

# ENVIRONMENTAL CATALYSIS FROM NANO- TO MACRO-SCALE

## OKOLJSKA KATALIZA OD NANO- DO MAKROVELIKOSTI

**Adrián Manuel Tavares da Silva**

Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal  
adrian@fe.up.pt

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In today's highly sensitive ecosystem, environmental protection is a great challenge to be faced by industry, with regulations becoming more restrictive in the future. Advanced oxidation processes (AOPs) – or technologies (AOTs) – are promising end-line solutions for waste water treatment, involving liquid-phase oxidation of pollutants by means of highly reactive species, such as hydroxyl radicals. In general, installation costs of AOPs are comparable with the ones associated to biological treatments; however, operating costs of AOPs are higher due to the use of costly chemicals. Development of highly active heterogeneous catalysts is a key approach to scale-up cost-effective environmental technologies, minimizing the needs in chemicals and increasing the level of treatment obtained. This paper is an overview of some different steps involved in the field of environmental catalysis engineering to develop suitable materials from a nano-scale point to a macro-scale application.

Keywords: environmental protection; heterogeneous catalysts; advanced oxidation processes (AOPs);

V današnjem občutljivem ekosistemu je varovanje okolja pomemben izziv, ki ga srečuje industrija, še posebej zaradi predpisov, ki bodo v prihodnosti še bolj omejujoči. Napredni oksidacijski procesi (AOP) in tehnologije (AOT) so obetajoče končne rešitve za obdelavo odpadnih voda in temeljijo na oksidaciji nečistoč z visoko reaktivnimi snovmi, kot so hidroksilni radikali. V splošnem so stroški AOP-naprav podobni tistim za biološko obdelavo, vendar so obratovalni stroški AOP višji zaradi uporabe dragih kemikalij. Razvoj visokoaktivne heterogene katalize je ključni pogoj za napredek cenovno učinkovite okoljske tehnologije, ker minimizira porabo kemikalij in poveča kakovost obdelave. Ta članek je pregled različnih stopenj na področja inženirstva okoljske katalize, ki ima za cilj razviti primerne materiale z nano- do makroobmočjem uporabe.

Ključne besede: varovanje okolja, heterogena kataliza, napredni oksidacijski procesi (AOP)

## 1 INTRODUCTION

The treatment of effluents is one of the major social, economical and political problems of our days. As consequence, many researchers have focused their scientific interests in environmental issues. Scientific journals with high impact factors, as well as traditional and new congresses include now environmental themes. This was a crucial step in order to alert industry stakeholders to the importance of reducing the industrial impact on the environment, assuring a good quality of life. The objective of the so-called *green chemistry* is mainly directed to emerging technologies by designing environmentally benign processes<sup>1</sup>. However, operation issues, deep research, long time consuming and high economical investment are some shortcomings found at industrial level when applying this concept to processes already installed in traditional industries. Consequently, the treatment of pollutants by remedial end-line technologies is still important.

Conventional biological processes have associated significant disadvantages, such as inhibition of microorganisms by certain pollutants, impossibility to treat high concentrations of organic compounds and production of sludge, which is another source of pollution. AOPs are alternatives in this domain. In brief, the Fenton process consists in the chemical oxidation of

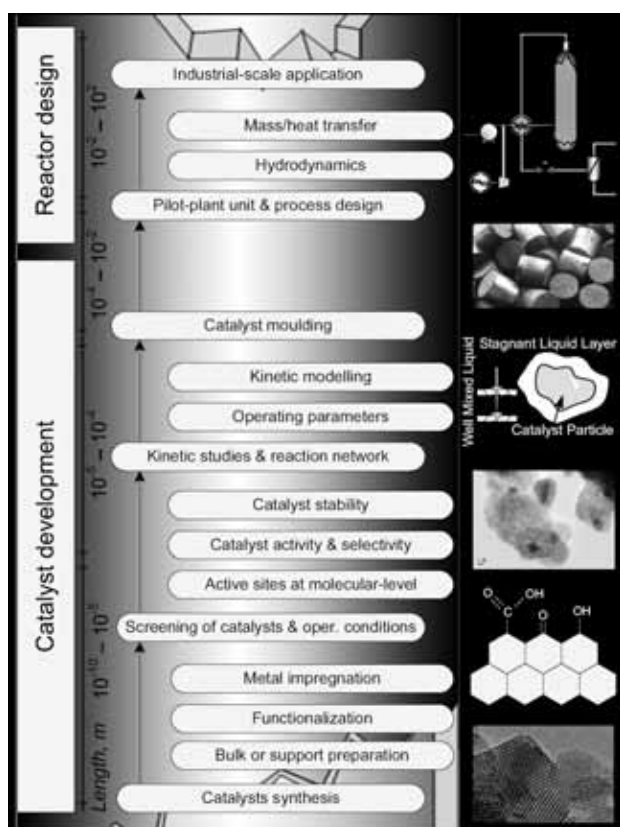
pollutants by means of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and iron acting as catalyst, based in the Fenton reaction known for over 100 years<sup>2</sup>; ozonation is based in the strong oxidant properties of ozone; photocatalysis uses the photonic activation of the catalyst by light irradiation producing reactive electron-holes; and in catalytic wet oxidation (CWO) the pollutant molecules are oxidized with pure oxygen or air at elevated temperatures (130–250 °C) and pressures (5–50 bar). Other AOPs such as sonolysis, which consists on the ultrasonically induced acoustic cavitation, or the electrochemical oxidation, which produces large amounts of hydroxyl radicals directly in water, are at an earlier stage of development. Each technology requires a different catalytic material as well as the optimization of their catalytic properties. Different metal oxides (e.g., Zn, Mn, Fe, Co, Ni, Cr, and Bi oxides) and noble metals (e.g., Ru, Pt, Pd, Rh and Ir) supported typically on CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> or carbon materials have been used in CWO studies<sup>3,4</sup> and few of them applied in ozonation<sup>5</sup>. TiO<sub>2</sub>-based materials are the preferred photocatalysts<sup>6</sup> and iron ions are the base of the Fenton reaction<sup>7,8</sup>.

