

Advanced oxidation processes (AOP) for water purification and recovery

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Abstract

All advanced oxidation processes (AOP) are characterised by a common chemical feature: the capability of exploiting the high reactivity of HO radicals in driving oxidation processes which are suitable for achieving the complete abatement and through mineralization of even less reactive pollutants. The different AOP are considered and critically presented according to their specific features with reference, whenever possible, to their real applications for water pollution abatement. The experimental apparatus and working procedures which can be adopted for carrying out waste water treatments by AOP application are examined. Some remarks upon treatment economics are provided on the basis of the main parameters affecting the AOP costs. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the last 10 years, a rather fast evolution of the research activities devoted to environment protection has been recorded as the consequence of the special attention paid to the environment by social, political and legislative international authorities leading in some cases to the delivery of very severe regulations [1].

The fulfilment of severe quality standards is especially claimed for those substances exerting toxic effects on the biological sphere preventing the activation of biological degradation processes.

The destruction of toxic pollutants as also that of the simple biologically recalcitrant compounds must be therefore demanded to other, non biological technologies. These technologies consist mainly of conventional phase separation techniques (adsorption processes, stripping techniques) and methods which destroy the contaminants (chemical oxidation/reduction).

Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganics or, at least, at their transformation into harmless products.

Obviously the methods based on chemical destruction, when properly developed, give complete solution to the problem of pollutant abatement differently from those in which only a phase separation is realised with the consequent problem of the final disposal.

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Table 1

Second order rate constants for ozone and hydroxyl radical for a variety of compounds

Organic compound	Rate constant ($\text{M}^{-1} \text{s}^{-1}$)	
	O_3^{a}	$\text{HO}^{\bullet\text{b}}$
Benzene	2	7.8×10^9
Toluene	14	7.8×10^9
Chlorobenzene	0.75	4×10^9
Trichloroethylene	17	4×10^9
Tetrachloroethylene	<0.1	1.7×10^9
<i>n</i> -Butanol	0.6	4.6×10^9
<i>t</i> -Butanol	0.03	0.4×10^9

^a From [9].

^b From [8].

It has been frequently observed [2–4] that pollutants not amenable to biological treatments may also be characterised by high chemical stability and/or by strong difficulty to be completely mineralized. In these cases, it is necessary to adopt reactive systems much more effective than those adopted in conventional purification processes.

A lot of researches have been addressed to this aim in the last decade pointing out the prominent role of a special class of oxidation techniques defined as advanced oxidation processes (AOP) which usually operate at or near ambient temperature and pressure [5–7]. This discussion points to a synoptic presentation of these oxidation techniques with special attention given to fundamental chemical aspects.

2. General survey

Advanced oxidation processes although making use of different reacting systems, are all characterized by the same chemical feature: production of OH radicals.

OH radicals are extraordinarily reactive species, they attack the most part of organic molecules with rate constants usually in the order of 10^6 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ [8,9] (Table 1).

They are also characterised by a little selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. The versatility of AOP is also enhanced by the fact that they offer different possible ways for OH radicals production thus allowing a better compliance with the specific treatment requirements.

- $\text{H}_2\text{O}_2 / \text{Fe}^{2+}$ (Fenton)
- $\text{H}_2\text{O}_2 / \text{Fe}^{3+}$ (Fenton - like)
- $\text{H}_2\text{O}_2 / \text{Fe}^{2+} (\text{Fe}^{3+}) / \text{UV}$ (Photo assisted Fenton)
- $\text{H}_2\text{O}_2 / \text{Fe}^{3+}$ - Oxalate
- Mn^{2+} /Oxalic acid/Ozone
- $\text{TiO}_2 / \text{hv} / \text{O}_2$ (Photocatalysis)
- $\text{O}_3 / \text{H}_2\text{O}_2$
- O_3 / UV
- $\text{H}_2\text{O}_2 / \text{UV}$

Fig. 1. Advanced oxidation processes.

A suitable application of AOP to waste water treatments must consider that they make use of expensive reactants as H_2O_2 , and/or O_3 and therefore it is obvious that their application should not replace, whenever possible, the more economic treatments as the biological degradation. A list of the different possibilities offered by AOP is given in the Fig. 1.

