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Degradation of organic pollutants in water by photochemical reactors

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Abstract

The degradation of glycolic acid in aqueous media was performed by homogeneous photochemical and heterogeneous photocatalytic processes using different kinds of chemical reactors. The efficiency of the degradation processes was evaluated by measuring both the reactant conversion and the decrease of the total organic carbon (TOC) of the solution. The best results were obtained by using a continuous reactor with a fixed supported photocatalyst. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Water purification; Supported photocatalyst

1. Introduction

Most of the organic pollutants contained in waste waters can be effectively removed by biological oxidation and other well-known processes. In some cases the presence of toxic and refractory compounds prevents the application of the conventional technologies and the so-called advanced oxidation processes (AOPs) must be used [1,2]. An interesting class of AOPs consists of the photoactivated processes. A key feature of these processes is the possibility to achieve the complete oxidation of refractory organics to water and carbon dioxide at room temperature and atmospheric pressure. The photoactivated chemical reactions are characterised by a free radical mechanism initiated by the interaction of photons of a proper energy level with the molecules of chemical species present in the solution or with a catalyst. The radicals can be easily produced using a UV radiation by the homogeneous photochemical degradation of oxidising compounds like Hydrogen peroxide and Ozone [3–5]. An alternative way to obtain free radicals is the photocatalytic mechanism occurring at the surface of semiconductors (like titanium dioxide). In this case electrons of the semiconductor crystalline structure are excited from the valence to the conduction energy bands creating electron–vacancy pairs. The charged carriers can be captured by intrinsic traps of the solid surface or simply recombine, but their life can be sufficiently long to give rise to interaction with different compounds (electron donors and acceptors) adsorbed at the catalyst surface [6,7].

The photocatalytic process can be carried out by using a slurry of fine particles of the solid semiconductor dispersed in the liquid phase. In this case the performance of the reactor might be severely affected by the low irradiation efficiency due to the opacity of the slurry. After the oxidation treatment the solid catalyst must be separated from the liquid. This is

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not an easy operation because of the small size of the particles (usually below 1 micron). A further problem is the fouling of the surface of radiation source due to the deposition of the catalytic particles.

At present time, the application of the slurry photocatalytic treatment in large scale reactors seems to be quite problematic. In recent years fixed supported photocatalysts have been investigated in order to improve the feasibility of the process on an industrial scale [8–11]. The key points in the development of a supported photocatalyst are the possibility to obtain an active crystalline structure and the stability of the catalyst layer in the reacting media. Films obtained by wash-coating using a suspension of commercial products with a well-known photocatalytic activity satisfies the first condition, but can be very sensitive to the erosion by the flowing liquid [8]. Durable supported films can be obtained by different techniques like physical and chemical vapour deposition (PVD and CVD), but in this case the crystalline structure of the final product and consequently the catalytic activity might be difficult to control.

In the present work glycolic acid was chosen as the test molecule to evaluate the performance of different chemical reactors. The deep oxidation of aliphatic acids in aqueous media is also of practical interest because these organic compounds (e.g. formic, glycolic and citric acid) are contained in waste waters produced by cleaning of boilers in power plants. The degradation of the test reactant in aqueous solution was performed by the following photo-activated processes:

1. heterogeneous photocatalysis using either supported or dispersed catalyst (titanium dioxide in the Anatase form);
2. homogeneous photochemical oxidation in the presence of hydrogen peroxide;
3. combination of photocatalytic and photochemical process.

2. Experimental

Two pilot-size reactors have been used to perform the experimental tests. Both the reactors were equipped with UV (low pressure mercury) lamps characterised by an almost monochromatic emission at a wavelength of 254 nm. The various reactors were different in size and radiation power, but had the same tubular configuration with an axial cylindrical UV lamp and an annular free space for the gas and the liquid flowing upward. The experimental results obtained by different reactors could be used to compare the various degradation processes since the radiation distribution along the reaction zone was very similar (55–65 W/m).

The experiments with the suspended solid catalyst were carried out by using the reactor A (Table 1). The slurry was obtained by dispersing fine particles of commercial Titania (Degussa P25) in the liquid. The dispersion of the catalytic particles in the liquid was improved by the sonication of the slurry in a 20 kHz ultrasound bath for 10–15 min. The apparatus was operated as a batch system by recycling the liquid contained in a mixed vessel.

