

**SIMULTANEOUS PHOTOCATALYTIC REDUCTION OF SILVER AND
OXIDATION OF CYANIDE FROM DICYANOARGENTATE SOLUTIONS AND
SPENT PLATING BATHS**

María-José López-Muñoz*, José Aguado, Rafael van Grieken and Javier Marugán
Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan
Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain.

Corresponding author:	e-mail:	mariajose.lopez@urjc.es
	Phone:	+34 91 6647464
	Fax:	+34 91 4887068

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Abstract

The feasibility of heterogeneous photocatalysis for the treatment of dicyanoargentate complexes using titanium dioxide was investigated. The best results were obtained in the presence of oxygen, as the simultaneous deposition of metallic silver on the catalyst and oxidation of released cyanide ions to cyanate species was achieved. It is proposed that O_2 plays a dual role in the reaction: it supports the reduction of metal acting as intermediate in the transfer of electrons and acts as reagent in the oxidation of released cyanide to cyanate species. The influence on the kinetics of the addition of methanol was studied. In anoxic conditions the rate of silver reduction was increased, what is attributed to the effectiveness of methanol as hole scavenger and its ability to form reducing radicals, whereas the oxidation of released CN^- was inhibited. On the contrary, in aerobic medium the presence of the alcohol had a detrimental effect on the metal reduction but no cyanide accumulation was produced. The photocatalytic treatment of an industrial spent silver plating bath was carried out. In anoxic conditions it was achieved the recovery of silver upon deposition on the catalyst as Ag^0 , therefore showing the feasibility of the process. As the large amount of organic matter in the solution inhibited the oxidation of cyanide ions, a two-step procedure is proposed for the overall treatment of those wastewaters.

Keywords

Photocatalytic reduction; photocatalytic oxidation; Silver recovery; Cyanide; Dicyanoargentate; Plating baths

1. Introduction.

Cyanides are widely used in electroplating, mining and photographic processes due to their unique properties for complexing metals such as silver, gold, copper or zinc. As a consequence, wastewaters coming out from these activities usually contain large amounts of metal cyanide complexes with the general formula $[M(CN)_n]^{x-}$, where M represents the metal cation, n is the number of bound cyanide ions, and x is the total anionic charge of the complex [1,2]. Despite many of them are considered as weakly toxic because they are relatively stable, metal cyanide complexes are species of environmental concern for their potential release of CN^- ions under uncontrolled ambient conditions. For that reason, it is important the treatment of effluents containing these cyanocomplexes previously to their discharge into the environment [3]. Common cyanide oxidation processes such as alkaline chlorination or advanced oxidation technologies based on the use of ozone or peroxides, do not achieve the complete removal of metal cyanide complexes [4]. In contrast, heterogeneous photocatalysis has shown a high efficiency in the removal not only of free cyanides [5,6], but also of iron [7,8], copper [9] and gold cyanocomplexes [10]. To the best of our knowledge, however, there are no references in open literature to date concerning the photocatalytic treatment of silver-cyanide complexes, what constitutes the purpose of the present work.

To achieve an effective treatment of silver cyanide complexes not only the oxidation of the CN^- groups but the recovery of silver would be desirable in order to accomplish a double objective: to avoid cyanide and metal pollution and to reuse silver in new processes. Previous studies have shown the feasibility of removal and recovery of dissolved metal ions from wastewater by heterogeneous photocatalysis with titanium dioxide. The process involves the reduction and deposition of metals onto the semiconductor surface, followed by their extraction through chemical or mechanical procedures [11 and references therein]. The photocatalytic deposition on TiO_2 of a variety of metals such as gold [10, 15], palladium [15], platinum [16, 17], rhodium [18] and silver [19-25] from their respective inorganic salts solutions has been reported. Although it is thermodynamically feasible to achieve the direct reduction of the metallic ions by the photogenerated electrons as far as the potential of the conduction band of the semiconductor is more negative than the reduction potential of the M^{n+}/M couple, in practice the photocatalytic reduction rate is governed by the kinetics [12]. Therefore, it is essential to acquire the knowledge of what operational variables or added reactants can influence on the photocatalytic reduction efficiency. In that respect, it has been proved that metal deposition can be enhanced by the addition of reducing organic species,

what has been explained in terms of a synergism between the oxidation of the organic compound and the simultaneous reduction of the metal cations [11]. For instance, Szabó-Bárdos et al. found that silver photoreduction on TiO_2 was enhanced in the presence of oxalic acid [22]; Chen and Kay reported the promoting effect of a variety of organics on the photocatalytic reduction of Hg (II) [12]; Kriek et al. observed no rhodium deposition on TiO_2 from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ unless ethanol was added to the system [18]; Schrank et al. investigated the simultaneous photocatalytic Cr (VI) reduction and a dye oxidation with TiO_2 [14]. They found a beneficial effect of the dye on the metal photoreduction, explained by means of an efficient consumption of the holes by the dye with the subsequent attenuation of charge carriers recombination.

On the other hand, negative results in terms of metal deposition are obtained when both the metal ions to be reduced and the oxidisable organic groups belong to the same chemical entity as it occurs with metal-EDTA complexes, species widely used in industrial applications. The photocatalytic treatment of Cr(III), Cu(II), Ni(II), Pb(II), Zn(II), Cd(II), Hg(II), Fe(III), Co(II) and Mn(II) complexed with EDTA showed that whereas the oxidation of the EDTA organic ligands was achieved in most cases, the reduction of metal ions was not attained. The observed removal of metals from the solution was due to either a simultaneous adsorption of the free metal cations over the titanium dioxide surface or the precipitation of metal derivative species, with no reduction to the metallic state [25].

The present work is focused on the study of the photocatalytic performance of TiO_2 for achieving the simultaneous reduction of silver and oxidation of cyanide from aqueous dicyanoargentate(I) solutions and spent silver plating baths. Operating parameters such as presence or absence of dissolved oxygen and addition of methanol as hole scavenger at different concentration levels have been investigated. It should be noted that most studies in photocatalysis dealing with silver and organics are mainly focused on the metal influence on the TiO_2 activity for the degradation of the organic compounds rather than in the process of Ag recovering. On this basis, further investigations are required in order to establish the feasibility of the whole process for the treatment of waste effluents. Moreover, in addition to the goals of cyanide removal and silver recovery the photocatalytic treatment of silver-cyanide complexes has a considerable interest for mechanistic reasons because of the fact that both target chemical groups to be oxidized and reduced belong to the same molecule and understanding the mechanism of these type of processes can be decisive for many practical applications.

2. Experimental.

2.1. Materials.

Degussa P25 TiO₂ was used as the photocatalyst. This commercial titanium dioxide, commonly used as standard material in photocatalytic studies, consists of anatase and rutile crystalline phases in a ratio of 4:1 respectively. It shows a B.E.T. specific surface area of 50 m²g⁻¹ and an average particle size of *ca.* 30 nm although in suspension larger polycrystalline aggregates are formed. All other chemicals mentioned hereafter were of reagent grade and used as received without further purification. Solutions were prepared with water from a Millipore Milli-Q water purification system.

2.2. Experimental set-up and procedure.

Photocatalytic reactions were carried out in a 1 litre cylindrical Pyrex reactor, provided with internal irradiation through a 150 W medium pressure mercury lamp (Heraeus TQ-150). The light source was surrounded by a water-cooled jacket to both filter UV ($\lambda < 300$ nm) and IR radiations and to maintain the temperature of the suspension at $25 \pm 1^\circ\text{C}$. Withdrawing of samples and bubbling of gases were carried out through two openings in the upper part of the reactor.