The potentialities offered by AOP can be exploited to integrate biological treatments by an oxidative degradation of toxic or refractory substances entering or leaving the biological stage.

Another aspect concerning the opportunity of AOP application is that referring to the polluting load of wastes normally expressed as COD. Only wastes with relatively small COD contents ($\leq 5.0 \text{ g/l}$) can be suitably treated by means of these techniques since higher COD contents would require the consumption of too large amounts of expensive reactants. Wastes with more massive pollutants contents can be more conveniently treated by means of wet oxidation or incineration [10] (Fig. 2).

Wet oxidation makes use of oxygen or air to achieve pollutant oxidation at high temperatures (130 – 300°C) and pressure (0.5 – 20 Mpa). Since oxidation is an exothermic process, simple thermal balance shows that wastes with COD contents higher than approximately 20 g/l undergo autothermic wet oxidation, whereas fuel consumption should be taken into account to achieve combustion temperatures for leaner wastewaters. For these wastes, the cost evaluation of

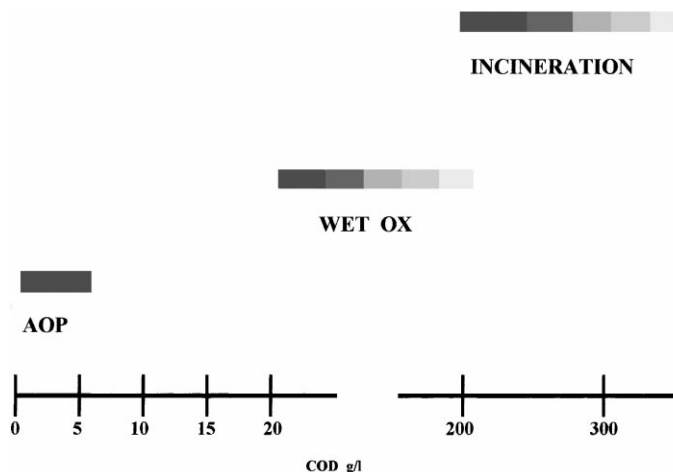


Fig. 2. Suitability of water treatment technologies according to COD contents.

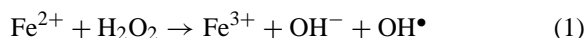
fuel consumption will give the selection criteria for the application of AOP or wet oxidation treatment.

3. Fenton processes

The renewed interest of researchers for this classic, old reactive system, discovered by Fenton the last century [11], is today underlined by a significant number of investigations devoted to its applications in wastewater treatments.

It has been demonstrated that Fenton's reagent is able to destroy toxic compounds in waste waters such as phenols and herbicides.

Production of OH radicals by Fenton reagent [12] occurs by means of addition of H_2O_2 to Fe^{2+} salts

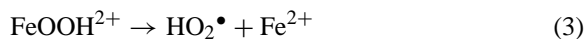


This is a very simple way of producing OH radicals neither special reactants nor special apparatus being required.

This reactant is an attractive oxidative system for waste water treatment due to the fact that iron is very abundant and non toxic element and hydrogen peroxide is easy to handle and environmentally safe.

It must be stressed that the behaviour of the system cannot be completely explained on the basis of the sole reaction (1). In fact, as it has been pointed out in many recent studies [13] the adoption of a proper

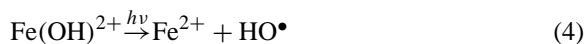
value of pH (2.7–2.8) can result into the reduction of Fe^{3+} to Fe^{2+} (Fenton-like)



proceeding at an appreciable rate. In these conditions, iron can be considered as a real catalyst.