The continuous reactor B was used to test the supported photocatalyst. A thin film of Titania was fixed on a cylindrical (32 mm i.d.) surface of AISI 316 stainless steel by physical vapour deposition (PVD) [12]. The product of this first step was an amorphous phase that was converted into the active crystalline

Table 1
Experimental equipments

	Reactor A	Reactor B
Operating regime	Batch-recycle	Continuous-single pass
Flow regimes	Single liquid and biphase upward	Single liquid and biphase upward
Reactor internal diameter (mm)	76	32–76
UV lamp diameter (mm)	25	25
UV lamp length (mm)	230	750
Reactor volume (cm^3)	1000	277–2721
Liquid hold-up (%)	85–100	81–100
Lamp input power (w)	15	40

structure of the catalyst (Anatase) by a thermal treatment at 500°C. The cylindrical catalyst supports were placed in the reactor coaxial with the UV lamp so that an almost uniform radiation of the whole active surface could be obtained.

The homogeneous photodegradation in the presence of hydrogen peroxide was performed both in the batch and in the continuous reactors A and B.

In the reactor B a gas/liquid separator was placed at the outlet and the samples were collected at its outlet. In the reactor A the samples were taken between the tank and the pump. The residence time in the reactor B was varied by changing the liquid flow rate. Experiments were carried out both in monophasic regime (solution saturated with air) and in biphasic liquid/gas flow. In this last case the gas hold-up in the reactor was experimentally determined. The hold-up does not change with the liquid flow rate but varies sensibly with the gaseous flow rate. At the operating conditions tested in this work (1.5 l/min for the continuous system and 5 l/min for the batch equipment) the gas hold-up ranged from 19% in the reactor B to 15% in the reactor A.

The effective residence time was determined on the basis the actual liquid hold-up inside the reactor. For the batch reactor A the actual residence time in the photoactivated zone was calculated by considering the ratio between the volume of the reactor and the total volume of liquid (including the storage tank and the recycling tubes).

The initial concentration of the glycolic acid was 200 mg/l for all the tests presented in this work. The reactants were supplied by Carlo Erba (purity grade higher than 99%) and were used as received. A TOC instrument (Fisons Instruments), equipped with an oxidation and a reduction reactor and an FID detector, was used to measure the content of Total Organic Carbon of the solutions. The concentration of the organic acids was measured by a Dionex suppressed ionic chromatograph DX-100, equipped with an AS4A-SC (4×250 mm) anionic exchange column and a conductivity detector. A 3 mm borate buffer at pH 9.8 was used for the analysis, and retention time were $t_R=2.34$ and 2.84 min for formic and glycolic acid, respectively. The concentration of hydrogen peroxide was measured by a titanium based colorimetric method [13]. The absorbance was measured at 415 nm by a Hewlett-Packard diode array spectrophotometer.

3. Results and discussion

The following process/equipment combinations have been tested:

1. photocatalytic oxidation by a supported catalyst in reactor B;
2. photocatalytic oxidation by a dispersed catalyst in reactor A;
3. photochemical degradation in the presence of H_2O_2 in reactors A and B;
4. combination of photocatalytic and photochemical oxidation in reactors A, B.

Some preliminary tests were carried out to verify that the removal of the organic reactant is only due to the photo-activated processes. It has been proved that glycolic acid is not stripped by the gas flow, that it is stable in the darkness in the presence of the catalyst and/or the hydrogen peroxide. The direct photolysis is not responsible for the observed decrease of the TOC. As a matter of fact short chain aliphatic compounds like the glycolic acid and the intermediates produced by its oxidative degradation are stable in the tested range of UV ($\lambda>240$ nm).

3.1. Continuous photocatalytic reactor (reactor B)

In order to find the best operating conditions a first set of tests was carried out by using both a monophasic flow of the solution saturated with air and a biphasic air–liquid flow (air=1.5 l/min). The fastest TOC conversion was observed in the case of the biphasic flow (Fig. 1). This might be interpreted as an experimental evidence that mass transfer of the reactants towards the catalyst surface is the rate controlling phenomena. The gas flow is very important because the bubbles increase the turbulence in the system enhancing the mass transfer phenomena. Moreover the presence of a gas flow prevents the decrease of the concentration of the oxygen in the liquid phase along the reactor. The role of the oxygen dissolved in the liquid is fundamental in the photocatalytic degradation process [7] because it prevents the recombination of the electron–vacancy pairs. These experimental results confirm the

