Overview on Photocatalytic and Electrocatalytic Pretreatment of Industrial Non-Biodegradable Pollutants and Pesticides

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Abstract. Electrochemical and photochemical catalytic pretreatments were studied on diverse non-biodegradable industrial or toxic pollutants using different catalysts. This approach turned out also to be useful to degrade recalcitrant industrial waste waters markedly enhancing the biodegradability and biocompatibility of the treated effluents. In the case of p-toluenesulfonate, a completely non-biodegradable material from the dye industry, the TiO_2 photocatalytic material applied for two hours affected total dearomatization allowing efficient subsequent biological degradation. A photochemical-biological flow reactor has been built to attain full mineralization of large volumes of diluted solutions of this xenobiotics as found in polluted water reservoirs. Fenton and photo-Fenton systems have been extensively studied in the abatement of the highly soluble Orange azo-dyes. They induce rapid destructive and low cost degradation of these textile dyes comparable to flocculation/coagulation techniques.

Introduction

Photocatalytic and electrocatalytical pretreatment of toxic, non-biodegradable industrial pollutants has been the subject of intensive research in our laboratory during the last few years [1–3]. Although biodegradation of common household effluents is an efficient process, a large and increasing number of industrial pollutants are resistant to bacterial degradation. Photocatalytical and electrochemical pretreatments [4] coupled with biological degradation seems to be an effective and inno-vative procedure to abate recalcitrant aromatic compounds. The optimization of the initial pretreatment stage renders the solution biocompatible [5]. The ensuing bacterial process (no cost step) is capable of degrading the aliphatics left in solution to a very low carbon level (< 10 ppm C TOC (= total organic carbon) or < 17 ppm C DOC (= dissolved organic carbon) acceptable in treated waters). The work of our group in 1995 was directed toward the use of new and improved catalysts, photocatalysts, and integrated processes to attain these objectives. Different aspects of the problem under study were dealt with separately and are dicussed next.

i) a. Oxidation of hazardous pollutants through an integrated flow reactor.
b. Photocatalytic flow reactor with in situ electrochemical generation of H_2O_2.

ii) Electrochemically and/or photocatalytically coupled degradation of industrial pollutants or non-biodegradable industrial effluents.

iii) Degradation/decoloration of soluble textile azo-dyes via Advanced Oxidation Technologies (AOT's).

iv) Degradation of non-biodegradable effluents from wine and oil processing.

v) Preparation and use of catalytic materials active in pollutant pretreatment: TiO_2, Fe-metal, Fe_2O_3, Fe-zeolites, CuO aerogel.

vi) Degradation of commercial brighteners: The case of Tinopal CBS-X and Tinopal DMS-X with relatively large polycyclic structures and molecular weights (Mw) 500–1000.
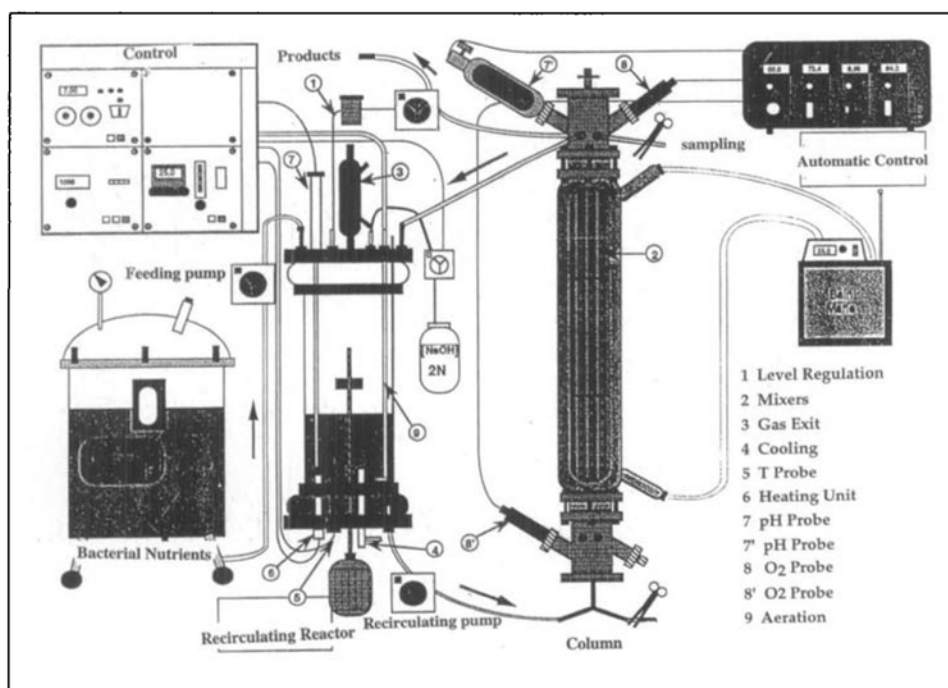
Catalytically-Biologically Integrated Flow Reactors Useful in Pollutant Abatement

A photocatalytical reactor has been built using a medium pressure Hg-lamp to dearomatize via TiO_2. p-Nitrotoluenesulfonate (p-NTS) in the presence of H_2O_2 was effectively degraded. The p-NTS is a non-biodegradable intermediate found in dye manufacture in Switzerland [3]. The

Fig. 1. Schematic of flow reactor used in the degradation of recalcitrant pollutants

Control
Products
sampling
Automatic Control
Feeding pump
NaOH 2N
1 Level Regulation
2 Mixers
3 Gas Exit
4 Cooling
5 T Probe
6 Heating Unit
7 pH Probe
7' pH Probe
8 O2 Probe
8' O2 Probe
9 Aeration
Bacterial Nutrients
Recirculating Reactor
Recirculating pump
Column

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initial dissolved organic carbon degraded from 400 mg C/l to 100 mg C/l in a few hours rendering a biocompatible solution with low toxicity. Quicker degradation was observed using the *Fenton* reagent $(Fe^{+3} + H_2O_2)$ under light illumination in an homogeneous type of pretreatment. This photocatalytical pretreatment allows acceptable degradation kinetics in the first stage recycling up to 20 l/h. The treated solution was fed into the biological second stage. The core of this reactor consists of immobilized bacteria attached to Biolite (*Fig. 1*).