4. Photoassisted Fenton processes

The rate of degradation of organic pollutant with Fenton–Fenton like reagents is strongly accelerated by irradiation with UV-VIS light [14,15]. This is an extension of Fenton process which takes advantage from UV-VIS light irradiation at wavelength values higher than 300 nm. In these conditions, the photolysis of Fe^{3+} complexes allows Fe^{2+} regeneration

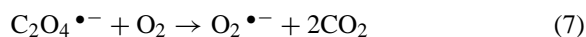
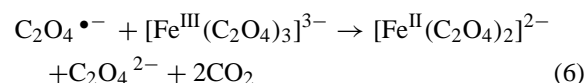
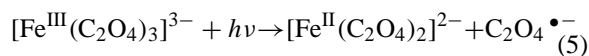


and the occurrence of Fenton reactions due to the presence of H_2O_2 (Reaction 1).

Despite of the great deal of work devoted by researchers to these processes scanty indications have been found about their industrial applications. This is not surprising since Fenton processes application requires strict pH control and sludges can be formed with related disposal problems.

4.1. UV/ Fe^{3+} -Oxalate/ H_2O_2

An improvement of photoassisted Fenton processes is the UV-VIS /Ferrioxalate/ H_2O_2 system which has been very recently demonstrated [16] to be more efficient than photo-Fenton for the abatement of organic pollutants:



Ferrioxalate is the oldest and best known photo-active example of Fe^{3+} -polycarboxylate complexes [17]. Irradiation of ferrioxalate in acidic solution generates carbon dioxide and ferrous ions Fe^{2+} free or complexed with oxalate which in combination with H_2O_2 provides a continuous source of Fenton's reagent. Ali Safarzadeh [18] reports that the energy required for treating the same volume of selected wastewater (toluene, xylenes, mek) is about 20% of the energy required by photo-Fenton system. The high efficiency of this process as compared to other UV processes is attributed to the fact that:

- ferrioxalate absorbs over a broad range of wavelengths (200–400 nm) thus utilising more efficiently the UV-VIS radiation;
- the quantum yield of Fe^{2+} formation is 1.0–1.2 over the range of irradiation whereas that of Fe^{2+} with photo-Fenton process decreases from 0.14 at 313 nm to 0.017 at 360 nm;
- a great difference in the efficiency is observed with wastewaters containing aromatic pollutants whose hydroxyderivatives produced in first oxidation stage strongly absorb in the same UV range as H_2O_2 and Fe^{3+} leading to a very slow rate of destruction of the parent molecules.

5. Photocatalysis

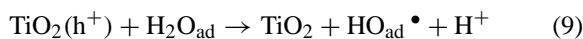
Photocatalytic processes make use of a semiconductor metal oxide as catalyst and of oxygen as oxidizing agent [19]. Many catalysts have been so far tested, although only TiO_2 in the anatase form seems to have

the most interesting attributes such as high stability, good performance and low cost [20,21].

The initiating event in the photocatalytic process is the absorption of the radiation with the formation of electron-hole pairs

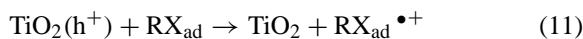


The considerable reducing power of formed electrons allows them to reduce some metals and dissolved oxygen with the formation of the superoxide radical ion $\text{O}_2^{\bullet-}$ whereas remaining holes are capable of oxidizing adsorbed H_2O or HO^- to reactive HO radicals:



These reactions are of great importance in oxidative degradation processes due to the high concentration of H_2O and HO^- adsorbed on the particle surface.

Some adsorbed substrate can be directly oxidized by electron transfer:



Unfortunately a significant part of electron-hole pairs recombine thus reducing the quantum yield.

In the most part of the works devoted to the photocatalysis the possible exploitation of the wavelengths of the solar spectrum is stressed. However, this is only partially true since the overlapping between the absorption spectrum of TiO_2 and that of the sun at ground is rather poor [21].

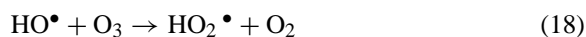
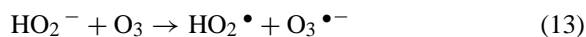
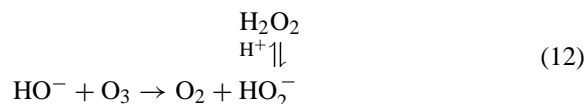
Intensive researches are carried out worldwide to obtain modified (doped) TiO_2 with broader absorption spectrum and characterized by higher quantum yield.

