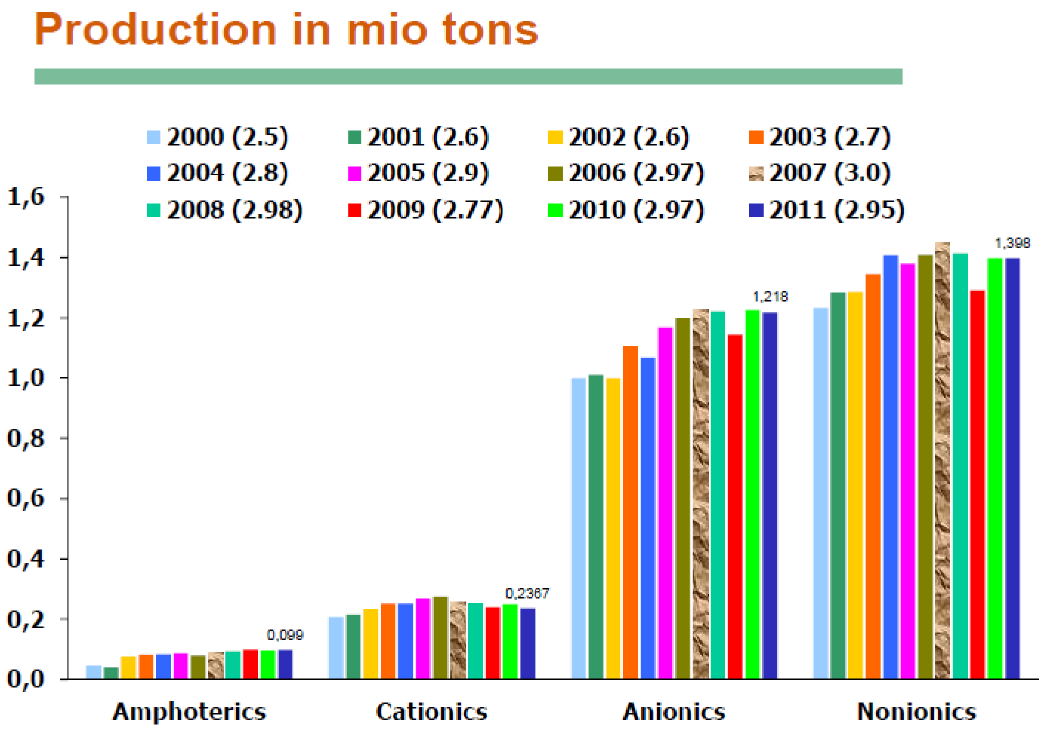


Figure 3. Surfactants production in millions tones in Western Europe 2000 - 2011 [5].

1.1.1. Types of surfactants

1.1.1.1. Anionic surfactants

Most detergents contain a large amount of anionic surfactants [6]. Anionic surfactants are surface-active compounds consisting of a hydrophobic alkyl chain and an anionic hydrophilic group. Anionic surfactants are negatively charged in aqueous solutions due to the presence of a sulfonate, sulfate, carboxylate or phosphate groups [7] (Figure 4).

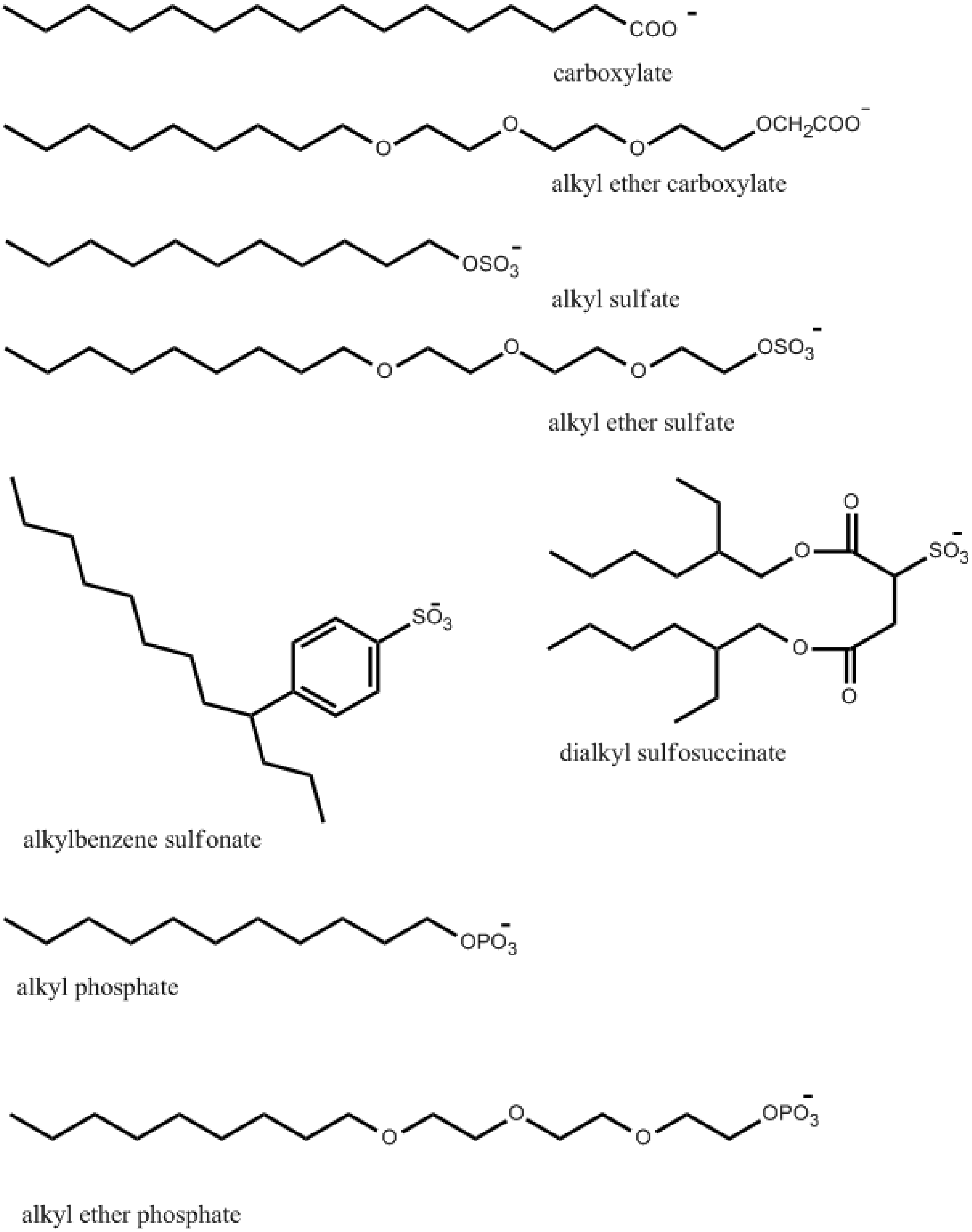


Figure 4. Chemical structures of some anionic surfactants.

Commercial anionic surfactants contain mixtures of homologues with different alkyl chain lengths. For some surfactant groups, the existence of different isomers also add to the complex nature and versatile application of these substances. [7]. The largest volume of anionic surfactants is used in the consumer products like, e.g., laundry detergents, cleaning and dishwashing agents as well as the personal care products.

Another important application of anionic surfactants includes cleaning agents designed for the industrial and institutional market. By volume, the most important groups of anionic surfactants are fatty acid soaps, linear alkylbenzene sulfonates, alkyl ether sulfates and alkyl sulfates [7].

Soap has remained the largest surfactant by volume worldwide. It is still the surfactant of choice in many countries. A decreased use of soap can be found in laundry detergents, due to its sensitivity to water hardness. In Europe, the primary function remaining for the soap is a foam regulator in the laundry detergents [6].

The production of soap is carried out on a large scale. The prevalent manufacture process is hydrolysis of triglycerides with the sodium hydroxide. This method coproduces glycerol and the sodium salt of the fatty acid (soap). The triglycerides used in the soap manufacturing are commonly derived from beef tallow and several vegetable oils (*i.e.* coconut, palm and palm kernel oils) [8].

In Europe, USA, and Japan soap has been largely replaced by the synthetic anionic surfactants, such as linear alkylbenzene sulfonate (LAS). LAS show very good detergency performance and, as a result of their high solubility, LAS are also frequently used in the formulations for liquid detergents. Like soap, LAS are sensitive to water hardness [6, 9]; the detergency performance of LAS is reduced with increasing water hardness. [6]

Linear alkylbenzene sulfonate (LAS) is one of the most used synthetic anionic surfactants worldwide. They were introduced in the sixties as the principal component of household detergents to replace the highly branched alkylbenzene sulfonates (ABS). The use of LAS was favored because of the high biodegradability, excellent detergent properties and lower production costs [10, 11]. The European consumption of LAS in 2005 was 430 kt, from which more than the 80% was used in the formulation of household cleaning products [10, 12].

LAS are produced by the sulfonation of dodecylbenzene (commonly referred to as linear alkylbenzene, LAB) with sulfuric acid or sulfur trioxide. Almost 90% of the produces dodecylbenzene is consumed in the manufacture of LAS. Dodecylbenzene is produced by the alkylation of benzene with dodecene in the presence of an aluminum chloride catalyst. Dodecene can be produced by the thermal cracking of wax paraffin to (alpha)-olefins [an (alpha)-olefin is a hydrocarbon with a double bond between the first (alpha) and second (beta) carbon atoms] [8].

Alkyl sulfates (AS) are used in the laundry detergents, frequently in combination with other anionic surfactants. AS are used in special products, including wool-washing agents, soap bars and liquid bath soaps, hair shampoos, and toothpastes. Most of the AS used in the consumer products are linear primary AS but some linear and branched secondary AS are also being used [7].

Alkyl sulfates are produced either from natural fatty alcohols or from petrochemical substances. Their use has increased especially in the concentrated products [6].

Secondary alkyl sulfonates SAS are seen as special anionic surfactants for consumer products. The SAS include high solubility, fast wetting and good chemical stability. Their properties are very similar to LAS in terms of detergency and water hardness sensitivity. They are completely insensitive to hydrolysis, even at extreme pH values, due to the presence of the stable carbon–sulfur bond [6].

Alkyl ether sulfates (AES), or alkyl ethoxy sulfates, are being used increasingly, frequently in the combination with other anionic and nonionic surfactants, in liquid bath soaps, hair shampoos, and mechanical dishwashing agents. [7].

1.1.1.2. Nonionic surfactants

The term nonionic surfactant usually refers to derivatives of ethylene oxide and/or propylene oxide with an alcohol containing an active hydrogen atom. Nevertheless, other types such as alkyl phenols, sugar esters, alkanolamides, amine oxides, fatty acids, fatty amines and polyols are all produced and used widely throughout the world in a multitude of industries [13] (Figure 5).

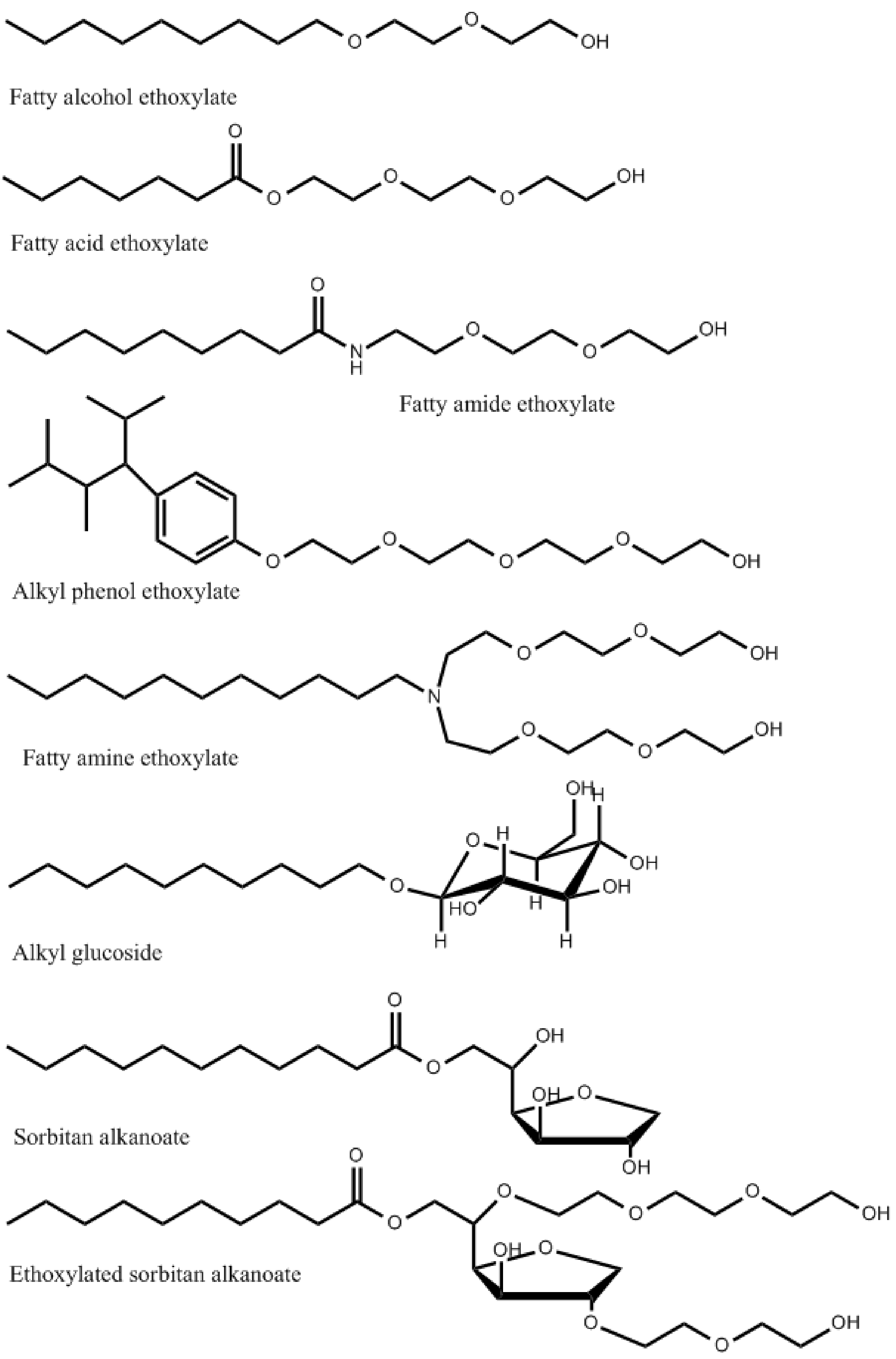


Figure 5. Chemical structures of some nonionic surfactants.

Nonionic surfactants do not have an electrical charge, which makes them resistant to deactivation caused by water hardness. They are excellent grease removers, which are used in the laundry products, household cleaners and hand dishwashing liquids. The most of laundry detergents contain both nonionic and anionic surfactants as they complement each other's cleaning action. Nonionic surfactants contribute to the feature that makes the surfactant system less hardness sensitive. The most commonly used nonionic surfactants are ethers of fatty alcohols [14].

One of the main advantages of the nonionic surfactants is their compatibility with all other surfactants. This property is attributed to the presence of the non-charged head group in the structure of nonionic surfactants [15, 16]. In general, nonionic surfactants have lower CMC levels than anionic and cationic ones. [17].

Nonionic surfactants, like most ethylene oxide derivatives, exhibit inverse solubility characteristics and may precipitate with the solution’s temperature increase . This sometimes precludes their use in high temperature applications but can be an advantage if is desired to destroy surfactant activity by temperature elevation [18].

Most non-ionic surfactants are not single compounds but rather the products of a reaction between ethylene oxide and organic compounds such as alkyl alcohols, alkylphenols and fatty acids. These reactions produce mixtures, which have a range of ethoxymer chain lengths. The trivial nomenclature for these compounds is generally based on their average ethoxymer chain length with for example 'NP9' being used to describe a nonylphenol ethoxylate formulation with an average ethoxymer chain length of nine. The parent compound of this type of surfactant is described as the alkylphenol polyethoxylate (APEO). An estimated 350 000 tons per year of APEOs are currently used in the US, Western Europe and Japan [19].

The growing popularity of nonionic surfactants in the surfactants market is due to several factors including [20]:

1) Their inherent electrical neutrality is desirable in many applications.

2) Importance of low foaming nonionic surfactants like ethylene oxide/propylene oxide (co-polymers) EO/PO block copolymers in the new generations of washing machines.

3) Compatibility with other ionic types for suitable surfactant blends, often resulting in synergism.

4) Availability of a wide range of nonionic surfactants to suit specific needs.

5) The important role of some nonionic as intermediates for the production of key anionic such as alcohol ether sulfates (AES).
6) The growing importance of ethoxylates in the detergent, cosmetics, food and other industrial sectors and the growing preference for narrow range ethoxylates.
7) A reasonable price structure and current globalization of surfactant markets.
8) Growing preference for natural-based nonionic products such as alkylpolyglucosides (APG) and alkylglucosides (AGA).

Alcohol ethoxylates AE are the most important nonionics in detergent formulations. By varying the length of carbon chain and the degree of ethoxylation, these nonionic surfactants can be tailor-made with respect to the washing temperature [6].

Fatty acid alkanolamides FAA alone have little application in laundry detergents. Their most important feature is foam boosting, *i.e.* adding desired stability to the foam produced by detergents prone to heavy foaming [6].

Alkylamine oxides AO are produced by oxidation of tertiary amines with hydrogen peroxide. They show cationic behavior at acidic conditions and behave as nonionic surfactants at neutral or alkaline conditions. Despite the good detergent properties, they are rarely included in laundry detergent formulations due to the high costs and low thermal stability [6].

N-Methylglucamides (NMG) are a new type of nonionic surfactants that has been introduced into detergents market in the 1990s. They are increasingly used as co-surfactants in powder and liquid detergent formulations [6].

Alkylpolyglycosides (APG) consists of an alkyl chain (hydrophobic) and sugar derivate (hydrophilic) and have distinct lathering characteristics, especially in combination with anionic surfactants [6, 21, 22]. Due to their good foaming properties APGs are predominantly used in the dishwashing detergents, liquid detergents, and special detergents for fine fabrics [6].

Nonylphenol ethoxylates (NPEs) are highly effective surfactants that have been safely used for more than 40 years in a number of industrial sectors including textiles, pulp and paper, paints, adhesives, resins and protective coatings. NPEs are also used in a variety of cleaning products and detergents for home and institutional use [23]. There are three main reasons why the nonylphenol ethoxylates have been the material of choice in the pulp and paper industry: cost effectiveness, score on Draves' wetting test, and stability under harsh condition [23].

1.1.1.3 Amphoteric surfactants

Amphoteric surfactants may contain two charged groups of different sign. They can be anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) in the solution, depending on the acidity or pH of water. They are compatible with all other classes of surfactants and are soluble and effective in the presence of high concentrations of electrolytes, acids and alkalis. Whereas the source of the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, sulphonate) [14, 25, 26].

Amphoteric surfactants include two main groups, *i.e.* betaines and real amphoteric surfactants based on fatty alkyl imidazolines (Figure 6). The key functional groups in the chemical structures are the more or less quaternized nitrogen and the carboxylic group. Betaines are characterized by a fully quaternized nitrogen atom and do not exhibit anionic properties in alkaline solutions, which means that betaines are present only as 'zwitterions'. Another group of amphoterics are designated imidazoline derivatives because of the formation of an intermediate imidazoline structure during the synthesis of some of these surfactants. This group contains the real amphoteric surfactants that form cations in acidic solutions, anions in alkaline solutions, and 'zwitterions' in mid-pH range solutions [7]. The mid-pH range (isoelectric range) in which the surfactant has a neutral charge is compound specific and depends on the alkalinity of the nitrogen atom and the acidity of the carboxylic group [7].

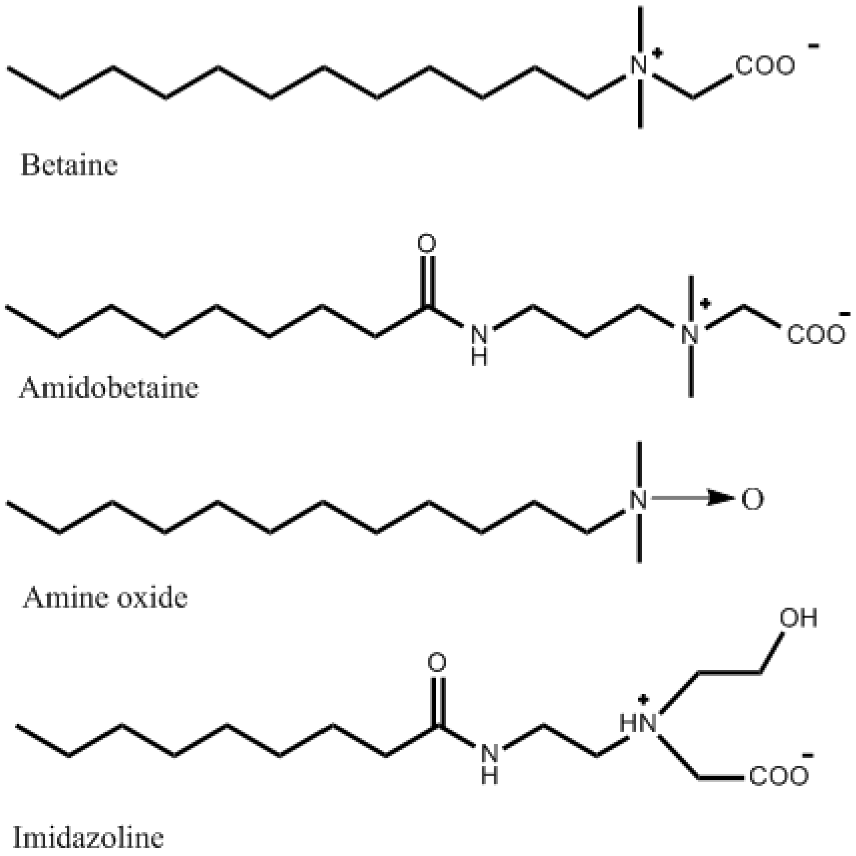
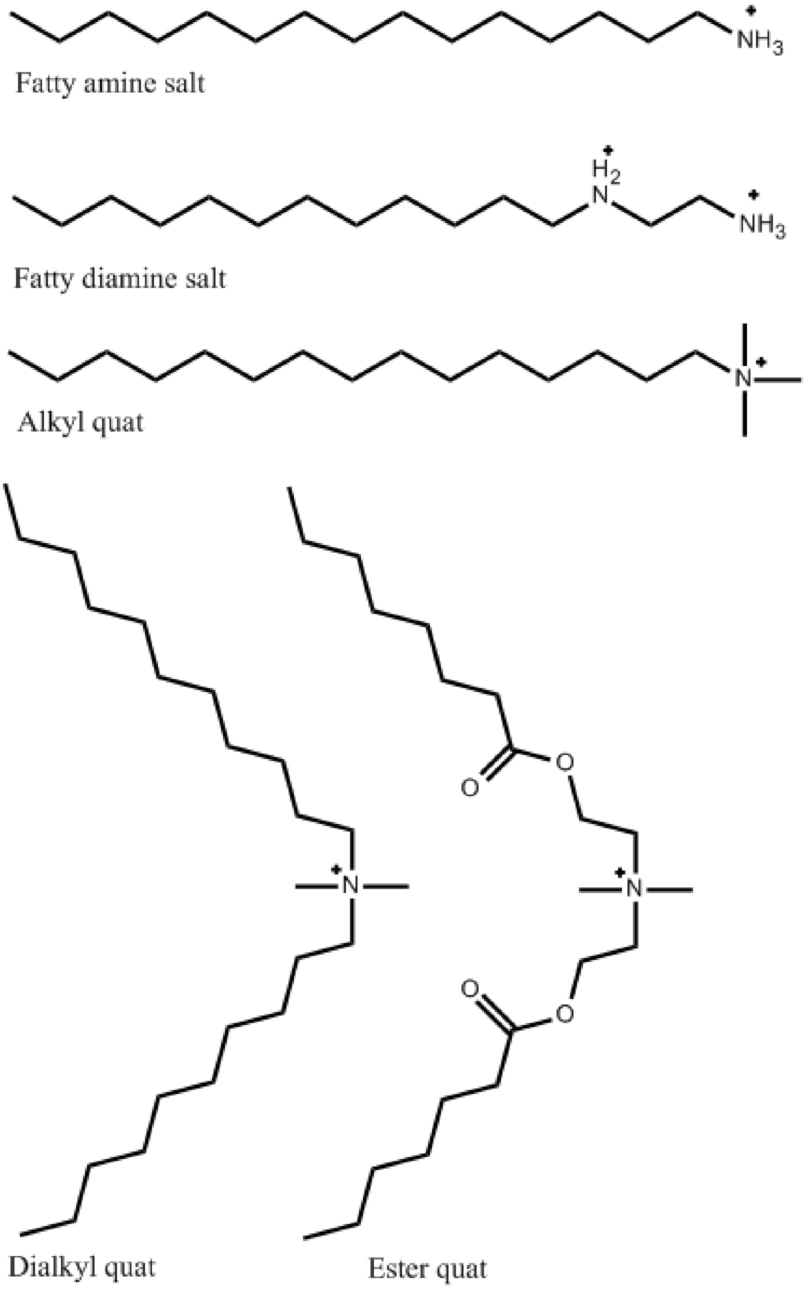


Figure 6. Chemical structures of some zwitterionic surfactants.

Amphoteric surfactants are mainly used in manual dishwashing and body care products. The most important types of amphoterics are: alkyl betaine, alkylamidopropyl betaine, betaines derived from imidazolines, alkylamphoacetates [6]. They are used in personal care products (*e.g.* hair shampoos and conditioners, liquid soaps, and cleansing lotions) and in all-purpose industrial cleaning agents [7].

1.1.1.4 Cationic surfactants

Cationic surfactants are surface-active compounds with at least one hydrophobic alkyl chain and a hydrophilic group carrying a positive charge. [7]. Cationic surfactants are positively charged in the aqueous solutions. The quaternary ammonium compounds are especially used in the commercial products [7, 14] (Figure 7).



Fatty amine salt

Fatty diamine salt

Alkyl quat

Dialkyl quat

Ester quat

Figure 7. Chemical structures of some cationic surfactants.

A positively charged quaternary nitrogen atom characterizes the structure of quaternary ammonium compounds. Commercial raw materials are normally derived from natural oils, which imply that homologous mixtures of surfactants with different alkyl chain lengths are used in the products [7].

Cationic surfactants represent one of the smaller classes of surfactants when compared to anionic and nonionic surfactants. Annual worldwide production of cationics is estimates for 500 000 metric tons [13].

The mostly used cationic surfactants are fatty amines, their salts and quaternary derivatives. Actually, fatty amines are not cationic but anionic surfactants. However, they are generally classified with cationics because they are mostly used at acid pH, in which their salts are cationic [26].

