Sustainable Water Use and Technologies*

by Gabriele Centi and Siglinda Perathoner

The sustainable use of water is becoming a critical issue in Europe and requires a new management approach in water use. Water pollution must be lowered in its contamination and new technologies for water purification developed. Water use and quality in Europe are briefly reviewed and advanced technologies for water purification are discussed with emphasis on the role of catalysis in these technologies.

The sustainable use of water is beginning to be recognized as a critical issue in Europe [1] and worldwide. The population growth and industrial development are the driving forces for increased water demand which leads to increased water stress and damage to ecosystems and human development. Inadequate amount of water or poor water quality create a conflict between human demand for water and wider ecological needs, both in highly industrialized regions and in countries where low rainfall results in low water availability and a lack of water quality [2]. The solution to this problem requires an integrated approach between better management of water resources and cycling, an increase in water recycling, a reduction in both point and diffuse water pollution as well as the development of advanced technologies for water purification and for the reduction of both direct and indirect pollution.
After a brief review of the key aspects on water use and quality in Europe which are discussed in more detail in the cited "Sustainable use of Europe's water?", a report of the EEA (European Environment Agency) [1], advanced technologies for water purification are discussed here with emphasis on the role of catalysis in these technologies.

Water use and quality

On average in Western Europe, 16% of the fresh water supply is withdrawn from available sources to be used for anthropogenic activities, but this percentage can reach as much as 50% in some Mediterranean countries, because the water sources are far from evenly distributed. In addition, the water needed to sustain aquatic life should be considered. Therefore, although less than one-fifth of the available water is consumed, there are resources problems in several European regions with a consequent sharp increase in the cost of water in recent years. Furthermore, most water withdrawn from a particular source is not returned to that source but rather returns to the overall water supply at a different point from where it was obtained. This causes a significant impact on water sources, even though the net consumption of water is relatively small. About 50% of major wetlands in Europe are classified as "endangered status" as a result of overexploitation of groundwater resources.
On average in Europe, 18% of the water consumed is used as public water supplies, 30% for agriculture, 14% for industry (excluding cooling water) and 38% for power and other uses. All these uses cause relevant alterations to the water cycle, such as (i) damming to provide hydroelectricity or water resources, modifying river flow patterns, (ii) population growth, lowering of water resources due to consumption for public supplies and irrigation, (iii) land sealing by urbanisation and (iv) agricultural drainage and flood control, modifying the hydrological cycle and water balance. A more sustainable use of water resources requires improving water management in all these areas, and especially reducing water consumption, such as measures to increase the awareness about water conservation, reducting leakage in water distribution systems, and increasing reuse of wastewater. Several of these aspects are included in the recent EU "Water Framework Directive" (COM(97) 49 final) which, when adopted by the single states, will rationalize EU water legislation and establish a framework for water protection.
Water pollution is the other result of human activity with a massive influence on the water cycle. Pollution may be broadly classified as point and diffuse pollution. Point

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**Based on a lecture given at the ICS-UNIDO Workshop "Catalytic Processes for Clean Chemistry and Water and Air Depollution", Hammemet (Tunisia), Nov. 2000.*

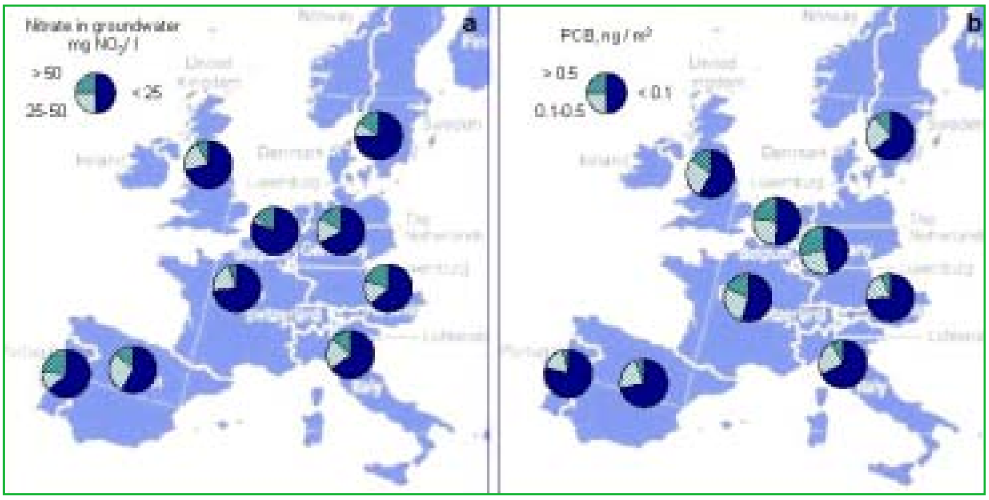

Figure 1 - Distribution map of nitrate in groundwater and PCB (polychlorinated biphenyls) in Europe. EEA (http://www.eea.eu.int/) and EMEP (http://www.emep.int/) sources

