Pilot Photoreactor for Cyanides Degradation

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Heterogeneous photocatalytic method has been used for detoxifying an aqueous effluent containing free cyanide ions.
A continuously stirred tank photoreactor at pilot plant scale has been designed, constructed and tested. The reactor contained a suspension of photoactive catalyst irradiated by near-UV light. The photoreactor treated an aliquot of the waste water produced by a power plant located at Puertollano (Spain).

Among the advanced oxidation processes developed in these last years, heterogeneous photocatalysis in the presence of semiconductor materials seems the most promising one for solving a variety of problems of environmental interest in water and air purification [1-3]. This new method has shown to be effective for the conversion and/or destruction of a lot of organic and inorganic contaminants with a measurable rate up to negligible concentration levels. The basic principles of heterogeneous photocatalysis [4-7] may be summarised as follows. When a photon with an energy of $h\nu$ (h, Planck's constant and ν, frequency) matches or exceeds the band gap energy, E_g, of the semiconductor photocatalyst, an electron is promoted from the filled valence band into the empty conduction band leaving a hole behind. Depending on many factors, the photogenerated pairs (excited-state conduction-band electrons and valence-band holes) can undergo different fates. They can: (i) recombine and dissipate the input energy as heat; or (ii) get trapped in metastable surface states; or (iii) induce redox reactions with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. In this last case redox reactions can be driven; in fact, the valence-band holes are powerful oxidants (+1.0 to +3.5 V vs. NHE depending on the semiconductor and pH),

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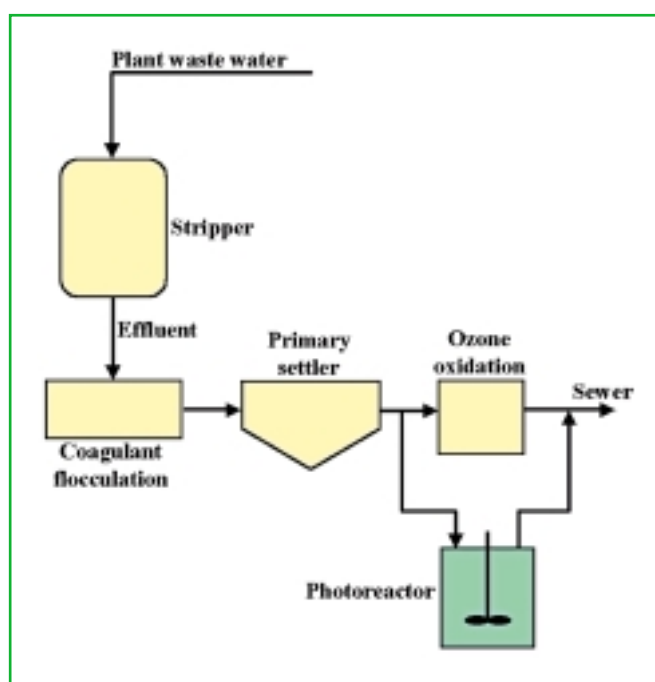

Figure 1 - Block diagram of the decontamination process; the yellow blocks represent the existing units of the water treatment system of the IGCC plant

while the conduction-band electrons are good reductants (+0.5 to -1.5 V vs. NHE). On this ground the main difference between a traditional "thermal" catalyst and a photocatalyst is that the first one is always active *per se* while the second one turns active *only* when it is irradiated.