Actually, the sustainable technological implementation of AOPs as new solutions at the macro-scale depends on the understanding of fundamental catalytic processes taking place at the nano-scale. Development of active, selective and economic catalysts, which permit to

increase the process efficiency and decrease the consumption of chemicals, is one of the main challenges<sup>9</sup>. The present paper does not intend to give an extensive survey on the published work regarding catalytic materials and reactor configurations that has been used in AOPs, since this information can be found in many reviews of the Fenton process<sup>8,10</sup>, ozonation<sup>5</sup>, photocatalysis<sup>10–15</sup> and CWO<sup>3,4,10,16–23</sup>, but rather to give an introductory background on the catalysis engineering steps and tools to develop heterogeneous catalysts, with the final aim of applying these materials in industrial-scale reactors. In contrast with CWO, the ozonation and the Fenton processes are relatively simple and have been widely installed for the treatment of effluents<sup>5,7</sup>. Photocatalysis differs from the other AOPs since a light-irradiation is used and, as consequence, the main concepts involved are also different when. Therefore, in

this paper, particular emphasis is given to CWO and photocatalysis as two examples of AOPs with different complexity.

Environmental catalysis engineering can be considered as an interdisciplinary integration of fundamental and applied knowledge on materials, chemistry, physics and engineering. The different levels of catalyst development are strongly linked with basic concepts of all these areas and they cannot be isolated if the aim is to produce sustainable development of catalytic reactors. In a catalytic point of view, at the nano-scale the reactivity of the active sites is influenced by the surrounding environment at a supramolecular level. This environment drives the local adsorption/desorption of reactants and products; for instance, local pH around the active site can be different from the bulk pH depending on the characteristics of the catalytic cavities. For this reason, adequate tuning of catalysts at the nano-scale level allows enhancement of the catalytic properties. The nano-scale differs from the molecular level since the later refers to the direct interaction between the active site and these molecules. The nano-sized catalytic materials should be assembled at the micro-scale with the aim of obtaining optimal spatial distribution and catalyst composition in a final macro-structured catalyst (e.g., pellets, membranes, monoliths, foams)<sup>24</sup>. Optimization of catalytic properties and reactor design involves testing and modelling at different levels (reaction and kinetic studies under different operating conditions, mass/heat transfer and hydrodynamic investigations, simulation and experimental work in pilot-units and final scale-up to industrial level). In order to provide an integrative point of view, the multidisciplinary strategy for development of catalysts was divided in seven main stages, as shown in **Figure 1**: catalyst synthesis; catalyst screening and operating conditions; kinetic studies and reaction network; catalyst stability and activity; catalyst screening and operating conditions; pilot-plant unit and process design; industrial-scale application. The length associated to each step is only indicative and although they are sequentially presented and described in the next sections, in practice there are overlaps between the different steps when optimizing catalytic materials/processes.



**Figure 1:** Schematic diagram representing different levels of catalyst development and application. Figures at the right side from bottom to top: (i) HRTEM micrograph of nanosized ceria particles ( $\approx 3$  to  $8$  nm); (ii) representation of a functionalized carbon surface; (iii) HRTEM micrograph of Pt nanoparticles (dark spots  $\approx 2$ – $4$  nm) supported on Ce-Ti-O; (iv) scheme of a particle of catalyst in a liquid media; (v) example of a shaped catalyst ( $6.4 \times 6.4$  mm); (vi) WO Zimpro diagram.

