

Activated sludge respirometry to assess solar detoxification of a metal finishing effluent

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Received 26 June 2007; received in revised form 10 September 2007; accepted 11 September 2007

Available online 14 September 2007

Abstract

Inhibition of the respiration of activated sludge has been tested as a convenient method to estimate toxicity of aqueous solutions containing copper and cyanide, such as metal finishing effluents; according to this method, an EC_{50} of 0.5 mg/l was determined for CN^- and 3.0 mg/l for copper. Solar detoxification of cyanide-containing solutions was studied using TiO_2 , but this process was unfavourable because of the inhibitory role that plays the copper ions present in real effluents on the oxidation of cyanide. On the other hand, the oxidative effect of hydrogen peroxide was greatly enhanced by Cu^{2+} and solar irradiation, as complete elimination of free and complexed cyanide could be accomplished, together with precipitation of copper, in experiments carried out at pilot plant scale with real metal finishing effluents. Under these conditions, total detoxification was achieved according to respirometric measurements although some remaining toxicity was determined by more sensitive *Vibrio fischeri* luminescent assay. © 2007 Elsevier B.V. All rights reserved.

Keywords: Detoxification; Cyanide; Sunlight; Activated sludge; Metal finishing effluents

1. Introduction

Generation of important volumes of effluents polluted with hazardous chemicals is one of the most serious environmental concerns related with industrial activities. Toxicants have to be removed before water can be either re-used, or discharged into aquatic systems [1]. Furthermore, toxic compounds are not compatible with activated sludge-based biological reactors, which are among the most widely employed methods for wastewater treatment [2]. For this reason, development of specific methods to remove efficiently these pollutants seems meaningful.

Primary elimination of most inorganic or organic hazardous species can be accomplished using chemical processes. In particular, considerable information is now available on the use of

advanced oxidation methods to treat a wide range of chemicals such as pesticides, antibiotics, phenols and chlorophenols, dyestuffs, surfactants, cyanides or paper industry contaminants [3–6]. However, a study on the remaining toxicity of the treated effluent appears to be a key factor in order to evaluate the applicability of the chemical treatment, above all, when dealing with real wastewaters [7]. Furthermore, in most cases the final goal of photocatalysis is to improve the biocompatibility of the effluent in order to apply a biological treatment [8–10].

There are several ways to measure toxicity, but in all cases bioassays are employed and results are rather variable [11,12]; thus, the effect of toxicants towards living systems is not easy to predict. The inhibition of the bioluminescence of *Vibrio fischeri*, a marine microorganism, is commonly employed in toxicity determination [13]; however, results obtained by means of this assay cannot be easily related with the effect of the toxicant towards biomass of biological reactors, as *V. fischeri* seems to be too sensitive [14]. Assays involving activated sludge could be more suitable for this purpose, as this sludge consists in a

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consortium of microorganisms commonly present in biological reactors [15].

Respiration of activated sludge could be a good parameter to be used for this purpose, as the concentration of dissolved oxygen can be easily determined, and it can be employed in oxygen uptake rate (OUR) calculation [16,17]. Inhibition of the respiration of activated sludge has proven to be a useful tool to estimate their response towards toxicants. In particular, an adaptation of the OECD test 209 has been used to estimate detoxification of aqueous solutions of several commercial pesticides when submitted to TiO₂-based solar photocatalysis [18–20]; this method proved to be suitable to determine the short-term effect of the pollutant on the microorganisms.

The use of activated sludge respirometry to estimate solar detoxification by photocatalysis of the wastewaters of a metal finishing industry seems interesting. A number of papers have been published dealing with the use of photocatalytic methods to remove cyanides; titanium dioxide [21–24] and hydrogen peroxide [25–27] have been shown to oxidise efficiently this toxicant using UV lamps or even sunlight [28,29]. However, as far as we know, the effect of the treated solutions towards activated sludge remains to be explored. With this background, this work studies the solar detoxification of a real metal finishing effluent containing important amounts of copper and free and complexed cyanides, using catalytic TiO₂ or sacrificial H₂O₂. The role of the copper ions has been checked and toxicity has been determined according to activated sludge respirometry and compared with the widely employed *V. fischeri* test.

2. Experimental

2.1. Reagents

Sodium cyanide (95%) employed to prepare synthetic wastewaters was purchased from Aldrich. Degussa P-25 titanium dioxide was used as photocatalyst. Hydrogen peroxide (30%, v/v, Panreac) was used as oxidising agent in some (photo)-reactions; all the other chemicals were also purchased from Panreac, but sodium cyanate which was obtained from Aldrich. Solutions were prepared with Milli Q grade water.

