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LABORATORY AND PILOT SCALE PHOTODEGRADATION OF CYANIDE-CONTAINING WASTEWATERS

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Cyanide degradation efficiency using advanced oxidation methods was investigated. Model cyanide solutions in TiO₂/UV and H₂O₂/UV systems were degraded for different pH, temperature, gas phase, and kind of catalyst. Laboratory experiments of cyanide photodegradation were carried out in homogeneous UV/H₂O₂, and heterogeneous UV/TiO₂ systems using different forms of catalyst. For the first time cyanide degradation using TiO₂ supported on glass microspheres has been studied. Photodegradation of cyanide was enhanced by addition of hydrogen peroxide and copper ions. Almost 20 % increase in cyanide oxidation efficiency was observed for photocatalytical oxidation of copper cyanide complexes. Moreover, cyanide photodegradation in an Air Sparged Hydrocyclone (ASH) unit was examined.

Key words: cyanide, titanium dioxide, photodegradation, hydrogen peroxide

INTRODUCTION

BACKGROUND

Free cyanide is a highly toxic chemical that is found in the environment at low concentrations coming from natural sources. It reaches toxic levels mostly through industrial processes such as mineral processing, electroplating, and paper-making. Cyanide is also a regulatory target because of its toxicity, incompatibility with most publicly-owned treatment plants, and danger to sewer workers and aquatic life.

Cyanides are harmful for the environment especially in a free, uncomplexed form. Thus one of detoxification methods is complexation with ferrous ions. Alkaline chlorination, one of the most popular cyanide detoxification method, is characterized as a fast reaction but has limited application in the case of cyanide complexes. Toxic

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chlorine compounds can be generated for particular composition of wastewaters. The SO₂/air method is another way for cyanide oxidation. The reaction is performed in the presence of Cu²⁺ ions as a catalyst and at pH 9 to 10 maintained with lime addition. In this method large quantities of solids are generated, thus polluting the environment. In recent years, methods of biological degradation have become more important (White 1998, White 2000). Biodegradation of cyanides is limited to low CN⁻ concentration and the kinetics is slow which makes treatment of large streams of wastewater difficult.

In this regard, there is a necessity of developing clean and efficient methods for the treatment of cyanide wastes. Cyanide degradation using Advanced Oxidation Processes (AOPs), particularly photocatalytic oxidation has been proposed and evaluated in laboratory and pilot scale experiments. Photochemistry is a fast developing area both in terms of research and commercial activity and appears to be strong, and growing (Mills 2002).

AOPs often require costly reactants such as H₂O₂ and O₃, therefore they should not replace, whenever possible, more economic treatment such as the biological degradation. AOPs can be integrated with biological treatment of toxic substances entering or leaving the biological stage (Malato 2002).

Photooxidation of CN⁻ using TiO₂, CdS, ZnO, V₂O₅ and Fe₂O₃ as catalysts has already been studied (Schiavello 1988, Mihaylov 1993, Wu 2000, Frank 1977, Matatov-Meytal 1998, Yeber 1999, Dąbrowski 2002, Ismail 2003). Another application of semiconductor-based photocatalysis has been demonstrated in the degradation of surfactants, and aliphatic and aromatic chlorinated hydrocarbons (Dąbrowski 2000, Chen 1999, El-Morsi 2000, Gallardo 2003, Hilgendorff 1996, Krichevskaya 2001). Many researchers agree that titanium dioxide is the best photocatalyst for environmental application at present since it is highly active, stable to light illumination, inexpensive, and nontoxic (Kaneko 2003).

RECENT RESEARCH

Hydroxyl radicals are formed on a hydrated and hydroxylated surface of a catalyst and may be formed from H₂O₂ via oxygen anion radical[•]O₂⁻ and via photolysis of H₂O₂ (Pelizzetti 1994). Increased intensity of photodegradation is also observed in the presence of oxygen (Artuna 1999). When investigating the degradation of triphenylmethane in the UV-TiO₂ system (anatase), Yang et al. (Yang 2001) demonstrated that adsorption of the compound at the surface of the catalyst takes place first, and its oxidation by activated hole-electron pairs and surface-bounded hydroxyl radicals follows. For that reason, the change of pH of the solution will cause positive or negative charging of catalyst particles and, by the same token, will change the rate of adsorption of the compound being degraded. For this reason, a decrease in pH causing positive charging of TiO₂ surface should promote adsorption of CN⁻ ions, thus enhancing efficiency of cyanide degradation. From the other hand, a decrease in pH

below pH 11 initiates conversion of free cyanide from ionic to anionic form, and volatile HCN gas is formed. Also, alkaline environment and aeration are conducive of generation of hydroxyl radicals. Therefore, both effects should be taken into account.