1.1.2. Environmental fate of surfactants

Surfactants are regarded as one of the major and most undesirable pollutants detected in the aquatic and terrestrial environment. Due to the excessive occurrence of surfactants and their continuous presence in the environment, there is a considerable interest in environmental fate of surfactants [27]. After use, the residual surfactants and their degradation products are discharged to sewage treatment plants or directly to surface waters, and then dispersed into different environmental compartments. Due to their widespread use and high consumption they have been detected at various concentrations in surface waters, sediments and sludge-amended soils. In order to assess their environmental risks, we need to understand the distribution, behavior, fate and biological effects of these surfactants in the environment.

TABLE 1. Concentrations of surfactants in sewage influents and effluents.

Surfactant	Location	Influent (mg/L)[a]	Effluent (µg/L)	Ref.
LAS	Germany	0.5–3.5	7–16	29
LAS	The Netherlands	3.1–7.3	<8.1–491	30
LAS	UK	1.73–5.58	40–1090	31
LAS	Italy	3.4–10.7	21–290	32
LAS	The Netherlands	3.4–8.9 (5.2)	19–71 (39)	33
AES(C12C15)		1.2–6.0 (3.2)	3.0–12 (6.5)	33
AS(C12C15)		0.1–1.3(0.6)	1.2–12 (5.7)	33
Soap		14–45 (28)	91–365 (174)	33
AE(C12C15)		1.6–4.7 (3.0)	2.2–13 (6.2)	33
AE(C12C15)	United States	0.68–3.67	11–114	34
NPE	United States		<LOD–332 (9.3)	35
NPE	Italy		2–27 (10)	36
NPE	Greece	1.18–1.62 (1.4)	35–130 (62)	37

[a] Concentration range and median in parentheses. LOD = limit of detection.

Surfactants in raw sewage or wastewater can easily be treated by modern treatment technologies at high rates [28]. The removal efficiency of a surfactant depends on its physiochemical properties, treatment plant design and waste load. Results of the removal efficiency for some wastewater treatment plants are given in Table 1 [28].

In addition to the surfactants, their degradation products are also widely detected in sewage effluent. Of greatest concern are alkylphenols, which are the degradation products of nonionic surfactant APE. During sewage treatment, APE are biodegraded through a mechanism involving stepwise loss of ethoxy groups to shorter APE homologues, carboxylated products (alkylphenol ethoxycarboxylates, *i.e.*, APECs), and finally alkylphenols such as nonylphenol (NP) and octylphenol (OP) [28]. NP and OP are known to be more toxic than their ethoxylate precursors and to mimic the effect of the hormone estrogens [28]. The concentrations of NP and OP in the final sewage effluents vary widely among various sewage treatment plants from less than the limit of detection (LOD) to 343 µg/L (Table 2).

TABLE 2. Concentrations of alkylphenols in effluents of sewage treatment plants [28].

Location	Sample no.	Concentration (mg/L)[a] NP	Concentration (mg/L)[a] OP
Canada	8	0.8–15.1 (1.9)	0.12–1.7 (0.69)
United Kingdom	16	< 0.2–5.4 (0.5)	
Switzerland	2	5–11	
Spain	3	6–343	
Japan	10	0.08–1.24	0.02–0.48
United States	1	16	0.15
United States	6	0.171–37 (1.02)	< LOD–0.673 (0.072)
Germany	16	< LOD–0.77 (0.111)	< LOD–0.073 (0.014)
Italy	12	0.7–4 (1.8)	

[a] Concentration range and median in parentheses. LOD = limit of detection.

In wastewater treatment, a proportion of the surfactants are being removed by adsorption on sewage solids during the primary settlement of sewage. In many countries, the treated sludge (biosolids) may be applied onto agricultural lands as fertilizers for plants. High concentrations of surfactants were found in treated sludge. Surfactants in aerobically treated sludge are found in much lower concentrations than in anaerobically digested sludge because of their quicker aerobic biodegradation. Bruno *et al.* [38] determined the surfactants and their metabolites in untreated and anaerobically digested sludge and found that the removal rates for anionic surfactants LAS, AS, and AES (7%, 28%, and 8%) were lower than for nonionic surfactants AE and NPE (54% and 63%) [28].

TABLE 3. Concentrations of surfactants in treated sludge [28].

Surfactant	Location	Treatment	Concentration (mg/kg dry weight)
LAS	Switzerland	Anaerobically digested sludge	2900–11.900
LAS	Germany	Aerobically treated sludge Anaerobically digested sludge	182–432 1327–9927
LAS	Spain	Aerobically treated sludge Anaerobically digested sludge	100–500 7000–30200
LAS	United States	Aerobically treated sludge Anaerobically digested sludge	152 ± 119 10.462 ± 5.170
LAS	Italy	Anaerobically digested sludge	4342
AS			47
AES			69
AE			143
NPE			81
OP			17
Np			308

However, OP and NP concentrations in the sludge increased after the treatment from 14 and 242 mg/kg to 17 and 308 mg/kg, respectively. This is because OPE and NPE in the sludge were degraded into OP and NP during the anaerobic digestion. Surfactant concentrations up to 416 µg/L have been reported in surface waters (Table 4). Waters and Feijtel [9] summarized the LAS monitoring data in European rivers with concentrations ranging from under 2.1 to 130 μg/L in water and from 0.49 to 5.3 mg/kg in sediment. Sulfophenyl carboxylates, main degradation product of LAS was also found in the drinking water samples from Niteroi, Sao Goncalo, and Rio de Janeiro, with its concentration ranging from 1.4 ± 0.2 μg /L to 3.7 ± 0.7 μg /L [28,39].

TABLE 4. Concentrations of surfactants in surface waters and sediments.

Surfactant	Location	River water (μg/L)[a]	Sediment (μg/L)	Ref.
LAS	Brazil	14–155		39
LAS	Philippines	1.2–102		40
LAS	Switzerland		190–3400	41
LAS	Taiwan	11.7–135		42
LAS	The Netherlands	< 2.1–168		30
LAS	United Kingdom	22–130		43
LAS	United Kingdom	5–416		44
AE	United States	2–37		35
NPE	United States	< LOD–17.8 (6.97)		36
NPE	Taiwan	2.8–25.7 (21.3)		42

[a] Concentration range and median in parentheses.LOD = limit of detection.

The occurrence of APE degradation products (NP, OP) has been widely reported in surface waters (rivers, lakes, and coastal waters as well as aquatic biota) around the world (Table 5). Concentrations in surface waters were found to be up to 644 μg/L for NP and up to 0.47 μg/L for OP, respectively. Owing to their hydrophobic nature, the reported alkylphenol levels in the sediments were much higher than in the corresponding surface waters. Their concentrations varied between less than 0.1 and 13,700 μg/kg for NP and up to 670 μg/kg for OP in the sediment.

TABLE 5. Concentrations of alkylphenols in a surface waters and sediments.

Location	Concentration (μg/L) in water [a] NP	Concentration (μg/L) in water [a] OP	Concentration (μg/kg) in sediment NP	Concentration (μg/kg) in sediment OP	Ref.
Canada	<LOD–0.92	<LOD–0.084	0.1–72	<LOD–1.8	45
United Kingdom	(<LOD) <0.03–53 (1.3)	(<LOD) <0.2–22 (<0.2)	(10.6)[b] <0.1–1(<0.1)	(0.41)[b]	46 47

Switzerland	0.7–26 (2.7)^{b}				48
	<LOD–0.48				49
Spain	<LOD–644 (51)				49
Japan	0.05–1.08	0.01–0.18	30–13000	3–670	50
	0.11–3.08	<LOD–0.09			51
	<LOD–1.9 (0.25)^{b,c}				52
	<LOD–3.0 (0.15)^{b,d}				53
United State	<LOD–1.19 (1.52)	<LOD–0.081 (0.017)			35
	12–95 (48)^{b}				54
	0.077–0.416 (0.2)	0.00156–0.007 (0.002)	6.99–13700 (2107)^{b}	<LOD–45 (30)^{b}	55
	<0.11–0.64 (0.12)^{b}		< 2.9–2960 (162)^{b}		56
Germany	0.0067–0.134 (0.023)	0.0008–0.054 (0.0038)			57
Taiwan	1.8–10 (3)				42

[a] Concentration range and median in parentheses LOD = limit of detection

[b] Arithmetic mean (± standard deviation) in parentheses for the data in this row

[c] Summer sampling

[d] Autumn sampling

Once surfactants enter the environment they undergo many processes, such as sorption, bioaccumulation, degradation and solubilisation of other organic compounds. Sorption of a surfactant onto sediment/soil depends on its physiochemical properties, sediment nature and environmental parameters. The information from sorption process of a surfactant can be used to estimate the distribution of the surfactant in different environmental compartments (sediment/soil and water) and to estimate their bioavailability. Sorption also has a significant influence on the degradation of the surfactant in the environment. Surfactant molecules may sorb directly onto solid surfaces or may interact with sorbed surfactant molecules. The sorption mechanism is dependent on the nature of the sorbent and the surfactant concentration. At low concentrations, the surfactant molecules may be sorbed to a mineral surface or clean sediment that has very few sorbed surfactant molecules, and sorption may occur mainly due to van der Waals interactions between the hydrophobic and hydrophilic moieties of the surfactant and the surface. As the surfactant concentration increases, active sorption sites on the solid surface become less and less available, and more and more hemimicelles start forming. At higher concentrations, such sorption may entail the formation of more structured arrangements, including the formation of monomer surfactant clusters on the surface or a second layer, for which these arrangements may be governed mainly by interactions between hydrophobic moieties of the surfactant molecules. Therefore, two-stage sorption isotherms (Figure 8) have been reported for nonionic surfactants NPE and AE and anionic LAS, although the sorption behavior is different for nonionic and anionic surfactants [28].

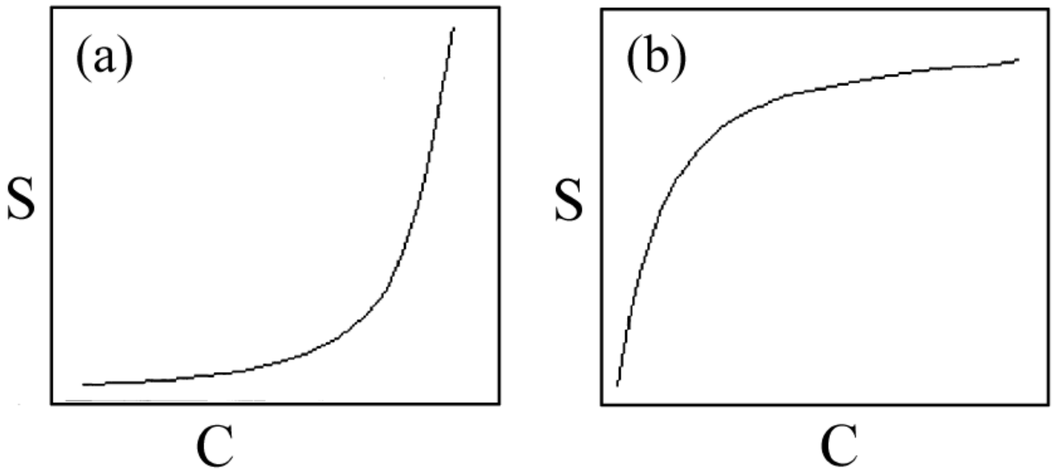


Figure 8. Sorption isotherms for anionic and nonionic surfactants (a.LAS; b.APE and AE, S is the sorbed surfactant concentration and C is the surfactant concentration in the solution).

The sorption of LAS on natural soils has two stages. At low LAS concentration (<90 µg/cm^3), the sorption isotherms were linear and the sorption coefficient (K_d) ranged from 1.2 to 2.0. At high levels (>90 µg/cm^3), cooperative sorption was observed and the sorption amount of LAS increased exponentially with the increasing of LAS concentration in the solution [81]. In a real soil environment or aquatic environment, where LAS levels are rather low, the LAS sorption ability of a soil or sediment is very weak. In contrast, the sorption of a nonionic surfactant reached a maximum on the solid surface when the solution is near or just at the CMC level of the surfactant. The decreased sorption of nonionic surfactants (APE and AE) on sediment at higher concentrations was observed [28].

At concentrations above the CMC level, surfactants have the ability to solubilize more hydrophobic organic compounds than would be dissolve in water alone. The effectiveness of surfactants in solubilizing water insoluble or poorly soluble compounds is dependent on the sorbed compounds, the environmental media and the surfactant [58]. Surfactants may affect the mobility and degradation of hydrophobic organic compounds in soil or sediment [59,60]. Aronstein *et al.* (1991) [58] found that the extent of phenanthrene biodegradation was markedly increased at nonionic surfactant concentrations of 10 µg/kg soil in both a mineral and organic soil, despite the lack of desorption enhancement in the organic soil.

Ying *et al.* [61] also found that small percentages (> 1%) of surfactants in water could mobilize triazines in the contaminated soils, which have been previously stabilized by the activated carbon. Kile and Chiou [62] studied the effect of anionic, cationic and nonionic surfactants on the water solubility of DDT and trichlorobenzene. As would be expected, the solubility was enhanced when the surfactant was present at concentrations greater than the critical micelle concentration. There was also a solubility enhancement at surfactant concentrations less than the CMC levels. However, the studies by Klumpp *et al.* [63] and Edwards *et al.* [59] found that surfactants below CMC enhanced the sorption uptake of hydrophobic organic pollutants due to the formation of hemimicelles. At higher concentrations, the same surfactants in micellar form remobilized those hydrophobic compounds already adsorbed by solubilization.

Bioconcentration is the accumulation of a chemical in or on an organism when the source of chemical is solely water. Bioconcentration is a term that was created for use in the field of aquatic toxicology. Bioconcentration can also be defined as the process by which a chemical concentration in an aquatic organism exceeds that in water as a result of exposure to a waterborne chemical. Bioconcentration factor can also be expressed as the ratio of the concentration of a chemical in an organism to the concentration of the chemical in the surrounding environment. In surface water, the BCF is the ratio of a chemical's concentration in an organism to the chemical's aqueous concentration. BCF is often expressed in units of liter per kilogram (ratio of mg of chemical per kg of organism to mg of chemical per liter of water) [28].

It has been found that longer LAS homologues have higher K_{ow} values (Table 6). LAS are taken up from water via the fish gills rather than skin [64]. The concentrations of the selected LAS homologues (C10LAS to C13LAS) in the liver and the internal organs of juvenile rainbow trout increased rapidly demonstrating fast uptake into systemic circulation. The bioconcentration factors (BCFs) in rainbow trout ranged between 1.4 and 372 L/kg. The BCFs in fathead minnows were higher, ranging from 6 to 990 L/kg [64]. In the terrestrial environment, BCFs are significantly lower than in the aquatic environment and a bioaccumulation of LAS in terrestrial biota is mostly unlikely [65].

TABLE 6. Octanol/Water partition coefficients (K_{ow}) and critical micelle concentrations (CMC) of surfactants [28].

Compound	Log Kow	CMC(mM) (distilled water)
C12LAS	1.96	1.1
C13LAS	2.54	0.46

Tolls *et al.* [64] produced data for bioaccumulation factors for alcoholethoxylate in fathead minnows (*Pimephales promelas*). The influence of both the alkyl and the ethoxylate chain length was studied. The BCF increased with increasing length of the alkyl chain and decreasing length of the ethoxylate chain. The bioconcentration factors (BCF) ranged between < 5 and 390 L/kg.

NP and OP also may bioaccumulate in aquatic organisms. This has been documented in some fish species from natural waters and from controlled laboratory exposure (Table 7). The reported bioconcentration factors (BCF values) in whole fish ranged from 21 to 1300 for 4-NP and 267 to 471 for 4-t-OP. The differences in the BCF values of NP and OP among fish species are probably due to their different metabolic abilities, functioning of their gills, etc. [28, 66].

TABLE 7. Bioconcentration factor (BCF, wet weight) data for alkylphenols [28].

Species	4-Nonyphenol	4-t-Octylphenol
Ayu fish (field)	21 ± 15	297 ± 194
Killifish	167 ± 23	267 ± 62
Sticklebacks (field)	1300	
Salmon	282	
Fathead minnow	270–350	
Rainbow trout		471

1.1.3. Biodegradation of surfactants

The primary transformation of surfactants occurring in the environment is degradation through the microbial activity. Biodegradation is an important process for treating surfactants in sewage treatment plants, and it also enhances the removal of these surfactants in the environment.

TABLE 8. Biodegradability of surfactants in the environment [28].

Surfactant	Aerobic condition	Anaerobic condition
LAS	Degradable	Persistent
SAS	Readily degradable	Persistent
Soap	Readily degradable	Readily degradable
Fate acid ester (FES)	Readily degradable	Persistent
AS	Readily degradable	Degradable
AES	Readily degradable	Degradable
Cationic surfactants (*e.g.*, TMAC, DTDMAC)	Degradable	Persistent
APE	Degradable	Partially degradable
AE	Readily degradable	Degradable

During biodegradation, microorganisms can either utilize surfactants as substrates for energy and nutrients or cometabolize the surfactants by microbial metabolic reactions. The most important factors that affect biodegradation of a surfactant in the environment are chemical structure and the physiochemical conditions of the environmental media. Different classes of surfactants exhibit different degradation behavior in the environment (Table 8). The most of the surfactants can be degraded in the environment by microbes, although some surfactants, such as LAS, may be persistent under anaerobic conditions [28, 67].

Biodegradation of LAS is initiated with a ω-oxidation of the alkyl chain followed by successive cleavage of C2 fragments (B-oxidation) (Figure 9). The reaction occurring during ω- and β-oxidations generate sulpho phenyl carboxylates (SPCs) resulting in the loss of interfacial activity and toxicity [68-70]. (SPCs aromatic ring cleavage then follows to achieve LAS mineralization.

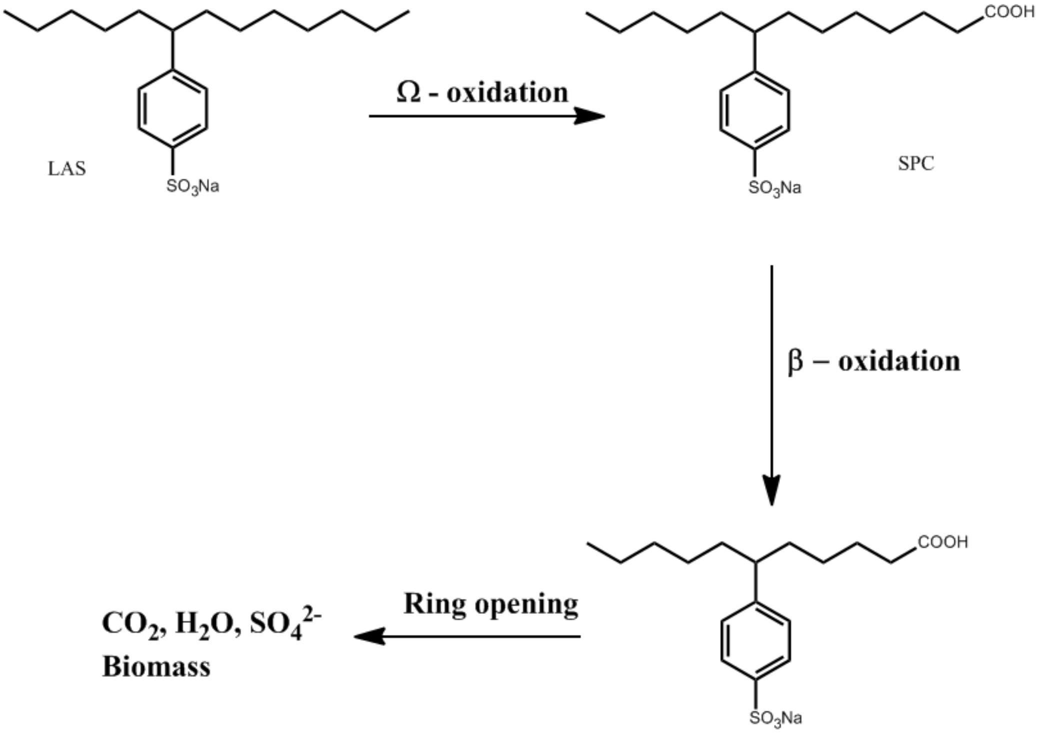


Figure 9. Biodegradation pathway of alkyl benzene sulfonate (LAS) [71]..

Alkyl sulfates (AS) are among the most rapidly biodegradable surfactants. Both primary and ultimate biodegradations are fast and complete in a wide range of test designs. The biodegradation is found to involve the enzymatic cleavage of the sulfate ester bonds to give inorganic sulfate and a fatty alcohol. The alcohol is oxidized to an aldehyde and subsequently to a fatty acid, with further oxidation following the oxidation pathway, thus achieving ultimate biodegradation [68].

The primary alkyl sulfatase in the bacterium initiates the biodegradation of SDS and hence 1-dodecanol is formed. It is then oxidized to 1-dodecanoic acid by the action of alcohol dehydrogenase. Finally it is metabolized by B-oxidation pathway, the pathway of SDS degradation in Figure 10 [72].

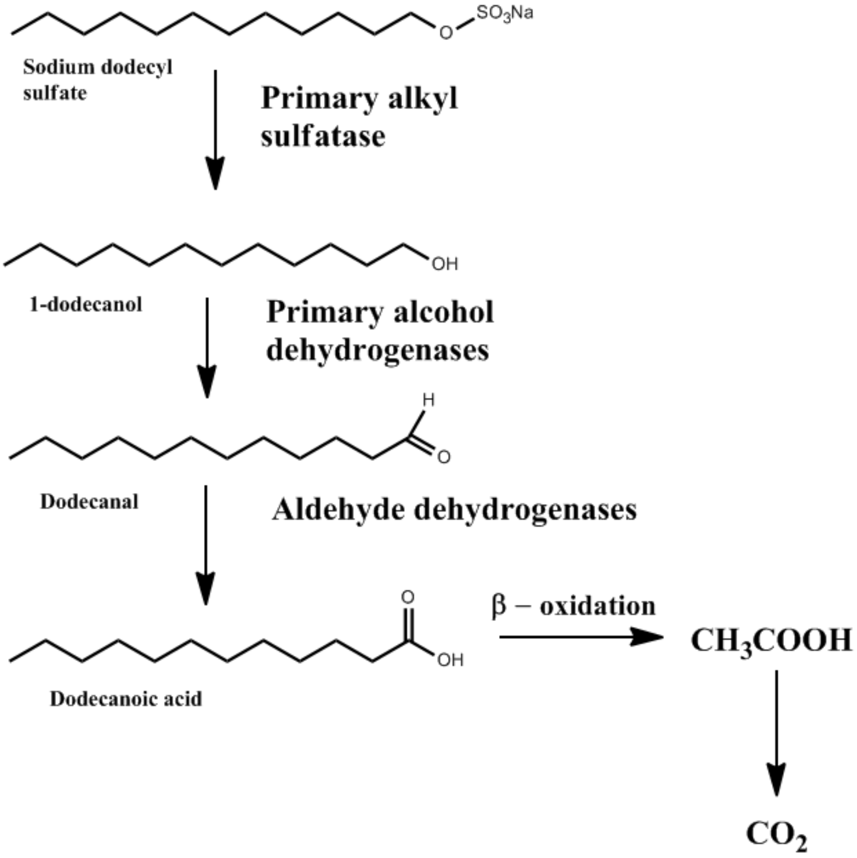


Figure 10. The degradation of sodium dodecyl sulfate (SDS).

The biodegradation of APE in conventional sewage treatment plants is generally believed to start with a shortening of the ethoxylate chain, leading to short-chain APE containing one or two ethoxylate units. Complete deethoxylation with formation of alkylphenols (AP) has been observed only under anaerobic conditions producing mainly alkylphenoxy ethoxy acetic acid and alkylphenoxy acetic acid [28]. The three most common groups of intermediates reported were: (a) alkylphenols (*e.g.*, NP and OP); (b) short-chain alkylphenol ethoxylates having 1–4 ethoxylate units, with APE2 predominating; (c) a series of ether carboxylates, including alkylphenoxy acetic acid and alkylphenoxy ethoxy acetic acid. Recalcitrant decarboxylated NPE biotransformation products with the alkyl chain carboxylated (CAPEs) were also detected in a sewage treatment plant effluent. Previous investigations showed that APE metabolites degraded more easily under the aerobic than under the anaerobic conditions [76].

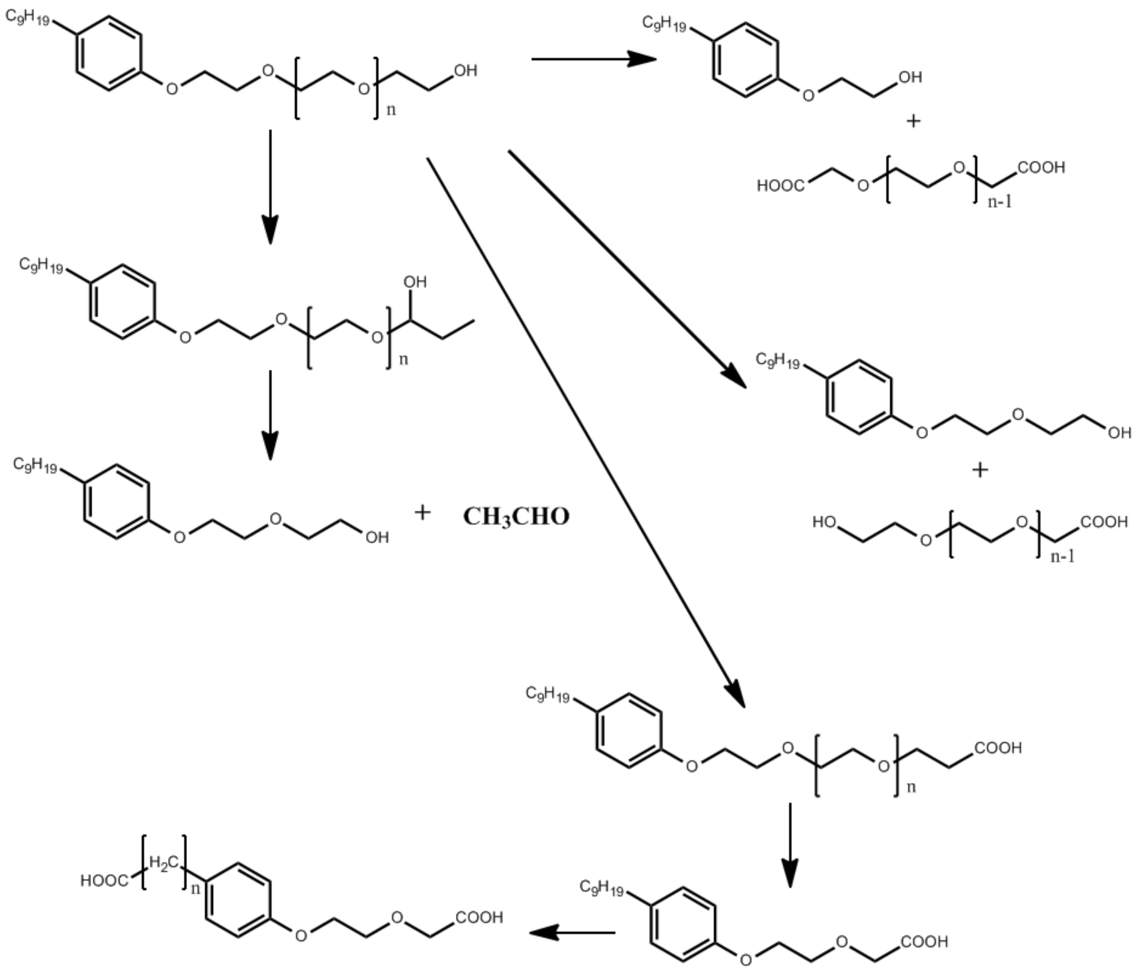


Figure 11. Proposed pathways of aerobic degradation of nonylphenol ethoxylates [76].