sources include discharges from sewage treatments and industrial processes. Diffuse sources are less clearly identified and derive from several activities such as run-off from agricultural land and urban areas, and pollution from waste disposal. While relevant progress has been made in controlling point sources, diffuse pollution has been scarcely addressed.

Water pollutants include organic matter (which may be further classified in biodegradable, recalcitrant or hardly-biodegradable, POPs - Persistent Organic Pollutants - which include several pesticides, and toxic substances), phosphorus, nitrogen (from excess application of fertilizers and manure, but also from urban wastewater treatment plants) and heavy metals.

Phosphorus and nitrogen in rivers (a main source of drinking water in Europe) can cause eutrophication with excessive growth of plants, which on death and decay can deplete water oxygen levels and water suitability for consumption, besides the negative impact on the ecosystem. In many European rivers, the phosphorus concentrations decreased significantly between the late 1980s and the mid 1990s, whereas nitrate concentrations increased rapidly in the same period.

Nitrate is a significant problem in several part of Europe. The EU Drinking Water Directive indicates a level of 25 mg NO_3/l, but in over 50% of the tested groundwater areas in the EU more than a quarter of the sampling sites exceed this guide level. Figure 1a shows that a large proportion of the sampling sites is above the recommended value of 25 mg NO_3/l and around 10-20% also above the threshold value of 50 mg NO_3/l.

Pesticides represent another relevant issue in Europe. The most commonly found pesticides in groundwater appear to be atrazine, simazine and lindane. However, of approximately 800 active substances registered for pesticide use in Europe, only a fraction is effectively monitored. Several sampling sites have a level of pesticides greater than the Drinking Water Directive maximum allowable concentration of 0.1 μg/l. Figure 1b shows that in several cases in Europe the concentration of PCBs (polychlorinated biphenyls) exceeds the threshold value of 0.1 μg/l. Chlorinated hydrocarbons, which derive from old landfills, contaminated industrial sites and industrial, energy or military activities, are also important groundwater pollutants.

Ammonia is also an important potential pollutant, being toxic to aquatic life. It comes from sewage effluents and run-off from fields spread with animal manure. Although data are not complete, the available information indicates that ammonia is a potential problem in many European rivers and above the threshold value of 0.5 mg/l.

Surface water acidification derives mainly as a secondary effect of air pollution by nitrogen and sulphur oxides. Although acidification remains a problem in many areas, controls on sources of acid emissions have brought about substantial improvements in the alkalinity in northern and central Europe. Pollution of groundwater by heavy metals (mostly by leaching from dumping sites, mining activities and industrial discharges) has also been relevantly reduced, but remains a severe problem in Eastern Europe.

There are thus different levels of problems regarding water pollution. The reduction of pollution is possible for point sources by extending the use of cleanup technologies or improving their performances using advanced methodologies, and using “water-care” production processes or improving water recycle and management. For diffuse sources, a more rational use of resources (for example, pesticides and fertilizers) and improved control in solid waste management is needed, but it is also needed the development of “on-site” remediation methodologies and technologies for water purification.

Sustainable water use thus requires a complex, interdisciplinary and multilevel approach, which includes an intensified effort in improving or developing new technologies for water treatment or reuse.

Technological needs for sustainable water

Although relevant progress has been made in the last decade, sustainable water use requires a change in the approach to water and wastewater management, but also advances in scientific and technological knowledge. In terms of scientific advances, critical topics are the understanding of the impact of existing pollutants (and of emerging ones), including improved modelling techniques and analytical tools, and of new water management approaches. But of equal relevance is also the need for developing new advanced technologies.

In terms of water quality issues, there are problems which are progressively reduced with current methodologies/technologies such as those of phosphorus levels, acidification of surface water, and contamination by heavy metals and those which need further effort in developing better and sustainable technologies. These include, but are not limited to:

- reduction of the contamination of groundwater and especially drinking water by nitrates, and by pesticides (or other POPs) and chlorinated hydrocarbons;
- improved technologies which allow reuse of wastewater;
- advanced technologies for the elimination of chemicals having a toxic effect on microbiological activity from diffuse sources such as elimination of polyphenol emissions in agro-food production.

