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Advanced Oxidation Processes based on photocatalysis for the degradation of organic contaminants in water

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ABSTRACT

Many organic pollutants are daily released into the environment or pass through the wastewater treatment plants contaminating surface and drinkable water. Part of these pollutants belongs to the category of the emerging organic contaminants since they are still unregulated or in process of regularization. They give cause of concern since they are dangerous for human health and for the survivor of a large number of living organisms. The implementation of wastewater treatment plants against the emerging contaminants is one of the challenges for the enhancement of the water quality, and advanced oxidation processes represent new technologies very promising as tertiary treatments. The research activity carried out during my PhD course focused on degradation test on aqueous solutions contaminated with different class of pollutants such as surfactants, pharmaceuticals and personal care products, both as single compound solutions and mixture of contaminants. The photocatalytic process was studied developing a new pre-industrial pilot plant and testing new TiO_2-based photocatalysts in a view of a technological transfer of the photocatalytic methodology. The reuse of a photocatalyst consisting of TiO_2 supported on a solid substrates was also investigated with the aim to avoid some problems related to the use of a dispersed catalyst. Photocatalytic process coupled with ultrasounds was also examined in order to speed up the decomposition of the pollutants. The disappearance of every pollutant was followed by HPLC analysis and the mineralization was assessed by the determination of total organic carbon.

In the end, the energy consumption related to the processes tested on the mixture of contaminants was calculated in order to establish the best methodology to obtain good degradation rate with reasonable costs.

KEYWORDS: wastewater treatment plants, advanced oxidation processes, emerging organic contaminants, photocatalytic process, TiO_2-based photocatalysts.

1. INTRODUCTION

Water is the most precious resource of the earth because no life is possible without water. It regulates ecosystems, grows our food and powers our industry. Hardly any economic activity can be sustained without water.

The principal sources of water for human use are lakes, rivers, soil moisture and relatively shallow groundwater basins. These sources represent only 0.01% of all water on Earth. Unfortunately, the excessive use and continued mismanagement of freshwater resources for human development have led to water shortages, increasing pollution of freshwater, loss of biodiversity, and degraded ecosystems across the world.[1]

1.1 WATER ISSUES IN THE WORLD

Critical issues which threaten water resources are described below.

1.1.1 Water scarcity

Europe is not widely regarded as an arid continent, so it may be surprising to know that nearly half the EU's population lives in 'water-stressed' countries, where the abstraction of water from existing freshwater sources is too high. Water scarcity affects 33 EU river basins and many people in the world still lack access to basic water services. In the future, the water shortage could be enhanced by the melting of alpine glaciers due to climate changes. A 2013 report by WHO and UNICEF concluded that 768 million people in the world remain without access to a safe source of water and 2.5 billion people remain without access to improved sanitation.[2]

Global water demand is largely influenced by population growth, urbanization, food and energy security policies, and macro-economic processes. Global water demand is projected to increase by some 55% by 2050, mainly because of growing demands from manufacturing (400%), thermal electricity generation (140%) and domestic use (130%).

Water resources, and the essential services they provide, are among the keys to achieving poverty reduction, inclusive growth, public health, food security, lives of dignity for all and long-lasting harmony with Earth's essential ecosystems.[3]
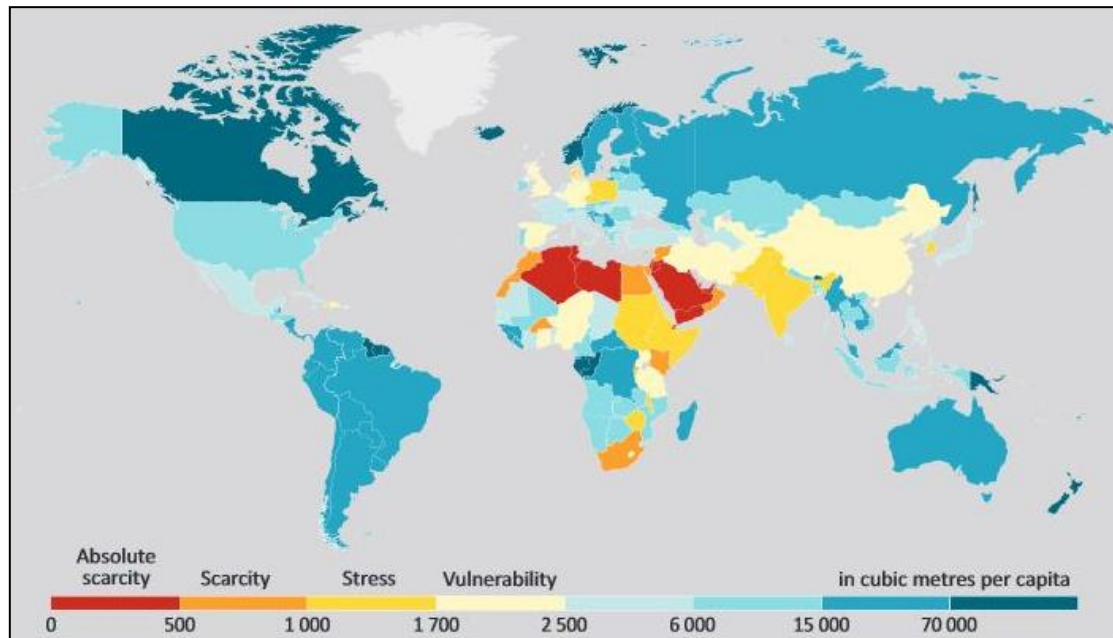
Figure 1.1 Renewable water resources per capita in 2010 (UN FAO Aquastat database)

1.1.2 Water pollution

Water quality is just as important as water quantity for satisfying basic human and environmental needs, since polluted water that cannot be used for drinking, bathing, industry or agriculture may effectively reduce the amount of water available for use in a given area.

The major source of water pollution are from human settlements and industrial and agricultural activities, which produce a large number of contaminants compounds classified into three main groups:

1. Bacteria, virus, protozoa and all agents which cause diseases.
2. Inorganic compounds which are water soluble, such as acids, salts and toxic metals (cadmium, lead, mercury). Radioactive waste also belongs to this group, they are unstable elements that decay by emitting ionizing radiation.

3. Organic compounds, such as saturated, unsaturated and aromatic hydrocarbons; they constitute oils, detergents and emulsifiers, plastics and pesticides.

One drop of dangerous substance could pollute thousands of liter of water. Most of the contaminants are characterized by their persistence, bioaccumulation and toxicity. Nowadays water pollution could remain in groundwater for generations. Groundwater is crucial for the livelihoods and food security of 1.2 to 1.5 billion rural households in the poorer regions of Africa and Asia, and for domestic supplies of a large part of the population elsewhere in the world.

Water pollution is aggravated by population growth, rapid urbanization and uncertain impacts of climate change and it is expected to get worse over coming decades.

Approximately 3.5 million deaths are related to inadequate water supply, sanitation and hygiene.

1.1.3 Eutrophication

High concentrations of sewage or fertilizers in water systems can cause eutrophication, promoting the growth of weeds that disrupt normal ecosystems, deprive fish of oxygen and interfere with water treatment. There are signs of eutrophication in some 40% of European rivers and lakes, as well as coastal waters.

1.1.4 Morphological changes

The building of dams, reservoirs and irrigation systems can cause damage by changing water levels, placing obstacles in the way of the natural flow of the rivers and thereby destroying ecosystems or cutting off natural flood plains from water courses.

1.1.5 Ecological impacts

Temperature changes, for instance due to the use of water for cooling purposes, and the increasing presence of alien species in our waters.[4]

One possible solution for a more rational use of water resources is the possibility to recover wastewater after an appropriate depuration treatment in order to reuse it for other employments. The choice of the process and degree to be practiced depends on the source of the starting water and the use of treated water. Depurated water can be reused for industrial processes, for extinguishing a fire, for washing streets and cars , for irrigation in the agricultural field, or by the civic network as drinking water.

1.2 CONVENTIONAL WATER TREATMENTS

Conventional wastewater treatment plants (WWTPs) do not remove pollutants definitively, therefore their effluents are among the major sources responsible for water pollution, especially regarding the emerging organic contaminants (EOCs).

WWTPs consist of a combination of physical, chemical and biological processes. These treatments are divided into preliminary, primary, secondary and tertiary (Figure 1.2).

Preliminary treatment is basically mechanical and its main function is to remove large materials, suspended or floating solids as sand, wood and oils which could block or inhibit the subsequent biological step of depuration.

Primary treatment is designed to eliminate organic and inorganic solids by the physical processes of sedimentation. Some organic nitrogen, organic phosphorus and heavy metals associated with solids are also removed during primary sedimentation, producing a mud potentially contaminated but colloidal and dissolved constituents are not affected. In this phase some pharmaceuticals can be removed by absorption in the mud, whereas others remain in the water. The effluent of primary treatment contains mainly colloidal and dissolved organic and inorganic solids.

The secondary treatment consists of biological treatment of wastewater by employing many different types of microorganisms in a controlled environment.

The tertiary treatment improves the quality of the effluents, so it removes nitrogen and phosphorus and brings bacteria down.[5]

The main processes of wastewater treatment plants are described below.

1.2.1 Coagulation

Coagulation removes organic matter and turbidity from water. Dissolved and small substances are the most hardly removable substances and coagulation neutralizes the charges of these substances in order to promote the formation of a cluster. During this process, a chemical positive charged substance (aluminium or iron salt, polymer) is added to water while it is strongly mixed.

1.2.2 Flocculation

Flocculation consists in the cohesion of particles in water into flocks which will sediment in the further sedimentation process. Flocks are formed due to a slow and extended mixing which allows the collision of particles.

1.2.3 Sedimentation

The aim of this process is to produce clarified water. It consists in the sedimentation of flocculated particles on the bottom of a tank as a result of gravity. Precipitate solids are removed and they have to be treated in the appropriate manner.

1.2.4 Filtration

During the filtration, filters are used to divide suspended solids from water. The aim of the filtration is to remove small particles and pathogens which have not been eliminated during the previous processes.
The most used means to filter is constituted of sand or sand and anthracite. Also active carbon can be used as a filter since it absorbs a lot of organic substances, but this kind of filters could release the absorbed material when they reach the maximum saturation.

1.2.5 Chlorination

Chlorination consists in the addition of chlorine to water in order to inactivate pathogenic microorganism. Chlorine is used as sodium hypochlorite, $NaClO$, and when it dissolves in water, it produces hypochlorous acid ($HOCl$) and hypochlorite ion (ClO^-). The hypochlorous acid, which is a neutral compound, penetrates throughout the cell wall of pathogens, which is negatively charged, causing the death of microorganisms.

1.2.6 Biological Processes

Microorganisms are the primary agents of biological wastewater treatment. They develop and grow in the sludge to be treat, converting organic matter into simpler substances. The biological treatment can come first or after than a chemical physical treatment depending on the type of wastewater.

1.2.7 Reverse osmosis and nanofiltration

Reverse osmosis and nanofiltration can remove dissolved and non biodegradable compounds. These processes are based on the implementation of a different pressure to the two side of a membrane: water can pass throughout the membrane which is impenetrable to the solute. The membrane cost and the energy consumption to obtain the difference of pressure, are the main drawback of this process.
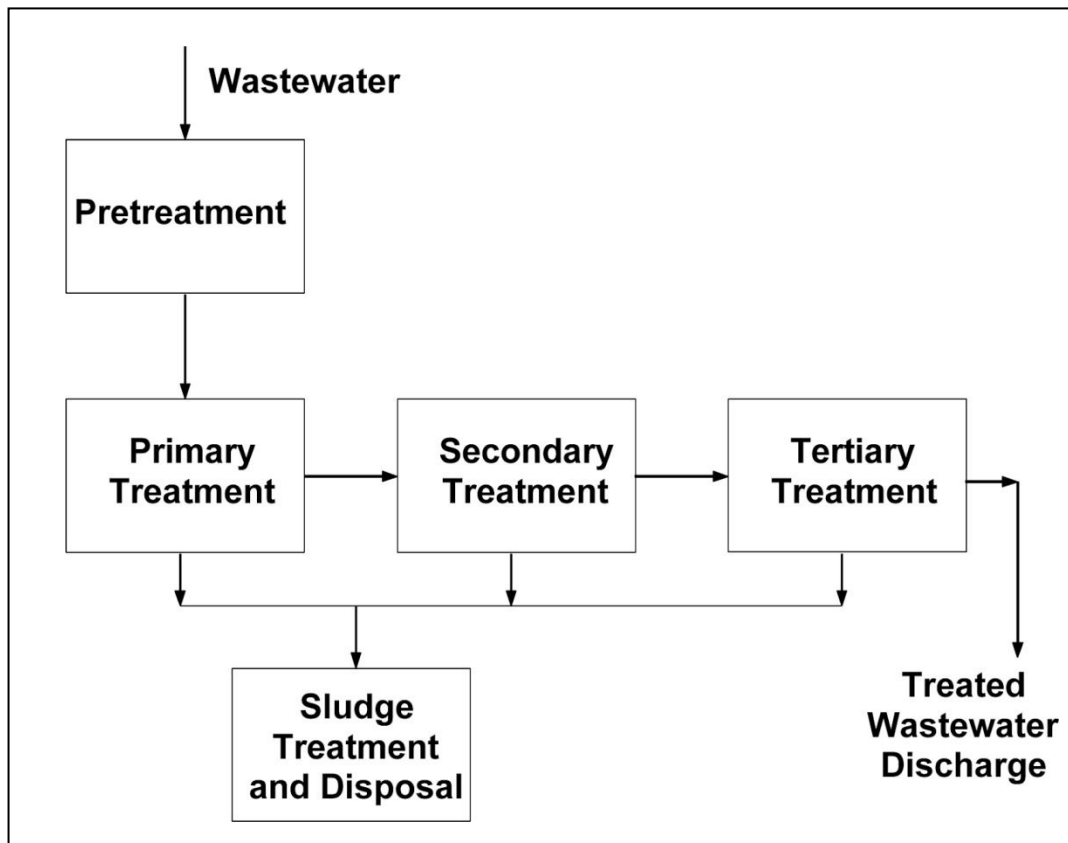
Figure 1.2 Scheme of processes of a conventional WWTPs.

1.2.8 Disadvantages of conventional wastewater treatment plants

Although most of the WWTPs follow the regulatory requirement for wastewater treatment, the removal of the most of EOCs is still incomplete. It is because the plants were not intended to handle these contaminants, and most of them and their metabolites survive the degradation making wastewater treatment plant discharges the primary sources of these pollutants. Another problem is that although organic pollutants may be removed by processes such as sedimentation and sand filtration, they are only temporarily stored in the sand particles by partitioning into the sludge component of the processes, which may be eventually sprayed in landfill sites, incinerated or amended to agricultural soils, posing potential additional cost and threats to the environment. Also biological treatments are not effective since wastewater include an increasing number of synthetic molecules which are not biodegradable, persisting in the water and in the environment.

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One more disadvantage is the formation of byproducts. Chlorination, used to remove pathogen agents from treated water, leads to the formation, with the natural organic compounds of the water (i.e. fulvic and humic acids), of chloride hydrocarbon considered carcinogenic. These compounds are generally removed with active carbon which is later burned, producing chlorine oxides which in turn can form carcinogenic dioxins.

Only a complete degradation will provide a lasting solution to preventing EOCs exposure to the environment.

1.3 WATER QUALITY

Water quality may be defined by its physical, chemical, and biological characteristics. Physical parameters include colour, odour, temperature, and turbidity. Insoluble contents such as solids, oil and grease, also fall into this category. Solids may be further subdivided into suspended and dissolved solids as well as organic (volatile) and inorganic (fixed) fractions. Chemical parameters associated with the organic content of wastewater include biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and total oxygen demand (TOD). Inorganic chemical parameters include salinity, hardness, pH, acidity and alkalinity, as well as concentrations of ionized metals such as iron and manganese, and anionic entities such as chlorides, sulfates, sulfides, nitrates and phosphates. Bacteriological parameters include coliforms, fecal coliforms, specific pathogens, and viruses. Both constituents and concentrations vary with time and local conditions.

2. EMERGING ORGANIC CONTAMINANTS

The research activity of this thesis has been focused on water pollution, especially on the EOCs, most of which are dangerous for human health e for the survivor of a large number of living organisms since they are characterized by their persistence, bioaccumulation and toxicity.

EOCs are new products or chemicals that are still unregulated or are currently undergoing a regulation process, since their levels in the environment have only recently begun to be quantified and acknowledged as potentially hazardous to ecosystem.[6] The problem of EOCs is the lack of knowledge of their impact in the middle or long-term effect on aquatic environment, ecosystem and human health. Globally, concentrations measured in aquatic environment were in the ηg L^{-1} to μg L^{-1} range. The detection of such low concentrations has been made feasible by the advances in analytical technology.[7] Although parts per billion concentrations may not pose much acute risk, it is completely unknown whether other receptors in non target organisms are sensitive. Moreover they occur in the environment as multi-component mixtures having an ecotoxicity rate higher than any single compound. In the end, EOCs may still pose risks to aquatic species under chronic long-term exposure. Chronic toxicity data are only available for a minority of the EOCs.[8]

The elimination of EOCs in the conventional WWTPs is often incomplete and the effluents of these plants have been recognized as the main source of EOCs in the environment. Their release into surface, ground and costal water affects water quality and drinking water supplies.

EOCs include different chemical classes of pollutants such as pharmaceuticals, surfactants and personal care products.[9] These classes of compounds represent the object of this research activity and they are described below.

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2.1 SURFACTANTS

Surfactants are organic compounds containing both hydrophobic and hydrophilic groups. They lower the surface tension of aqueous solutions, making them substances with foaming properties and wetting agents which can dissolve water-insoluble substances in aqueous solutions.