Alkyl ethoxylates (AE) are easily degradable under aerobic and anaerobic conditions. High primary biodegradation (96 ± 0.5%) was found for AEs in the continuous-flow activated sludge test with a high concentration of metabolites, free fatty alcohol (FFA) and poly (ethylene glycols) (PEG) [76]. However, in a static test, a primary degradability of 75%–98% in an aqueous environment was achieved in 10 days, without significant accumulation of metabolites PEG. This fact is suggesting that AE can be readily biodegraded in a variety of different soil types, suggesting AE will not accumulate in aerobic sludge-amended soils.

It is believed that the mechanism for aerobic biodegradation of AE was initiated by the central cleavage of the molecule, leading to the formation of PEG and FFA, followed by ω- or β-oxidation of the terminal carbon of the alkyl chain and the hydrolytic shortening of the terminal carbon of the polyethoxylic chain [28]. In contrast to the aerobic biodegradation, where central cleavage prevails, the first step of anaerobic microbial attack on the AE molecule is the cleavage of the terminal ethoxy unit, releasing acetaldehyde stepwise and shortening the ethoxy chain until the lipophilic moiety is reached [28].

1.1.4. Ecotoxicity of surfactants

Ecotoxicity, the subject of study of the field of ecotoxicology (a portmanteau of Ecology and Toxicology) refers to the potential for biological, chemical or physical stressors to affect ecosystems. Such stressors might occur in the natural environment at densities, concentrations or levels high enough to disrupt the natural biochemistry, physiology, behavior and interactions of the living organisms that comprise the ecosystem.

The Organization for Economic Cooperation and Development (OECD) test guideline has developed specific tests to determine toxicity level in organisms. Ecotoxicological studies are generally performed in compliance with the international guidelines. Concentration required to cause adverse effect in half the members of a tested population (LC_{50}) is the acute toxicity test that tests for the concentrate of tissue at which it is lethal to 50% within 96 hours. The test may include eggs, embryos, or juveniles and last from 7 to 200 days.

The EC_{50} is the effective concentration at 50%, which is the concentration that causes adverse effects in 50% of the test organisms.

Lowest Observed Effect Concentration (LOEC) – The lowest test concentration that has a statistically significant effect over a specified exposure time.

No Observed Effect Concentration (NOEC) – The highest test concentration for which no effect is observed relative to a control over a specified exposure time.

Aquatic toxicity data are widely available for anionic, cationic, and nonionic surfactants. Lewis [77] has summarized the chronic and sublethal toxicities of surfactants to aquatic animals and found that chronic toxicity of anionic and nonionic surfactants occurs at concentrations usually greater than 0.1 mg/L. Some published toxicity data for anionic and nonionic surfactants on several test organisms (algae, invertebrates or fish) from the literature is presented in Table 9. and 10. [28].

TABLE 9. Aquatic toxicity data for anionic surfactants

Chemical	Species	Toxicity value	Ref.
C10LAS	*Daphnia magna*	LC_{50}—48 h, 13.9 mg/L	9
C12LAS		LC_{50}—48 h, 8.1 mg/L	
C14LAS		LC_{50}—48 h, 1.22 mg/L	
C12LAS	*Dunaliella sp.(green alga)*	EC_{50}—24 h, 3.5 mg/L	78
C11–12LAS	*Oncorhynchus mykiss (rainbow trout)*	NOEC—54 d, 0.2 mg/L	79
C12LAS (SDBS)	*Salmo gairdneri (rainbow trout)* *Gammbusia affinis (mosquito fish)* *Carassius auratus (gold fish)*	Immobilization, EC_{50}—48 h, 3.63 mg/L Immobilization, EC_{50}—48 h, 8.81 mg/L Immobilization, EC_{50}—48 h, 5.1 mg/L	80
C12AS (SDS)	*Salmo gairdneri (rainbow trout)* *Gammbusia affinis (mosquito fish)* *Carassius auratus (goldfish)*	Immobilization, EC_{50}—48 h, 33.61 mg/L Immobilization, EC_{50}—48 h, 40.15 mg/L Immobilization, EC_{50}—48 h, 38.04 mg/L	80
Sodium dodecyl ethoxy sulfate (SDES)	*Salmo gairdneri (rainbow trout)* *Gammbusia affinis (mosquito fish)* *Carassius auratus (goldfish)*	Immobilization, EC_{50}—48 h, 10.84 mg/L Immobilization, EC_{50}—48 h, 13.64 mg/L Immobilization, EC_{50}—48 h, 12.35 mg/L	80

TABLE 10. Aquatic toxicity data for nonionic surfactants

Chemical	Species	Toxicity value	Ref.
C12EO6	*Salmo gairdneri(rainbow trout)* *Gammbusia affinis (mosquito fish)* *Carassius auratus (goldfish)*	Immobilization, EC_{50}—48 h, 22.38 mg/L Immobilization, EC_{50}—48 h, 29.26 mg/L Immobilization, EC_{50}—48 h, 28.02 mg/L	80
C9–11EO6	*Pimephales promelas (fathead minnow)*	LC_{50}—10 d, 2.7 mg/L	81
OPEO6	*Salmo gairdneri (rainbow trout)* *Gammbusia affinis (mosquito fish)* *Carassius auratus (goldfish)*	Immobilization, EC_{50}—48 h, 6.44 mg/L Immobilization EC_{50}—48 h, 9.65 mg/L Immobilization, EC_{50}—48 h, 9.24 mg/L	80
NPEO8	*Australian native frogs*	Full narcosis, EC_{50}—48 h, 2.8–3.8 mg/L	82
NPEO9	*Fathead minnow* *Daphnia magna*	LC_{50}—96 h, 4.6 mg/L LC_{50}—48 h, 14 mg/L	83
NP	*Fathead minnow* *Daphnia magna*	LC_{50}—96 h, 0.3 mg/L LC_{50}—48 h, 0.19 mg/L	83

Some recently published toxicity data for the three classes of surfactants on several aquatic species have been presented in Table 11. They found that cationic surfactants were more toxic than anionic and non-ionic surfactants [84].

TABLE 11. Chronic toxicity of surfactant to aquatic species.

Organisms	Species	Surfactants	Toxicity value	Conc. mgL^{-1}
Bacteria	*Vibrio fischeri*	LAS	EC_{50}-Luminescence 30 min	109.7
	Vibrio fischeri	QAC	EC_{50}-Luminescence 30 min	
	Photobacterium	QAC	EC_{50}-immobilization 24 h	0.5
	phosphoreum	LAS	EC_{50}-24 h	
	Dunaliella sp.	QAC	EC_{50}-24 h	0.15–0.63
	Dunaliella sp.			3.5
				0.79
Algae	*Scenedesmus subspicatus*	AEO	EC_{10}	0.03
	Selenastrum	AEO	EC_{10}	9.791
	Pseudokirchneriella subcapitata	PFOS	EC_{50}	146µM

	C.vulgaris	PFOS	EC_{50}	96 µM
Crustaceans	*Daphnids* *Daphnia magna*	QAC (benzalkonium chloride) QAC	LC_{50} EC_{50}-immobilization 24 h	0.1–1.0 0.13–0.38
Amphipod	*Echinogammarus tibaldii*	QAC (cetyltrimethyl ammonium bromide)	LC_{50}	7.7
Invertebrate	Daphnia magna	AEO	EC50	0.36 -50.5

Significant amounts of surfactants can enter into the soils through sewage sludge, which is increasingly applied on agricultural lands as fertilizers for plants. The occurrence and the distribution of these surfactants in soil by the application of sewage sludge present a potential ecotoxicological risk. Exposure of soil to surfactants makes this environment hostile for microorganisms. The effects of surfactant on microorganisms were mainly due to the reactions at the cell surface. According to Jensen (1999) [65], a depolarization of the cell membrane by the absorption of surfactant may result in a decreased absorption of essential nutrients and oxygen consumption or a decreased release of toxic metabolic products from the cell leading to a build-up [85]. The toxicological effect of surfactants on terrestrial environment is presented in Table 12 [84].

TABLE 12 Toxicity of different type of surfactants against various terrestrial organisms.

Organisms	Species	Surfactants	Toxicity value	Conc. mg/L
Soil fauna	*Eisenia foetida*	LAS	Mortality (14 days)	1000 mg/kg in OECD soil
	Lumbricus terrestris	LAS	Mortality (14 days)	1000 mg /kg in OECD soil
	Platynothrus peltifer	LAS	Mortality (LC_{50})	319 mg/kg in LUFA soil
	Isotoma viridis	LAS	Mortality (LC_{50})	661 mg /kg in OECD soil
Bacteria	*Azobacter sp.*	NP		18.8–37.6 mg/kg
Algea	*Navicula peliculosa*	LAS	EC_{50}, 96 h	1.4
Crustaceans	*Arcatia tonsa*	LAS	EC_{50}, 48 h	1.11
	Arcatia tonsa	NPEs	LC_{50}, 48 h	359
Fish	*Pleuronectes plateas*	LAS	EC_{50}, 96 h	1.0
	Promelas Pimephales	NPEs	LC_{50}, 96 h	190
Invertebrate	*Folsomia fimetaria*	NP	EC_{50} (21 days)	5–133 mg /kg
	Folsomia candid	NP	EC_{50} (21 days)	5–133 mg/ kg
Terrestrial	*Brassica rapa*	LAS	EC_{50} (14days)(Growth)	137.7 mg/ kg
Plants	*Malvia pusilla*	LAS		204.2 mg/kg
	Solanum nigrum	LAS		169.2 mg/kg
	Chenopodium album	LAS		164.3 mg/kg
	Ryegrass Lolium	LAS		500 kg ha^{-1}, strong effects

Although the toxicity of alkylphenol ethoxylates (APEOs) is relatively low, concern over their metabolites has received a great attention, especially for those with one or two ethoxylate groups or those with none (alkylphenols). Borghi *et al.* (2011) [86] have indicated that nonylphenol ethoxylates and octylphenol ethoxylates are much less toxic to aquatic organisms than their degradation products (nonylphenol and octylphenol), which are classified as endocrine-disrupting chemicals. They alter the normal functioning of the hormonal system of mammalians, fishes and amphibians [84].

1.2. Advanced Oxidation Process (AOPs)

Advanced oxidation processes are defined as the processes that generate hydroxyl radicals in sufficient quantities to be able to oxidize majority of the complex chemicals present in the effluent water. The hydroxyl radical is a powerful oxidant and a short lived, highly reactive and non-selective reagent that is easy to produce. Thanks to high reactivity and non-selective properties of hydroxyl radicals, AOP's are considered as very important methods for treatment of toxic waste in water systems [87, 88].

TABLE 13. Oxidizing potential for conventional oxidizing agents in acid [89].

Oxidation agent	Standard potential (V, NHE)
Fluorine (F_2)	3.03
Hydroxyl radical ($^{\bullet}OH$)	2.80
Oxygen (atomic)	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.77
Potassium-permanganate ($KMnO_4$)	1.67
Hypobromous acid (HBrO)	1.59
Chlorine dioxide (ClO_2)	1.50
Hypochlorite (HClO)	1.49
CHLORINE (CL_2)	1.36
Oxygen (molecular)	1.23
Bromine (Br_2)	1.09

Half-life of hydroxyl radical is about 10^{-9} seconds. Short half-life and extremely reactive properties influence the process of its production and application. Because of its high reactivity, hydroxyl radical cannot be contained and it must be generated "*in situ*" when needed. The underlying reactions and $OH^{\bullet}$ formation efficiencies of various approaches such as the Fenton reaction (Fe^{2+}/H_2O_2), photo-Fenton reaction (Fe^{3+}

/H_2O_2/$h\nu$), UV/H_2O_2, peroxone reaction (O_3/H_2O_2), O_3/UV, O_3/activated carbon, O_3/dissolved organic carbon (DOC) of water matrix, ionizing radiation, vacuum UV, and ultrasound are reviewed [90].

AOPs show great flexibility at practical use, because of fact that they can be used separately or in combination with some other classic methods for water treatment. Besides, another great advantage of AOPs over classic methods for wastewater treatment is the possibility for doing the treatment at ambient conditions, *i.e.* atmospheric pressure and room temperature and so called ambient AOPs can be used for low loaded wastewater.

Advanced oxidation processes (AOPs) have already been used for the treatment of wastewater containing recalcitrant organic compounds such as pesticides [92], surfactants [17], coloring matters [92], pharmaceuticals [93] and endocrine disrupting chemicals. Moreover, they have been successfully used as pretreatment methods in order to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes [94].

AOPs can provide effective technological solutions for water treatment. Such solutions are vital for supporting and enhancing the competitiveness of different industrial sectors, including the water technology sector, in the global market. The main goals of academic, research and industrial communities through the development and implementation of environmental applications of AOPs will be [95]:

1) New concepts, processes and technologies in wastewater treatment with potential benefits for the stable quality of effluents, energy and operational cost savings and the protection of the environment.

2) New sets of advanced standards for wastewater treatment.

3) New methodologies for the definition of wastewater treatment needs and framework conditions.

4) New know-how for contributing to enhancing the European water industry competitiveness.

1.2.1. Ozone O_3

Ozone O_3 was discovered in 1840 and the structure of the molecule as triatomic oxygen was established in 1872. The first use of ozone was reported at the end of the 19th century as a disinfectant in many water treatment plants, hospitals, and research centers [96].

O_3 is known as a very reactive agent in both water and air, which is attributed to its electronic configuration. O_3 can be represented as a hybrid of four molecular resonance structures (see Fig. 12). As can be seen, these structures present negative and positively charged oxygen atoms, which in theory imparts to the ozone molecule the characteristics of an electrophilic, dipolar and even nucleophilic agent [97].

Figure 12. Chemical structure of the ozone molecule.

The O_3 can be generated artificially in the ozone generators. There is two ways of generating ozone by ozone generators: (a) the cleavage of oxygen molecules under the influence of strong electrical field and (b) the same mechanism like in nature, the photolysis of oxygen [96].

The direct oxidation of organic components by ozone ($M + O_3$) is a selective reaction with slow reaction rate constants, typically being in the range of (K_D =1.0-10^6 $M^{-1}s^{-1}$).

The ozone molecule reacts with the unsaturated bonds due to its dipolar structure and leads to a splitting of the bond, which is based on the so - called Criegee mechanism (see Fig. 13), which was developed for non-aqueous solutions.

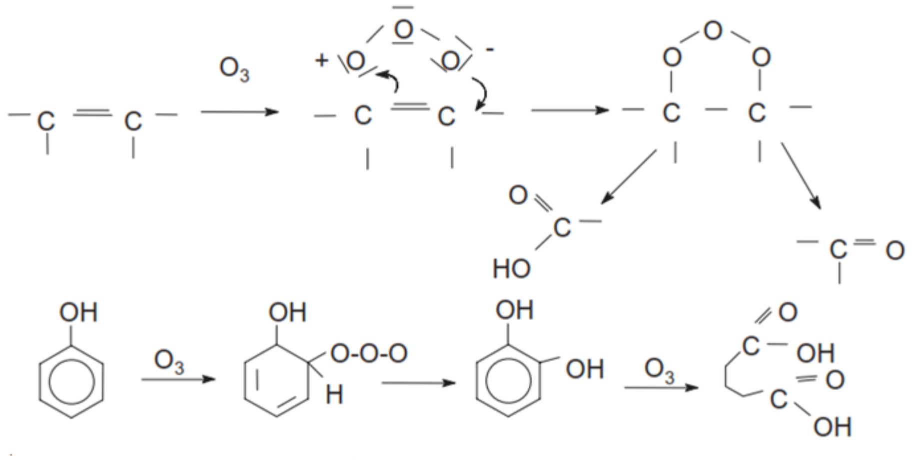


Figure 13. Plausible aqueous reactions with ozone.

In general, ozone reacts faster with the organic water contaminants, the ones having the higher electron density, *i.e.*, the degree of nucleophilicity. Ozone will react faster with certain types of aromatic and aliphatic compounds, for example, those carrying electron - supplying substituents such as hydroxyl or amine groups. If there is no such substituent the rate of ozonation is much slower. The following order of reactivity toward ozone can be used as a rule of thumb for the various target compound groups: saturated aliphatic < aromatic ring < unsaturated aliphatic e^- - detracting substitutes < non-substituted < e^- - supplying substitutes undissociated < dissociated.

Table 14 gives some general and specific examples of the reactivity of organic compounds toward ozone [98, 99].

TABLE 14. Oxidation of organic compounds by ozonation.

Compound	Type	KD ($M^{-1}s^{-1}$)
	Aliphatic: saturated, alkanes Aliphatic: e^- supplying substitutes, alcohols Aliphatic: unsaturated, alkenes Aromatics: nonsubstituted	10^{-2} 10^{-2}–1 1–10^4 1–10^2
Benzene	Aromatic ring: nonsubsituted	2
Chlorobenzene	Aromatic ring: e^- detracting substitutes	0.8
Phenol	Aromatic ring: e^- supplying substitutes undissociated	1.3×10^3
Phenol	Aromatic ring: e^- supplying substitutes dissociated	1.4×10^9

This type of reaction is important in acid media and this route leads to a very limited mineralization of the organic compounds. Its use for the removal of pollutants must be reinforced by modification of the method.

The stability of ozone largely depends on the water matrix, especially its pH, the type and content of natural organic matter (NOM) and its alkalinity.

The pH of water is important because hydroxide ions initiate ozone decomposition that involves the following reactions (Eq. 1-7) [100, 101]:

$$O_3 + HO^{-} \rightarrow O_2 + HO_2^{-} \tag{1}$$

$$HO_2^{-} + O_3 \rightarrow O_3^{\bullet -} + HO_2^{\bullet} \tag{2}$$

$$HO_2^{\bullet} \Leftrightarrow O_2^{\bullet -} + H^{+} \tag{3}$$

$$O_2^{\bullet -} + O_3 \rightarrow O_3^{\bullet -} + O_2 \tag{4}$$

$$O_3^{\bullet -} + H^{+} \rightarrow HO_3^{\bullet} \tag{5}$$

$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \tag{6}$$

$$O_3 + HO^{\bullet} \Leftrightarrow O_2 + HO_2^{\bullet} \tag{7}$$

Thus, the decay of ozone initiated by the hydroxide ion leads to a chain reactions, producing fast-reacting and nonselective OH radicals. The •OH reacts with the target molecule at the position with the highest electron density due to its electrophilic properties. Detailed information on kinetics of the oxidation of selected organic compounds with ozone and OH radicals at ambient temperature can be found in relevant literature [102].

Four nonionic groups of surfactants with the trade names Triton (polyethyleneglycol-mono-(p-(1,1,3,3-tetramethylbutyl) phenol-ether), Tergitol (polyethyleneglycol 2,6,8-trimethyl-4 nonanol ether), Synperonic (polyethyleneglycol nonyl phenol ether), and Brij (polyethyleneglycol cetyl ether) with initial concentrations over and below a critical micelle concentration are decomposed by ozone. Authors found that presence of the benzene ring made decomposition difficult compared to molecules without it. A 28% reduction of Triton X-100 (120 mg/dm^3) and a 94.1% reduction of Tergitol TMN10 (100 mg/dm^3) were achieved. Molecules with a large number of ethoxylated units were more easily degraded than the molecules with a shorter chain. For a lower concentration, when the surfactant is in the monomeric form, the reaction rate is higher than in the case when it appears in the micelle form: linear molecules were more quickly decomposed than the corresponding molecules with a branched aliphatic chain [103].

In other paper two commercial surfactants (sodium dodecyl sulphate and tetraethylammonium dodecylbenzen sulphonate have been submitted to ozone treatment. At neutral pH (around 6.2) only 20% elimination of SDS was achieved after 30 min treatment (according to MBAS method). In basic medium ozonation of same surfactant was more efficient (70% elimination). In the case of SDBS author obtained significantly better results at neutral pH than those obtained for SDS (50% of degradation after 30 min). In basic medium degradation of SDBS was 80% [104].

1.2.2 Ozone/ UV - Radiation O_3 / UV

Ozone in aqueous solution absorbs UV radiations between 200 and 360 nm with a maximum at 253.7 nm ((low-pressure Hg lamp - λ = 253.7 nm)) (molar absorption coefficient ε max = 3600 L mol^{-1}cm^{-1}). The photolysis of ozone in water leads to the formation of $^{\bullet}OH$ radicals, according to the following successive and competitive steps (Eq. 8-12) [105]:

$$O_3 + H_2O + h\upsilon \rightarrow 2\,^{\bullet}OH + O_2 \quad (8)$$

$$O_3 + ^{\bullet}OH \rightarrow HO_2^{\bullet} + O_2 \quad (9)$$

$$O_3 + HO_2^{\bullet} \rightarrow ^{\bullet}OH + 2\,O_2 \quad (10)$$

$$^{\bullet}OH + HO_2^{\bullet} \rightarrow H_2O + O_2 \quad (11)$$

$$2\,^{\bullet}OH \rightarrow H_2O_2 \quad (12)$$

In their paper Amat *et al.* [19] examine degradation of SDS and SDBS with ozone and combination of ozone and UV (low-pressure Hg lamp 254 nm). They compare results of decrease of surfactants concentration (MBAS method) after 30 min of treatment with ozone and combination ozone/UV. In the case of SDS decrease of SDS concentration with ozone at neutral pH was 20% and with ozone/UV around 90%. In the case of SDBS decrease of concentration was 60% for ozone and 90% for ozone/UV.

In another paper significant increase in COD (16.71% ozone, 77.42 ozone UV medium pressure) and TOC 3.7 ozone, 64.27 ozone UV medium pressure) reduction were achieved after NPEO40 solution treatment [106].

1.2.3 Ozone + Hydrogen Peroxide (O_3/H_2O_2)

The reaction of H_2O_2 with O_3, often termed peroxone process, is one of the AOPs that produce hydroxyl radicals ($^{\bullet}OH$) in aqueous solution with $^{\bullet}OH$ yield per O_3 close to 50%.
Mechanism of hydroxyl radical is presented in reactions (Eq. 13-18).

$$H_2O_2 \rightarrow H^+ + HO_2^- \qquad (13)$$

$$HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet -} \qquad (14)$$

$$HO_2^{\bullet} \rightarrow O_2^{\bullet -} + H^+ \qquad (15)$$

$$O_2^{\bullet -} + O_3 \rightarrow O_2 + O_3^{\bullet -} \qquad (16)$$

$$O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet} \qquad (17)$$

$$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2 \qquad (18)$$

Recently, this mechanism has been modified by assuming that the electron transfer in reaction 14 is preceded by adduct formation (reaction 19), and the conversion of $O_3^{\bullet -}$ into $^{\bullet}OH$ must proceed *via* reactions 20 and 21 rather than by reactions 17 and 18.

$HO_2^- + O_3 \rightarrow HO_5^-$ (19)

$HO_5^- \rightarrow HO_2^{\bullet} + O_3^{\bullet -}$ (20)

$O_3^{\bullet -} \rightarrow O_2 + O^{\bullet -}$ (21)

$O^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^-$ (22)

$HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet -}$ (23)

$k_{11} = 2.2\times10^{6}\ M^{-1}\ s^{-1}$

In the case of ozonation of SDS and SDBS in the presence of hydrogen peroxide nearly complete elimination of the surfactant species was accomplished but degradation was lower compared with the ozone/UV treatment [104].

In other study authors found that presence of H_2O_2 considerably increased the removal rate during SDBS ozonation and decrease was virtually double that removed by the use of ozone alone [107].

1.2.4 Hydrogen Peroxide – UV Radiation (H_2O_2/UV)

The direct photolysis of hydrogen peroxide H_2O_2 leads to the formation of ${}^{\bullet}OH$ radicals (Eq. 24) [108].

$H_2O_2 \xrightarrow{hv} 2\ {}^{\bullet}OH$ (24)

Also HO_2^-, which is in an acid–base equilibrium with H_2O_2, absorbs the UV radiation of the wavelength 254 nm (Eq. 25 and 26):

$H_2O_2 \rightarrow HO_2^- + H^+$ (25)

$HO_2^- \xrightarrow{hv} {}^{\bullet}OH + O^{\bullet -}$ (26)

The basic concept of these systems is the decomposition of H_2O_2 with the formation of free radical intermediates, especially the hydroxyl radical. This radical is capable of reacting with a variety of organic compounds leading to either partial or complete degradation of these compounds to CO_2, H_2O and inorganic ions.

Factors affecting UV-H_2O_2 treatment are presented as following [109]:

1) Usually there is an optimum concentration beyond which the presence of hydrogen peroxide is detrimental to the degradation reaction due to the scavenging action. (Eq. 27 and 28).

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \qquad k = 2.7 \times 10^{7}\ M^{-1}\ s^{-1} \tag{27}$$

$$^{\bullet}OH + HO_2^{-} \rightarrow HO_2^{\bullet} + OH^{-} \qquad k = 7.5 \times 10^{9}\ M^{-1}\ s^{-1} \tag{28}$$

2) Presence of compounds (*e.g.* humic acid), which results in strong absorption of incident UV light is another factor that needs to be considered while adjusting the dose of hydrogen peroxide.

3) Lower operating pH (in the range 2.5–3.5) is usually preferred for the combination technique of UV photolysis coupled with H_2O_2.

4) Synergism between UV photolysis and H_2O_2 will be beneficial only for the contaminants, which require a relatively higher level of oxidation conditions (higher activation energies).

In their paper Sanz *et al.* examined photochemical degradation of LAS with UV-H_2O_2 system. They found that pH has no significant influence on oxidation and that the degradation is favored by the amount of peroxide up to a certain critical value (molar ratio H_2O_2/LAS around 20). Beyond this value there are no improvement in degradation [110].

In another paper Arslan Alaton *et al.* [111] optimized reaction parameter for degradation of mixture of alkyl ethoxylate. COD value of treated sample was in the range 150-900 mg L^{-1}. They found that complete organic carbon removal could be achieved after 60 min, corresponding to UV dose of 21 kWh/m^3 and H_2O_2 concentrations 30 - 40 mmol/L. Degradation of the original surfactant traced via HPLC analyses occurred appreciably faster (*ca.* 15–20 min).

Degradation of NPE-9 was tested for UV-C runs in the absence and in the presence of H_2O_2 (1:1 and 1:0.5 NPE-9/H_2O_2 molar ratios). Dark reactions with H_2O_2 gave less than 15% degradation in 3 h. Although NPE-9 could be very well degraded by

UV-C light alone (reaching 75% depletion in 180 min), H_2O_2 addition increased the rate, but no significant differences were found between the two H_2O_2 concentrations used [112].