Despite the great efforts devoted to the study of photocatalytic processes no indications have been found in the literature of their application on industrial scale.

6. Ozone water system

To illustrate the fundamental chemistry upon which $\text{O}_3/\text{H}_2\text{O}_2$ and O_3/UV processes are based, a reference to the ozone chemistry in aqueous alkaline solutions is required. This argument has been extensively and successfully studied by Hoigné and co-workers [22] in the attempt of giving a chemical explanation to the

short life time of ozone in alkaline solutions. Hoigné showed that the ozone decomposition in aqueous solution develops through the formation of OH radicals. In the reaction mechanism OH^- ion has the role of initiator:



The mechanism also elucidates the role exerted by H_2O_2 since it is formed during the ozone decomposition in aqueous solution.

It is clear therefore that the addition of hydrogen peroxide to the ozone aqueous solution will enhance the O_3 decomposition with formation of OH radicals. The influence of pH is also evident, since in the ozone decomposition mechanism the active species is the conjugate base HO_2^- whose concentration is strictly dependent upon pH. The increase of pH and the addition of H_2O_2 to the aqueous O_3 solution will thus result into higher rates of OH radicals production and the attainment of higher steady-state concentrations of OH radicals in the radical chain decomposition process [23].

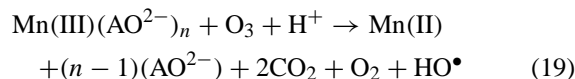
It must be remarked that the adoption of the $\text{H}_2\text{O}_2/\text{O}_3$ process does not involve significant changes to the apparatus adopted when only O_3 is used, since it is only necessary to add an H_2O_2 dosing system.

6.1. Mn^{2+} /oxalic acid/ozone

The system Mn^{2+} /oxalic acid can be conveniently used to enhance ozone decomposition to produce HO radicals.

Mn^{2+} catalysed ozonation of oxalic acid has been shown to develop according to a radical mechanism at pH >4.0 at which Mn(III)-dioxalate and

Mn(III)-trioxalate are formed. In these conditions, the oxidation process proceeds presumably through the formation of OH radicals



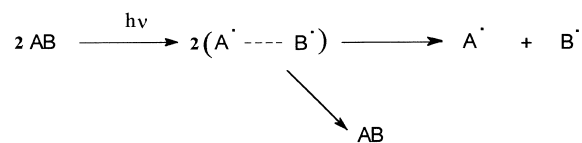
as a result of a reaction between manganese complexes and ozone [24]. The system has been demonstrated to be effective for the abatement of refractory pollutants such as pyrazine and pyridine [25].

6.2. H_2O_2 photolysis

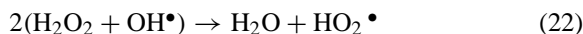
This process is effected by irradiating the pollutant solution containing H_2O_2 with UV light having wavelengths smaller than 280 nm. This causes the homolytic cleavage of H_2O_2 [26].



In aqueous solution, the cage effect of water molecules lowers the primary quantum yield to 0.5:



Since H_2O_2 itself is attacked by OH radicals



the overall quantum yield becomes one.

The major drawback of this process is due to the small molar extinction coefficient of H_2O_2 which is only $18.6 \text{ M}^{-1} \text{ cm}^{-1}$ at 254 nm, only a relative small fraction of incident light is therefore exploited in particular in the cases where organic substrates will act as inner filters.

The rate of photolysis of aqueous H_2O_2 has been found to be pH dependent and to increase when more alkaline conditions are used [1]. This may be primarily due to the higher molar absorption coefficient of the peroxide anion HO_2^- which at 254 nm is $240 \text{ M}^{-1} \text{ cm}^{-1}$.

6.3. O₃/UV

O₃/UV process is an advanced water treatment method for the effective oxidation and destruction of toxic and refractory organics in water. Basically, aqueous systems saturated with ozone are irradiated with UV light of 254 nm in a reactor convenient for such heterogeneous media. The extinction coefficient of O₃ at 254 nm is 3600 M⁻¹ cm⁻¹ much higher than that of H₂O₂.