Photocatalytical oxidation of cyanide has been proposed as a possible option for cyanide treatment (Mihaylov 1993, Augugliaro 1997), and an alternative for conventional chemical methods. Hidaka et al. reported photodegradation of CN^- in industrial wastewater using suspended TiO_2 as a catalyst (Hidaka 1992). The evolution of CO_2 , consumption of O_2 , evolution of N_2 and formation of the OCN^- intermediate ions were examined quantitatively. The catalytic activity of Degussa P-25 catalyst and TiO_2 (rutile) were examined. Irradiation was carried out in laboratory scale. The 546 ppm CN^- solution was photodegraded using TiO_2 catalyst in an alkaline environment (initially pH=12). The effect of different amounts of TiO_2 catalyst was examined for the 500 ppm solution. The optimum amount of TiO_2 was found to be 1 g/dm^3 (Hidaka 1992). The photocatalytic oxidation of cyanide using Degussa P-25 catalyst was investigated by Pollema et al. (Pollema 1992). It was confirmed that cyanide was first oxidized to cyanate and further through nitrite to nitrate.

Mihaylov et al. (Mihaylov 1993) investigated photocatalytic oxidation of cyanide in the presence of TiO_2 (anatase and rutile), ZnS , ZnO , CdS , V_2O_5 , SiO_2 and Fe_2O_3 . Only TiO_2 and ZnO yielded satisfactory results. Photodegradation of cyanide in UV/ V_2O_5 - SiO_2 system in laboratory scale was investigated by Ismail et al (Ismail, Ibrahim and Mohamed 2003). Reaction was performed at pH 8-10 for different temperatures 30 – 60 °C and different microstructure of V_2O_5 - SiO_2 catalyst. An increase in temperature caused a decrease in cyanide degradation efficiency. 98.5 % of cyanide removal was achieved after 3 hours of reaction, for best conditions (30 °C and form of the catalyst characterizing the highest surface area). Overall kinetics for degradation of cyanide was found to be of first order. It was concluded that the surface area of the catalysts plays an important role for improving their photoactivities.

Cyanide can volatilize as HCN during degradation, especially when solution is sparged with the gas phase. The amount of HCN volatilized is a function of the pH, temperature of the solution, the surface area of the catalyst, and increases with decreasing pH and increasing temperature and surface area. Alicilar et al. (Alicilar 2002) investigated air oxidation of aqueous cyanides in a countercurrent fixed bed reactor. They used model cyanide solution with relatively high CN^- initial concentration within the range 0.005 – 0.1 M. Although they obtained 89 % cyanide conversion under optimum conditions at 60 °C, the gas phase leaving the system was not analyzed for HCN.

Frank and Bard reported photo-oxidation of cyanide in the presence of TiO_2 in both anatase and rutile forms (Frank and Bard 1977, Frank 1977). The reaction was studied for several cyanide concentrations using a 450 W xenon lamp, 2500 W mercury-xenon lamp and direct (unfocused) sunlight. Under all conditions the reaction proceeded at a measurable rate resulting in CNO^- as the final product of oxidation. They anticipated further oxidation of CNO^- , but found no evidence of other products (Frank 1977).

Removal of cyanide in presence of Cu (II) ions in UV/TiO₂ system was examined by Barakat et al. (Barakat 2004). Results revealed that about 78 % of free cyanide (10⁻³ M) was removed after illumination for 4 hours in the presence of 1 g/dm³ (TiO₂) at pH 11. The co-existence of Cu (II) and cyanide enhanced the removal efficiency of both copper and CN⁻. The removal percentage increased with an increase in Cu:CN molar ratio reaching a complete removal for both copper and cyanide at a ratio of 10:1 at the same previous conditions of free cyanide.

Chiang et al. (Chiang 2002) investigated degradation of cyanides in UV/TiO₂, using TiO₂ particles doped with CuO. They found that the rate of photooxidation of cyanide slightly increased for 0.10 % Cu, and any further increase of the copper dopant concentration caused a decrease in the cyanide oxidation. In contrast to Bakarar et al., results they showed that the presence of Cu²⁺ ions within the range 0.002 to 0.5 mM in the solution decreased the photocatalytic degradation of cyanide. Reduced activity was explained in terms of the competition reaction of Cu (I) cyanide complex ions for surface hydroxyl radicals.

Photocatalytic oxidation is accelerated by scavenging conduction band electrons thus preventing the recombination between electron and positive hole. Several oxidants such as H₂O₂, K₂S₂O₇, and KIO₄ are used for this purpose (Kaneko 2003). Among them H₂O₂ may be the best from practical point of view, because no reaction product is left after the treatment.

In photocatalytic water treatment the difficulty in recovering TiO₂ powder from treated water is a major obstacle for the instrumentation. To solve this problem several immobilization methods have been studied, including coating of TiO₂ powder with binder, preparation of the thin film using sol gel method, and coating on supporting substrates of varying shapes (Matatov-Meytal 1998, Yeber 1999, Nozawa 2001, Rzechula 1998). Photocatalytic efficiency of such catalysts is often lower because of smaller surface area than powder, and both powder and immobilized TiO₂ are now used on a commercial basis (Kaneko 2003).