The degradation products during advanced oxidation of the nonionic surfactant nonylphenol decaethoxylate with the H_2O_2/UV-C were also investigated [113]. H_2O_2/UV-C ensured complete removal of NP-10 and partial mineralization (79%), which was accompanied by the generation of polyethylene glycols with 3–8 ethoxy units. PEGs containing 3–8 ethoxy units, aldehydes and carboxylic acids including formic, acetic and oxalic acids were identified as the degradation products of NP-10 by the H_2O_2/UV-C.

1.2.5 Fenton System (H_2O_2/Fe^{2+})

Fenton and related reactions encompass reactions of peroxides (usually H_2O_2) with iron ions to form active oxygen species that oxidize organic or inorganic compounds when they are present [114-116]. The history of Fenton chemistry dates to 1894, when Henry J. Fenton reported that H_2O_2 could be activated by Fe (II) salts to oxidize tartaric acid.

The mechanism for decomposition of H_2O_2 in acidic solution in the dark and in the absence of an organic compound consists of the sequence of reactions 29–35 [117].

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + OH^- + HO^\bullet \quad (29)$$

$$\mathrm{Fe(III)} + H_2O_2 \rightarrow \mathrm{Fe(II)} + HO_2^\bullet + H^+ \quad (30)$$

$$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \quad (31)$$

$$HO^\bullet + \mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)} + OH^- \quad (32)$$

$$\mathrm{Fe(III)} + HO_2^\bullet \rightarrow \mathrm{Fe(II)} + O_2H^+ \quad (33)$$

$$\mathrm{Fe(II)} + HO_2^\bullet + H^+ \rightarrow \mathrm{Fe(III)} + H_2O_2 \quad (34)$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (35)$$

Fenton process is strongly dependent on the solution pH due to iron and hydrogen peroxide speciation factors. The optimum pH for the Fenton reaction was found to be around 3 [118].

At higher pH the activity of Fenton reagent is reduced due to formation of ferric hydroxide precipitate and the presence of relatively inactive iron oxohydroxides [119]. At pH below 3, decrease in degradation efficiency was observed [120]. At very low pH values, iron complex species $[Fe(H_2O)_6]^{2+}$ exist, which reacts more slowly with hydrogen peroxide than other species. Usually the rate of degradation increases with an increase in the concentration of ferrous ion [121]. However, the extent of increase is sometimes observed to be marginal above a certain concentration of ferrous ion. Concentration of hydrogen peroxide plays a crucial role in deciding the overall efficiency of the degradation process. Usually it has been observed that the pollutant’s degradation percentage increases with an increase in the dosage of hydrogen peroxide [122].

Elements with multiple redox states (like chromium, cerium, copper, cobalt, manganese and ruthenium) can also decompose H_2O_2 into hydroxyl radical through conventional Fenton-like pathways. The *in situ* formation of H_2O_2 and decomposition into $HO^{\bullet}$ can be also achieved using electron transfer mechanism in zero-valent aluminum/O_2 system. Mechanisms and practical limitations influencing their environmental applications have been reviewed [123]**.** Photo-Fenton process, a combination of hydrogen peroxide and UV radiation with Fe^{2+} or Fe^{3+} oxalate ion, produces more hydroxyl radicals compared to conventional Fenton method or photolysis and in turn increases the rate of degradation of organic pollutants [124,125].

Fenton reaction accumulates Fe^{3+} ions in the system and the reaction does not proceed once all Fe^{2+} ions are consumed. In photo-Fenton reaction, photo-reduction of ferric ions (Fe^{3+}) regenerates ferrous ions (Fe^{2+}). The newly generated ferrous ions react with H_2O_2 and generate hydroxyl radical and ferric ion, and the cycle continues.

Working at an initial pH value of 8, a Fe^{2+} dosage of 600 mgL^{-1} and a H_2O_2 dosage of 120 mgL^{-1}, the chemical oxidation demand (COD) and linear alkylbenzene sulfonate (LAS) were decrease from 1500 and 490 mgL^{-1} to 230 and 23 mgL^{-1} after 40 min of fenton oxidation, respectively. Advanced oxidation pretreatment using Fenton reagent was very effective at enhancing the biodegradability of this kind of wastewater [126].

Fenton's reagent has shown high efficacy in SDBS transformation at pH 2 but does not mineralize the dissolved contaminant and is ineffective at pH 7. The efficacy of this advanced oxidation process is mainly determined by the amount of Fe(II) used, whereas H_2O_2 only affects the rate of the process, dissolved oxygen had little effect except at pH 7. This is because (i) dissolved oxygen can compete with H_2O_2 for the oxidation of Fe(II) only at pH>5 , because Fe(II) is not oxidized by O_2 at low pH, (ii) at pH 7, the Fe(III) formed from oxidation of Fe(II) with H_2O_2 precipitates as $Fe(OH)_3$ and therefore no longer takes part in the catalytic reaction, and (iii) according to Fe(II) speciation, it is well known that Fenton's reaction is not effective at neutral or basic pH.

Fenton oxidation of 10 nonionic surfactants (6 alcohol ethoxylates and 4 alkylphenol ethoxylates) was investigated. Oxidation reactions were quite fast (less than 5 min) [42] and led to a maximum surfactants removal of 96–99%. The dosages of Fenton reagents (H_2O_2 and Fe^{2+}) necessary for achieving the maximum removal linearly increased with the length of the surfactants ethoxy chain [128].

Fenton and photo-Fenton processes were tested for the degradation of a sodium dodecyl sulphate. When soft conditions are employed (1 mM Fe^{2+}; 4 mM H_2O_2), only a 14% of degradation is achieved in 60 min. By increasing the iron and the oxidant concentration around one magnitude order, the removal efficiency of SDS improved 63% approximately in the same reaction time At the same reaction conditions tested (10 mM $FeSO_4$; 60 mM H_2O_2), 63% of SDS degradation was achieved in the absence of solar radiation whereas a 79% of SDS removal was obtained in the CPC reactor (tubular pyrex glass reactor located in the focus of a compound parabolic concentrator) [129].

Similar results were obtained in Fenton and photo-Fenton process degradation of NPE-9. With the same concentrations of reactants (1:1:0.5 NPE-9/H_2O_2/Fe^{2+}) authors obtained significantly better results in photo-Fenton reactions (degradations of 9_NPE in Fenton reaction was 60 % and in photo-Fenton reaction 96 %) [112].

A wide range of solid materials, such as transition metal exchanged zeolites have been proposed as heterogeneous catalysts for the oxidative degradation of organic compounds through the Fenton-like reaction [130]. Commercial linear alkylbenzene sulphonic acids (LAS) have been chosen as model compound in photo-Fenton reaction with heterogenous Fenton catalysts. Good results, comparable with classic photo Fenton reaction, have been obtained with H_2O_2/FeOOH and H_2O_2/[Fe(III)/SiO_2 (3%)] and sunlight.

Advantages of heterogenous system have been: extent of mineralization of the same order of homogeneous photo activated method, recycling of catalyst with low material cost and no sludge formation [131].

1.2.6 Photocatalytic Oxidation (UV/TiO_2)

Among AOPs, heterogeneous photocatalysis has proved to be efficient tool for degrading aquatic organic contaminants Heterogeneous photocatalysis involve the acceleration of photoreaction in presence of semiconductor photocatalyst. One of the major applications of heterogeneous catalysis is photocatalytic oxidation to effect partial or total mineralization of liquid phase contaminants. Even though degradation begins with a partial degradation, the term ‘photocatalytic degradation’ usually refers to complete photocatalytic oxidation or photomineralization, essentially to CO_2, H_2O, NO^{3-}, PO_4^{3-} and halide ions. Heterogeneous photocatalysis has attracted constant research since its infancy considering the high number of excellent reviews and books devoted by many researchers [132-134].

Many chalcogenide semiconductors such as TiO_2, ZnO, ZrO_2, CdS, MoS_2, Fe_2O_3 and WO_3 have been examined and used as photocatalysts for the degradation of organic contaminants [135]. In spite of the constant vigorous research activities over two decades in search for an ideal photocatalyst, titanium dioxide in its anatase modification (Degusa P-25) has remained a benchmark against which any emerging material candidate will be measured since it was reported to have the best combination of photoactivity and photostability.

In order to activate the degradation process, pure TiO_2 requires photo-excitation with light at wavelengths exceeding the band gap of the active anatase phase of 3.2 eV, that is, wavelengths of ≤ 387 nm, This produces electron-hole (e^- / h^+) pairs (Eq. 36).

$$TiO_2 + h\nu = e^-\ cb\ (TiO_2) + h^+\ vb\ (TiO_2) \qquad (36)$$

Where cb is the conduction band and vb is the valence band.

Thus, as a result of irradiation, the TiO_2 particle can behave either as an electron donor or acceptor for molecules in contact with the semiconductor. The electron and hole can recombine, releasing the absorbed light energy as heat, or they can participate in redox reactions with adsorbed species as the valence band hole is strongly oxidizing while the conduction band electron is strongly reducing. On the semiconductor surface, the excited electron and the hole can participate in redox reactions with water, hydroxide ion ($OH^–$), organic compounds or oxygen leading to mineralization of the pollutant.

Photodegradation of a commercial detergent whose major components are an anionic surfactant in aqueous TiO_2 dispersions under irradiation with concentrated sunlight in the presence of air was examined. Authors found that the optimal operational parameters for this detergent were, respectively: TiO_2 loading, 6 gL^{-1}; circulation flow rate, 4.9 L min^{-1}; and pH 4.9. The increase in surface tension as the degradation proceeded was faster than the temporal degradation of the detergent [136].

In another paper [137] SDBS surfactant was degraded photocatalytically in a batch mode with a circulation system exposed to concentrated sunlight using a parabolic round sunlight concentrator Applied PRC reactor essentially consisted of a parabolic round mirror concentrator for geometric concentration of solar light, that was equivalent to 70 suns (aperture diameter 1.0 m, mirror area 0.785 m^2), and a round bottom flask photoreactor (Pyrex walls; volume, 1.3 l).

They also examined the effect(s) that additives such as potassium persulfate ($K_2S_2O_8$) have on the process. Authors found that enhancement of TOC removal depend on the pH, the TiO_2 loading and the quantity of the $K_2S_2O_8$ additive. At pH 5.0 and at a TiO_2 loading of 5.0 g $L^{−1}$ the degradation of SDBS was not enhanced on addition of the extraneous $K_2S_2O_8$ oxidant in the concentration range between 1.0 and 30 mM. However, on using a loading of 0.20 g $L^{−1}$ of TiO_2 the degradation of SDBS was significantly enhanced in the presence of persulfate additive ($K_2S_2O_8$, 5.0 and 20 mM).

Sodium lauryl sulfate (0.1–0.6 mM) in aqueous solution was photocatalytically decomposed in the fluidized bed reactors with UV illumination by a TiO_2 photocatalyst immobilized on a porous SiO_2 support [138]. As the lamp intensity increased, the photon rate became higher and a higher photoefficiency was obtained. It was also found that the pH is another important parameter in determining the reaction rate and the acidic conditions were favorable for the sodium lauryl sulfate and TiO_2 system.

In photocatalytic degradation of 9-NPE (TiO_2-UV-C) authors found decrease of 9-NPE concentration (89%) and TOC decrease (42.7%). TOC decreased rapidly in the first 5 min and then stopped, indicating the formation of recalcitrant intermediates [112].

1.3. Non-thermal plasma

Plasmas are ionized gases. They consist of positive and negative ions, electrons, as well as neutral species. The plasma state is often referred to as the fourth state of matter. Much of the visible matter in the universe is in the plasma state.

All plasma systems, in terms of thermodynamic equilibrium (related to electronic density and temperature), are defined into two categories: thermal and non-thermal plasma [139]. Thermal plasma (arc discharges, torches or radio frequency plasma) is associated with sufficient energy introduced to allow plasma constituents to be in thermal equilibrium. Non-thermal plasma is obtained using less power (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.

Thermal plasma is sustained with introducing high electrical energy, so that a high flux of heat is created, which can be used in processing even the most recalcitrant wastes via thermal incineration processes. It is a promising alternative to conventional and industrially mature thermal processes for waste treatment [140].

Non-thermal plasma produced in water solutions forms the basis of innovative AOPs for the water treatment [141,142]. The non-thermal plasma process can remove chemical and biological wastes in all three states (gas, liquid and solid). The method can be used in treatment of wastewater with both high and low concentration of organic matter, even in a large flux.

1.3.1. Types of non-thermal plasma

Based on the plasma-phase distribution, electrical discharges with liquids can be subdivided into three main groups, namely, electrical discharges above liquid surface, direct electrical liquid discharges and discharges in bubbles/vapor in liquids (Figure 14) [143].

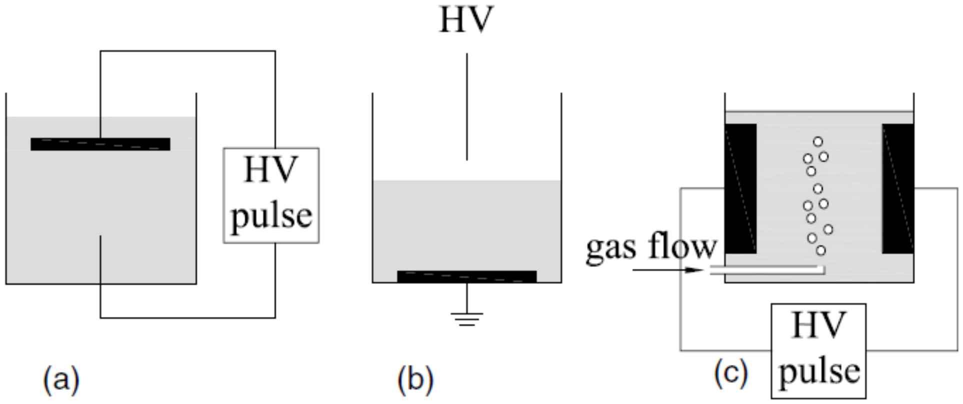


Figure 14. Typical electrode configurations for the three different types of discharges in contact with liquids. (*a*) Direct liquid phase discharge reactor (*b*) gas phase discharge reactor with liquid electrode (*c*) example of bubble discharge reactor [143].

The discharge directly in the liquid, so-called direct liquid streamer or corona discharges are almost always generated by pulsed excitation in a pin-to-plate configurations or in plate–plate configurations [144,145]. The most commonly used excitation method is the capacitor discharging by means of a spark gap or another triggering device or to produce pulsed excitation with use of pulse forming lines as used in high power water switching. Electrical breakdown is generally defined as the moment when a conductive plasma channel forms an electrical connection between the two metal electrodes inside the liquid. Historically, regarding the breakdown initiation in liquids under pulsed excitation two principal schools of thought emerged a few decades ago. The first favours an electron multiplication theory in the liquid, whereas the second favors a bubble mechanism breakdown theory or more generally a phase change mechanism breakdown theory. Discussion of this two thoughts and experiments that confirm theory and influence of different factors on electrical breakdown in liquid have been reviewed [143].

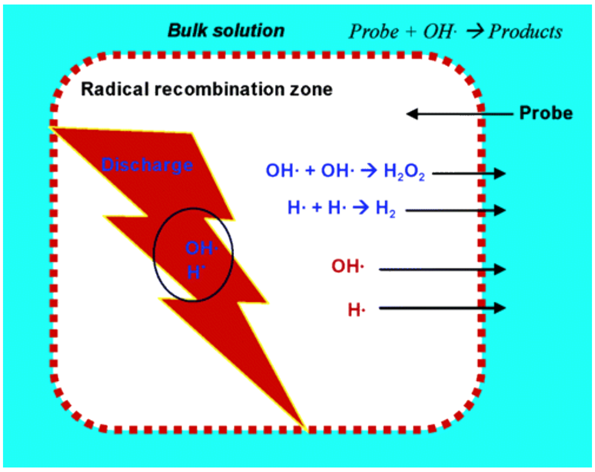


Figure 15. Various reaction zones involved in the production and reactions of reactive species formed by the high voltage electrical discharge in water. [146]

In their paper Sahni and Locke [146] proposed three critical reaction zones in the pulsed streamer discharge processes (Figure 15): a high temperature electrical discharge zone (depicted by the orange region) where the radicals such as $OH^{\cdot}$ and $H^{\cdot}$ are formed from water dissociation (eq 37), a radical recombination zone (depicted by the white region) where the radicals recombine to yield molecular products such as H_2O_2, H_2, and O_2 that diffuse into the bulk (eqs 38–40), and the zone representing the bulk solution (depicted by the blue region) where radicals and molecular species diffusing into the bulk react with molecular species (Eq. 41 and 42 these two reactions may also occur in the recombination zone).

$$H_2O \rightarrow OH^{\bullet}+H^{\bullet} \qquad (37)$$

$$OH^{\bullet} +H^{\bullet} \rightarrow H_2O_2 \qquad (38)$$

$$H^{\bullet} +H^{\bullet} \rightarrow H_2 \qquad (39)$$

$$OH^{\bullet} + H^{\bullet} \rightarrow H_2O \qquad (40)$$

$$OH^{\bullet} + \text{probe} \rightarrow \text{products} \qquad (41)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (42)$$

Experiments over a wide range of probe concentrations strengthen the hypothesis that the hydroxyl radical is the predominant precursor of hydrogen peroxide formation. They also found that by increasing the power input linear increase in the rate of production of hydroxyl radicals is observed.

In the cases of electrical discharges above liquid surface, the plasma generation and gas phase breakdown above liquid surface is mostly similar to the gas electrical discharge. Fast imaging of electrical breakdown in a metal-to-water electrode system with DC applied voltages shown that the Taylor cone is fully developed before the electrical breakdown occurs [147] (Figure 16).

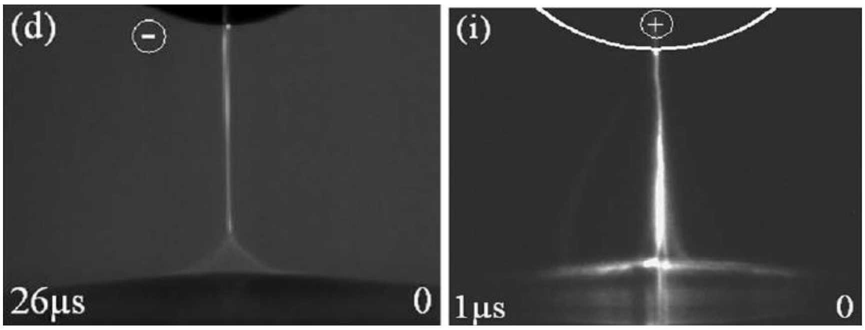


Figure 16. Taylor cone formation and electrical breakdown.

Overview of important reactions in the air plasma–liquid cathode interaction was reviewed. In general in this type of non-thermal plasma, the solution pH decrease as a result of nitric acid formation. Also, conductivity of solution increase as a consequence of formation of nitric acid and the formation of the H_3O^+ ions in the water due to the electronic and ionic bombardment. The formation of hydrogen peroxide, hydroxyl radicals and ozone strongly depends on reactor configuration [148].

Pulsed electrical discharges in a single bubble in water has been studied fundamentally, in the case with a metal needle electrode of which the tip extends inside a bubble and a disk counter electrode immersed in the de-ionized water (Figure 17) [149].

Authors observed two distinct types of discharges. The discharge is fundamentally different from unipolar dielectric barrier when a bubble covers the entire gap between the electrodes and no dielectric covers either electrode.

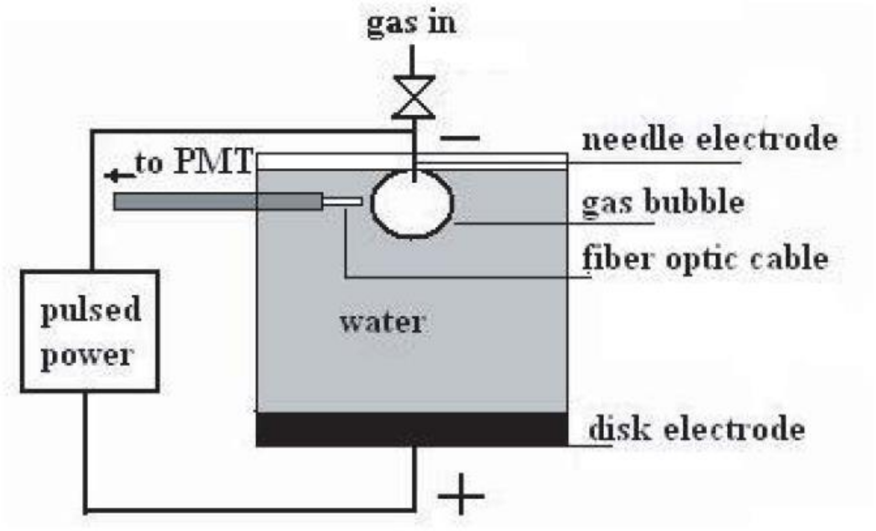


Figure 17. Schematic diagram of the bubble – water arrangement showing the bubble around the needle electrode with the disk electrode immersed in water. Gas is fed through the needle and a stationary bubble forms surrounding the tip of the needle [149].

1.3.2. Physicochemical properties of non-thermal plasma

. Non-thermal plasma produced by gas discharges is a mixed atmosphere consisting of high-active species, such as electrons, ions, radicals, excited atoms and molecules [150,151]. The addition of water molecules into electrical discharge process leads to generating $OH^{\bullet}$ and $H^{\bullet}$ via dissociation, ionization and vibrational/rotational excitation of water molecules. For example, the pulsed streamer discharge process produces charged particles having energies of about 5–20eV, which can initiate the reactions of vibrational/rotational excitation of water (threshold energy < 1 eV), dissociation of water (threshold energy ≈ 7.0 eV) or even ionization energy of water (threshold energy ≈ 13 eV) as Eq. (43-46) [152].

Dissociation: $H_2O + e^- \rightarrow OH^\bullet + H^\bullet + e^-$ (43)

Ionization: $H_2O + e^- \rightarrow 2e^- + H_2O^+$ (44)

$H_2O^+ + H_2O \rightarrow OH^\bullet + H_3O^+$ (45)

Vibrational /rotational excitation: $H_2O + e^- \rightarrow H_2O^* + e^-$ (46)

$H_2O^\bullet + H_2O \rightarrow H_2O + H^\bullet + OH^\bullet$ (47)

$H_2O^\bullet + H_2O \rightarrow H_2 + O^\bullet + H_2O$ (48)

$H_2O^\bullet + H_2O \rightarrow 2H^\bullet + O^\bullet + H_2O$ (49)

Eq. (47-49) demonstrated that vibrationally/rotationally excited water molecules relax into a lower energetic state through which some active radicals can be produced.

When oxygen is exposure to electrical discharge, O atom ($E^0_{O/H2O}$ =2.42 V) can be generated according to equation via dissociation of $O_2^\bullet$. Generated oxygen atom boosts the rate of production of $OH^\bullet$.

$e^{-*} + O_2 \rightarrow O^\bullet + O^\bullet + e^-$ (50)

$O^\bullet + H_2O \rightarrow 2OH^\bullet$ (51)

Furthermore, O atom can directly react with contaminants and also takes part in the reactions with O_2 resulting in the formation of O_3 ($E^0_{O3/O2}$ = 2.07 V).

$O^\bullet + O_2 + M \rightarrow O_3 + M$ (52)

Ozone as a strongly oxidizing allotropic form of oxygen reacts best when it can act as an electron transfer acceptor for the oxidation of metal ions, as an electrophile for the oxidation of phenol and other activated aromatics, and as a dipole addition reagent by addition to carbon–carbon multiple bonds. Ozone is unstable and decomposes through a cyclic chain mechanism to produce hydroxyl radicals in neutral and basic solutions (Figure 18).

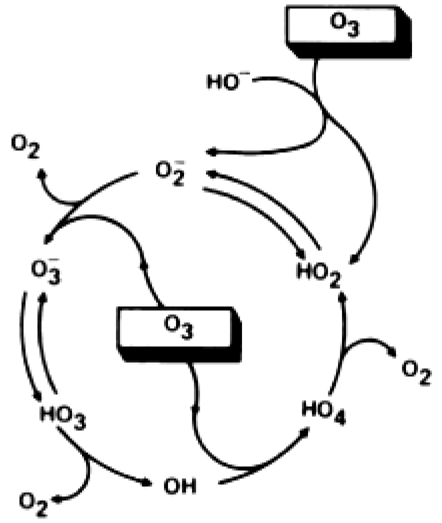


Figure 18. Cyclic chain mechanism of ozone decomposition [153].

Moreover, with the presence of H_2O_2 in plasma system, ozone can react with HO_2^- giving $OH^\bullet$ [101].

$$H_2O_2 \rightarrow H^+ + HO_2^- \tag{53}$$

$$O_3 + HO_2^- \rightarrow {}^\bullet O_2^- + OH^\bullet + O_2 \tag{54}$$

$OH^\bullet$ radicals have very short lifetime in a gas (3.7×10^{-9} s), and low diffusion distance (approximately 6×10^{-9} m) [154]. So their diffusion from the plasma zone into the surrounding water seems unlikely. Recombination of $OH^\bullet$ radicals formed long-lived plasma chemical product, hydrogen peroxide ($E^0_{H2O2/H2O} = 1.77$ V), especially in the cases of underwater plasmas. Hydrogen peroxide does not significantly react with most organic compounds, but in his presence much more $OH^\bullet$ can be directly or indirectly generated *via* various reactions (*e.g.*, dissociation, photolysis and metal-based catalytic reactions).

Plasma discharges in air usually generate not only oxygen and water dissociation species but also nitrogen oxide compounds known as reactive nitrogen species (RNS). RNS include nitric oxide, nitrous acid and peroxynitrous acid, which can diffuse into the bulk water phase and further be oxidized into undesirable toxic species (NO_2^- and NO_3^-). This can result in an increased toxicity of treated water and a pH decrease. Nitric oxide (NO) and nitrogen dioxide (NO_2) formed in the plasma phase can be dissolved in water and react with plasma-generated active species such as hydroperoxyl radical, ozone or hydrogen peroxide in order to give other RNS such as nitrous acid (HONO) and peroxynitrous acid (ONOOH). Detailed mechanism of RNS formation was described [155] *via* Eq. 55-66:

$$O_2 + e^- (+M) \rightarrow 2O^\bullet + e^- (+M) \qquad (55)$$

$$N_2 + O^\bullet \rightarrow {}^\bullet NO + N^\bullet \qquad (56)$$

$$N^\bullet + O^\bullet \rightarrow {}^\bullet NO \qquad (57)$$

$$N^\bullet\ ({}^2D) + O_2 \rightarrow {}^\bullet NO + O^\bullet \qquad (58)$$

$${}^\bullet NO + {}^\bullet OH \rightarrow ONOH \qquad (59)$$

$$NO + O \rightarrow ONO \qquad (60)$$

$$ONO + NO + H_2O \rightarrow 2ONOH \qquad (61)$$

$$NO^\bullet + HO_2^\bullet \rightarrow ONOOH \qquad (62)$$

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \qquad (63)$$

$$NO_2 + {}^\bullet OH \rightarrow H^+ + NO_3^- \qquad (64)$$

$$ONOOH \rightarrow NO_3^- + H^+ \qquad (65)$$

$$3NO_2^- + 2H^+ \rightarrow NO_3^- + 2NO + H_2O \qquad (66)$$

In study of the behavior of an anthraquinonic dye (ARS) exposed to gliding arc discharge in presence or absence of incorporated sulphamic acid known for its ability to inhibit the formation of nitrite ions and their derivatives, authors found that nitrite and peroxynitrite ions are the key agents of the degradation process [156].

