ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 6, pp. 793–800. © Pleiades Publishing, Ltd., 2010.

VIII INTERNATIONAL CONFERENCE
ON MECHANISMS OF CATALYTIC REACTIONS

Environmental Photocatalysis in Action for Green Chemistry[1]

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Received November 23, 2009

Abstract—Heterogeneous photocatalysis is a recent discipline particularly well adapted to environmental problems since it operates at room temperature by replacing catalyst's thermo-activation by photo-activation (or replacing phonons by photons). In fine chemistry, high initial selectivities (100%) are obtained in dry organic media in selective mild oxidation of gaseous or liquid hydrocarbons. Similarly, 100% selectivities were obtained in sulfur-involving photocatalytic reactions, noted as "thio-photocatalysis". Environmental photocatalysis is active in water and air decontamination and can advantageously use the UV-A solar spectrum for outside applications.

DOI: 10.1134/S0023158410060030

Photocatalysis appeared as a new discipline in the mid sixties and later became an emerging "Advanced Oxidation Process", with more than 2000 recent publications on the subject [1] whose bases have recently been established [2–4] to prevent some misconceptions. "Green Chemistry" is that which follows twelve principles defined in [5].

(1) prevention (i.e., it is better to prevent waste than to treat or clean up waste after it has been created),

(2) atom economy,

(3) less hazardous chemical synthesis,

(4) designing safer chemicals,

(5) safer solvents and auxiliaries,

(6) design for energy efficiency,

(7) use of renewable feedstocks,

(8) reduce derivatives,

(9) catalysis,

(10) design for degradation,

(11) real-time analysis for pollution prevention, and

(12) inherently safer chemistry for accident prevention.

This article wants to exemplify "Green Chemistry" by photocatalysis.

TITANIA'S APTITUDES IN BOTH FINE AND ENVIRONMENTAL CHEMISTRY

Photocatalysis is alternatively able to induce either mild and selective or total oxidation reactions depending on the absence or presence of water, respectively [6], as summarized in table.

Photocatalysis in fine chemicals versus environmental chemistry

Parameters	Fine chemicals	Environmental catalysis
Main reaction	Mild oxidation	Total oxidation
Initial selectivity	100%	To selectivity
Final products for organics	C=O	CO_2
Medium	Dry medium	Water, humid air
Active species	O*	$OH^{\bullet}$
Reaction of formation	$(TiO_2) + h\nu \longrightarrow e^- + h^+$ $O^-_{ads} + h^+ \longrightarrow O^*_{ads}$ $(H_2O \rightleftharpoons H^+ + OH^-) + h^+ \longrightarrow H^+ + {}^{\bullet}OH$	

[1] The article is published in the original.

GREEN PHOTOCATALYTIC CHEMISTRY IN FINE ORGANIC CHEMISTRY

Selective Photocatalytic Mild Oxidation in Fine Chemicals

Photocatalysis is one of the heterogeneous catalytic processes able to functionalize light *n*-alkanes at room temperature into (aldehydes + ketones), either in gas or in liquid phase [7, 8]:

$$C_nH_{2n+2} + O_2 + [TiO_2 + h\nu + \text{air}] \longrightarrow C_nH_{2n}O + H_2O\ (n \geq 2).$$

Substituted aromatic hydrocarbons such as alkyltoluenes or *o*-xylenes are 100% regioselectively oxidized on the methyl group into alkylbenzaldehydes, both in gas or liquid phase, by mere irradiation of titania at room temperature [9]:

$$RC_6H_4CH_3 + O_2 + [TiO_2 + h\nu + \text{air}] \longrightarrow RC_6H_4CHO + H_2O.$$

The photocatalytic mild oxidation of olefins (propylene [10], cyclohexene [11]) gives a 100% initial selectivity in epoxides, which however decompose when increasing the conversion because of their high inherent reactivity. Primary and secondary alcohols, either gaseous or liquid, are 100% selectively oxidized in their corresponding aldehydes and ketones [12]:

$$RCHOH{-}R' + O_2 + [TiO_2 + h\nu + \text{air}] \longrightarrow RCOR' + H_2O.$$

Selective Photocatalytic Reactions Involving Sulfur: Thio-Photocatalysis

A recent review was devoted to sulfur compounds [13]. H_2S was chosen as a convenient and reactive source of sulfur [14], provided that the medium is oxygen-free, since otherwise H_2S would be preferentially oxidized in sulfate. The conversion of propene in 1-propanthiol was successfully obtained:

$$CH_3CH{=}CH_2 + H_2S \longrightarrow CH_3CH_2CH_2SH.$$

This result was unexpected since secondary 2-propanthiol is, in general, preferentially obtained in conventional processes. The addition of H_2S is of the anti-Markownikow-type [14]. This is indicative of a radical intermediary reaction. Actually, the overall reaction is not a redox one since carbon remains at its 2^- oxidation state. It is a simple addition resulting from the heterolytic dissociative adsorption of H_2S at the surface of the catalyst as $H^+ + SH^-$, followed by the neutralization of SH^- anions by photoholes (h^+):

$$h\nu + (\text{catalyst}) \longrightarrow e^- + h^+,$$

$$H_2S \longleftrightarrow H^+ + SH^-,$$

$$SH^- + h^+ \longrightarrow {}^{\bullet}SH,$$

$$CH_3CH{=}CH_2 + {}^{\bullet}SH \longrightarrow CH_3\dot{C}HCH_2SH.$$

Simultaneously, since the reaction is performed in reducing conditions without air, the free photo-electrons generated can readily react with adsorbed protons to generate $H^{\bullet}$ radicals which recombine with the thiolic radical into thiol:

$$e^- + H^+ \longrightarrow H^{\bullet},$$

$$H^{\bullet} + CH_3\dot{C}HCH_2SH \longrightarrow CH_3CH_2CH_2SH.$$

This reaction was extended to other sulfur-containing molecules. Octanthiol could be selectively (96%) added on octene to produce dioctylsulfide [15]:

$$C_6H_{13}CH{=}CH_2 + C_8H_{17}SH \longrightarrow C_8H_{17}SC_8H_{17}.$$

These reactions were performed using either CdS or TiO_2. Surprisingly, TiO_2 was revealed to be much more active than CdS. This is accounted for by the possible sulfidation of titania's surface, underlining the adaptability of this oxide and of its surface to new challenges, despite unusual and aggressive environments [14].

Selective Mild Oxidation of Substituted Aromatics to Illustrate Green Chemistry Principles 1–6, 8, and 9

As an example of green chemical photocatalytic reactions, let us consider the synthesis of an important intermediate in industrial fine (perfume) chemistry—4-*tert*-butylbenzaldehyde. Actually, it is environmentally-hostilely prepared in industry by the stoichiometric oxidation of 4-*tert*-butyltoluene (4-TBT) by permanganate. According to redox thermodynamics, this reaction requires a highly acidic medium, which has to be subsequently neutralized and generates a lot of (in-)organic by-products:

$$4\text{-}tert\text{-}C_4H_9C_6H_4CH_3 + 4KMnO_4 + 6H_2SO_4 \longrightarrow 4\text{-}tert\text{-}C_4H_9C_6H_4CHO + 2K_2SO_4 + 4MnSO_4 + 11H_2O.$$

By contrast, the oxidation of 4-TBT is 100% selective, both in gas or liquid phase, in 4-*tert*-butylbenzaldehyde by the mere near UV irradiation of titania used in. suspension in ambient air at room temperature [9]:

$$4\text{-}tert\text{-}C_4H_9C_6H_4CH_3 + O_2 + [TiO_2 + h\nu] \longrightarrow 4\text{-}tert\text{-}C_4H_9C_6H_4CHO + H_2O.$$

The photocatalytic oxidation of 4-TBT is a typical example of green chemistry with the use of air and a cheap, stable and recyclable titania catalyst which does not need solvents nor heating but only UV-A light provided by lamps whose technology is permanently improving.

The high selectivity was ascribed to the oxidation by a photoactive neutral, atomic oxygen species, which results from the neutralization of a dissocia-

tively chemisorbed O^-_{ads} species by positive photogenerated holes h^+:

$$O^-_{ads} + h^+ \longrightarrow O^*_{ads}.$$

The precursor O^-_{ads} has been detected by photoconductivity measurements as a function of the partial pressure of oxygen. This reaction only occurs in gas or liquid pure organic phase in the absence of water.