The relatively short aliphatic chains coming into this second stage are further oxidized to CO_2 at a rate that is compatible with the volume dearomatized in the unit time to allow meaningfull coupling of the two stages. Preliminary results indicate the advantage of process integration in regards to the size of the reactor respect to the volume of pollutants it can handle [6]. The high pH, temperature, and salinity stability of the hybrid reactor when dealing with toxic substances like halocarbons, pesticides, atrazine, phenols, and diverse organic acids seem also promising. Work is under way to improve the type and variety of catalyst used, catalyst fixation and to decrease of light requirements for optimal energy use. This last item makes up to 60% of the cost of the integrated process.

Design and Construction of a Photocatalytic Reactor with an Electrochemical H_2O_2 Generator

An ergonomic unit of this type has been the subject of intensive research cooperation betwen Russia and Switzerland (INTAS contract 094-642, 1994). The destruction and decontamination of toxic man-made waste materials from the defense industry and agriculturally toxic residues has led to a cooperation between Russia and Switzerland since it is problem common to these two countries. A two-stage reactor is being developed consisting of a primary photocatalytic TiO_2 head and a second unit consisting mainly of an electrolyzer (*Fig. 2*) generating the H_2O_2 needed in the process.

This electrolyzer is fed by state-of-the-art solar-cell panels which should decrease considerably the cost of the energy necessary for the detoxification under suitable atmospheric conditions [7]. Common level of phenolic pollutants found in contaminated waters are of the order of 20 ppm or 10^{-5}M with a Mw of *ca.* 200. If 6 ml/min or 20 l/h water are treated, this are *ca.* 2mg C/

Cathode: granulated carbon subunit
$$O_2 + 2H^+ + 2e \rightarrow H_2O_2$$

Air

water mixture

Anode: Ti foil
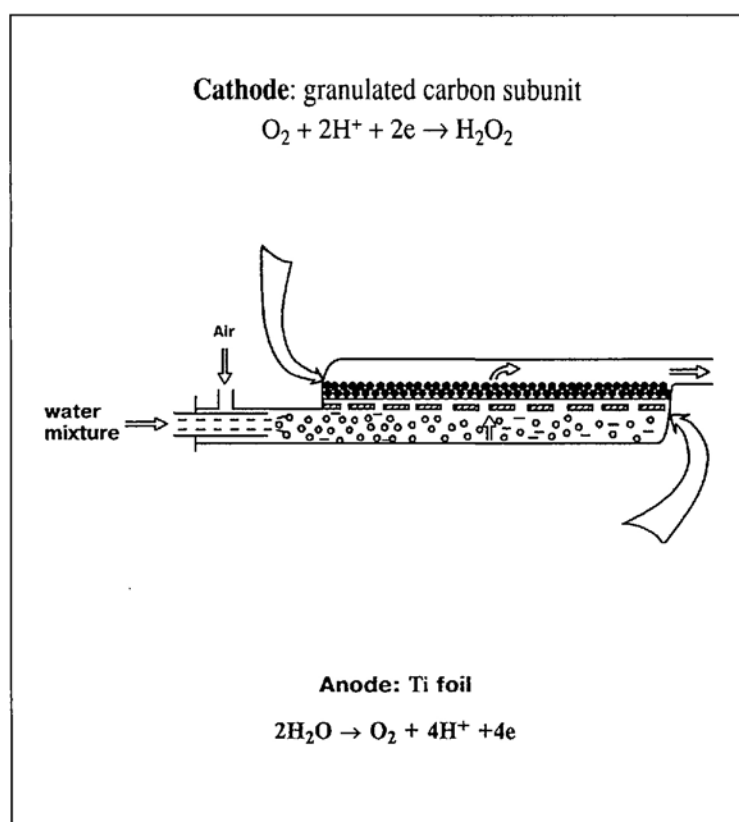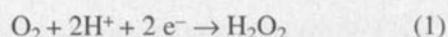$$2H_2O \rightarrow O_2 + 4H^+ + 4e$$

Fig. 2. *Electrolyzer unit used in the electrochemical generation of H_2O_2 to feed an ergonomic flow reactor aimed at the degradation of industrial pollutants*

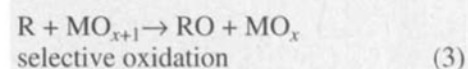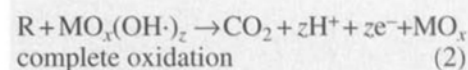l. To abate 10^{-5} ml C/s or 10^{-7} mol C/min we need to generate H_2O_2 as shown.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

This is the same as stating that 10^{-7}M pollutant/min need *ca.* 10^{-5}M H_2O_2/min. Since 1 ampere (A) = $6 \cdot 10^{-4}$ moles e^-/min then the equivalence is 10^{-5} moles H_2O_2/min = $2 \cdot 10^{-5}$ moles e^-/min and the charge necessary during the degradation is $2 \cdot 10^{-5}$ moles e^-/ min = 0.03 A or 30 mA a value in the range of the solar-cell output under AM 1 conditions used to feed the electrolyzer. The abatement of pollutants had been found to be strongly depending on the solution pH [8].