Aqueous contaminants can be removed by reductive degradation pathways due to the presence of reductive species in electrical plasma. Aqueous electron, as a strong reducing agent (E^0 H_2O/e^- aq= - 2.77 V), can be formed by the irradiation of water with high-energy electrons [157]. Additionally, H radicals are formed directly by the electron collision with water molecules and from the reaction of hydrated electrons with acids. The H radicals, as strong reducing agents ($E^0_{H_2O/H'}$ = - 2.30 V), undergo two general types of reactions with organic compounds: (i) hydrogen addition to unsaturated bond and (ii) hydrogen abstraction saturated compounds [158].

As a result of excited species (generated from the collisions between electrons and neutral molecules) relaxation to lower energetic states, all plasmas containing water have UV light emission. UV light participates in degradation of organic molecule in two ways. Organic molecule (M) irradiated by UV light absorbs the radiation and gets to an excited state ($M^{\bullet}$). The excited molecules $M^{\bullet}$ have short lifetime (10^{-9}–10^{-8} s) and immediately returns to the ground state through which excited molecule can decompose into new molecules [159]:

$$M + hv \rightarrow M^{\bullet} \rightarrow \text{products} \tag{67}$$

Another way is photolytic dissociation of the hydrogen peroxide and ozone thereby causing hydroxyl radical generation in the plasma system [160]. These supplementary hydroxyl radicals in turn destroy the pollutants and thus enhance the utilization of input electrical energy.

Due to the limited space in the water, plasma cannot spread freely, and a pressure as high as 105-107 MPa is generated. Because of the incompressibility of the water, the high pressure would transform into impact shock wave in water. Thus, shockwave can be produced by high electric energy only directly introduced in the liquid or bubbles [161]. Streamer-like discharges in liquid produce shock [162], and diaphragm-like discharges in bubbles in the liquid can generate weaker shockwaves at the moment of bubble implosion [163]. Gas-phase plasmas normally do not induce any shockwaves in the liquid, but they can affect the liquid motion under three plasma generation situations, namely, cold plasma jets or plumes, ionic wind and the formation of Taylor cones in plasma–water interface [164].

1.3.3 Reactors for plasma treatment

Varieties of different reactors with liquid phase or gas–liquid phase electrical discharges have been developed. Representative reactors were discussed in Jiang review [141], according to the classification of discharge types. They classified reactors as following:

a) **Pulsed corona/streamer/spark discharge**

Pulsed discharge reactor is driven by a pulsed electric generator able to create a very sharp high voltage pulse with a range of nanosecond or microsecond of the duration time. In this discharge process, only free electrons gain high energy with producing energetic electrons leading to non-thermal plasma generation [165]. The typical configurations involve two asymmetric electrodes, one is very high curvature electrode (*e.g.*, needle [166], ring [167] or wire [168]) and the other one is small curvature such as a plate. The discharge inception voltage in this configuration was reduced because uniform electric field generated on the large curvature electrode can induce a high potential gradient. Types of pulsed discharge plasma reactors are: (a) liquid discharge reactor [169], (b) gas discharge reactor, (c) hybrid gas–liquid discharge reactor [170], (d) wires-plate reactor [168], (e) electrostatically atomized ring–mesh reactor [171] and (f) aerosol reactor [172].

b) **DC pulseless corona discharge**

The pulseless corona system can obtain a high flux of electrons from DC electrical discharge in gases or liquids. This system supplies active radical species like hydroxyl radical, ozone and atomic hydrogen, for chemical oxidations. The advantage of the DC corona is that it can continuously produce radical species. Disadvantage is that it consumes more energy because of the continuous operation. These types of reactors are also significantly affected by water conductivity. Some types of DC pulseless corona discharge reactors are: (a) submerged capillary point electrode reactor [173], (b) multiple wires-plate reactor [174], (c) wire-cylinder wetted-wall reactor [175].

c) Dielectric barrier discharge

This discharge type is based on the use of at least one dielectric barrier (quartz, glass, mica and alumina, ceramics) in the discharge gap with time varying voltages applied to the electrodes. Dielectric barrier prevents spark formation, eliminates electrode etching and corrosion and distributes the discharge almost uniformly over the entire electrode area. Industrial generation of ozone with oxygen or air feed is based on dielectric barrier discharge (DBD) technology. In this type of electrical discharge systems a large number of chemical active species with very high oxidation potentials are produced. Some types of described DBD reactors are: (a) multiple tubes-liquid electrode reactor [176], (b) rod-cylinder reactor [177], (c) coaxial cylinder reactor [178] and (d) rotating drum reactor [179].

d) Gliding arc discharge

The gliding arc discharge (GAD) exhibits a dual character of thermal and non-thermal plasma. A typical reactor consists of insulating cover, „knife-edge“ divergent electrodes, high voltage power supply, the nozzle and impedance [180]. High voltage is introduced between two or more thin “knife-edge” divergent electrodes and when the electric field reaches approximately 3 kV mm^{-1} in air, at the narrowest point electrical breakdown results in the arc discharge. High velocity gas flows through the nozzle and the length of the arc (actually a thermal plasma) increases. The temperature of the ionized gas decreases, so that it becomes a non-thermal quenched plasma upon breaking into a plasma plume. After the decay of the plasma plumes, the evolution repeats from the initial breakdown. This technique allows introduction of high electrical power and consequently results in the larger yields of short-lived active species.

Interestingly, hydrogen peroxide and ozone were not detected for any working gas in the solution for this type of discharge. Presence of water vapor strongly suppresses ozone formation and the hydroxyl radicals generated in the plasma do not recombine to produce measurable levels of hydrogen peroxide [181].

e) DC glow discharge

In DC glow electrical discharge process, a thin wire anode is in contact with the surface of the electrolyte. The DC glow discharge is initiated in a thin sheath film of vapor covering the electrode surface. Vapor phase water molecules are electrolytically dissociated at a high temperature with generations of active species such as $OH^{\bullet}$, $H^{\bullet}$ and $HO_2^{\bullet}$. Under the influence of the large electric field driving force, H_2O^+ gas ions produced from vapor H_2O molecules bombard the gas–liquid interface and subsequently react with liquid H_2O molecules to form additional OH and H radicals [182]. In efforts to improve the treatment efficiency, multiple anodes can be used to generate large volume plasma [183]. In the case submersed glow discharge electrolysis technologies are used, two electrodes are placed in liquid so the power dissipation in the vicinity of the electrode is large enough to evaporate the liquid. The glow plasma is generated in the vapor layer and covers the metal electrode [184].

Advantage of glow discharge technology is that it can be operated under high-salt containing water, because the aqueous solution itself serves as the cathode in glow discharge processes [185].

Some described types of glow discharge reactors are (a) contact glow discharge reactor [186], (b) contact glow discharge reactor with two cells [187], (c) submerged glow discharge reactor [184] and (d) DC diaphragm glow discharge reactor [188].

f) DC arc discharge

Thermal plasma has also been applied for water treatment. Due to its high temperatures and energy densities, reduction or oxidation atmosphere and rapid quenching rate (10^5–10^6 K s^{-1}), it can produce non-equilibrium chemical compositions [189]. The widely utilized thermal plasma generation reactor is a torch configuration. In this type of reactors the contaminated solution is usually directly introduced into torch as plasma forming gas. When the arc is ignited, the aqueous solution evaporates spontaneously to provide the generation of 100%-water plasma due to enormous heat from an anode. Anode is cooled by the water evaporation; therefore no cooling-controlled units are required [190].

In his paper Malik [191] compares relative energy yields (value expressing the amount of pollutant converted divided by the energy input required at 50% conversion of the pollutant) of about 27 major types of plasma reactors. The results reveal dramatic differences in the energy yields, up to five orders of magnitude. The most efficient are pulse-powered reactors, in which plasma is formed in gas phase and the waste solution is sprayed into it.

1.3.4 Catalysis in plasma treatment

There are many papers that describe use of catalyst in plasma treatment in order to improve energy efficiency. Some of most interesting catalyst are activated carbon materials (mechanism of degradation are based on sorption of organic compounds and oxidizing molecules) [192]. Activated carbon fibers [193] and multiwalled carbon nanotubes [194] are also applied as catalyst in the plasma treatment. In plasma-photocatalysis process, the high electric field is thought to be able to prevent recombination of electrons with holes on the surface of TiO_2, which could improve the quantum effect of photocatalysis [195]. TiO_2 mounted on activated carbon can significantly improve the decomposition of phenol adsorbed on activated carbon and the simultaneous regeneration of the saturated activated carbon [196]. Some other oxides, *e.g.*, Fe_3O_4, NiO and Ag_2O were also applied for assessing the synergistic effect for organic abatement in plasma system [197,198].

Addition of ferrous salt in plasma system is an attractive alternative arising from the fact that adding iron salts can catalytically transform previously formed H_2O_2 into hydroxyl radicals via Fenton reactions [178]. In addition, the Fenton reaction in plasma system can be activated by self-generated „white light“ containing wavelengths from 200 nm in the UV range to 1000 nm in the infrared range. Other metal ions like Mn and Co could also catalyze the plasma treatment [199].

1.3.5 Application of non-thermal plasma in degradation of organic contaminants

Plasma, as reagentless technique (no external reagents needed) and with high removal efficiencies of a large variety of contaminants within a short contact time, could be competitive in comparison to the other AOPs. Applications of non-thermal plasma technologies to decontaminate waters from organic contaminants are recently reviewed [142]. Magueranu *et al*. recently reviewed degradation of pharmaceutical compounds [200]. In Table 15 application of plasma treatment for some selected compounds are reviewed.

TABLE 15. Application of plasma treatment for some selected compounds.

Ref.	Plasma properties	Target properties
Phenol and derivatives		
201	gas corona discharge Non-pulsed direct current (DC), high voltage (13.7–19 kV)	Phenol (50 mg/L)
202	streamer corona discharge and spark discharge	Phenol (500 μmol/L)
203	pulsed high-voltage corona discharge plasma	Phenol (100 mg/L)
204	DBD reactor (≈17 kV, 50 Hz),	Phenol (47 mg/L)
205	coaxial DBD (16 kV, 50 Hz, 0.56 mA)	Resorcin and pyrocatechol (59 mg/ L)
206	pulsed-electric discharge reactor (60 kV).	2,4-dichlorophenol (1 g /L)
207	three parallel coaxial DBD reactors (20 kV)	2-chlorophenol, 4-chlorophenol and 2,6-dichlorophenol 20 mg /L)
208	multi-tube parallel surface discharge plasma reactor (20–30 kV, 30–150 W)	p-nitrophenol (40 L, COD 80 mg L^{-1})

209	nonthermal plasma hybridseries gas–liquid electrical discharge reactor (45 kV, 60W).	Catechol, resorcinol, hydroquinone), (2-, 3-, and 4-chlorophenol) and (2-, 3- and 4-nitrophenol)
Pesticides		
210	DBD, 80 V , 1–2.5 A	Nitenpyram
211	gas–liquid hybrid discharge reactor a needle-plate electrode	Diuron
212	wire–cylinder dielectric barrier discharge reactor, 50 W	Atrazine
213	pulsed electrical discharge, 45 kV, 60 Hz	Atrazine
214	DBD, applied power = 85 W, airgap distance = 5 mm, and treatment time = 7 min.	Dimethoate
215	Dielectric barrier discharge	Mesotrione
216	Dielectric barrier discharge, 170 W	Acetamiprid (50 mg/L)
217	Dielectric barrier discharge (DBD) reactors; one was a conventional batch reactor (R1) and the other a coaxial thin-falling-water-film reactor	Atrazine, chlorfenvinfos, 2,4-dibromophenol, and lindane), (1–5 mg/ L)
Dyes		
218	Glow discharge electrolysis	Polar brilliant B concentration of 50 mg/L
219	Contact glow discharge electrolysis, f 480 V and a current of 65–80 mA	Methyl orange dissolved in sodium sulfate (0.015 M)
178	Dielectric barrier discharge	Reactive Black 5, Reactive Blue 52, Reactive Yellow 125, and Reactive Green 15 (100 ppm)
220	Dielectric barrier discharge, t 22 kV with a frequency of 10.5 kHz.	Methylene blue, 100 mg/L
221	Dielectric barrier discharge	Azo dyes (Astrazon Red, Realan Red RC, Realan Golden Yellow RC, Optilan Blue MF-2RLA, Optilan Golden Yellow MF-RL, Lanaset Yellow 4GN) Anthraquinone dyes

		(Realan Blue RC, Lanaset Blue 2R) Indole dyes (Astrazon Yellow, Astrazon Brilliant Red), Mixed dyes (Astrazon Blue)
222	Contact glow discharge electrolysis, o 580V, 80 mA	Reactive Yellow 176 (Y3RS), Reactive Red 239 (R3BS) and Reactive Black 5 (B5) (50 mg/L
223	Gliding arc	Orange I, Crystal Violet, and Eriochrome Black T
224	Pulsed discharge plasma, : (i) streamer, (ii) spark, (iii) spark–streamer mixed mode	Rhodamine B (basic dye), Methyl Orange (acid dye), and Chicago Sky Blue
225	Pulsed discharge reactor with TiO_2-loaded activated carbon fiber	Methyl orange
226	Gas–liquid series highvoltage pulsed discharge water treatment reactor	Basic dyes (Basic Orange, Methylene Blue), acid dyes (Methyl Orange, Eosin Yellowish)
Pharmaceuticals and personal care products		
227	DBD with falling liquid film	Antibiotics (amoxicillin, ampicilin, oxacilin (100 mg/L)
228	Point to plate corrona with gas bubbling	Antibiotic Tetracycline (50 mg/L)
229	DBD with falling liquid film	Anticonvulsant carbamazepine (20 mg/L)
230	Wetted wall corrona discharge	Anti-inflamatory ibuprofen (60 mg/L)
231	DBD with falling liquid film	Anti-inflamatory ibuprofen (60 mg/L)
232	Corona with liquid shower	Analgesic, paracetamol (100 mg/L)
233	Corona with liquid shower	Hormone, 17β-estradiol (3 mg/L)
234	DBD with falling liquid film	vasodilatator, pentoxyfiline (100 mg/L)

2. Materials and methods

2.1. Chemicals

The anionic surfactants, sodium dodecyl sulfate SDS and sodium dodecylbenzene sulfonate SDBS were purchased from Sasol S.P.A (Italy) and used without further purification. The non-ionic surfactant TX-100 was purchased from ICN Biomedicals and used without further purification. Homogeneous catalysts used in degradation reactions were hydrogen peroxide (30% H_2O_2, Carlo Erba, Italy) and ferrous sulfate ($FeSO_4 \cdot 7\ H_2O$, Merck, Germany). Other chemicals for spectrophotometric determination purchased from Merck (Germany) and Sigma Aldrich were of analytical grade. All solutions were prepared with deionized water with conductivity between 1.0 and 1.5 μS cm^{--1}. Syringe filters (13 mm, PTFE membrane 0.45 μm) were purchased from Supelco (USA). Solvents used in HPLC and UPLC-MS analysis were purchased from Sigma Aldrich and were HPLC and HPLC-MS grade, respectively.

2.2 Water falling film DBD reactor (WFF DBD)

The degradation of surfactants using a coaxial dielectric barrier discharge DBD was designed as an atmospheric non-thermal plasma reactor for the treatment of various water solutions. In this reactor water forms a falling film that is in direct contact with the plasma, as shown in Figure 19.

A cylindrical reactor was prepared with Pyrex tubes that had an internal diameter of 28.5 mm and length of 600 mm. The outer electrodes were made with aluminum foil, which was sealed on an outer glass tube with 400 mm in length. The inner electrode was a glass cylinder with a diameter of 20 mm that was silver-plated on the inside.

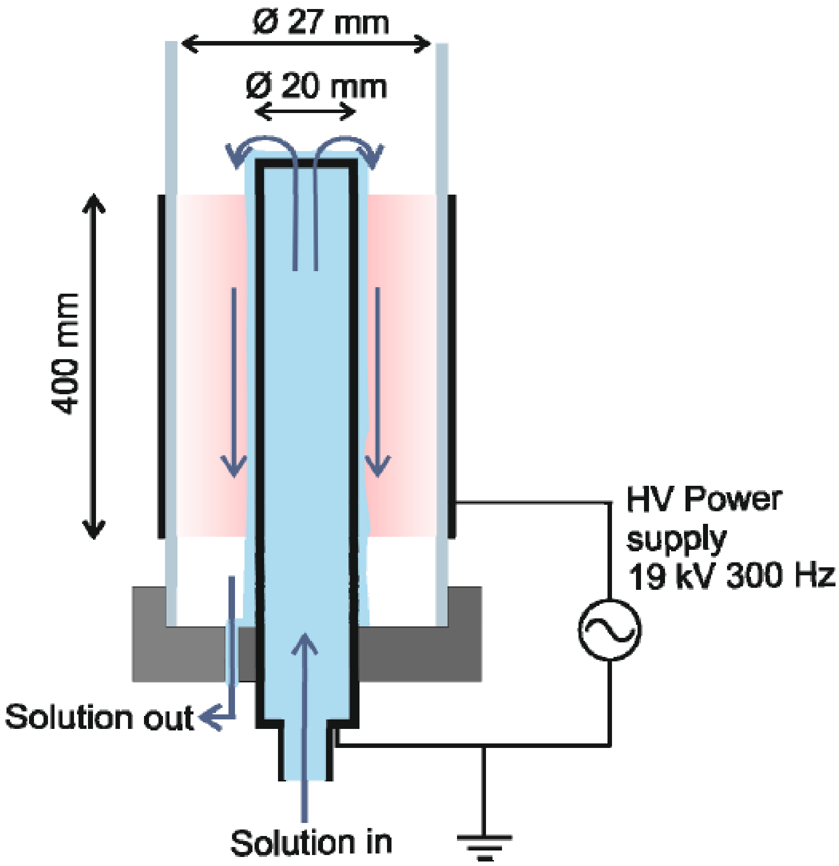


Figure 19. Water falling film dielectric barrier discharge (DBD) reactor used in the experiments.

A solution of surfactant flows up through a vertical hollow cylindrical electrode and flows down, thus making a thin dielectric film over the inner electrode. A barrier discharge is generated in air within a 3.5 mm gap between the dielectric and the water layer by applying a sinusoidal voltage of 19 kV on the peak.

The thin layer of water is in direct contact with the plasma, and oxidative species are transferred from the plasma into the liquid phase, where the reactions with the pollutants occur, which is of great importance, especially for short-living active species. To increase the total flow of the treated solution, three discharges are connected in parallel. The plug-in power for this system of discharges was 180 W. After the treatment, the solution was collected in a reservoir at the bottom of the reactor. The collected solution was re-introduced through the reactor for the next treatment, when the total amount of solution from the previous run had already passed.

The energy density (ED) of ~ 45 kJ L^{-1} was introduced into the solution with one pass through the reactor. Applied energy density was increased by recirculating the solution up to the point when applied energy density reached 450 kJ L^{-1}.

A high voltage transformer was used as a power supply, which allows the variation of the sinusoidal voltage up to 20 kV. The frequency for the plasma reactor was set at the optimal value of 300 Hz. The total flow rate through three parallel DBD reactors was 210 cm^3 min^{--1}. In all experiments, the treatment was started with 2 L of the surfactant solutions at a concentration of 100 mg L^{-1}.

2.3 Analytical procedures

2.3.1. Determination of pH value

All measurements of pH value were done using a pH meter (Microcomputer pH-vision 6071, JENCO Electronics Ltd. Taiwan) with combined electrode type HI 1131 (Hanna Instruments). The pH of all samples was adjusted to 7.0 ± 0.2.

2.3.2. Spectrophotometric analysis

Spectrophotometric measurements were done by GBC Cintra 10 (GBC Scientific Equipment Pty Ltd., Australia) spectrometer at a fixed slit width (1 nm) with quartz cuvettes (1 cm long optical path), 5 minutes after the plasma treatment.

2.3.2.1. Determination of anionic surfactants as methylene blue active substances

Methylene blue reagent was prepared by dissolving 100 mg methylene blue in 100 cm^3 water. 30 cm^3 of prepared solution was transfered to 1000 cm^3 flask. 500 cm^3 water, 41

cm^3 3M H_2SO_4 and 50 g sodium phosphate, (monobasic, monohydrate, $NaH_2PO_4 \cdot H_2O$) was added. After dissolving, the solution was diluted to 1000 cm^3.

A 5 cm^3 sample of each of the above solutions was used for the analysis (instead of 100 cm^3, as used in the standard method). Each sample was placed in a test-tube (20 mm x 150 mm). The sample was adjusted to alkaline pH using NaOH, with the pH exceeding 8.3 as indicated by the phenolphthalein in end-point. The pink colour from phenolphthalein was then discharged by the addition of a few drops of H_2S0_4. Then 2 cm^3 of chloroform and 2 cm^3 of Methylene Blue reagents were added to each sample. The samples were shaken for 30 s using the vortex mixer. After allowing the phases to separate, the surfactant complex with the chloroform in the organic phase, was transferred into a second test-tube using a Pasteur pipette. This extraction procedure was repeated twice on the solution in the first test-tube using 2 cm^3 of chloroform each time.

Then 10 cm^3 of the wash solution was added to the second test-tube with the first phase extract (approximately 6 cm^3). The tube was shaken for 30 s using the vortex mixer. After settling of the contents, a Pasteur pipette was used to transfer the washed organic phase with MBAS into a third test-tube. The solution in the second test-tube was extracted twice using 2 cm^3 chloroform each time. This washed extract of the organic phase with MBAS (about 10 cm^3) was filtered through glass wool to transfer it into a fourth 20 cm^3 marked test-tube.

The third test-tube was rinsed twice with 2 cm^3 of chloroform each time. The chloroform was transferred into the 20 cm^3 marked fourth test-tube, through the glass wool. The final volume in the fourth test-tube was made up to 20 cm^3 with chloroform, making sure that all blue-coloured surfactant complex was transferred from the glass wool into the test-tube. This 20 cm^3 final extract solution was used for measuring the absorbance at 652 nm against a blank of $CHCl_3$.

2.3.2.2. Determination of nonionic surfactants as cobalt thiocyanate active substances

Sample volume of 10 cm^3 was transferred to centrifugal cuvette. The pH was adjusted to 7. After that 3 cm^3 of cobalt thiocyanate reagents (prepared by dissolution of 6.2 g ammonium-thiocyanate (NH_4SCN) and 2.8 g cobalt-nitrate hexahydrate

(($Co(NO_3)_2{\bullet}6H_2O$) in demineralized water and diluted to 100 cm^3) and 3 g of sodium chloride were added. Solution was shaken until salt dissolution. After dissolution, 15 cm^3 of chloroform was added. Mixture was shaken and after that centrifuged 5 minutes. Organic phase was transferred to spectrometer cuvette and absorbance was determined on 320 nm against the blank of chloroform.

The efficiency of degradation is defined as a percentage decrease of absorbance of surfactant derivatives according to Eq. (68):

$$Decolorization\ (\%) = \frac{A_0 - A}{A_0} \times 100 \qquad (68)$$

Where A_0 presents the absorbance of starting solution at the wavelength that 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.

2.3.2.3. Hydrogen peroxide determination

The titanium sulfate test reagent was prepared by reaction 1 g of anhydrous titanium dioxide with 100 cm^3 of sulfuric acid (specific gravity 1.84) for 15 to 16 hours on a sand bath at a temperature of 150° C. The solution was cooled, diluted with 4 parts (by volume) of distilled water, and filtered prior to use.

A standard hydrogen peroxide solution was made by diluting 20 cm^3 of 30% hydrogen peroxide solution to 1 liter with distilled water and standardized by titration with permanganate.

1 cm^3 of titanium sulfate reagent was added to 10 cm^3 of solution and absorbance was measured at 407 nm.

2.3.2.4. Indigo colorimetric method for ozone determination

a) Indigo stock solution: Add about 500 cm^3 distilled water and 1 cm^3 conc. phosphoric acid to a 1-L volumetric flask. Add 770 mg potassium indigo trisulfonate, $C_{16}H_7N_2O_{11}S_3K_3$ (commercially available at about 80 to 85% purity). Fill to mark with distilled water. A 1:100 dilution exhibits an absorbance of 0.20 ± 0.010 at 600 nm. The stock solution is stable for about 4 months when stored in the dark. Discard when absorbance of a 1:100 dilution falls below 0.16. Do not change concentration of dye for higher ranges of ozone residual. Volume of dye used may be adjusted.

b) Indigo reagent I: To a 1-L volumetric flask add 20 cm^3 indigo stock solution, 10 g sodium dihydrogen phosphate (NaH_2PO_4), and 7 cm^3 conc. phosphoric acid. Dilute to mark. Prepare solution fresh when its absorbance decreases to less than 80% of its initial value, typically within a week.

c) Indigo reagent II: Proceed as with indigo reagent I, but add 100 cm^3 indigo stock solution instead of 20 cm^3.

Spectrophotometric, volumetric procedure:

1) Concentration range 0.01 to 0.1 mg O_3/ L—10.0 cm^3 indigo reagent I was added to each of two 100-cm^3 volumetric flasks. One flask (blank) was filled to mark with distilled water. Other flask was filled to mark with sample. Absorbances of both solutions were measured at 600 nm. 10-cm cell was used.

2) Range 0.05 to 0.5 mg O_3/L—Proceeded as above using 10.0 cm^3 indigo reagents II instead of reagent I. Absorbance was measured in 5-cm cells.

3) Concentrations greater than 0.3 mg O_3/L—Proceeded using indigo reagent II, but for these higher ozone concentrations correspondingly smaller sample volume was used. Resulting mixture was diluted to 100 cm^3 with distilled water.

Ozone concentrations were calculated according to Eq. 69:

$$mg\ O_3 L^{-1} = \frac{100 \times \Delta A}{f \times b \times V} \tag{69}$$

Where:

ΔA = difference in absorbance between sample and blank,

b = path length of cell, cm,

V = volume of sample, cm^3 (normally 90 cm^3), and

f = 0.42.

2.3.3. Determination of OH radicals

Four milliliter samples (pH 7.0) taken from the reactor vessel, 5 cm^3 of 0.5 mol L^{-1} phosphate buffer (NaH_2PO_4-H_3PO_4, pH 4.0), and 0.4 cm^3 of 6 mmol L^{-1} DNPH were mixed and diluted to 10 cm^3. Thus formed hydrazone was equilibrated to room temperature for 30 min and then analyzed on analytical column Hypersil Gold aQ C18 (150 mm, 3 mm, 3 μm) at 30 °C. Mobile phase consisted of 40% of water as component A and 60% of methanol (HPLC grade, Sigma Aldrich) as component B. The chromatographic elution was conducted at flow rate of 0.4 cm^3 min^{-1} in isocratic mode. An injection volume of 20 μL was used each time. Detector was set at 355 nm, and calibration curve was made with formaldehyde (HACH Company, USA; Formaldehyde standard solution CH_2O=4000 mg L^{-1}, ampules). Samples were filtered through syringe filters (25 mm, PTFE membrane, pore size 0.45 μm) purchased from Supelco (Bellefonte, PA, USA). Data analysis was performed by software Chromeleon, v6.8 (ThermoFisher Scientific, Bremen, Germany).