Real cyanide-containing wastewaters were supplied by a metal finishing factory from Eastern Spain; they were taken from the inlet of the wastewater treatment system. The main parameters of this effluent were systematically inside the following ranges: pH, 10.5–11.0; conductivity, 2.2–2.5 mS/cm; free cyanide, 100–150 mg/l; copper, 250–350 mg/l; total carbon, 500–800 mg/l; less than 30 mg/l organic carbon and trace amounts of other metals, such as zinc or nickel.

Activated sludge employed in the respirometric experiments was taken from the wastewater treatment plant of Alcoy (East Spain). The initial amount of suspended solids was in the range 2–3 g/l; before the experiments they were diluted to adjust this value to 1–1.5 g/l. Sludge was employed without previous adaptation to the pollutants. Lyophilised bioluminescent bacteria (*Vibrio fischeri*, NRRL B-11177) were purchased from

Macherey-Nagel; they were kept at –18 °C until they were used.

2.2. Reactions

Preliminary experiments were carried out with synthetic solutions containing an initial concentration of cyanide of 100 mg/l, prepared from solid NaCN. When titanium dioxide was used as photocatalyst, its amount was in the range 0.2–1.0 g/l. In some cases, 50 mg/l of Cu²⁺ were added to the cyanide solution. Finally, different amounts of hydrogen peroxide were employed as sacrificial oxidising agent in some experiments. Reactions involving real wastewaters were also carried out either adding catalytic titanium dioxide (0.2–1.0 g/l) or hydrogen peroxide.

Laboratory scale reactions were performed in 250 ml open glass vessels. They were irradiated by means of a solar simulator (Oriol Instruments, Model 81160) equipped with a 300 W xenon lamp, whose spectrum closely matches that of sunlight reaching the Earth surface. In all cases, magnetic stirring was kept all along the reaction time and water was periodically added in order to compensate for evaporation losses. Reactions with real wastewaters were scaled up using a pilot plant for wastewater detoxification (Solardetox Acadus-2006). It was based on compound parabolic collectors [30], CPCs, able to treat up to 50 l of wastewater (3.0 m² irradiated surface, 24 l irradiated volume). A picture of the plant can be observed in Fig. 1. Accumulated and instantaneous UV radiation was measured by means of a UV radiometer and expressed as t_{30W} . This is a convenient parameter to normalise the changing irradiation conditions typical of solar experiments: t_{30W} is calculated by considering an average intensity of 30 W/m², which is typical for sunny days in the South East of Spain [18]. Eq. (1) has been used in the t_{30W} (in seconds) calculations, where UV_{ac} is the accumulated solar radiation (J/m²), V_i the irradiated volume (l) and V_t the total volume (l).

$$t_{30W} = \frac{UV_{ac} V_i}{30 V_T} \quad (1)$$

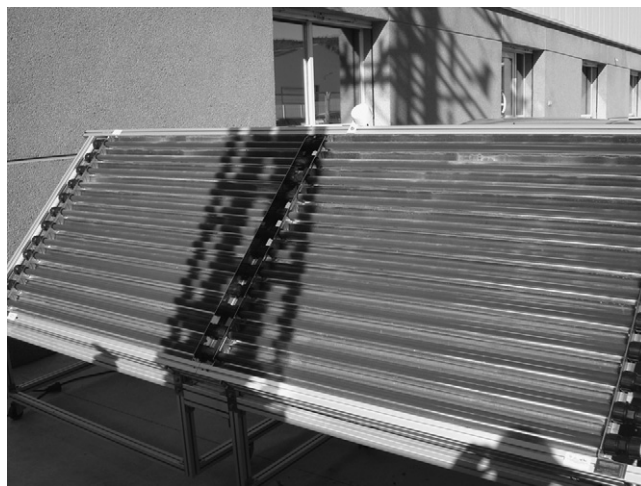


Fig. 1. Picture of the pilot plant for solar detoxification of wastewater.