CURRENT RESEARCH

The main research objective was the evaluation of UV/TiO₂ and UV/H₂O₂ system in degradation of cyanides.

The influence of the amount and catalyst type, gas phase, and pH on the efficiency of cyanide degradation was studied. Since there were questionable results in the available literature pertaining to the influence of metal ions, particularly copper, on the efficiency of cyanide oxidation, solutions containing free and complexed cyanides were also investigated. Wastewaters discharged during metal processing and metal extraction processes besides cyanide contain metal ions. Thus evaluation of a complexed cyanide system was an integral part of the research.

Cyanide degradation photocatalytical methods can be achieved using the Air Sparged Hydrocyclone. The ASH is an efficient contactor for the gas/liquid phase and

in case of photodegradation, provides thin layer of an aqueous phase around UV lamp. Therefore, application of ASH technology for degradation of cyanides using photooxidation methods was evaluated.

EXPERIMENTAL

MATERIALS

In all experiments of cyanide degradation at the laboratory scale, sodium cyanide NaCN reagent grade (POCh Lublin, or Fisher Scientific Co.) was used as source of CN^- ions. Solutions were prepared by dissolution of NaCN in deionized water, alkalinized with NaOH to pH 12, unless stated otherwise in the text. In laboratory scale experiments stock cyanide solution ($\sim 1000 \text{ mg/dm}^3 \text{ CN}^-$) was prepared first and cyanide concentration was determined by titration with AgNO_3 . Then it was diluted to desired cyanide concentration for particular degradation experiments or calibration of analytical instruments and methods. Solutions of sodium hydroxide NaOH reagent grade (POCh Lublin, or Fisher Scientific Co.) and sulfuric acid H_2SO_4 reagent grade (POCh Gliwice, or Mallinckrodt Baker, Inc.) were used for pH correction.

In photocatalytical experiments titanium dioxide in anatase and rutile forms, and as TiO_2 supported on glass hollow microspheres (Rzechula 1998) was used as catalyst. Additionally, H_2O_2 (30 % solution, ACS reagent grade, Mallinckrodt Baker, Inc. or "STANDARD" Lublin) was used during photocatalytical degradation of cyanides in a homogeneous system.

Chemicals used for determination of free cyanides included aqueous solution of silver nitrate AgNO_3 ACS reagent grade (Fisher Scientific Co.) with combination of 5-(4-dimethylamino-benzylidene), rhodanine indicator (99 %, ACROS Organics) dissolved in acetone (ACS, reagent grade, Aldrich Chemical Co., or POCh Gliwice). In preparation of standard solutions for analysis of WAD cyanides the following chemicals were utilized: picric acid (98 %, Aldrich Chemical Co.), diethylenetriamine-pentaacetic acid DTPA (Sigma Chemical Co.), sodium tetraborate $\text{Na}_2\text{B}_4\text{O}_7$ (min. 99.0 %, Sigma Chemical Co.) and sodium carbonate Na_2CO_3 reagent grade (Mallinckrodt Baker, Inc.).

LABORATORY REACTORS

Investigations of efficiency of cyanide degradation were performed in laboratory set-up presented in

Fig. 1, equipped with medium-pressure mercury lamp (150 W Heraeus TQ-150). The gas phase was delivered to the reaction environment through a glass porous frit. Volumetric flowrate of the gas phase was measured by flow meter installed in the gas path. The content of the reactor was mixed with magnetic stirrer and continuously circulated with a peristaltic pump (Elpin Model 272.C, or Masterflex Model 7562-00) through the measuring cell. The temperature and pH were monitored during reaction

using pH combination electrode (EPS-1 Elmetron, or 300729.1 Denver Instruments Company) and mercury thermometer, both placed in the measuring cell. The cell was also equipped with cyanide ion-selective electrode (ECN-01 half cell in connection with RL-100 Ag/AgCl reference electrode, or ISE-8780 combination electrode Omega Technologies Company). The data was collected by computer (Elmetron Model CX-742, or Denver Instruments Company Model 225).

Also any cyanide that could volatilize during sparging with the gas phase was absorbed in a 100 ml washer containing 0.5 M NaOH solution.

