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Feasibility analysis of photocatalytic wastewater treatment

I. Mazzarino
Politecnico di Torino, Italia

Abstract

Since the early 80's the photocatalytic oxidation is well known as a way to degrade organic compounds in aqueous solutions. A wide number of scientific publications has proved the efficiency of photocatalysis with most classes of organic pollutants. The complete degradation of the organic compounds occurs at room temperature and atmospheric pressure. In spite of these positive features the photocatalysis is still considered as an experimental technology and up to now it has not been applied for waste waters treatment in large scale plants. In this work the feasibility of the photocatalytic purification process was investigated by evaluating the cost of water treatment in several practical cases. The examined system is a tubular reactor packed with a fixed bed of supported catalyst and equipped with commercial UV-A lamps. The performance of the system was simulated by integrating the local mass balance and radiation field equations. The cost of the water treatment was calculated by considering the energy consumption, the periodical replacement of the lamps and the durability of the supported photocatalyst. The results show that the photocatalytic oxidation is not competitive with most of the traditional water treatments in the case of common water pollutants. The field of application of photocatalysis is limited to the case of waters contaminated by pollutants not degradable by the conventional technologies.

1 Introduction

The abatement of organic pollutants in wastewaters can be performed by various chemical processes. Some of these, like aerobic and anaerobic biological treatments, are well known and can be considered, today, as current industrial technologies. On the other hand, a relevant number of organic compounds, usually called "refractory pollutants", are not degradable by the above mentioned processes. The purification of wastewaters contaminated by these pollutants is a very important problem because most of the refractory organics are highly toxic and persistant in the environment. In last decades many "advanced processes" for the degradation of toxic pollutants in water has been investigated. One of these is the photocatalytic oxidation [1,2].

The mechanism of the photocatalysis is initiated by the impact of photons on the surface of a photoconductor. If the energy of the photons is sufficiently high the impact lead to the formation of a heterogeneously charged couple: an excited electron and a positive electronic vacancy. Both these sub-atomic entities can interact with chemical species absorbed on the solid surface starting a radicalic reaction mechanism. The usual final result of this chain process is the conversion of the organic compounds to water and carbon dioxide. This mechanism is well known since the early 80's as well as its potential application in pollutants degradation. The research work was first carried out by teams of chemists investigating the complex path of the reactions for a wide number of pollutants. The experimental tests were performed in lab-size mixed equipments using a slurry (suspension of fine catalytic solid particles in the polluted water). This kind of system showed to be uneffective in pilot-size photocatalytic converters because of the very short depth of penetration of the UV radiation in the slurry [3, 4]. Moreover, the separation of the solid particles after the treatment is not easy because of their very small size and the cost of this operation can affect sensibly the practical feasibility of the process. The question seemed to be solved by the use of fixed-bed systems with supported photocatalysts. The supported catalysts showed to be sufficiently active and durable even in the presence of a flowing liquid phase [5].

The following step in scaling up the process to the industrial size is the estimate of the overall cost of treatment per unit volume or mass of the effluent. A supposed advantage of photocatalysis consists of the mild operating conditions required to performe the complete degradation of the pollutants. In fact, the process can be carried out at room temperature and atmosferic pressure and is effective with most of the organic compounds. Notwithstanding the moderate conditions, the energy required to degrade a unit mass of pollutant by a photocatalytic reactor is not small. First of all the efficiency of the conversion of the electrical energy to light by commercial UV lamps is low (from 20 to 50%). Furthermore, not all the photons emitted by lamp have energy sufficient to excite the electrons. Finally, the couple electron-vacancy produced by an effective photonic impact can easily recombine without any chemical effect. The experimental measurement of the energy efficiency of photocatalysis gave values between 2 and 5% in the case of pollutants with a simple molecular structure and lower than 1% for more complex organic compounds [6].

In this work the feasibility of the photocatalytic purification of wastewaters was evaluated by simulating the performance of a continuous photoreactor with a fixed bed of supported catalyst. The tested system has a tubular configuration with an axial UV source. The catalyst consists of glass particles (5x5 mm Rashig rings) coated by a thin layer of photocondutor. The transparency of the supporting material and the very small thickness of the active material allows to a significant fraction of the radiation to penetrate through the bed activating the process also in the zones far from the light source.