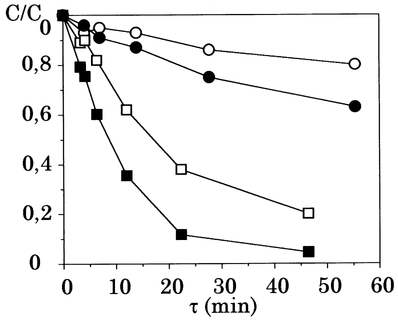

Fig. 1. Glycolic acid and TOC conversion by supported photocatalyst: (■ ●) acid conversion; (□ ○) TOC conversion; (● ○) single liquid flow; (■ □) two-phase flow.

findings of previous investigations on the photocatalytic degradation of other organic compounds [12].

The degradation of the acid seems to occur via an apparent first order decay, as it was already observed during batch experiments with a suspended catalyst [7]. The decrease of the TOC content is significantly slower than the acid conversion. This indicates that a significant amount of intermediates are produced before the deep oxidation of the substrate. Formic acid has been identified as one of these intermediates. The concentration of the formic acid shows a maximum around a residence time of 20 min when almost 90% of the initial substrate has already been decomposed (see Fig. 2).

A set of tests was carried out both with single phase and two-phase flow in the presence of hydrogen peroxide. An excess of H_2O_2 with respect to the stoichiometric amount (the concentration required to mineralize the substrate) was employed. It is interesting to note that, while in the absence of hydrogen peroxide the performance in single and two-phase flow is quite different, the degradation time is nearly the same in the two cases when H_2O_2 is used. The results in Fig. 3 show that with an initial concentration of hydrogen peroxide equal to 5 times the stoichiometric quantity, the complete oxidation of the glycolic acid is achieved in 25 min, while in the absence of H_2O_2 the same result is obtained with a biphase flow after more than 60 min. This result proves that the contribution of the photocatalytic process is negligible if compared with the photochemical reaction promoted by the hydrogen peroxide. In fact, in this case, the performance of the reactor is independent of the hydrodynamic regime, while the photocatalytic process is greatly influenced by this factor. The homogeneous photochemical process takes place in all the reactor volume and is not affected by mass transfer phenomena. The role of the dissolved oxygen in the homogeneous photo-activated degradation has not been elucidated completely. In any case, the UV-induced decomposition of the hydrogen peroxide probably maintains the liquid saturated by oxygen.

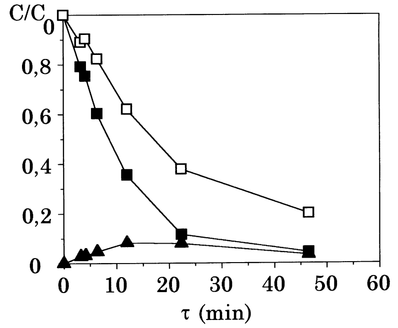

Fig. 2. Glycolic acid (■), TOC (□) and formic acid (▲) conversion by supported photocatalyst with biphase gas–liquid flow regime.

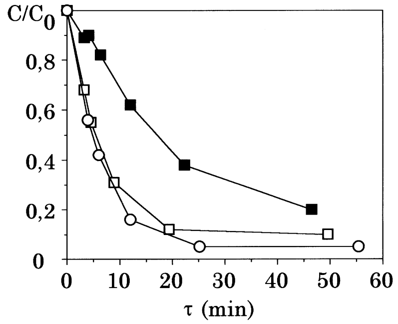

Fig. 3. TOC conversion by complementary photocatalytic and photochemical degradation: (■) only catalyst with biphase flow; (□) biphase flow with H_2O_2; (○) liquid flow with H_2O_2.

The experiment carried out in the same operating conditions, but in the absence of the catalyst confirms that the homogeneous reaction is the main degradation way in the combined process (see Fig. 4).