Sustainable water technologies, besides being economic and easily manageable should avoid secondary pollution or the simple transfer of the pollutants from one stream to another.

Water treatment technologies are often multistep processes which include:

- *primary treatments* - They are based mainly on physical action; examples are screening, sedimentation, filtration and flotation;
- *secondary treatments* - They are based on chemical and biological processes which convert the chemical structure of the constituents of wastewater to products either innocuous or less hazard; examples are neutralization, precipitation, and active sludge;
- *tertiary treatments* - They are used to convert chemicals difficult to convert or not converted by secondary treatments, and when more stringent water quality is required; examples are active carbon adsorption, ion exchange, reverse osmosis and the AOPs (Advanced Oxidation Processes) which will be discussed in more detail in the following sections.

The typical efficiency in pollutant removal is less than 50% for primary treatments, in the 70-90% range for secondary treatments and over 95% for tertiary treatments. While primary and secondary treatments are well established, the improvement of final water quality in cleanup technologies and therefore the reduction of its impact on the environment and global water cycle requires the use and further development of tertiary treatments. Typical tertiary treatments such as ion-exchange, reverse osmosis, active carbon adsorption, and electrodialysis do not convert pollutants, but rather transfer them from a diluted to a concentred stream. Therefore, it is preferable in a sustainable water approach to use other technologies such as AOP methods which convert pollutants and toxic chemicals to innocuous or not hazardous products, although these methods are usually more expensive and require further development. There is thus a technological need for further developing these technologies and not only for their more extensive application.

Furthermore, these methods find application in combination with other treatments in converting recalcitrant chemicals or in improving water quality in the treatment of a wide range of industrial wastewater effluents. For example, they may be used for converting toxic compounds to chemicals (such as acetic acid, for example) which then can be treated by active sludge in a biological downstream unit.

Although active sludge remains the main technology to reduce the BOD (Biological Oxygen Demand, an index of the content of biodegradable organic substances in water) in wastewater, new technologies are required which can be more flexible in terms of organic loading (often, when there is a peak in the wastewater content of organics the active sludge plant is bypassed and the effluent is directly sent to the river) and content of toxic elements (various chemicals such as phenols, cyanide, etc. and heavy metals are toxic for microrganisms). There is, however, a new driving force which is related to social acceptance of wastewater treatment plants. Typical active sludge plants have a visual negative impact and produce odours which often makes difficult (sometimes impossible) their localization in or near cities. New advanced technologies may hide away the wastewater plant in an office-type block which makes its acceptance by society much easier.

Another problem related to active sludge is the disposal of the sludge. The EU Urban Wastewater Treatment Directive has put severe limitations on the landfill disposal, typical method up to now used (after stabilization, dewatering and thickening). Alternatives are incineration, which is a costly method and may produce relevant amounts of gaseous pollutants, or wet oxidation, either catalytic or not catalytic, briefly discussed in the following sections.

The question of water recycle in industry

There are several types of production which have an intensive use of water, such as automobile and heavy manufacturing, agri-foods and dairy products, the electronics industry and chemical and paper manufacturing. Water is used in processing, washing, cooling and as service water. Water contamination and therefore the possibility of its recycle greatly depends on the specific treatment. Water used in cooling and as service water may be easily recycled, while processing and washing water requires one or more treatments before recycle. Due to the large volumes of water used in washing or processing in some companies, an effort in this direction is mandatory. However, processing and washing water often is characterized by the presence of several toxic or non-biodegradable chemicals. Typical solutions adopted are ion-exchange, reverse osmosis, active carbon adsorption, and electrodialysis, but as discussed in the previous section the development of more sustainable technologies is preferable.

Large efforts have been made by several companies to recycle water. Water recycle, besides reducing the use of water resources and allowing better water management in the company, can also be a relevant economic opportunity, especially when high water quality is required for the production [3]. As discussed in more detail in the cited reference [3], water recycle in printed boards production, semiconductor fabrication and the textile dying industry can lower the cost of water by about 5-15% which, taking into account the large volumes of water used in these processes (typically from 100,000 m^3/y to up to 1 million m^3/y), may represent a very large economic opportunity, besides reducing the negative impact on water resources.