For real processes of polluted water remediation the features of the "optimum" photocatalyst are the classical ones required by thermal catalysts (high activity, stability, selectivity, low cost etc.). In addition, however, owing to the fact that the photocatalytic process needs a radiation source, the photocatalyst would have narrow band gap in order to use the most cheap radiation source, i.e. solar light. Various semiconductor materials (e.g. TiO_2, ZnO, Fe_2O_3, CdS, ZnS etc.) have been tested as oxidation photocatalysts. However, as result of different problems mainly related to the photocatalyst stability under irradiation in water, it is generally accepted that TiO_2, in the anatase form, is the most suitable material for waste water treatment [8]. Aqueous suspensions of this semiconductor
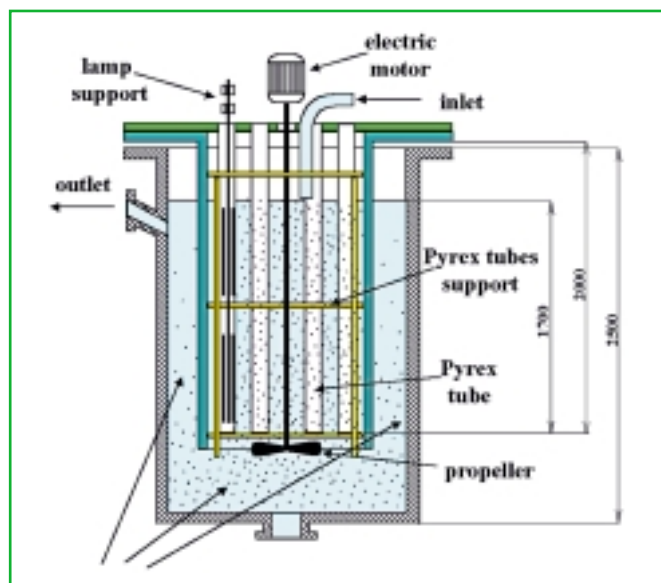
*Figure 2 - Scheme of the pilot plant photoreactor.
The figures indicate millimetres*

material can be activated by irradiation with light of wavelength lower than 380 nm and, in this situation, a lot of redox reactions can occur on the catalyst surface.

Up to now heterogeneous photocatalysis has attracted great attention mainly from the scientific community. A large number of studies on basic aspects of the photooxidation of many pollutants in water have been published, but only recently those methods are starting to be used to solve real problems raised by the presence of pollutants in water.

This paper reports the results of an investigation project devoted to study the possibility of utilising the photocatalytic method for the oxidation of free cyanide ions contained in a process waste water. The project, funded by the European Community of Steel and Carbon (ECSC, Contract no. 7220-ED/052), lasted from January 1994 to June 1998. The main participants to the investigation were the research group from the "Dipartimento di Ingegneria Chimica dei Processi e dei Materiali" of the University of Palermo (Italy) and that from the "Instituto de Catálisis y Petroleoquímica" of CSIC (Madrid, Spain).The project developed in two consecutive parts. During the first part an investigation at laboratory scale on the kinetic and mechanistic aspects of cyanide photodegradation in the presence of near-UV irradiated TiO_2 catalyst was performed. In the second part, which was carried out in a power plant located at Puertollano (Spain), a pilot plant continuous photoreactor was designed, constructed and tested for detoxifying an aliquot of the waste water produced by the plant. The features of the pilot photoreactor required the preparation of a TiO_2 photocatalyst supported on Al_2O_3 particles. This supported catalyst fulfilled the fluidodynamic requirements of the photoreactor while maintaining an appropriate intrinsic activity for effluent treatment.

The treated wastewater

The contaminated waste water, used in this work to test the performance of the photocatalytic method, was produced in a power plant of advanced technology built at Puertollano (Spain) by a Consortium of the main European electrical companies. The power plant utilises an integrated gasification combined cycle (IGCC) based on a coal gasification process. The IGCC is a new technology that represents an attractive option for conversion of coal to electricity. Compared with the power plants based on the well established process of pulverised coal combustion (PCC), IGCC plants show the following main advantages: (i) a net energy efficiency of 42.5%; (ii) a sulphur removal efficiency of 97-99% compared to about 90% for PCC; (iii) a NO_x removal down to 90 g/GJ (without selective catalytic reduction) compared to 120 g/GJ for PCC; and (iv) a lower amount of CO_2 emission to the atmosphere due to the higher energy efficiency.

To promote the development of IGCC, two demonstration plants of this type have been built in Europe, a 250 MW plant in Buggenum (The Netherlands) and a second one of 335 MW, using European technology, in Puertollano (Spain). In the line of promoting a new technology and considering the social alarm that pollution problems arise, ECSC funded specific target projects in 1992 and 1993 to study new ways to treat gas and waste water emissions from IGGC plants. These studies were not planned to influence the design of the gas and waste water treatment systems of the two mentioned demonstration plants, that were already built or in construction, but to obtain some information that could be useful if the demonstration plant produced pollution problems. On this ground our project was funded to study the applicability of an advanced oxidation process such as heterogeneous photocatalysis for treating process waste water.