Synthetic surfactants have become a significant fraction of dissolved organic pollutants in the water ecosystems. At present the non-ionic surfactants of alkylphenyl polyetoxylate type (APnEO) are the most widely industrial scale used surfactants, they are used in the production of detergents, emulsifiers, wetting agents, solubilizers and dispersants. But, when they interact with living organisms, they can mimic natural hormones and thus have the potential to act as endocrine disrupters in aquatic organisms, wildlife and even humans. They are found in WWTPs or they are present in the environment as a result of the bacterial degradation. The degradation reactions that occur in the environment are shown in Figure 2.1.
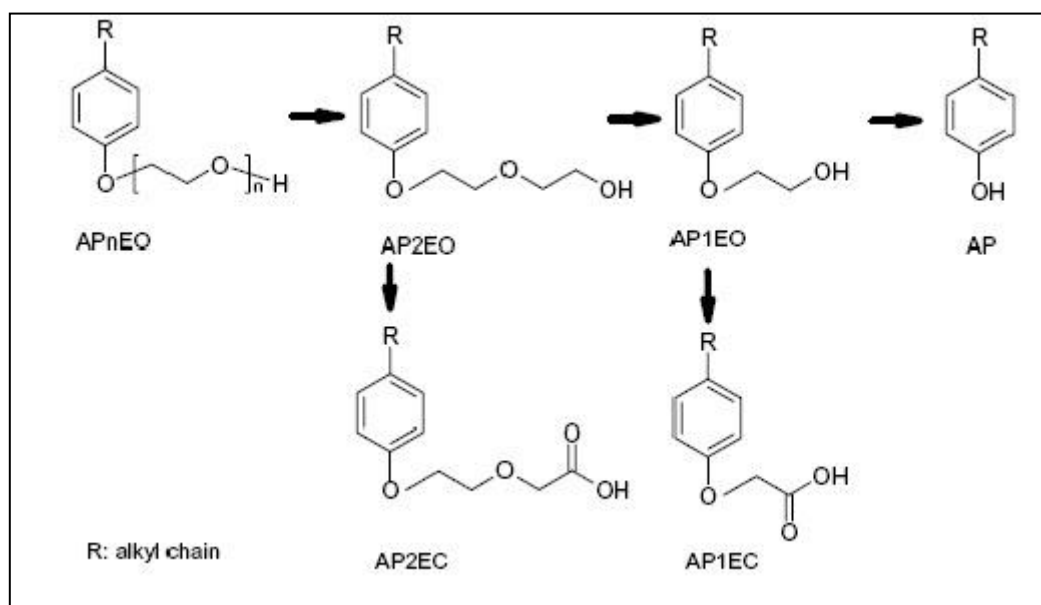
Figure 2.1 Degradation process of APnEO in aquatic environment (Ning B., Graham N.J.D., Zhang Y., 2007).

In the category of non-ionic surfactants, Triton X-100 (TRX) (Figure 2.2) possesses wide practical applications in almost every type of liquid, paste, and

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powdered cleaning compounds, ranging from heavy-duty industrial and agrochemical products to gentle detergents.[10]
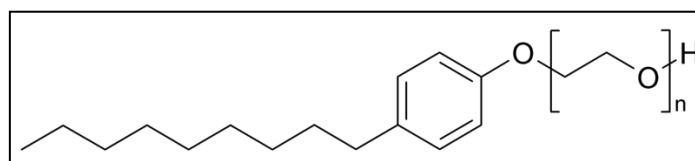
Figure 2.2 Chemical structure of Triton X-100.

2.2 PHARMACEUTICALS

Pharmaceuticals have a great impact on aquatic ecosystem since their consumption is increasing, their biodegradability is poor and they are molecules designed to act at very low concentrations. The most commonly pharmaceuticals categories detected in water are: analgesics/anti-inflammatories, antibiotics, antidiabetics, antifungals, antihypertensives, barbiturates, beta-blockers, diuretics, lipid regulators, psychiatric drugs, receptor antagonist, hormones, beta-agonists, antineoplastics, topical products, antiseptics and contrast agents. Several hundred thousand tons of pharmaceuticals are used yearly for the treatment of human and animal diseases also in livestock and aquaculture. After their consumption by humans, pharmaceuticals can be excreted through feces or urine in unmetabolized form or as active metabolites leading to concentrations up to μg L^{-1} in surface water of developed countries and up to mg L^{-1} in developing countries.[11] They are released into the sewage system, pass through WWTPs and enter the water system producing a complex mixture of compounds that may have synergetic effects. Pharmaceuticals used in the veterinary medicine are excreted onto the ground or directly into surface waters without passing through a WWTP. To date, more than 200 different pharmaceuticals alone have been reported in river waters globally, with concentration up to a maximum of 6.5 mg L^{-1} for the antibiotic ciprofloxacin.[12]

Carbamazepine (CBZ) and Diclofenac (DCF) are two of the most common pharmaceuticals found in the soil. Their chemical structure is described in Figure 2.3. They enter into the soil through the reuse of wastewater for

agriculture irrigation, especially in places that suffer from serious water shortage. Moreover, since CBZ and DCF are poorly removed by WWTPs, they are detected with high frequency in the effluents, surface water and groundwater. Generally their concentration at the effluents are higher than the one found in groundwater and freshwater resources. The low removal rate of CBZ can be ascribe to its resistance to biodegradation and low sorption rate. DCF has high log K_{ow}, so it could be removed by sorption to activated sludge with effective rate, but at the typical environmental pH range (5-8), DCF almost entirely exists in the anion form and have therefore a lower tendency to be sorbed to clay minerals and organic matter of the sediments. CBZ sorption affinity for sediments is negligible due to the fact that it mainly occurs in the environment in its neutral form.
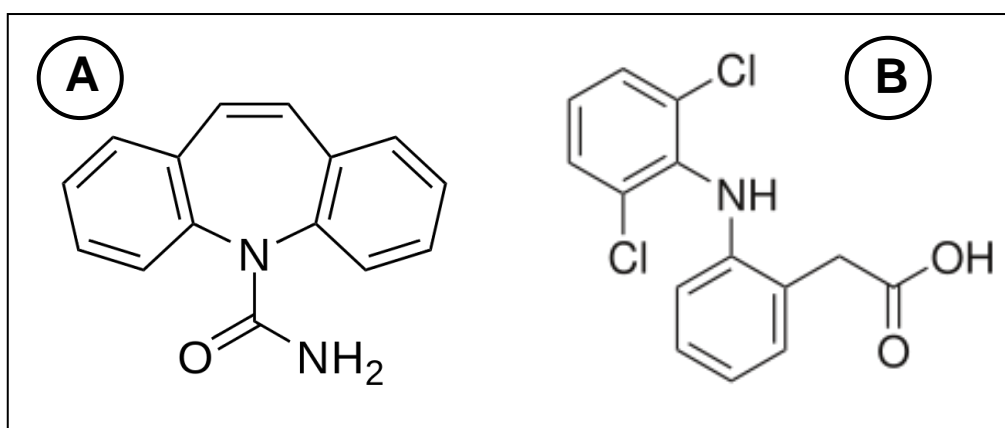
Figure 2.3 Carbamazepine (A) and Diclofenac (B).

2.3 PERSONAL CARE PRODUCTS

Personal care products are chemicals used as active ingredients or preservatives in cosmetics, toiletries, or fragrances. They are not used for treatment disease, but some may be intended to prevent diseases (e.g. sunscreen agents, biocides). Benzophenones are UV filters, among them, benzophenone-3 (BP3) and benzophenone-4 (BP4) (Figure 2.4) are, at the present, the most frequently used in cosmetic formulation such as sunscreens, skin care, facial makeup and lip care products. Many personal care products contains biocides such as triclosan, triclocarban as preservatives and

antimicrobials, benzotriazoles are used as anti-corrosives in dishwasher detergents and anti-icing fluids.[13] [14]

These compounds have come into focus because of their extensive use, furthermore some of them are lipophilic and therefore have a potential for bioaccumulation. These compounds can be directly introduced into the environment, for example they can be released into recreational waters or volatilized into the air. Because of this direct release they can bypass possible degradation in WWTPs.[15]

Since personal care products are continually infused into the environment, also those compounds that might have low persistence can display the same exposure potential as truly persistent pollutants since their removal rates can be compensated by their replacement rates.
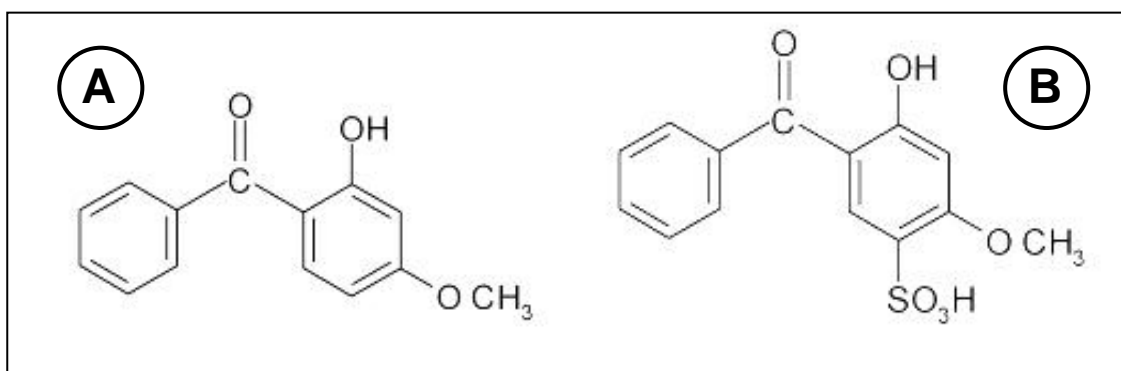
Figure 2.4 Benzophenone-3 (A) and Benzophenone-4 (B).

2.4 FATE IN THE ENVIRONMENT

The fate of the EOCs in the environment depends on their degree of natural attenuation and its physico-chemical properties, such as the octanol-water partition coefficient (K_{ow}) and the solubility in water (S_w). These parameters can both give an indication of compound mobility and affinity to sorption. The compounds with higher molecular weight and a log K_{ow} > 5 are more easily sorbed to sediments and removed by coagulation. On the contrary, those with log K_{ow} < 2.5 have low sorption and incline to remain in the surface water.[12] In surface water some natural removal mechanisms of EOCs occurs, such as biodegradation and photodegradation. Biodegradation is the dominant fate pathway for the removal of some EOCs from the aqueous phase of wastewater

and surface waters, but the process may take several months, especially in anaerobic conditions. Photolysis is another natural attenuation process due to the presence of aromatic rings, heteroatoms and other functional groups. The compounds with these properties can absorb solar radiation or react with photogenerated transient species in natural waters. As with biodegradation, the effects of natural photodegradation to EOCs are unsatisfactory since many environmental factors, such as depth of river, shading from bankside vegetation, presence of particulate matter and season, affect the photolysis process.

Depending on the environmental pH, the EOCs can be either neutral or positively or negatively ionized. The degree of their ionization affects the sorption that can occur by interaction with mineral surfaces (surface complexation) and with organic matter.

2.5 TOXIC AND ECOLOGICAL EFFECTS

The effects of EOCs and their metabolites in the aquatic environment is not well known since often unpredicted and unknown side effects exist. Moreover, they often occur in the environment as multi-component mixtures having an ecotoxicity rate higher than any single compound.[8] Also, it must be taken into account that although concentrations in environmental water bodies are at low levels, EOCs may still pose risks to aquatic species under chronic long-term exposure and also low exposure may lead to effects in non-target organisms.

Some studies have investigated a combination of various chemicals and the result was that they produced a detectable effect. The antiepileptic carbamazepine and the lipid lowering agent clofibric acid (which belong to very different therapeutic classes), exhibited stronger effects to Daphnia magna during immobilization tests than the single compounds at the same concentration.[16] Furthermore, Cleuvers (2004) reported considerable acute toxicity for a mixture of non-steroidal antinflammatory (diclofenac, ibuprofen, naproxen and aspirin) at the same concentration where little no effect was observed for the chemicals individually.[17]

Fishes are one of the most vulnerable species to the high concentration of pharmaceuticals. A part from the fishes, the adversely effects on algae in

aquatic environment might lead to serious ecological results. A study have reported that the increase in concentration of Carbamazepine and Diclofenac leads to the adverse effects on the chloroplasts in algae, causing the reduction of photosynthesis and affecting their survival. Moreover, the dead algae leads to the eutrophication and the disruption of food chain and this affects the entire aquatic equilibrium.[18]

A significant concern has been mostly focused on antibiotics or steroids compounds that may cause resistance among natural bacterial populations or in the case of steroids, can cause serious ecological effects even at low concentration because they are very active biological compound. The occurrence of hormone compounds in the environment might lead to endocrine disrupting to most of the animals including mammals, bird or fishes.[19]

Endocrine disruptors have lipophilic properties and they can pass through the cell membrane and accumulate in the adipose tissue. Bioaccumulation play a great role in the toxicological effects of these compounds which can produce biological effects in animals even if they are present in the environment at low concentrations. A consequence of the bioaccumulation process is the biomagnification which consists in an increase of the concentration of a substance along the food chain since predators assume not only endocrine disruptors present in the environment, but also those present in the preys. Therefore, especially big predators, including man, are exposed to these substances.

2.6 EUROPEAN LEGISLATION IN THE FIELD OF WATER POLICY

Our rivers, lakes, coastal and marine waters as well as our groundwaters are valuable resources to protect.

European water legislation dates back to the latter half of the 1970s. A 1988 review identified gaps to be filled, leading to further measures obliging Member States to control sewage from urban areas, nitrogen fertilizers from farmland, and pollution from factories and industrial plants. The outcome was the 2000 Water Framework Directive (WFD) (Directive 2000/60/EC), one of the most ambitious and comprehensive pieces of EU legislation ever. It has been established with the aim to set up a legal framework for the protection of water

quality in European countries (for river water, sea water, groundwater and coastal water). The directive recognized that specific measures have to be adopted in order to reduce the level of pollution for 33 priority substances (Annex X). Priority Substances are chemical pollutants that pose a significant risk to (or via) the aquatic environment at EU level.

The list of the priority substances was replaced by the Directive on Environmental Quality Standards (Directive 2008/105/EC), which set the maximum allowable concentrations for the substances in surface water, sediments or biota, that are the environmental quality standards (EQS), and confirmed their designation as priority or priority hazardous substances. The directive also takes into account other substances (Annex III) for possible identification as priority or priority hazardous substances.

The Directive 2013/39/UE replaced the Annex X of the Directive 2000/60/EC adding other 12 chemicals to the starting list of priority substances. The maximum concentration levels in water of these new substances will be set and enforced by 2018. Moreover, the Commission established a watch list of substances for which Member States gather monitoring data at selected representative monitoring stations over at least a 12-month period.

The Commission established the first watch list on 14 September 2014 and update it every 24 months thereafter. When updating the watch list, the Commission remove any substance for which a risk-based assessment can be concluded without additional monitoring data. The duration of a continuous watch list monitoring period for any individual substance shall not exceed four years.

Member States report to the Commission the results of the monitoring and the Commission adopt implementing acts establishing and updating the watch list. Three pharmaceutical have been added to the watch list. Effectively the compounds - an anti-inflammatory drug and two hormonal ingredients - have been put on probation and may be added to the priority list at a later date. Ethinylestradiol (EE2) is a synthetic steroid. The most frequent use is as the estrogen component of combined oral contraceptives. Beta-estradiol is the most active of the naturally occurring estrogenic hormones and is also a key intermediate in industrial synthesis of other estrogens and of various hormonal 19-norsteroids. DCF is non-steroidal anti-inflammatory drug used by patients for

the treatment of inflammation and pain predominantly via oral and dermal application.[20] The watch list of substances has been enforced in the Annex of Commission implementing decision (UE) 2015/495 of 20 March 2015, and other compounds were added to the list: 2,6-Ditert-butyl-4-methylphenol, 2-Ethylhexyl 4-methoxycinnamate, Macrolide antibiotics, Methiocarb, Neonicotinoids, Oxadiazon, Tri-allate.

In Italy the EU Water Framework Directive was transposeded by the D.Lgs.n.152 3 April 2006.

3. ADVANCED OXIDATION PROCESSES

Taking into account recent studies on EOCs, conventional WWTPs do not solve completely the problem of water pollution since the removal of parent contaminant molecules does not necessarily translate into removal of the toxicity suggesting that a great number of transformation products (of unknown toxicity and persistence) exits in final effluent and reaches surface water.

Regarding pharmaceutical compounds, parent chemicals are often excreted from the human body with a number of associated metabolites which can themselves be pharmacologically active.[21] For example, the major metabolite of CBZ (carbamazepine epoxide) has been found in influent wastewater at concentrations ranging from 880 to 4026 ng L^{-1} whereas the parent compound was found at <1.5-113 ng L^{-1}. Metabolites can also be persistent during secondary wastewater treatments.[22]

Over the last decades there has been a particular attention to the development and optimization of the advanced oxidation processes (AOPs) which can represent a valid alternative or an implementation of the conventional systems for water purification. In fact, through these processes, the polluting molecules can be destroyed in an effective and sustainable way.

AOPs are chemical – physical systems which have been developed as new technologies for water purification. AOPs make use of different types of energy such as ionizing radiation (for example gamma rays and electron-beam), ultrasounds, non thermal plasma, UV light (with hydrogen peroxide or ozone or photocatalysts like TiO_2 or ZnO), to generate a number of reactive species that attack refractory and/or toxic pollutants in wastewaters. Among the reactive species produced by the AOPs, hydroxyl radical ($^{\bullet}OH$) plays a major role, it behaves as a molecular chisel converting organic compounds into carbon dioxide and pure water (mineralization process).

Different AOP techniques, hence different possible ways for OH radicals production allow a better compliance with the specific treatment requirements. AOP can be exploited to integrate biological treatments by an oxidative degradation of toxic or refractory substances entering or leaving the biological stage.

Advanced processes are recognized to attain the elimination of contaminants and not merely their separation. Separation, in fact, may produce excellent water quality, but does not solve the problem of contaminants disposal. In fact, they are often accumulated in smaller volumes where toxicity increases, creating areas with higher ecological risk. Many AOPs work in atmospheric condition and ambient or sub-ambient temperatures without any chemical supply.

Moreover, some AOPs are able to remove compounds which are adsorbed on mud or soil surface, since radical species pass them into the aqueous phase where they undergo the oxidation process.

Choosing the most appropriate AOP for water purification, it is necessary to keep in mind the following considerations:

- nature and physical - chemical properties of the water (or wet matrix) to treat;
- nature, chemical – physical properties and concentration of the pollutant to remove;
- pollutant biodegradability;
- presence of OH radical scavengers and compounds which absorb UV radiation;
- pertinence of wastewater to treat: pH of the solution have to be carefully regulated because of the balance which settle the OH radical production;
- presence of other components in the water which could interfere with the reaction intermediates.

However, primary evaluations have to be the rate of removal to reach and the possible existing alternatives.

In the end, the cost of the system is an important aspect: components which increase the production of the OH radical (O_3, H_2O_2, TiO_2) have high cost such

that only water with a COD value ≤ 5 g/L can be treated with an AOP method, whereas a higher value of COD would require the consumption of big amount of expansive reagents.

As in the metabolic process (for example the oxidation of formaldehyde in eq. 1), AOPs work an aerobic demolition of the molecular structure of organic substances.

(1) $CH_2O + O_2 \rightarrow CO_2 + H_2O$

The difference is that the advanced oxidation processes use a radical oxidation (eq. 2), which is more efficient.

(2) $CH_2O + 2\ ^{\bullet}OH \rightarrow CO_2 + H_2O + H_2$
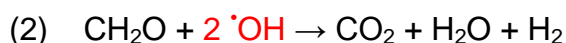
3.1 THE MAIN ADVANCED OXIDATION PROCESSES

The main advanced oxidation processes are described below.