Potassium dicyanoargentate (I) (Aldrich) was used for the preparation of the reacting solutions. The TiO₂ powder (0.5 g L⁻¹) was added to the silver cyanocomplex solution, for which the initial concentration was fixed at 0.385 mM. In order to facilitate total mass balance calculations in all the figures and throughout the results and discussion, the concentrations of dicyanoargentate (I) and its detected oxidation products, mainly cyanate, have been expressed in terms of their equivalence to ppm of CN⁻ (*i.e.*, a 0.385 mM [Ag(CN)₂]⁻ solution contains 20 ppm of CN⁻ ions whose oxidation would yield 32.3 ppm of CNO⁻ species).

The initial pH value was adjusted at 12 by addition of a NaOH (Scharlab) solution. Before starting the irradiation, oxygen or helium was bubbled for 30 minutes through the suspension in order to reach either the saturation or the elimination of oxygen respectively, depending on the purpose of the experiment. In the meantime, the lamp was switched on outside the reactor to stabilise the light emission.

When required, methanol (Scharlab) was added to the solution as additional oxidizable compound. Reactions using the industrial spent plating bath solution provided by Metalor

Technologies Ibérica S.A. were carried out without any previous treatment, except for dilution.

Along the reaction runs, that usually lasted 4 hours, oxygen or helium was continuously bubbled into the stirred suspension. Aliquots were taken at time intervals, following filtration through 0.22 μm Nylon membranes in order to remove the suspended solids before being analysed.

The initial photonic efficiencies were calculated as follows:

$$\xi^0 (\text{mol}_{\text{Ag}} \text{Einstein}^{-1}) = \frac{r^0 (\text{mol}_{\text{Ag}} \text{L}^{-1} \text{s}^{-1})}{I^0 (\text{Einstein} \text{L}^{-1} \text{s}^{-1})}$$

where r^0 is the initial slope of the dicyanoargentate degradation profile and I^0 is the incident photon flow per liter, whose value ($I^0 = 1.37 \cdot 10^{-5} \text{ Einstein L}^{-1} \text{ s}^{-1}$) was determined by ferrioxalate actinometry according to the procedure described by Hatchard and Parker [26].

2.3. Analytical procedures.

Total cyanide concentration (free cyanide plus weak acid dissociable cyanocomplexes such as dicyanoargentate (I)) was determined through a standard colorimetric method using a pyridine-barbituric acid reagent to form a highly coloured complex with maximum absorbance at 575 nm [27]. The absorption measurements were performed with a Varian Cary 500 Scan UV-Vis-NIR spectrophotometer. Free cyanide concentration was potentiometrically determined by using a CN^- -selective electrode in an expandable ion analyser (Orion 720A). Cyanate concentration was measured by ion chromatography in a Metrohm equipment (Separation centre 733, IC detector 732, Pump Unit 752). An aqueous solution of NaHCO_3 (2.0 mM), and Na_2CO_3 (1.3 mM) was used as eluent at a flow rate of 0.8 ml min^{-1} .

The concentrations of dissolved silver species were determined with a Varian Vista AX inductively coupled plasma-atomic emission spectrometer (ICP-AES). The spectral line at 328.068 nm was used with quantification purposes after calibration with certified standards. This analysis was also performed to evaluate the silver content of the catalysts recovered after the reaction following their treatment with nitric acid.

X-ray diffraction (XRD) patterns of the recovered solids were acquired on a Philips X'PERT MPD apparatus using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$). Scans were made in the 2θ range $20\text{-}70^\circ$ with a step size of 0.02° and a step time of 1 second, enough to obtain a good

signal-to-noise ratio in all the studied reflections. The morphology of the solids was examined by transmission electron microscopy (TEM) using a JEOL JEM-2000 FX instrument operating at an accelerating voltage of 200 kV. The powder was ultrasonically dispersed in acetone and the suspension was deposited on a carbon-coated copper grid.

Total organic carbon (TOC) content of the spent plating baths was determined using a combustion/non dispersive infrared gas analyzer model TOC-V Shimadzu.

3. Results and discussion.

3.1. Blank and adsorption experiments

Blank experiments were performed without addition of TiO_2 in order to determine whether any photochemical reactions could occur in the absence of catalyst. No photolytic degradation of dicyanoargentate was observed after 6 h of irradiation under the different reaction atmospheres investigated, namely helium purged and oxygen saturated, thus assuring the photocatalytic nature of the subsequent results in the presence of titania. Also the adsorption of $[\text{Ag}(\text{CN})_2]^-$ on the titania surface was evaluated by analyzing the dicyanoargentate(I) content of the supernatant solution after stirring a suspension of the catalyst and the complex for 1 h in the dark at pH 12. The results indicated negligible dark adsorption of $[\text{Ag}(\text{CN})_2]^-$ on the titania surface, what can be explained by the electrostatic repulsion for the approach of the anionic complex to the negatively charged semiconductor surface at the studied pH value.

3.2. Photocatalytic degradation of $\text{Ag}(\text{CN})_2^-$ in the absence of oxygen.

Figure 1 shows the concentration profiles of the photocatalytic degradation of pure potassium dicyanoargentate(I) solutions with TiO_2 . The reaction was carried out in the absence of dissolved oxygen by purging the solution with helium, as described in the experimental. It may be observed that a slow degradation of the $\text{Ag}(\text{CN})_2^-$ complex was produced, together to the formation of cyanate species derived from the oxidation of cyanide ligands. It is worth noting that the total CN^- mass balance was achieved between the silver-cyanide complex and cyanate species and that no free cyanide ions (CN^-) were detected in the medium along the reaction.

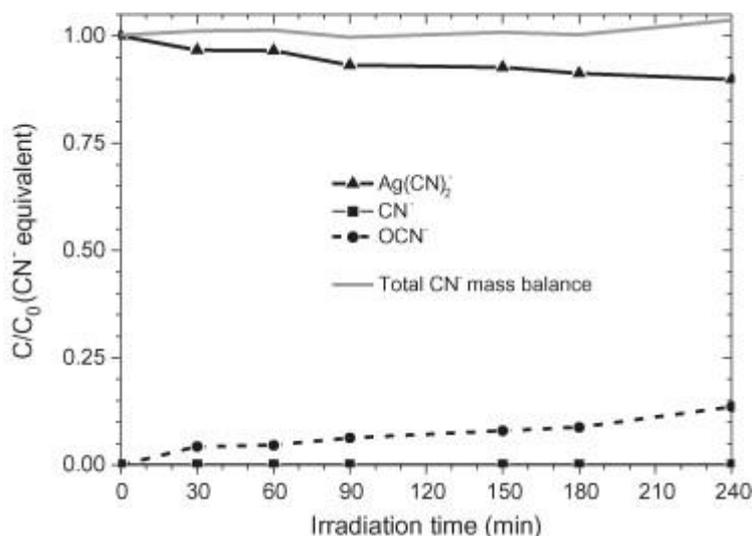
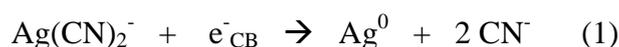


Figure 1. Photocatalytic degradation of $\text{Ag}(\text{CN})_2^-$ in the absence of oxygen.