The term "process waste water" of IGCC plant covers waters collected from different stages of the gas treatment process. These waters have alkaline pH and contain among other compounds: ammonia, carbonates, sulphides, cyanides, thiocyanates, thiosulfates, formates, chlorides and traces of heavy metals. Analytical investigations of process waste waters have shown that the composition and concentration of trace compounds change as a function of the fed coal and the process parameters (pressure, temperature, coal/water ratio etc.).

The treatment system of IGCC plant at Puertollano is mainly formed by an oxidation step using ozone and several process steps of neutralisation and coagulation/flocculation, settlers, homogenisation, clarification and filtering, that leave the waste water clean enough to be discharged into the water stream. The elimination of free cyanides is carried out before the neutralisation of the waste water alkalinity. In fact, when the waste water pH is lower than 9.5, free cyanides react by producing hydrogen cyanide, a gaseous compound of very high toxicity. The treatment specifications are chosen by taking into account the European Regulations on the limits to discharge dangerous compounds into public sewer net-

*Figure 3 - Picture
of the photoreactor*

Figure 4 - View of the external vessel and jacket of the photoreactor

works or into natural water streams. For cyanide ions the maximum concentration value in effluents to public sewers is below 0.5 ppm for all the European countries.

Guidelines for the pilot plant photoreactor design

The reactor configuration chosen for performing the cyanide oxidation at the pilot plant scale was that of a continuous slurry stirred tank reactor with immersed lamps. The choice of this photoreactor was based on the following considerations:

i) by increasing the catalyst concentration, a maximum of activity, i.e. of local volumetric reaction rate, can be reached;

ii) the mass transport resistance between the bulk of the liquid phase and the irradiated surface of the catalyst can be minimised depending on the agitation degree of the system;

iii) the irradiation efficiency, i.e. the ratio between the total photon flow emitted by the lamp and that absorbed by the whole suspension, can approximate the unity value as the catalyst concentration of the suspension can be chosen in order that no radiation is transmitted by the suspension.

The main operative drawback of a continuous slurry reactor is that the exit flow consists of the inside reacting suspension so that the wash out of the catalyst eventually occurs. It is therefore necessary a solid-liquid separation equipment coupled with the reactor in order to recovery the catalyst and a solid conveyor for recycling the catalyst to the photoreactor. In order to avoid the need of the separation-transportation unit, it was decided to design the photoreactor with an inside settling zone so that the exit flow did not contain solid particles. This choice allowed to simplify the photoprocess operation but involved that the catalyst particles did possess particular features; in particular the particles should have a high settling velocity.
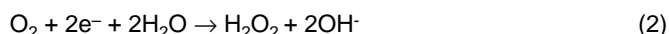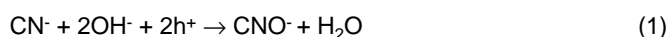
The process of cyanide photodegradation was arranged in parallel with the chemical treatment performed on the gross contaminated effluent of the industrial plant. In Figure 1 the block diagram of the decontamination process is reported; the yellow blocks represent the existing units of the water treatment system of the plant. The photoreactor was designed for treating a flow rate of 1 m^3/h of the liquid effluent feeding the ozonization reactor and for performing a conversion of cyanides of at least 98%.

Laboratory scale investigation

Preliminary reactivity runs showed that no oxidation reactions occurred in the absence of light and/or of catalyst and/or of oxygen. Oxygen was not a reactant limiting the process rate as the reactivity results obtained by using pure oxygen or air

did not show appreciable difference. The analyses performed on the reacting system indicated that the cyanate species was the unique intermediate product while the final oxidation products were nitrate and carbonate ions. The oxidation of CNO^- started to be significant only after the almost complete disappearance of CN^-. NO_3^-, in fact, appeared when the CN^- concentration reached a negligible value. The indication given by carbonate analysis was the same: carbonate ions concentration substantially increased only when cyanide concentration reached very low values. The measured values of cyanide, cyanate, and nitrate concentration quite well satisfied the nitrogen molar balance.

