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WATER REMEDIATION 2.0: ADVANCED OXIDATION PROCESSES

MANY SYNTHETIC MOLECULES CONTAMINATE THE AQUATIC ENVIRONMENT THREATENING THE BIOSPHERE AND HUMAN HEALTH. AMONG THEM, PHARMACEUTICALS AND PERSONAL CARE PRODUCTS ARE BECOMING OF CONCERN BECAUSE OF THEIR INCREASING DIFFUSION AND RESISTANCE TO CONVENTIONAL DEPURATION PROCESSES. ADVANCED OXIDATION PROCESSES ARE INNOVATIVE AND EFFECTIVE TERTIARY TREATMENTS TO MINERALIZE BIORECALCITRANT ORGANIC CONTAMINANTS

Canale Navile, Bologna. In the background the new building of the Department of Chemistry

The co-authors dedicate this article to dr. S.S. Emmi on the occasion of his retirement.

Water and societal challenges

The societal challenges of the Europe 2020 strategy have been defined as :

i) health, demographic change and wellbeing;
ii) food security, sustainable agriculture and forestry, marine and maritime and inland water research, and the bioeconomy;
iii) secure, clean and efficient energy;
iv) smart, green and integrated transport;
v) climate action, environment, resource efficiency and raw materials;
vi) Europe in a changing world - inclusive, innovative and reflective societies;
vii) secure societies - protecting freedom and security of Europe and its citizens.

Even if water is named only in one challenge, it is clearly involved in any of the other ones, with the sole possible exclusion of transportation. In fact, abundant and healthy water is at the base of the wellbeing and food production but water is also a key component of the environment and a raw material for many manufacturing process and its depuration is an energy intensive activity. The water capture, treatment and distribution use about the 15% of the produced energy but water itself is involved in the energy production as well as in food production and industrial processes [1]. A low fossil fuels intensive technology to water depuration will have a wide impact in the life of Europeans, as this technology will contribute to mitigate climate change effects through highly efficient drinking water production. Furthermore, being water one of the primary good for human life, its availability at low price for all the citizen produce cohesion and stability. Water, energy and food are connected in a chain to which our society is hanging, the lack of one of them results in a breakdown of the accessibility to the other two, especially for the most vulnerable part of the population. About 1,500 m^3 of water is what each person needs annually for a decent life. Roughly 2 m^3 of highest quality for drinking, 20 m^3 for hygiene and cooking, and 250 for services and industrial needs, all of it, comes from the aquifers (water usable by humans) that constitute the 1% of the global water. The rest of the above water amount is for growing food and mainly is rain water. Today there are around seven billion people on Earth and according to the official United Nations (UN) projections, by 2050 the world population is expected to reach around ten billion people [2]. To satisfy the human needs of such a population an almost proportional increasing of safe and cheap water is as important as the energy availability. Statistics indicate that around 1/5 of world population lives in areas of water scarcity, and another 1/4 faces economic water shortage [3], also related to climate changes. In fact, seasonally and spatially variable precipitation patterns and river transporting the run-offs govern the local and regional availability of water. Finally, only 0.3% of freshwater sources is readily drinkable [4] and these sources must be protected from pollution.