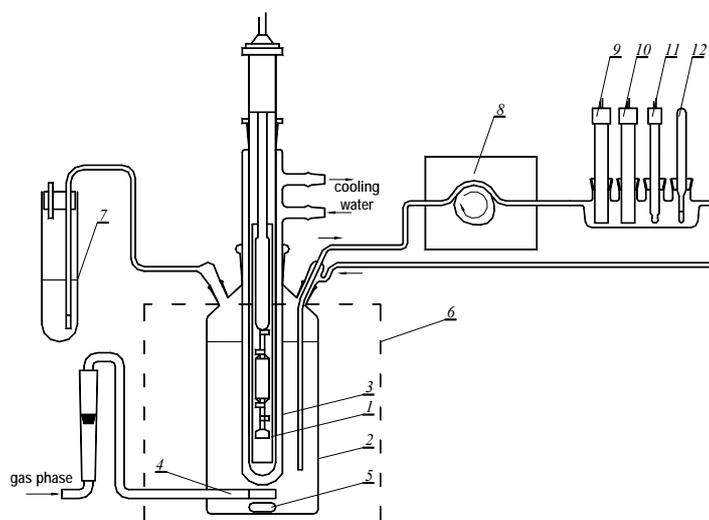


Fig. 1. Experimental set-up used for elimination of cyanides from aqueous solutions: 1- Heraeus medium pressure mercury lamp, 2- glass reactor, 3- UV lamp cooling system, 4- sparged gas system, 5- magnetic stirrer, 6- thermostat, 7- washer with NaOH solution, 8- peristaltic pump, 9- ion-selective electrode, 10- reference electrode, 11- pH electrode, 12- thermometer

ASH SYSTEM

Photocatalytical degradation of cyanides was carried out in a pilot scale set-up presented in Fig. 2. The system consisted of 150 dm³ tank which was connected with 3" ASH unit equipped with polyethylene porous tube and UV lamp. There was control of the air and liquid phases fed into the ASH.

During laboratory investigations on HCN stripping efficiency it was found that there is no HCN release to the gas phase once pH of cyanide solution is ≥ 12 . Since photodegradation of cyanides was carried out at pH 12, there was no further treatment of the gas phase leaving the system. The ASH system was monitored for pH and temperature of the reaction solution. The cyanide aqueous solution was irradiated using 2.0 kW Hanovia medium pressure mercury lamp.

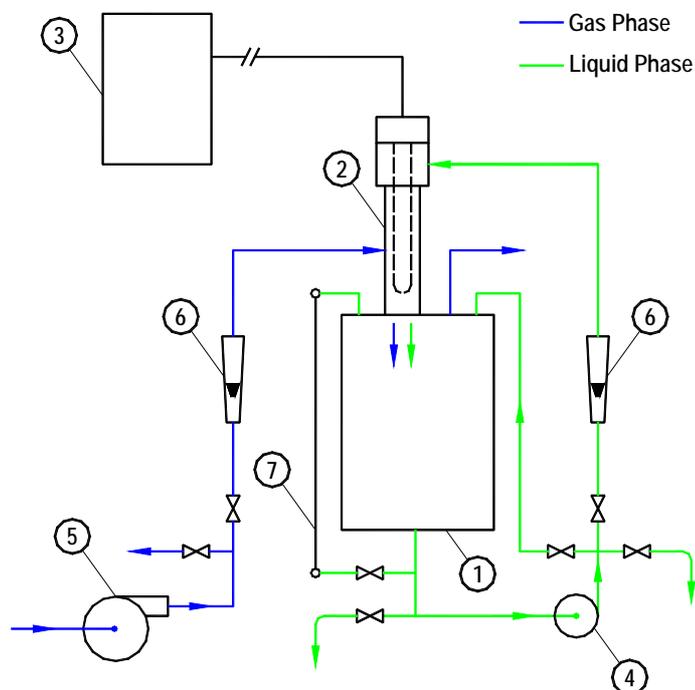


Fig. 2. Simplified flow sheet for cyanide photodegradation from aqueous solutions using ASH technology: 1- reactor, 2- ASH unit equipped with UV lamp, 3- control panel for UV lamp, 4- pump, 5- blower, 6- flow meter, 7- viewing tube

ANALYTICAL METHODS

The following analytical techniques were used for the research program: titration with AgNO_3 , the picric acid method, and electrochemical analysis with ion selective electrodes. All analytical measurements were performed in duplicates unless there was an *on-line* collection of the data.

RESULTS AND DISCUSSION

LABORATORY INVESTIGATIONS

In all our runs the amount of stripped HCN was less than 0.05 % of the total, initial cyanide amount as determined by analysis of the 20 ml NaOH absorption solution. The rate of cyanide degradation for different forms of titanium dioxide is contrasted to the rate in the absence of catalysis in Fig. 3.