Effects of Electrochemical and Photocatalytical Pretreatments on Industrial Waste Waters

Electrochemical pretreatment was tried on industrial waste waters originating from a swiss flavor-manufacturing facility. *Fig. 3* presents the reduction for the TOC values for a solution containing 150 ml effluents using anodes either of Pt or Ti/SnO_2 as a function of the charge passed at the rate of 50 mA/cm². The two anodes were used because good electrochemical degradation was obtained for phenol [9][10] and benzoquinone [11] as model for industrial pollutants. Pt is used as anode material due to its stabiliy and long life-

time and because its catalytic properties are close to the Ti/IrO_2 commercial anode. Chlorine formation from chloride was observed along TOC abatement in *Fig. 3*.

The generated chlorine is suggested to accelerate the degradation of the pollutants in the waste waters since it enhances anodic oxidation. The electrolysis produces either $\cdot$OH radicals adsorbed on the electrode surface or chemisorbed active oxygen MO_{x+1} capable of acting as oxidation agent on the anode. This is shown below by *Eqns. 2* and *3*, respectively [12]:

$$R + MO_x(OH\cdot)_z \rightarrow CO_2 + zH^+ + ze^- + MO_x$$
complete oxidation $\quad (2)$

$$R + MO_{x+1} \rightarrow RO + MO_x$$
selective oxidation $\quad (3)$

The energy needed to decrease about 58% the initial TOC found in industrial effluents was estimated to be around 40 Wh/l. The energy cost was of the order of 5.2 US$ per m³, compatible with nondestructive techniques as the more traditional methods of desorption and flocculation.

Photochemical degradation of these waste waters was also carried out during this study. *Fenton* reagent was added and photolyzed with the effluent in homogeneous solution. After 10 h the TOC reduction attained *ca.* 60%, but in the absence of light this value only reached *ca.* 20%. The $\cdot$OH radicals are generated photochemically due to the 250–400 nm

light of the solar simulator (90 mW/cm²). About 58% of the initial TOC of these industrial effluents content is seen to abate over a few hours [13]. In effect, preliminary results show that the cost of the energy necessary for photochemical degradation was several times higher than waste treatment by electrochemical means. This is due to low efficiency in the electrical/light energy conversion of the order of 5 to 10% depending on the irradiation device used. This makes solar irradiation very suitable as a low-cost energy source.

In a separate study degradation *via* photo-*Fenton* reactions of nitrophenols have been reported by our laboratory [14]. The nitrophenols as such dissapeared in < 30 min and the TOC was abated in < 4 h. The efficient reduction of the non-biodegradable aromatics under light irradiation during *Fenton* reaction is due to the photocatalytically produced Fe^{+2} ions generating ·OH radicals and hydroxylating the ring(s) as long as H_2O_2 is available in solution.

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + \cdot OH \quad (4)$$

$$Fe^{+3} + PhH + \cdot OH \rightarrow Fe^{+2} + PhOH + H^+ \quad (5)$$
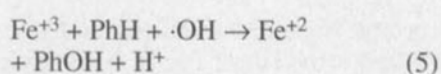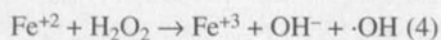
The optimal pH for such reactions was observed to be between 2 and 4 for many aromatic pollutants. The H_2O_2 decomposes into water and oxygen at pH values > 5.5 rather than generating ·OH radicals necessary in *Eqn. 4*. Another point to consider here is that Fe^{+3} begins to precipitate at pH > 4 decreasing its intervention efficiency at higher pH values.

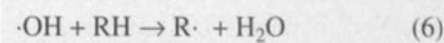## Degradation/Decoloration of Soluble Textile Azo-Dyes *via* Advanced Oxidation Technologies

Azo-dyes comprise about one half of the textile dyes used today and relatively large amounts of these highly water-soluble dyes leach out in the vicinity of manufacturing sites. We have taken Orange II as a model compound to study the degradation of this type of dyes. It is a commercial product, widely used and not biologically degradable. *Fig. 4* shows that the total mineralization of Orange II solutions due to the classical *Fenton* reagent using $(Fe^{+3} + H_2O_2)$ under light occurs within 8 h [15]. Orange II as such dissapeared in less than 10 min rendering in the oxidative environment used 4-hydroxybenzenesulfonic acid and naphthalene-1,2-diol. These latter two intermediates once generated were observed to be biologically degradable.

Spectroscopic evidence indicated that photocatalytic degradation of the azo-dye proceeded in acid media (pH < 5) through chelation between Fe^{+3} and Orange II. When starting from solutions with pH > 6 the pH in the solution was observed to shift by itself during the reaction to the acid region. The release of H^+ into the system allows the Fe^{+3} ions to be in soluble form and further chelate the Orange II promoting the photocatalysis.

Decoloration of the concentrated solutions of Orange II, an undesirable feature of dye-polluted streams was observed to abate in less than 2 h. The quantum yields observed for Orange II disappearance as a function of wavelength follows the point by point adddition of the absorbance of Fe^{+3} and H_2O_2 of the solution used during the photolysis [16]. Cu^{+2} is seen in *Fig. 4* to be less efficient in photodegradation of Orange II while an equimolar mixture of $Cu^{+2} + Fe^{+3}$ improved the dark oxidation efficiency of Fe^{+3}.