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2 Reactor model

The model is based on the local mass balance equations of the organic pollutant. The system is assumed to be isothermal because of the low concentration of the reactants and the high thermal capacity of the aqueous media. The expected axial concentration gradients are moderate thus the axial dispersion phenomena in the catalytic bed can be neglected. On the contrary, the radial dispersion may have significant effects since the rate of reaction decrases remarkably with the distance from the lamp and a sharp radial concentration gradient may take place [7]. Under these assumptions the model equations are:

$$\begin{cases} -v_L \cdot \dfrac{\partial C_{AL}}{\partial z} + \dfrac{D_r}{r} \cdot \dfrac{\partial C_{AL}}{\partial r} + D_r \cdot \dfrac{\partial^2 C_{AL}}{\partial r^2} + k_s a \cdot (C_L - C_S) = 0 \\ k_s a \cdot (C_L - C_S) = R_A \end{cases}$$

The boundary conditions are:

$$\begin{cases} z = 0 \quad R_0 \le r \le R \quad C_L = C_0 \\ z > 0 \quad r = R_0 \quad \dfrac{\partial C_L}{\partial r} = 0 \\ z > 0 \quad r = R \quad \dfrac{\partial C_L}{\partial r} = 0 \end{cases}$$

In the case of high pollutant concentration the consumption of the oxygen can not be neglected and the mass balances of this reactant must also be considered:

$$\begin{cases} -v_L \cdot \dfrac{\partial C_{OL}}{\partial z} + \dfrac{D_r}{r} \cdot \dfrac{\partial C_{OL}}{\partial r} + D_r \cdot \dfrac{\partial^2 C_{OL}}{\partial r^2} + \\ + k_s a \cdot (C_{OL} - C_{OS}) - (ka)_l \cdot (C_{OG} - C_{OL}) = 0 \\ \\ k_s a \cdot (C_{OL} - C_{OS}) = R_O = R_A \cdot v_O \end{cases}$$

Liquid to solid and gas to liquid mass transfer coefficients can be calculated by literature correlations as well as the radial dispersion. The rate of the photocatalytic process R_A depends on the so-called "local volumetric rate of energy absorption" (e^a). In the case of a tubular lamp with a very high ratio between the axial length and the radius the light source can be considered monodimensional. By assuming a monochromatic radiation emission in parallel planes, e^a can be evaluated by the following relation:

$$e^{a} = \mu_{v}\frac{E_{L}}{2\pi L_{L}}\frac{1}{r}\exp\left(-\int_{R_0}^{R}\mu_{v}dr\right)$$

Unfortunately the activation of the photocatalytic process is not the lot of all the photons emitted by the lamp. A wide fraction of them is reflected by the solid surface giving rise to the phenomenon of scattering of the radiation. Assuming that the reflection is unelastic the energy of the photons does not change and the balance of energy is described by the following equation:

$$\frac{dI_{v\omega}}{ds} = -(\mu_{\lambda}+\sigma_{\lambda})I_{v\omega} + \frac{\sigma_{\lambda}}{4\pi}\int_{4\pi} I_{v\omega}p_{\lambda}(\omega',\omega)d\Omega$$

Where s is the linear coordinate along the incident photon direction ω, ω' is the direction of the scattered one, σ_{λ} is the scattering coefficient and p_{λ} is the probability that a photon with direction ω' is scattered on the ω direction (phase function). The scattering equation was solved by Monte Carlo method [8].

The numerical integration of the model equations performed by the finite elements method allows drawing bidimensional profiles of the concentration of the reactants. This makes possible to calculate the conversion of the organic pollutants in the treated water at various values of parameters like the inlet concentration, the effluent flowrate and the reactor size.

3 Water treatment cost

The feasibility of the photocatalytic purification is related to the cost of treatment per unit volume of water. If the kinetic of the reaction is known the model can simulate the behavoiur of the photocatalytic converter and it is possible to identify the residence time and the size of the equipment required to achieve a certain conversion.

In our study we first consider the case a model pollutant "A" with inlet concentrations from 10 to 500 ppm. The kinetic of the photocatalytic oxidation of this compound is similar to that experimentally determined for various easily degradable organic compounds (phenols, short chain carboxilic acids and others). In order to evaluate the feasibility of the process in a wide range of operating conditions two other pollutants "B" and "C" with sensibly slower kinetics of degradation were also examined.