2.3. Analysis

Samples were periodically taken from the reactors to be analysed; all of them were filtered through nylon filters (0.45 μm) before analysis. Different standardised procedures have been employed for CN^- determinations [31]. High concentrations of free cyanide (above 10 mg/l) were analysed potentiometrically (106613 electrode, from WTW), while the 1,3-dimethylbarbituric acid spectrophotometric method was used for lower concentrations. In order to measure total cyanide, the solution was submitted to an acidic distillation before analysis; briefly, it consists in adding HCl to the effluent to convert free and complexed cyanide into gaseous HCN which is bubbled through a NaOH solution to obtain NaCN, which can be determined as free cyanide. Total dissolved carbon (TC) was determined by means of Shimadzu model TOC-V CSH provided with an autosampler; carbonates were precipitated with calcium chloride and the samples filtered before TC analyses.

Dissolved metals (copper, zinc, nickel) were determined by inductively coupled plasma-optical emission spectroscopy (ICP). An ICP Optima DV2000 apparatus, supplied by Perkin-Elmer was employed.

Respirometric assays were carried out using an activated sludge respirometer BM3-LAB (Neurtek) equipped with an oxygen sensor (WTW-Cell Ox). Oxygen uptake rate was calculated from the difference in the concentration of oxygen in the activated sludge when it is pumped to the oxygen sensor through two different length pathways [32]. The OUR inhibition experiments were based on the standardised norm ISO 8192; activated sludge (500 ml) was brought to its maximum oxygen uptake rate (OUR_{max}) by addition of solid sodium acetate (1 g). Then, a sample of the effluent (in the range 1–250 ml) was added and the final oxygen consumption (OUR_f) was measured; the percentage of inhibition (I) was calculated by Eq. (2a). Dilution of the sludge by addition of the liquid sample was responsible of some decrease in the OUR as determined by blank experiments (I_B); thus, a corrected inhibition has to be calculated by means of Eq. (2b):

$$I = \frac{\text{OUR}_{\text{max}} - \text{OUR}_f}{\text{OUR}_{\text{max}}} \times 100 \quad (2a)$$

$$I_C = \frac{I - I_B}{100 - I_B} \times 100 \quad (2b)$$

Luminescent assays were carried out according to the standardised ISO 11348-3 norm, using lyophilised bacteria (*Vibrio fischeri*, NRRL B-11177). The standard procedure was employed for reconstitution of the bacteria, using a salty solution obtained from Macherey-Nagel. The luminescence was measured by a Luminometer Lumifix-Bio-10, also supplied by Macherey-Nagel. Toxicity was determined after 15 min incubation. Distilled water and zinc sulphate were used in control experiments. All samples were filtered and neutralised before analysis.

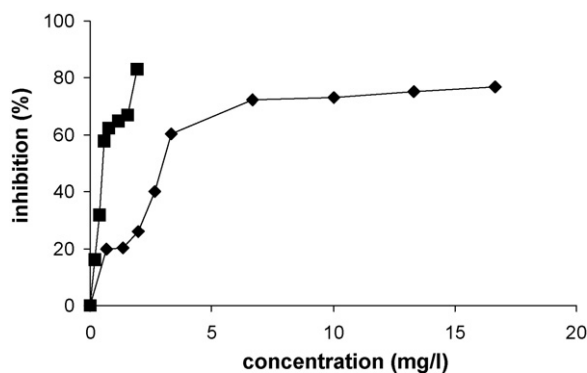


Fig. 2. Inhibition of the oxygen uptake rate of activated sludge produced by different concentrations of cyanide (■) and copper cation(II) (◆).

3. Results and discussion

The toxicity of CN^- and Cu^{2+} towards activated sludge was estimated respirometrically. For this purpose, solutions containing different concentrations of the toxicant were tested in consecutive experiments, and the corrected inhibition values (I_C) were calculated. A plot of the I_C vs. the concentration of CN^- and Cu^{2+} can be observed in Fig. 2; qualitatively CN^- resulted to be more toxic, although copper ions also show a significant toxicity at concentrations close to 1 mg/l. The EC_{50} is a useful parameter to quantify and compare toxicities, as it expresses the effective concentration of a toxicant causing 50% inhibition of the microorganisms activity [33]: a value of 3.0 mg/l was obtained for Cu^{+2} while that for CN^- was 0.5 mg/l. On the other hand, the toxicity of cyanate, major intermediate in the oxidation of cyanide [22,25] was also tested following the same procedure, and it resulted to be negligible in the range 1–100 mg/l.