In the absence of oxygen, silver atoms of dicyanoargentate(I) are the acceptors of electrons generated by irradiation of the semiconductor:



As a consequence, cyanide ions are released from the complex and can be subsequently oxidized by holes, as the detection of cyanate species in the solution proves:



Because of the low reduction driving force of $\text{Ag}(\text{CN})_2^-$, for which reduction potential (vs. NHE) is -0.2 V [28], the recombination of photogenerated electrons and holes can be a competing process inhibiting reaction (1). Such detrimental effect can be partially overcome by the oxidation of the cyanide ions through reaction (2) thus avoiding the recombination of charge carriers. However, the availability of CN^- ions to act as hole scavengers is limited in turn by their release from the complex and therefore the global kinetics might be controlled by the decomposition rate of the dicyanoargentate(I) complex through the reduction reaction (1). Accordingly, such limitation should be taken into account for any strategy directed to increase the efficiency of the overall process. On the basis of the above considerations, the influence on the kinetics of the addition of sacrificial electron donors was investigated by performing further experiments in the presence of methanol. As it is well known, this alcohol behaves as an efficient scavenger of holes in photocatalytic reactions thereby suppressing the electron-hole recombination. Figure 2 displays the concentration profiles obtained upon addition of increasing concentrations of methanol and Table 1 summarises the values of the

initial reaction rates and the photonic efficiencies for the photodeposition of silver from dicyanoargentate(I) solutions on TiO_2 in the absence of oxygen. It is clearly shown that the presence of the organic compound indeed enhanced the photocatalytic degradation of the dicyanoargentate(I) complex, increasing up to 13-fold the photonic efficiency.

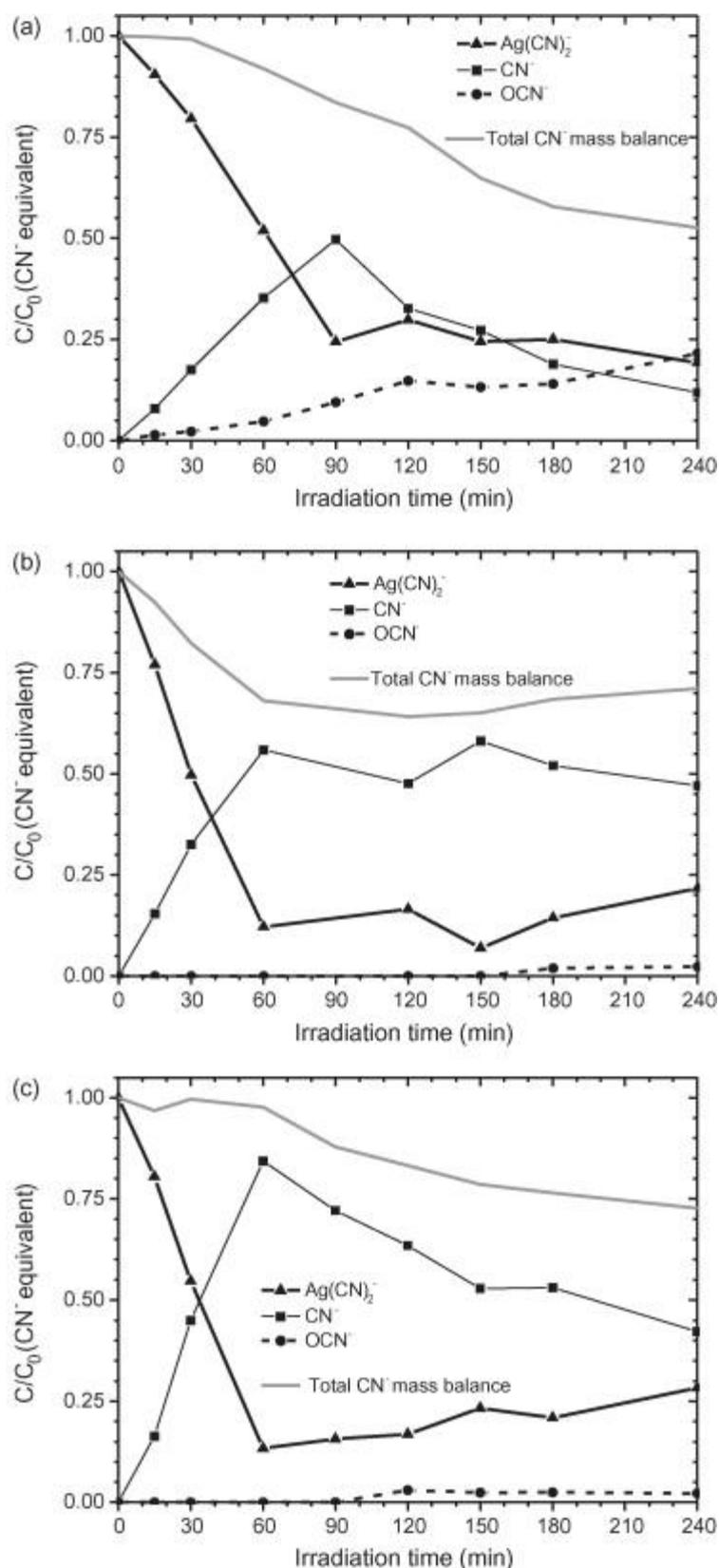


Figure 2. Photocatalytic degradation of $\text{Ag}(\text{CN})_2^-$ in the absence of oxygen upon addition of methanol 0.1 mM (a), 1 mM (b) and 10 mM (c).

Table 1. Initial reaction rates and photonic efficiencies of the photodegradation of $\text{Ag}(\text{CN})_2^-$ with Degussa P25 TiO_2 in the absence of oxygen.

	Initial reaction rate r^0 ($\text{ppm Ag}^0 \text{ min}^{-1}$)	Initial photonic efficiency ξ^0 ($\text{mol}_{\text{Ag}^0} \text{ Einstein}^{-1}$)
Degussa P25, without O_2	0.0470	$5.32 \cdot 10^{-4}$
Degussa P25, without O_2 , 0.1 MeOH	0.3327	$3.76 \cdot 10^{-3}$
Degussa P25, without O_2 , 1.0 MeOH	0.5997	$6.78 \cdot 10^{-3}$
Degussa P25, without O_2 , 10.0 MeOH	0.6142	$6.94 \cdot 10^{-3}$

It is noticeable, however, that even though the degradation of $\text{Ag}(\text{CN})_2^-$ was improved, the presence of methanol had a detrimental effect on the photocatalytic oxidation of released cyanides to cyanates, thereby producing a significant increase of the concentration of free CN^- in the solution. In fact, for methanol concentrations higher than 1 mM the inhibition of CN^- ions oxidation was almost complete. The results obtained confirm that the photocatalytic degradation of the dicyanoargentate(I) complex is limited by the efficiency of its decomposition rate through the reduction reaction (1). The addition of the hole scavenger in solution has an accelerating effect, increasing the reduction efficiency and thereby enhancing the release of free cyanides from the complex. However, those cyanide groups must compete with methanol molecules for holes and/or adsorption sites to undergo oxidative reaction. The experimental results prove that a preferential photocatalytic oxidation of the alcohol takes place: at low methanol loading, part of cyanide ions is able to be oxidized to cyanate species whereas the increase of methanol concentration inhibits such reaction.