Water pollutants

The "Directive 2013/39/EU of the European Parlament and the Council of the 12 August 2013 amending Directive 2000/60/EC and 2005/105/EC regards priority substances in the field of water policy", contains a list of 45 "priority substances whose concentration must be below the environmental quality standards (EQSs) that range from 0.1 to 10 μg L^{-1}. Among them, 41 are organic or organohalogenate compounds and almost 25 of them are pesticides, the other are related to industrial activity. Also the ten substances of the new "watch list" provided in the directive above mentioned, and recently established by the Decision 2015/495 of European Commission, are organic compounds. These substances, that after the monitoring period can become "priority substances", include: pharmaceuticals (17-α-ethinylestradiol; 17-β-estradiol and estrene; diclofenac; macrolide antibiotics such as erythromycin, clarithromycin, and azithromycin), a personal care product (2-ethylhexyl-4-methoxycinnamate), an antioxidant (2,6-ditert-butyl-4-methylphenol), and several pesticides, yet (methiocarb, oxatiazon, tri-allate; and neonicotinoids such as imidacloprid, thiacloprid, thiamethoxam, and clothianidin). In Italian rivers, 17 pesticides (dieldrin, AMPA, sinazine, terbutylazine, diuron, 2,4-DB, 2,4-D, terbutryne, cadusafos, endosulfan sulfate, azoxystrobin, malathion, metolachlor, pendimethain, bentazone, alacholor and linuron) have been found above the EQSs of the directives. Another class of contaminants to be taken in evidence for the quality of water are the so called emerging organic contaminants (EOCs) that the United States (US) Environmental Protection Agency in 2014 defined as new chemicals without regulatory status and whose impact on the environment and on the human health is poorly understood although potentially harmful [5]. The studies on EOCs has been taken into account to compile the above mentioned "watch list" and will be used to update it. Usually, the knowledge of EOCs impact on aquatic environment and human health in the middle or long-term is poor but the precaution principle suggests their check and limitation. EOCs include chemicals which have just appeared on the market, or those already present in the environment but whose significance is yet under investigation [6]. The EOC concentrations measured in the aquatic environment generally range from ngL^{-1} up to μg L^{-1}, and only recent advances in analytical techniques [7] enabled the detection of such low concentrations both in surface [8] and drinkable water [9]. Furthermore, in some effluents of pharmaceutical manufacturing farms and in some influents of municipal wastewater treatment plants (WWTPs), the maximum concentration of some pharmaceuticals have been found in the order of mgL^{-1}, for example: carbamazepine 0.84 mgL^{-1} and venlafaxine 11.7 mgL^{-1} [10], ciprofloxacin 31 mgL^{-1} [11], salicylic acid and naproxen 0.6 mgL^{-1} [12], and diclofenac 0.2 mgL^{-1} [13]. EOCs are also natural contaminants as, for example, caffeine that, in a survey over 23 European countries (164 sampling sites), has been detected with a frequency of 83% (l.o.d. 1 ngL^{-1}) with an average concentration of 13 ngL^{-1} and a maximum value of 89 ngL^{-1} [14]. Since most EOCs are not completely removed by conventional WWTPs, they occur in the environment as multi-component mixtures having an ecotoxicity rate higher than any single compound [15]. In many cases, bacteria detected in the effluents of WWTPs showed resistance to several antibiotics [16]. In a US survey dealing with 65 organic contaminants, the most frequently found on 47 ground water sampling sites, were diethyltoluamide (an insect repellant, frequency of detection 35%), bisphenol A (from the polymer industry, 30%), tri(2-chloroethyl)-phosphate (fire retardant, 30%), sulfamethoxazole (veterinary and human antibiotic, 23%), carbamazepine (anticonvulsant, 20%), tetrachloroethylene (solvent, 24%), 1,7-dimethylxanthine (caffeine metabolite, 16%), and 4-octylphenol monoethoxylate (derivative of surfactants, 19%).

Fig.1
The main emission way of EOCs to the environment are WWTP effluents

In a study on 164 ground water samples across Europe [17] perfluorooctanoic acid (PFOA) was detected (l.o.d. 0.4 ngL^{-1}) with the frequency of 66%, an average concentration of 3 ngL^{-1} but a maximum concentration of 9 ngL^{-1}. PFOA and perfluorooctylsulfonate (PFOS) have been recently suspected to interact with endocrine system. They are very stable compounds and their sources are mainly industrial effluents consequently they can be easily intercepted and treated.

In addition to anthropic contaminants, some natural contaminants should be considered, for example, in many European countries cyanotoxin and microcystins, toxins produced by some algae flourishing in summertime, occasionally contaminate the fresh water basins and sometime pass through the depuration plants reaching municipal waterworks [18].

The main emission way of EOCs to the environment are the WWTP effluents and the sewage leakage from municipal pipelines, but the use of the WWTP effluents and their sludge as fertilizer in agriculture can introduce the biorecalcitrant molecules in the ground.