The simulations were carried out with a flowrate of 1 m^3/h of wastewater and a 90% final conversion of the pollutants. A key parameter of the photocatalytic converter is the depth of the catalytic bed ($R - R_0$). With a high depth the radiation emitted by the lamp is better exploited since a small fraction of energy reaches the reactor shell. On the other hand, the zone of the catalytic bed far from the UV source is less active because of the lower intensity of the radiation. By simulating the performance of the system with various values of the depths of the catalyst bed an optimal one should be determined. The table 1 shows the main operating parameters of the examined cases.

Table 1: Operating conditions (1 m^3/h of treated water, 90% conversion)

#	Pollutant	C_{A0} (ppm)	S (m)	τ (min)	Lamps	Power (kW)
1	A	10	0.019	9.0	26	2.1
2	A	20	0.019	13.7	39	3.1
3	A	50	0.019	25.8	74	5.9
4	A	50	0.03	34.2	53	4.2
5	A	50	0.04	43.1	44	3.5
6	A	50	0.05	54.4	40	3.2
7	A	50	0.06	67.6	38	3.0
8	A	50	0.09	123.8	36	2.9
9	A	100	0.019	43.1	123	9.8
10	A	500	0.019	155.1	444	35.5
11	B	100	0.019	263.3	754	60.3
12	B	100	0.03	350.0	543	43.4
13	C	100	0.019	595.2	1705	136.4
14	C	100	0.03	789.9	1226	98.1

The total cost of the photocatalytic purification was splitted in two main items: the operative cost and the apparatus cost. The first term account for the energy consumed to generate the UV radiation and for the periodical replacement of the UV sorces. This last item is far from being negligible because of the relatively short life of the lamps. Commercial UV-A sources should be replaced after 2000 hours to avoid a significant decrease of the efficiency. Shorter wavelenght sources have a quite longer life (5000 to 7000 h) and a higher light efficiency but are more expensive. Moreover a short wavelength radiation require the use of catalyst supports made of quartz while the much less expensive glass can be used with UV-A lamps. The table 2 shows the operating costs per unit volume of treated effluent for the various polluted streams.

Table 2: Operative cost

#	Energy (€/m^3)	Lamps (€/m^3)	Total operative (€/m^3)
1	0.16	0.34	0.50
2	0.24	0.50	0.75
3	0.46	0.96	1.41
4	0.33	0.68	1.01
5	0.27	0.57	0.84
6	0.25	0.52	0.76
7	0.24	0.49	0.73
8	0.22	0.46	0.69
9	0.76	1.59	2.35
10	2.75	5.73	8.49
11	4.67	9.74	14.41
12	3.37	7.01	10.38
13	10.57	22.02	32.59
14	7.60	15.83	23.43

The data reported in the table shows that the replacement of the lamps is about 65-70% of the operative cost. The reduction of the cost of the UV sources seems to be more effective than the increase of the energy effiency of the process. On the other hand one must consider that a more efficient systems can work with a reduced number of lamps and conseguently the cost of sources replacement is proportionally lower.

The cost of the apparatus for the photocatalytic water purification is nearly equal to that of the supported catalyst since the contributions of the vessel and the auxiliary equipments are negligible. The fixed photocatalyst is prepared by coating transparent supports by thin layers of photoconductive materials. For small productions (1'000 to 5'000 kg corresponding to 1 - 5 m^3 reactors) the current market prise of properly sized and shaped borosilicate glass supports is about 60'000 €/m^3. The deposition of the photocatalytic active layer can be performed by various techniques. Some of these like washcoating uses low cost raw materials, but must be repeated several times in order to obtain a uniform layer of photoconductor. Other techniques like sol-gel processes or impregnation by chemical precursors, require more expensive chemicals, but are carried out in one step only. On the basis of our esperience in installing pilot size photocatalytic converters the cost of the coating and the following thermal treatments in the case of small productions can be estimated in 30'000 €/m^3.

As far as the life period of the supported photocatalyst is concerned the tests carried out at lab-scale proved that no significant decrease of the catalytic activity occurs during two years. This time period can be assumed as the minimum life for the supported catalyst also in the case of industrial installation. No experimental data is available for more extended periods, but it seems reasonable to suppose that the catalyst could survive for a longer time. In our calculations we assumed a maximum life of five years. The table 3 shows the results of cost calculations in these two cases (low catalyst production LP).