Other authors have previously determined the toxicity according to the inhibition of the luminescence of *Vibrio* bacteria. A EC_{50} of 0.5 mg/l was obtained for the copper cation [34], while the EC_{50} of cyanide was 38 $\mu\text{g/l}$ [35]. Trends are coincident with the respirometric assays, but the luminescent bacteria seem to be more sensitive towards pollutants than activated sludge; as stated in Section 1, this is a well-known behaviour that has already been reported for different pollutants [14]. For this reason, activated sludge-based measurements could be employed to predict the effect of the effluent towards wastewater treatment plants, while the luminescent assay is more suitable to ensure complete detoxification.

Variation in the toxicity of cyanide-containing solutions submitted to solar-based photochemical treatments was studied. First, TiO_2 solar photocatalysis was tested in a series of bench-scale experiments: 250 ml of a 100 mg/l solution of cyanide were irradiated with a solar simulator for 3 h in the presence of different dosages of TiO_2 (0.2, 0.5 and 1 g/l) in order to determine the influence of this parameter. The final concentration of the pollutant was determined potentiometrically and the inhibition of the sludge respiration was measured by adding 10 ml of the cyanide solution to 500 ml of activated sludge. Table 1 indicates that the initial inhibition was 90%, and the photocatalytic process resulted in a noticeable detoxification, although final toxicity depended on the remaining amount of cyanide. The concentra-

Table 1

Effect of the amount of TiO₂ on the detoxification of cyanide-containing aqueous solutions: inhibition of the OUR and cyanide concentration at the beginning of the experiment (initial, first row) and after 3 h of irradiation using different amounts of TiO₂

	<i>I_c</i> (%)	CN ⁻ (mg/l)	Total carbon (mg/l)
Initial (<i>t</i> =0 h)	90	100	46
0.2 mg/l TiO ₂ (<i>t</i> =3 h)	55	29	32
0.5 mg/l TiO ₂ (<i>t</i> =3 h)	25	18	28
1.0 mg/l TiO ₂ (<i>t</i> =3 h)	21	14	20

tion of photocatalyst had some influence on the results: when 0.2 g/l were used, 55% inhibition of OUR was detected after 3 h; the best results were obtained with the highest amount of TiO₂ (1 g/l) where 85% of CN⁻ was removed, and the final *I_c* decreased to 21%.

It is described in the literature that titanium dioxide catalyses the oxidation of CN⁻ into cyanate (CNO⁻) as major product, which in turn can react to form nitrate and carbonate [22]. Table 1 shows the total dissolved carbon remaining in the solution after precipitation of carbonates; this indicates that important concentration of cyanate and carbonate was still present at the end of the treatment. However, the high toxicity of cyanide, together with the negligible effect that cyanate, nitrate and carbonate ions have in this range of concentrations towards respiration of the activated sludge, could explain the important detoxification that was achieved.

Real metal finishing effluents contain important amounts of transition metals such as copper, which might have a remarkable influence on the process. To clarify this point, a 250 ml sample of this kind of effluent (see Section 2.1. for more details) was submitted to irradiation (solar simulator) for 3 h in the presence of TiO₂ (0.5 g/l). Respirometric curves obtained when 10 ml of the treated and non-treated solutions are added to 500 ml of activated sludge in two separate experiments, are shown in Fig. 3; they indicate that although the *I_c* values were reduced from 95 to 50%, the persistent high toxicity might make this process unattractive. Although some authors have reported high con-

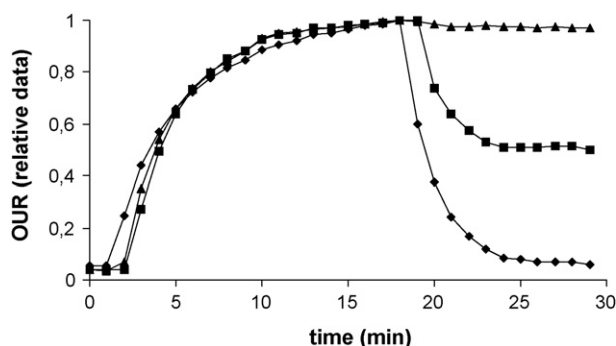


Fig. 3. Respirometric curves obtained for the effluent of a metal finishing industry before treatment (◆), after 3 h of irradiation in the presence of titanium dioxide (■) and after 15 min irradiation in the presence of hydrogen peroxide (▲). In all cases, sodium acetate (1 g) was added to 500 ml of the sludge at the beginning of the experiment to achieve its maximum OUR. Then, 10 ml of the sample were added (*t*=18 min) and the decrease in the respiration was determined.

centration of copper to play a favourable role in the process [24], probably due to the enhanced degradation of complexed cyanides, the removal of more toxic free cyanides is inhibited by a competitive process [23]. Furthermore, the toxicity of copper, which is not efficiently eliminated from the solution, could also explain the important toxicity at the end of the process.