ENVIRONMENTAL PHOTOCATALYSIS: WATER DECONTAMINATION

Besides the selective mild oxidation of organics performed in gas or liquid organic phase, UV-irradiated titania becomes a total oxidation catalyst once in presence of water because of the generation of OH radicals obtained by neutralization of OH^- surface groups by positive holes [2, 3]:

$$OH^- + h^+ \longrightarrow {}^\bullet OH.$$

Inorganic Pollutants

Inorganic pollutants cannot be removed from water but can be detoxified. Various toxic anions are converted into harmless or less toxic compounds. Generally, the key element (S, N, P, C, etc.) is oxidized at its maximum and-harmless oxidation state [2, 3]. In parallel, heavy (noble) metals (**M**), which are generally toxic for human beings since they accumulate in the body, can be removed from industrial waste effluents [16, 17] by photo-reduction as small crystallites deposited on the photocatalyst according to

$$M^{n+} + H_2O + [TiO_2 + h\nu] \longrightarrow M^0(\downarrow) + nH^+ + n/4O_2$$

provided the redox potential of the cation metal couple is higher than the flat band potential of the semiconductor.

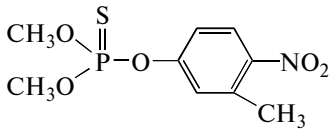
Organic Pollutants

This is the main field of water photocatalytic decontamination. Most of aliphatic and aromatic pollutants are totally mineralized into CO_2 and innocuous inorganic anions. More complex molecules such as pesticides (herbicides, insecticides, fungicides, etc.) or dyes are totally destroyed. This results from the unselective attack of organics by ${}^\bullet OH$ radicals, known as the second strongest oxidant (after fluorine). The unselective total oxidation of organics by ${}^\bullet OH$ radicals proceeds via the attack of a C–H bond, forming a water molecule plus a radical $R^\bullet$, which subsequently undergoes several attacks by ${}^\bullet OH$. Carboxylic intermediates react directly with holes h^+ which induce decarboxylation according to the photo-Kolbe reaction [18]:

$$RCOO^- + h^+ \longrightarrow RCOO^\bullet \longrightarrow R^\bullet + CO_2(\text{gas})$$
$$\longrightarrow C_{n-1} \longrightarrow C_{n-2} \longrightarrow C_{n-3} \longrightarrow \ldots \longrightarrow CO_2.$$

This reaction generates the first evolved CO_2(gas) molecule and accounts for the loss of C atoms as CO_2(gas) in total degradation of pollutants in water decontamination. A long list of photocatalytically degradable pollutants has been established by Blake [1].

The degradation pathways are generally very complex and require many advanced techniques. Dangerous chemicals such as organophosphorus are totally destroyed, as for instance insecticide fenitrothion [19], whose formula is



The mass balance analyses corresponded to the overall equation:

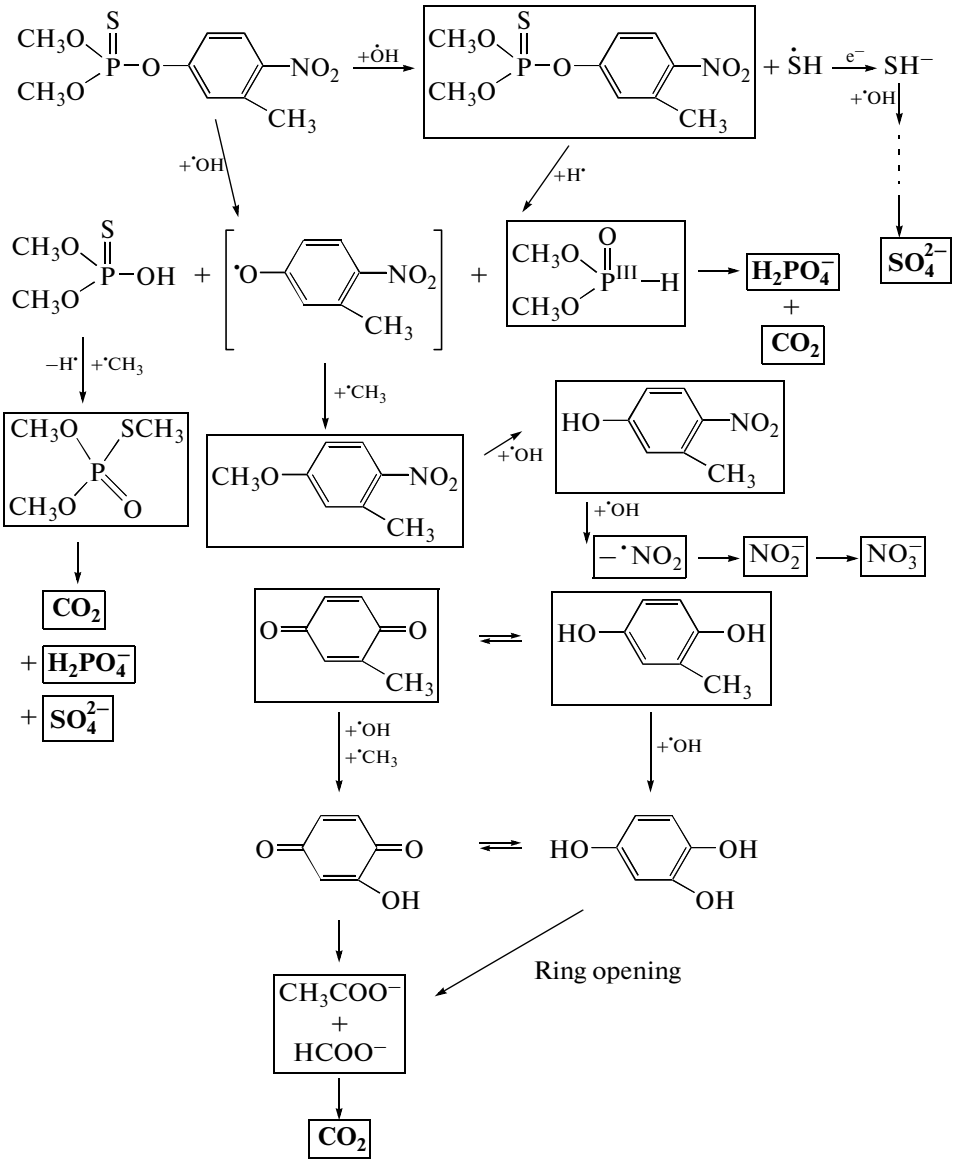
$$(CH_3O)_2P(S)OC_6H_3(NO_2)CH_3 + 27/2O_2$$
$$\longrightarrow 9CO_2 + 3H_2O + 4H^+ + H_2PO_4^- + SO_4^{2-} + NO_3^-.$$

The degradation pathway is complex as shown in Scheme 1. This particular efficiency of titania has been utilized for producing efficient photocatalytic gas masks for the US army in contaminated areas [20].

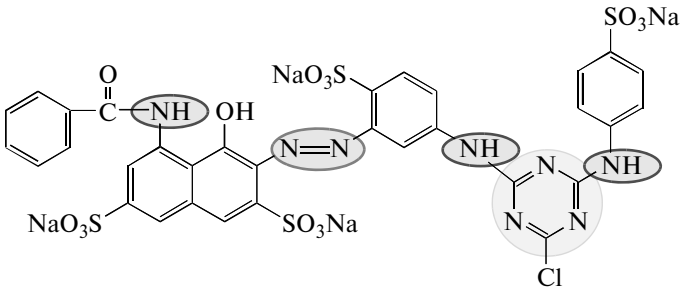
Dye Removal Case Study of Azo-Dyes

Dyes are not only decolorized by photocatalysis but also totally destroyed. Presently, half of them are azo-dyes (i.e., containing the –N=N azo-group). Several ones (Congo Red [21], Methyl Red [21], Orange G [21], Amaranth [22], Orange Yellow and Patented Blue) were all successfully destroyed and totally mineralized. The stoichiometric coefficients of the total degradation as well as the mass balances were established for different elements (carbon, hydrogen, oxygen, sulphur), except for nitrogen. Nitrogen has always been a complex element in chemistry because of its apparent inertness as N_2 but with multiple oxidation states, ranging from 3^- to 5^+. The nitrogen mass balance established in the aqueous solution based on nitrate and ammonium ions was not complete. What about the fate of total organic nitrogen? Using an airtight batch slurry photoreactor connected to an airtight gas chromatograph, an evolution of N_2 in the gas phase could be detected and quantified.