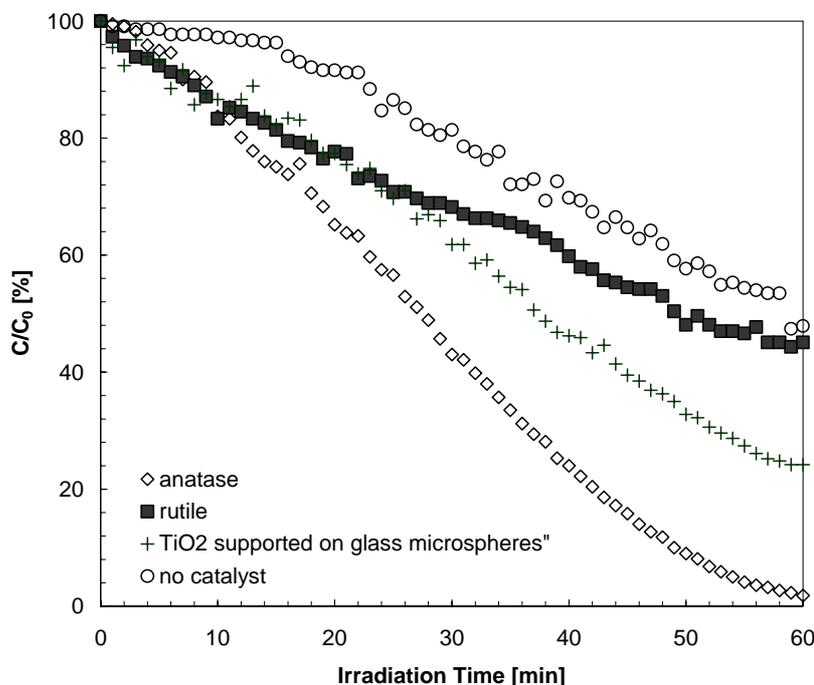


Fig. 3. Impact of catalyst type on elimination of free cyanides from aqueous solution at pH 12

Better efficiency of cyanide removal was obtained for powdered anatase or anatase supported on glass hollow microspheres than for powdered rutile. After 60 min. irradiation of an aqueous solution initially containing 20 mg/dm^3 of CN^- , free cyanides were eliminated in 97 %, 75 % and 55 % for suspended anatase, supported anatase and suspended rutile, respectively. The catalyst effectiveness after one hour reaction are revealed in Table 1. It is evident, that anatase is most effective followed by supported anatase and then rutile. The results suggest that commercial anatase and anatase supported on glass hollow microspheres are the most effective catalysts for photocatalytic degradation of free cyanide.

At the beginning of the reaction a similar decrease of cyanide concentration was observed for the supported anatase and rutile. But after 30 min. irradiation the activity of rutile dropped, probably due to an irreversible dehydroxylation of the catalyst surface. As a consequence, impaired potential for O_2 adsorption reduced the photoactivity, an explanation given earlier by Palmisano et al. (Palmisano 1994). On the other hand, lower performance of the supported anatase compared to the same amount of the unsupported powdered anatase can be explained to be due to the much smaller overall TiO_2 content on the glass microspheres (up to 0.5 % by wt.).

Table 1. Effects of catalyst form, sparging gas, initial CN⁻ concentration, temperature and pH on photo-oxidation rate of cyanide

CATALYST FORM	Catalyst loading [g/dm ³]	Initial amount of cyanide [mg/dm ³]	Gas phase	Gas flow rate [dm ³ /h]	Temperature [°C]	pH	k ₁ [min ⁻¹]
-	-	20	oxygen	20	20	12	0.006
anatase	1	4	oxygen	20	20	12	0.112
anatase	1	20	air	20	20	12	0.023
anatase	1	20	oxygen	10	20	12	0.027
anatase	1	20	oxygen	20	20	12	0.028
anatase	1	100	oxygen	20	20	12	0.020
anatase	1	20	oxygen	20	35	12	0.028
rutile	1	20	oxygen	20	20	12	0.012
TiO ₂ supported on glass microspheres	0.005	4	oxygen	20	20	12	0.015
TiO ₂ supported on glass microspheres	0.005	20	oxygen	20	20	12	0.016

Frank and Bard (Frank, 1977 #257), in their investigations reported weak oxidation of CN⁻ at best in the absence of a photocatalyst (less than 1 % of the free CN⁻ was destroyed). However, the results of Pollema et al. showed otherwise. After 2 hours irradiation of a 5 µg/cm³ cyanide solution, with pH adjusted to 10 and saturated with O₂, a complete loss of cyanide was observed. Our results confirm cyanide degradation in the UV/O₂ system. In the absence of titanium dioxide 46% of the free cyanide was eliminated after 60 min. irradiation at pH=12, and it is only a few percent lower than for the UV/TiO₂ system with rutile as a catalyst.

The influence of the initial cyanide concentration on the efficiency of cyanide destruction is shown in Fig. 4. The reaction was carried out at three initial CN⁻ concentrations: 4 ppm, 20 ppm and 100 ppm. All free cyanides were removed after 18 min. irradiation for the lowest cyanide concentration (4ppm). The same time of irradiation resulted in elimination of approx. 30 % in the case of the solutions initially containing 20 ppm and 100ppm of sodium cyanide. Our results confirm data from the literature regarding the pseudo-first order kinetics for higher cyanide concentration. The first-order rate constants, obtained under different experimental conditions, are presented in Table 1.

The data in Table 1 reveal that for a constant amount of anatase, pH value and temperature, smaller rate constants were obtained for air than for oxygen. Similar results were obtained by Pollema et al. in photocatalytic oxidation of 10 µg/ml cyanide solution using Degussa P-25 catalyst (Pollema 1992).