Advanced oxidation processes

The removal of organic pollutants from water are currently carried out by means of separation processes (sedimentation, flocculation, filtration, electrocoagulation, absorption in active carbons etc.) or biological digestion. However, separation processes concentrate contaminants in sludge or solids that must be destroyed elsewhere and biological digestion is not able to remove many biorecalcitrant pollutants. On the other hand, several chemical oxidation processes can be used for water sanitization (chlorination, ozonation) but they do not abate total organic carbon (TOC) and sometime generate hazardous byproducts (i.e. dichloromethane from humic acids after chlorination). Several advanced oxidation processes (AOPs) have been recently developed to destroy the organic pollutants into the water bulk transforming them in non-harmful compounds, without the need of separation and post-treatment processes. AOPs include photolysis of H_2O_2 or O_3, photo-catalysis (light based AOPs), electron-beam, plasma technologies, supercritical water oxidation, wet air oxidation, water sonolysis, and other (dark AOPs) [19]. AOPs are based on the generation of the hydroxyl radical, a strong oxidant with E°=1.9÷2.7 V vs. NHE, depending on pH [20], and have the advantage to destroy organic pollutants directly into water with plants smaller than the biological ones. The employment of these new technologies would provide a complete decomposition of biorecalcitrant compounds preventing them from persisting in the environment [21] but also allowing the recycling of water in the perspective of the circular economy. Some of these processes do not generate only $^{\bullet}OH$ (Tab. 1, eq. 1÷6) but also reducing species (i.e. hydrogen atoms and/or solvated electrons) and are occasionally also called "advanced remediation processes". In 2010, the International Atomic Energy Agency (IAEA) started a Coordinated Research Project entitled "Radiation treatment of wastewater for reuse with particular focus on wastewater containing organic pollutants", due to end in 2016, where the comparison of ionizing and non-ionizing radiation technologies is the task entrusted to the authors of the present article.

Tab. 1

Radical reactions in AOPs

(R = aliphatics; Ar = aromatics)

Radical oxidation of organic molecules	
(1)	$RH + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}R$
(2)	$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$
(3)	$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$
(4)	$ArH + {}^{\bullet}OH \rightarrow ArH(OH)^{\bullet}$
(5)	$ArH(OH)^{\bullet} + O_2^{\bullet} \rightarrow [ArH(OH)OO]^{\bullet}$
(6)	$[ArH(OH)OO]^{\bullet} \rightarrow ArH(OH) + HO_2^{\bullet}$
UV photolysis	
(7)	$O_2 + h\nu\ (185\ nm) \rightarrow 2O^{\bullet}$
(8)	$O^{\bullet} + O_2 \rightarrow O_3$
(9)	$H_2O + h\nu \rightarrow 1/2H_2 + {}^{\bullet}OH$
(10)	$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O$
Photocatalysis	
(11)	$MOx + h\nu \rightarrow MOx^{*}\ (e^{-}, h^{+})$
UV and H_2O_2	
(12)	$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH$
(13)	$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet}$
(14)	$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$
O_3 and UV/O_3	
(15)	$O_3 + H_2O \rightarrow 2{}^{\bullet}OH + O_2$
(16)	$O_3 + HO^{-} \rightarrow O_2^{\bullet -} + HO_2^{\bullet}$
(17)	$O_3 + h\nu \rightarrow O_3^{*} \rightarrow O_2 + O^{\bullet}$
(18)	$O^{\bullet} + H_2O \rightarrow H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH$
Sonolysis	
(19)	$H_2O \rightarrow H^{\bullet} + {}^{\bullet}OH$
(20)	$O_2 \rightarrow 2O^{\bullet}$
(21)	${}^{\bullet}O + H_2O \rightarrow 2{}^{\bullet}OH$
Electrochemical AOPs	
(22)	$H_2O \rightarrow {}^{\bullet}OH + H^{+} + e^{-}$
(23)	$2{}^{\bullet}OH \rightarrow H_2O_2$
(24)	${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$

Light AOPs

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 [22].