An example is the case of the electronics industry which uses very large volumes of high quality water in the several steps of its production lines [3]. Typically rinse water in the electronics industry is produced in the several steps of (i) cleaning (removal of oil, particles and other contaminants), (ii) etching, (iii) layer deposition and (iv) layer removal. The composition of the rinse water is very complex, due to the presence of different chemicals, although in low concentrations, such as [1] organic acids (methane sulfonic acid, *p*-toluensulfonic acid, formic acid, citric acid, etc.), [2] organic

bases (triethanolamine, thiourea, amines, etc.), [3] surfactants (polyglycol ether, alkyl benzene and alkanes sulfonates, α-sulfo fatty acid esters, soap, fatty alcohol polyglycol ether, etc.), [5] complexing, wetting agents and organic stripping agents (cyanides, tartrate, polyethylene oxide, etc.), [5] other organics (alcohols, resorcinol, γ-butirrolactone, formaldehyde, etc.), and [6] inorganics (H_2SO_4, HBF_4, HCl, K-citrate, NaF, NH_4Cl, Cu, Sn, Ni, Pb).
The development of technologies to recycle this rinse water requires an intense research effort and the combination of different water treatment technologies [3]. Although other types of production processes may have less demanding requirements, the development of water treatment technologies for its recycle requires generally large and costly research activity. The economical, management and environmental advantages in recycling the water can be good incentives for companies having a more long term and strategic perspective of the environmental problem and water sustainability. However, the extensive recycle of water in industrial production requires the adoption of both incentives for research and legislative measures, partly included in the cited EU "Water Framework Directive".

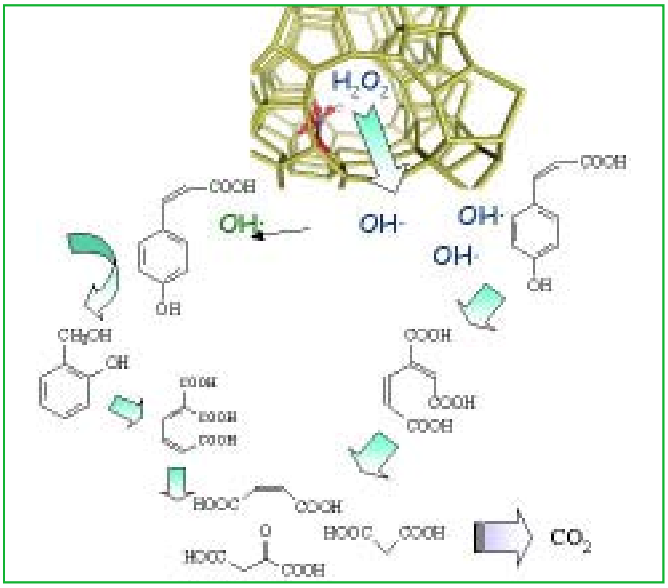

Figure 2 - H_2O_2 activation by a heterogeneous Fenton-type Fe/ZSM-5 catalyst and mechanism of degradation of a model phenol present in olive oil mills wastewater

The issue of wastewater emissions from agro-foods production

Wastewater emissions from agro-foods production, although formally belonging to the class of point sources, may also be included in the class of diffuse sources, because often agro-foods production units are small-size, but widespread over a territory. The total volume of wastewater produced in Europe is quite high and it often contains biostatic or phytotoxic chemicals. As an example, the total volume of wastewater produced from olive-oil mills, wineries and breweries (all characterized by high contents of phenols and polyphenols) is over 10-15 million m^3/y in Europe. Often these agro-foods production units are very small-size, and thus a technology for wastewater treatment should have characteristics different from those possible in industry and, on the other hand, the collection of wastewater in a centralized localization is not feasible. We will discuss this problem in more detail with reference to the case of olive-oil mills wastewater [4].
Olive oil mills produce around 5.5 million m^3 of wastewater characterized by a very high COD (in the 10-60 kg O_2/m^3 range). This waste water contains a very high amount of organics (up to 15% by weight) present in the form of phenols, polyphenols, pectine, colloids, etc. Due to the phytotoxic characteristics of the wastewaters, the development of efficient, cost effective and environmentally acceptable methods for their disposal is a major problem, especially in the countries of the Mediterranean area.
Olive oil wastewater may be treated using different technologies, such as evaporation and incineration, ultrafiltration, reverse osmosis, anaerobic digestion, wet oxidation, chemical addition and photocatalytic treatment, but the analysis of their feasibility, efficiency, practicalness, cost and ecocompatibility evidences that most of them are inadequate. Anaerobic digestion allows only a 80-90% COD removal, insufficient to permit discharges of effluents into the environment, and physical and chemical technologies are not cost effective because of the seasonal character of production and the small size of extraction plants. Interesting results have been obtained with a photocatalytic approach [5], using TiO_2 as the photocatalyst (however, high dilution rates are necessary) or using a photoactivated Fenton reaction, H_2O_2/Fe^{2+} (however, a centralized treatment unit is required).
The waste water from olive oil processing has the following characteristics: i) it is produced in a limited time range, ii) the sources are widespread over the production area and iii) technical personnel is not available. A centralized treatment unit is thus not a feasible solution, and it is necessary to develop a compact, small-size technology requiring simple operations and which can be moved from one site to another. Furthermore, it must be economical. The technology should convert the recalcitrant and non-biodegradable (phytotoxic) chemicals to produce a wastewater which can be introduced in the available collectors to be sent to a conventional biological water treatment unit. Furthermore, the treatment must stabilize the wastewater and thus eliminate the formation of malodours and other biological processes which limit the storage and transport of the wastewater as such.
Wet air oxidation requires reaction temperatures of the order of 200 °C or above, and thus requires the use of an autoclave, the operation of which is made difficult by the creation of foams, volatile organic compounds, catalyst deactivation, etc. Therefore, it is preferable to use a different oxidant which makes it possible to work at a temperature below about 80 °C (thus without autoclave) and which eliminates bubbling of gas into solution. H_2O_2 is a suitable reactant for these reasons, but homolytic splitting of the hydrogen peroxide molecule is necessary to create the hydroxyl radicals which are the effective powerful oxidizing agents. This can be made using UV-light radiation, but the process is costly, or adding Fenton-type catalysts (iron ions).
A pilot plant using H_2O_2 as the oxidant for the detoxification of the olive oil effluent followed by aerobic active sludge treatment has been reported [6]. High efficiencies are pos-