This effect could be explained by *Eqns. 6–8*. The Cu^{+2} ions would react with the organic radicals and subsequently reduce the Fe^{+3} ions in solution making the degradation of the azo-dye catalytical in iron- and copper-containing solutions.

$$\cdot OH + RH \rightarrow R \cdot + H_2O \quad (6)$$
$$RH = Orange\ II$$

$$R \cdot + Cu^{+2} \rightarrow R^+ + Cu^+ \quad (7)$$

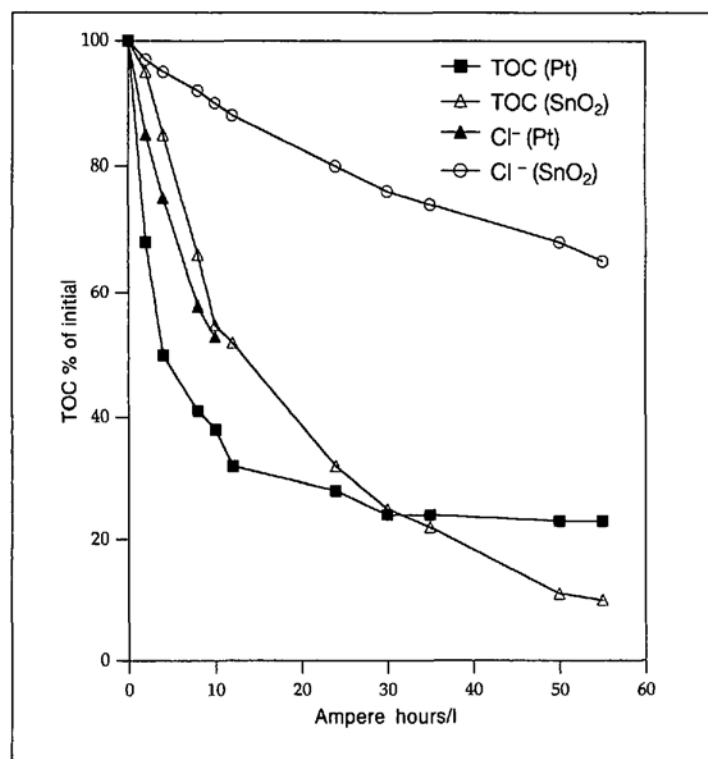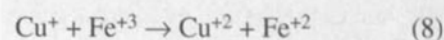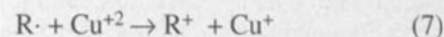$$Cu^+ + Fe^{+3} \rightarrow Cu^{+2} + Fe^{+2} \quad (8)$$

Fig. 3. *TOC decrease* vs. *Ah/l when 150 ml of industrial effluents of the flavor industry are electrolyzed with a) Pt electrodes, b) SnO₂ electrodes.* The percentage decrease of initial chloride for the same solution are also reported in the plot.
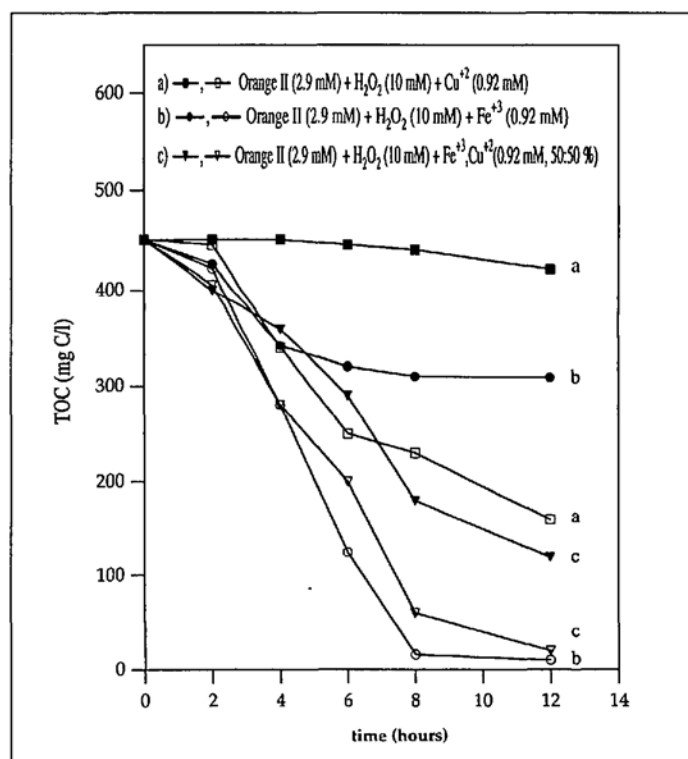

Fig. 4. *TOC decrease* vs. *time for light-induced runs* (open points) *and dark reactions* (full points) *for concentrated solutions of Orange II* (2.9 mM) *and H_2O_2* (10 mM) *with a) Cu^{+2}* (0.92 mM) b) *Fe^{+3}* (0.92 mM), *and c) Cu^{+2} and Fe^{+3} ions adding up to 0.92 mM.*

Different metal ions like Cr^{+2}, Mn^{+2}, and Co^{+3} were assayed besides Fe^{+3} and Cu^{+2} to affect *Fenton*-like photodegradation of Orange II. The results obtained suggested that the thermodynamic potential of the redox couple was not the most important factor controlling the efficiency during the abatement of this dye.