2.3.4. Determination of the chemical oxygen demand (COD)

Chemical oxygen demand (COD) value of initial solutions (0 kJ L^{-1}) of two anionic surfactants and the solutions after the plasma treatment (450 kJ L^{-1}) was determined. COD value was determined for plasma-treated samples with applied energy density of 45 and 450 kJ L^{-1}. COD determination, was done using microwave digestion at high temperature and pressure (up to 100 bar). Microwave digester was ETHOS 1. Advanced microwave digestion System, Milestone Italy with segmented rotor HPR-1000/10S. In this type of apparatus, with poly Teflon vessels up to ten samples can be done simultaneously which considerably speeds up the process.

2.3.5. Determination of the total organic carbon (TOC)

Total organic carbon (TOC) analysis was done in accordance with method ISO 8245:2007 [235]

2.3.6. Ultra-high pressure liquid chromatography – Orbitrap - Mass (UHPLC-Orbitrap-MS)

The degradation products were identified using the UHPLC-Orbitrap-MS (Thermo Fisher Scientific). A column Acclaim Surfactant (150 × 3 mm, 3 μm, Thermo Scientific) was used for separation. The mobile phase was composed of 0.1 M ammonium acetate as component A and acetonitrile (both HPLC grade, Sigma Aldrich) as component B. The compounds were eluted at a flow rate of 400 μL/min, and the injection volume was 10 μL. The system was operated in the full spectral acquisition mode in the mass range of 50-900 m/z. The mass spectrometer was operated in the positive ionization mode. HESI-source parameters were as follows: source voltage 3 kV, capillary voltage −20 V, tube lens voltage −150 V, capillary temperature 275°C, and sheath and auxiliary gas flow (N_2), 30 and 8 (arbitrary units). Collision-induced dissociation (CID) was accomplished at collision energy of 40 eV.

The UHPLC system was coupled to a linear ion trap-Orbitrap hybrid mass spectrometer (LTQ Orbitrap MS) equipped with a heated electrospray ionization probe (HESI-II, Thermo Fisher Scientific, Bremen,Germany). Instrument control, data acquisition and data analysis were handled by computer equipped with Xcalibur software.

2.4 Toxicity tests

Each sample was centrifuged for 10 min at 2000 rpm. The supernatant was separated for toxicity tests. The hydrogen peroxide present in the samples was removed prior to toxicity analysis using the catalase enzyme.

2.4.1 *Vibrio fischeri* (*V. fischeri*)

The toxicity of the treated solutions was tested with *Vibro fischeri* NRRL B-11177, according to ISO 11348-3 [236]. Using BioFix Lumi freeze-dried bacteria (Macherey-Nagel, Duren, Germany), toxicity was measured as the inhibition of bacterial bioluminescence when the bacteria were exposed to surfactant solution before and after DBD treatment.

The osmolality and pH of all samples were adjusted to 2% NaCl and 7.0 ± 0.2 (0.1 M NaOH or HCl). Tests were carried out in three replicates. The exposure time was 15 min (at 15°C), and the EC_{50} (effective concentration of 50% inhibition) value was calculated using Microsoft Excel 2003 and OriginPro 8.0 software.

2.4.2 *Artemia salina* (*A. salina*)

Artemia salina cysts were purchased from Dajana Pet (Czech Republic). *They* were hatched and larvae were reared in synthetic sea water (Reef Salt, Aqu Medic, Germany) at 32 ± 0.5% [237]. In order to produce instar larvae, the entire suspension was illuminated by a tungsten filament light and continuously gently aerated.

An acute toxicity test was performed in darkness at 25 ± 1°C. The highest concentrations of untreated (100 mg L^{-1}) and treated (100% v/v) samples after the tenth recirculation (ED ≈ 450 kJ L^{-1}) through the DBD reactor were tested in triplicate. The osmolality and pH were adjusted to 32 ± 0.5‰ and 8.0 ± 0.2 (0.1 M NaOH or HCl). With a Pasteur pipette, 40 larvae were placed into vessels containing 50 cm^3 of the solution. Tests were considered valid if the mortality in the control did not exceed 10% and if the reference toxicant tests ($K_2Cr_2O_7$) were within the range of acceptable values.

The lethal concentration LC_{50} values (lethal concentration of effluent which causes mortality of test organism by 50%) with 95% confidence limits were estimated by Spearman–Karber regression model.

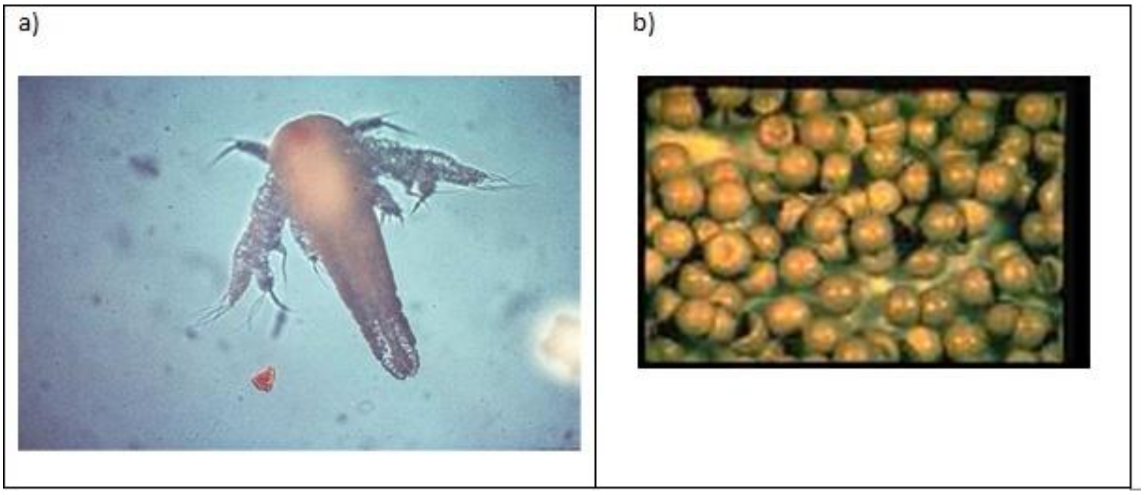
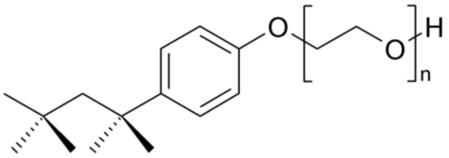
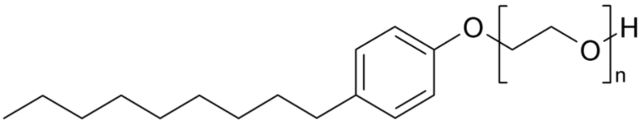
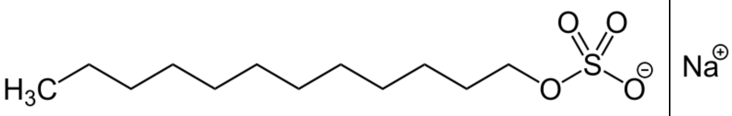
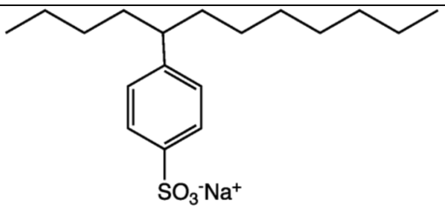


Figure 20. Photography of a) brine shrimp *Artemia salina*; b) *Artemia salina* cysts

3. Results and Discussion

In the present study, the degradation of four surfactants (two anionic - sodium dodecyl sulphate and sodium dodecyl benzene sulphonate, and two nonionic - nonylphenol ethoxylate and Triton X-100) was studied using non-thermal plasma based on coaxial dielectric barrier discharge reactor (DBD). Their structures are presented in the Table 16.

TABLE 16. Chemical structure of treated surfactants.

Name **CAS number**	**Chemical structure**
Triton X-100 **CAS No.: 9002-93-1**	
Nonylphenol ethoxylate **CAS No.: 68412-53-3**	
Sodium dodecyl sulphate **CAS No.: 151-21-3**	
Sodium dodecyl benzene sulphonate **CAS No.: 25155-30-0**	

Synthetic surfactants are widely used in detergents and cleaning products, ranging from household detergents and cleaners to personal care and toiletry products, with a range of specialized hygiene products used in institutional and industrial applications. Other applications of surfactants are in agrochemical, textile, pulp and paper industry, as well as paint and coating industry. Surfactants examined in this research are predominantly used in formulations of laundry detergents and for industrial cleaning application. They are used in large amounts and significant amount of surfactants can be found in the water.

Due to their significant effects on the aquatic environment, degradation of surfactants is subject of many research papers. In addition to the classical wastewater treatment a lot of research is addressed to the usage of advanced oxidation process for removal of various surfactants.

Dielectric barrier discharge reactor with water falling film constructed at Faculty of Physics (University of Belgrade) was previously successfully used for treatment of dyes, pesticides, phenols and its derivatives, as well as ibuprofen. Dielectric-barrier discharges are characterized by the presence of one or more insulating layers between the metal electrodes in addition to the discharge space. In our case the reactor were composed of two insulating layers of glass. The outer electrodes were made from aluminum foil, which was sealed on an outer glass tube and inner electrode was a glass cylinder, silver-plated on the inside.

Transformer was used as a power supply, which allows variation of the sinusoidal voltage up to 20 kV. The frequency for the plasma reactor was set at the optimal value, 300 Hz. Water forms a falling film that is in the direct contact with plasma. As water constantly flows over the top of the reactor, thin water film constantly regenerates, *i.e.* reactor works on the principle of the flow reactor. Hence, a thin layer of water is in direct contact with the plasma, oxidative species are transferred from the plasma into the liquid phase, where the reactions with the pollutants occur, which is of great importance, especially for short-living active species. To increase the total flow of the treated solution and efficiency of the treatment, three discharges are connected in parallel. The plug-in power for this system of discharges was 180 W.

Usage of homogenous catalysts in chemical and technological processes has several advantages compare to the heterogeneous catalysis. Homogenous catalysis is a lot simpler to perform, especially for industrial wastewater treatment because it is not needed for catalysts to be removed from system afterwards. Heterogeneous catalysts must be removed from the system after the catalytic cycle.

The necessary condition that must be met is that all homogenous catalysts used in those treatments are not toxic. Some of them, like H_2O_2, decompose during time to water and oxygen, and even considered as green catalysts. Others like Fe^{2+}, $Fe^{3+}$and Mn^{2+} are easily deposited by changing the redox conditions in water or by adjusting the pH value.

The goal of this thesis was to determine the degradation efficiency of the dielectric barrier discharge reactor with water falling film and effects of homogenous catalysts (Fe^{2+} and H_2O_2) on the efficiency of surfactants degradation, chemical oxygen demand (COD) and total organic carbon (TOC). Toxicity of the samples after degradation was examined by *Artemia salina* test (*A. salina*) and in case of Triton X-100 by *Vibrio fischeri* test.

3.1. Spectrophotometric determination of surfactants

Each series of experiments started with the recirculation of 2 L surfactant solution (concentration of 100 mg L^{-1} and the native pH value). An energy density (ED) of 45 kJ L^{-1} was introduced in the solution with each pass through the reactor. ED was defined as the dissipated discharge power divided by the flow rate of the water solution. Each solution was recirculated ten times and total energy density introduced after ten passes was 450 kJ L^{-1}. The total flow rate through three parallel DBD reactors was 210 cm^3 min^{-1}. After recirculation, a small aliquot was taken to record the absorption spectra according to the corresponding spectrophotometric method (MBAS for anionic and CTAS for nonionic surfactants) [238].

Water-soluble anionic surfactants (Methylene blue active substances - MBAS) such as linear alkyl sulfates form a 1:1 ion pair with the water-soluble cationic dye, methylene blue (MB). The ion pair is effectively neutral and is therefore extractable into a water-insoluble organic solvent such as dichloromethane (DCM). The intensity of the resulting blue color complex in the organic phase is measured at 650 nm.

Cobalt thiocyanate active substances (CTAS) are those that react with aqueous cobalt thiocyanate solution to give a cobalt-containing product extractable into an organic liquid in which it can be measured. Nonionic surfactants exhibit such activity, as may other natural and synthetic materials; thus, estimation of nonionic surfactants as CTAS is only possible if substantial freedom from interfering CTAS species can be assured.

The changes in the UV-visible absorption spectra of the derivatized surfactant solution with different energy density introduced are shown in Figure 21. With the increase of energy density the absorbance of complex was reduced in the whole spectrum. In the case of anionic surfactants, in addition to a decrease in absorption at 320 nm, which originates from the surfactant – ammonium cobaltothiocyanate complex, a decrease in absorption at 280 nm could be also observed.

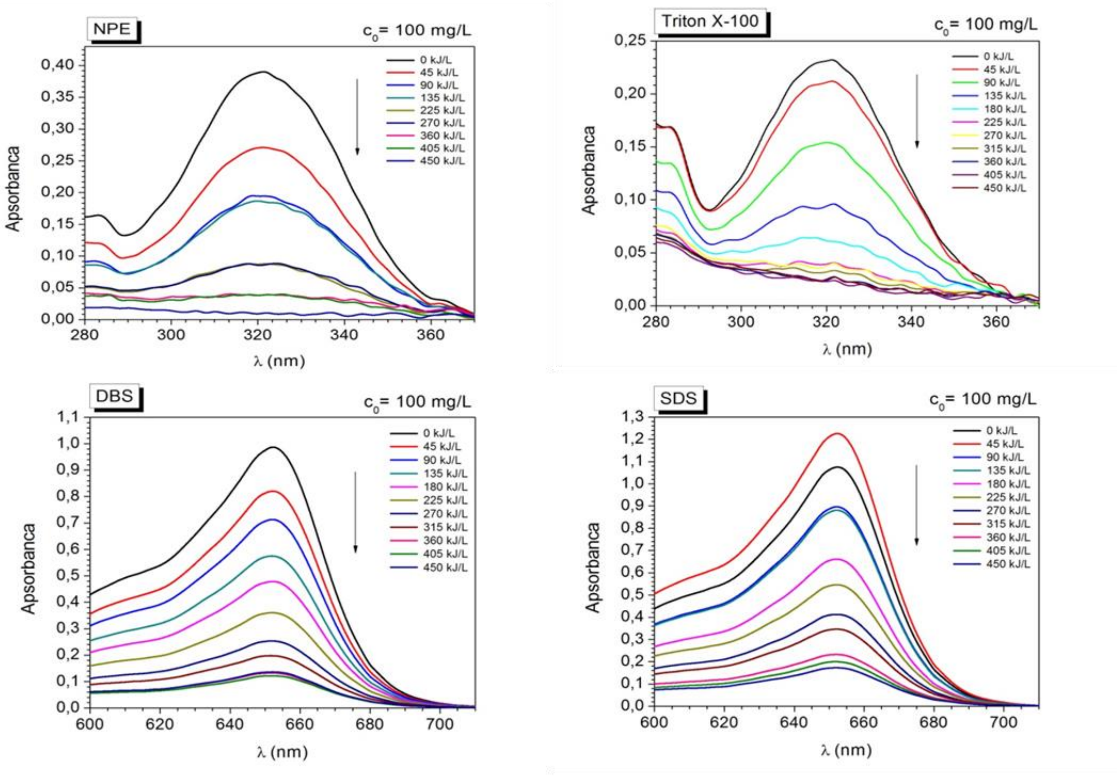


Figure 21. The changes in the UV-visible absorption spectra of the derivatized surfactant solution with different energy density introduced.

3.2 Degradation of non-ionic surfactants

3.2.1. Degradation of Triton X-100 in DBD reactor

Triton X-100 was chosen as the model compound for detailed examination of the degradation process. At first it was treated without a catalyst. Absorbance measurements of all samples (with different energy density introduced) were performed 5 min and 24 h after the plasma treatment in order to examine the post treatment reactions. Figure 22 shows that the difference in the degradation percentage at 5 min and 24 h is negligible.

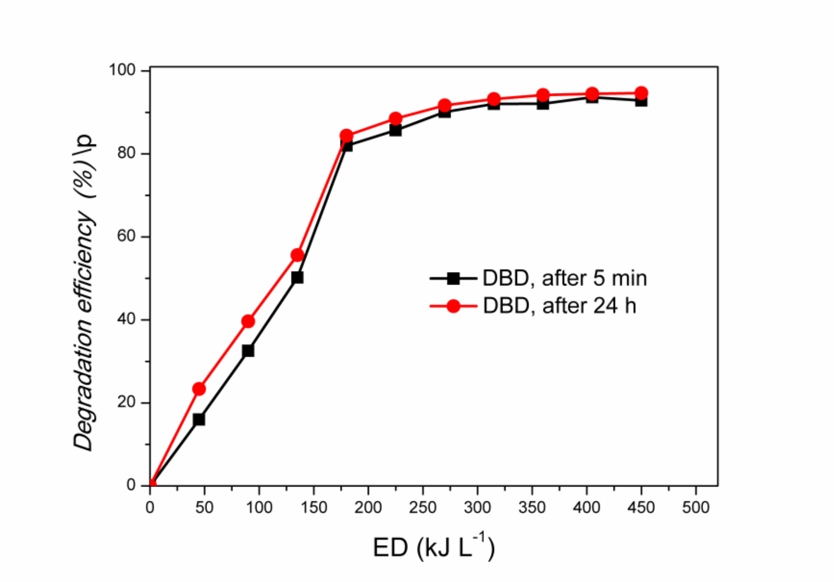


Figure 22. Degradation efficiency of TX-100 in DBD reactor after 5 min and 24 h.

As described in introduction part, various oxidizing species are formed in the treated solution during the plasma treatment. Most of these oxidizing species are active radicals with a very short lifetime, so they can react only with the pollutant molecules while the solution is flowing through the DBD reactor. Additionally, more stable O_3 and H_2O_2 molecules were also generated and they may still influence the degradation of surfactants after the treatment. The oxidation potential of O_3/H_2O_2 is based on the fact that the conjugate base of H_2O_2 can initiate ozone decay, which leads to the formation of $OH^{\bullet}$. This combination is usually called peroxone [239]. There was not a considerable difference in the degradation percentage after 5 min and 24 h of the plasma treatment, therefore we conclude that the main species responsible for the degradation of TX-100 are very reactive, short-living radicals. Among these radicals, $OH^{\bullet}$ was the major oxidative specie because it has the highest oxidation potential and is not selective in the degradation reactions. These results are different than results published in previous paper where the same reactor was applied for degradation of dyes. In the treatment of reactive dyes authors obtained significant percentage of decolorisation with low energy input (45 and 90 kJ) after 24 h in comparison with results after 5 minutes. This difference can be explained with the fact that chromophore in the reactive dyes can be oxidized with long-lived species (hydrogen peroxide) and in case of surfactants this species could not oxidize active groups.

3.2.2. Effect of H_2O_2 on the degradation of surfactants

In order to optimize concentration of hydrogen peroxide, three different concentrations of H_2O_2 (5, 10, and 20 mmol L^{-1}) were added to the surfactant solution to examine the effect on the degradation efficiency in the DBD reactor. Higher degradation efficiency was expected with H_2O_2 due to a more efficient generation of $OH^{\bullet}$ radicals, according to the following Eq. (24 and 70):

$$H_2O_2 \xrightarrow{hv} 2\,{}^{\bullet}OH \qquad (24)$$

$$H_2O_2 + {}^{\bullet}O_2 \xrightarrow{hv} {}^{\bullet}OH + OH^{-} + O_2 \qquad (70)$$

However, in the presence of ozone, which is one of the reactive species in the plasma reactors, H_2O_2 can initiate both ozone decay and the formation of $OH^{\bullet}$, a combination called peroxone [239]. Figure 3 shows that for ED = 45 kJ L^{-1}, the percentage of degradation in DBD was lower than in the catalytic system H_2O_2/DBD. Almost the same percentage of degradation was obtained for 10 and 20 mmol L^{-1} H_2O_2, thus increasing the H_2O_2 concentration further will not change the efficiency of surfactant degradation.

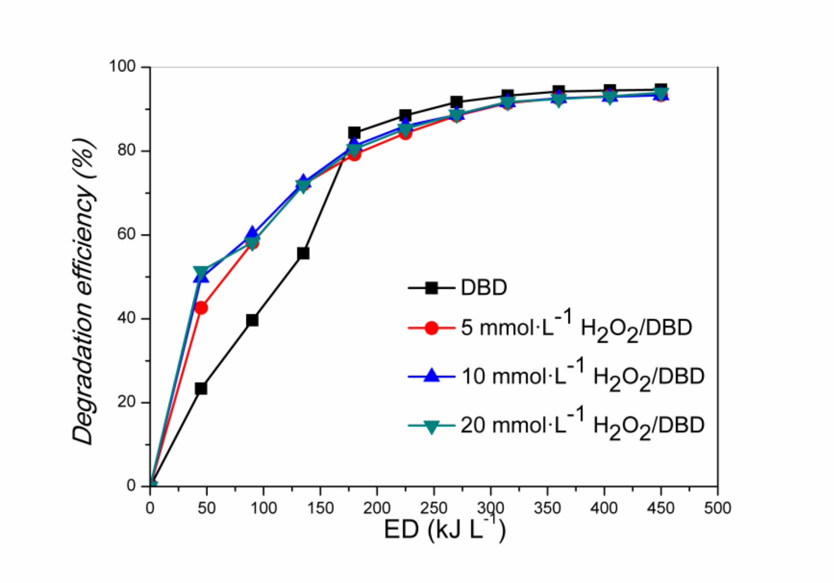


Figure 23. Degradation efficiency of TX-100 in the DBD reactor with the addition of H_2O_2.

Nevertheless, the results in Figure 23 show a lower degradation with H_2O_2 for ED = 200 kJ L^{-1}. These results can be explained by the consumption of $OH^{\bullet}$ by additional H_2O_2 through the reactions below (Eq. 31 and 11):

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (31)$$

$$^{\bullet}OH + HO_2^{\bullet} \rightarrow H_2O + O_2 \qquad (11)$$

When the initial peroxide concentration is very high and concentration of target compound is low, generated $OH^{\bullet}$ radicals react primarily with the excess peroxide and produce hydroperoxyl radicals (HO_2•; Eq. (31)), who are less reactive than $OH^{\bullet}$, and the rate of TX-100 degradation is thus decreased. The generated $OH^{\bullet}$ radicals can also further react with $HO_2^{\bullet}$ and produce water and oxygen (Eq. 11). In this way, the concentration of $OH^{\bullet}$ that is available for TX-100 degradation also decreases [241]. Thus, at ED = 200 kJ L^{-1}, the concentration of H_2O_2 is sufficiently high that this mechanism becomes more significant. As a result, the effective levels of both H_2O_2 and $OH^{\bullet}$ are reduced, and the degradation of TX-100 is inhibited in the presence of H_2O_2.

3.2.3. Effect of Fe^{2+} on the degradation of surfactants

As mentioned above, H_2O_2 is formed in the solution during the plasma treatment. DBD reactor produces H_2O_2 based on Eq. (71and 72) [240]:

$$2\,H_2O + e^{-}\,{}^{\bullet}\!\rightarrow H_2O_2 + H_2 + e^{-} \qquad (71)$$

$$O_3 + hv + H_2O \rightarrow H_2O_2 + O_2 \qquad (72)$$

The content of H_2O_2 in the deionized water was quantified 5 min after the treatment. The reaction with titanium sulphate reagent was used for determination of hydrogen peroxide [241]. The yellow color was produced due to the formation of pertitanic acid. The reaction equation is usually written as:

$$Ti^{4+} + H_2O_2 + 2H_20 = H_2Ti0_4 + 4H^{+} \qquad (73)$$

Nevertheless, some chemists prefer to write the formula of pertitanic acid as $TiO_2.H_20_2$, showing a true peroxide structure. The results are shown in Fig. 24.

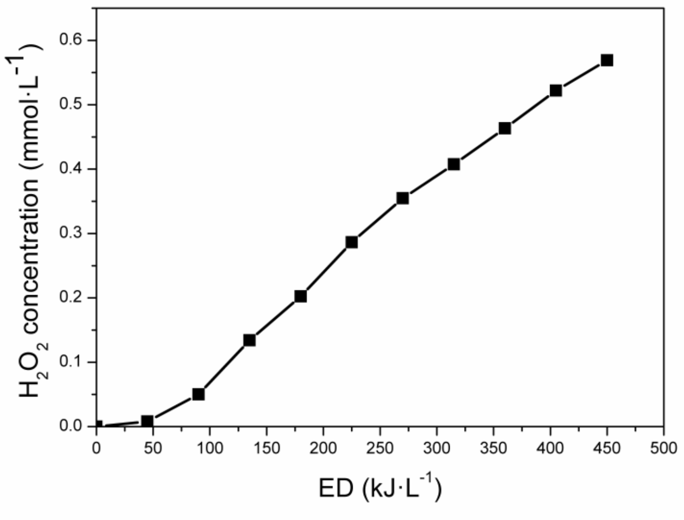


Figure 24. Production of H_2O_2 in the DBD reactor with different ED values

The peroxide concentration increased with each pass through the reactor. Therefore, Fe^{2+} was added to the treated solution to initiate the Fenton reaction. The formation of hydroxyl radicals and regeneration of Fe^{2+} by photo-reduction from Fe^{3+} can be represented by the following reactions [117]:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^{\bullet} + HO^{\cdot} \quad (29)$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet} + H^{+} \quad (30)$$

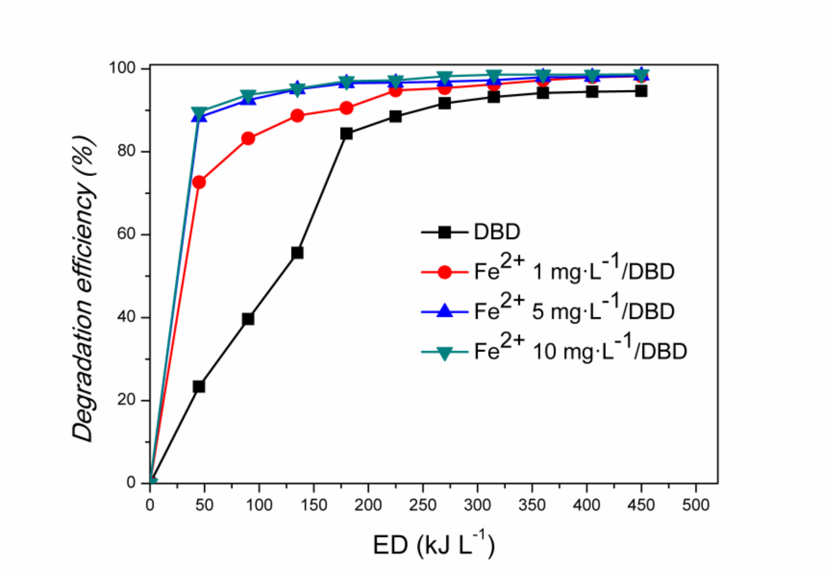


Figure 25. Degradation efficiency of TX-100 in the DBD reactor with the addition of Fe^{2+}.