It is also worthy to note the concentration profiles obtained upon addition of 1 and 10 mM of methanol, where the $\text{Ag}(\text{CN})_2^-$ decreased by more than 85% in 1 h. By this time, however, the rate of silver deposition on TiO_2 slowed down and even a slight increase of dissolved silver was detected concomitantly to a decrease of free cyanide concentration. A limitation caused by the lack of hole scavengers can be ruled out to explain these results taking into account both that similar profiles were obtained by increasing the methanol loading and that CN^- ions in solution were available to be oxidized. Neither a saturation of the titania surface by deposited metallic silver can be considered according to the TEM analysis of the spent catalyst, as it will be later discussed. In a previous work focused on the enhancement of the photocatalytic oxidation of oxalic acid by silver deposition on TiO_2 [22]

Szabó-Bardos et al. found a breakdown in the increase of metal deposition rate at various conversions. They proposed that the phenomenon could be explained by considering the silver ion transport to the surface and its adsorption processes. Upon irradiation, the consumption of silver ions at the titania surface would be faster than their diffusion to the surface from the bulk. As a consequence, the rate of silver reduction would be determined by the diffusion process therefore resulting in a decrease of the photoinduced electron transfer reaction at low concentrations of silver ions in the aqueous phase. Huang et al. [24] studied the removal of silver in photographic processing waste by titanium dioxide-based photocatalysis and found that using a fixer containing about 6 000 ppm Ag^+ and a total concentration of TiO_2 of 0.2 wt%, the final concentration of metal in solution could not be lowered below 200 ppm even though fresh TiO_2 was added to the solution. The authors attributed their results to either that the deposited Ag metal could block light from entering the TiO_2 making it incapable of accepting any more silver or to the fact that at such silver loading the rate of Ag re-dissolution could become equal to the rate of deposition making impossible any further removal of dissolved silver. The much lower concentrations of silver ions used in the present work as compared with reference [24] and the lack of saturation of the titania surface observed by TEM, point out that a blocking of light by deposited metal must not be responsible for the cease of silver deposition. We neither consider that restrictions in the diffusion and adsorption of silver ions cause the breakdown of silver deposition since the stirring of solution must be able to provide a proper diffusion rate of silver ions to the non-porous titania surface used in the present work. On the other hand, previous studies have shown the nearly complete removal (99.7%) of dissolved Ag(I) by photocatalytic reduction of AgNO_3 solutions with TiO_2 P25 [12, 19]. One significant difference that should be noticed between works that report the complete deposition of silver and those that do not achieve it is the absence or presence of complexing organic compounds respectively in the solution. In the latter cases, a breakdown of silver deposition is observed whatever the nature of the organic species: oxalic acid [22], thiosulfate [24] or cyanide ions (present work), therefore indicating that the role of those organics coexisting in the solution should be taken into account to elucidate the results. In that respect, a plausible proposal is that the presence in the solution of chemicals able of stabilizing silver ions in solution as it is the case of CN^- , oxalate or thiosulphate, avoids the complete metal photocatalytic deposition on TiO_2 . This hypothesis is supported by the complete silver removal achieved in the presence of non-complexing sacrificial organics such as 4-nitrophenol [12]. On this basis, the complete recovery of silver would require the simultaneous oxidation of cyanide ligands. The accumulation of free

cyanide ions in the solution may also favour the cyanidation of a small fraction of silver deposited on the semiconductor surface thus leading to the formation of $\text{Ag}(\text{CN})_2^-$, what would account for the slight increase of dissolved silver detected at longer times (figure 2).

It should be finally mentioned that, independently of the amount of methanol added, no CN^- mass balance was achieved in any of the reactions. This topic will be discussed later in more detail.

3.2. Photocatalytic degradation of $\text{Ag}(\text{CN})_2^-$ in the presence of oxygen.

Reactions (1) and (2) show that for the photocatalytic treatment of the $\text{Ag}(\text{CN})_2^-$ complex one electron is required to attain the reduction of the silver ion whereas 4 holes are needed to achieve the oxidation of the two CN^- ions released. This unbalanced charge carriers consumption could result in a build up of electron concentration thus leading to increased recombination rates and lowered efficiency. Therefore, the addition of an electron scavenger as molecular oxygen might have a beneficial influence on the kinetics of the photocatalytic degradation of dicyanoargentate(I). It is well established in the literature that oxygen is efficiently reduced by photogenerated electrons leading to the formation of superoxide ions:



As it is shown in Figure 3, under oxygenated conditions a high conversion was achieved not only for silver photodeposition but also for cyanide oxidation to cyanate. In fact, it is worthy to notice that no free cyanide ions were detected in the medium and the total CN^- mass balance was accomplished between the dicyanoargentate and cyanate species present in the solution. Likewise the experiments performed under anoxic reaction environment, the effect on the kinetics of the addition of methanol was also investigated. The concentration profiles obtained, displayed in figure 4, show significant differences comparing with the previous experiments where oxygen and methanol were independently evaluated. In the presence of oxygen the addition of alcohol had a detrimental effect, decreasing the efficiency for silver deposition as the methanol concentration is increased. Table 2 summarizes the initial reaction rates and photonic efficiencies of the photodegradation of dicyanoargentate solutions in the presence of oxygen, without and with methanol. The addition of methanol resulted in a decrease of the photodeposition rate down to ten-fold. On the other hand it is noticeable that, in contrast with the results obtained in the absence of oxygen, no accumulation of free cyanides in the solution was observed upon methanol addition. From the

above results two main conclusions can be drawn about the photocatalytic treatment of dicyanoargentate complexes: the first one is that the presence of oxygen does not avoid silver deposition on titania; and the second one is it prevents the accumulation of free cyanides in the solution, independently of the presence of methanol.

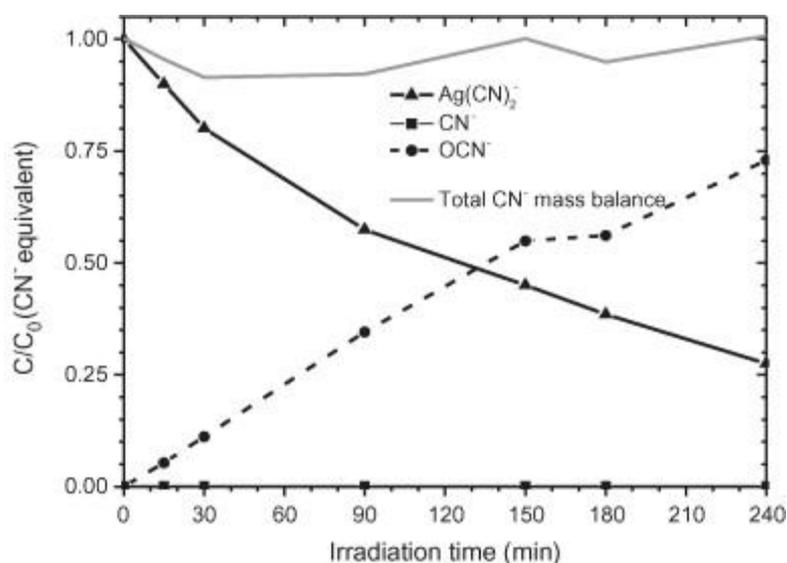
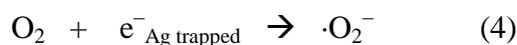


Figure 3. Photocatalytic degradation of $\text{Ag}(\text{CN})_2^-$ in the presence of oxygen.

Most studies dealing with photocatalytic deposition of metals on TiO_2 from aqueous solutions of their respective ions, generally report that the presence of oxygen inhibits the reduction process. It is the case of silver, mercury, palladium, rhodium and platinum, what has been explained in terms of a competition between metal ions and O_2 for conduction band electrons [11 and references therein]. On the other hand, works focused on increasing the photocatalytic activity of titanium dioxide for oxidation of organic compounds by deposition of silver on the semiconductor report contradictory results about the influence of oxygen. Whereas some studies have found a detrimental effect of the presence of molecular oxygen, no significant differences between ambient and oxygen-enriched conditions have been obtained in specific cases, and even a beneficial influence of O_2 has been reported. For instance, the photoactivity of silver metal-modified titania particles for sucrose mineralization was observed to decrease by 25% under oxygen-enriched atmosphere in comparison with ambient conditions [21]. In the same study, however, it was found that the rate of salicylic acid mineralisation was improved in oxygen-enriched photocatalyst suspensions and similar

photoactivities for the oxidation of phenol under both ambient and oxygen-enriched conditions were obtained. By contrast with the latter results, Sclafani et al. [29] reported that the photoactivity of anatase for phenol degradation was enhanced by the simultaneous presence of Ag^+ and oxygen, suggesting that silver photodeposited onto TiO_2 could react with peroxidic species produced in the photoreduction of oxygen. A similar beneficial effect of the molecular oxygen was also found in the oxidation of 2-propanol with Ag-TiO_2 samples [20] what, considering the good catalytic properties of silver for oxygen reduction, was attributed to the formation of superoxide radicals on silver deposits with an overvoltage lower than on TiO_2 .