3.1.1 Ultraviolet disinfection and photolysis

Ultraviolet light (UV) is successfully applied for disinfection of wastewater and drinking water. Electromagnetic radiation is an effective agent for microorganism inactivation in the wavelength ranging from 240 to 280 nm, which kill microorganisms by causing irreparable damage to their nucleic acid.[23] Besides to its disinfection effectiveness, UV can also degrade organic compounds by direct photolysis of photolabile compounds as a consequence of light absorption,[24] or it is used in order to quantify the contribution of the electronic excitation of the organic pollutant in mediated oxidation processes. UV alone is not considered an AOP because it does not directly produce oxidants. However, small amounts of O_3 and $^{\bullet}OH$ can be generated in some side reactions. The vacuum UV (VUV) radiation emitted by low pressure mercury and excimer lamps are able to dissociate molecular oxygen to atomic oxygen (eq. 3) that reacts with O_2 to produce O_3 that is dissociated by the 254

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nm radiation (eq. 4).[25] In addition, the VUV radiation dissociates H_2O (eq. 5) producing $^\bullet OH$ that attacks the dissolved or dispersed organic matter (eq. 6). The VUV process is very simple, it has the advantage that no chemicals need to be added.[26]

(3) $O_2 + h\nu$ (185 nm) $\rightarrow 2O^\bullet$

(4) $O^\bullet + O^2 \rightarrow O^3$

(5) $H_2O + h\nu \rightarrow 1/2\ H_2 + {}^\bullet OH$

(6) $^\bullet OH + RH \rightarrow R^\bullet + H_2O$
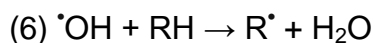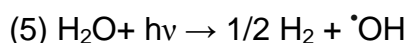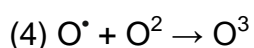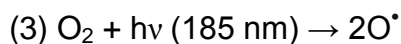
3.1.2 Photocatalysis

Photocatalysts are usually semiconductors. Photoexcitation with light of energy greater than the semiconductor band-gap promotes an electron from the valence band to the conduction band, and leaves an electronic vacancy or hole (h^+) in the valence band, as described in eq. 7. The hole is highly oxidative and quickly reacts with organic molecules adsorbed on the photocatalyst surface leading to their degradation. In addition, h^+ and e^- react with adsorbed water molecules and dissolved O_2, respectively, producing $^\bullet OH$ and $O_2^{\bullet-}$ that in turn degrade the nearby organic molecules.[27]

(7) $MOx + h\nu \rightarrow MOx^\bullet$ (e^-, h^+)
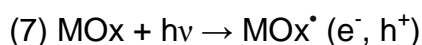
TiO_2 is the most used photocatalyst for environmental applications because it has a strong oxidizing power under UV irradiation, high chemical stability, low cost and low toxicity. It mainly occurs in nature in three forms: anatase, rutile and brookite. Anatase exhibits the highest photocatalytic activity.[28] Photocatalytic pollutant degradation using semiconductor materials has attracted considerable attention due to the possibility of exploiting the solar radiation that could ensure more economic solutions to the problem of water purification and recovery.

TiO$_2$ catalysis proceeds through the production of $^\bullet$OH radicals and other reactive species that are able to degrade the organic molecules at the solid-liquid interface. The mechanism of action lies on the effectiveness of charge separation between h$^+$ and e$^-$ created upon absorbing a radiation of sufficient energy (UV photons, e-beam and γ-rays). As TiO$_2$ particles in water are widely hydroxylated, h$^+$ escaping annihilation, migrate to the surface and oxidize adsorbed water molecules and hydroxyl ions. Oxygen adsorbed at the surface captures electrons preventing their recombination with **h$^+$**, and therefore increases the $^\bullet$OH radical yield.

As the band-gap of anatase TiO$_2$ (3.2 eV, λ = 387.5 nm[29]) can exploit only a little percentage of the sunlight, in order to extend the photocatalytic activity of TiO$_2$ from UV to visible light region, various strategies have been adopted such as doping or coupling with other functional materials. Carbon based materials have been recently considered very effective since they do not introduce defect states in the TiO$_2$ band-gap. Among these materials graphene have received increasing attention for their unique properties: a monolayer of carbon atoms gives a large surface area, high chemical stability, mechanical flexibility and superior electrical conductivity.[30]

Even if artificial UV radiation with λ ~ 254 nm is energy demanding it represents a better choice than solar light for high water flux, because it can run 24 hours per day, it needs smaller plants, and because it also activates direct photolysis.

Most of the photocatalysis applications involved suspensions in water[31,32] but the immobilization of the photocatalyst on suitable solid matrices would ensure some advantages, such as an easy recovery of the catalyst and an higher specific surface area available and consequently an higher contact area to the solution. Moreover, from a practical point of view, the suspended system requires an additional treatment in order to remove the catalyst from the treated aqueous solution.[33] In the last years, some research activities have been devoted to the development of new TiO$_2$-based photocatalytic systems with the aim of enhancing the photocatalytic activity. An exhaustive review on TiO$_2$ has been recently published showing the technological readiness of this process.[34] In our opinion the photocatalysis, especially if coupled with light emitting diodes (LEDs), is a promising technique for small size plants because the systems

require only the power connection and potentially works for a long time with a variety of water with a low level of contamination.
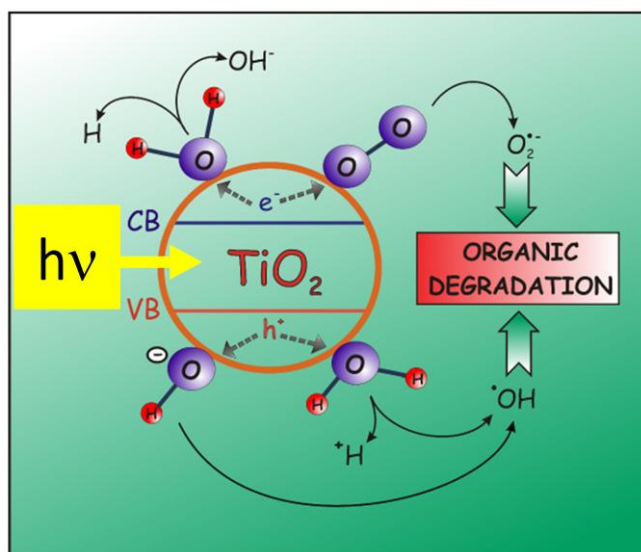
Figure 3.1 Reaction that occur as a result of the interaction between a photon and a TiO_2 particle

3.1.3 UV and H_2O_2

This AOP process is performed by irradiating the polluted water added with a proper amount of H_2O_2 with UV light having wavelengths smaller than 280 nm. The absorption of light then causes the homolytic break of H_2O_2 (eq. 8). The back reaction of $^{\bullet}OH$ with H_2O_2 itself is slow and of limited importance, however the perydroxyl radical formed may participate to the oxydation process of pollutants or regenerate H_2O_2 (eq 9 and eq. 10).

(8) $H_2O_2 + h\nu \rightarrow 2\ ^{\bullet}OH$

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

(10) $2\ HO_2^{\bullet} \rightarrow H_2O_2 + O_2$
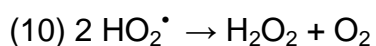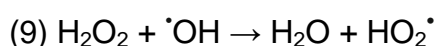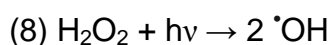
Attention has to be paid to the cases where organic substrates act as inner filters: since the molar extinction coefficient of H_2O_2 at 254 nm is small (18.6 M^{-1} cm^{-1}), the fraction of incident light absorbed may be reduced with a fall of

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efficiency. The photolysis of aqueous H_2O_2 is pH dependent and increases when more alkaline conditions are used.[26] This is due to the higher molar absorption coefficient of the peroxide anion HO_2^- which is 240 M^{-1} cm^{-1} at 254 nm.

3.1.4 UV and O_3

Since past times, ozone is widely applied for disinfection and depollution of water because it shows high reactivity with organic molecules due to a high affinity for π systems and a relatively high oxidation potential (1.19 ÷ 1.60 V vs. NHE[35]). Ozone is easy to be produced from air by using electrical discharges. In water, O_3 decomposes into the more powerful oxidant $^\bullet OH$, and the milder $O_2^{\bullet-}$ (eq. 11 and eq. 12). When irradiated with UV light at 254 nm (ε_{O3} = 3600 M^{-1} cm^{-1} [36]), ozone enhances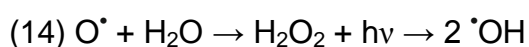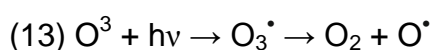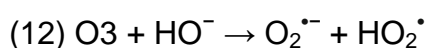 the production of $^\bullet OH$ (eq. 13 and eq. 14), and of a variety of other reactive oxygen species, which accelerate the removal of organic matter. Therefore the UV/O_3 system constitutes one of the most appreciated AOP method.[29]

(11) $O_3 + H_2O \rightarrow 2\ ^\bullet OH + O_2$

(12) $O3 + HO^- \rightarrow O_2^{\bullet-} + HO_2^\bullet$

(13) $O^3 + h\nu \rightarrow O_3^\bullet \rightarrow O_2 + O^\bullet$

(14) $O^\bullet + H_2O \rightarrow H_2O_2 + h\nu \rightarrow 2\ ^\bullet OH$
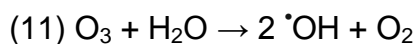
3.1.5 Sonolysis by ultrasound cavitation

Sonolysis of water is a relatively new process demonstrating already a certain effectiveness in the destruction of some varieties of pollutants. Sonolysis is obtained by producing in water the acoustic cavitation phenomenon through the application of an alternating field of compressing and decompressing ultrasonic *waves.* Acoustic cavitation is a cyclic process characterized by the formation (nucleation), growth (expansion), and adiabatic implosion (collapse) of gaseous

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microbubbles. In other words, absorbing the ultrasound energy, the microbubbles grow up to a critical resonance size and then collapse, creating local hot spot, living in the subsecond domain, and having temperatures around 5000°C, and pressures of about 1000 atm. Because of these extreme conditions, within the bubble and at the bubble-solution interface, the trapped molecules of vaporized water and those of the dissolved gasses, achieve excited states which dissociate into highly reactive free radicals[37] (see for example eq. 15 and eq. 16 where))) indicates the ultrasounds). Governing the conditions to produce cavitation and monitoring it are not yet easy activities and many investigations worldwide are focused on them. However, even if cavitation is not reached, ultrasounds, because of their efficiency in solution stirring, accelerate every reaction limited by the transport of mass.

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

(16) $O_2 +))) \rightarrow 2\, O^{\bullet}$

(17) $O^{\bullet} + H_2O \rightarrow 2\, {}^{\bullet}OH$
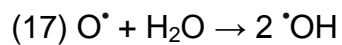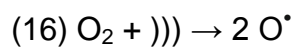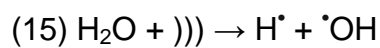
Figure 3.2 Cavitation bubble
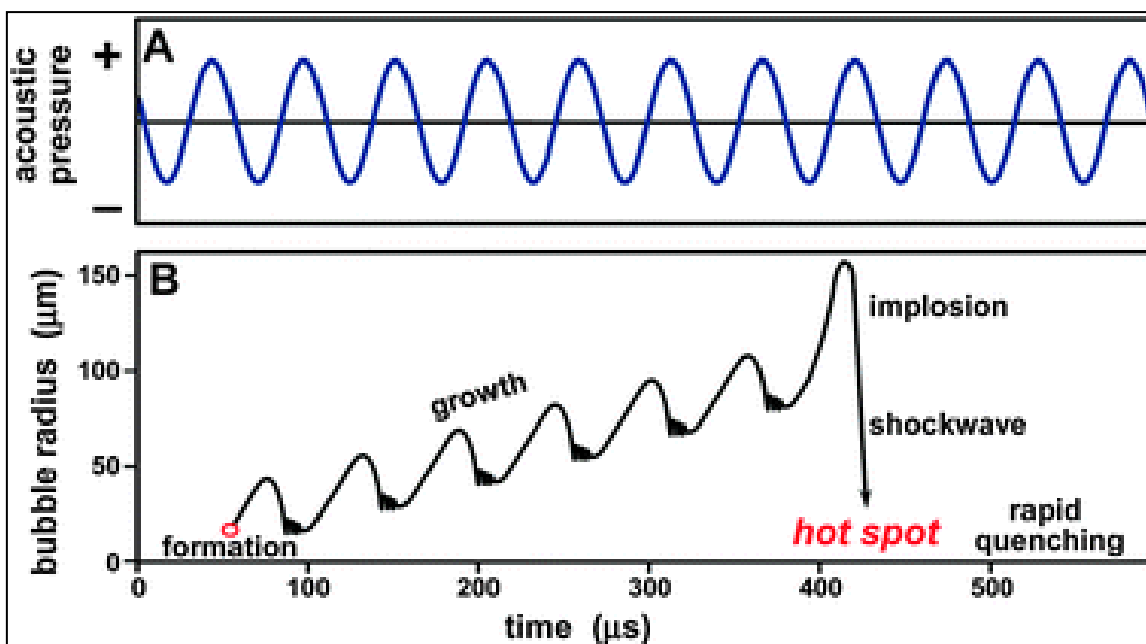
Figure 3.3 Mechanism of acoustic cavitation

3.1.6 Electrochemical AOPs

Electrochemistry is the regular method to impose reduction and oxidation processes on a solution but it can be yet considered an advanced process (EAOP) when non-conventional electrodes are used or when it is coupled to other physical techniques. These methods are based on the electrochemical generation of the $^{\bullet}OH$ in solution. EAOPs include heterogeneous processes like anodic oxidation and photoelectrocatalysis methods, in which $^{\bullet}OH$ is generated at the anode surface either electrochemically or photochemically, and homogeneous processes like electro-Fenton, photoelectro-Fenton, and sonoelectrolysis, in which $^{\bullet}OH$ is produced in the bulk solution. EAOPs have been suggested to treat water with the widest chemical oxygen demand (COD) content, ranging from 0.01 to 100 g L^{-1}, whereas biological treatments are useful from 0.001 to 1 g L^{-1} and other AOPs from 0.01 to 10 g L^{-1}.

To date, a large-scale application of EAOPs is the automated disinfection of swimming pool water using boron doped diamond anodes. Compared with the other disinfection methods, these systems have the advantages that there is no chlorine smell, no accumulation of chemicals in the pool, no need of anti-algae, and there is a residual action to avoid non regular disinfections. Other

applications are already on the market for water disinfection and industrial wastewater treatments.

These EAOPs are based on the production of oxygen-based agents, such as $^\bullet$OH (see for example eq. 18 on boron doped diamond, BDD[38]) and O_3, directly by water electrolysis, providing high disinfection rate with relatively low energy consumption, without the addition of chemicals and with the possible oxidation of organic matter. Other EAOPs, based on porous electrodes under oxygen flux, are a way to produce H_2O_2 and supply reactants for the Fenton oxidation.[39]

(18) $H_2O \rightarrow {}^\bullet OH + H^+ + e^-$ $E \sim 2$ V vs. Ag/AgCl on BDD

(19) $2\,{}^\bullet OH \rightarrow H_2O_2$

(20) ${}^\bullet OH + H_2O_2 \rightarrow HO_2{}^\bullet + H_2O$
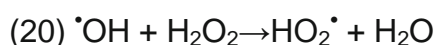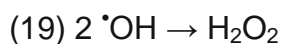
3.1.7 Sonoelectrochemistry

The term sonoelectrochemistry, or acoustoelectrochemistry, refers to the use of acoustic waves, mainly ultrasounds in the range from 20 kHz to 2 MHz, during electrochemical processes. In liquids, the acoustic energy is transferred via alternated compression and rarefaction, that is via longitudinal pressure waves, further transversal waves can involve the surfaces of liquids and solids. When ultrasounds pass through water are partially adsorbed producing radiation forces, that depend on position and direction and induce liquid motion known as acoustic streaming. This phenomenon depends on the cell shape and, if the working electrode is involved in the acoustic streaming, the current is not diffusion driven but meets the shape of the methods involving forced convection.[40] The limiting current depends on the ultrasounds intensity and on the distance between the acoustic wave source and the working electrode.

As shown before, ultrasounds in water produce the cavitation that is the formation, grown and collapse of microbubbles whose oscillation and collapse produce violent, uneven and disorderly convection in the solution, different from relatively ordered acoustic streaming, that invests working electrode enhancing current but also noise. Anyway, this effect is detectable only if the working

electrode is located in the region where cavitation take place, in contrast to acoustic streaming that involves the main part of the cell.

Decreasing the size of the working electrode down to less than 1 mm of diameter, the signal-to-noise ratio decrease and the current shape shows two contributions: a relatively constant but less intense increase due to turbulent motion, and a large number of very intense individual peaks due to the microjets provoked by the interaction of the bubble collapse to the planar electrode wall. The collapses of microbubbles can form very high pressure pulses that are called shock waves and that are one of the possible mechanisms of solid material erosion by cavitation. In electrochemistry experiments, shock waves can be connected to the renewal of the electrode surface that enhances the current, especially if the electrode is activated because of the removal of a passive layer. In 2010, Gonzalez-Garcia et al. reported a wide overview of the literature on sonoelectrochemistry in two short articles.[41,42] The acoustic energy concentrated into the microbubbles, within time scale of the order of 1 ns, leads to extreme conditions of pressure and temperature.[43] Sonoelectrochemistry has been used to destroy some organic contaminants directly, such as trichloroacetic acid[42] or bovine serum albumine[44], or coupled with Fenton reagents, to destroy pollutants such as 2,4-dichlorophenoxyacetic acid, 4,6-dinitro-o-cresol, and azobenzene.[45]

3.1.8 Non-thermal effect of microwaves

In order to enhance the activity of photocatalysts, in 2002 Horikoshi *et al.* proposed the coupling of macrowaves to UV radiation. The author tested the absorption of microvawes radiation on TiO_2 semiconductor nanoparticulates and observed the increase of the formation of $^{\bullet}OH$ which was monitored by electron spin resonance spectroscopy. Although the photon energy (10^{-5} eV) of the microwaves of frequency 2.45 GHz is several orders of magnitude lower than the band-gap energy required to activate the TiO_2 semiconductor, microwave non-thermal effects contribute significantly to the enhancement of a TiO_2-photoassisted reaction, as it may affect both the surface and the crystalline structure of the metal oxide toward reactions taking place at the surface.[46]

3.1.9 Wet air oxidation

Wet air oxidation (WAO) is one of the most economically and technologically viable AOPs for wastewater treatment. In this process, the organic pollutants are oxidized in the liquid phase at high temperature (125 ÷ 320°C) and pressure (0.5 ÷ 20 MPa), in the presence of gaseous oxygen (or air) as oxidant. Many studies have reported that the reaction pathway of WAO proceeds via free radical reactions which can oxidize organic contaminants into CO_2 and H_2O along with simpler forms which are biodegradable. WAO has a great potential for the treatment of effluent containing a high content of organic matter (about 10 ÷ 100 g L^{-1} of COD) and toxic contaminants for which direct biological treatment is not feasible. Many researchers carried out the WAO of aqueous solution of phenol achieving destruction efficiencies exceeding 90%. Devlin and Harris studied the oxidation of phenol demonstrating that it is firstly oxidized to dihydroxybenzenes (hydroquinone and catechol) which are converted into benzoquinones. Rings of benzoquinones are then opened with the formation of appropriate acids which are further oxidized to short-chain carboxylic acids.[47]

3.1.10 Supercritical water

Supercritical water oxidation (SCWO) destroys aqueous organic wastes by oxidizing them to CO_2 and H_2O. SCWO operates above the critical point of water (374°C and 22.1 MPa), and since most organic chemicals have unlimited miscibility with supercritical water, it can serve as a solvent, catalyst as well as a reactant in the chemical decomposition of organic compounds. SCWO takes advantage of the miscibility of organics, H_2O, and O_2 to rapidly oxidize the organics in the single-phase mixture. Organic feed destruction ratios are usually better than 99.99%. Because of the lower than incineration operating temperatures and high concentration of supercritical water, pollutants such as NO_X and SO_X are not generated in noticeable concentrations.[48] Processes in a supercritical water environment require the construction of expensive and complex equipment. The presence of high pressure will require using durable materials, and the high-temperature performance significantly limits the choice

of these materials. Due to these difficulties the SCWO process is not yet common in industrial practice.[49]

3.1.11 Plasma based AOPs

Plasma is a gas consisting of electrons, free radicals, ions and neutral species, obtained by a variety of electrical discharges or high intensity radiofrequencies. Based on the relative temperatures of these species, plasma treatments are classified as "thermal" or "non-thermal". Thermal plasma is associated with sufficient energy introduced to allow plasma constituents to be in thermal equilibrium. Non-thermal plasma is obtained using less power which is characterized by an energetic electron temperature much higher than that of the bulk-gas molecules.[50] In a non thermal plasma, the production of e^- can activate the gas molecules by collision processes and subsequently initiate a number of reaction paths generating additional $^\bullet O$, $^\bullet OH$ or $^\bullet HO_2$ for decomposing pollutants.