**Slika 1:** Shematični grafikon, ki predstavlja različne stopnje razvoja in uporabe katalizatorjev. Slike od desne spodaj navzgor: (i) HRTEM-mikroposnetek nanoziranih delcev cerijevega oksida ( $\approx 3$ – $8$  nm); (ii) funkcionalizirana površina ogljika; (iii) HRTEM-posnetek nanodelcev Pt (temne točke  $\approx 2$ – $4$  nm) na Ce-Ti-O-podlagi; (IV) shema delca katalizatorja v tekočem mediju; (V) primer oblikovanega katalizatorja ( $6.4 \times 6.4$  mm); (VI) WO Zimpro-diagram

## 2 CATALYST SYNTHESIS

In general, the chemical processes can be classified according to the number and type of phases (liquid, gas and solid) or to the nature of the catalyst (heterogeneous or homogeneous). Gas-liquid reactions with solid catalysts are one of the largest chemical commercial applications, including oxidations, since the use of homogeneous catalysts requires its removal from the wastewater with a posterior recovery step. The concept of heterogeneous catalysts is normally associated to solids or mixtures of solids which accelerate chemical fluid reactions without changes in the solids. During

many years (essentially until 1970's), development and preparation of heterogeneous catalysts was considered more as alchemy than science, consuming many efforts, money and time without guaranty of the final results <sup>25</sup>. Nowadays, the relation between catalysis and other emerging sciences, such as analytical or solid state chemistry, makes possible to reduce the wide number of variables in preparing heterogeneous catalysts to a series of elementary steps. A heterogeneous catalyst is characterized mainly by the relative amounts of different components (active species, physical and/or chemical promoters, and supports), shape and size, pore volume and distribution, and surface area. The nature of the active species is always the most important factor. Various research projects worldwide investigate possible applications of active and stable heterogeneous catalysts in AOPs for the oxidation of various pollutants.

The first steps in heterogeneous catalytic ozonation date back to 1970s <sup>26</sup>, but only now interesting perspectives are reappearing <sup>5</sup>. In the Fenton process the formation of sludge, a source of pollution and the reason of catalyst loss, is the main shortcoming of using iron in the typical homogeneous form. Iron-based heterogeneous catalysts, or solid sources of iron, such as minerals, are some alternatives <sup>8</sup>. Attention has been also paid to new heterogeneous catalysts for CWO and photocatalysis. Catalysts able to oxidize typical refractory end products of biological processes have been well accepted.

According to the most common preparation procedures, the catalysts can be classified as <sup>25</sup>: *bulk catalysts or supports* where the catalyst is generated as a new solid phase (e.g., precipitation, sol-gel) and *impregnated catalysts* where the active phase is introduced or fixed on a pre-existing solid (e.g., impregnation, ion exchange, adsorption, deposition-precipitation and chemical- or physical-vapour deposition). The formation and *precipitation* of a crystalline solid occurs by supersaturation with physical (e.g., variations in temperature) or chemical (e.g., addition of bases or acids) perturbations of a solution, formation of stable small particles by nucleation and growth by agglomeration of those particles. The *sol-gel* method consists on the transformation of a solution into a hydrated solid precursor (hydrogel). This method has gained importance due to the better control of different properties such as texture and homogeneity. *Impregnation* is based in the contact between the solid support and a certain volume of solution, which contains the precursor of the active phase. The method is called *wet impregnation* when an excess of solution is used and *incipient wetness impregnation* if the volume is equal or slightly less than the pore volume of the support. The *ion exchange* method is based on the replacement of ions on the surface of a support by electrostatic interactions. *Adsorption* consists in the controlled attraction of a precursor contained in an aqueous solution by charged sites on the support. In the *deposition-precipitation*

method, slurries are formed and the precipitation occurs in interaction with a support surface by addition of an alkali solution. The prepared solids are separated from the mother liquor with filtration, decantation, centrifugation, etc., usually washed with distilled water (or specific organic solvents) for complete removal of impurities and submitted to thermal treatments (e.g., *drying* and *calcination-heating*). After calcination, modification of the nature and/or structure of the phases and stabilization of mechanical properties occur.