The comparison of the data displayed in Figures 1 and 3, clearly show that the presence of oxygen enhances the deposition of silver from the dicyanoargentate(I) complex on TiO_2 and promotes the oxidation of released cyanide ions to cyanate species. Hence, even though oxygen can compete with Ag(I) for scavenging photogenerated electrons, the efficiency of electron transfer from the TiO_2 conduction band to silver ions seems to be more favoured than to adsorbed oxygen. The electron transfer from the conduction band of irradiated titania to the silver particles that are gradually deposited on the semiconductor surface is thermodynamically possible because the Fermi level of titanium dioxide is higher than that of silver [30 and references therein]. The electronic interaction between deposited metal and semiconductor results in the formation of Schottky barriers at metal-semiconductor contact regions, improving the efficiency of the separation of the photogenerated electron-hole pairs and thus the charge transfer to electron acceptors available on the TiO_2 surface, such as molecular oxygen [22]. Therefore, deposited metallic silver might promote the formation of superoxide radicals through reaction (4):

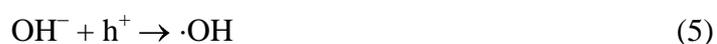


Even though this electron transfer must be a fast process, the fact that oxygen does not avoid silver reduction indicates the faster electron transfer from the titania conduction band to silver. It is plausible to consider that once superoxide radicals are formed by reaction (3) they can subsequently transfer the electrons to Ag(CN)_2^- species approaching the surface, therefore contributing to the reduction process. This role of the oxygen as intermediate in the transfer of electrons has been previously proposed by Giménez et al. [31] to explain the beneficial effect of molecular oxygen in the process of reduction of chromate species. On the other hand, the fact that in all reactions performed under aerobic conditions oxidation of released cyanides to cyanate species was always achieved, even in the presence of methanol, suggests that oxygen

must also have a direct participation in the oxidative process as reactant, most likely through the different oxygenated radicals that can be formed in the photocatalytic process. This dual role of oxygen as electron acceptor and reactant in the photocatalytic process has been also proposed in previous studies [22, 32, 33].

Taking into consideration the good results obtained in terms of silver deposition upon addition of either methanol or oxygen separately, it is quite striking the drastic decrease in the metal reduction induced by their simultaneous presence, more pronounced as methanol concentration is increased. An hypothesis to explain the above findings is that methanol undergoes different pathways and subsequently plays different roles depending on whether the photocatalytic treatment of $\text{Ag}(\text{CN})_2^-$ takes place in anoxic or aerobic environment. As a consequence, its ability for enhancing silver photoreduction from the cyanocomplex strongly depends on the experimental conditions used.

The process by which methanol acts as an efficient hole scavenger in photocatalytic reactions has been described in the literature as follows. The reaction of photogenerated holes with hydroxyl groups leads to formation of OH radicals (reaction 5) that readily react with methanol molecules through abstraction of a hydrogen atom from the C-H bond therefore generating α -hydroxymethyl radicals (reaction 6) [34]:



The α -hydroxymethyl radicals formed are species with a strong reducing power that can either react with other species adsorbed on the titania surface or inject an electron into the conduction band of the semiconductor, process known as current doubling effect [35]. That means, that in the absence of oxygen, methanol enhances the reduction of $\text{Ag}(\text{CN})_2^-$ not only because it minimizes charge carriers recombination but due to the formation of reducing intermediates capable of donating an electron to the metal ion. This two-fold effect of organic additives on metal ion reduction in UV-irradiated TiO_2 suspensions has been previously stated to explain the enhancement of the photocatalytic reduction of Cd [36] and Se ions [37]. In the presence of oxygen, however, the improvement of Ag(I) reduction induced by methanol is significantly diminished as the results displayed in figure 4 show. It is suggested that in this case, $\cdot\text{CH}_2\text{OH}$ radicals preferentially react with O_2 thus fading their reductive role. Chuang et al. [32] have proposed that in the absence of oxygen, methoxide species formed upon adsorption of methanol on TiO_2 surface react with photogenerated holes to form $-\text{OCH}_2\cdot$

radicals, which can dissociate to yield formaldehyde. In the presence of O_2 , however, $\cdot OCH_2$ incorporates O_2 to generate peroxy radicals that can recombine with $\cdot OOH$ radicals to produce $-OCH_2OOOOH$ tetraoxides, which at last decompose to formic acid and water molecules.

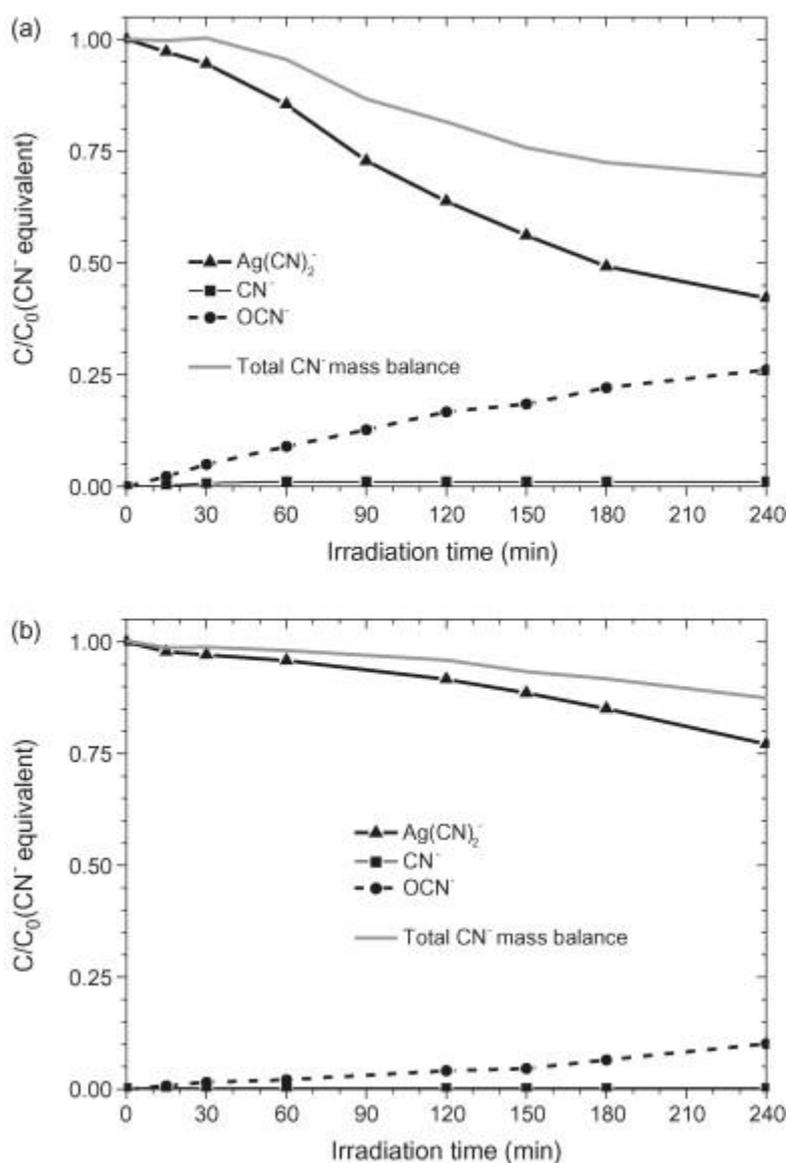


Figure 4. Photocatalytic degradation of $Ag(CN)_2^-$ in the presence of oxygen upon addition of methanol 1 mM (a) and 10 mM (b).