Hydrogen peroxide was tested to detoxify the solution. This reagent has been employed to oxidise cyanide, and its effect is greatly enhanced by the presence of some metal cations such as copper [36]. As this reaction has been reported to be accelerated by UV irradiation [25], the use of sunlight to treat metal finishing is an attractive alternative.

A series of laboratory scale experiments were devoted to clarify this point. First, hydrogen peroxide (5 mmol) was added to 250 ml of a cyanide solution (100 mg/l, approximately 1 mmol) and the mixture irradiated with a solar simulator. Total elimination of free cyanide was achieved after 90 min of photochemical treatment (Fig. 4), corresponding to approximately 1.5 kJ in the UV-A range of the spectrum (6 kJ/l); on the other hand, H₂O₂ in the dark was not able to remove significant amounts of CN⁻ even after 3 h of reaction. Although efficient photolysis of hydrogen peroxide only occurs under UVC irradiation, some formation of highly reactive hydroxyl radicals, which are able to react efficiently with the pollutant, should not be ruled out to explain the enhanced oxidation of cyanide under sunlight irradiation [37]. In agreement with these data, respirometric assays indicated complete detoxification at the end of the experiment carried out under irradiation. Although dissolved carbon only suffered a slight decrease after removal of carbonates, non-toxic cyanate could be the predominating species under these conditions and further chemical treatment of the effluent would be disadvantageous. However it was not possible to decrease significantly the amount of H₂O₂ employed in the reaction, as when the photochemical experiment was performed with 2.5 mmol of hydrogen peroxide, 10 ml of the treated sample produced and *I_c* of 50%.

Chemical photo-oxidation of cyanide with hydrogen peroxide was also studied in the presence of Cu²⁺ in order to confirm the possible photocatalytic role of this cation. After 1 h of irradiation, activated sludge assays indicated that detoxification of the effluent was achieved. At this moment, potentiometric measurement after acidic distillation indicated complete removal of free and complexed cyanide; furthermore, TC analysis after precipitation of carbonates, indicate that approximately 30% of the

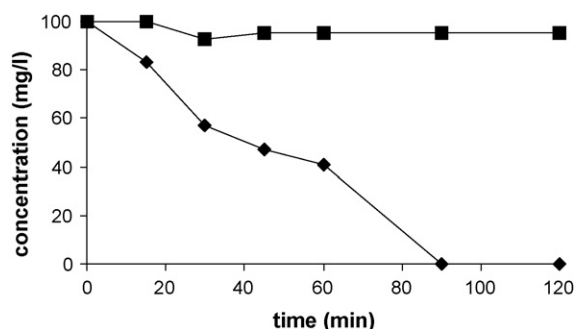


Fig. 4. Removal of cyanide in aqueous solution by hydrogen peroxide: (◆) solution irradiated with a solar simulator, (■) in the dark.

initial CN^- was oxidised to CO_3^{2-} . In addition, a solid was formed during the photo-treatment; this precipitate has been previously observed by other researchers and characterised as copper hydroxide [25]. Thus, the presence of copper favours the UVA-based elimination of cyanides by H_2O_2 as: (a) enhances the photo-oxidation of cyanides, (b) copper is removed as non-soluble hydroxide and (c) detoxification of the solution requires shorter irradiation periods.

The reaction was tested with real effluents at bench-scale, showing that hydrogen peroxide in the presence of sunlight was able to remove 90% of the carbon present in the solution and no free cyanide was detected in the effluent, probably due to the photocatalytic effect of copper cation. In addition to this, precipitation of metals occurred at basic pH (pH of the effluent was around 10) and no copper was detected in the solution after filtration (Fig. 5). In agreement with these data, complete detoxification of the solution was achieved after 3 h of irradiation. Experiments were also carried out under sunlight and similar results were observed.