3.1.12 Electron-beam

When ionizing radiation is applied to water, it produces highly reactive species that rapidly disinfect water and mineralize organics. The ionizing radiation can be produced by means of a γ-radiation source (such as ^{60}C) or of an electron accelerator (electron beam or e-beam). As the high-energy electrons travels through water, they transfer their energy and slow down to thermal values. Along their pathway they form three reactive species (hydrated electrons, $^\bullet OH$ and $^\bullet H$) responsible for the destruction of the organic compounds.

The e-beam process is an on-off technology that does not use any radioactive materials, does not produce any radioactive waste, and is probably one of the most environmentally sustainable technologies, given that electricity comes from renewable sources. Furthermore, it works at room temperature and atmospheric pressure. So far, the e-beam technology is the most powerful AOP, as it surpasses any other process in the production rate of reactive agents by many order of magnitude. Also its efficiency in converting electromagnetic energy into chemical energy is around 60 ÷ 80% (DC type accelerators), much

better than other radiation sources. Running cost becomes convenient when treating volume of water above 1000 m^3 per day. Therefore, e-beam fits the need of medium-large WWTPs which treat strongly polluted effluents, for example those coming from dye, textile, and paper mill industries, hospitals, municipal and animal-breeding plants.[51][52][53]

3.2 HYDROXYL RADICAL

AOPs involves generation of highly reactive radicals species, mainly the hydroxyl radical ($^\bullet$OH).

The hydroxyl radical is a powerful oxidant, having a standard reduction potential of 2.7 V in acidic solution and 1.8 V in neutral solution. Furthermore the hydroxyl radical is a short lived, highly reactive and non-selective reagent. It attacks most organic molecules with elevated reaction rate constants that range from 10^6 to 10^9 $M^{-1}s^{-1}$, which are close to the diffusion-controlled limit. The hydroxyl radical can oxidize organic and inorganic substrates by different types of reactions:

(1) $^\bullet$OH + R-H $\rightarrow$ R$^\bullet$ + H_2O *abstraction of hydrogen atom*

(2) $^\bullet$OH + R_2C=CR_2 $\rightarrow$ $^\bullet$CR_2-C(OH) R_2 *electrophilic addition to unsaturated bond*

(3) $^\bullet$OH + M^{n+} $\rightarrow$ $M^{(n+1)+}$ + OH^- *electron transfer*
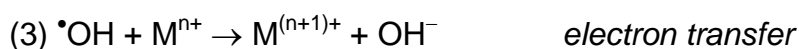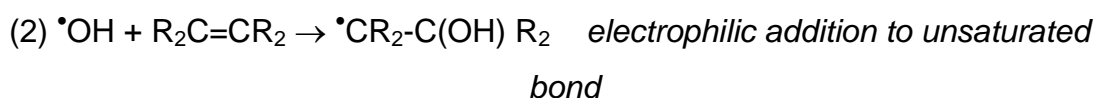
Radical-radical recombination must also be taken into account:

(4) 2 $^\bullet$OH $\rightarrow$ H_2O_2
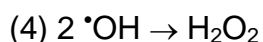
3.2.1 Scavenging effect

Although the high reactivity of $^\bullet OH$ offers the benefit of oxidizing mixtures of organic compounds, it has the drawback of reacting also with the background water components, consequently its efficacy depends on the water quality. The omnipresent bicarbonate or carbonate ions can compete successfully for OH radicals, especially at low loads of organic matter. All reactions that do not result in the degradation of the target pollutants are called scavenging reactions.

The scavenging reactions of OH radicals by carbonate or bicarbonate ions are usually referred to as electron transfer reactions.

(5) $^\bullet OH + CO_3^{2-} \rightarrow HO^- + CO_3^{\bullet -}$ $k_{\bullet OH,M} = 3.9 \times 10^8$ L mol^{-1} s^{-1} (Buxton et al., 1988)

(6) $^\bullet OH + HCO_3^- \rightarrow HO^- + HCO_3^\bullet$ $k_{\bullet OH,M} = 8.5 \times 10^6$ L mol^{-1} s^{-1} (Buxton et al., 1988)
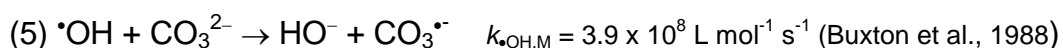
However, the bicarbonate and carbonate radicals ($HCO_3^\bullet$, $CO_3^{\bullet -}$) may act as very selective oxidant. The composition of the CO_2 (H_2CO_3) / HCO_3^- / CO_3^{2-} system in water is strongly dependent on the pH of the solution (Figure 3.4). When carbon dioxide is dissolved in water, only a small amount (about 0.1%) reacts to form carbonic acid (H_2CO_3). In fact, most of the undissociated acid is actually present as $CO_{2(aq)}$ at pH values lower than 4.3. At a pH of 8.2 the system consists mostly of bicarbonate ions and at higher pH values, above 12, carbonate ion is mainly present.
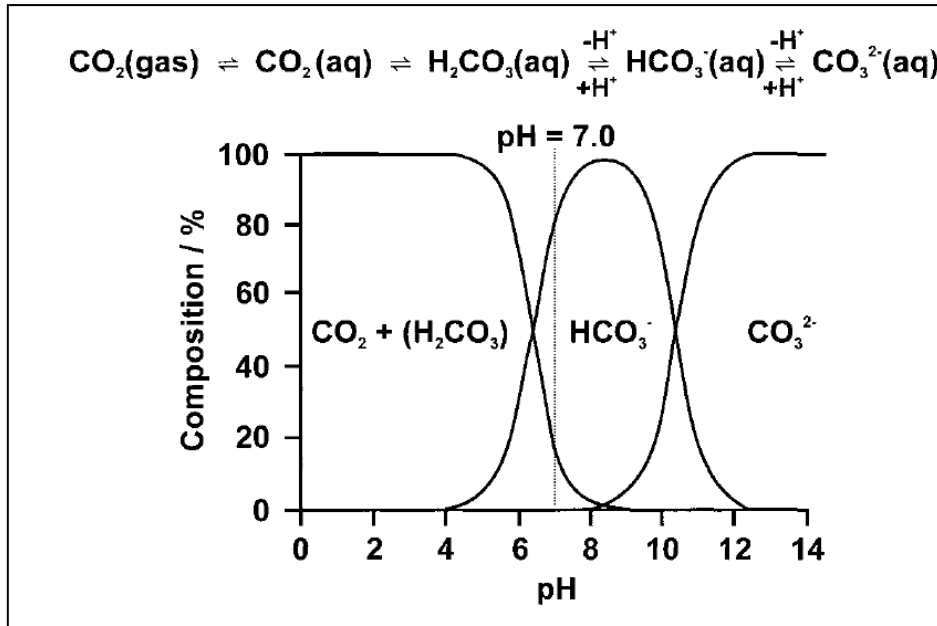
Figure 3.4 Composition of the $CO_2/(H_2CO_3)/HCO_3^-/CO_3^{2-}/H_2O$ system as a function of pH

The AOPs studied in the present thesis are based on UV radiation, which is widely used for wastewater disinfection. UVC radiation alone cannot be considered a plain oxidation process, and in some cases it may lead to unexpected results because of the direct photolysis of photolabile compounds. In the last decades, its oxidative effect has been enhanced by coupling it with additives and photocatalysts. TiO_2 photocatalysis has recently proved to be an effective water

disinfection option, since it does not need the addition of chemicals which can concur to form toxic byproducts. TiO_2-based photocatalytic processes seem not only sustainable and reliable solutions for a wide variety of water remediation issues but also economically rewarding.

4. EXPERIMENTAL SECTION

4.1 MATERIALS

All the chemicals were reagent grade or higher and were used without any further purification. Sodium dodecylbenzenesulfonate (SDBS), Hexadecyltrimethylammonium bromide (HTAB), BP3, BP4, CBZ, DCF, TRX, titanium tetraisopropoxide 98%, HCl 37% aqueous solution, and acetylacetone were supplied by Sigma-Aldrich. Lorodac, C12–C14-alcohol polyethylene glycol ethers (7 EO), 100% by weight, was supplied by Sasol. TiO_2 VP Aeroperl P25/20 from Evonik (TiO_2-mp), was a mixture of 80% anatase and 20% rutile with an average particle size of 20 μm and a tapped density of 0.7 g cm^{-3}. The average geometrical area results 0.2 m^2 g^{-1}. Absolute ethanol and the quartz wool (density 2.2 ÷ 2.6 g cm^{-3}) were supplied by Carlo Erba. Deionized water (DW) (resistivity = 18 MΩ cm at 25 °C, absorbance = 0.07 at 254 nm) was produced by a MilliRO 15 water purification system (Millipore). Tap water (TW) was collected from municipal waterworks of Bologna, Italy (absorbance = 0.13 at 254 nm), and the concentrations of the main metals and anions, determined by ion chromatography, titration and inductive coupling plasma atomic spectroscopy following the standard methods, were listed in table 2 with TOC and conductivity.

Table 4.1 Main metals and anions in Bologna's waterworks.

Parameter	value	s.d. [a]	units	l.o.q. [b]
pH	7.64	-	-	-
HCO_3^-	226.54	-	$mg\,L^{-1}$	-
CO_3^-	0	-	$mg\,L^{-1}$	-
NO_2^-	<0,02	-	$mg\,L^{-1}$	0.02
NH_4^+	<0,02	-	$mg\,L^{-1}$	0.02
NO_3^-	4.7	0.7	$mg\,L^{-1}$	0.5
F^-	<0.1	-	$mg\,L^{-1}$	0.1
ClO_2^-	134	27	$\mu g\,L^{-1}$	100
BrO_3^-	<2	-	$\mu g\,L^{-1}$	2
Br^-	258	8	$\mu g\,L^{-1}$	2
ClO_3^-	<100	-	$\mu g\,L^{-1}$	100
Cl^-	30	1	$\mu g\,L^{-1}$	2
SO_4^{2-}	60	6	$mg\,L^{-1}$	2
TOC	0.9	0.2	$mg\,L^{-1}$	0.2
Fe	11	2	$\mu g\,L^{-1}$	10
Mn	8	2	$\mu g\,L^{-1}$	5
Al	145	44	$\mu g\,L^{-1}$	20
Ca	81	8	$mg\,L^{-1}$	0.4
Mg	14	1	$mg\,L^{-1}$	0.2
Na	18	3	$mg\,L^{-1}$	0.2
K	1.8	0.3	$mg\,L^{-1}$	0.1
°F	26	-	-	-
conductivity	0.47	-	$mS\,cm^{-1}$	-

[a] standard deviation; [b] limit of quantification.

4.2 UV AND PHOTOCATALYTIC TREATMENTS

Different aqueous solutions of contaminants were treated by UV radiation with and without photocatalyst. Three selected surfactants (SDBS, Lorodac and HTAB) and the second rinse water from the laundry machine were treated only on laboratory scale, an aqueous solution of five organic contaminants (MIX 5), composed by BP3, BP4, CBZ, DCF, TRX, was treated both on laboratory and pre-industrial scale.

All the above mentioned contaminants will be described in the following chapter.

4.2.1 Laboratory scale

The UV light source was a Multilamp Rayonet (Figure 4.2) provided with 16 lamps (Sylvania G8W) with maximum emission centred at 254 nm and absorbed power 8W (UVC flux in the centre of the reactor was 25 mW cm^{-2}). The lightening system include an air blowing cooler.
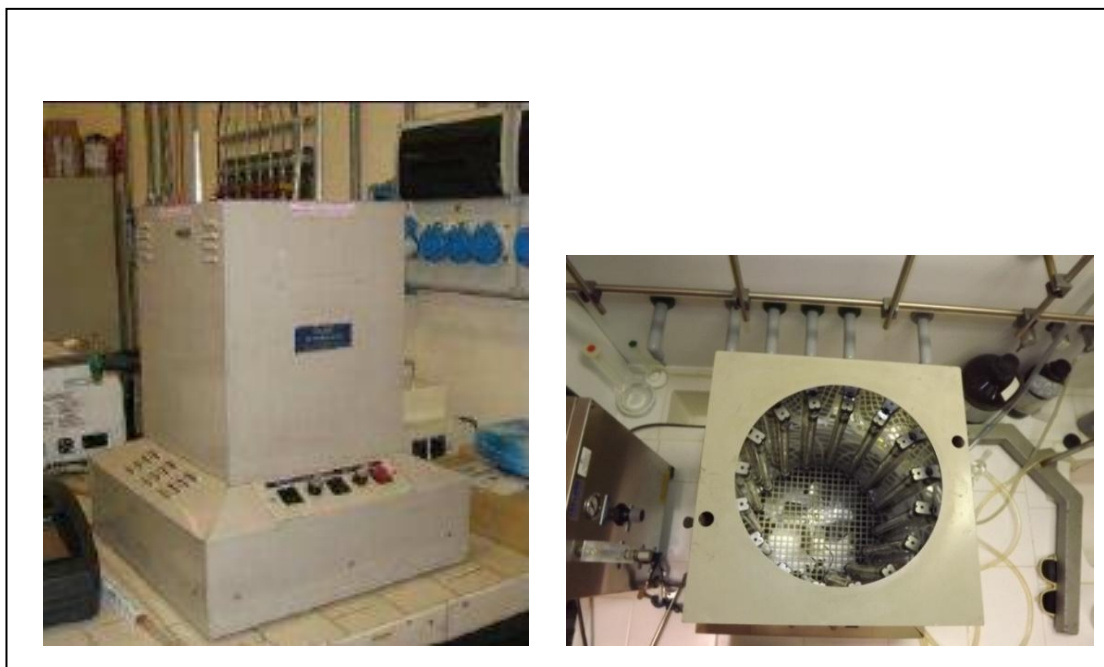

Figure 4.2 Rayonet photochemical reactor

The experiments were carried out in a quartz tube (diameter 4 cm) equipped with a condenser, to avoid water evaporation, and a Teflon capillary pipeline to supply the air bubbles that provide the stirring and suspend the eventual catalyst particles. The tube included 0.25 L of solution containing 25 mg L^{-1} of contaminant in the treatment of the single surfactants and 5 mg L^{-1} of each contaminants in the treatment of the MIX 5. Solution of single surfactants were prepared using only DW, MIX 5 solution was tested both in DW and TW. The solutions to be treated were magnetically stirred at room temperature in the dark for 48 hours and then the concentration of the contaminants was checked. Before starting the treatment, the solution was equilibrated under air bubbling in the dark for 5 min.

The test on single surfactant were treated using both UVC (254 nm) and UVA (368 nm) radiation. UVA radiation was tested in view of a commercial application of the photocatalytic process that combines water and energy saving, and it was used at lower power (64 watt) than the UVC treatment (128 watt). Furthermore, at the present only gas discharge lamps are available as UVC sources and their structure, basically made by quartz glass, does not match the specifications for domestic appliances. On the other hand, UVA radiation can be obtained by solid state LEDs that allow a wide variety of optical designs. At the present, UVA LEDs are commercialized with emission power lower than a watt per piece and with moderate conversion efficiency, but their performances are increasing day by day.

In the treatment with UVC radiation, TiO_2 was added at the concentration of 0.01 %, while with UVA radiation, TiO_2 concentration was 0.2%.

The photocatalyst was used as micropearls dispersed in the solution (TiO_2-mp).

Experiments on the second rinse water were designed in a view to the technological transfer of the photocatalytic process on real samples. Treatments were performed with UVA radiation (68 watt) testing different concentration of TiO_2-mp: 0.01%, 0.05% and 0.2%.

In the test carried out on MIX 5, three specimens of solutions were treated as follows: (i) UVC, (ii) UVC, TiO_2-mp 0.01%; and (iii) UVC, TiO_2

supported on quartz wool (TiO$_2$-qw) at the same concentration of the previous treatment.