For the photocatalytic oxidation of cyanides in the presence of polycrystalline TiO_2 in aqueous medium, the following mechanism, which implies the oxidation of the inorganic species by the holes photogenerated in the semiconductor and the reduction of oxygen by the conduction band electrons, has been proposed [9]:

$$CN^- + 2OH^- + 2h^+ \rightarrow CNO^- + H_2O \qquad (1)$$

$$O_2 + 2e^- + 2H_2O \rightarrow H_2O_2 + 2OH^- \qquad (2)$$

$$1/2O_2 + 2e^- + H_2O \rightarrow 2OH^- \qquad (3)$$

The CNO^- ion is the first product in the photooxidation process. The observed absence of NO_2^- and of NH_3 among the reaction products, probably due to the strong oxidant conditions used in all the experiments, indicates that CNO^- is subsequently oxidised to CO_3^{2-} and NO_3^- ions according to the following overall reaction:

$$CNO^- + 10OH^- + 8h^+ \rightarrow NO_3^- + CO_3^{2-} + 5H_2O \qquad (4)$$
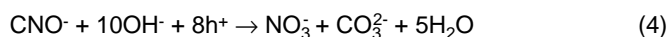
As above reported, a continuous stirred tank photoreactor with an internal settling zone was chosen as the pilot plant re-
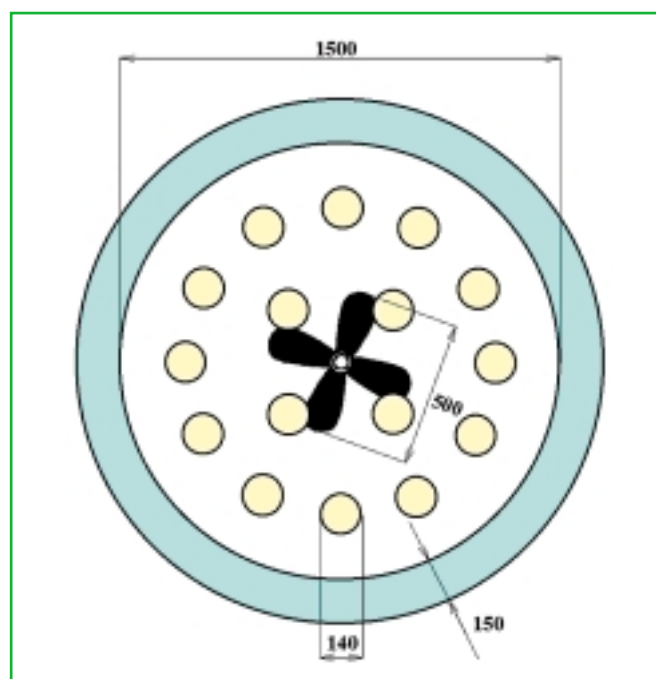

Figure 5 - Photoreactor top view showing the distribution of Pyrex tubes containing the lamps. The figures indicate millimetres

Figure 6 - Picture
of the photoreactor cover

actor configuration. The photocatalyst to be used in this reactor should exhibit appropriate mechanical and fluidodynamic characteristics in addition to good catalytic properties. The main features to be satisfied by the catalyst were the following ones: (i) the particles did not break with the formation of very fine powders, which would leave the reactor with the exit flow; (ii) the catalyst particles were easily suspended; and (iii) the specific gravity and size of particles allowed their easy separation from the exit liquid flow.

Commercial titania did not fulfil the previous requirements as their particle size is very small; therefore, two possible methods were tested: a) preparation of pure TiO_2 with large particle size; and b) loading with TiO_2 big particles of a material having high mechanical strength. The first method was unsuccessful; in fact, when this powder was used for cyanide photodegradation runs, the particles broke to form particles with sizes similar to those of commercial TiO_2.

As far as the second method is concerned, titania catalysts supported on alumina were prepared by different techniques and tested. Alumina showed to be stable during the cyanide photodegradation so that it was chosen as the support of all the new prepared catalysts.

In order to check the mechanical durability of the catalyst under the fast mixing conditions prevalent during the occurrence of the photoreaction, the following procedure was used. First, specimens of the supported catalysts were stirred in water for different periods of times, using experimental conditions (pH, stirring rates, concentration of catalyst etc.) equal to those used for performing the photocatalytic activity tests. At the end of each planned duration of stirring, the agitation was stopped and the fine material detached from the support and remaining in suspension (i.e. slowly settling or not at all in times below 1 minute) was removed. Therefore the remaining solid (i.e. all the particles that settled in a time less than 1 minute) was washed and tested in order to compare its photoactivity with that of the starting material. The results indicated that the supported photocatalysts prepared by hydrolysis of organotitanium precursors were the most satisfactory ones. In fact, the amount of titania which remained on the catalyst grains even after prolonged mixing (over 64 hours) was enough to keep a sizeable photoactivity level for the cyanide photooxidation reaction.