Different concentrations of Fe^{2+} (1, 5, and 10 mg L^{-1}) were added to the TX-100 solution, and the results are presented in Figure 25. The addition of Fe^{2+} ions significantly increased the degradation percentage. Concentrations of 5 and 10 mg L^{-1} of Fe^{2+} were more efficient than 1 mg L^{-1} Fe^{2+}. They gave almost complete removal of TX-100 (97%) for ED = 200 kJ L^{-1}. A similar degradation percentage was obtained for these two Fe^{2+} concentrations, so we can conclude that catalyst concentrations > 5 mg L^{-1} do not lead to further improvement in efficiency. Increased efficiency of degradation in systems that contain Fe^{2+} can be explained by Fenton's reaction and reaction of Fe^{2+} with ozone [243]:

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \quad (29)$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + HO^{\bullet} + O \quad (30)$$

3.2.4. Degradation of nonylphenol ethoxylate

Nonylphenol ethoxylate was treated in the same experiments as Triton X-100 with the optimized concentration of catalyst. Similar behavior was noticed in comparison to Triton X 100 (Figure 26).

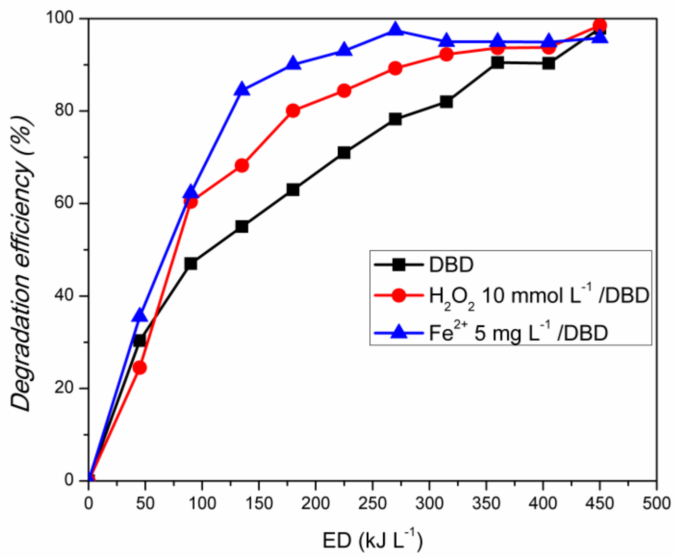


Figure 26. Degradation efficiency of NPE in the DBD reactor with catalyst and without catalyst

Since the structures of these two non-ionic surfactants are quite similar, these results are expected.

3.2.5. Identification of oxidation products and degradation mechanism of TX-100

The assessment of degradation products was the critical point that yields important information about the overall efficiency of the process because some of the created products might have an inhibitory effect on certain species. Samples were collected after introducing ED = 200 kJ L^{-1} into the TX-100 solution and using UHPLC-Orbitrap-MS analysis to identify the products and understand the mechanism of TX-100 decomposition in non-thermal plasma reactors. The degradation products were identified in non-catalytic DBD treatment and in the two catalytic systems that gave the highest degradation efficiency, 10 mmol L^{-1} H_2O_2/DBD and 5 mg L^{-1} Fe^{2+}/DBD. Degradation products were identified according to the corresponding spectral characteristics: mass spectra, accurate mass, and characteristic fragmentation.

All of the identified products in the three degradation systems are shown in Figure 27.

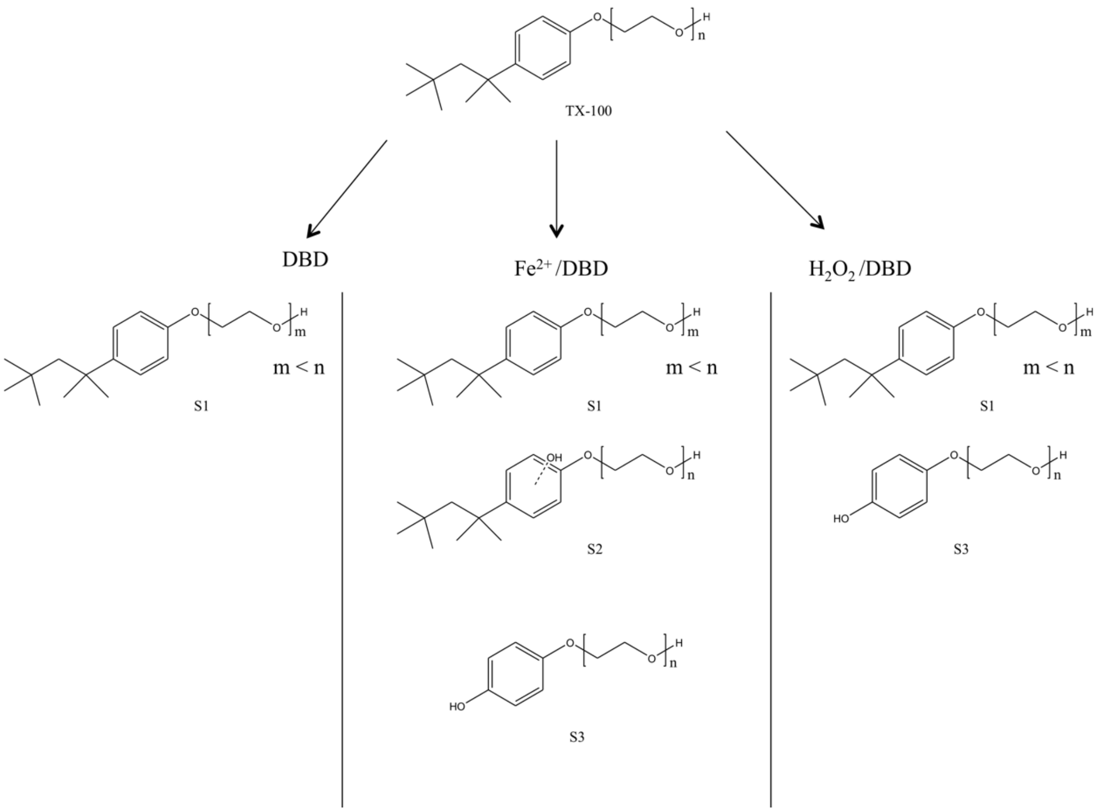


Figure 27. Degradation scheme of TX-100 decomposition with non-catalytic and catalytic DBD treatments.

In the non-catalytic DBD treatment, TX molecules with a cluster of mass signals separated by 44 mass units (Fig. 29, structure S1) were observed at a retention time of

3.5–6.0 min, which corresponded to the characteristic masses of the TX molecules (M = 206+44 n) ($5 \leq n \geq 16$) with H^+ ion attached (positive MS mode; 427.3, 471.3, 515.4, 559.4, 603.4, 647.4, 691.5, 735.5, 779.5, 823.5, 867.6, 911.6) or with a water molecule attached (444.3, 488.4, 532.4,576.4, 620.4, 664.5,708.5, 752.5, 796.5,840.6, 884.6, 928.6). Their mass spectrum is shown in Fig. 29. Mass spectrum of starting compounds is shown in Fig. 28.

No extra peaks from degradation products were observed, but the intensity of the peaks characteristic of long ethoxy chains was reduced, which indicated the continuous attack of $OH^\bullet$ radicals on ethoxy units and degradation through the shortening of the ethoxy chain. Nonylbenzene, a structurally related compound, is attacked via the v- or b-oxidation of the side chain, so the degradation of TX-100 can be assumed to proceed through the breakdown of the alkyl chain [244]. However, TX-100 molecules have highly branched octyl chains, which prevent b-oxidation, and the primary degradation thus begins at the ethoxy chain. We can therefore conclude that the degradation of TX-100 in the DBD reactor occurs mainly via shortening of the ethoxy chain (Fig. 27, structure S1).

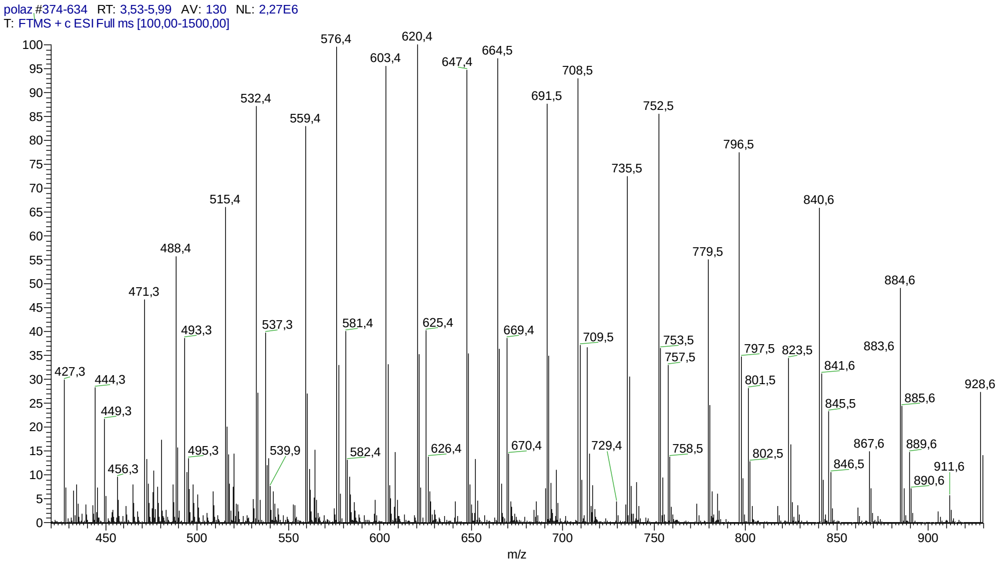


Figure 28. Mass spectrum of Triton X-100 molecules

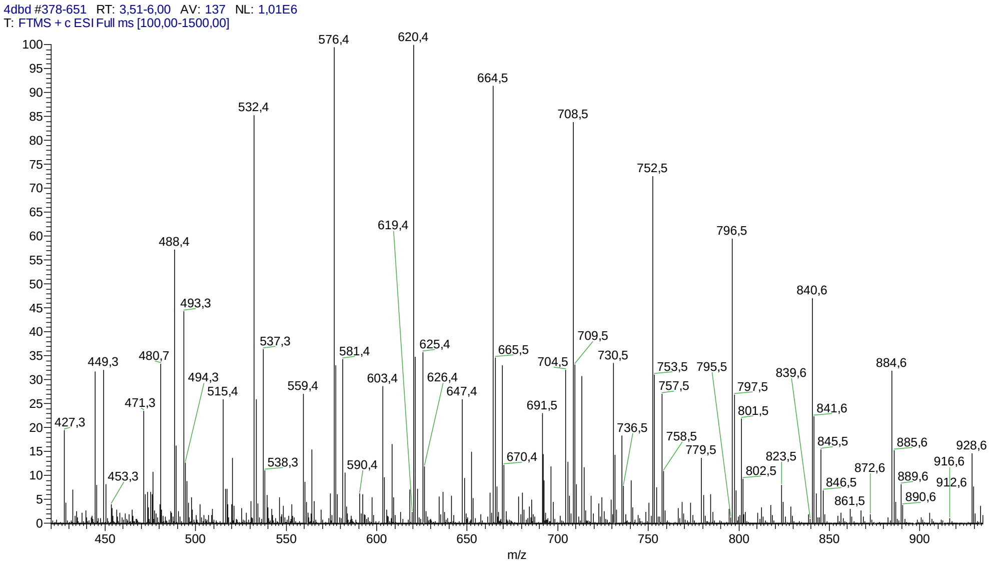


Figure 29. Mass spectrum of Triton X-100 solution after degradation in the non-catalytic DBD with introduced energy density of 180 kJ L^{-1}

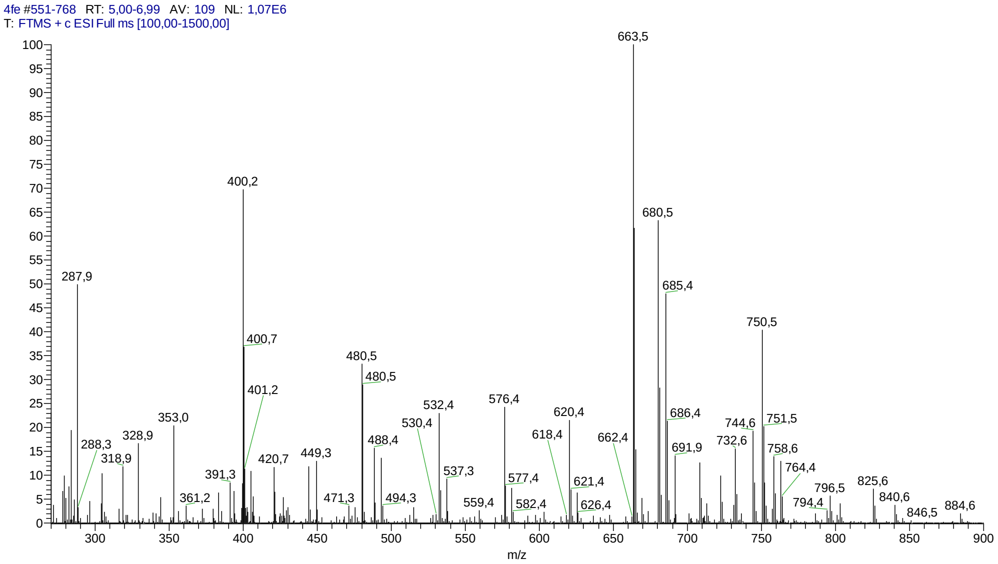


Figure 30. Mass spectrum of Triton X-100 solution after degradation in the Fe^{2+} DBD system with introduced energy of 180 kJ L^{-1}

The mass spectra of the main degradation products for the Fe^{2+}/DBD treatment are shown in Fig. 30, and their structures are shown in Fig. 27 (structures S1, S2, and S3). The TX molecules with long ethoxy chains have almost completely disappeared (Fig. 27, structure S1). Products S2 are attributed to the series M = 222+44 n, and the most intense peak belongs to this series (663.5 with H^+ ion and 680.5 with H_2O attached). These products are formed by the addition of the $OH^•$ radical to the aromatic ring. The cleavage of the bond linking the alkyl chain to the aromatic ring forms polyethoxylated phenol and characteristic masses of S3 products are M = 110+44 n. The most intense peak of this series has the mass 287.9 with the H^+ ion attached.

In the system H_2O_2/DBD, a higher concentration of TX molecules is identified than in the Fe^{2+}/DBD system (structures S1). The most intense are those peaks with the mass 287.9 (with H^+ ion attached) and 480.3 (with H_2O_2 attached) that belong to series S3 (M = 110+44 n) (Figure 31).

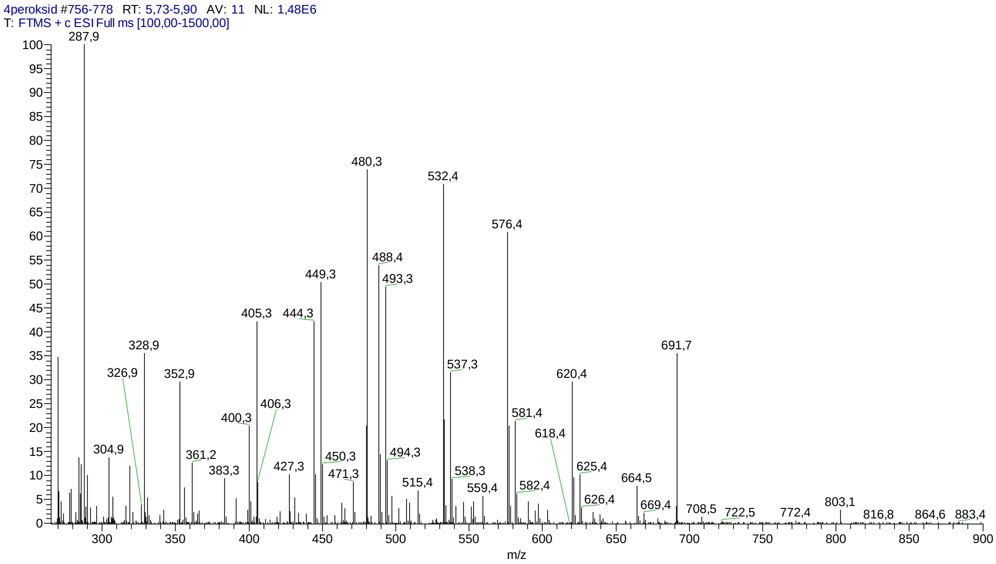


Figure 31. Mass spectrum of Triton X-100 solution after degradation in the H_2O_2 /DBD system with introduced energy of 200 kJ L^{-1}

However, the H_2O_2/DBD system showed the highest TOC removal efficiency, which can be explained by the presence of a high concentration of less reactive species that react with degradation products but not with TX molecules. Thus, the presence of H_2O_2 increases the total oxidation power of the plasma.

TX with a lower ethoxy chain (n = 1–3) was not detected, likely because of the short treatment time.

3.2.6. Ecotoxicity assessment of surfactants after the DBD treatments

Ecotoxicology connects specific substance / mixture with effects they cause in bioassays. Surfactants and their residuals from hospital, municipal and industrial wastewaters through sewage system can reach various aquatic environments or be transported from the Arctic to the tropics terrestrial environments. These contaminants can even be present in the air where foliar uptake (plants) or respiratory exposures can occur. Organisms at risk from chemical exposures include plants, fungi, and algae (primary producers); invertebrates (such as worms, bugs, beetles, and mollusks); fish; amphibians; reptiles; birds; and mammals. In our case aquatic environment is potentially at risk so we decided to compare adverse effects of untreated and treated solution in toxicity screening with water organism *Vibrio fischeri* and *Artemia salina*.

In ecotoxicology, as a measure of toxicity for tested compound, LC_{50} and EC_{50} values are used. The LC_{50} (lethal concentration, 50%) is a measure of the lethal dose of a toxin. The value of LC_{50} for a substance is the concentration required to kill half the members of a tested population after specified test duration. The LC_{50} values are frequently used as a general indicator of a substance's acute toxicity. A lower LC_{50} is indicative of increased toxicity.

The EC_{50} is effective concentration at 50%, which is the concentration that causes adverse effects in 50% of the test organisms.

For the toxicity studies, a treated TX-100 solution was studied after introducing ED 450 kJ L^{-1}. The applied amounts of Fe^{2+} or H_2O_2 were, respectively, 5 mg L^{-1} or 10 mmol L^{1}, the most efficient for the degradation of TX-100 in combination with DBD.

The TX-100 EC_{50} value for *V. fischeri* was reported to be 63.6 mg L^{-1} [245], similar to the data obtained in this study (EC_{50} = 56.6 mg L^{-1}). The inhibition (%) of bioluminescence (toxic effect) was < 10% for all tested samples after DBD treatment with and without the addition of a catalyst (H_2O_2 or Fe^{2+}). Therefore, the final degradation products of the treated solutions did not cause any significant toxic effect to *V. fischeri*.

In the toxicity screening with *A. salina*, a difference in mortality % was observed between untreated and solution-treated samples in the DBD reactor (with or without a catalyst). When *A. salina* was exposed to the initial solution of TX-100 (100 ppm), the observed mortality was 76%. However, after the application of the DBD treatment, the toxic effect was reduced to 16% of mortality. When the homogenous catalysts Fe^{2+} or H_2O_2 were added to DBD, the toxic effect was further reduced to 10% in the case of Fe^{2+} and to 6% in the case of H_2O_2. These values were equal or lower than the validity criterion for mortality in the control group. In the case of nonylphenol ethoxylate, the toxicity of starting solution was significantly lower than in the case of Triton X-100. It was around 30%. After the DBD treatment without catalyst it decreases to only 2%. After the treatment with iron as catalyst their toxicity was as in the case of Triton-X. Similar results were obtained with hydrogen peroxide as catalyst.

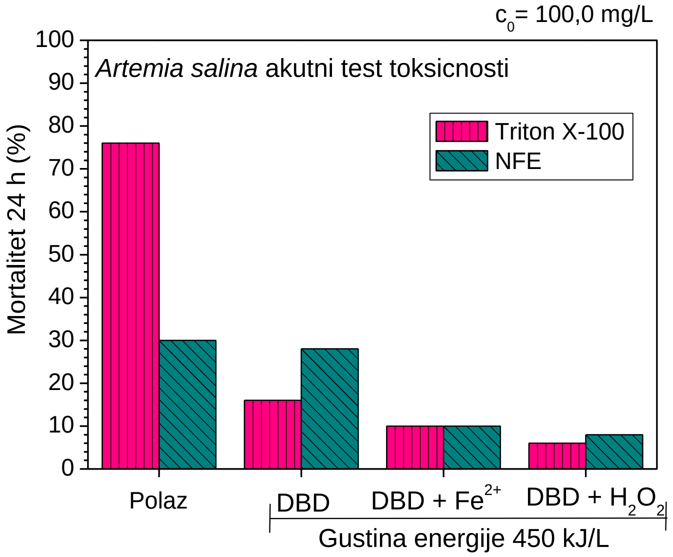


Figure 32. *Artemia salina* toxicity test results for Triton X-100 and NPE

3.2.7 Chemical oxygen demand analysis

Chemical oxygen demand has been defined as the amount of oxygen that would be needed when all the organic ingredients would be oxidized completely. According to the name, the oxidation takes place chemically, so the chemical oxygen demand can only be defined indirectly. The result of a chemical oxygen demand test indicates the amount of water-dissolved oxygen (expressed as parts per million or milligrams per liter of water) consumed by the contaminants. The higher the chemical oxygen demand the higher the amount of pollution in the test sample.

In the case of nonionic surfactants the measured values after the tenth pass through the DBD reactor (450 kJ L^{-1} introduced energy density) show that treatment without a catalyst show decrease in COD value (around 35%). Degree of mineralization was similar for both surfactants. In the case of catalyzed treatment better results were obtained with hydrogen peroxide as catalyst (around 58%) in comparison to iron (50%). Both catalyst increase mineralization efficiency compared with treatment without catalyst. Similarities in results were expected because their structures were similar. Catalyst favors the attack on aromatic ring and this fact explains the increase in mineralization.

3.2.8 Total organic carbon analysis

Total organic carbon (TOC) represents the amount of organic carbon present in the sample. It is used as an indicator of water quality and it is a non-specific method, *i.e.* it cannot be used for identification of organic substances present but only for a determination of their amount.

Analysis of TOC was performed to compare the differences in the mineralization efficiency between the catalytic systems. The initial solution was 100 mgL^{-1} TX-100 before degradation. The TOC value was measured after ten passes of the TX-100 solution through the reactor, *i.e.*, at ED = 500 kJ L^{-1}. The mineralization efficiency in the non-catalytic DBD treatment was very low (1%). The addition of the homogenous catalysts H_2O_2 or Fe^{2+} significantly improved the mineralization efficiency of TX-100. The catalytic system H_2O_2/DBD resulted in a mineralization efficiency in the range of 4–34%, (depending on the H_2O_2 concentration) whereas the Fe^{2+}/DBD mineralization efficiency was in the range of 2–21% (depending on the Fe^{2+} concentration).

The best result was obtained in the system with 20 mmol L^{-1} H_2O_2, although this system was not the most efficient at removing the surfactant molecules. This result can be explained by the formation of less reactive species, such as hydroperoxyl radicals ($HO_2^{\bullet}$), which were formed at a high concentration of H_2O_2. Based on the UV–Vis spectra, we concluded that the species responsible for the degradation of TX-100 are likely very reactive, short-living radicals.

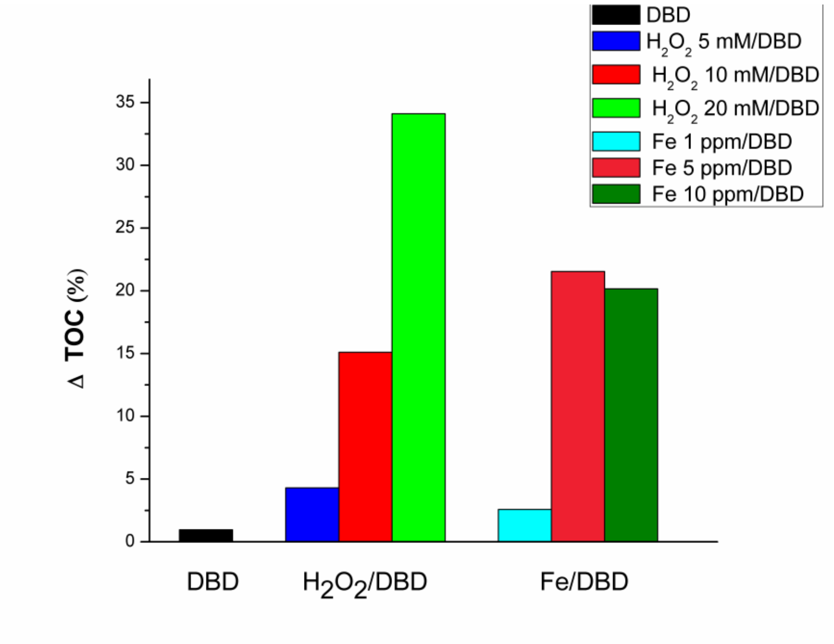


Figure 33. Mineralization efficiency after Triton x-100 degradatiton in the DBD reactor

3.3 Degradation of anionic surfactants

3.3.1 Efficiency of degradation without a catalyst

Efficiency of degradation was monitored with MBAS test for both surfactants. In both cases the loss of surfactant activity was observed (Figure 34). Degradation of dodecylbenzene sulphonate was faster and this fact is in accordance with results of ozonization of this two surfactants. Dodecylbenzene sulphonate undergo ozonization but sodium dodecyl sulphonate degrade only 20% under neutral conditions. In our case we obtained better results for SDS degradation.

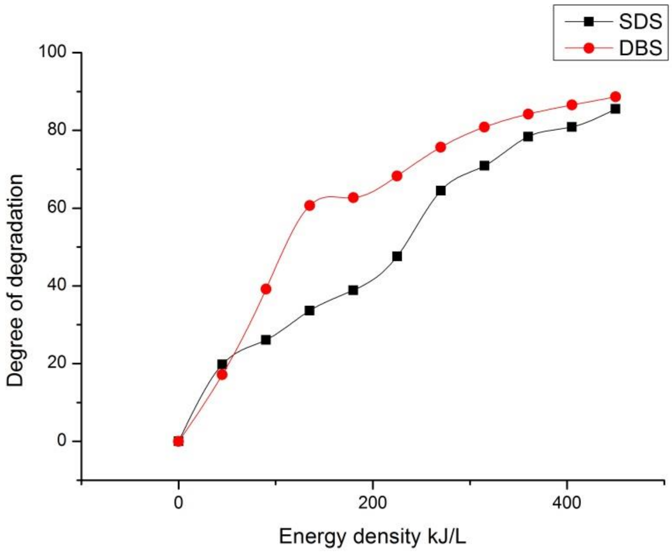


Figure 34. Degradation efficiency of SDBS and SDS with dielectric barrier discharge.