Besides to its disinfection effectiveness, UV can also degrade organic compounds by direct photolysis of photolabile compounds as a consequence of light absorption [23], 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 amount 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. 7) which, reacting with O_2, produces O_3 that is dissociated by the 254 nm radiation (eq. 8) [24]. In addition, the VUV radiation dissociates H_2O (eq. 9) producing $^{\bullet}OH$ that attacks the dissolved or dispersed organic matter (eq. 10). The VUV process is very simple, it has the advantage that no chemicals need to be added [25].

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. 11. 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 [21] (Fig. 1). 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 [26]. 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

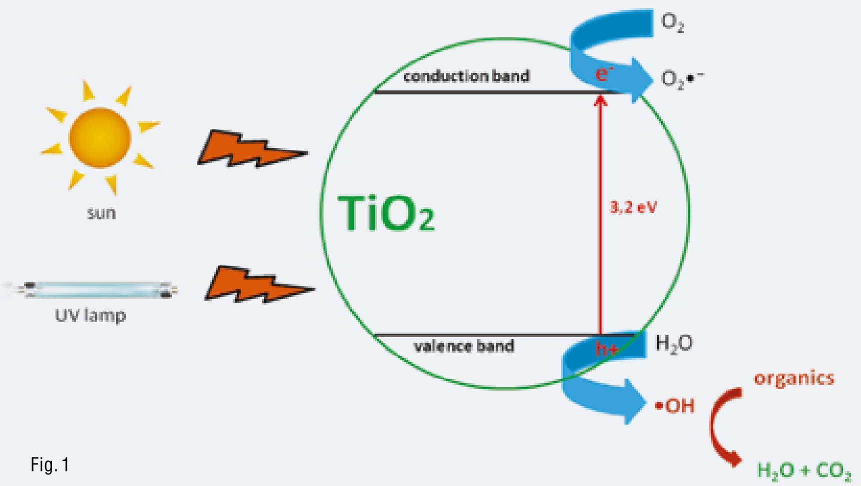

Fig. 1
Scheme of photocatalysis

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, holes 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 [27]) 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 coupling with other functional materials. Carbon based materials have been 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 [28]. 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 [29, 30] but the immobilization of the photocatalyst on suitable solid matrices would ensure some advantages, such as 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 [31]. 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 [32]. In a recent project on domestic appliances funded by the Italian Ministry of Economic Development (program *Industria 2015* for the industrial development), the photocatalytic AOP was studied by the authors of this article, to reuse the second rinsing water for the following washing cycle in the domestic laundry machines.

UV and H_2O_2

This AOP process is performed by irradiating the polluted water added of 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. 12). 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. 13, 14). 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 efficiency. The photolysis of aqueous H_2O_2 is pH dependent and increases when more alkaline conditions are used [25]. 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.

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 [20]). In water, O_3 decomposes into the more powerful oxidant $^{\bullet}OH$, and the milder $O_2^{\bullet}$ (eq. 15, 16). When irradiated with UV light at 254 nm (ε=3,600 $M^{-1}cm^{-1}$ [33]), ozone enhances the production of $^{\bullet}OH$ (eq. 17, 18), 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 [27].

Dark AOPs

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 microbubbles. In other word, 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 5,000 °C, and pressures of about 100 MPa. 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 [34]. Governing the conditions to produce cavitation and