Table 3: Photocatalytic treatment cost (LP catalyst, 2 and 5 years of life)

#	Catalyst 2years (€/m^3)	Catalyst 5years (€/m^3)	Total 2years (€/m^3)	Total 5years (€/m^3)
1	0.53	0.21	1.03	0.71
2	0.80	0.32	1.54	1.06
3	1.51	0.60	2.92	2.02
4	1.99	0.79	3.00	1.81
5	2.49	0.99	3.33	1.84
6	3.15	1.26	3.92	2.03
7	3.97	1.59	4.70	2.31
8	7.23	2.89	7.92	3.58
9	2.51	1.00	4.86	3.35
10	9.06	3.62	17.55	12.11
11	15.39	6.15	29.80	20.56
12	20.34	8.14	30.72	18.52
13	34.79	13.92	67.38	46.50
14	45.93	18.37	69.36	41.80

The contribution of the catalyst is 30 to 55% of the total cost of the photocatalytic treatment.

According to our past experiences the key points in producing the catalyst supports are the shape and size of the bodies. The market price of row or standard manufactured (tubes and slabs) high-grade glass is about six times lower than the mentioned value of 60'000 €/m^3. For large-scale production of photocatalyst the cost of the supports should not be very different from that of standard shape bodies. The table 4 shows the calculated total cost of the photocatalytic tretament assuming a price of 10'0000 €/m^3 for the support in the case of high catalyst production (HP). In this case the catalyst contributes with 15 to 35% of the total cost of the water purification.

Table 4: Photocatalytic treatment cost (HP catalyst, 2 and 5 years of life)

#	Catalyst 2years (€/m^3)	Catalyst 5years (€/m^3)	Total 2years (€/m^3)	Total 5years (€/m^3)
1	0.24	0.09	0.73	0.59
2	0.35	0.14	1.10	0.89
3	0.67	0.27	2.09	1.68
4	0.88	0.35	1.90	1.37
5	1.11	0.44	1.95	1.28
6	1.40	0.56	2.17	1.33
7	1.76	0.71	2.49	1.43
8	3.21	1.29	3.90	1.97
9	1.12	0.45	3.47	2.80
10	4.03	1.61	12.51	10.10
11	6.84	2.74	21.25	17.15
12	9.04	3.62	19.42	13.99
13	15.46	6.19	48.05	38.77
14	20.41	8.17	43.85	31.60

The figure 1 shows that the cost of the periodical replacement of the lamps is sensibly higher than those of the catalyst and the energy consumption even in the case of small production and short life of the catalyst.

All the costs increase linearly with the pollutant concentration with the exception of very diluted solution (C_{AO} below 50 ppm). This behaviour depends on the kinetic rate equation of the photocatalytic degradation and has been experimentally confirmed.

The influence of the depth of the catalytic bed on the total cost of the photocatalytic process is shown in figure 2. The optimal value, corresponding to a minimum of the cost, depends on the catalyst production and life. In the case of small production and short life the cost of the catalyst represents a high fraction of the total. In this case the energy efficieny is less important and the minimum of the cost is obtained with small size reactors where the activity of the catalyst is better exploited. As the cost of catalyst decreases the influence of the energy and the lamp replacement terms increases and the optimal point moves to higher values of the bed depth.

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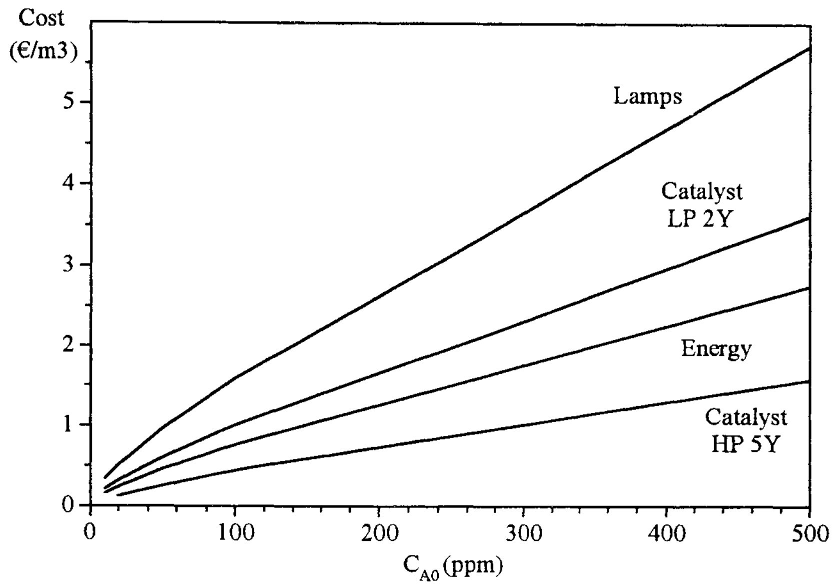

Figure 1: Catalyst, lamps replacement and energy costs vs. the inlet concentration of the pollutant A (90% final conversion).