Pretreatment of Non-Biodegradable Effluents in Wine and Oil Refining. *p*-Coumaric Acid as a Model Compound

p-Coumaric acid is one of the common recalcitrant compounds found in olive and wine processing. It inhibits the biological degradation of waste waters of agricultural origin in Switzerland and along the Mediterranean shore. The oxygen in solution was monitored *via* a *Clark* electrode and in the gas phase *via* gas chromatography. This information in addition to the detection of the H_2O_2 consumption during the reaction (detection limit to 0.5 mg peroxide/l) allowed the optimization of H_2O_2 addition indicating the exact timing for the oxidant intervention after the previous aliquot of oxidant has been used up.

Fig. 5 shows the accelerated degradation of *p*-coumaric acid through a classical *Fenton* system. In the dark, slow degradation is observed of *p*-coumaric acid due to the reaction,

$$Fe^{+3} + H_2O_2 \rightarrow HOO \cdot + Fe^{+2} + H^+ \quad (9)$$

but also due to the formation of Fe/coumaric acid/H_2O_2 complexes which decarboxylate slowly in the dark. These complexes enter in the dark with much difficulty into reactions involving Fe-intermediates in *Fenton* cycles [17]. Under light these Fe-complexes formed in combination with H_2O_2 may form complexes that effectively participate in *Fenton* reactions active in *p*-coumaric-acid decomposition in addition to the free ·OH hydroxyl radicals described by *Eqns. 4–5*. These complexes showed significative tailing into the visible region beyond that of *p*-coumaric acid at $\lambda = 380$ nm and that of Fe^{+3}(aq) at $\lambda = 390$ nm and were sensitive to visible-light irradiation.

Decoloration of *p*-coumaric acid in concentrated solutions which is an environmental important aspect was observed in < 2 min. Photocatalytic degradation has to be effective within a few minutes to be worth of practical application *(Fig. 5)*. If not, the energy cost becomes to high compared with more traditional treatment methods. The cost involved in *p*-coumar-
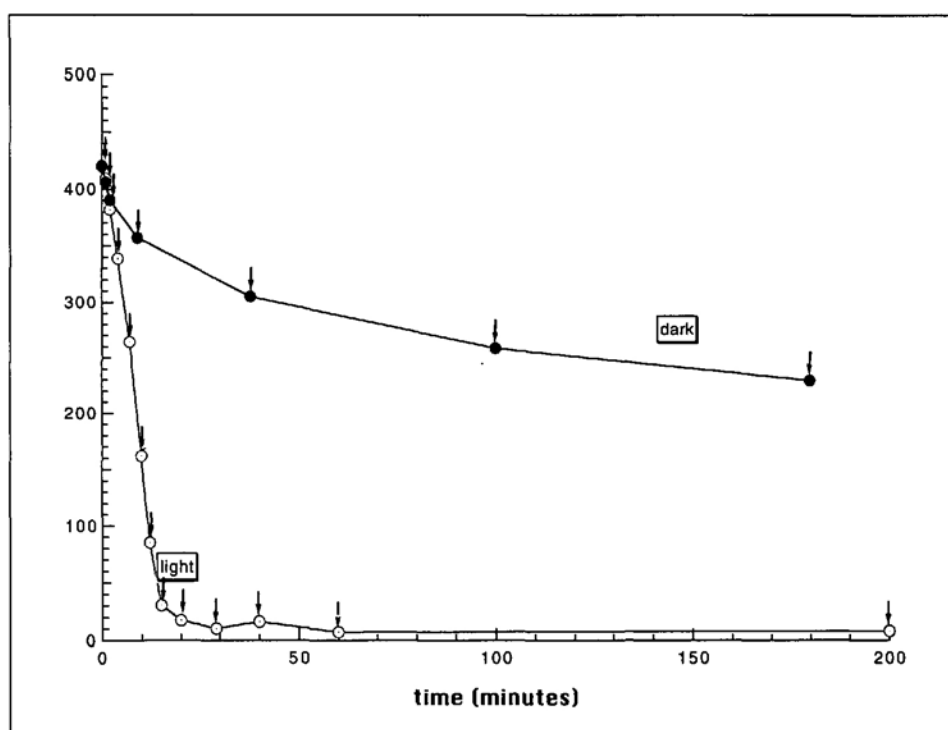

Fig. 5. *TOC* vs. *time during reaction in the dark and under irradiation when H_2O_2* (10 mM) *aliquots are added immediately after the consumption of the previous addition into a solution of* p-coumaric *acid* (3.95 mM) *and* Fe^{+3} (2.6 mM)

ic-acid mineralization was shown to depend on the volume of the waste water, the amount of oxidant, the time of illumination, and the dye concentration. The energy for the solar simulator (80 mW/cm^2) operation during 1/3 h on a reactor area of 48 cm^2 for 40 ml irradiated solution is *ca.* $0.08 \cdot 48 \cdot 1/3 : 0.04 = 31.7$ Wl/h. At 0.13 US$ per kWh the treatment of 1 m^3 solution would require an electricity input of *ca.* 4.1 US$. Adding the cost of the H_2O_2 used (1 l/m^3 at 1.9 US$/l) a total cost is *ca.* 6 US$/m^3 is estimated when mineralizing a concentrated coumaric-acid solution of 450 mg C/l. This cost of in the range of non-destructive flocculation/filtration processes [6] to treat industrial pollutants with the advantage that the pollutant is mineralized during the degradation process. In view of the latter result other acids like: gallic, gentisic, and caffeic acids are currently investigated since these substances also inhibit the biological treatment of waste waters of agricultural origin.