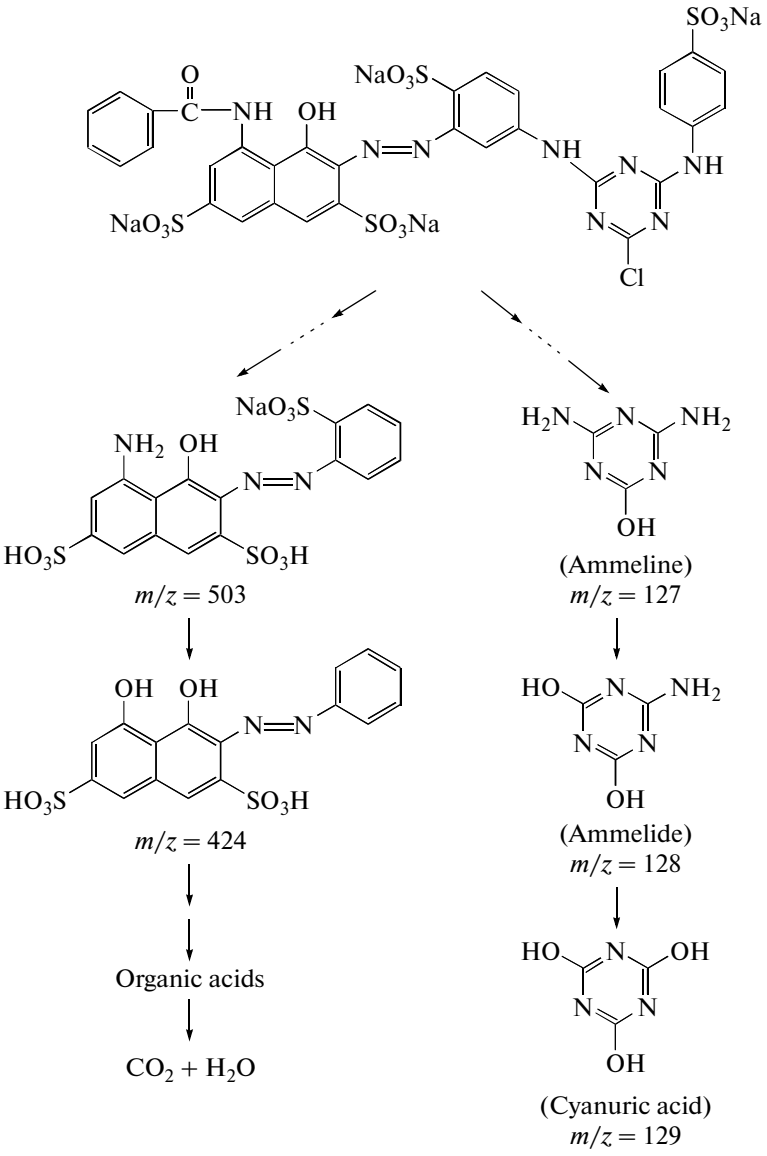
For example, azo-dye Reactive Red-4 (Cibacron Brilliant Red 3B-A), whose formula is given in Scheme 2 and which absorbs $\lambda_{max} = 517$ nm, was decomposed according to Scheme 3. It contains three nitrogen-containing functions: 1 azo group, 3 secondary amines and 1 triazinic ring. The three –N-groups gave ammonium and nitrate ions, whereas the atomic ratio of evolved nitrogen to total nitrogen $2n_{N_2}/n_{NT}$ was found equal to 0.25, i.e., just corresponding to the ratio 1/4 of the number of N atoms contained in the



Scheme 1. Photocatalytic degradation pathway of organophosphorus fenitrothion (the framed molecules correspond to those actually detected).



Scheme 2. Reactive Red-4 (Cibacron Brilliant Red 3B-A).



Scheme 3. Initial degradation pathway of reactive Red-4.

double –N=N azo-groups (n_{N_2}) to the total number of N atoms (n_{NT}).

This means that photocatalytic degradation of azo-compounds is 100% selective in generating gaseous dinitrogen from the azo-groups. This is the first example—to our knowledge—of a nitrogen evolution during the aqueous photocatalytic degradation of complex N-containing pollutants [21, 22]. This constitutes an ideal example of water decontamination in line with green chemistry. However, the complexity of nitrogen chemistry is underlined by the lower right part of Scheme 3. The triazinic ring remains unopen and thence undegraded! This was first observed by Pelizzetti et al. [23]. The triazinic ring is so stable that even the Total Organic Carbon Analyzer indicated a wrong 100% mineralization of carbon since it was unable to detect it. Therefore, this observation is useful to researchers who could be induced in a wrong interpretation of their own results based on an inefficient analytical tool. However, even if this ultra-aromatic ring remains unopen, photocatalysis remains the only technique able to "neutralize" it from the toxicity view point. Via ammeline and then ammelide, it is finally converted into cyanuric acid $C_3H_3N_3O_3$ (Scheme 3) so stable that it is unreactive and thence non-toxic. This is in line with the oxidation degree of carbon, which is already at the 4^+ state as in CO_2!