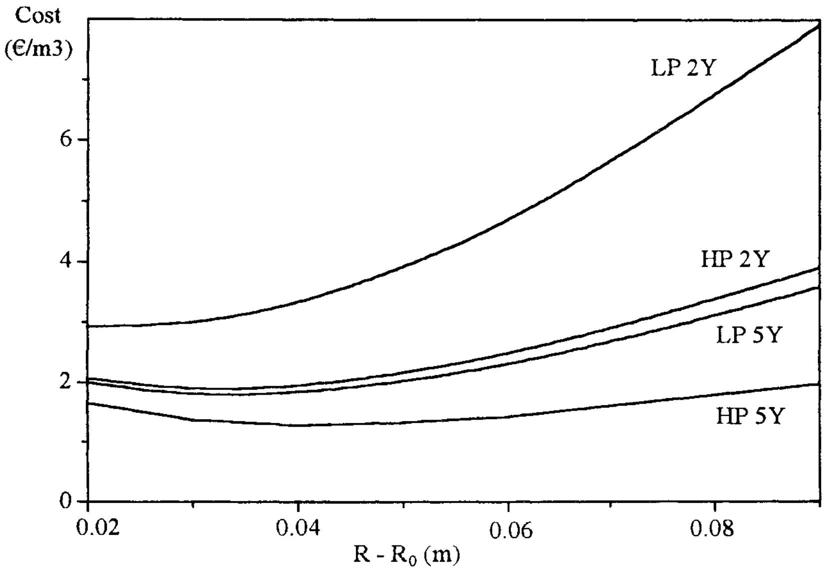

Figure 2: Total cost of the photocatalytic purification vs. the depth of the catalytic bed (pollutant A, C_{A0} = 50 ppm, 90% conversion)

4 Conclusions

The results of the feasibility analysis show that the cost of the photocatalytic treatment of wastewaters is quite high. The process is not competitive with the current purification technologies in the case of common water pollutants. For this reason the field of applications of the photocatalytic treatment is strictly limited to the case of refractory pollutants not degradable by the conventional pocesses.

The key factors limiting the feasibility of the process at a real scale are the low energy efficiency and the short life of the UV sources that must be periodically replaced. The cost of the catalyst seems to be of a secondary importance, but it should not be neglected since it might influence the optimal values of the operating conditions.

A detailed system model accounting for mass and radiation transfer phenomena appears to be a necessary tool to evaluate the process feasibility and to identify the optimal process parameters.

The analysis procedures illustrated in this work have been applied to the designe a pilot-size photocatatyc converter with a volume of 1 m^3 and a power of about 50 kW. This unit will operate by the end of 2001 year for the treatment of industrial wastewaters contaminated by chlorinated organic pollutants.

Notations

a	Specific area of interface, m^{-1}
C_{AL}	Concentration of the organic pollutant in the liquid, kmole m^{-3}
C_{AS}	Concentration of the organic pollutant at the catalyst surface, kmole m^{-3}
C_{OL}	Concentration of the oxygen in the liquid, kmole m^{-3}
C_{OS}	Concentration of the oxygen at the catalyst surface, kmole m^{-3}
D_r	Radial dispersion, m^2 s^{-1}
e^a	Local volumetric rate of energy absorption (LVREA), J s^{-1} m^{-3}
E_L	Lamp energy, J
k_L	Gas-liquid mass transfer coefficient, m s^{-1}
k_S	Liquid-solid mass transfer coefficient, m s^{-1}
I_v	Radiation intensity, J m^{-2}
L_L	Lamp length, m
r	Radial coordinate, m
R_A, R_O	Reaction rates, kmole s^{-1} m^{-3}
R_0	Lamp radius, m
R	Reactor radius,
v_L	Superficial velocity of liquid phase, m s^{-1}
z	Axial coordinate, m
ε	Bed porosity, -
μ_v	Lambert-Beer coefficient, m^{-1}
ν_0	Oxygen stoichiometric coefficient, -

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