Experiments were then scaled up to treat real effluents which contained 360 mg/l of Cu^{2+} , 120 mg/l of free cyanides and 850 mg/l of total cyanides; the pH of the solution was 10.9. The plant was loaded with 50 l of the effluent and hydrogen peroxide was periodically added throughout the experiment. Samples were periodically taken and analysed after filtration; data are shown in Fig. 6. A very vigorous reaction was observed with formation of a green/brownish precipitate. The amount of total CN^- was negligible even in the first sample ($t_{30\text{W}} = 14$ min), with a peroxide consumption of approximately 150 g. With these data, a ratio of 2.6 moles of H_2O_2 per mole of CN^- was estimated, well above the stoichiometric relationship (1:1) needed for quantitative oxidation of cyanate; this is attributable either to partial oxidation of cyanate into carbonate (as indicated by the TC decrease) or to decomposition of H_2O_2 . Copper ions were also removed by precipitation of $\text{Cu}(\text{OH})_2$ at the basic pH conditions, after destruction of the cyanide.

As a consequence of these processes, detoxification of the solution was achieved. The inhibition of the oxygen uptake rate of activated sludge decreased from 100% of the untreated solution, to 0% in the sample taken at $t_{30\text{W}} = 14$ min (see Fig. 3). Also more sensitive assay based on the inhibition of the lumi-

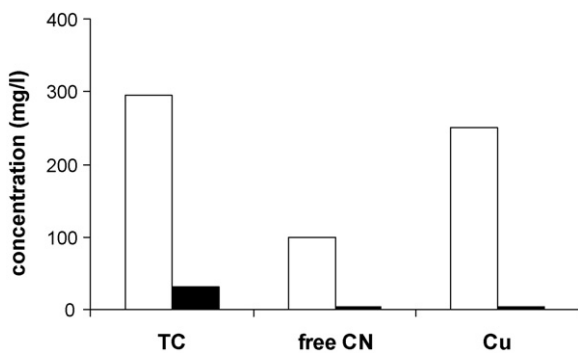


Fig. 5. Concentration of dissolved carbon (TC), free cyanide and copper in a metal finishing effluent before (white bars) and after 3 h of irradiation in the presence of hydrogen peroxide (bench-scale experiment).

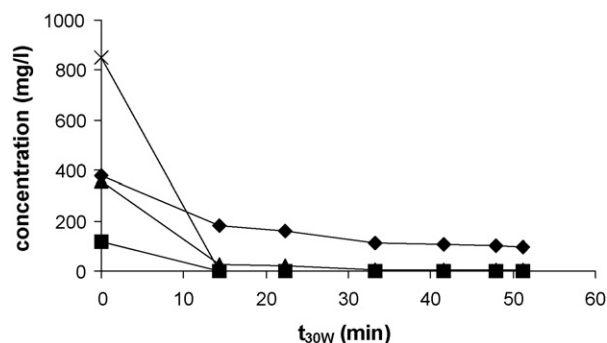


Fig. 6. Treatment of metal finishing effluents with hydrogen peroxide under sunlight in a wastewater treatment plant. Plot of the concentration of free cyanide (■), total cyanide (×), total carbon (◆) and copper (▲) vs. irradiation, expressed as $t_{30\text{W}}$.

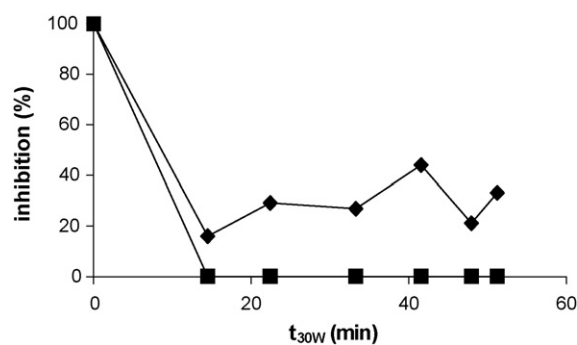


Fig. 7. Treatment of metal finishing effluents with hydrogen peroxide under sunlight in a wastewater treatment plant. Plot of the inhibition of the luminescence of *V. fischeri* (◆) and respiration of the activated sludge (■) vs. irradiation, expressed as $t_{30\text{W}}$.

nescence of *V. fischeri*, showed a remarkable variation, from the initial 100% to the range 10–20% in the treated samples (see Fig. 7).

4. Conclusions

Hydrogen peroxide has proven to be an efficient oxidising agent to remove free and complexed cyanides from a metal finishing effluent. The process was very fast under solar irradiation, possibly due to the photocatalytic effect of copper ions that are also present. Furthermore, precipitation of the metal cation also occurred once the complex was destroyed. On the other hand, Cu^{2+} inhibits the catalytic effect of TiO_2 , making this process unfavourable.