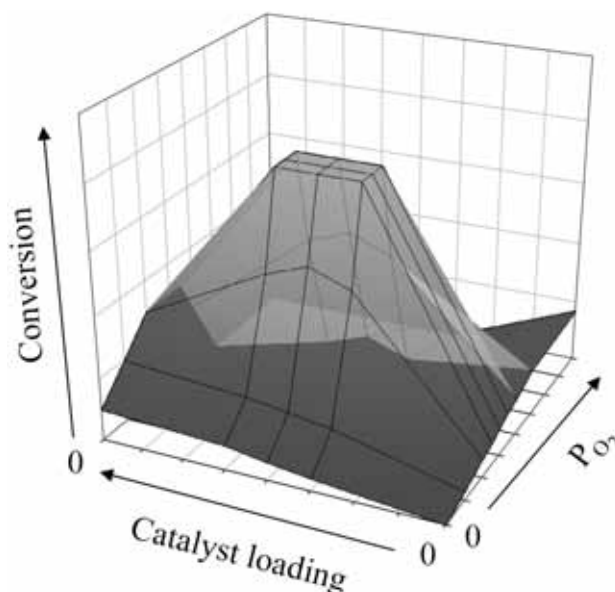
Thorough chemical, textural and structural analysis of catalytic materials is possible nowadays due to several available techniques. Electron microscopy constitutes a family of very powerful catalyst characterization techniques. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) or high resolution TEM (HRTEM) are analytical techniques used to identify structural constitution of heterogeneous catalysts, including shape, atomic structure and dispersion of active nanoparticles supported on high surface area materials (e.g., Figure 1-iii showing Pt-nanoparticles supported on Ce-Ti-O), which are key information in catalysis. When coupled with other techniques, such as energy-dispersive X-ray spectroscopy (EDXS) or selected-area electron-diffraction (SAED), catalyst composition data can be obtained in diverse phases of the sample, since it is possible to analyze selected areas at the nano-size scale. New devices have been coupled with microscopes in order to increase the analytical potentialities. For instance, the high-angle annular dark-field detector (HAADF) and the field emission gun (FEG) are appropriate to identify some metals (e.g., gold) at the nano-scale in catalytic materials. X-ray diffraction (XRD) is a common technique used to identify the structure of materials as well as to determine crystallite sizes with the Scherrer equation. X-ray photoelectron spectroscopy (XPS) is frequently used to analyze oxidation states. Textural characteristics (BET surface area, micropore, mesopore and macropore constitution) are determined from the nitrogen adsorption isotherm obtained at 77 K and using specific calculation methods such as t-method, Stoeckli and Dubinin equations. Temperature-programmed desorption (TPD) has gained special relevance in the chemical analysis of surface oxygen groups on carbon materials, since CO and CO<sub>2</sub> are formed and released when applying heating ramps <sup>27</sup>. By means of the deconvolution of the TPD spectra, it is possible to determine the amounts of the diverse surface groups (carboxylic acids; carboxylic anhydrides; lactones; phenols; carbonyl or quinones). This makes possible to finely tune the surface chemistry of functionalized carbon materials (representative image on **Figure 1-ii**) which provides a proper control of chemical reactivity. The referred techniques are only few examples among many other important methods that are used to characterize heterogeneous catalysts.



### 3 CATALYST SCREENING AND OPERATING CONDITIONS

In AOPs the appropriate catalyst will be the one that operating in amenable reaction conditions shows the highest level of pollutant degradation to carbon dioxide and water or to less toxic/refractory compounds. Many parameters should be evaluated and several materials and compositions must be tested in order to increase the probability of identifying a suitable candidate for the process. Catalyst deactivation must be investigated as well, being normally due to sintering, poisoning of active sites, dissolution of active components to the liquid phase (leaching) or fouling of the catalyst surface as a result of deposition of reaction intermediates. Examination of fresh and used catalysts allows to identify possible changes on the catalyst during the reaction, essential for understanding the catalyst deactivation. Therefore, an initial idea of catalyst activity/stability may be obtained in batch reactor experiments by recycling the catalyst for a small number of cycles. Experiments that are more definitive may require operation with a continuous reactor over hundreds or possibly thousands of hours of operation. The level of pollutants degradation to be achieved with a certain technology is defined by process economic considerations, where the cost of the catalyst replacement is considered as part of the global economical analysis. Novel methods have been developed for monitoring *in situ* in which way the metal sites interact chemically with the surrounding molecules, interconnecting classical studies with advanced analysis of the chemical events taking place at the atomic/molecular level. Sum Frequency Generation (SFG) is one example <sup>28</sup>.

The activity of catalysts depends on the operating conditions used. Catalyst loading, solution pH and substrate concentration/nature are variables that should be considered among all the different catalytic-AOPs. Other parameters are specific for each process. Of importance is the oxygen partial pressure and the temperature in CWO, the light intensity in photocatalysis and the ratio Fe:H<sub>2</sub>O<sub>2</sub> in the Fenton process. The ozonation process is strongly dependent on the media pH. At low pH the direct and selective reaction of molecular ozone with pollutants occurs, while at high pH ozone is mainly decomposed in hydroxyl radicals which in turn attack the pollutants <sup>5</sup>. In CWO, the increase of temperature leads to a consequent increase in the oxidation rate. Regarding possible effects of oxygen partial pressure and catalyst loading, a hypothetical behaviour of the total organic carbon (TOC) conversion in a generalized reaction system at constant temperature is represented in **Figure 2**. Without catalyst and increasing the oxygen partial pressure the conversion obtained will be small if the pollutant is of difficult oxidation by non-catalytic WO. If the experiment is performed without oxygen but in the presence of a catalyst, some conversion can be achieved depending on the nature of the catalytic material. Increasing both oxygen and catalyst loading, a plateau of



**Figure 2:** Conversion of total organic carbon as a function of catalyst loading and oxygen partial pressure ( $P_{O_2}$ ), in CWO.