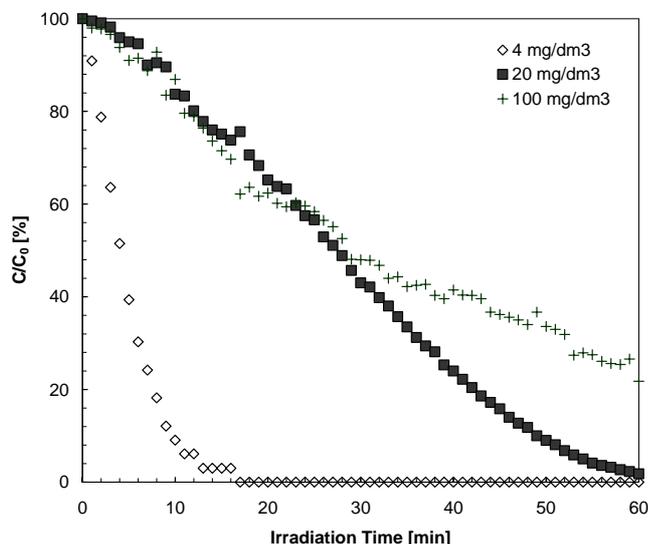


Fig. 4. The influence of initial cyanides concentrations on the elimination rate at pH 12 in the presence of suspended anatase (1 g/dm^3) and O_2 sparged at $20 \text{ dm}^3/\text{h}$

The influence of oxygen concentration on the rate of cyanide degradation in the UV/ TiO_2 system is presented in Fig. 5. As expected, free cyanide was not destroyed after 60 min. irradiation in the absence of oxygen. In this case photogenerated electrons in the conduction band accumulate and recombination between electrons and positive holes increases, thus inactivating action of a photocatalyst.

In order to obtain the deoxygenated solution, argon was sparged through a titanium dioxide (anatase) aqueous suspension for 30 min. before irradiation and than during processing at a flow rate of $20 \text{ dm}^3/\text{h}$. It is evident that, not much difference in rate was recorded for air and oxygen at 20 ppm initial cyanide concentration. It means that for such flowrate saturation of the solution with oxygen exceeds oxygen demand. Although presence of dissolved oxygen is crucial for the photodegradation of cyanide, the results revealed that further decrease in air/oxygen flowrate could be applied to the photocatalytical system.

Also the oxidation rate of cyanide did not depend on the alkalinity of the reaction environment, see Fig. 6. No difference in the oxidation efficiency at pH 10 and 12 for either air or oxygen was observed. Peral et al. reported, that the amount of photo-oxidized free cyanide decreased when the pH was changed from 10.5 to 13 (Peral 1990). Such a behavior was explained by the increasing negative charge on TiO_2 particles in more alkaline environment as the result of competitive adsorption of OH^- which limited the access of CN^- ions to the TiO_2 surface. Assuming that hydroxyl radicals plays important role in degradation of cyanide ions it could be expected that lowering pH below 10 would decrease efficiency of cyanide oxidation. In addition,

below pH 11 cyanide ions transform to anionic form and below pH 8, cyanide exists practically only as HCN. Thus removal of cyanide by stripping with gas phase becomes competitive against degradation in aqueous phase.

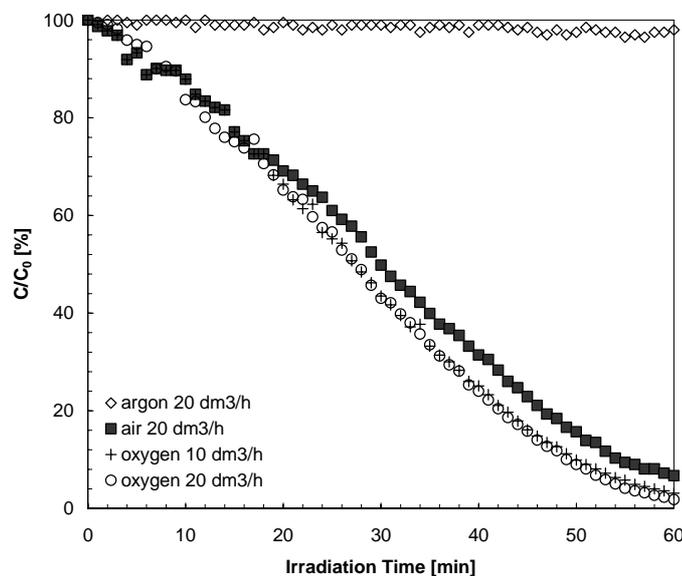


Fig. 5. The influence of air, oxygen and argon on eliminations of cyanides; initial cyanide concentration: 20 mg/dm³; pH 12; gas flow rate: 20 dm³/h; photocatalyst: suspended anatase (1 g/dm³)

Photodegradation of free and complexed cyanides in an aqueous medium in homogeneous and heterogeneous systems irradiated with UV and near-UV light was investigated by Augugliaro et al. (Augugliaro 1997, Augugliaro 1999). The reaction kinetics was affected by the catalyst content, the concentration of chlorides, and the intensity of UV radiation, but remained independent on the initial cyanide concentration and the pH.