4.2.2 Pre-industrial scale

A pilot plant to treat contaminated solutions was realized at the ISOF-CNR Institute laboratory in a view of an industrial employment (Figure 4.3). It consists of a tank (10÷25 L), a recycling pump, four UVC lamps (36 W each) and an air blower.
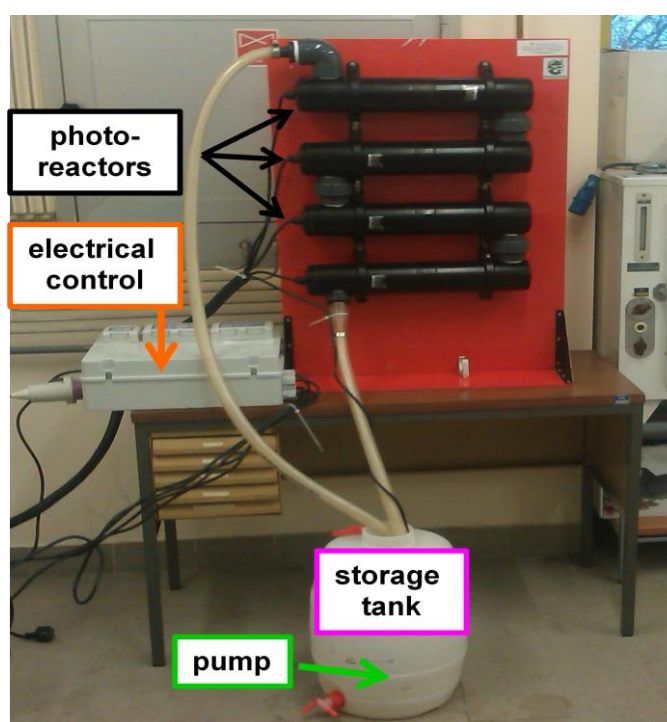

Figure 4.3 Pre-industrial pilot plant realized at ISOF-CNR Institute

For this prototype, different TiO$_2$ photocatalysts supported on different solid substrates were developed. The aim was to avoid some practical problems due to the use of dispersed TiO$_2$, such as the need to remove the catalyst from the aqueous suspension at the end of the whole degradation process. The immobilization of TiO$_2$ on solid surfaces was realized by PURETi Italia company, using the PURETi Clean photocatalytic system. Two different solid substrates covered with this photocatalyst was tested. In the first case, TiO$_2$ was spread on the inner layer of the tubes which include the UV lamps (Figure 4.4), in the second case it was spread on four nets of fiberglass inserted around the UV lamps (Figure 4.5). Each net had 42 holes in 1 cm^2, 3 mm thickness and

an average absorbance of 0.15 (standard deviation 0.04). The measures of the four samples were reported in the Table 4.2.

Figure 4.4 Tube with TiO$_2$ on the inner layer

Figure 4.5 UV lamp covered with the TiO$_2$ net of fiberglass

Table 4.2 Data of the nets treated with the PURETi coating

Sample	Width/cm	Lenght/cm	Weight/ g	BaseCoat	Clean
A	20.5	36	7.69	7.73	7.82
B	21	36	8.05	80.9	8.15
C	20.5	36	7.93	7.94	8.05
D	20.5	36	7.94	7.97	8.04

For each treatment in the prototype, 10 L of MIX 5 solution was used at the concentration of 25 mg L^{-1}.

Photodegradation treatments consisted of pre- and post-treatment phases, described below:

- Pre-treatment: the tank of the prototype was filled with the aqueous solution to be treated and the prototype was activated turning off the UV lamps. After 5 minutes a sample representing the 0 time was collected.

- Post-treatment: the prototype was washed for 4 hours by using 20 L of DW turning on the UV lamps in order to clean the plant of any residue of the previous treatment.

During both the irradiations on laboratory and pre-industrial scale, 5 mL samples were withdrawn at specific times and stored in the dark at 4°C before the analysis. In the case of the TiO_2 suspension, the sample was centrifugated before the high performance liquid chromatography (HPLC) analysis.

4.2.3 Technological testing on laundry machine wastewater

An Ariston Aqualtis AQXXL129 laundry machine, supplied by Indesit Company S.p.A., was used for the testing on real second rinsing water.

In a laundry machine, the washing cycle is constituted by three different phases: a washing phase and two rinse phases. The second rinse water (volume = 20 L) was treated since it has the smaller organic carbon content. Degradation treatment was carried out with the Rayonet photochemical reactor using UVA radiation and 64 watt of power in the perspective of the technological use of the photocatalytic process. The washing cycle (white cotton 60°C) was realized following the official protocol nr. 59D/332/DC of the International Electrotechnical Commission which establishes the rules for tests that are performed on washing machines. These rules establish that during the washing cycle, standard detergent and cotton strips including the standard dirty have to be used. In Figure 4.6 the standard strip are represented.

Figure 4.6 Standard strip used during the laundry machine washing cycle.

Also, to complete the loading of the washing machine drum, white cotton swatches are needed as replenishment material.

Second rinse water was saved into a tank and three degradation treatment were performed using UVA radiation with different TiO_2 concentration (0.01%, 0.05%, 0.2%).

4.2.4 Ultrasounds - UVC coupled system

For the contemporary irradiation of about 1 L of the MIX 5 solution, an Elmasonic P30H ultrasound source (frequency: 37 kHz and power: 36 ÷ 120 W or frequency: 80 kHz and power 30 ÷ 100 W) was equipped with 2 UV lamps (Philips TUV PL-S, $\lambda_{max} \sim$ 254 nm, 9 W), a pure air blower and a cooling coil. The ultrasound bath, the lamps and the safety power/system are shown in figure 4.7.

Figure 4.7 Apparatus for the ultrasounds / UVC - TiO$_2$ hybrid technique.

Different investigations were carried out: UV and ultrasounds were tested alone and as a coupled process. Treatments with TiO_2-mp were also tested, and the

photocatalyst was added at growing concentrations in order to assess the most suitable amount for the used experimental system.

For each treatment, 1 L of MIX 5 solution at the concentration of 25 mg L^{-1} was used. The molecules were dissolved in DW and the solution was put directly inside the tank of the instrument. The samples were collected at different time intervals up to 4 hours.

4.3 ANALYTICAL METHODS

The concentration of Sodium dodecylbenzenesulfonate and the MIX 5 contaminants was determined by a HPLC Agilent 1260, equipped with a diode array detector and a luminescence detector. Sample injection volume was 40 µL and analytes were separated on a reverse phase Zorbax C8 column (4.6 x 150 mm, 5 µm). A linear gradient was employed, from 0.1% trifluoroacetic acid in water to 100% acetonitrile, at flow rate of 1.0 mL min^{-1}. The detection was carried out at 285 nm for all the compounds with the exception of TRX which was detected by using an in-line Varian Pro Star 363 fluorescence detector (λ_{ex}= 229 nm and λ_{em}= 302 nm).

The concentration of the non ionic surfactant Lorodac was detected by a Termo Fisher TSQ 40600 HPLC instrument equipped with a diode array detector, an electrospray ionization (ESI) interface and a triple quadrupole detector.

The concentration of the cationic surfactant was detected by the charged aerosol detector (CAD), which is based upon a combination of HPLC with electrical aerosol technology. A simplified scheme of how CAD works is illustrated in Figure 4.8.
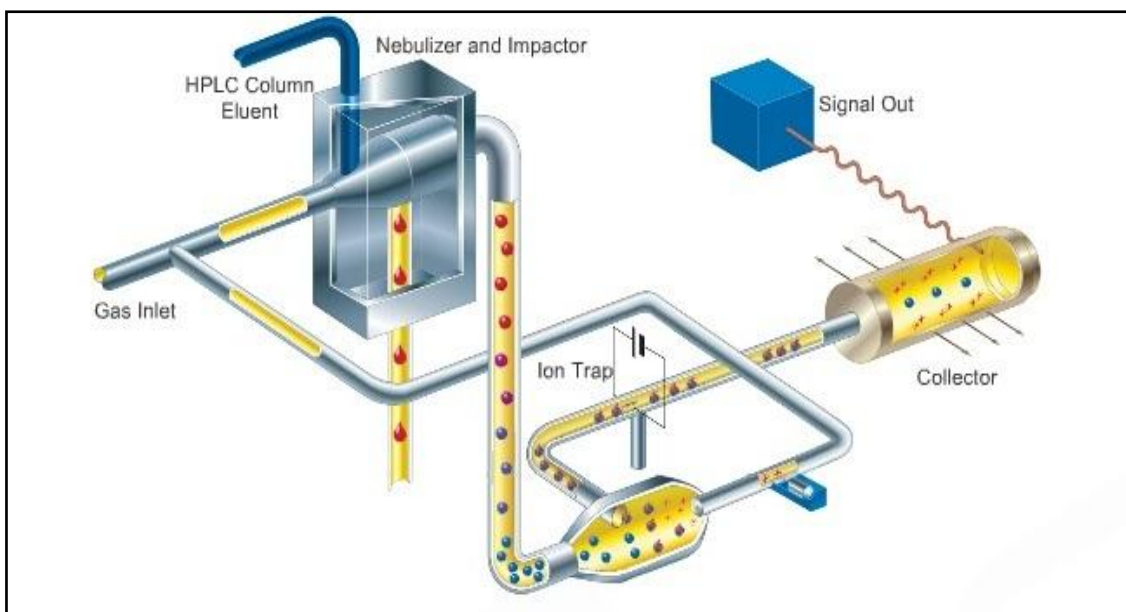
Figure 4.8 Corona™ Veo™ Charged Aerosol Detector.

Regarding the experiments carried out with the laundry machine wastewater, the concentration of anionic and non ionic surfactants was detected by the Hach Lange kit: LCK 332 for the anionics and LCK 333 for non ionics.

TOC concentration was measured by means of a Hach-Lange DR5000 spectrophotometer and LCK-385 test-in-cuvette with limit of detection 3 mg L^{-1}.

The pH was measured by an Orion Research Expandable Ion analyzer EA940 equipped with a Hanna Instruments HI 1111 electrode.

The temperature was monitored with a Delta Ohm HD 9219 thermometer equipped with a Pt100 sensor.

4.4 SYNTHESIS AND CHARACTERIZATION OF TiO$_2$-qw

Some treatments in the Rayonet photochemical reactor and in the home-made prototype were carried out with TiO$_2$-qw.

TiO$_2$-qw was produced at ENEA (Faenza) by the deposition of a TiO$_2$ thin film on quartz wool by sol-gel technique. The sol was obtained by mixing

titanium tetraisopropoxide, absolute ethanol, acetylacetone and 1 mol L^{-1} HCl aqueous solution in 1/0.5/3/34 ratio. Acetylacetone was used as complexant in order to avoid the precipitation of titanium byproduct, whereas HCl was added in order to introduce the required amount of water and to promote the polymeric sol synthesis by acidic catalysis. The obtained yellow sol was clear and stable for several days.

Four specimens of the sol were dried under atmospheric conditions up to sol-gel transition and the solvent evaporation was completed under infrared lamp. The obtained solids were treated for 30 min at four different temperatures: 350, 400, 450, and 500 °C, respectively. On these specimens, X-ray diffraction (XRD) was performed with a Philips PW 1710 diffractometer using Cu Kα radiation (λ=1.5406 Å) in order to select the temperature that gives the more crystalline anatase with the lower rutile content.

The samples of commercial quartz wool were soaked in the TiO_2 sol previously diluted in ethanol with a volume ratio of 1:5. This dilution ratio was chosen in order to avoid a thick deposition on the fibres, which would exhibit fragile behaviour and low adhesion. The solvent was then evaporated under atmospheric conditions for about 20 min and the densification was performed for 30 min at 450 °C that is the better temperature rising from XRD studies. The obtained samples were washed with water to remove the unbounded TiO_2 and dried at 120 °C for 20 min. A loading of 35 mg of TiO_2 per gram of TiO_2-qw was determined by weight.

The scanning electron microscopy (SEM) observations were performed on TiO_2-qw with a scanning electron microscope Leo 438 VP, using both secondary electrons and backscattering electrons detectors, in partial vacuum conditions, with and without sample metallization. Absorbance has been evaluated by Perkin-Elmer Lambda 9 spectrophotometer.

Four specimens of TiO_2-qw were prepared depending on the treatment temperature to which the sol-gel samples were treated. In the four specimens of powders, the two main TiO_2 phases, anatase and rutile, were confirmed by XRD (Figure 4.9). Anatase, the phase with the most promising photocatalytic

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activity,[54] [55] appeared after treatment at 350 °C, but mainly in amorphous form. The rutile phase was detected at 500 °C together with anatase of the highest crystallinity than that observed after thermal treatment at lower temperatures. On the basis of the XRD results, a temperature of 450 °C was chosen for the densification of TiO_2 nano-coating on a relevant amount of quartz wool (about 50 g), in order to obtain anatase with the highest crystallinity together with the minimum content of rutile phase.
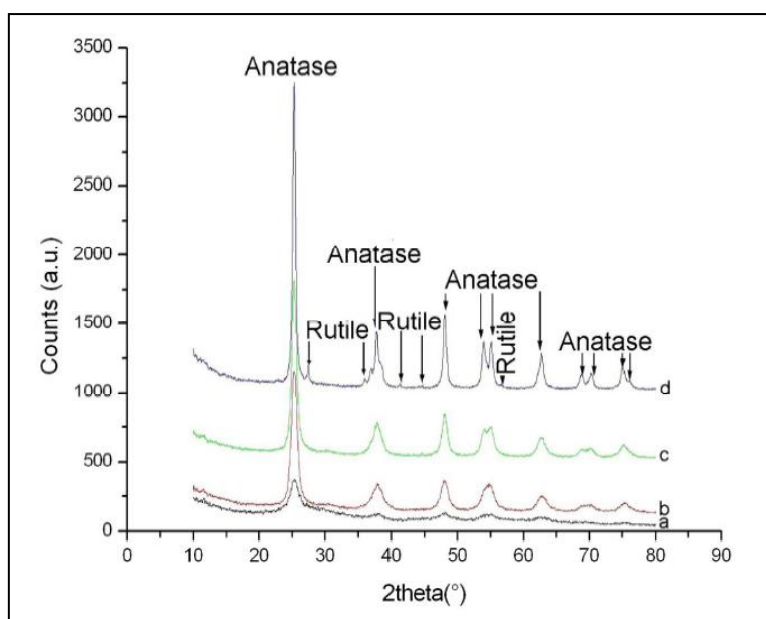

Figure 4.9 XRD patterns of the TiO_2 powders heated at the following temperatures: 350 °C (a); 400 °C (b), 450 °C (c), and 500 °C (d).

The SEM characterization of the TiO_2-qw was done on specimens with and without gold sputtering. In both cases very good resolutions were obtained, but observations without sputtering and using the secondary electron partial vacuum detector were preferred, in order to avoid any possible interference from gold deposition. The backscattering electrons detector was used to find the coating defects, exploiting its sensitivity to the mean atomic weight, which is lower for quartz than for titania. Some micrographs on the obtained coated quartz fibres before use are reported in Figure 4.10. The diameter of the fibres spans from 6 to 20 μm, consequently TiO_2-qw geometric surface is estimated in the range 0.28 ÷ 0.08 m2 g-1 that is comparable to that of TiO_2-mp. Because of the characteristics of the quartz substrate and because of the coating method

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(dipping in a precursor solution, gelling and drying), very variable coating thicknesses and also defects were observed. In particular, some fibres show crystallites grown perpendicularly to the fibre axis and, sometimes, mass accumulation appears near the fibre crossings. In the region without defects, the thickness of the TiO_2 coating results about 400 nm.
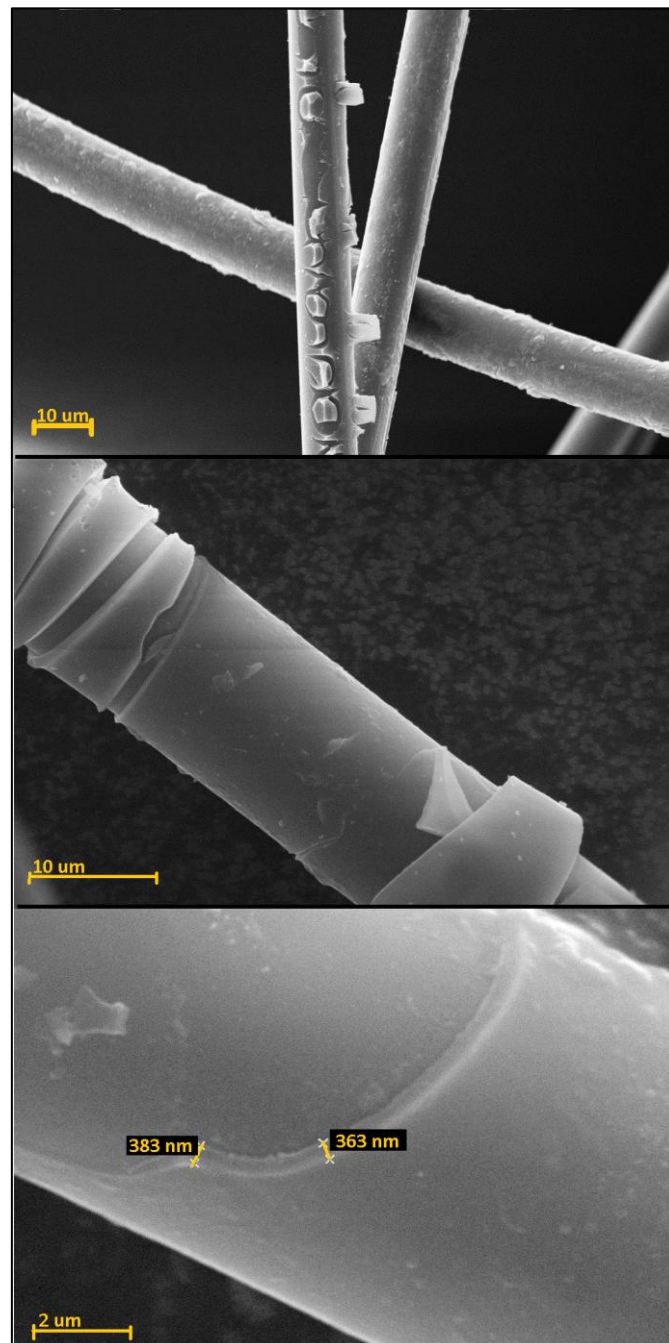

Figure 4.10 SEM images of TiO₂-qw before use (secondary electron detector in partial vacuum conditions). Thickness data are reported on a sample without gold coverage.

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5. RESULTS AND DISCUSSION

5.1 TEST ON AQUEOUS SOLUTIONS OF SURFACTANTS

Degradation test on aqueous solutions of surfactant were carried out selecting three surfactants as representative of the compounds found in the laundry machine wastewater. SDBS and Lorodac are the anionic and non ionic surfactants respectively of the standard detergent used during test on laundry machines; HTAB is representative of the category of cationic surfactant. The chemical structure of these three surfactants are described in Figure 5.1.
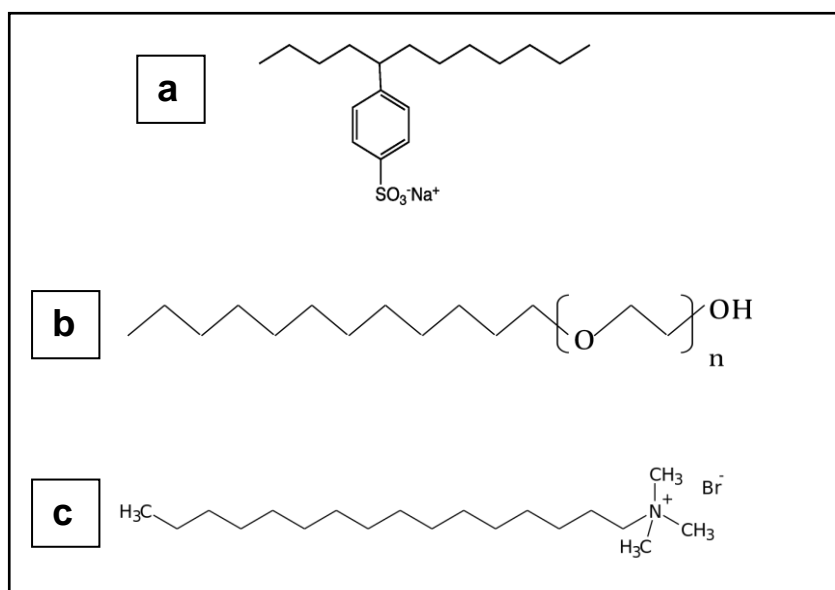

Figure 5.1 a) SDBS (anionic surfactant); b) Lorodac (ionic surfactant); c) HTAB (cationic surfactant).