**Slika 2:** Popolna organska konverzija na CWO kot funkcija obremenitve katalizatorja in parcialnega pritiska kisika ( $P_{O_2}$ )

maximum efficiency can be observed in a region where changes in the correspondent values do not affect the global conversion. Moreover, for higher oxygen partial pressures decrease in conversion is represented as well, in order to account for the possible occurrence of over-oxidation by the catalyst, as referred in the literature <sup>29</sup>. At a constant oxygen partial pressure, decrease in conversion with higher amounts of catalyst represents the eventual acceleration of the *termination* step mechanism by the catalyst <sup>30</sup>.

Regarding photocatalysis, it is quite well established that the reaction rate is proportional to the radiant flux and to the mass of catalyst in slurry conditions, up to a certain loading for which all the particles are fully illuminated (usually between 0.6–2.5 g/L). For higher mass of catalyst, scattering effects can decrease the efficiency of the process <sup>12</sup>. In contrast to CWO, in photocatalysis heating is not required since the process is based in a photonic activation of the catalyst. In fact, increase of temperature can have a negative effect in the activity, since the adsorption of pollutants decreases and tends to decelerate the reaction. Thus, photocatalytic reactors operate at normal temperature and pressure. This advantage together with the possibility of using solar energy makes this technology very promising. Development of immobilized photoactive materials in the visible-light region ( $> 400$  nm) is the main challenge.

### 4 KINETIC STUDIES AND REACTION NETWORK

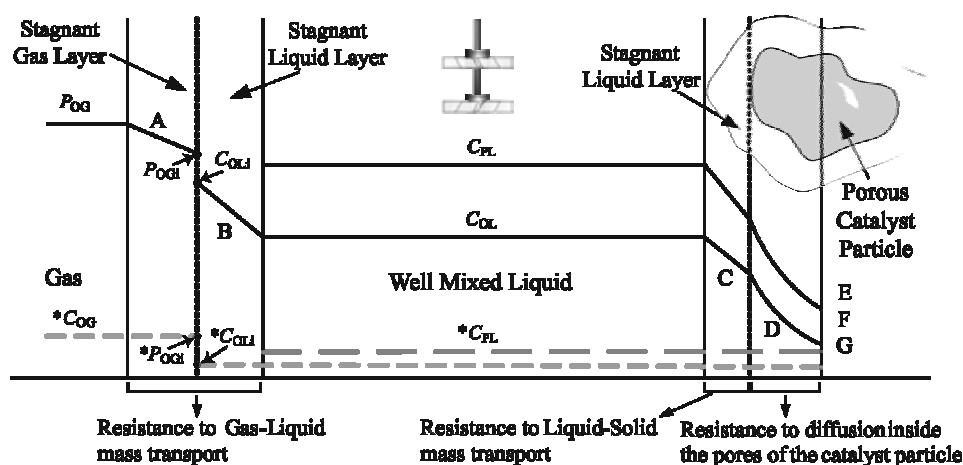
Multiphase reactions often consist of multiple reaction pathways with series of parallel reactions networks. Identification of intermediates is usually an essential

issue, normally requiring both experimental analysis and postulates from the available information. In AOPs the strong oxidation media leads to the formation of several intermediates. The difficulty in the development of a reaction network increases in complex reactions when many compounds are involved, which is of special importance when using industrial effluents. For this reason, besides Langmuir-Hinshelwood expressions, kinetic models based in lumped parameters grouping pollutants with similar reactivity have been widely used for AOPs<sup>16,31,32</sup>. Moreover, in general, the mechanisms are not well understood but it is quite consensual that free radicals participate actively. For this reason, the normal strategy when studying AOPs is to oxidize as much as possible the pollutants and look to the organic pollutants obtained at the end of the experiments, which are usually more resistant to oxidation than those degraded along the process.