Complete detoxification of the solution has been achieved according to respirometric measurements, once elimination of the highly toxic Cu^{2+} and CN^- was accomplished. This is in agreement with the high toxicity that these two species showed towards the activated sludge.

Acknowledgements

We want to acknowledge the financial support of Generalitat Valenciana (Investigadores Emergentes, GV06/118), Spanish Ministerio de Educación y Ciencia (PETRI program, PTR1995-

0934-OP) and Spanish Ministerio de Medio Ambiente (project 318/2006/3-11.1).

References

- [1] J. Blanco-Gálvez, P. Fernández-Ibáñez, S. Malato-Rodríguez, Solar photocatalytic detoxification and disinfection: recent overview, *J. Sol. Energy Eng.* 129 (2007) 4–15.
- [2] D. Mantzavinos, E. Psillakis, Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment, *J. Chem. Technol. Biotechnol.* 79 (2004) 431–454.
- [3] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, *Chem. Rev.* 93 (1993) 671–698.
- [4] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Jiménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal. B* 47 (2004) 219–256.
- [5] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment. I: Oxidation technologies at ambient conditions, *Adv. Environ. Res.* 8 (2004) 501–551.
- [6] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment. II: Hybrid methods, *Adv. Environ. Res.* 8 (2004) 553–597.
- [7] M.J. Farré, S. Brosillon, X. Domènech, J. Peral, Evaluation of the intermediates generated during the degradation of Diuron and Linuron herbicides by the photo-Fenton reaction, *J. Photochem. Photobiol. A* 188 (2007) 34–42.
- [8] P.P. Scott, D.F. Ollis, Integration of chemical and biological oxidation processes for water treatment: review and recommendations, *Environ. Progr.* 14 (1995) 88–103.
- [9] A. Marco, S. Esplugas, G. Saum, How and why combine chemical and biological processes for wastewater treatment, *Water Sci. Technol.* 35 (1997) 321–327.
- [10] C. Pulgarin, M. Invernizzi, S. Parra, V. Sarria, R. Polania, P. Péringier, Strategy for the coupling of photochemical and biological flow reactors useful in mineralization of biorecalcitrant industrial pollutants, *Catal. Today* 54 (1999) 341–352.
- [11] M. Farré, D. Barceló, Toxicity testing of wastewater and sewage sludge by biosensors, bioassays and chemical analysis, *Trends Anal. Chem.* 22 (2003) 299–310.
- [12] M.E. Lapertot, C. Pulgarin, Biodegradability assessment of several priority hazardous substances: choice, application and relevant regarding toxicity and bacterial activity, *Chemosphere* 65 (2006) 682–690.
- [13] S. Parvez, C. Venkataraman, S. Mukherji, A review on advantages on implementing inhibition test (*Vibrio fischeri*) for acute toxicity prediction of chemicals, *Environ. Int.* 32 (2006) 265–268.
- [14] M. Gutierrez, J. Etxebarria, L. de las Fuentes, Evaluation of wastewater toxicity: comparative study between Microtox[®] and activated sludge oxygen uptake inhibition, *Water Res.* 36 (2002) 919–924.
- [15] S. Ren, Assessing wastewater toxicity to activated sludge: recent research and developments, *Environ. Int.* 30 (2004) 1151–1164.
- [16] G. Ricco, M.C. Tomei, R. Ramadori, G. Laera, Toxicity assessment of common xenobiotic compounds on municipal activated sludge: comparison between respirometry and Microtox[®], *Water Res.* 38 (2004) 2103–2110.
- [17] N. Checchi, S. Marsili-Libelli, Reliability of parameter estimation in respirometric models, *Water Res.* 39 (2005) 3686–3696.
- [18] A. García, A.M. Amat, A. Arques, R. Sanchís, W. Gernjak, M.I. Maldonado, I. Oller, S. Malato, Detoxification of aqueous solutions of the pesticide “SevnoI” by solar photocatalysis, *Environ. Chem. Lett.* 4 (2006) 169–172.