5.1.1 Procedure of degradation treatments

Each type of surfactant was treated with UVC and UVA radiation with the addition of dispersed TiO_2 photocatalyst and the reactions were performed in the Rayonet photochemical reactor. UVA was used at the power of 64 watt, and the UVC at 128 watt.

TiO$_2$-mp was added at the concentration of 0.01 % p/v and 0.2 % p/v in the UVC and UVA treatment respectively. The bigger concentration of the photocatalyst had the aim to provide for the low power and efficiency of the UVA light. The samples were analyzed by HPLC developing a specific analytical method for each kind of surfactant using specific columns and detectors.

5.1.2 Test on anionic surfactant

Regarding the anionic surfactant, the HPLC analysis after the UVC treatment was carried out using the fluorescence detector. It revealed that SDBS was almost totally decomposed after 30 minutes. For the UVA treatment, the analysis was carried out with HPLC-MS instrument and it revealed that the concentration of the compound decreased of 80% after 30 minutes.

Measurement about the organic content proved that the UVC decreased the TOC faster than the UVA radiation, since it involves not only the photocatalytic reaction, but also the direct photolysis. Figure 5.2 represents the variation of TOC during the treatments with the two radiations, demonstrating that the TOC almost completely decayed after two hours and four hours with UVC and UVA treatments respectively.
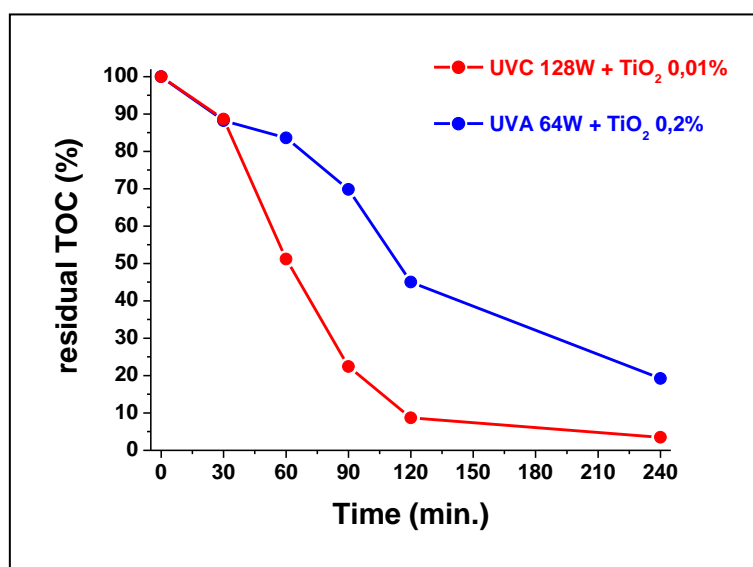

Figure 5.2 Comparison of variation of TOC during the degradation treatments of the anionic surfactant with UVC+TiO$_2$-mp 0,01% and UVA+TiO$_2$-mp 0,2%.

5.1.3 Test on non ionic surfactant

Both UVC and UVA degradation treatments led to the total decomposition of Lorodac after 30 minutes. The variations of concentration were measured with HPLC-MS analysis. Figure 5.3 demonstrates that different mineralization grade of the surfactant were obtained with the two treatments: TOC was completely removed after 90 minutes with UVC and after 4 hours with UVA.
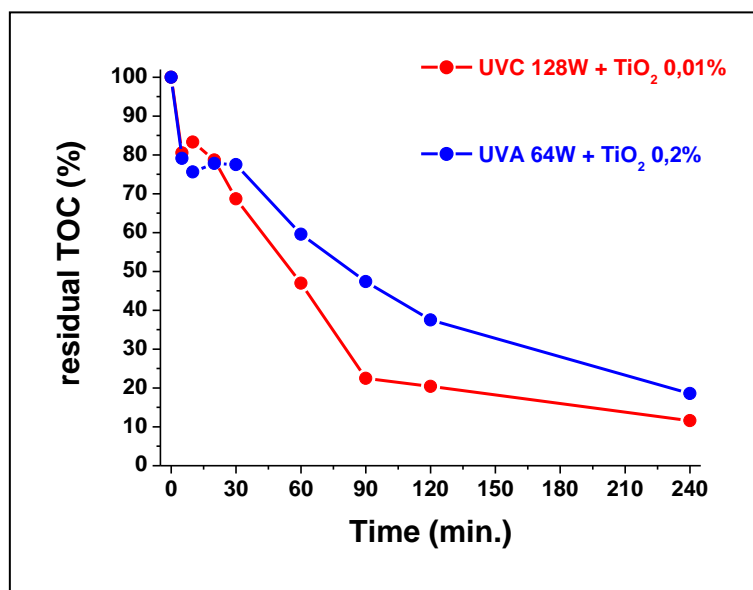

Figure 5.3 Comparison of variation of TOC during the degradation treatments of the non ionic surfactant with UVC+TiO$_2$-mp 0,01% and UVA+TiO$_2$-mp 0,2%.

5.1.4 Test on cationic surfactant

Samples of HTAB treated with UVC radiation were analyzed with Corona detector. The cationic surfactant was almost totally decomposed after 30 minutes. HPLC-MS was used to measure the concentration of surfactant during the UVA treatment and the results were the same.

TOC analysis demonstrated that both UVC and UVA radiations mineralize the cationic compound slower than previous experiments with anionic and non ionic surfactants. After 2 hours, TOC decreased of about 50% (Figure 5.4).

Cationic surfactant resulted the most difficult surfactant to decompose, indicating that its chemical structure undergoes scarcely the attack of OH radical.
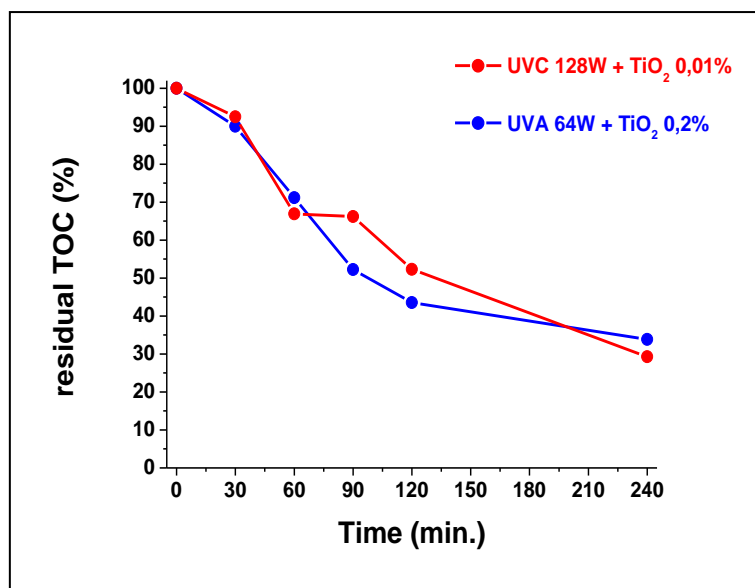
Figure 5.4 Comparison of variation of TOC during the degradation treatments of the cationic surfactant with UVC+TiO$_2$-mp 0,01% and UVA+TiO$_2$-mp 0,2%.

5.1.5 Photocatalytic treatments on laundry machine wastewater

Degradation of real samples were experimented testing photocatalytic process on laundry machine wastewater. These samples of water included surfactants, all the component of detergents and the dirty of the washed material. The treatments were performed using UVA radiation with different TiO$_2$ concentration.

The concentration of non ionic surfactant decreased faster than the anionic one (Figure 5.5), demonstrating that the Lorodac ethoxylated group is more attacked by oxidant species than the SDBS benzene ring.

The increase of TiO$_2$ concentration allowed to obtain the best degradation. In Table 5.1 the percentage of the degradation of the three surfactants during this treatment is described. Figure 5.6 demonstrates that after two hours TOC decreased of 35%. About this, it is important to consider that real samples are complex mixtures, so the mineralization process takes longer than samples including a single compound and prepared synthetically in the laboratory.
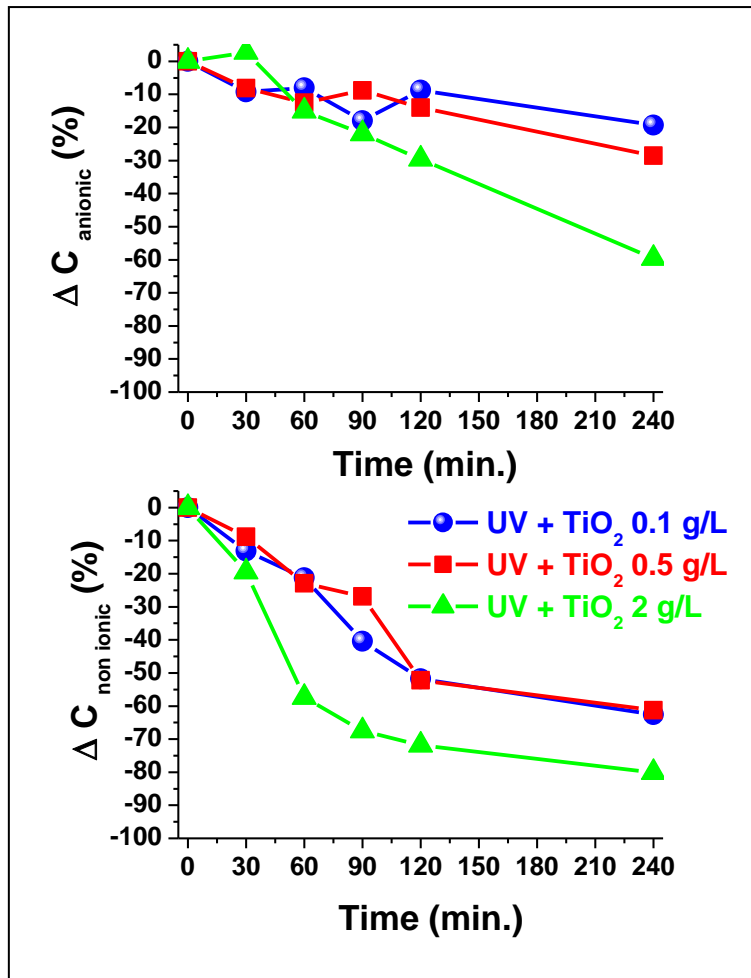
Figure 5.5 Variation of anionic and non ionic surfactants concentration during the treatments with UVA radiation with different concentration of TiO$_2$-mp.

Table 5.1 Percentage of degradation of the three surfactants during the treatment with UVA and 0,2% TiO$_2$-mp.

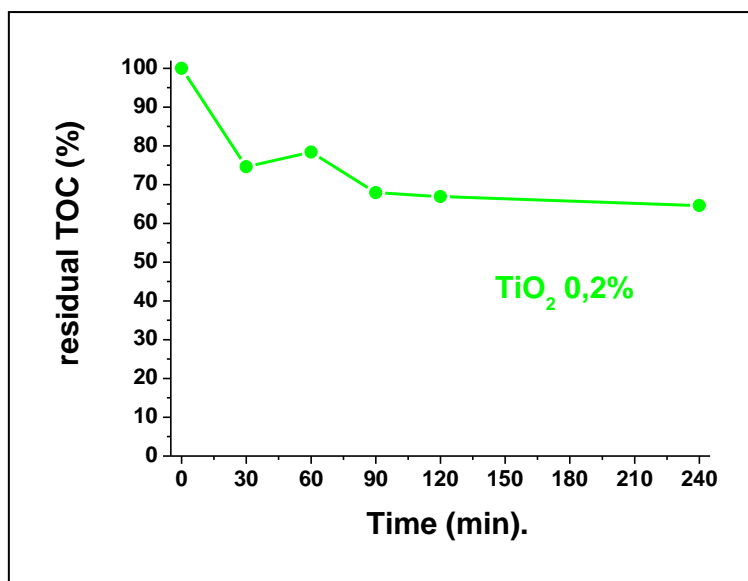|	SDBS	LORODAC	HTAB	2° rinse
Δ TOC (after 4 hours)	-80%	-80%	-70%	-35%

Figure 5.6 Variation of TOC of the laundry machine wastewater during the treatment with UVA+TiO$_2$-mp 0,2%.

5.2 TEST ON AQUEOUS SOLUTIONS OF MIX 5

Degradation test on aqueous solutions of MIX 5 were carried out selecting five emerging organic contaminants (EOCs). The components of the MIX 5 solution were described below.

BP3 and BP4 are two of the most commonly used UV filters in personal care products and they were found in untreated municipal wastewater in different countries at concentrations between 1.5 and 19 µg L^{-1}.[56] Their occurrence both in water and in sediments raises concern regarding possible estrogenic effects.[57] They have similar structures, good stability to the light, but different solubility.
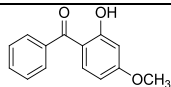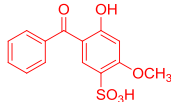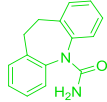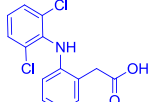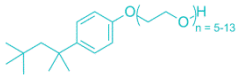
CBZ is a neutral molecule containing a strong polar group. It is an anticonvulsant used in the treatment of epilepsy and bipolar disorder. It is the most frequently detected pharmaceutical residue in water bodies and its removal efficiency in wastewater treatment plants is less than 10% due to its resistance to the biodegradation.[58]

DCF is a non-steroideal anti-inflammatory agent recently included by the European Commission in the "watch list" to be monitored in surface waters. Many studies found DCF concentrations > 1 µg L^{-1} in wastewater treatment plants effluents and in the future DCF may be classified as priority substance

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with environmental quality standards values ranging from 10 to 100 ng L^{-1}.[59] DCF has been selected also because it is usually commercialized as a sodium salt, and because it is sensitive to UV radiation, showing spontaneous photolysis in the environment with half-lives from 0.19 to 0.27 hours.[60] Finally, TRX is an amphiphilic molecule (non ionic surfactant) widely used in almost every type of liquid paste, and powdered cleaning formulates, ranging from heavy-duty industrial and agrochemical products to gentle detergents.[61] It is a toxic and poorly biodegradable compound that can mimic natural hormones, therefore having the potential to act as an endocrine disrupter in aquatic organisms and even humans.[62]

Table 5.2 describes the five organic molecules mixed in the MIX 5.

Table 5.2 Components of the MIX 5.

Name	CAS #	m. w. (g mol^{-1})	formula
benzophenone-3 (BP3)	131-57-57	228.24	
benzophenone-4 (BP4)	4065-45-6	308.31	
carbamazepina (CBZ)	298-46-4	283.27	
diclofenac (DCF)	15307-79-6	296.15	
triton X-100 (TRX)	9002-93-1	625 (average)	

Degradation treatments were performed in the Rayonet photochemical reactor. A preliminary treatment was carried out by means of UV photolysis and it was compared with the photocatalytic ones which were performed with TiO_2-mp and TiO_2-qw. TiO_2-qw life cycle was also evaluated. Every treatments was carried out both in DW and TW.

The efficiency of the three degradation treatments was determined by following the disappearance of the parent molecules by HPLC and evaluating the degree of mineralization via total organic carbon analysis. Figure 5.7 indicates the chromatograms relative to the MIX 5 molecules. Each peak has a different

lambda maxima, Triton is the only compound monitored by using the fluorescence detector.
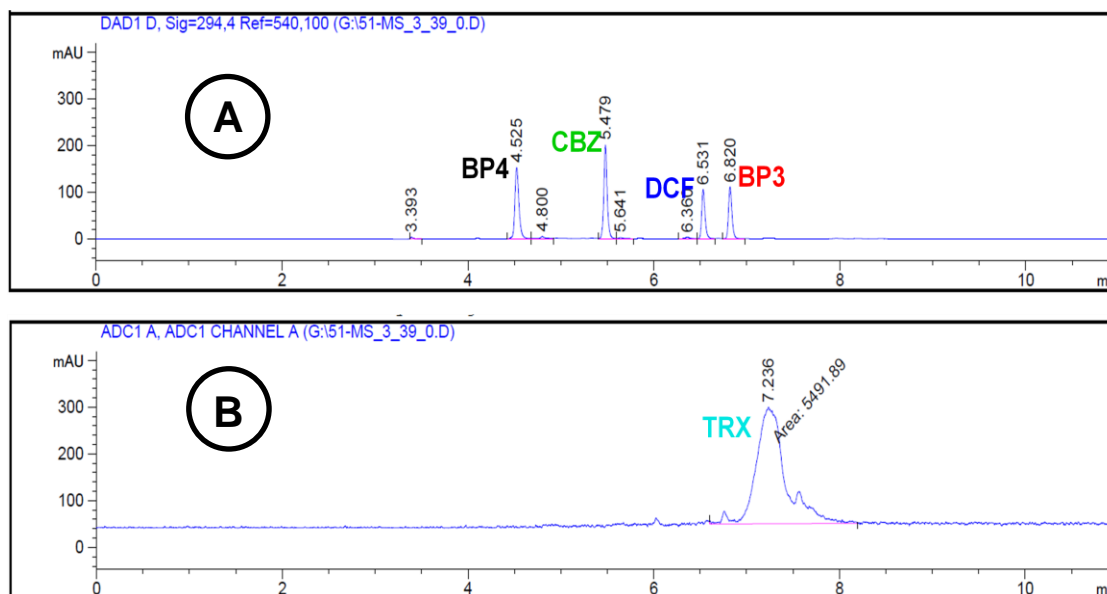

Figure 5.7 Chromatograms relative to the mixture of five EOCs. Chromatogram A represents the peaks of BP4, CBZ, DCF, BP3 resulted from the diode array detector; chromatogram B represents the peak of TRX resulted from the fluorescence detector.

5.2.1 Preliminary treatment

The UVC treatment represented the starting point for the evaluation of direct photolysis. Figure 5.8 describes the residual amounts of the five compounds during the degradation treatment. All pollutants almost completely disappeared in 2 hours in DW and in 4 hours in TW. As expected, DCF was the most photo-labile compound that completely disappeared during the first 5 minutes of irradiation in DW as well as in TW.