Since the efficiency of the UV-H_2O_2 degradation process showed to be independent of the presence of a gas flow, the influence of the initial concentration of hydrogen peroxide on the reaction rate was investi-

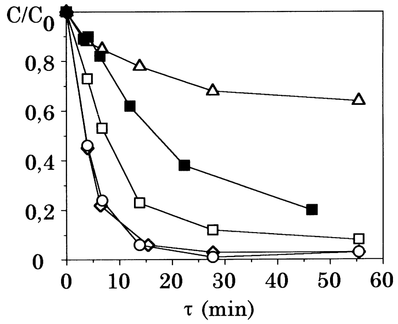

Fig. 4. TOC conversion versus residence time in photochemical processes: (■) only catalyst with biphase flow; liquid flow with different H_2O_2 concentrations: 5 (◇), 2 (○), 1 (□), and (△) 1/3 of stoichiometric.

gated by using a single liquid flow regime. As expected, the higher the peroxide concentration the higher is the degradation rate, but the latter seems to reach a limiting value with initial concentration of hydrogen peroxide more than the double the stoichiometric value. The reaction rate observed in presence of a sub-stoichiometric concentration of peroxide is lower than that obtained by the photocatalytic process. A slight increase of the reactor performance can be obtained only by a high concentration of H_2O_2. Notwithstanding the better performances, the homogeneous photochemical process seems to be less attractive for industrial applications due to the cost of the oxidative reactant and to its high residual concentration in the treated water. Better results might be obtained by using UV sources with a shorter wavelength since the dissociation of the hydrogen peroxide is significantly faster at 180–200 nm.

3.2. Slurry photocatalytic reactor (reactor A)

The amount of suspended catalyst was varied in the range 10–1000 mg/l to evaluate the influence of this parameter both in the monophasic and in the biphasic regime (Figs. 5 and 6). The concentration of the catalyst seems to play a secondary role; as a matter of fact the differences observed in the abatement yield are not impressive. The degradation rate increases a little, both in single and two-phase flow, when the catalyst amount changes from 10 to 100 mg/l, in agreement with the results of batch experiments [7].

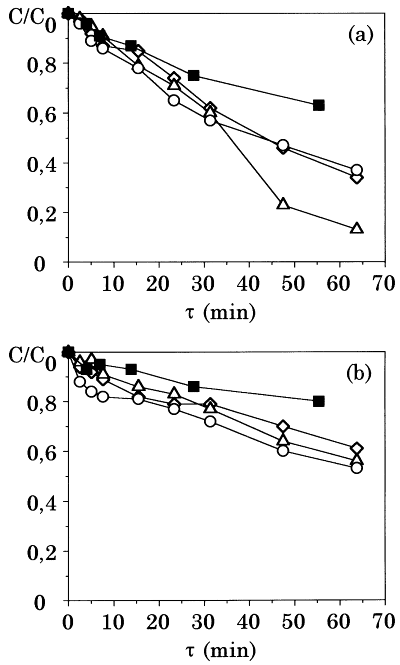

Fig. 5. Glycolic acid (a) and TOC (b) conversion versus residence time with monophasic regime: supported catalyst (■); dispersed TiO_2: (◇) 10, (△) 100, and (○) 1000 mg/l.

A further increase of the catalyst load is not effective, probably because of the higher opacity of the suspension preventing the penetration of the UV radiation in the liquid. In these conditions, the rate of degradation is not affected by the reactor volume since the photocatalytic process occurs only in a small zone close to the UV source.

By comparing the experimental results obtained with the two catalysts one can notice that the slurry system is slightly more efficient with a monophasic liquid flow. In this case the performance of the supported catalyst reactor is severely limited by the mass transfer of the reactants. On the contrary, with a biphasic flow the continuous reactor is more efficient. With the fixed catalyst 80% of the initial concentration of total organic carbon is converted during 45 min of irradiation, while at the same time only the 30% is degraded with the suspended catalyst.

The combined photocatalytic–photochemical process was carried out also in the batch reactor A both with and without the suspended catalyst. The tests were performed with a catalyst load of 100 mg/l and

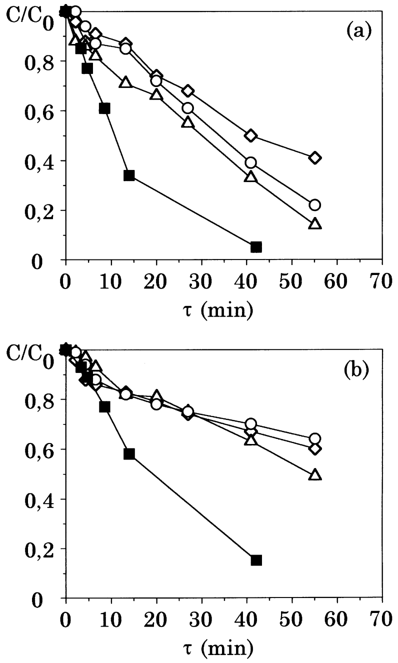

Fig. 6. Glycolic acid (a) and TOC (b) conversion versus residence time with biphasic gas–liquid flow regime: supported catalyst (■); dispersed TiO_2: (◇) 10, (△) 100, and (○) 1000 mg/l.

an initial concentration of hydrogen peroxide double the stoichiometric amount.