The kinetic parameters are generally obtained in slurry operation batch-experiments for AOPs. **Figure 3** shows the typical concentration profiles of a general gas-liquid-solid system with external mass transfer and intraparticle diffusion resistances for the oxidant gas (O) and the pollutant (P). The local temperature is assumed to be constant throughout the different phases and the liquid backmixed. For the reactants the steps can be described as: (A) transport of O from the gas bulk to the gas-liquid interface; (B) transport of O from the gas-liquid interface to the liquid bulk; (C) transport of O and P from the liquid bulk to the catalyst surface; (D) intraparticle diffusion of the reactants into the catalyst pores; (E) adsorption of the reactants on the active catalyst sites; (F) surface reactions of O and P to yield reaction products; and (G) desorption of the products into the liquid bulk. Therefore, before the reaction at the active catalyst sites, different transport and reaction processes take place. In order to model the intrinsic reaction kinetics, the laboratory reactor should be

selected and operated with the aim of conducting the experiments under conditions where interparticle and intraparticle concentration and temperature gradients are absent. With mechanically agitated reactors, it is possible to eliminate or reduce the magnitude of these resistances in a gas-liquid-solid catalyzed system and, therefore, it becomes easier to obtain intrinsic reaction rates directly or derived from the experimental data. Continuous fixed-bed reactors have been also used for this purpose in CWO<sup>33</sup>; however, elimination of these gradients may be difficult.

For slightly soluble gas oxidants in water (e.g., oxygen), the transport of the oxidant in a gas phase constituted by two or more components (e.g., oxygen and nitrogen) is faster than in the liquid. The gas phase resistance can be then neglected, being the liquid film resistance the controlling mass transfer. Different experimental procedures can be considered in order to eliminate the concentration gradients on the system; (1) For the gas-liquid mass transfer resistance the preferred approaches are to improve the gas-liquid contacting or to increase the concentration of reactant in the gas phase. The first case can be obtained by means of some reactor specifications such as impeller rotational speed, design, size, location or gas sparger design, vessel baffles and other internals; (2) Concerning the liquid-solid mass transfer resistance, the elimination of this phenomenon is associated with the amount of catalyst, catalyst particle size, impeller diameter and location, baffles and other internals. The increase of the impeller rotation speed decreases the liquid-solid resistance, having, however, little effect once the speed attains the minimum value required for complete and uniform solids suspension; (3) The internal diffusion resistance can be reduced with the amount of catalyst as well as with the particle diameter since, consequently, the effectiveness factor increases<sup>34-35</sup>.



**Figure 3:** Schematic representation of typical concentration profiles for the gas ( $C_O$ ) and the liquid pollutant ( $C_P$ ) in a gas(G)-liquid(L)-solid(S) catalytic system with and without(\*) external mass transfer and intraparticle diffusion resistances ( $i = \text{interface}$ ).

**Slika 3:** Shematična predstavitev tipičnih koncentracijskih profilov za plinski ( $C_O$ ) in tekoči onečiščevalec ( $C_P$ ) v tekočem (L) in v trdnem katalitskem sistemu z zunanjim prenosom mase in brez njega(\*) ter difuzijska odpornost med delci (1 – mejna površina)

CWO experiments are conducted in stainless steel (or titanium) high-pressure autoclaves equipped with thermocouples and mechanically driven impellers for proper control of temperature and agitation velocity, respectively. In contrast, typical batch photocatalytic reactors consist of a glass external cylindrical reaction vessel, where is placed the reaction mixture, with magnetic agitation, and an inner double-wall compartment immersed inside the liquid housing the lamp and acting as a cooling water jacket. This compartment is made of glass or quartz depending on the type of irradiation that is studied (UV or UV/VIS). Therefore, batch reactors in slurry conditions are used to perform kinetic studies in both CWO and photocatalysis. However, the reactors are quite different in what respect configuration and construction materials.

## 5 CATALYST MOULDING

The optimal catalyst composition defined by slurry screening tests can differ when the experiments are performed with shaped catalysts. In this context, the different steps of catalyst development should be always strongly connected. The solid catalysts are typically used as a powder (slurry), or as irregularly shaped granule, table, sphere, or extrudate. Usually, the catalysts used in slurry have average particle diameters between 50  $\mu\text{m}$  to 450  $\mu\text{m}$  and the larger pellet catalysts used in fluidized and fixed-bed processes between 0.8 mm to 10.0 mm (an image of a shaped catalyst is shown in Figure 1-v). Structured catalysts, such as monoliths, membranes, foams and fibre catalysts are new attractive alternatives<sup>24</sup>. Shaped catalysts can be produced by traditional processes such as press and extrusion, or using new technologies as powder injection moulding (PIM). Some studies should be done to optimize the heating rate, sintering temperature, time and atmosphere composition. In particular for photocatalysis, the use of typical pellets is not feasible since the semiconductor catalyst has to be fully irradiated. For this reason, most of the known systems use fine powdered catalyst dispersions/suspensions, requiring a final step of filtration. As solution, photocatalytic materials can be immobilized onto glass or other supports as a film. Since these coatings are still not mechanically robust for the traditional and complex waste waters treatments, they are actual motive of intensive research<sup>13</sup>.