The degradation of the five EOCs in TW was slower than in DW due to the scavenging effect of the inorganic ions on the radical reactions.[63] Even if the samples irradiated for short times showed a yellowish coloration, and the corresponding HPLC analysis had slightly increased baseline signal, the concentrations were lower in the byproducts than in the parent compounds. Therefore it is very likely the byproducts remained undetectable by the used analytical procedure.
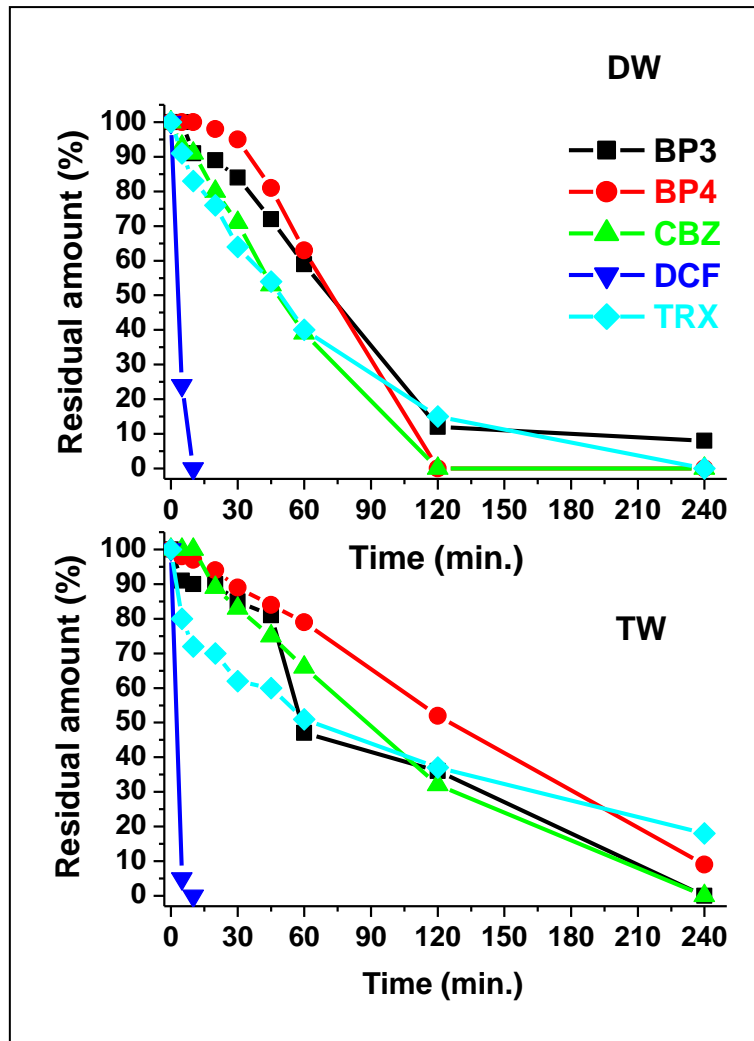
Figure 5.8 Residual amounts of the five compounds during the treatment with UVC radiation in DW and TW.

Also about the TOC analysis, the mineralization process was faster in DW than in TW, and this is explained by the presence of bicarbonate and carbonate ions in TW that can quench the reactive hydroxyl radicals leading to production of hydroxide anions. In order to support this explanation, a further analysis on the TW solution with TiO_2 in dispersion was performed, measuring the pH value and the concentration of bicarbonate and carbonate ions at the beginning (time 0) and at the end of the process (after 4 hours). The table 5.3 indicates that the pH increased as a result of the enhance of hydroxide anions, at the same time the amount of the carbonate and bicarbonate ions decreased as a consequence of their reaction with OH radicals (producing carbon dioxide).

Parameter	0 min.	240 min.	Units
pH	7.64	8.97	
HCO$_3^-$	226.54	49.6	mg/L
CO$_3^{2-}$	0	3.59	mg/L

5.2.2 Photocatalytic treatment of MIX 5

Photocatalytic processes resulted to be effective in the decomposition of the 5 pollutants with both the two types of photocatalysts, at the same concentration (0.01%): TiO$_2$-mp (Figure 5.9 A) and TiO$_2$-qw (Figure 5.9 B). In both cases the degradation reactions proceeded with a similar trend even thought in the case B, the process was slightly faster than the case A. This is explained by the higher active area of the supported photocatalyst on equal amount of TiO$_2$ used in the two different treatments.

As in the preliminary experiments, the degradation reactions were faster in DW than in TW for the same reason explained before. HPCL revealed no detectable byproducts.
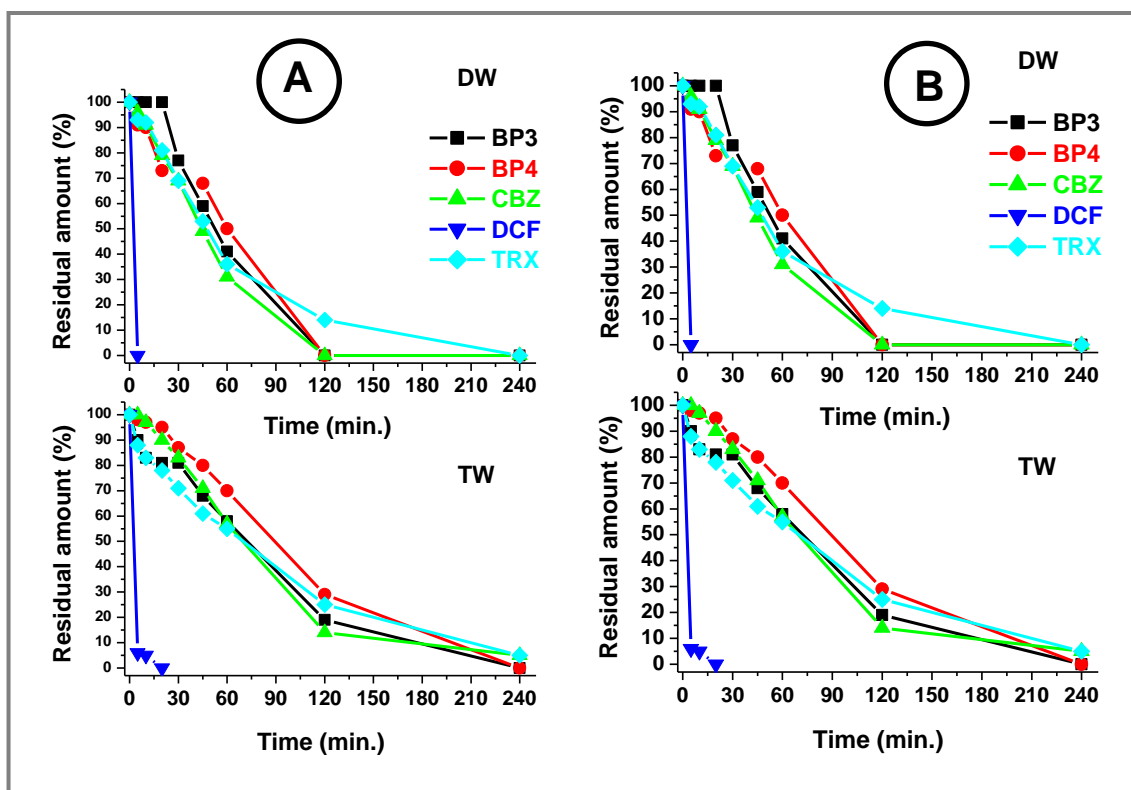
Figure 5.9 Residual amounts of the five compounds during the treatment with UVC - TiO$_2$-mp (A) and UVC - TiO$_2$-qw (B) in DW and TW.

5.2.3 Mineralization and catalyst life-cycle

Figure 5.10 shows the comparison of the average residual amount of the five EOC after 120 min. (A) and the residual TOC after 240 min. (B), in the two water matrices.

The temperature during all the six experiments increased in the same way from (24 ± 2) °C to (53 ± 2) °C, so it cannot be considered the responsible of the different degradation and mineralization rates. In DW the three UVC based treatments, after 120 min, reduced the average EOC concentration of one order of magnitude, but in TW, only the AOP treatment with TiO$_2$-qw was able to reach this goal (Fig. 5.10 A). Also the opposite trends of pH in DW and TW suggests different degradation pathways depending on the matrices. In the case of TW, the EOCs mineralization needed longer times than in DW (Fig. 5.10 B). Even if in DW the three UVC based mineralization processes can be considered satisfactory after 240 min, in TW, UVC mineralized only the 30% of the EOCs. However, the photocatalysis significantly enhanced the EOC

mineralization process achieving the best performance with TiO_2-qw (residual TOC about 30%). In this case, a larger photocatalytic area is exploited, compared with the same amount of TiO_2-mp. Furthermore, the use of a solid support facilitates the recovery and reuse of the catalyst itself.
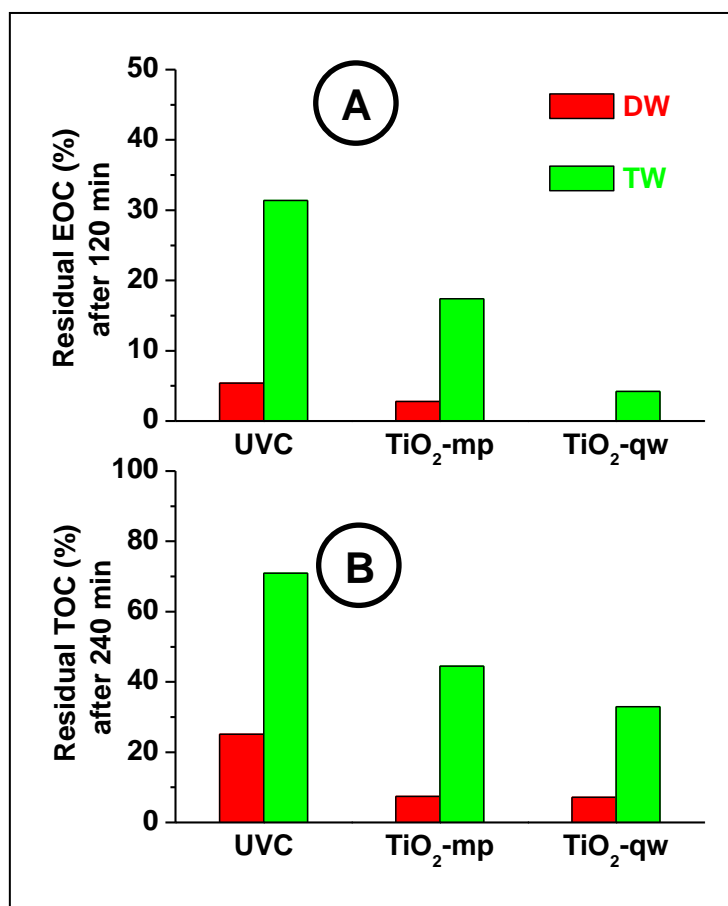

Figure 5.10 Average amount of EOC after 120 min. (A) and residual amount of TOC after 240 min. (B) of the three UVC - air based treatments.

Figure 5.11 shows the performance of TiO_2-qw in TW over repeated treatment with UVC and air. After every 240 min. long treatment, TiO_2-qw was recovered, washed three times in DW to remove residual salts and organic matters, dried at 120 °C for 18 hours and weighted. The weight loss after every cycle was less than 0.5%. The fitting to a constant residual amount shows that the average EOC residual after 120 min. (12%) stays within the confidence band (confidence level 95%), but TOC residual after 240 min (45%) at the 8th cycle, exceeds the confidence band. However, a recent study encourages the use of regeneration processes to enhance the cycle-life of the immobilized photocatalysts. After the 8 cycles, the used TiO_2-qw was analysed by SEM

once again and the images are reported in Figure 5.12. A comparison of these images with those of Figure 4.10 demonstrates that the coating morphology of the catalyst was essentially unchanged after 8 cycles even if a loss of TiO_2 appears in the defects and thicker points.
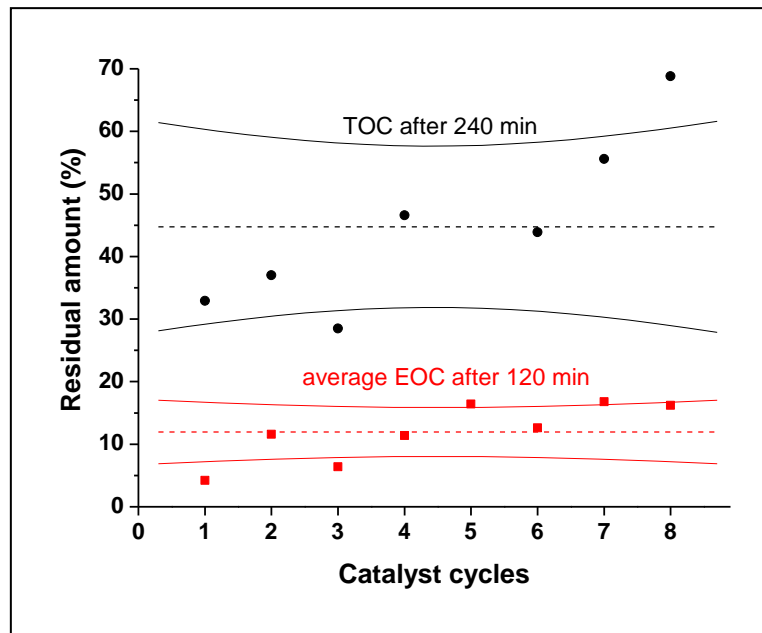

Figure 5.11 Performance of TiO$_2$-qw in TW over repeated treatment with UVC and air.
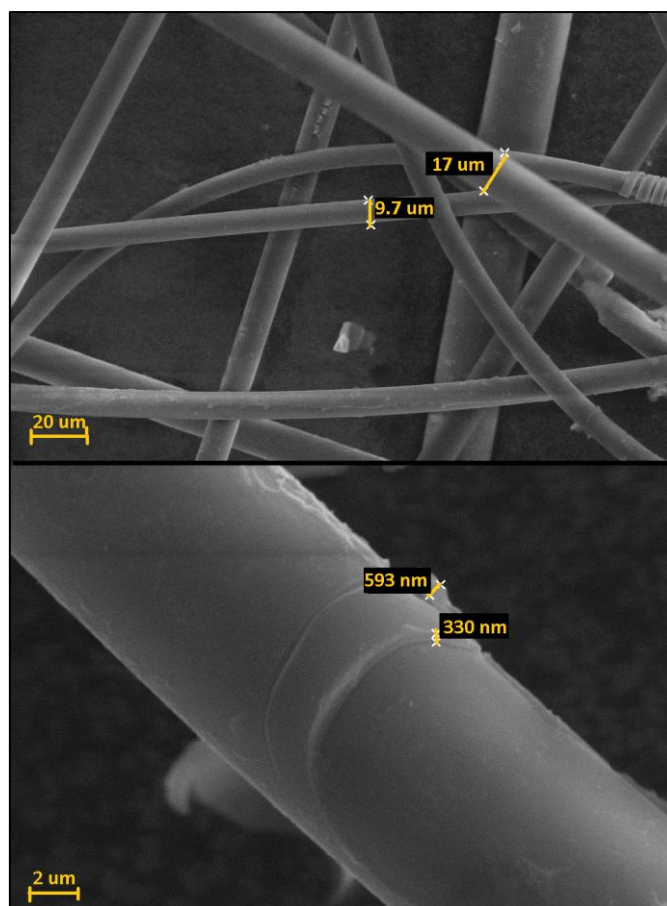
Figure 5.12 SEM images of TiO$_2$-qw after 8 cycles.

5.3 TEST ON AQUEOUS SOLUTIONS OF MIX 5 PERFORMED IN THE PROTOTYPE

Degradation treatments were performed in the prototype using UVC radiation and different supported photocatalysts.

Three types of treatment were performed. The first one represented the reference test and it was carried out using UVC radiation alone without the photocatalyst. The second treatment was executed with TiO$_2$ spread on the inner layer of the plastic tubes which included the UVC lamps. In the third treatment TiO$_2$ was spread not only on the tubes but also on plastic nets included around UVC lamps.

Figure 5.14 indicates that at the end of the first treatment, the degradation rates of the five molecules were good: BP3 was decomposed of 46%, CBZ 60%, TRX 66% and BP4 88%.
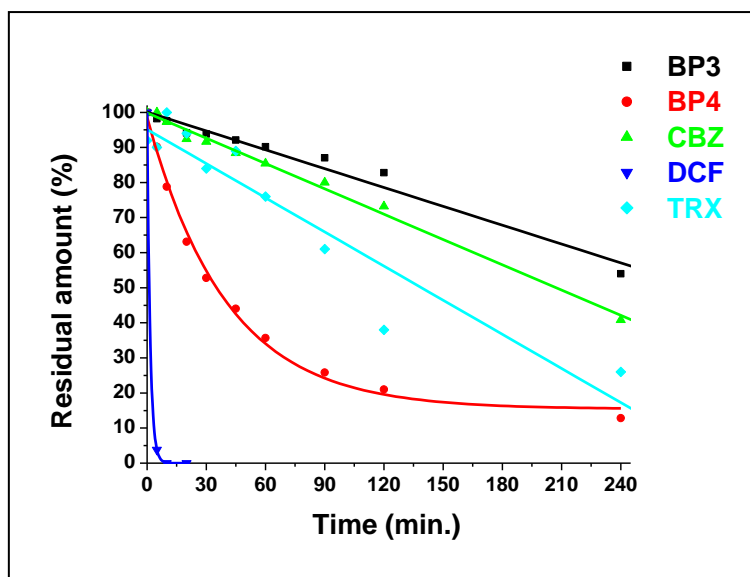
Figure 5.14 Residual amounts of the five compounds during the treatment with UVC radiation in the prototype.

The results related to the treatment with the photocatalytic tubes were comparable to the previous treatment (Figure 5.15).

Figure 5.15 Residual amounts of the five compounds during the treatment with the photocatalytic tubes in the prototype.