Catalytic Materials Efficient in Pollutants Pretreatment

Our laboratory is actively seeking new and more advanced catalytic material to effectively dearomatize recalcitrant industrial waste at reasonable cost. The main findings over the last two years to be published in 1996 are described briefly below:

TiO_2: The most widely semiconductor used due to its high surface activity and chemical as well as corrosion stability in heterogeneous photocatalysis [18] has been used successfully in our studies involving the degradation of anthraquinone-2-sulfonic acid [1], *p*-nitrotoluenesulfonic acid [3], waste waters [4][5]. Since TiO_2-related degradation processes of pollutants have been known for the last 15 years no further details are given in this overview.

*Fe^0*: The abiotic oxidative degradation of the herbicide atrazine by zero valent iron was activated beneficially by visible light and has been reported recently out of our laboratory [19]. This study involved nanosized iron powder under simulated solar radiation. Atrazine was seen to degrade in acidic pH within 2 h but the total elimination of Cl$^-$ took up to 25 h indicating the existence of long-lived intermediates during the degradation. The most important factors controlling the degradation rate were seen to be the nature, preparation, and surface area of the iron used.

α-Fe_2O_3: The results of the photocatalytic degradation of 2-aminophenol has been published recently [20]. The catalyst α-Fe_2O_3 reacted only with aminophenols having electron-donating character through the formation of a surface complex but not with phenol, 2-nitrophenol, and 2-chlorophenol.

Fig. 6 shows the values for the oxidation potentials for these phenols with the exception of 2-chlorophenol having an

oxidation potential > 1.2 V *vs.* NHE. These values were 0.295, 0.669, and 0.949 V *vs.* NHE, for 2-aminophenol, phenol, and 2-nitrophenol, respectively.

These latter results show that the electron-donating capacity is an important parameter controlling the degradation of 2-aminophenol on the iron oxide. The electron-donor capacity of 2-aminophenol may allow the formation of donor-acceptor complexes due to the low oxidation potential of aminophenol in addition to the *ortho* effect of the NH$_2$ group in the ring. Oxygen has beeen observed to play an important role in the degradation of this substrate. This effect is understood in terms of the reaction

$$:NH_2-R + O_2 \rightarrow (R-NH_2\cdots O_2) \rightarrow$$
$$R-NH_2^+ + O_2^- \qquad (10)$$
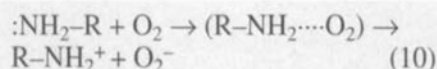
Oxidation of the nitrophenol complex formed *via* a ligand-to-metal charge transfer and concomitant reduction seem to proceed at the oxide surface. In the ensuing reaction the surface is reoxidized in the presence of air. The photocatalyzed degradation of 2-aminophenol is more related to a surface complex and not to a semiconductor-assisted photodegradation.

Fe-ZSM-5 zeolite: The degradation of 4-nitrophenol was also possible and has been reported using a 1.5% Fe-zeolite catalyst [21]. The photo-oxidation proceeded well at pH ≈ 3 where 3 moles of H$_2$O$_2$/mol of 4-nitrophenol were required under light to mineralize the substrate. During the photodegradation Fe^{+3} corrosion is observed in acidic media. The substrate abatement proceeds through hydroxylation of the ring as followed by ^{1}H-

NMR spectroscopy during the time of the reaction. The rate of 4-nitrophenol disappearance was observed to be a multistep process depending on the amount of zeolite used, the concentration of the substrate and peroxide used, the reaction temperature, and pH. The rates obtained for the degradation were a composite of processes taking place at the zeolite surface, the dark or thermal reaction steps and the *Fenton* light-induced efficient H$_2$O$_2$ decomposition.

CuO aerogel: The catalytic oxidation and photooxidation of nitrophenols by a strong oxidant generated *in situ via* CuO aerogel has been recently reported out of our laboratory [22][23]. Nitrophenols were catalytically degraded with high efficiency by a novel CuO-aerogel powder prepared by sol-gel methods with a surface area (20 m^2/g). By XPS the surface Cu species was seen to contain of 80% Cu(I), 15% Cu(II), and 5% Cu^0. *Fig. 7* presents copper dissolved during thermal and light experiments for the first and third cycle in solution. It is seen that copper in solution decreases more steeply for irradiated solutions than in the case of thermal reactions. This effect is more pronounced for Cu^{+1} ions either in the dark or under light. The copper in solution has been assessed *via* the neo-cuproin reagent following the absorption of the Cu-neocuproin complex in chloroform solution. The absorbance at λ = 457 nm was measured against appropiate blanks. To identify specifically the Cu^{+1} ion present we added Fe^{+3} ions (1 mM) at pH 2.5. The Cu^{+1} reacts with Fe^{+3} and the resulting Fr^{+2} complexes with *o*-phenanthroline. The Fe-phenanthroline complex showed a peak at λ = 510 nm (ε = 1.2·10^4 M^{-1} cm^{-1}).

Up to six consecutive degradations showed no decrease in the catalyst efficiency confirming the stability during the reaction. After each 24 h cycle, fresh nitrophenol was added after washing the catalyst several times with water before reuse. Hydroxylic sites on the CuO were suggested to be involved in the substrate degradation process when Cu^{+1} is reoxidized by oxygen in the presence of light in acidic media:

$$2Cu^{+1} + O_2 \rightarrow (Cu_2O_2)-H^+ \rightarrow$$
$$CuO-OH^+ \qquad (11)$$
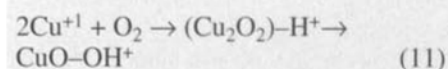
Cu$_2$O$_2$ reacts with O$_2$ generating peroxides. This has been known for the last two decades [8].