In the presence of the catalyst the reactor performance is not significantly enhanced by using the hydrogen peroxide (Fig. 7). On the other hand, the efficiency of the homogeneous photo-degradation is remarkably higher in the absence of the catalyst (Fig. 8). This might be explained by considering that the contribution of the photocatalytic process is negligible and the presence of suspended particles reduces sensibly the average UV light intensity in the reactor.

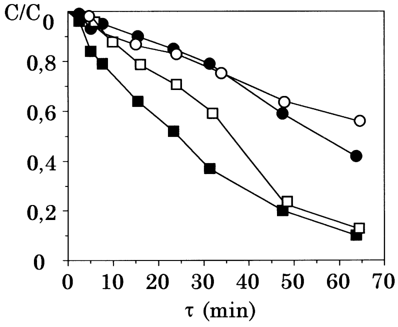

Fig. 7. Slurry reactor: single phase Glycolic acid (■ □) and TOC (● ○) conversion; (■ ●) combined; (□ ○) photocatalytic.

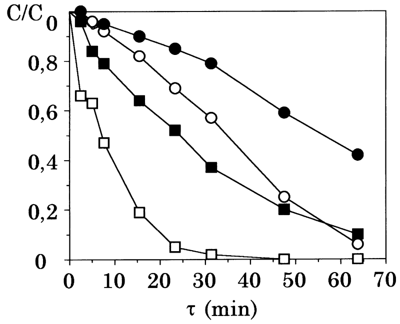

Fig. 8. Slurry reactor: single phase Glycolic acid (■ □) and TOC (● ○) conversion; (■ ●) combined; (□ ○) UV+H_2O_2.

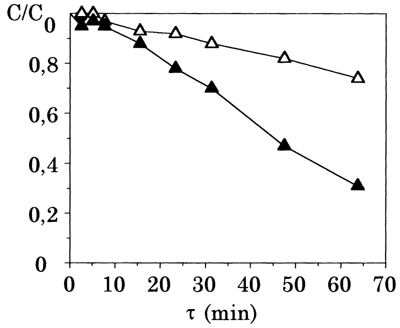

Fig. 9. Hydrogen peroxide conversion versus time (H_2O_2 double the stoichiometric value): (▲) no soid particles; (△) slurry.

The residual concentration of hydrogen peroxide at the end of the process is quite high (Fig. 9). The experimental results show that in the absence of a suspended catalyst, 30% of the initial amount of H_2O_2 has not been decomposed after 65 min of irradiation, when the TOC is almost completely converted. In the presence of a solid phase more than 70% of hydrogen peroxide remains in the liquid phase when the conversion of TOC is already higher than 50%.

4. Conclusions

The complete degradation of the glycolic acid to inorganic compounds can be achieved both by heterogeneous photocatalytic oxidation and by homogeneous photochemical oxidation in the presence of hydrogen peroxide.

The fixed photocatalyst obtained by physical vapour deposition of titanium dioxide on a stainless steel support showed to be very active and durable. The performance of the supported catalyst seems to be better than that of a dispersed photocatalyst. The use of the fixed photocatalyst might improve significantly the feasibility of the photocatalytic process on a real scale by solving the typical problems of the slurry systems.

The complementary use of the hydrogen peroxide and the heterogeneous photocatalyst leads to a higher degradation efficiency, but a large excess of the peroxide is required to achieve a sufficient conversion of the organic pollutant. The degradation occurs mainly via the homogeneous photochemical reactions and the contribution of the photocatalytic mechanism to the overall conversion rate seems to be negligible. Furthermore, the presence of a suspended solid catalyst prevents the irradiation of the liquid phase reducing significantly the efficiency of the homogeneous degradation.

Notwithstanding the high degradation efficiency, the photochemical process in presence of hydrogen peroxide seems to be less attractive for an industrial application. This is due to the additional cost of the oxidising compound and to the large residual concentration of this reactant which can be considered as a secondary water pollutant.

5. Nomenclature

C	concentration (mg/l)
C_0	inlet concentration (mg/l)
τ	residence time (min)

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