The change of temperature from 20 to 35 °C did not influence the oxidation rate in the presence of titanium dioxide, see Fig. 7. The impact of temperature in the range 25 – 55 °C on CN⁻ photo-oxidation was investigated by Peral et al. (Peral 1990). The degradation efficiency increased only from 74.8 % at 25 °C to 75.8 % at 35 °C, i.e. the results are similar to our data. Peral et al. calculated an activation energy of 5.5 kJ/mol. Such a low value is characteristic for a fast electron transfer reaction.

The influence of H₂O₂ on cyanide degradation efficiency was tested in UV/H₂O₂ system. The comparison of the results obtained in homogeneous system with the cyanide degradation in UV/TiO₂ system is presented in Fig. 8. Photodegradation of cyanides was over 15 times more effective for UV/H₂O₂ system. The difference in efficiency of cyanide degradation is connected with increased amount of •OH radicals generated in UV/H₂O₂ system.

Degradation of cyanide in UV/H₂O₂ system is effective way of fast detoxification of cyanide wastes. However, from the economical point, application of UV/TiO₂ systems, although less efficient in terms of kinetics of cyanide oxidation, could be more favorable, especially for large industrial streams or environmental applications.

The effect of addition of copper ions was investigated in UV/TiO₂ system, where catalyst was in the form of microspheres with attached TiO₂. Different molar ratios of Cu²⁺ to CN⁻, 1:1 and 5:1 were evaluated. Obtained data is presented in Fig. 9. It is shown that copper ions have positive effect on degradation of cyanide. About 11 % better efficiency of cyanide degradation was observed for higher Cu²⁺:CN⁻ ratio. Moreover, there was about 18 % more cyanide removed than in case where no copper ions were present in the reaction environment.

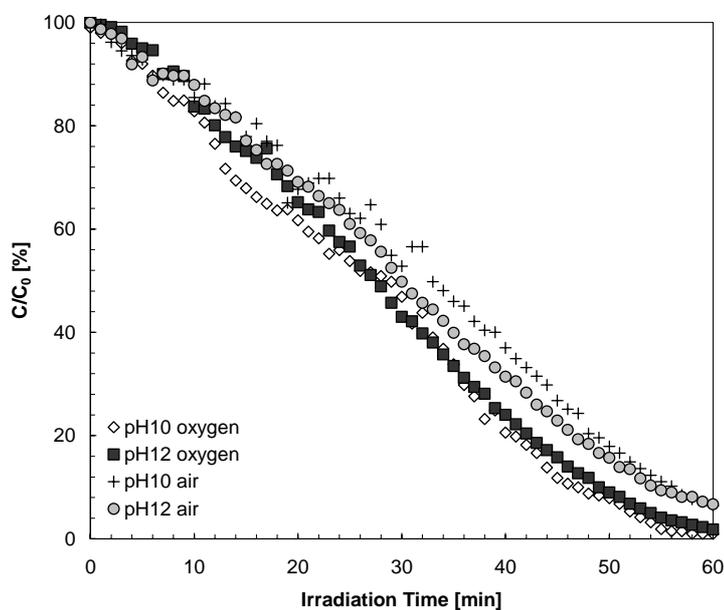


Fig. 6. Free cyanides elimination from aqueous solutions at different pH for air and oxygen; 20 mg/dm³ initial cyanide concentration; pH 12; 20 dm³/h gas flow rate; suspended anatase (1 g/dm³)

The rate of oxidation of cyanide by ozone, which enters a cyclic oxidation-reduction pathway, was found to increase in the presence of copper (Gurol 1988). Barakat et al. (Barakat 2004) also showed that presence of Cu (II) enhanced the removal of cyanide for UV/TiO₂ system. On the other hand, results of Chiang et al. (Chiang 2002) indicated that addition of Cu²⁺ ions has an adverse effect on efficiency of cyanide oxidation.

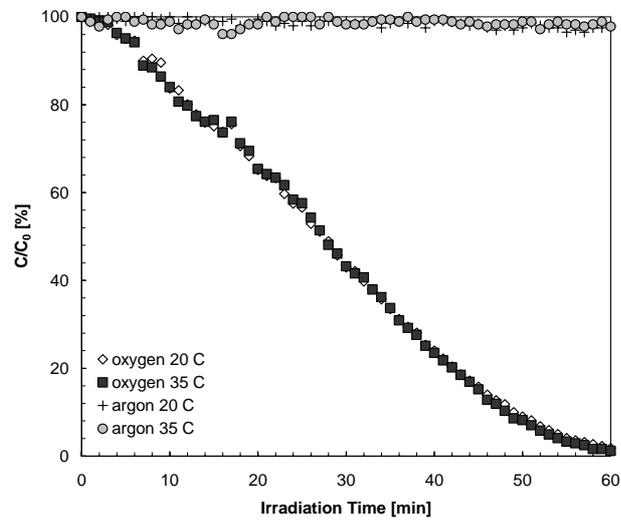


Fig. 7. The influence of temperature on kinetics of cyanide elimination for oxygen and argon; initial cyanide concentration: 20 mg/dm³; pH 12; gas flow rate: 20 dm³/h; suspended anatase (1 g/dm³)