By way of cyclic voltammetry a half-wave oxidation potential for the Cu^{+1}/Cu^{+2} couple was detected at 0.23 V *vs.* NHE. This value is different to the value
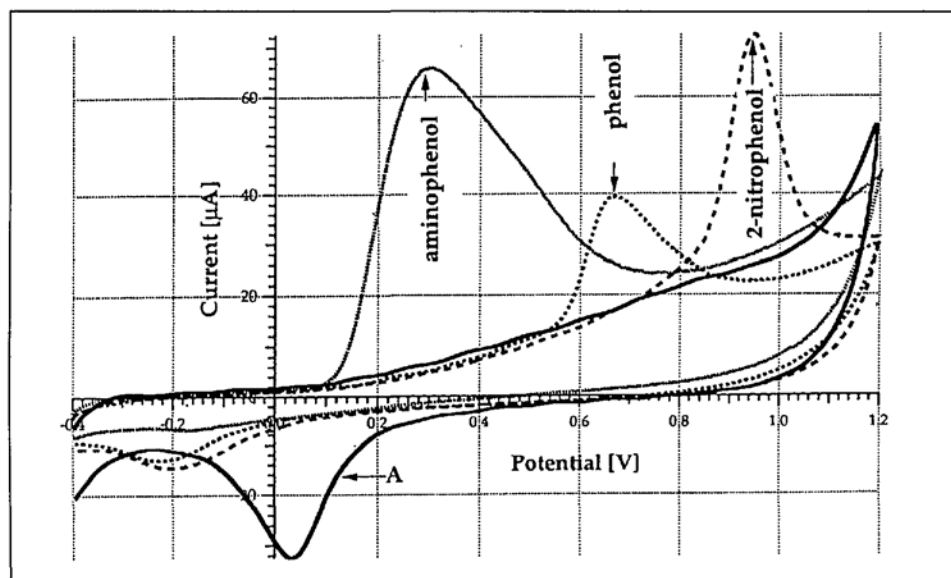
Fig. 6. *Cyclic voltammetry showing the oxidation potentials V vs. NHE* (normal hydrogen electrode) *for the phenols described.* For other details see text.
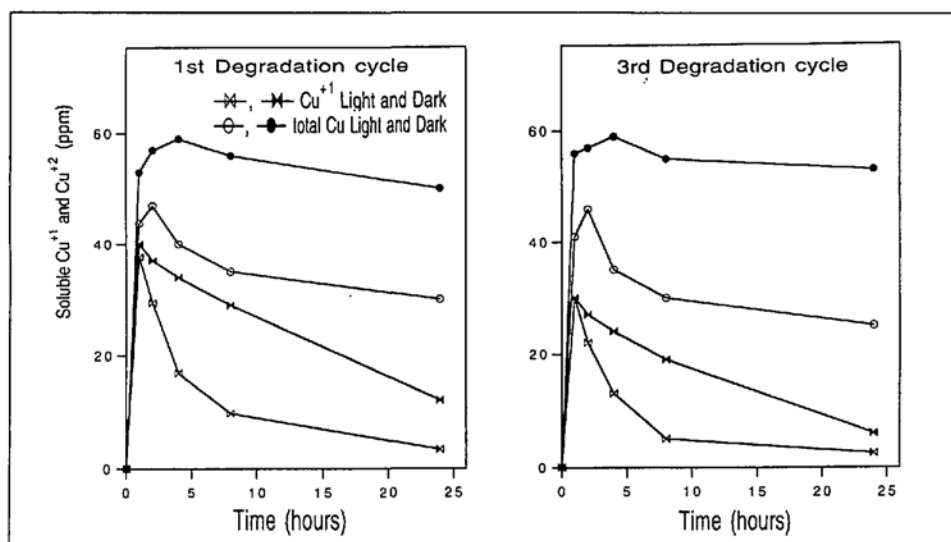
Fig. 7. *Thermal* (dark points) *and light reactions* (open points) *for the catalytic degradation of a solution of 2-nitrophenol* (0.8·10^{-3}M) *with 1 g/l CuO aerogel*

for the potentials of this couple in homogeneous solution (0.16 V). It was also observed that Cu^{+1} ions added homogeneously in solution did not induce 2-nitrophenol degradation either in the dark or under irradiation. We suggest, therefore, that Cu ions adsorbed on the CuO aerogel are the precursors active during the degradation which would be heterogeneous-homogeneous in nature. The adsorbed Cu^{+1} and Cu^{+2} ions react with oxygen adsorbed on the CuO-aerogel surface where the concentration of $Cu^{+1} >> Cu^{+2}$ as seen by XPS. Since the nitrophenol degradation was favored respect to air and even more to Ar-purged solutions, the evolution of Cu^{+1} shown in *Fig. 7* could be stated

$$d[Cu^{+1}{}_{solution}]/dt = \\ k\,[Cu^{+2}{}_{CuO\ aerogel}]\cdot[O_2] \qquad (12)$$

Degradation of Commercial Brighteners

Two cases have been investigated as listed below:
a) Photodegradation *via Fenton* systems of Tinopal CBS-X.
b) Degradation via TiO_2 suspensions of Tinopal DMS-X.