Table 2. Initial reaction rates and photonic efficiencies of the photodegradation of $\text{Ag}(\text{CN})_2^-$ with Degussa P25 TiO_2 in the presence of oxygen.

	Initial reaction rate r^0 ($\text{ppm Ag}^0 \text{ min}^{-1}$)	Initial photonic efficiency ξ^0 ($\text{mol}_{\text{Ag}^0} \text{ Einstein}^{-1}$)
Degussa P25, with O_2	0.2753	$3.11 \cdot 10^{-3}$
Degussa P25, with O_2 , 1.0 mM MeOH	0.1010	$1.14 \cdot 10^{-3}$
Degussa P25, with O_2 , 10.0 mM MeOH	0.0291	$3.28 \cdot 10^{-4}$

Summarising, the role of methanol as hole scavenger thereby decreasing carriers recombinations would not be affected by the reaction environment. On the contrary, the availability of $\cdot\text{CH}_2\text{OH}$ reducing radicals to enhance the reduction of $\text{Ag}(\text{I})$ from the complex to metallic silver would be limited to anoxic conditions, as in aerobic conditions the predominant reaction is the photocatalytic oxidation of the alcohol with O_2 participation.

Finally, it is worthy to mention that similarly to the reactions performed in anoxic conditions, in the reactions displayed in Figure 4, CN^- mass balance was not achieved. In all cases, the CN^- mass balance was calculated as the sum of cyanides and cyanate concentrations. As indicated in the experimental, the former were analysed by the colorimetric method, which includes both free CN^- ions and dissolved cyanoargentate complexes whereas the CNO^- concentration was determined by ion chromatography. Additionally, concentration of free cyanide ions was potentiometrically measured with a selective electrode whereas dicyanoargentate(I) concentration was estimated by ICP/AES, analysing the silver content of the solution and assuming two cyanide ligands for each silver atom. A very good agreement was found between both independent determinations of free cyanide and dicyanoargentate species and the concentration of total cyanides measured by colorimetry, which indicates that complexed cyanides are mostly present as $\text{Ag}(\text{CN})_2^-$ species. Consequently, the lack of CN^- mass balance must be due to the formation of either insoluble species removed from the suspension after the catalysts filtration or soluble species not determined by the analytical techniques used in this work. Figure 5 schematizes the chemical species that can be formed in aqueous systems containing silver and cyanide [38, 39]. The species marked with an ellipse (Ag^0 , AgCN and AgOH) can be considered as insoluble in the experimental conditions used ($K_{\text{ps}} \text{AgOH} = 1.52 \cdot 10^{-8}$, $K_{\text{ps}} \text{AgCN} = 1.20 \cdot 10^{-16}$). Therefore the unique cyanide-containing insoluble compound should be AgCN , but no traces of these species were detected by DRX

analysis of the solids recovered after the reactions performed in the presence of methanol. The second possibility claims for the formation of non-detected soluble species. Taking into consideration that the lack of CN^- mass balance was found only in those reactions performed upon addition of methanol, it is reasonable to hypothesise the formation of species derived from the interaction between the alcohol or derivatives and cyanides. For instance, as cyanide radicals can be formed by either by direct oxidation with holes or by reaction with the hydroxyl radicals [40], it is plausible to hypothesize cross reactions between $\cdot\text{CN}$ and $\cdot\text{CH}_2\text{OH}$ species leading to the formation of nitriles:



3.3. Fate of silver.

According to the scheme presented in Figure 5 Ag^0 , AgCN and AgOH are the main silver-containing insoluble species that can be formed in the experimental conditions used. That means that they would be removed together with the catalyst in the filtration previous to the analysis. The presence of dissolved Ag^+ ions can be discarded because they would be precipitated as AgOH at the reaction pH. Moreover, the reduction potential of the Ag^+/Ag^0 pair ($E^0 = 0.8 \text{ V}$) indicates that Ag^+ reduction would be more favoured than that of dicyanoargentate(I) ($E^0 \text{ Ag}(\text{CN})_2^- / \text{Ag}^0 = -0.2 \text{ V}$) [28]. On this basis, it can be assumed that the results of silver analysis by ICP/AES of the solids recovered by filtration came from the sum of Ag^0 , AgCN and AgOH species formed, whereas the analysis of the solution once the solids have been removed included all the $\text{Ag}(\text{CN})_x^{(x-1)-}$ ($x = 2-4$) species present. It is worthy to note that, in contrast with the lack of CN^- mass balance above mentioned, the analysis for Ag content of solids and solutions established the achievement of silver mass balance in all reactions performed.

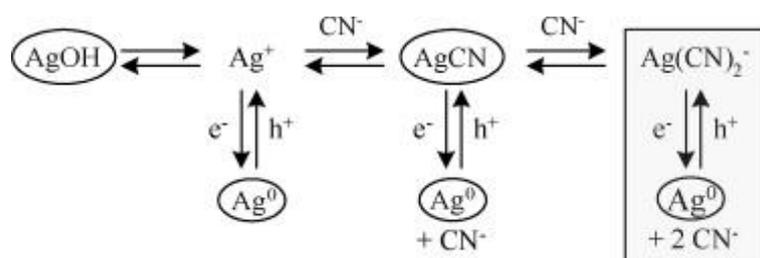


Figure 5. Scheme of plausible species in the aqueous silver / cyanide system

The spent catalysts recovered after the reaction showed a grey colour attributable to silver deposits, whose nature was investigated by XRD and TEM. Independently of the experimental conditions that had been used in the reaction, the powder X-ray diffraction patterns of the recovered catalysts always showed signals attributable to the presence of metallic silver. No other silver crystalline phases such as Ag_2O or AgCN were detected in any case. As a representative example, figure 6 displays the XRD patterns of the P25 sample recovered after the reaction performed in the presence of oxygen. Besides the peaks of anatase and rutile phases, the main peaks of Ag^0 at 2θ angles of 38.2° , 44.3° and 64.5° are clearly observed.

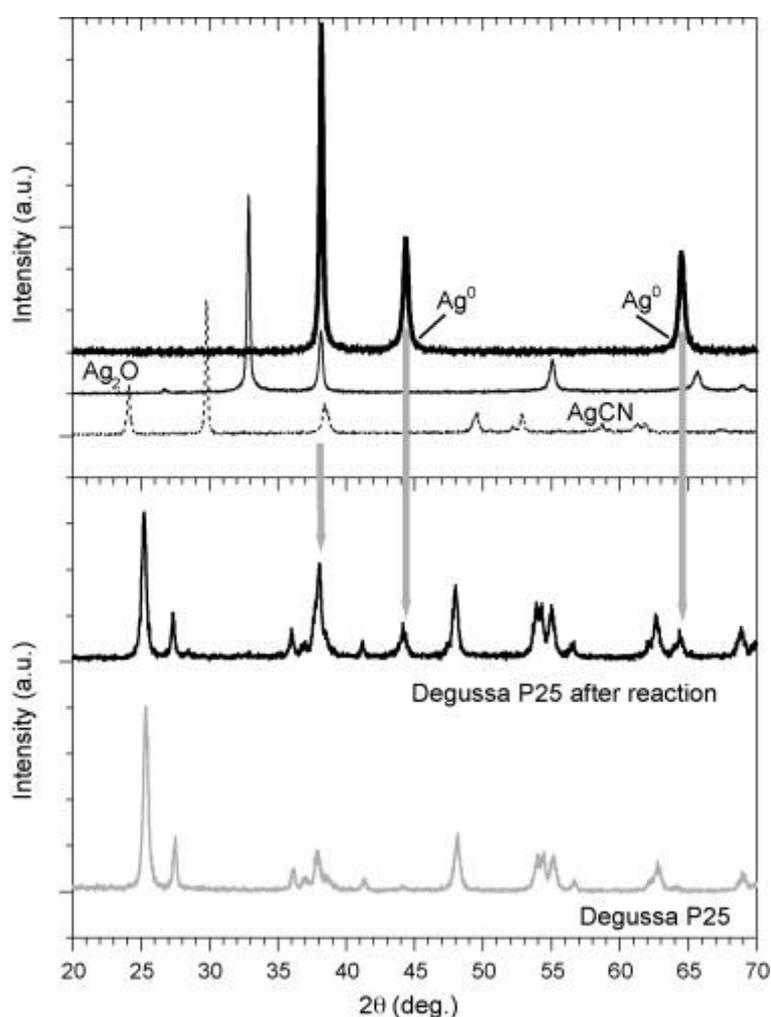


Figure 6. X-ray diffraction pattern of Degussa P25 TiO_2 recovered after photocatalytic reaction of $\text{Ag}(\text{CN})_2^-$ in the presence of oxygen.