O₃/UV oxidation process is more complex than the other ones, since OH radicals are produced through different reaction pathways. There is a general agreement about involved reactions [27]:



It is clear that under these conditions the system has the chemical behaviour of both O₃/H₂O₂ and H₂O₂/UV systems [1,6].

From the photochemical point of view, the absorption spectrum of ozone provides a much higher absorption cross section than H₂O₂, and inner filter effects by e.g. aromatics are less problematic [1].

7. AOP reactors

The adoption of oxidation treatments based on O₃/UV and H₂O₂/UV systems requires the use of suitable UV sources and of appropriate photochemical reactors [28,29].

Commercial AOP reactors have been recently developed for a full scale installation by Chemviron Carbon and Wedeco [30,31].

The reactor is normally provided with a device which allows a good mixing of dosed hydrogen peroxide. In the photoreactor design a careful attention must be paid to a proper sizing of the path length between quartz sleeve (housing the lamp) and the reactor walls. The rule generally adopted is that more than 90% of emitted light must be absorbed by the solution. A proper sizing of the pathlength renders useless the adoption of reflective reactor walls. The

use of special reflective materials is a controversial point since they are expensive and the benefits of the reflectors can be easily reduced or erased by the fouling in the case of waste waters containing suspended particles. The problem of fouling is more relevant for the quartz sleeve. It is essential that it remains clean during the operation. To this purpose the reactor is generally provided with a quartz sleeve cleaning device.

When ozone is admitted (O₃/UV), a gas–liquid contactor is required (i.e. a sparging device). Glaze [6] and Symmons [32,33] have recommended and used stirred tank photochemical reactors in order to obtain better results in mass transfer and to solve some of the remaining technical problems encountered in the scale up [1].

Scarce appear at the moment the information on scale-up procedures. In the most part of cases, the optimum residence time is determined by means of simplified first-order kinetics for the substrate consumption whereas for the oxidant dosage values ranging between $2.0 \times 10^3 \div 1.5 \times 10^4 \text{ mg l}^{-1}$ and $60 \div 2.4 \times 10^2 \text{ mg l}^{-1}$ are adopted respectively, for H₂O₂ and O₃ [34] for full-scale reactors. Optimum specific powers in the range $5 \div 100 \text{ W l}^{-1}$ are normally used in commercial reactors by means of UV lamps of $40\text{--}1.5 \times 10^3 \text{ W}$ [34].

8. Comparative comments

The following points have to be considered for a correct comparison of the three most applied AOP techniques (O₃/H₂O₂, H₂O₂/UV and O₃/UV).

8.1. Influence of pH

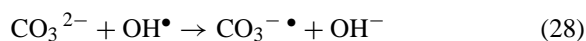
As previously discussed pH of the solution influences the rate of radical generation for the system O₃/H₂O₂, H₂O₂/UV and O₃/UV, proper values of this parameter must be therefore chosen.

It is important to consider that during photooxidation processes the pH of reaction medium decreases due to formation of acidic species. Therefore, it is necessary to adjust the pH of the treated water at the value (generally assessed by means of laboratory tests) which enables the achievement of the highest efficiency of pollutant abatement. For the most part

of common pollutants these values range between pH 3.0 and 5.0 [34].

8.2. Inhibition due to the scavenger presence

The presence in the treated water of carbonate can result in a significant reduction of the efficiency of abatement of pollutants as shown in some studies [34]. Carbonate acts as radical scavenger



since $\text{CO}_3^{\bullet-}$ is much less reactive than OH^\bullet . Inhibition by carbonate influences the behaviour of all three analyzed techniques.

8.3. Light wasting

It is clear that light based processes can be severely penalised by light absorption by substrate molecules (other than O_3 or H_2O_2). Although, in some cases it has been reported that organic substrates undergo photochemical reactions as a consequence of light absorption, rarely these transformations contribute to the TOC reduction. In this sense, the light absorbed by organic molecules can be generally considered as wasted light. Reduced efficiencies can also result during photolytic treatment of waste waters containing suspended material, since a fraction of irradiated energy is scattered by these particles [35].