sible and the technology is economically attractive, but the addition of transition metals (necessary for H_2O_2 activation) has a negative impact on the active sludge and being in large part complexed by the chemicals present in solution, does not allow an efficient catalytic homolytic splitting of H_2O_2 which thus is not efficiently used. Being a costly reactant, the optimisation of its use is a critical factor.
The use of solid heterogeneous Fenton type catalysts, based on isolated iron ions in a porous zeolite or clay matrix, may avoid the problems of homogeneous Fenton catalysts [7], allowing operation in a wider pH range and protecting iron ions from the complexation. The application to the case of olive oil mills wastewater is currently under study [6,8]. Figure 2 shows the concept of how a heterogeneous Fenton-type catalyst (Fe/ZSM-5) can activate H_2O_2 inside the channel structure producing hydroxyl radicals which diffuse out from the solid pore structure to degrade the polyphenols present in the olive oil mills wastewater. The mechanism of degradation of a model phenol (cumaric acid) is also outlined in Figure 2.
This example shows that the issue of wastewater emissions from agro-foods production units is not solved and new innovative approaches are required and under study to develop effective and economical technologies. However, the further step of application will require both legislative pressure and economic incentives, due to the small-size of the production units, although their global impact on the environment and water cycle is high.

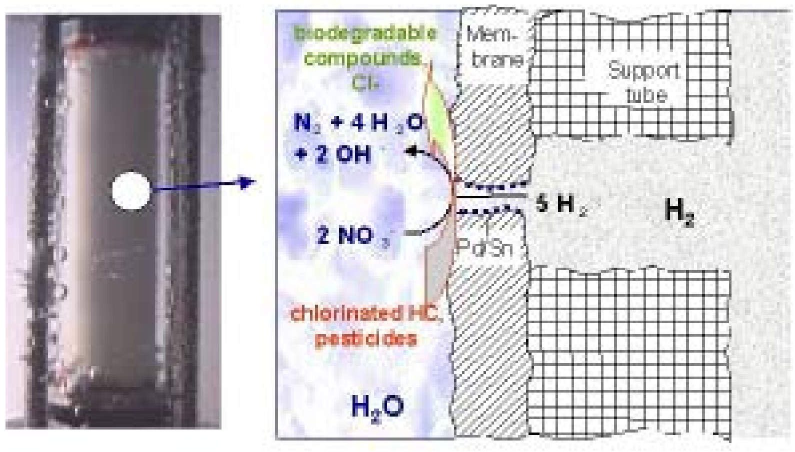

Figure 3 - Model of a catalytic membrane for water remediation by selective hydrogenation: conversion of nitrates, chlorinated hydrocarbons and pesticides on a Pd-based catalytic membrane