Examination of the solids by transmission electron microscopy showed the presence of dark crystals of size significantly larger than the titanium dioxide particles (figure 7). The microanalysis of these crystals by X-ray energy dispersive (EDX) confirmed that they consisted of metallic silver. As it can be observed, deposited Ag clusters are localized individually on the titania surface. The formation of large agglomerates upon silver photodeposition on titanium dioxide was also reported by Herrmann et al. [19]. They found that the process did not proceed through the formation of a silver monolayer or a silver film, but through the formation of huge crystallites that could be built up through agglomeration of Ag^0 atoms or by cathodic-like successive reduction processes. Additional EDX analysis of different zones of the recovered solids discarded the presence of significant amounts of C and N thus allowing to discard the formation of AgCN in all evaluated reaction conditions.

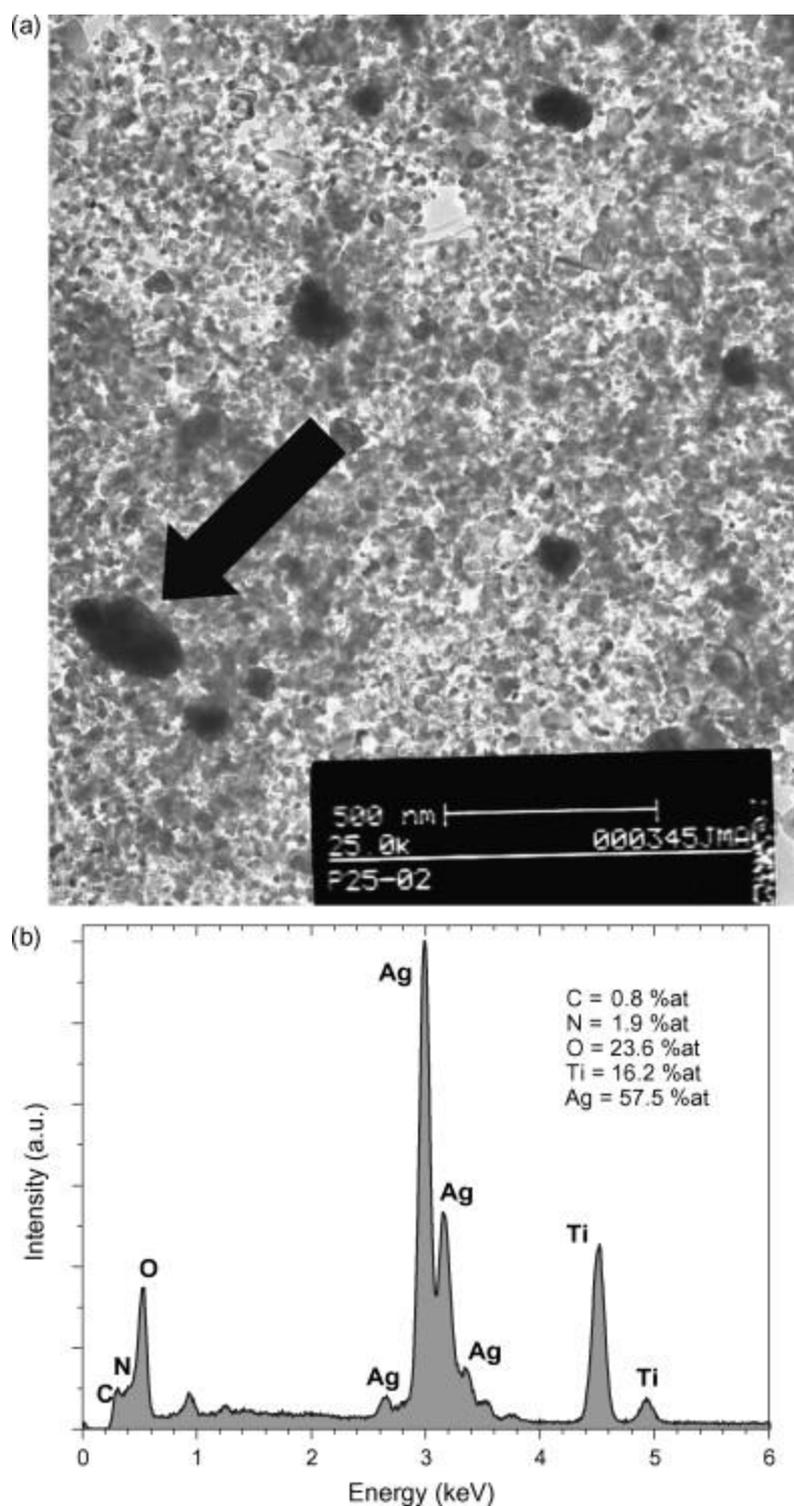


Figure 7. TEM micrograph of Degussa P25 recovered after photocatalytic reaction of $\text{Ag}(\text{CN})_2^-$ in the presence of oxygen (a) and EDX microanalysis of the pointed cluster (b).

Consequently, it can be concluded that under the investigated experimental conditions, the photocatalytic treatment of dicyanoargentate(I) aqueous solutions with TiO_2 results in the deposition of Ag(I) species as Ag^0 on the catalyst surface so that the solids separated after the

reaction consist of a mixture of titanium dioxide and metallic silver. Recovery of the latter can be done by nitric acid attack, producing the selective dissolution of the metal and allowing the reuse of the catalyst. Also sonication of the spent catalyst followed by sedimentation has been proposed by Huang et al [24] as a physical method to dislodge large particles of silver from the TiO₂ in the case of high Ag loadings.

3.4. Photocatalytic degradation of dicyanoargentate silver plating baths.

The feasibility of the photocatalytic process for the treatment of industrial silver plating wastewater was investigated carrying out experiments with a spent silver plating bath, whose composition is summarized in table 3. The pH value of the spent bath was 11.5. The difference between the potentiometric and colorimetric analysis indicated the presence of both free and complexed cyanides, the latter mostly due to silver and copper cyanides according to the measured metal concentrations. Taking into account that the sum of free and complexed cyanides would be equivalent to 17 500 mg l⁻¹ of organic carbon, it was inferred from the TOC value (39 500 mg l⁻¹) that large amounts of other organic compounds were also present in the bath. Most likely, this organic matter mainly comes from complexing agents and additives used in the formulation of the bath but their nature was not provided on grounds of industrial confidentiality.

Table 3. Composition of the spent silver plating bath.