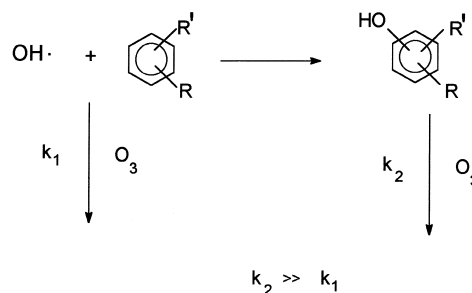
8.4. Mass transfer limitations

$\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV systems require that ozone molecules transfer from the gas stream to the liquid bulk in which they attack the organics. The overall process of absorption with reaction can develop according to different regimes [36].

It has been reported that mainly in the case of O_3/UV the rate of ozone consumption per unit volume can be so high that mass transfer limited regime for ozone absorption is established thus resulting in a decrease of quantum efficiencies and an increase of operating costs [35].

8.5. Direct ozone attack

With $\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV systems a part of the organic load can be reduced by the action of ozone alone which attacks some particular intermediates. This is for example the case of aromatic substrates which become much more reactive towards ozone after hydroxylation:



8.6. Additional equipments/material of construction

When O_3 is used in the oxidation process, there is the need of an ozone generator and its cooling system and of additional equipments such as pre-treatment section to dry the oxygen (air) fed to the ozonator and post-treatment reactor for the abatement of residual ozone in the off-gas [37]. Moreover, the powerful oxidative capability of ozone requires the choice of construction materials that can resist to its action. Typical material for the most part of pipings and the reactor is SS 304 or 316 although other materials are used for specific devices as reported by Roth [38]. These requirements influence significantly the capital costs.

8.7. Cost evaluation

The evaluation of the treatment costs is at moment one of the aspect which needs more attention.

The overall costs are represented by the sum of the capital costs, the operating costs and the maintenance. For a full-scale system these costs strongly depend on the nature and the concentration of the pollutants, the flow rate of the effluent and the configuration of the reactor.

Some efforts have been done for the evaluation of the operating costs to develop a procedure for the estimation of the electrical consumptions for UV lamps

[39,40]. According to this procedure after having fixed a reference level of removal (90%) of a specified pollutant or of the overall load (COD), a pseudo first order kinetic constant is estimated. The energy required for achieving the chosen level of abatement, for a fixed volume of waste water (i.e. 10^3 l), can be thus calculated through the following formula

$$E = \frac{P \times 1000}{V_0} \times \frac{\ln 10}{60} \times k \quad (\text{batch reactor})$$

where P is the lamp power (kW), k the pseudo first order constant (min^{-1}), V_0 the volume of the tested solution [1] and E is the energy in kWh required for achieving 90% destruction of pollutants in 1000 l of treated waste water. Values of E not higher than 2.5 are considered suitable for practical applications [39].

Only few data are reported in the literature for AOP overall costs [41–44] and due to their dependence on the effluent and plant characteristics their direct comparison is (often) meaningless. More interesting appear on the other hand the papers in which overall cost comparison is given for AOP and more conventional treatment techniques (air stripping, GAC adsorption, etc.) [43,44]. The results of these studies generally indicate that the overall costs of AOP treatments are comparable with those of well established technologies of pollutant abatement.

9. Conclusions

Advanced oxidation processes represent a powerful mean for the abatement of refractory and/or toxic pollutants in wastewaters.

Different AOP techniques have been developed thus allowing to make choices the most appropriate for the specific treatment problems.

Overall cost evaluations so far available indicate that AOP system are not more expensive than well established technologies for pollutant abatement.

Major attention should be devoted in the future by researchers to fill some specific gap which exists for these techniques in the areas such as identification of reaction intermediates, development of rate expressions based on established reaction mechanisms, identification of scale-up parameters and criteria for cost effectiveness and maximum destruction efficiency. Moreover, the improvement of these tech-

niques for a more efficient exploitation of sun radiation could ensure more economic solutions to the problem of water purification and recovery.

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