A usual preparation of

Figure 7 - Picture of the control
system panel used to check the
correct working order of the lamps

this supported catalyst took the following steps. Al_2O_3 was placed in a rotating flask to which titanium isopropylate was added. The mixture was stirred at room temperature for 1 h and, subsequently, the impregnated Al_2O_3 was placed in a stripping column of cylindrical shape having on the bottom a port through which a gaseous stream of wet N_2 was fed. The system was placed in an oven maintained at the temperature of 423 K.

The stripping operation, which lasted 6 hours, was carried out in order to hydrolyse the titanium isopropylate and to eliminate the organic moiety of the above reagent. Subsequently, the obtained brown powder was heated for 16 h at 773 K. The impregnation and stripping operations were carried out again four times and a thermal treatment lasting 2 hours at 773 K was performed every time. The catalysts were analysed by X-ray diffractometry and the results indicated that the supported TiO_2 is in the anatase phase.

Studies on the effect of the TiO_2 content indicated that catalysts with higher TiO_2 content showed a higher reactivity, suggesting that these catalysts should be preferred. However, these catalysts showed a significant release of TiO_2 during the reactivity run. On the contrary, the supported catalyst with less TiO_2 content showed a good mechanical stability, as concluded by the observation that the reaction solution was completely clear at the end of the runs. The catalyst with a TiO_2 content of 53% wt exhibited a high reactivity while maintaining its mechanical stability in the long term and it was therefore chosen for the runs to be performed in the pilot plant photoreactor.

As to concern the kinetics of cyanide photodegradation, the following information were drawn [9]:
a) the cyanide photooxidation reaction proceeds according to zero order kinetics at high concentration of cyanide;
b) the reaction turns to pseudo-first order kinetics at small concentration of cyanide;
c) the oxidation rate increases by decreasing the initial cyanide concentration;
d) the rate of cyanate photooxidation is quite smaller than that of cyanide.

Photoreactivity experiments of cyanide photooxidation were carried out at different pH's and concentrations of sulphate, sulphide and chloride ions. It was observed that the cyanide photooxidation rate is not affected in a significant way by the presence of chloride, sulphate and sulphide ions in the reacting mixture. As to concern the influence of the initial pH on the reaction rate, no significant differences were found, at least in the pH range (9.5-11) investigated in the course of the project. The quantum yield of cyanide photodegradation, defined as the ratio between the cyanide molecules reacted per unit time and the photons absorbed per unit time, had the value of 0.23. This figure is quite high; for the photooxidation of an organic molecule such as phenol the value of quantum yield, calculated in the same experimental conditions and using the same catalyst, is of about 0.1 [10].

Figure 8 - View of the opening
which allows the reacting
volume to be in contact
with the atmosphere

Figure 9 - Pyrex tube with the support containing eight lamps

Pilot plant scale investigation

The information obtained on the kinetics of cyanide photodegradation and on the quantum yield of the photoreaction was used for calculating the reacting volume of the photoreactor and the irradiation power.

The following values were used for the photoreactor set-up: reactor "design" volume: 0.84 m^3; security factor of 2.5; with the previous values the reacting volume of the photoreactor is 2 m^3. In Figure 2 the scheme of the photoreactor is reported. The reacting volume had the shape of a cylinder of 1,500 mm diameter and 1,700 mm height. In the scheme of the photoreactor an outer annular zone was allowed to separate the catalyst particles from the liquid solution leaving the reactor. In this way the outer diameter of the photoreactor was 1,800 mm. A rotating pump fed the liquid flow to the photoreactor while the exit stream left the photoreactor by gravity. Figures 3 and 4 show the pictures of the whole photoreactor and the external vessel, respectively. The irradiating system consisted of 16 Pyrex cylindrical tubes (ca. 2 m length), each of which contained 8 fluorescent actinic lamps (40 W, 60 cm height). Figure 5 reports a photoreactor top view showing the lamp distribution and Figure 6 the picture of the cover. In order to check that the lamps worked properly a control system with photodiodes was used. Figure 7 shows the panel of this system.