PHOTOCATALYTIC AIR TREATMENT

All pollutants in the aqueous phase can also be destroyed when they are in air phase, especially all the

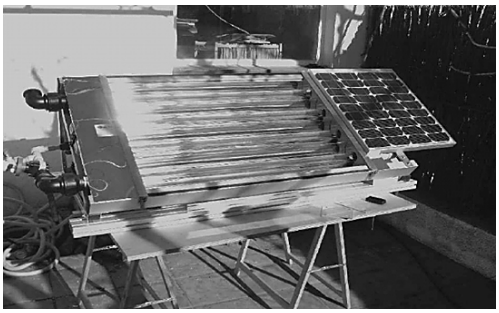


Fig. 1. SOLWATER and AQUACAT autonomous solar photoreactor prototype for water potabilization.

volatile organic compounds (VOC's). The air purification follows the same reaction mechanisms. However, the presence of a certain humidity is necessary to maintain an hydrated state of titania's surface, source of the hydroxyl groups, precursors of OH radicals, which are to be recalled as the second best oxidant after fluorine but as the first oxygen-containing one. In addition, this surface hydration is easily maintained by the formation of water during oxidation of the C–H bonds of organic pollutants to be destroyed.

For practical reasons, the photocatalyst has to be used in a fixed bed, or better deposited on a photoinert support. The optimum conditions for air treatment are based on the use of a fluidized bed described in [24–26]. The deposition of titania has been performed on various rigid supports including glass, quarz (actually, fused silica) or stainless steel [27]. A good anchoring of titania on such supports often requires controlled calcination, which induces interactions between both phases, in particular contamination and doping by foreign cations, which are detrimental for photocatalysis [27]. This is why we opted for a flexible support, paper, on the fibers of which commercial titania was merely bound using a UV-transparent silica binder. This has been done by J. Dussaud from Ahlstrom paper company.

In addition, it has been previously shown that the addition of activated carbon to titania in the aqueous phase created a strong interaction between both solid phases, with a kind of synergy: activated carbon adsorbs a great quantity of pollutants which are subsequently transferred to titania under the action of a driving force corresponding to an intense concentration gradient between activated carbon and "self-cleaning" titania. Such synergy exists in (humid) air treatment and enables one to absorb pollution peaks. In these conditions, UV-irradiated titania-based photocatalysis could be successfully applied to the elimination of air pollutants, VOC's, solvents, odors, chemicals, etc.

Concerning odors, air purification has been recently successfully applied to the removal of odors in confined atmospheres, in particular in domestic refrigerators [28]. An anti-odor domestic refrigerator prototype has been validated, patented and industrially produced in a first series at 40000 examplaries followed by a second one of 70000 units [28].

Other photocatalytic devices can equip kitchen ventilations, air conditioning systems in rooms or in cars. Some air purification devices are envisaged for the electronics industry, which requires a "molecular" purity of the ambient atmosphere for better performances of their nano-scale components. It can be noted that silicon-containing VOC's are destroyed, the organic part being mineralized as CO_2 and H_2O, whereas Si is converted in silica, which remains at the surface of titania, without troubles for photocatalysis since (i) it is transparent to UV-light and (ii) gathers as small islands, hard to detect by electron spectroscopy. We never reach saturation of coverage of titania by silica since gas impurities are lower than the ppm level.

The disinfection aptitude of titania-based photocatalysis evidenced in water was confirmed in air disinfection. For instance, virus H5N2, a model virus close to H5N1, responsible for the avian flu, could be photocatalytically deactivated in a dynamic photoreactor with a single pass of contaminated air at a flow rate of 60 m^3/h with an efficiency of 99.93%. This has been done in a specialized P3 medical laboratory of the medical school of the Lyon-1 University [29].

Air treatment has to be also associated to water and solid wastes treatment because of odors. This is done by covering water treatment ponds or lagoons by rafts on which large sheets of Ahlstrom papers are deposited, supporting associated titania-activated carbon (AC) catalysts which destroy odors with solar UV-photons in day time, whereas activated carbon traps odors during the night before their transfer to titania the next day, the driving force being the very strong concentration gradient between AC and self-cleaning titania.