Only in the third process the efficiency was improved. Two molecules (DCF and TRX) were totally decomposed, and the other three molecules were almost totally decomposed, as shown in Figure 5.16 .
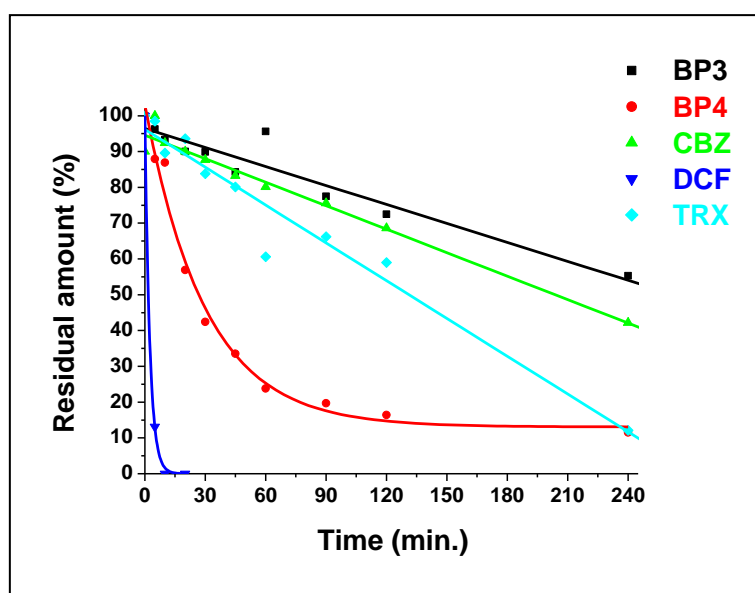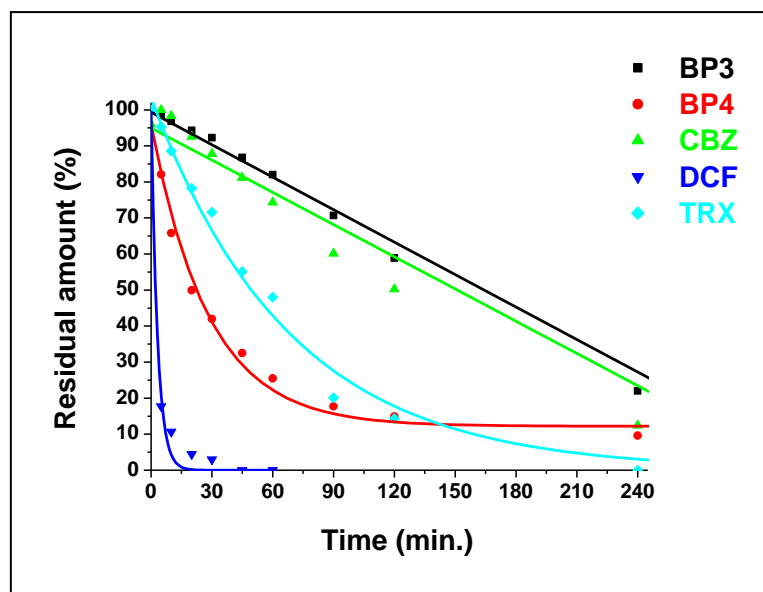
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Figure 5.16 Residual amounts of the five compounds during the treatment with the photocatalytic tubes and nets in the prototype.

5.4 UV IRRADIATION – ULTRASOUNDS COMBINED PROCESS

The combination of two different degradation techniques, UV irradiation and ultrasounds, was performed in order to speed up the decomposition of the pollutants.

Figure 5.17 represents the percentage of the residual amounts of the five molecules during the combined process with and without TiO_2. Figure 5.17 A is related to the UV-ultrasounds combined process without the photocatalyst. Only DCF, which is a photo-labile compound, was totally decomposed at the end of the treatment. BP4 concentration decreased of 55%, CBZ of 26% and TRX of 37%. BP3 was not decomposed. The treatment carried out with TiO_2-mp 0.01% (Figure 5.17 B) improved the degradation rates of the 5 compounds, especially BP3 concentration decreased of 60%. In this case, TiO_2 obviously increased the production of hydroxyl radicals due to its reaction with UV light. Moreover, it is reasonable to assume that ultrasounds speed up this reaction, and in order to verify this hypothesis, the treatment of the combined process with TiO_2 was compared with the same reaction performed without ultrasounds (Figure 5.18). The degradation rates related to the treatment with ultrasounds are bigger than those obtained in absence of ultrasounds, which have a mechanical effect because they mix the solution improving radical reactions between the oxidant

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species and the target molecules. Ultrasounds also improved the dispersion of TiO_2 in the solution.
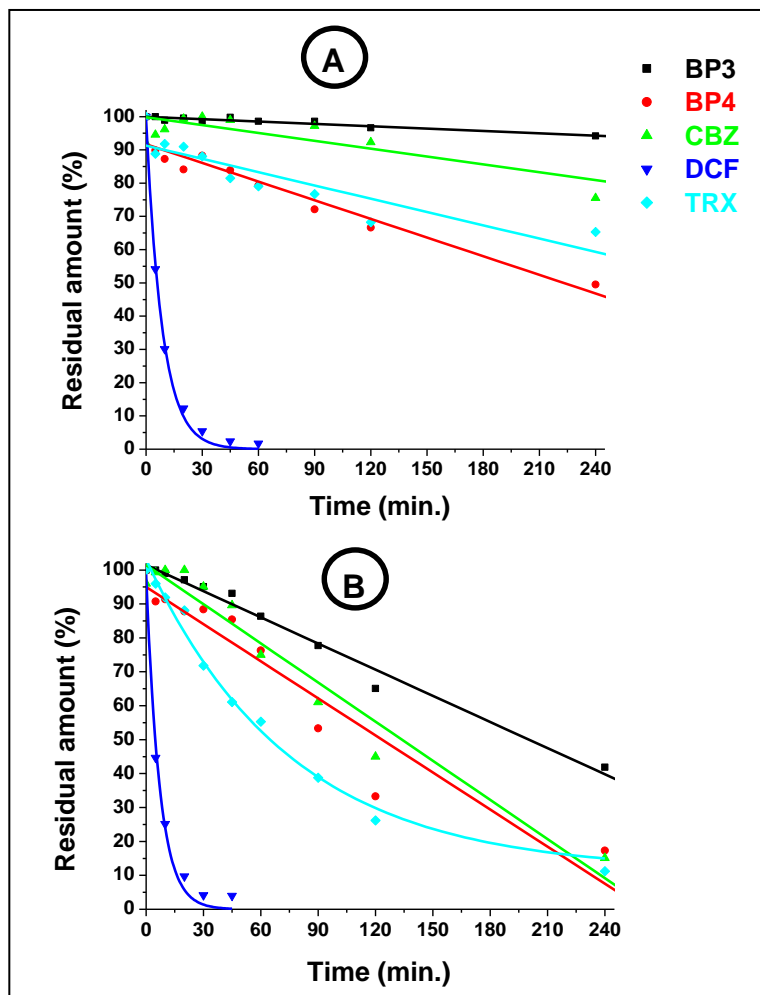
Figure 5.17 Residual amounts of the five compounds during the UV – ultrasounds combined process without TiO_2 (A) e with TiO_2 (B).
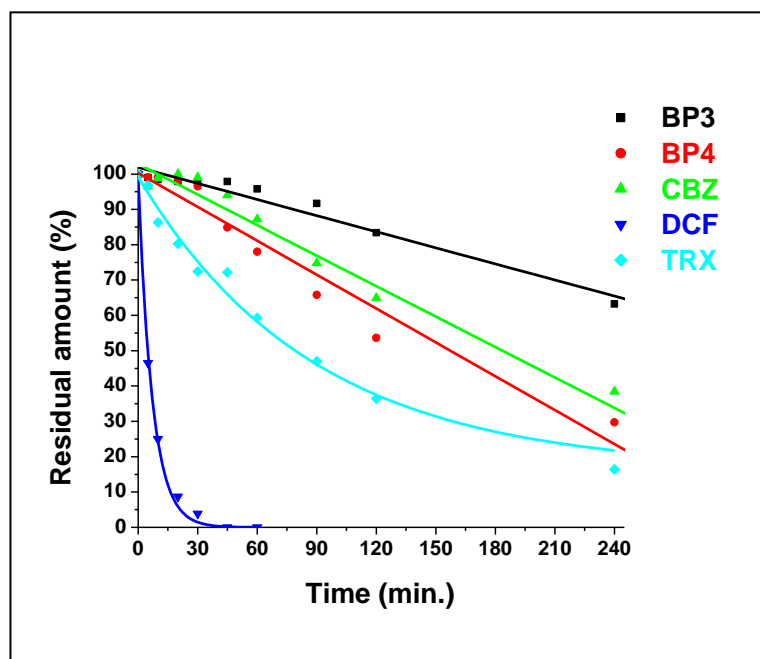
Figure 5.18 Residual amounts of the five compounds during the UV - TiO₂-mp without ultrasounds.

Since the presence of TiO_2 improved the efficiency of the degradation, growing concentrations of photocatalyst were tested. The treatment with TiO_2-mp 0.6% (Figure 5.19 A) allowed to obtain the same results of the treatment with 0.01% of photocatalyst in less time (90 minutes instead of 4 hours). Adding even more TiO_2 to the solution, 1 %, (Figure 5.19 B) the degradation rates did not change if compared to the previous treatment. It is possible to conclude that TiO_2-mp 0.6% was the optimum concentration for the UV light supplied by the experimented system.

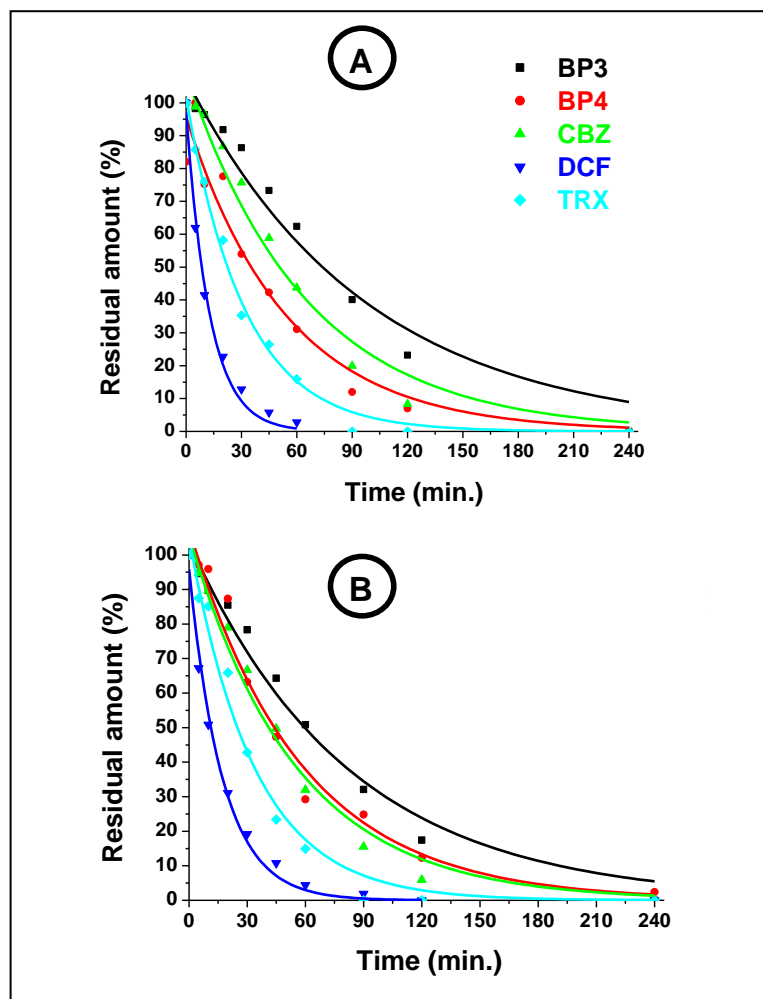**Figure 5.19 Residual amounts of the five compounds during the UV – ultrasounds combined process with TiO$_2$-mp 0.6% (A) and TiO$_2$-mp 1 % (B).**

5.5 ENERGY CONSUMPTION

All the three treatments on the MIX 5 solution were compared on the basis of the electric energy consumption. This parameter represents the main operating cost of each treatment and indicates if a process is convenient considering the ratio between the required energy and the results that can be obtained. Therefore the energy necessary to remove 1 g of pollutant after 2 hours of treatment was calculated, as suggested by the IUPAC, as follows:

$$E_{EM} = Pt / V (\gamma i - \gamma f)$$

The formula does not include chemical substances added to the treatment, neither materials and energy necessary to the installation, so the TiO_2 was not considered in the calculation. Figure 5.20 represents the results of this investigation, each bars of the histogram corresponds to the energy consumed by each treatment on MIX 5 reported in this thesis. The first bar is referred to photocatalytic test carried out on in the photochemical reactor. This test was on laboratory scale, it required more than 40 kWh/g of energy to decompose almost totally the MIX 5 compounds. Comparing this test to the one performed on pre-industrial scale (the last bar of the histogram), it results that the energy consumption was 16 times lower and the degradation rate was good, more than 70%.

The treatment related to the combined process with UV and ultrasounds which is the pink bar, allowed to decrease the MIX 5 concentration of 36% spending 10 kWh/g. In the presence of TiO_2, the energy consumption decreased and the degradation rate increased, especially when TiO_2 concentration was 0.6%, represented by the blue bar (in this case the MIX 5 was decomposed of 92% and the energy consumption was 5 kWh/g). The treatment performed in the ultrasound bath with UVC and TiO_2-mp 0.01%, without ultrasounds (green bar) allowed good degradation rate and the lowest energy consumption 1.4 kWh/g.
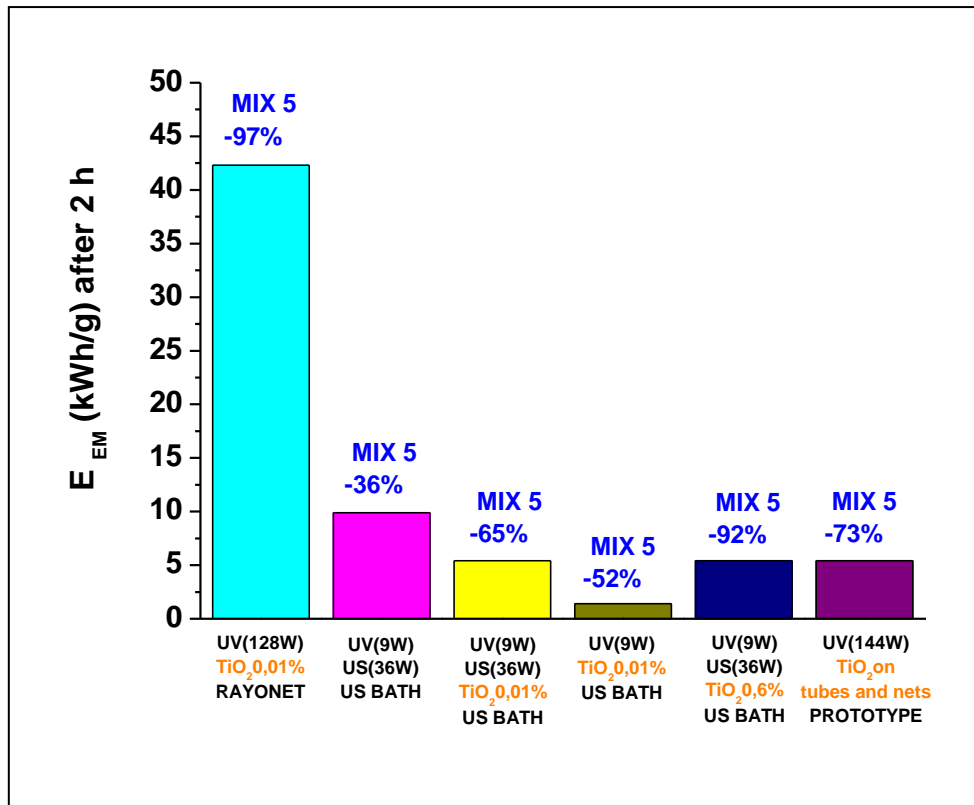
Figure 5.20 Comparison of electric energy necessary to remove 1 g of pollutant after 2 hours of all the treatments carried out on the MIX 5 solution.

6. CONCLUSIONS

The presence of organic pollutants in water bodies gives cause for concern, especially because of the toxic effects induced by these contaminants on aquatic organisms and humans.

The use of advanced treatments downstream of conventional biological processes would reduce considerably inputs of micropollutants in the ecosystem.

Photocatalytic processes experimented in the activity research of this PhD are considered an effective solution for the removal of organic contaminants from wastewater. Many research studies have been devoted to the development of such processes, however, most of them have been experimented for the removal of single compounds from synthetic aqueous solution by test on laboratory scale and without taking into account the issues related to the scale-up of the process. It is important to evaluate the treatment of mixture of different compounds as they are found in the environment and to study the conditions necessary for the implementation of the process on the real scale.

For this reason, in this study the photocatalytic process was studied for the removal of a mixture of emerging contaminants, selected from classes of pharmaceutical compounds and personal care products.

The simple treatment with UVC, already used as sanitizing post-treatment in wastewater treatment plants, has represented the reference process to evaluate the effectiveness of the photocatalytic process. If correctly powered and coupled with air, the use of UVC radiation can significantly decrease the concentration of the five molecules selected as representative of the main categories of EOCs.

Regarding the photocatalytic processes, both TiO_2 in suspended micropearls and supported on a quartz fiber resulted to be effective for the degradation of EOCs as well as all the classes of surfactants. However, the presence of inorganic ions in TW decreased the degradation rate for the plain UVC treatment as well as for the photocatalytic one.

TiO$_2$-qw leaded to better performances with respect to a commercial TiO$_2$-mp suspension of similar concentration, because it allowed a wider distribution of the photoactive material on the substrate surface. Pristine TiO$_2$-qw after 4 hours of UVC irradiation attained a mineralization of organic contaminants higher than 90% and about the 70% in DW and TW, respectively. Furthermore, it had the advantage to be easily recovered and reused 7 times without a relevant efficiency loss. Repeated treatment with UVC, TiO$_2$-qw and air in TW achieved an EOCs degradation of about one order of magnitude and an average mineralization of about 55% over 7 consecutive cycles, making it a promising technology to abate those EOCs showing to be refractory to the conventional WWTP.

The degradation of a more complex sample, the second rinse of laundry machine, using UVA radiation and TiO$_2$ led to the degradation of anionic and non ionic surfactants. However, under the condition described above, TOC decreases of 35% suggesting that, on real samples, the efficiency of the process decreases significantly and further specific investigations are needed.

The scale up of the photocatalytic process from less than 1 L to about 10 L allowed to obtain better degradation rates with lower energy consumption per mass unit of contaminant, improving the sustainability of the processes.

Regarding the coupled processes, ultrasounds speeded up the degradation rate, but energy consumptions increased significantly, consequently the use of ultrasounds is justified to improve the convection into the photoreactor and optimize the suspension of the photocatalyst.

In the end, choosing the degradation treatment, it is important to consider the aims to achieve, such as the costs and the degradation rates.

Even if a large number of economical and technical evaluations have to be carried out yet, AOPs represent a wide scope of technologies very promising as tertiary treatments to fight the large number of EOCs that pass through conventional WWTPs contributing to meet the environmental and societal challenges.

ACRONYMS

WWTP   wastewater treatment plant

EOC   emerging organic contaminant

AOP   advanced oxidation process

BOD   biochemical oxygen demand

COD   chemical oxygen demand

TOC   total organic carbon

TOD   total oxygen demand

APnEO   alkylphenyl polyetoxylate

TRX   triton X-100

CBZ   carbamazepine

DCF   diclofenac

BP3   benzophenone-3

BP4   benzophenone-4

WFD   water framework directive

UV   ultraviolet

TiO_2 titanium dioxide

LED   light emitting diode

EAOP   electrochemical advanced oxidation process

DW   deionized water

TW   tap water

TiO_2-mp TiO_2 micropearls

TiO$_2$-qw	TiO$_2$ quartz wool
HPLC	high performance liquid chromatography
CAD	charged aerosol detector
XRD	X-ray diffraction
SEM	scanning electron microscopy
E$_{EM}$	electric energy per mass

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