Technologies for water remediation

There are two main situation which require water remediation technologies: (i) localized contamination, generally associated with accidental spills, leaking, storage tanks, cleaning solvents and degreasers and (ii) diffuse contamination, mainly related to agricultural and industrial activities, but sometimes also to uncontrolled solid waste disposal activities. In the first case, if the contaminants are volatile organics, the most effective water remediation technology is air stripping associated with a second unit to recover or combust the stripped organics. The use of catalytic combustion is often the preferable and cost effective technology for the second unit.
Diffuse contamination requires different approaches. The most common case is the presence of nitrates, and pesticides or other chlorinated hydrocarbons in concentrations above the limits for use as drinking water and the necessity of using remediation technologies to decrease their concentration to acceptable values. As shown in the previous section (see Figure 1), this is a critical issue in Europe.
Due to the presence of chlorinated compounds, direct biological treatment is not possible, and a combination of AOP methods should be used such as ozonation (see following section) and biological denitrification units. However, a cost effective alternative technology, especially for small-size applications, is catalytic hydrogenation.
The introduction of a reducing step in drinking water treatment leads to the destruction of organochloro compounds and to the reduction of ions such as nitrates and bromates. Such an approach, based on the use of a catalytic hydrogenation step, has been developed both laboratory and pilot plant scales [9]. Catalysts based on Pd modified with Cu or Sn are effective both in nitrate reduction, and in dechlorination of pesticides or other organochlorocompounds, even if present in traces. However, a very critical issue is the selectivity of the reduction of nitrates, because ammonium ions tend to form in concentrations higher than the acceptable level (0.5 ppm).
Compared with catalytic gas-phase reactions, two critical problems are the possibility of the growth of micro-organisms and mass transfer limitations which are much more severe than for gas-phase reactions. Both these negative aspects could be decreased significantly by using more advanced reaction options such as the use of catalytic membrane reactors [10] which are schematically represented in Figure 3. These reactors, although more expensive, offer advantages in terms of (i) safety of operation, being the hydrogen feed physically separated from the water and air by the catalytic membrane, and (ii) improved selectivity in nitrate reduction. In fact, during nitrate reduction, OH^- ions are formed which increase the pH locally and favour the formation of ammonium ions. The hydrogenation reaction is very fast, thus maintaining a local pH around the Pd particles requires both minimizing the catalyst thickness and having an efficient back-diffusion of OH^- ions to the bulk solution where they can be neutralized by CO_2 added to the solution as a buffering agent.
The use of catalytic membranes makes it possible to optimise these factors and thus to improve selectivity in nitrate reduction, as well as avoid the presence of dead zones which favour biological growth [9].

Advanced technologies for water treatment

Considerable attention has been focused in the last decade on improving our understanding on advanced oxidation processes (AOP) which offer more environmentally feasible solutions for the chemical destruction of contaminants, still a major technology used for mineralization of pollutants.

Advanced oxidation processes, although making use of different reacting systems, are all characterized by the presence of the same reactive intermediate: OH radicals. The method of production of OH radicals, however, differs in the various methodologies. OH radicals are one of the most powerful oxidants, second only to fluorine.
Three types of reagents are used to produce OH radicals.

Dioxygen
Wet oxidation processes use O_2 or air as the reactant, but high temperatures (in the 130-300 °C range, and usually above 200 °C) are required as well as high pressures (0.5-20 Mpa). The oxidation of organic molecules may lead to the formation of partial oxidation products (aldehydes, especially) which participate in the mechanism of oxygen activation. Wet oxidation requires the use of an autoclave. Since acids are often produced as byproducts (acetic acid, especially), special corrosion resistant materials are necessary. The use of homogeneous or heterogeneous catalysts usually allow operation in less severe conditions and thus there is intense research in this area [11]. To have autothermic operations, the COD (Chemical Oxygen Demand, a parameter of the concentration of oxidizable organic species in wastewater) should be at least 20 g/l, a relatively high concentration of waste organic in solution. An alternative possibility is to use photoactivated O_2 on semiconductors such as TiO_2 [12]. This is a very efficient process for complete mineralization of several water pollutants, but usually cost effective only for very diluted aqueous solutions. Furthermore, UV radiation produced by lamps is necessary to have reasonable reaction rates, because the amount of visible light adsorbed by titania is only a few percent. Intense research is being carried out on the possibility of modifing titania to make it photoactive with visible light, but the results obtained are still unsatisfactory.