SOLAR DRIVEN PHOTOCATALYTIC DETOXIFICATION OF ORGANIC POLLUTANTS

Various contaminants (phenol, 4-chlorophenol, herbicide 2,4-dichloro-phenoxy-acetic acid, malic acid, formatanate, Congo Red, etc.) previously studied in our laboratory, were later photodegraded in the solar pilot plant at the "Plataforma Solar de Almeria" (PSA, Spain) [30]. The same kinetics of disappearance and the same intermediate products were found indicating identical reaction pathways. The rate was found proportional to the overall light flux including both direct and diffuse UV-light. The total mineralization followed by the disappearance of the total organic carbon was obtained generally within less than 1 h residence time, i.e., faster than the CO_2 evolution in laboratory experiments. This was ascribed to a more adapted reactor design, based on a plug-flow photoreactor connected to a tank, the ensemble corresponding to a resulting batch photoreactor. These photocat-

alytic engineering studies were later followed by two European programs (SOLWATER and AQUACAT) to design and build a new robust totally autonomous solar photoreactor, presented in Fig. 1, able to potabilize water by (i) decontamination (chemicals) and (ii) by disinfection (bacteria) for remote isolated populations living in sunny semi-arid areas.

In this reactor, water circulates in UV-transparent tubings located in the focal axis of sun compound parabolic collectors, in which titania is deposited on a special Ahlstrom paper fixed either on a glass fin or on a cylindrical co-axial support. The photo-voltaic panel is aimed at producing a dc-electrical current to run a pump for a permanent recirculation from a tank of water necessary to maintain it disinfected. Actually, photocatalysis is active in water disinfection as illustrated by the photocatalytic degradation of *Escherichia coli* (Fig. 2).

These results clearly confirmed that solar photocatalysis is a cheap way to decontaminate water in arid sunny areas. In addition, they confirm that solar activation, with a 3–5% UV-A energy content, is suitable for activating titania-coated objects. They perfectly illustrate principles 3 to 9 of green chemistry, in particular 6, concerning the design for energy efficiency and 7, the use of renewable feedstocks, presently UV-A photons from the sun.

CONCLUSIONS: PRESENT CHALLENGES FOR PHOTOCATALYSIS

Since the number of publications on photocatalysis presently increases exponentially, especially from emerging countries and from other communities such as materials science, experts in photocatalysis are now confronted to new comers in the domain. The actual challenges have to be clear defined, especially to avoid serious misconceptions recently orally described by the author and which will be published in the near future. Some of these challenges concern the following points.

(1) Are we "condemned" to exclusively work with titania?

(2) Can TiO_2 be photosensitized in the visible by doping? It is already known that cationic doping is not efficient and rather detrimental whereas anionic doping, still under investigation, has to be more clearly defined.

(3) Can we find a new photo catalyst, different from TiO_2 and directly active in the visible light?

(4) Can invisible titania thin layers be efficient enough when deposited on "self-cleaning" objects?

(5) Is photocatalysis suitable for preparative fine chemistry as exemplified in Fig. 1?

(6) Is photocatalysis enough bactericide in water and in air?

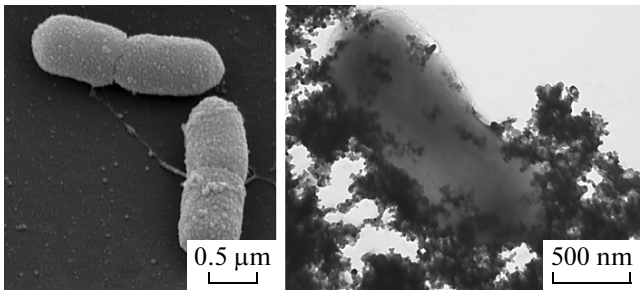


Fig. 2. Killing of *E. coli* before (left) and during (right) the adsorption before attack by UV-irradiated titania particles.

(7) Can photocatalysis be employed as a new medical tool in medicine ("cancericide effect" as reported in [31])?

(8) Are we able to define a few standardized and globally accepted tests for each photocatalytic application?

(9) Are we able to adapt to chemical engineering culture to promote environmental and "green" applications of photocatalysis?

This listing can constitute serious objectives for future researches in photocatalysis for the next years.

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