## 6 PILOT PLANT UNIT & PROCESS DESIGN

AOPs can be implemented in different three-phase reactors. Most used configurations are mechanically agitated reactors in slurry operation, bubble columns and packed-bed reactors. The complexity in modelling multiphase reactors with solid catalysts lies mainly in the fluid flow patterns, which depend on the reactor category. Prior to the intrinsic reaction that occurs at the

catalyst surface, the reactants have to diffuse from the gas and liquid phase to the active catalyst sites. In this context, the scale-up of a reaction system also involves evaluation of heat and mass transfer as well as gas-liquid hydrodynamics. Several models have been developed using various parameters such as interface mass transfer coefficients, intraparticle effective diffusion coefficients, axial dispersion coefficient, flow regimes, liquid hold-up, pressure drop and catalyst wetting<sup>23-24</sup>. These parameters depend on the hydrodynamic regime of the reactor and the physical properties of the phases (gas, liquid and solid). Interface mass transfer coefficients or external diffusion involve the resistances that are inherent to the reactor for transport from gas to liquid, liquid to solid, gas to solid and from dynamic to static liquid. The intraparticle diffusion or internal diffusion of reactants depends on the particle shape. The flow regime describes the flow pattern of liquid and gas throughout the reactor. The liquid hold-up consists of the interparticle and intraparticle fraction, of the total reactor volume, occupied by the liquid phase. The pressure drop depends on the liquid hold-up as the latter determines the effective void fraction available for the gas phase. The catalyst wetting deals with the average fraction of the external particle surface covered by the liquid. Many studies have been conducted at laboratorial scale to consolidate the knowledge in AOPs, but the bridge between laboratory and commercial scale is still a difficult task due to this high number of variables involved in the design of multiphase catalytic reactors.

Other specific issues should be also considered. For instance, in CWO experiments, it was found that heavy polymers are formed when some pollutants, such as phenol, are oxidized in slurry reactors. This phenomenon can be attributed to the high liquid-to-solid ratio in the slurry reactor, once these polymers can be formed through oxidative coupling. Afterwards, the polymers can be irreversibly adsorbed on the catalyst surface and progressively block the active sites. In this context, reactors with low liquid-to-catalyst volumetric ratio, such as packed-beds operating in trickle-bed regime, may be better options<sup>36,37</sup>. Moreover, catalyst stability should be addressed in continuous reaction application, taking as base the stability results obtained in batch operation. In fact, for a fresh catalyst, it is not unusual to show an initially high level of activity during short time testing. Nevertheless, sometimes, this is followed by a gradual or rapid decline with extended exposure, which may continue until some measure of activity reaches zero, or achieves a steady-state level caused by the deactivation of the catalyst.

Most of the studies performed in continuous operation deal with small-scale reactors. Relatively few studies have been published in the field of CWO in large-scale packed-bed systems, where mass transfer limitations are involved<sup>38</sup>. Therefore, experimental data, description of mass- and heat-transfer processes, reactor

simulation (e.g., using Computational Fluid Dynamics – CFD) and many other studies concerning continuous operation on CWO are object of research<sup>39,40</sup> being tested laboratorial pilot-scale reactors with lengths between 15–350 cm and diameters between 0.1 cm and 10 cm<sup>36,38,41,42,43</sup>.

Photocatalytic reactors differ in several aspects of design when compared with typical reactors. Selection of radiation sources (including solar light), respective design according to the radiation implemented, materials of construction and the need of other devices (such as reflectors, windows and cleaning setup) should be considered in their design<sup>13</sup>. Typical photocatalytic reactors consist of inner walled glasses housing the lamps in contact with the waste waters contained in an external reaction vessel. Other configurations consist of external or distributed light sources. Most of the reactors use powders as catalysts (slurry annular, open upflow, integrated flow membrane with filtration system, swirl flow, Taylor vortex and turbulent slurry reactors) or, less common, immobilized photocatalysts in solid matrix (falling film, fiber optic cable, multiple tube, packed bed, rotating disk and spiral glass tube reactors). Examples of solar reactors are the parabolic trough reactor, the

parabolic collecting reactor, the double skin sheet reactor, the tubular reactor and the solar pond<sup>13</sup>.

The deposition of photoactive films on the internal surfaces of the photoreactors is gaining more importance due to the increased control on the preparation of such materials. The liquid-phase processing methods that have been used specially to synthesize thin films, usually nanocrystalline, are (co-)precipitation and sol-gel methods while among the gas phase methods sputtering, spray pyrolysis deposition, chemical and physical vapour deposition are used. More investigation is needed regarding nano-adherence stability of crystalline films when applied over a rigid inert surface and explicit application of nano-films to photocatalytic reactors. Mechanical characterization of the films can be carried out by depth-sensing nanoindentation using Atomic Force Microscopes (AFM).