Ozone
Ozone may react with various organic and inorganic compounds, or may generate hydroxyl radicals. The second mechanism of action is preferable. Ozone is now being used in some European countries in large commercial applications for drinking water treatment, but its use can be expected to expand considerably over the next few years. The ozone decomposition to generate hydroxyl radicals is initiated by hydroxide ions, metal ions such as Fe^{2+}, H_2O_2, UV radiation and organic substances such as humic compounds and formate. This has lead to a range of different ozonation technologies such as in alkaline solution ($O_3 + OH^-$), photolytic ozonation (O_3/UV), and perozone ($O_3 + H_2O_2$). A new recent active area is also the use of homogeneous or heterogeneous catalysts for ozone activation [13]. Solid catalysts can also have the effect of adsorbing the organic compounds as well as ozone, favouring the reaction. The main limitation of ozone as the selective oxidant are (i) its cost of generation (it is produced on site by corona discharge), (ii) the short life time and (iii) low solubility in water. The typical application is for diluted aqueous solutions, *i.e.* having approximately a TOC (Total Organic Carbon) content below 0.1 mg C/l.

Hydrogen peroxide
Hydrogen peroxide is a convenient agent to generate hydroxyl radicals which, unlike ozone, is not limited by solubility problems, but in the past its application to water cleanup technologies was hindered by its high cost. However, the increased availability of H_2O_2 worldwide has largely cut its cost and thus there is renewed interest in its application to wastewater treatment. H_2O_2 must be activated to generate hydroxyl radicals and different technologies have been proposed depending on the modality of H_2O_2 activation. UV radiation is able to produce the homolytic splitting of H_2O_2 to generate two hydroxyl radicals (H_2O_2 photolysis), but the technology requires the use of UV lamps which are the costly part of the system. A classical method which has received renewed interest in recent years is the Fenton reaction based on iron salts:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$$
$$Fe^{3+} + H_2O_2 \rightarrow H^+ + FeOOH^{2+} \rightarrow HO_2^\bullet + Fe^{2+}$$

As discussed in the section related to wastewater emissions from agro-foods production, solid Fenton-type catalysts are under development to overcome some of the limitations of homogeneous Fenton catalysts. Interesting results are also obtained by combining Fenton catalysts and UV radiation (photo assisted Fenton reaction). The choice of the optimal solution depends on the type of waste in solution and range of concentrations. The method is typically employed, when the TOC values are in the 0.1-5 mg C/l range.
Active research is also being carried out in the field of total oxidation in supercritical water, due to the special properties of supercritical fluids in terms of ability to solubilize a wide range of chemicals and high mass transfer rates. However, the limitation is the necessity of working at very high temperatures and pressures (the critical point of water is 374 °C and 218 atm).
Due to the variety of situations encountered in wastewater treatment (in terms of composition and concentration of waste, and effluent flow rate) there is no one preferable technology, but each may be preferably applied in a certain range of concentrations. Research is now often directed towards the integration of various technologies, such as the combination of the AOP method with biological treatments. Although data are limited, economic indications suggest that the overall cost for AOP technologies, with respect to those for current methods, is comparable in several cases, but AOP technologies allow the impact of wastewater emissions on environment to be reduced.
AOP methods, in general, should be applied to wastewater of difficult biological conversion or containing chemicals having a toxic effect on biological activity, for diluted solutions and not very large volumes of effluents. Figure 4 reports a technological map of applications of the different technologies for wastewater treatment, although it must be kept in mind that this map gives only rough indications and specific techno-economical evaluations have to be made.

The role of catalysis in advanced water technologies

The use of catalysis in wastewater treatment may be considered still at the exploratory stage, even though there are a few examples of industrial applicatios. The most relevant is the "Osaka Gas" wet catalytic oxidation process for the treatment of high-concentration industrial effluents

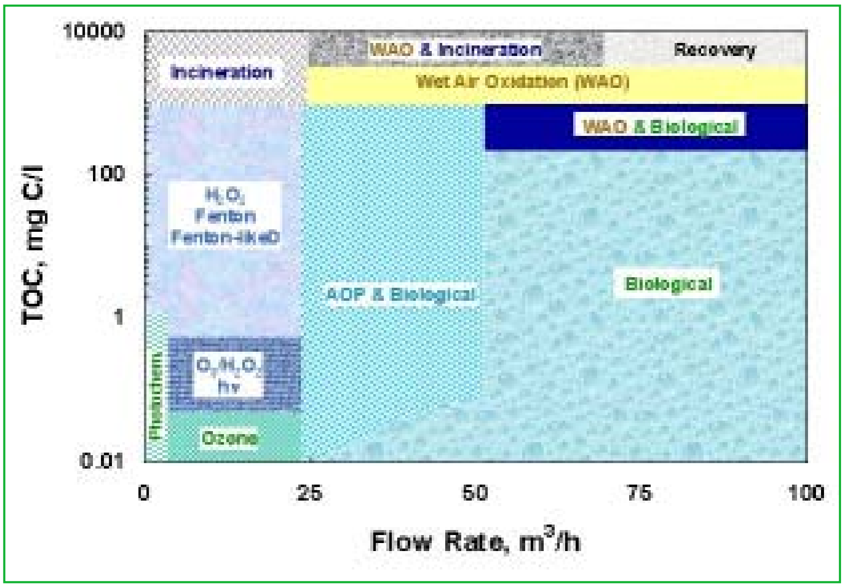

Figure 4 - Technological map for the applicability of different technologies of wastewater treatment