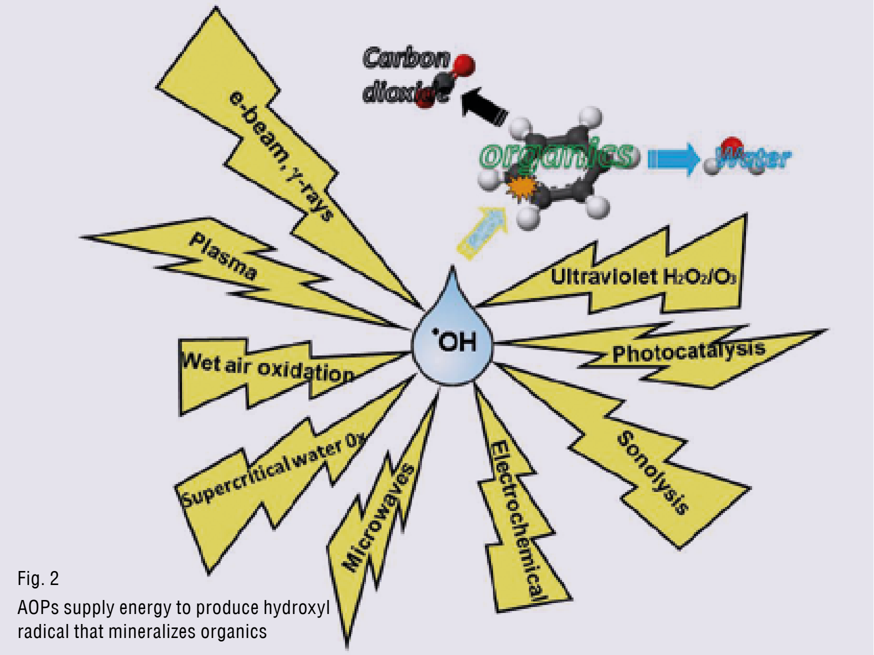

Fig. 2
AOPs supply energy to produce hydroxyl radical that mineralizes organics

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.

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 gL^{-1}, whereas biological treatments are useful from 0.001 to 1 gL^{-1} and other AOPs from 0.01 to 10 gL^{-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 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 [35].

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 absorbed 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 [36]. 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 electric 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. By decreasing the size of the working electrode down to less than 1 mm of diameter, the signal-to-noise ratio encreases 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 [37, 38]. The acoustic energy concentrated into the microbubbles, within time scale of the order of 1 ns, leads to extreme conditions of pressure and temperature [39]. Sonoelectrochemistry has been used to destroy some organic contaminants directly, such as trichloroacetic acid [38] or bovine serum albumine [40], or coupled with Fenton reagents, to destroy pollutants such as 2,4-dichlorophenoxyacetic acid, 4,6-dinitro-*o*-cresol, and azobenzene [41].

Non-thermal effect of microwaves

In order to enhance the activity of photocatalysts, in 2002 Horikoshi *et al.* proposed the coupling of microwaves to UV radiation. The author tested the absorption of microwaves 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 [42].

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 [43].

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 [44]. Processes in a supercritical water environment require the construction of expensive and complex equipments. 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 [45].

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 kinetic energies 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 [46]. 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.

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}Co) 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 1,000 m^3 per day. Therefore, e-beam fits the need of medium-large WWTPs which treat effluents strongly polluted, for example those coming from dye, textile, and paper mill industries, hospitals, municipal and animal-breeding plants [47].

Comparison of AOPs

Some authors compare the different AOPs on the basis of the effectiveness to remove the pollutants, even measured by cumulative concentrations such as natural organic matter (NOM), TOC and COD, but the $^{\bullet}OH$ concentration, and consequently the oxidation efficiency, strictly depends on the AOP conditions [48] so that the comparison of the method performance is not related to a single variable, but depends on a large number of parameters [49] that do not allow a rationalization of the results.

For example, comparing UV, O_3, H_2O_2/O_3,

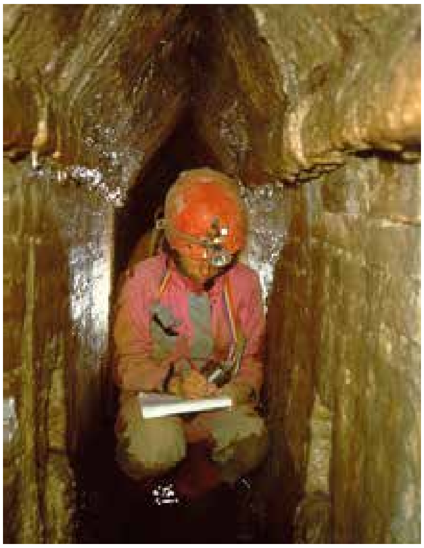

Fig. 3

The Roman underground aqueduct that connects Setta river to Bologna city with a gallery 18 km long

H_2O_2/UV, and O_3/UV treatments on surface river water in bench-scale, the authors [50] conclude that the last two processes are viable to partially remove the NOM decreasing the related formation of disinfection byproducts during the following process for drinking water production.