## 7 INDUSTRIAL-SCALE APPLICATION

Examples of commercial WO processes are schematized in **Table 1**<sup>19–20</sup>. As it can be observed, the WO technology has earned some place in the treatment of different waste waters. In particular, Zimpro (from

**Table 1:** Schematization of WO commercial processes

**Tabela 1:** Shematika komercijalnih WO-procesov

Process	N° Plants	Waste examples	Reactor	T/°C	P/bar	Catalyst
Zimpro	200 20 50	sewage sludge spent activated carbon industrial	bubble column (20 min – 4 h)	250–270 280–325 150–320	85–120 200 10–220	None (or homogeneous copper)
Kenox	n.s.	pulp & paper, metal finishing, petrochemical, food processing	recirculation reactor	204–260*	31–83	None (or impregnated in the static mixer)
Wetox	n.s.	n.s.	stirred tanks	207–247	40	None
VerTech	n.s.	sewage sludge	below-ground deep shaft	< 275*	< 110*	None
Oxyjet	n.s.	pharmaceutical and phenolic chemical wastes	jet mixer and tubular reactor (+ jet reactor)	< 300	n.s.	None (or in a jet reactor)
WPO	n.s.	n.s.	n.s. (H <sub>2</sub> O <sub>2</sub> as oxidant)	90–130	1–5	Fe <sup>2+</sup>
Ciba-Geigy	3	pharmaceutical, pulp & paper, petrochemical, hazardous waste landfill	n.s.	300	n.s.	Cu <sup>2+</sup>
Loprox	n.s.	Paper mill waste streams, municipal sewage sludge	Single or multi-stage bubble column	120–200	50–20	Fe <sup>2+</sup>
Orcan	n.s.	Textile	n.s.	120	3	Fe <sup>2+</sup>
ITECP**	n.s.	n.s.	n.s.	n.s.	n.s.	Bromide, nitrate and manganese ions
Athos	n.s.	municipal and industrial sludge	n.s.	240	44	Cu <sup>2+</sup> (heteroge- neous optional)
Osaka gas	n.s.	coal gasifier coke ovens cyanide sewage sludge	slurry bubble column	250	70	ZrO <sub>2</sub> or TiO <sub>2</sub> with noble or base metals
NS-LC	n.s.	phenol, glucose, acetic acid, etc	monolith	220	40	Pt-Pd/ TiO <sub>2</sub> -ZrO <sub>2</sub>
Kurita	n.s.	spent resins, ammonia	n.s.	< 170	n.s.	Supported Pt

n.s.: not specified; \*variable along the reactor; \*\*IT *Enviroscience catalytic process*.



USFilter, U.S.) is well established at an industrial level (WO diagram shown in **Figure 1-vi**). Treatment of sludge has been one of the main applications of WO and temperature ranges from 90 °C to 300 °C and pressures up to 220-bar have been used. Different reactor configurations have been developed, such as bubble column, tubular, stirred tanks, monolith and recirculation reactors. The commercial processes are essentially based in non-catalytic WO (five systems) or in homogeneous catalysts (six processes). The use of non-catalytic systems limits the application of the technology, increases considerably the operating conditions, and, therefore, the capital costs. Only few processes (three) involving heterogeneous catalysts, which are mainly based in expensive materials (Pt and Pd) are commercially developed. Regarding the use of photocatalysis for waste waters treatment, several companies are including this technology in their commercial portfolios. Commercial worldwide interest is clear, but many photocatalytic systems are still under development. Some cases of success are the solar plant in Almeria, Spain, and the systems commercialized by Purifics Environmental Technologies Inc., Canada<sup>13,15</sup>. Effective immobilization of catalysts that can operate under both artificial and solar light seems to be the main challenges for sustainable development of industrial-scale photoreactors. Therefore, the development of active and stable heterogeneous catalysts for industrial-scale application became still a key factor for enhancing the efficiency of AOPs.

## 8 FINAL REMARKS

Several criteria should be considered when selecting a given process for the treatment of waste waters. The development of catalytic materials is based on a methodical sequence of scientific and technological approaches to achieve a successful actual application. Identification of active phases by screening reactivity tests combined with the analysis of catalyst stability are the first steps in order to proceed with further kinetics and reaction network studies, which are particular of each reactional system, and consequently, of each type of waste water. In this domain, powerful analytical tools should be used especially for catalyst characterization and deep understanding of the catalytic reaction events. The integration of different AOPs have to be considered as a common strategy in laboratorial studies since better solutions can be obtained in an efficient-economic basis regarding both capital and operating costs when scaling-up these technologies. The catalyst powders should be transformed in suitable and mechanical robust forms for mass/heat transfer investigation and, eventually, hydrodynamic studies. In this task valuable computational tools can be used to simulate the catalytic processes, such as CFD, but kinetic data can be still only obtained with experimental work. Final testing in real

conditions is achieved after the scale of these technologies up to an industrial level.

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