Free cyanide (potentiometric analysis)	27 800	mg l ⁻¹
Weak acid dissociable cyanide (colorimetric analysis)	37 900	mg l ⁻¹
Total organic carbon	39 500	mg l ⁻¹
Silver	18 100	mg l ⁻¹
Copper	4 800	mg l ⁻¹
Zinc	290	mg l ⁻¹
Nickel	300	mg l ⁻¹
Potassium	550	mg l ⁻¹

The spent plating bath was diluted in order to work at concentrations comparable to those used in the study carried out with pure potassium dicyanoargentate solutions. As shown in Figure 8, the photocatalytic treatment of the spent plating bath in the presence of oxygen led to null deposition of silver on TiO₂. Additionally, no changes in the TOC and copper concentrations were detected whereas a slight reduction in the free cyanide concentration through oxidation to cyanate species was observed. These results agree with those obtained in the photocatalytic treatment of aqueous dicyanoargentate solutions upon methanol addition and prove the inhibition for silver deposition induced by the simultaneous presence of oxygen and organic compounds. In these conditions, a preferential oxidation of the organic compounds initially present in the spent plating bath solution takes place, although no mineralization is achieved according to the TOC measurements. On the contrary, the results displayed in figure 9 show that the photocatalytic treatment of the bath solution in the absence of oxygen led to a silver photodeposition rate of 0.3617 ppm_{Ag} min⁻¹, value very similar to that obtained for pure dicyanoargentate solutions in the presence of 0.1 mM methanol. This fact evidences that in anoxic conditions silver reduction and deposition rate is improved by the presence of the organic compounds present in the bath by acting either as hole scavengers or even supporting reducing agents. The analysis by XRD and ICP/AES of the catalyst recovered after the reaction confirmed the deposition of Ag⁰ on titanium dioxide. It is worthy to note that no other metallic phases such as copper, the second major metal cation present in the solution, were deposited on titania. It can be then assess that silver can be selectively recovered from the spent plating bath. The results obtained can be interpreted in terms of the more favourable reduction potential (vs. NHE) of the Ag(CN)₂⁻/Ag⁰ pair (E⁰ = -0.2 V) as compared with that of Cu(CN)₂⁻/Cu (E⁰ = -0.78 V) [9]. On the other hand, even though part of the copper in solution could be not complexed with cyanides, previous results about the photocatalytic treatment of an equimolar Cu²⁺-Ag⁺ solution have shown that Cu⁰ could not be photodeposited on titanium dioxide despite the slightly favourable redox potential with respect to the TiO₂ flat-band potential [19].

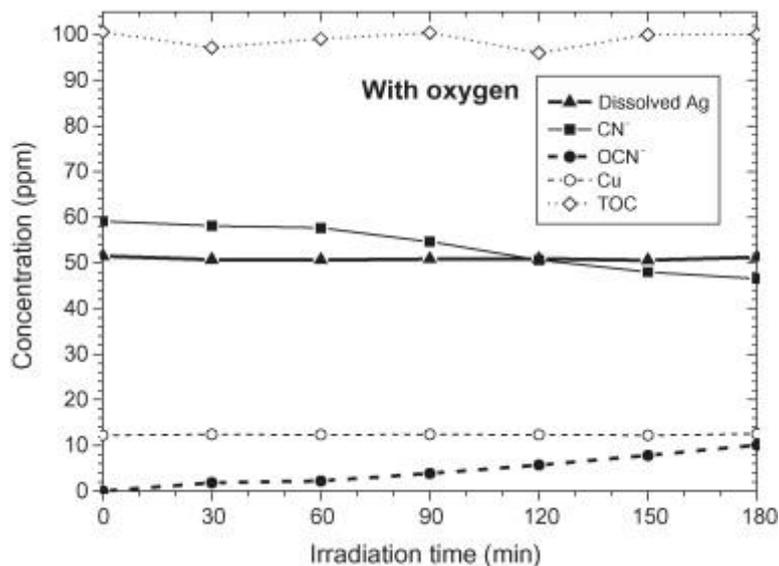


Figure 8. Photocatalytic degradation of an industrial spent silver plating bath in the presence of oxygen.

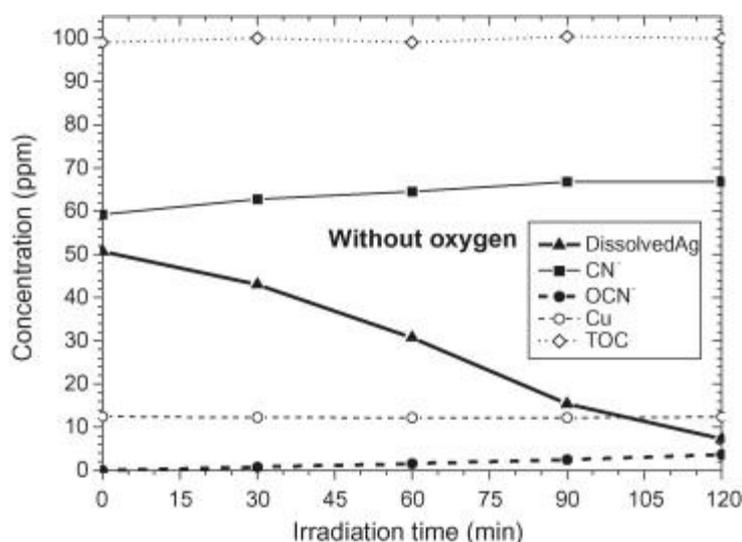


Figure 9. Photocatalytic degradation of an industrial spent silver plating bath in the absence of oxygen.

Summarising, the photocatalytic treatment of the spent silver plating bath solution in anoxic conditions allowed a selective recovery of metallic silver, which was photodeposited on the titania surface. Therefore, it is feasible the industrial application of heterogeneous photocatalysis for achieving a selective Ag⁰ deposition on TiO₂. It fails, however, in achieving the simultaneous Ag(I) reduction and cyanide oxidation attained in the experiments carried out with pure aerated dicyanoargentate solutions. Having in mind the simultaneous

presence of large amounts of organic additives, it can be proposed that the overall treatment of spent silver plating bath solutions with high TOC values could be performed in two steps. The first one, in the absence of oxygen, would lead to the selective photocatalytic recovery of silver. The second step, in aerobic conditions, would be focused on the oxidation of the free cyanides and organic compounds.

4. Conclusions

The photocatalytic performance of TiO_2 for the treatment of aqueous dicyanoargentate(I) solutions has been investigated. In anoxic conditions, the global kinetics are limited by the low reduction driving force of $\text{Ag}(\text{CN})_2^-$ to Ag^0 . The addition of methanol greatly enhanced the reduction of Ag(I) to metallic silver, but had the disadvantage of inhibiting the oxidation of released CN^- , thus resulting in an undesirable accumulation in the solution of such toxic species. The faster rate of Ag(I) ion photocatalytic reduction in the presence of methanol is attributed to both, the effectiveness of this organic molecule as hole scavenger and its ability to form reducing radicals. The best operating conditions for $\text{Ag}(\text{CN})_2^-$ treatment were observed to occur in the presence of oxygen, since both the simultaneous reduction of Ag(I), which is deposited as Ag^0 on the titania surface, and the oxidation to cyanate species of CN^- ions released from the complex were achieved. It is concluded that O_2 plays a dual role in the overall process. On one hand it supports the reduction process acting as electron intermediate and, on the other hand it actively participates in the cyanide oxidation. In aerobic conditions the presence of methanol noticeably slowed down the rate of silver deposition, which indicates that in this case the predominant reaction is the photocatalytic oxidation of the alcohol with O_2 participation.

The results obtained with a spent silver bath plating solution prove it is feasible the industrial application of the photocatalytic treatment for achieving a selective recovery of metallic silver. In cases of a high organic content in the solutions, the treatment procedure should be performed in two steps. In the first one, in the absence of oxygen, the silver recovery should be achieved. The second one, in aerobic conditions, would be focused to the cyanides and organic matter oxidation.

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