(http://www.oge.co.jp/English/hozen_e/hozenC01/hozenC01.htm). The process may be applied to wastewater from the chemical and pharmaceutical industries, pulp and food production, and gasification processes, the latter application being the original scope (coal gasifier effluents). The process operates in the 200-250 °C range using precious metals supported on titania or titania-zirconia carriers and used in the form of monoliths and is tailored to give a high conversion of ammonia and cyanide (present in the coal gasifier effluents). This is the only industrial process of wastewater treatment using a solid catalyst, while there are some examples of industrial processes of wet oxidation where transition metal ions (iron and copper, in particular) are added to promote activity [14].
The use of catalysts in AOP processes offers several potential advantages.

Operation in milder reaction conditions
Besides being less expensive and allowing relevant energy savings, carrying out wet oxidation at lower temperatures and pressures is of critical importance to reduce the possibility of corrosion associated with the formation of acids in the process of mineralization of the organics. This allows less costly materials to be used for the autoclave as well as safer operation.

Better engineering
More compact reactors, elimination of unwanted byproducts even if in traces, better reactor control and heat recovery can be achieved by advances in engineering.

Possibility of selective conversion
Using catalysts it is possible to achieve the preferential conversion of some chemicals, although this concept has not yet really been analysed in detail.

Possibility of combination of removal by adsorption and catalytic conversion in a separate step
Solid catalysts may act as adsorbent to remove pollutants present in diluted wastewater emissions, and act as catalysts to catalyse the conversion of adsorbed substances during a regeneration step [15]. This allows much better process energy use than wet (catalytic) oxidation for diluted wastewater. Also active carbon can be functionalized with a catalyst [16] to allow its regeneration by oxidative treatment at much lower temperatures (around 250 °C) than those used in the conventional regeneration method for active carbons (around 800 °C).
The use of catalysts, furthermore, is required in the processes of wastewater purification by reducing treatments (see section on the technologies for water remediation). Catalysts also find also application as complementary technologies to other wastewater treatment methods, such as in the control of odour, VOC, N_2O and NO_x emissions from wet oxidation treatments (for example, in the wet oxidation of industrial sludges), and of odours and VOC emitted from biological processes (aerobic and anaerobic). Although usually commercial catalysts are used in these cases, there are often unpredicted effects in treating complex mixtures and thus more specific catalysts would be preferable. The same is valid for catalysts used to convert stripped VOC from contaminated groundwater.
The use of solid catalysts to improve technologies for wastewater treatment is an area of potential importance, but further background knowledge is required, especially on the following aspects:
- *stability* of the catalyst under conditions of wastewater treatment (especially in relation to leaching of transition metal active components);
- synthesis of *catalysts not containing toxic elements* the leaching of which, even if in traces, may prevent the applicability of the technology according to current legislation;
- optimisation of the *catalyst pore structure*, because the mass transfer problems are completely different from the case of gas-phase reactions;
- *reactor engineering*, new advanced reactor engineering solutions are required in catalytic wastewater treatments.

Conclusions

Water sustainability is becoming an issue in Europe and a better balance between demand and availability is required which implies a change in the current approach. Water quality is decreasing in several regions in Europe due both to overconsumption and pollution, making water use increasingly more costly. Water reuse is becoming an economic opportunity and not only a necessity dictated by environmental protection considerations.
Water recycle, wastewater purification, and water remediation require further development of treatment technologies to improve their effectiveness and management, and decrease their cost. Due to the large variety of water and wastewater situations in terms of composition and flow rate, a range of different technologies, sometimes also a combi-

nation of different technologies, is required, being each technology suited for a limited range of situations.
The use of catalysts and especially of solid catalysts is beginning to be investigated in relation to water and wastewater treatment. Although it offers a range of potential advantages, it is necessary to further develop background knowledge to fully understand limitations and advantages. Present results are promising and already a few industrial examples of applications exist.

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