a) The aim of this work was to find ways to degrade Tinopal CBS-X from household effluents. Currently we only know that it is adsorbed up to 80% on the membrane walls of sewage bacteria in treatment plants [24]. The rest diffuses into natural streams and reservoirs, and is entrapped in sediments over longer time periods. We have used the photo-*Fenton* system to dearomatize this substrate in less than 1 h with complete mineralization over 5 h. Our approach is environmentally friendly due to the extremely low concentration of Fe^{+3} used. The H_2O_2 acting as an ecological oxidant generates $\cdot$OH and other oxidative radicals besides O_2 and a small amount of H_2 during the degradation. Intermolecular bond scission between the aromatic rings was found to be a much slower process than the intramolecular bond scission in the aromatic rings during the degradation. By means of the *Zahn-Wellens* test it was found that for the pretreated solutions the adsorption of Tinopal CBS-X proceeds much faster than when umpretreated substrate is fed on the activated sludge.

b) Degradation was carried out on Tinopal DMS-X a stilbene-type whitening agent (FWA) resistant to biological degradation. To degrade Tinopal DMS-X TiO_2 revealed itself effective in aqueous suspensions [25]. Tinopal DMS-X fluores-

cence decayed in less than 2 h showing the photooxidation of the substrate under illumination. Total mineralization took *ca.* 20 h. The titania-catalyzed Tinopal DMS-X photodegradation was observed to be cyclic in fashion. The catalyst was washed after each run and reused up to six runs not loosing any of his activity. The high photosensitivity of this solution has to be kept in mind when handling this compound during the experimental work. Tinopal DMS-X revealed itself also capable of sensitizing the fluorescence of humic acid. This study allowed to assign the energy transfer from Tinopal DMS-X to humic acid, as proceeding *via* a singlet mechanism.

[1] J. Kiwi, C. Pulgarin, P. Peringer, M. Grätzel, *New J. Chem.* **1993**, *17*, 487.

[2] J. Kiwi, C. Pulgarin, P. Peringer, M. Grätzel, *Appl. Catal. Environ.* **1993**, *3*, 85.

[3] L. Minsker, C. Pulgarin, P. Peringer, J. Kiwi, *New J. Chem.* **1994**, *1*, 793.

[4] J. Kiwi, C. Pulgarin, 'Beneficial effects of photochemical and electrochemical pretreatment of non-biodegradabale industrial pollutants and pesticides', in 'Environmental Catalysis', Ed. G. Centi, Italian Society of Chemistry, Roma, Italy, 1995, Vol. 1, p. 519.

[5] J. Kiwi, C. Pulgarin, 'Novel catalytic pretreatment methods allowing and accelerating the degradation of industrial pollutants', in 'Catalysis: Modern Trends', Eds. N. Gupta and D. Chakrabarty, Narosa Pub. New Dehli, 1995, Vol. 1, p. 405.

[6] C. Seignez, C. Pulgarin, S. Bosco, P. Peringer, J. Bandara, J. Kiwi, World Environmental Congress, London, Ont. Canada, 1995, Abstract p. 243.

[7] E. Savinov, I. Martianov, D. Bavykin, M. Fedotenko, J. Kiwi, World Environmental Congress, London, Ont. Canada, 1995, Abstract, p. 356.

[8] I. Martianov, E. Savinov, V. Parmon, J. Kiwi, World Environmental Congress, London, Ont. Canada, Abstract, 1995, p. 325.

[9] C. Comninellis, C. Pulgarin, *J. Appl. Electrochem.* **1993**, *23*, 108.

[10] C. Comninellis, C. Pulgarin, *J. Appl. Electrochem.* **1991**, *21*, 703.

[11] C. Pulgarin, N. Adler, P. Peringer, C. Comninellis, *Water Res.* **1994**, *28*, 887.

[12] C. Comninellis, *Electrochim. Acta* **1994**, *39*, 1857.

[13] P. Ribordy, C. Pulgarin J. Kiwi, P. Peringer, Am. Chem. Soc. Environmental Chemistry, Anaheim CA, 1995, Abstract, p. 109.

[14] Kiwi, C. Pulgarin P. Peringer, *Appl. Catal. Environ.* **1994**, *3*, 335.

[15] C. Morrison, J. Bandara, J. Kiwi, *Adv. Oxid. Technol.* **1996**, accepted for publication.

[16] J. Bandara, C. Morrison, J. Kiwi, C. Pulgarin, P. Peringer, *Photochem. Photobiol. A: Chem.* **1995**, in press.

[17] V. Nadtochenko , J. Kiwi, *J. Environ. Sci. Technol.* **1995**, submitted.

[18] M. Hoffmann, S. Martin W. Choi, D. Bahnemann, *Chem. Rev.* **1995**, *95*, 69.

[19] C. Pulgarin, J.-P. Schiwtzguebel, P. Peringer, G.-M. Pajonk, J. Banadara, J. Kiwi, *Adv. Oxid. Technol.* **1996** ,vol. 1, No 1, in press.

[20] C. Pulgarin, J. Kiwi, *Langmuir* **1995**, *11*, 519.

[21] C. Pulgarin, P. Peringer, P. Albers, J. Kiwi, *J. Molec. Catal. (Chemical)* **1995**, *95*, 61.

[22] J. Bandara, J. Kiwi, C. Pulgarin, P. Peringer, G.-M. Pajonk, P. Albers, *Environ. Sci. Technol.* **1996**, in press.

[23] J. Bandara, J. Kiwi, C. Pulgarin, G.-M. Pajonk, *J. Mol. Catal. Lett.* **1995**, submitted.

[24] C. Pulgarin, P. Peringer, J. Kiwi, *J. Adv. Oxid. Technol. (AOT's 1)*, **1996**, Vol. 1, No 1, in press.

[25] J. Bandara, R. Humphry-Baker, J. Kiwi, *Adv. Oxid. Technol (AOT's 2)*, **1996**, accepted.