The mixing of the reacting mixture was performed by a turbine impeller (500 mm diameter) with inclined blades in order to obtain a high axial flow. The impeller was positioned at about 1/6 of the liquid height from the bottom in order to better suspend the catalyst particles. The electric power needed to maintain a turbulent regime in the reaction volume was 3 kW; this figure was calculated from information obtained for standard baffled tank reactors. As it will be pointed out later, the mixing power was highly underestimated and it was necessary to change the motor in order to have a good particle suspension.

It is worth noting that no bubbling air or oxygen into the reacting mixture was needed; in fact, the photoreactor was designed for operating in contact with the atmosphere so that mixing of the suspension also allowed its oxygenation, which is essential in order to sustain the photocatalytic reaction. In Figure 8, it can be noted the opening which allows the reacting volume to be in contact with the atmosphere.

The equipment in contact with the reacting mixture (photoreactor vessel, impeller etc.) was stainless steel AISI 316L made, being the pH of the reacting mixture ca. 10.

The preliminary experiments carried out with the photoreactor working in a batch way concerned the testing of the efficiency of the mixing system for suspending the powder particles. It was immediately discovered that the power was greatly underestimated; its value was in fact determined having taken as reference baffled tanks. The presence inside of the mixed volume of 12 big Pyrex tubes containing the UV radiation sources determined a huge dissipation of energy. It was necessary to substitute the 3 kW electric motor

Figure 10 - Stainless steel support of the Pyrex tubes

driving the agitator with a 7 kW one to achieve good mixing conditions. Once this substitution was performed, the fluidodynamic behaviour of the photoreactor was satisfactory. Figure 9 shows a Pyrex tube with the support containing eight lamps and Figure 10 shows the stainless steel support of the Pyrex tubes.

The reactivity runs carried out by using the waste water produced by the plant showed a cyanide conversion higher than 98%. Each of these runs lasted 14-18 hours; it was not possible to carry out runs for longer times, because the IGCC plant was not working continuously. The duration of the runs was however sufficient in order that the photoreactor reached steady state conditions. In fact the whole volume of the liquid contained in the photoreactor (6 m^3) can be divided in two parts: that of the inner zone (2.5 m^3) can be considered perfectly mixed while that contained in the outer annulus can be considered as a plug flow. A stirred reactor needs about 4-5 times its mean residence time to reach steady state conditions for slow reactions. At the design liquid flow rate it means 8-10 hours to which 3.5 hours must be added for the delay introduced by the plug flow in series with the stirred zone. Consequently, about 12-14 hours of continuous operation are expected in order to reach steady state conditions at the exit of the photoreactor. Figure 11 shows a particular of the outlet of the photoreactor.

The influence of the amount of home prepared Al_2O_3-TiO_2 catalyst on the cyanide photodegradation rate was also studied. The dependence of the catalyst concentration on the degradation rate indicated that the optimum value was of about 2 g/l under the used experimental conditions.

A small detrimental effect of the increase of pH on the cyanide photodegradation rate in real waste water was also observed. This finding was not in accord with previous studies [9] which indicated a practical independence of CN$^-$ photodegradation kinetics of the pH. A likely explanation of this feature could be that the industrial wastewater contained organic substances for which an increase of pH favourably

Figure 11 - View of the outlet of the photoreactor

affected their photooxidation with a consequent detrimental effect on the cyanide degradation.

Conclusions

The feasibility of a process for cyanide degradation by mean of heterogeneous photocatalytic method has been satisfactorily checked at industrial level. The good performance of the pilot plant photoreactor allowed to obtain a liquid effluent with a concentration of free cyanide far below the 0.5 ppm value which is the maximum allowable one according to the EC law of environment protection.

The future prospects for the improvement of this photoprocess would mainly concern the optimisation of photoreactor operative conditions, first of all mixing conditions, and the increase of the specific reactivity.

For the first point it is likely that, owing to the internal geometry of the photoreactor, the mixing performed by a mechanical stirrer is not the most adequate (and economic) way for suspending the solid particles.

For the second point, it is likely that, due to the high ionic strength of the real industrial wastewater, the solubility of oxygen, which is an essential reactant for the occurrence of the photoreaction, is greatly reduced. Consequently, the obvious remedy would be the utilisation of another oxidant agent (gaseous or liquid) to be added to the solution, for example ozone or hydrogen peroxide.

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