- [19] A. Arques, A. García-Ripoll, R. Sanchís, L. Santos-Juanes, A.M. Amat, M.F. López, M.A. Miranda, Detoxification of aqueous solutions containing the commercial pesticide Metasystox by TiO₂-mediated solar photocatalysis, *J. Sol. Energy Eng.* 129 (2007) 74–79.
- [20] A. García-Ripoll, A.M. Amat, A. Arques, R. Vicente, M.F. López, I. Oller, M.I. Maldonado, W. Gernjak, Increased biodegradability of Ultracid[™] in aqueous solutions with solar TiO₂ photocatalysis, *Chemosphere* 68 (2007) 293–300.
- [21] V. Augugliaro, V. Loddo, G. Marci, L. Palmisano, M.J. Lopez-Muñoz, Photocatalytic oxidation of cyanide in aqueous titanium dioxide suspensions, *J. Catal.* 166 (1997) 272–283.
- [22] K. Chiang, R. Amal, T. Tran, Photocatalytic oxidation of cyanide: kinetic and mechanistic studies, *J. Mol. Catal. A: Chem.* 193 (2003) 285–297.
- [23] A. Bozzi, I. Guasaquillo, J. Kiwi, Accelerated removal of cyanides from industrial effluents by supported TiO₂ photo-catalyst, *Appl. Catal. B* 51 (2004) 203–211.
- [24] M.A. Barakat, Y.T. Chen, C.P. Huang, Removal of toxic cyanide and Cu(II) ions from water by illuminated TiO₂ catalyst, *Appl. Catal. B* 53 (2004) 13–20.
- [25] M. Sarla, M. Pandit, D.K. Tyagi, J.C. Kapoor, Oxidation of cyanide in aqueous solution by chemical and photochemical process, *J. Hazard. Mater.* 116 (2004) 49–56.
- [26] S. Malhotra, M. Pandit, J.C. Pandit, D.K. Tyagi, Photo-oxidation of cyanide in aqueous solution by the UV/H₂O₂ process, *J. Chem. Technol. Biotechnol.* 80 (2005) 13–19.
- [27] J. Ford, R. Hernandez, M. Zappi, Bench-scale evaluation of advanced oxidation processes for treatment of a cyanide-contaminated wastewater from an engine manufacturing facility, *Environ. Progress* 25 (2006) 32–38.
- [28] V. Augugliano, J. Blanco-Gálvez, J. Cáceres-Vázquez, E. García-López, V. Loddo, M.J. López-Muñoz, S. Malato-Rodríguez, G. Marci, L. Palmisano, M. Schiavello, J. Soria-Ruiz, Photocatalytic oxidation of cyanide in aqueous TiO₂ suspensions irradiated by sunlight in mild and strong oxidant conditions, *Catal. Today* 54 (1999) 245–253.
- [29] S. Malato, J. Blanco, A. Vidal, P. Fernández, J. Cáceres, P. Trincado, J.C. Oliveira, M. Vincent, New large solar photocatalytic plant: set-up and preliminary results, *Chemosphere* 47 (2002) 235–240.
- [30] S. Malato, J. Blanco, A. Vidal, C. Richter, Photocatalysis with solar energy at a pilot-plant scale: an overview, *Appl. Catal. B: Environ.* 37 (2002) 1–15.
- [31] Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA, 1998.
- [32] A.M. Amat, A. Arques, H. Beneyto, A. García, M.A. Miranda, S. Seguí, Ozonisation coupled with biological degradation for treatment of phenolic pollutants: a mechanistically based study, *Chemosphere* 53 (2003) 79–86.
- [33] D.E. Kritikos, N.P. Xekoukoulotakis, E. Psillakis, D. Mantzavinos, Photocatalytic degradation of reactive black 5 in aqueous solutions: effect of the operating conditions and coupling with ultrasound irradiation, *Water Res.* 41 (2007) 2236–2246.
- [34] V.P. Utgikar, N. Chadhary, A. Koeniger, H.H. Tabak, J.R. Haines, R. Govind, Toxicity of metals and metal mixtures: analysis of concentration and time dependence for zinc and copper, *Water Res.* 38 (2004) 3651–3658.
- [35] W. Liu, J.G. Jiang, G.Y. Shi, Y. He, Y. Liu, L.T. Jin, Toxicity assessment of cyanide and tetramethylene disulfotetramine (tetramine) using luminescent bacteria *Vibrio-qinghaiensis* and PbO₂ electrochemical sensor, *Chin. J. Chem.* 25 (2007) 203–207.
- [36] M. Kitis, E. Karakaya, N.O. Yigit, G. Civelekoglu, A. Akcil, Heterogeneous catalytic degradation of cyanide using copper-impregnated pumice and hydrogen peroxide, *Water Res.* 39 (2005) 1652–1662.
- [37] T. Oppenlander, Photochemical Purification of Water and Air, Wiley-VCH Verlag, Weinheim, Germany, 2003.