Since most AOPs are electric energy intensive methods, the use of renewable sources is desirable. Electric energy can also represent the main AOP operating cost, then a simple figure-of-merit based on energy consumption can be adopted to compare different AOPs. In 2001, the International Union of Pure and Applied Chemistry [51] published a report where some figures-of-merit were suggested. In particular, for high pollutant concentrations (TOC>0.1 gL^{-1}), the electric energy consumption per mass of organic pollutant removed from a stationary reactor (E_{EM}) in [$kWhg^{-1}$] is:

$$E_{EM} = Pt/[V(\gamma_i - \gamma_f)]$$

where P is the electric power [kW] input to the system, V is the volume [L] of water treated in the time t [h], γ_i and γ_f are the initial and final mass concentrations [gL^{-1}], respectively. By using the flow [Lh^{-1}] instead of the ratio between volume and time ($F=Vt^{-1}$), a similar formula can be obtained for flow reactors. However, E_{EM} is only one of the parameters useful for the life cycle assessment (ISO 14040-14044) that is becoming the standard procedure for the comparison of the different industrial processes, AOPs included.

The economical costs of AOPs, both investment and operating costs, strongly depend on the cost of the energy, the capital cost, the pay-back time, and the benchmark cost (i.e. the cost of water depuration by regular plants) that change over time and from a country to another, are not quickly comparable. In 2010 Mahamuni and Adewuiy [52] published a cost analysis of several AOPs involving ultrasounds that elucidates on the contribution of capital, labor, maintenance, and energy costs. The authors evaluated energy cost for the treatment of a cubic meter of wastewater contaminated by phenol, trichloroethylene, or reactive azo-dyes, starting from lab-scale rate constants and energy consumptions, and scaling-up them to 1 m^3min^{-1}.

The resulting costs in US Dollars ($) were widespread, ranging, for example for phenol degradation, from about 4000 $\$m^{-3}$ by using ultrasounds alone, to 23 $\$m^{-3}$ by using ultrasounds with UV and O_3. The use of ultrasounds alone is the most expensive treatment because of the inefficient conversion of electric energy to cavitation energy.

However, ultrasounds always contribute to lower the cost of any other AOPs because they enhance the mass transport toward the reaction site. A study on UV-based AOPs reports that, the sum of reagents and electricity (the last one stated as 0.1 $\$kW^{-1}$) costs for the degradation of the 50% of 3-methylindole 1 $molL^{-1}$ in ultrapure water, ranges from 144 for UV to less than 0.1 $\$m^{-3}$ for Fenton-based processes [53], depending strongly on the energy consumption. However, as the large number of assumptions made for the calculation does not allow an easy comparison to other authors, one can conclude that the cost of UV-based AOPs is in the order of magnitude of the dollars per mole of EOC destroyed, but the eventual matrix effects have not yet been evaluated. An industrial plant with an e-beam of 1 MeV and 400 kW, combined with biological WWTP for treating about 100 Ls^{-1} of textile dyeing wastewater, has operated

Fig. 2

The e-beam plant in Korea (courtesy of Mr. B. Han, EB-Tech Ltd.)

since 2005 in Korea (Fig. 2). This plant shows the reduction of chemical reagent consumption, and also the reduction in retention time with the increase in removal efficiencies of COD, Cr and BOD_5 up to 30÷40% with an estimated cost of 0.3 $\$m^{-3}$, all included, assuming 8000 hours per year of operating time and 20 years of life time [54].

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.

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Bonifica dell'acqua 2.0: processi avanzati di ossidazione

Molte molecole di sintesi contaminano le acque minacciando l'ambiente e la salute umana. Tra queste, i prodotti farmaceutici e per la cura della persona stanno diventando un problema per la loro crescente diffusione e resistenza ai processi di depurazione convenzionali. I processi avanzati di ossidazione promettono trattamenti terziari per mineralizzare contaminanti organici bioresistenti.

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