There are few explanations of these facts. At first in examined reaction pH is lowering during the treatment. In distilled water pH lower from 5.5 to 2.6 after 5 pass (Figure 35). Nitric oxide (NO) and nitrogen dioxide (NO_2) formed in the plasma phase can be dissolved in water and react with plasma-generated active species such as hydroperoxyl radical, ozone or hydrogen peroxide in order to give RNS such as nitrous acid (HONO) and peroxynitrous acid (ONOOH). Detailed mechanism of their formation was described [155].

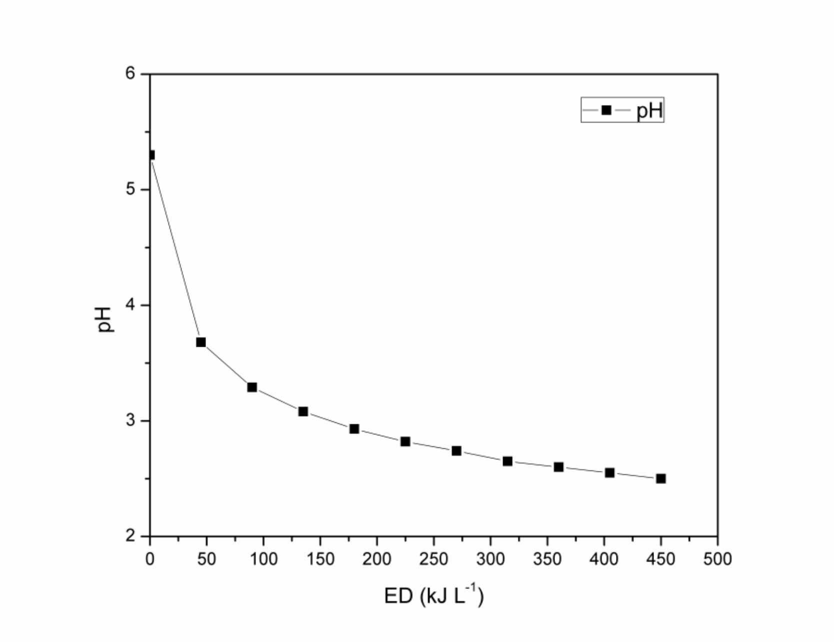


Figure 35. Changes of pH with introduced energy density.

At pH 2.6 SDS can undergo fast hydrolysis to sulphuric acid and dodecanol [246]. Conditions during plasma treatment (local high concentration of hydrogen ion and local increase of temperature) could significantly increase hydrolysis of SDS at higher pH. Dodecanol does not react in test with methylene blue. Other difference with classical ozonization is generation of hydrogen peroxide and hydroxyl radicals as oxidizing species in discharge. To confirm these facts concentration of ozone (Figure 39), hydrogen peroxide (Figure 24) and hydroxyl radical (Figure 38) in distilled water were measured.

The quantification of hydroxyl radicals was performed using DMSO as the probe compound [247]. The pathway of degradation of DMSO upon reaction with hydroxyl radicals has been extensively studied and results in the formation of methyl radicals and methane sulfinic acid as the primary intermediate products. Almost quantitative conversion of DMSO into methyl radicals upon reaction with hydroxyl radicals has been reported. Methyl radicals further reacts with oxygen and transform into peroxy radicals. Peroxy radicals undergo disproportionation in formaldehyde and methanol.

$(CH_3)_2SO + OH^{\bullet} \rightarrow CH_3SOOH + CH_3^{\bullet}$ (74)

$CH_3^{\bullet} + O_2 \rightarrow CH_3OO^{\bullet}$ (75)

$2\ CH_3OO^{\bullet} \rightarrow HCHO + CH_3OH + O_2$ (76)

$CH_3^{\bullet} + RH \rightarrow CH_4 + R^{\bullet}$ (77)

Formaldehyde was derivatized with a saturated solution of dinitrophenyl hydrazine and quantified using HPLC methods at 360 nm.

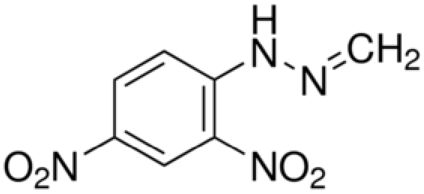


Figure 36. DNPH derivative of formaldehyde.

Chromatograms inserted in the Figure 37 present the changes in intensity of DNPH derivatives of formaldehyde with number of passes.

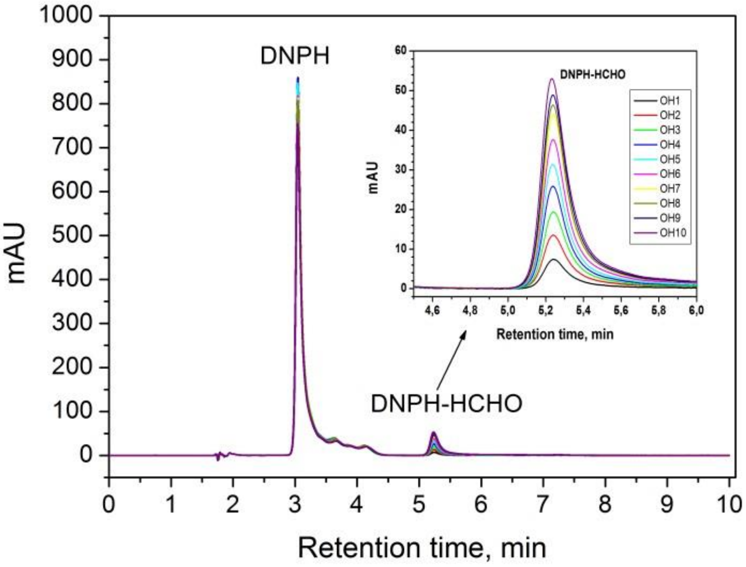


Figure 37. Chromatograms and changes in intensity of DNPH derivatives of formaldehyde with number of passes through the DBD reactor.

As we can see concentration of OH radicals increase with introduced energy density. After calculations, dependence of concentration of OH radicals on introduced energy density was plotted (Figure 38).

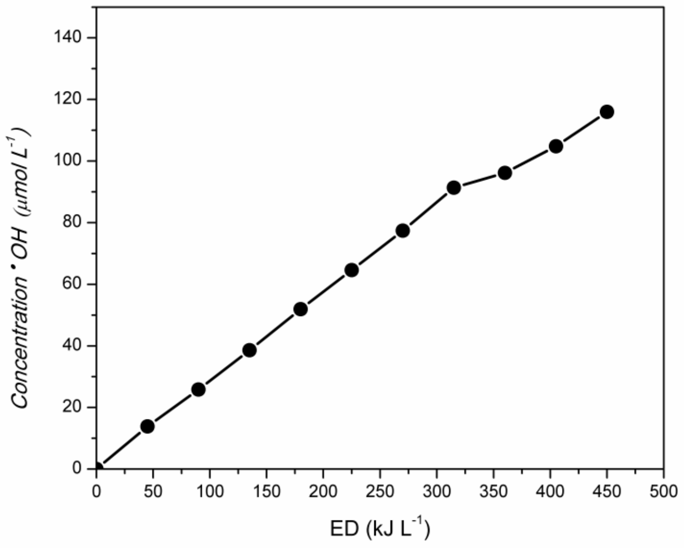


Figure 38. Changes in concentrations of hydroxyl radical in distilled water with introduced energy density

For determination of ozone in distilled water after treatment in reactor (Figure 40) indigo method was used [248]. With the indigo method, indigo trisulfonate dye immediately reacts with ozone (Figure 39). The color of the blue dye decreases in intensity in proportion to the amount of ozone present in the sample. Hydrogen peroxide (H_2O_2) and organic peroxides decolorize the indigo reagent very slowly. H_2O_2 does not interfere if ozone is measured in less than 6 h after adding reagents.

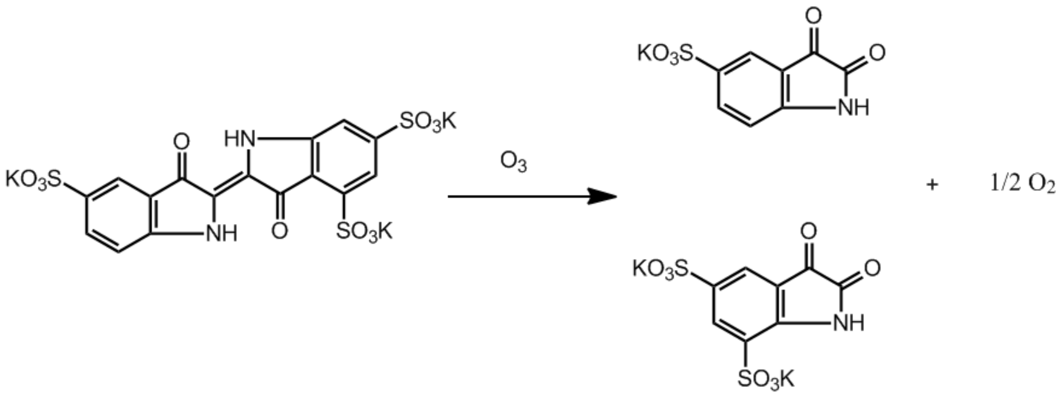


Figure 39. Reaction between ozone and indigo dye forming colorless products.

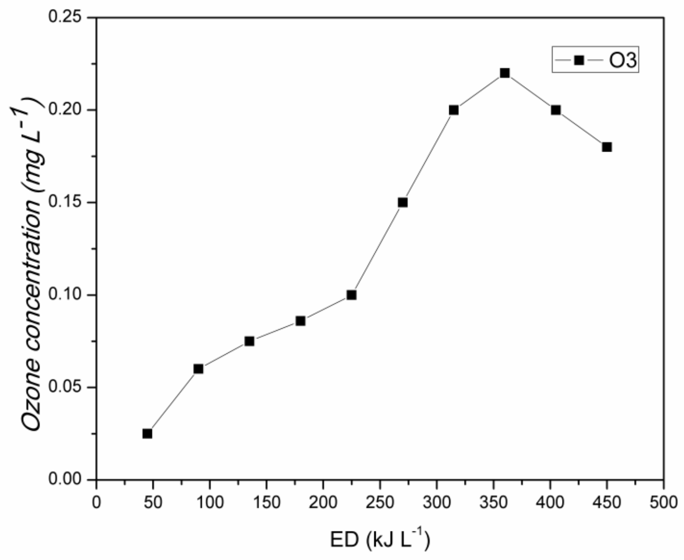


Figure 40. Changes of ozone concentration in distilled water with introduced energy density.

As we can see their concentrations in solution increase with introduced energy density. Those species can accelerate degradation of sodium dodecyl sulphate.

3.3.2 Influence of homogenous catalysts

Concentrations of catalyst optimized in experiments with Triton X-100 were used in further experiments with homogenous catalyst. As we can see from the Figure 41 both catalysts have an influence on the degradation of sodium dodecylbenzene sulphonate. Hydrogen peroxide has a greater impact on the degradation than iron (Fe^{2+}) as the 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 (Fe^{2+}) increase was around 10% for all passes. The final degradation efficiency for both catalysts (after ten passes through reactor) was increased around 10%.

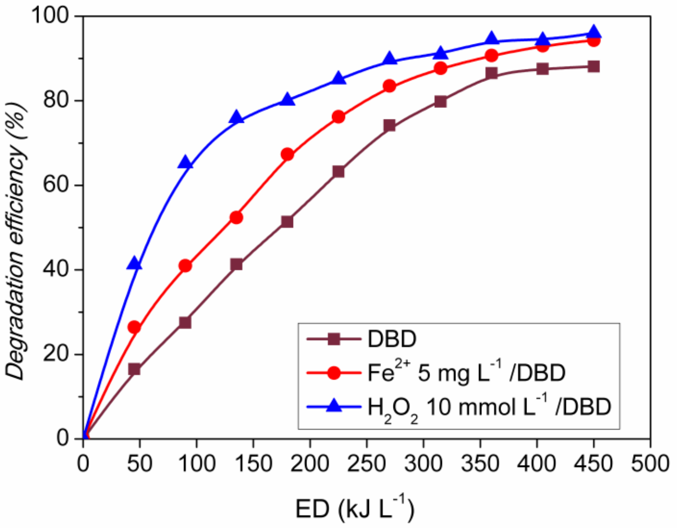


Figure 41. Degradation efficiency of SDBS in DBD reactor.

Increased efficiency of degradation in systems with H_2O_2 can be explained based on peroxone process, where in the reaction of ozone and hydrogen peroxide hydroxyl radical was generated. During discharge the UV light was generated so another way of hydroxyl radical generation was decomposition of hydrogen peroxide under UV radiation (Eq. 2). The hydroxyl radical is strong oxidant species that could attack aromatic ring and aliphatic part of a molecule. Another way of formation of hydroxyl radical was through the reaction of ozone with Fe^{2+}.

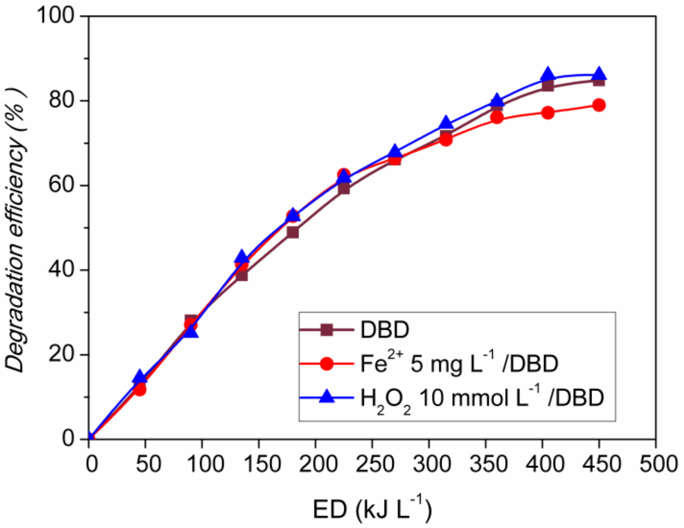


Figure 42. Degradation efficiency of SDS in DBD reactor.

Catalysts have no effect on surfactant degradation in the case of sodium dodecyl sulphate (Figure 42). This is in contrary with previous results of ozonization of SDS where adding hydrogen peroxide influenced SDS degradation [104] . However, the most significant difference between their and our work was the pH value. After first pass through the DBD reactor pH decreases from starting pH 7 to 3.5 in the case of SDS. After fifth pass pH decrease to 2.6. Similar results were obtained in the case of catalyzed reaction. We proposed that rate determination reaction in the case of sodium dodecyl sulphate was the hydrolysis of sulphate ester group and not degradation of surfactant. Iron (Fe^{2+}) and hydrogen peroxide have no influence on hydrolysis of ester group and so we could not see differences between experiments with and without a catalyst.

3.3.3 Toxicity tests

Toxicity of anionic surfactants, SDS and SDBS, was tested using *Artemia salina* test and expressed as a percentage of *Artemia salina* mortality. The toxicity of the plasma treated samples was significantly decreased in all systems tested (Figure 43). 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} (249). The toxicity effect (%) of initial solutions of both surfactants for the diluted samples (1:1) was higher in comparison to the treated solutions of SDS and SDBS in all systems (DBD, DBD + Fe^{2+}, 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 criterion (≤10%). A system with hydrogen peroxide as a catalyst (DBD+H_2O_2) had slightly higher toxicity effect, however, the mortality was under 20% (Figure 43). 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 a catalytic system with hydrogen peroxide (DBD+H_2O_2). Therefore, the most efficient reduction in mortality was achieved in the system where Fe^{2+} was used as a catalyst (DBD + Fe^{2+}).

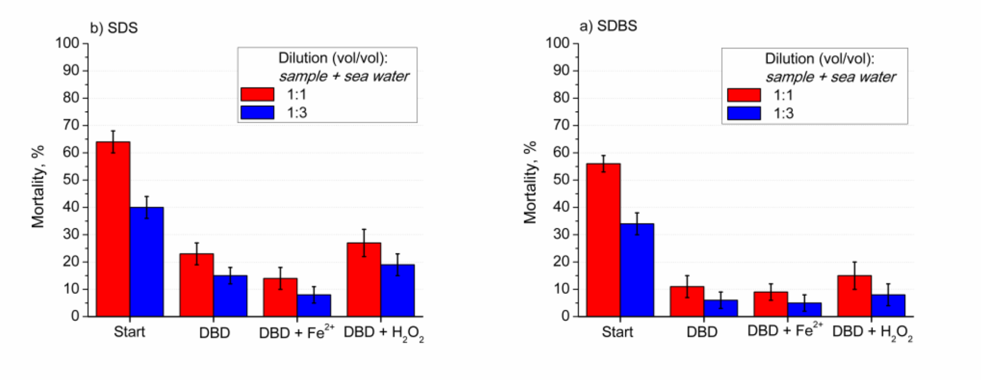


Figure 43. Toxicity of surfactant solutions before and after the plasma treatment (Number of replications: 3).

3.3.4 Chemical oxygen demand

The COD value of initial solutions (0 kJ L^{-1}) of two surfactants and the solutions after the plasma treatment (450 kJ L^{-1}) was determined. Determined values of COD are presented in Fig. 44. In the case of SDS we obtained a higher degree of COD removal with DBD treatment. This can be explained with the fact that higher alcohols have something higher value for reaction rate constant that SDBS [250]. Catalyst has an influence on COD removal and better results were obtained with hydrogen peroxide as catalyst. In the case of SDS the COD value was reduced by 38%. Better results in COD removal for SDS than SDBS can also be explained with the resistance of aromatic nucleus for oxidation.

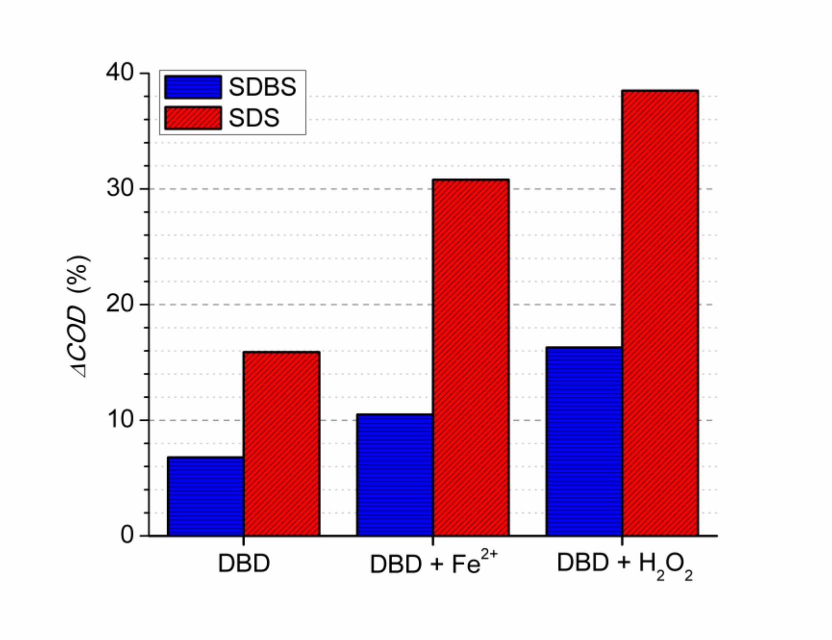


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Figure 44. Mineralization efficiency of plasma treated solutions presented as percentage decrease of COD value compared to solutions that didn't undergo plasma treatment.

3.3.5 Total organic carbon

Results obtained for two samples of surfactants, shown in Fig. 45. before and after the plasma treatment showed the decrease of TOC value for all systems tested. Better mineralization of SDS was achieved for the system where Fe^{2+} was used as homogenous catalyst. This could be explained by the fact that iron as catalyst favored degradation of oxalic acid (intermediate in alcohols oxidation) [251]. Iron has low influence on mineralization of SDBS. On the other hand, hydrogen peroxide has the greater influence on SDBS mineralization. In the case of hydrogen peroxide dominant mechanism of degradation was through hydroxyl radical that has no influence on mineralization of oxalic acid.

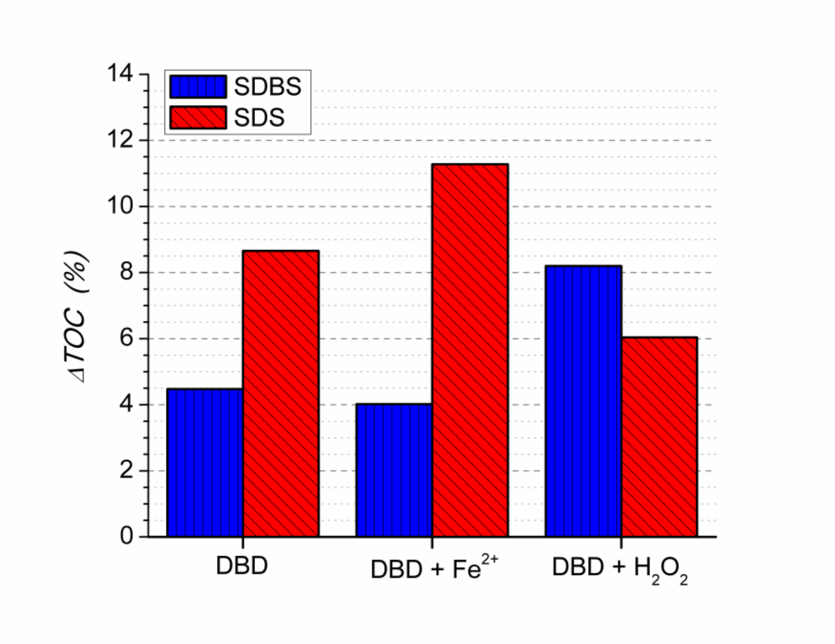

Figure 45. Mineralization efficiency of plasma treated solutions presented as percentage decrease of TOC value compared to solutions that didn’t undergo plasma treatment.

4. Conclusions

Degradation of four surfactants (two anionic surfactants: sodium dodecyl sulfate - SDS and sodium dodecylbenezene sulfonate – DBS; and two nonionic surfactant (Triton X-100 and nonylphenol ethoxylate - NPE) with non-thermal plasma (water falling film dielectric barrier discharge plasma reactor) were examined.

After ten pass through reactor and introduced energy of 450 kJ L^{-1} all surfactants were degraded with degradation efficiency higher than 80 %. Mineralization efficiency of reactions in DBD reactor was low (around 35 % COD decrease and 1 % TOC decrease in case of nonionic surfactants and around 10 % COD decrease and around 6-10 TOC decrease in the case of anionic surfactants).

Catalyst systems generally significantly improve degradation efficiency with except of sodium dodecyl sulfate. In case of sodium dodecyl sulfate we proposed that rate determination reaction is hydrolysis of sulfate ester under acidic conditions. During treatment, pH of solution decrease due to nitric and nitrous acid formation. Catalysts also improve mineralization efficiency for all tested surfactants.

Amounts of catalyst were optimized in experiments of Triton X 100 degradation. Best results were obtained for 5 mg L^{-1} Fe^{2+} and 10 mmol L^{-1} hydrogen peroxide. Those concentrations were used in all experiments.

In case of nonionic surfactants better results in degradation were obtained wit Fe^{2+} as catalyst especially in beginning of treatment (with introduced 135 kJ L^{-1} more than 80 % surfactants were degraded (around 50 % without catalyst and 65 % with hydrogen peroxide as catalyst). In the catalyzed treatment better results in COD decrease were obtained with hydrogen peroxide as catalyst (around 58%) in comparison to iron (50%). Hydrogen peroxide gave better results in TOC decrease for higher concentrations (20 mmol L^{-1}). In optimal concentrations iron gave better results in TOC decrease (21 %) than hydrogen peroxide (15 %) but both catalyst show better mineralization efficiency than treatment without catalyst.

Analysis of degradation products indicate that degradation of TX-100 in the DBD reactor without catalyst occurs mainly via shortening of the ethoxy chain. In experiments with catalyst among products with shorter ethoxylated chain products with breakdown of alkyl chain and hydroxylated aromatic nucleus were identified.

In case of anionic surfactants degradation of dodecylbenzene sulphonate in experiments without catalyst was faster. After ten pass and introduced energy of 450 kJ L^{-1} similar degradation was observed. Catalyst have not influence degradation of SDS and in case of DBS better results in degradation were observed with hydrogen peroxide (75 % for hydrogen peroxide, around 50 % for iron and around 40 % in experiments without catalyst for introduced energy of 135 kJ L^{-1}.

Decrease of COD value was increased with addition of catalyst and better results in decrease were obtained with hydrogen peroxide as catalyst. In all experiments higher degree of COD removal were obtained in the case of SDS. Better results in COD removal for SDS than DBS can be explained with the resistance of aromatic nucleus for oxidation.

Better mineralization of SDS was achieved for the system where Fe^{2+} was used as homogenous catalyst. This could be explained by the fact that iron as catalyst favored degradation of oxalic acid. On the other hand, hydrogen peroxide has the greater influence on DBS mineralization. In the case of hydrogen peroxide dominant mechanism of degradation was through hydroxyl radical that has no influence on mineralization of oxalic acid.

The toxicity effect (%) of all treated solutions of surfactants in all systems (DBD, DBD + Fe^{2+}, DBD+H_2O_2)was lower in comparison to the .initial solutions surfactants.

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Prilog:

Bibliografija kandidata kategorisana prema kriterijumima Ministarstva za nauku Republike Srbije:

M 21 – Radovi objavljeni u vrhunskim časopisima međunarodnopg značaja:

1. M. M. Aonyas, J. Nešić, **M. Jović**, M. Marković, B. Dojcinović, B. Obradović, G. M. Roglić, *Degradation of Triton X-100 in water falling film DBD reactor,* CLEAN - Soil, Air, Water 2016, 44 (4), 422–429 ISSN 1863-0650 IF_{2014} 1,945

M 23 – Radovi objavljeni u časopisima međunarodnog značaja

1. M. M. Aonyas, B. P. Dojčinović, S. D. Dolić, B. M. Obradović, D. D. Manojlović, M. D. Marković, G. M. Roglić, *Degradation of anionic surfactants using the reactor based on Dielectric Barrier Discharge (DBD***)** *J. Serb. Chem. Soc.* (2016), doi: 10.2298/JSC160303056A ISSN 0352-5139 IF_{2014} 0,871

Изјава о ауторству

Име и презиме аутора __**Munera Mustfa Aonyas**_

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Наслов рада *Degradacija surfaktanata primenom reaktora sa dielektričnim barijernim pražnjenjem, Degradation of surfactants using dielectric barier discharge reactor*

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5. **Ауторство – без прерада**. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, без промена, преобликовања или употребе дела у свом делу, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце. Ова лиценца дозвољава комерцијалну употребу дела.

6. **Ауторство – делити под истим условима**. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце и ако се прерада дистрибуира под истом или сличном лиценцом. Ова лиценца дозвољава комерцијалну употребу дела и прерада. Слична је софтверским лиценцама, односно лиценцама отвореног кода.