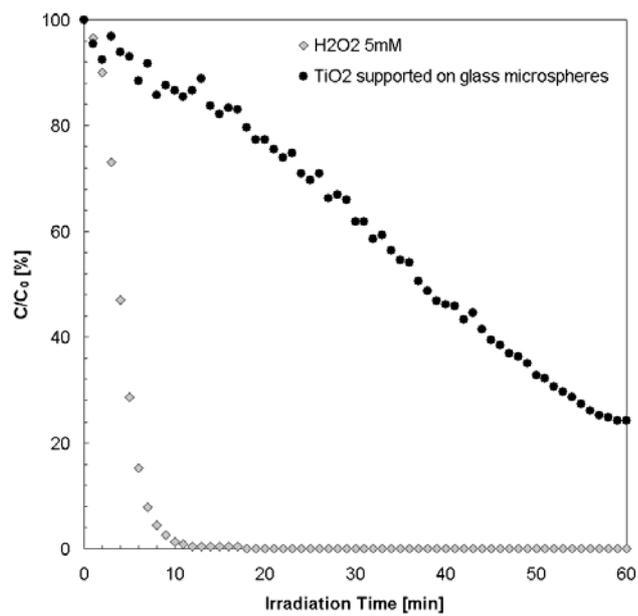


Fig. 8. Photodegradation of free cyanide solution in homogeneous and heterogeneous systems: initial cyanide concentration: 20 mg/dm³; pH 12; air flow rate: 20 dm³/h; amount of catalyst (1 g/dm³), temperature 20 °C

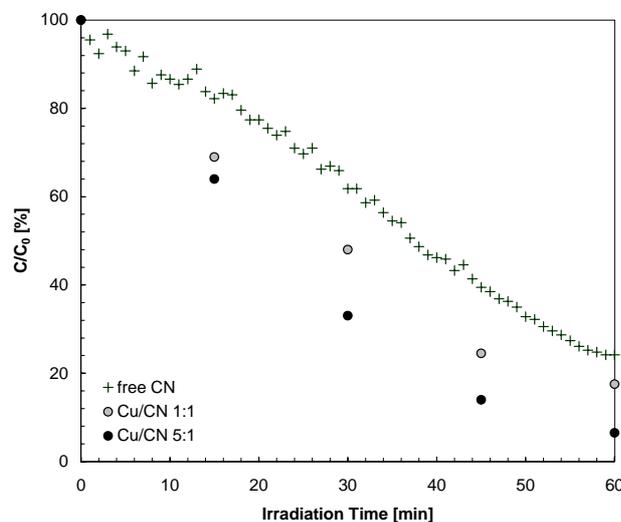
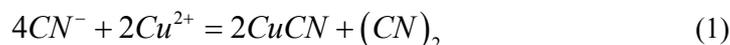


Fig. 9. The influence of addition of Cu^{2+} ions on kinetics of cyanide elimination; initial cyanide concentration: 20 mg/dm^3 ; pH 12; gas flow rate: $20 \text{ dm}^3/\text{h}$; TiO_2 supported on glass microspheres (1 g/dm^3)

Cu (II) is believed to be unstable in the presence of cyanide (Gurol 1988), and is reduced to Cu (I) according to Equation 1:



Thus in the presence of free CN^- copper should exist as Cu(I)-CN^- complexes in different speciations depending on the $\text{CN}^-:\text{Cu}$ ratio. It was postulated (Chiang 2002) that the negative effect of copper on photooxidation of cyanide could be the consequence of the competition reaction for hydroxyl radicals produced from the TiO_2 surface under UV irradiation. As a result of that competition from Cu(I) , CN^- would be oxidized less efficiently. On the other hand, all copper cyanide complexes display weak absorption above 250 nm with a maxima at 238–250 nm, which is below the operating wavelength of 350–385 nm of TiO_2 (Barakat 2004). Thus there will not be a decrease in the transmission of UV light to the reactor during photoreaction.

It can be proposed that holes generated at the valence band will oxidize the metal-cyano complexes. At the conduction band, the electrons will reduce the cyanide complex to Me(0) releasing the CN^- ions. This reaction can go through adsorption of copper cyanide complexes at photocatalyst surface, followed by oxidation of CN^- with removal and reduction of Cu^{2+} . In this case the presence of Cu^{2+} enhances the cyanide oxidation as it forms complexes in the adsorption process. Copper ions can also act as electrons scavengers and prevent the charge recombination in the photocatalytic process.

PILOT SCALE INVESTIGATIONS USING ASH TECHNOLOGY

Evaluation of applicability of the ASH technology for cyanide photodegradation was one of the objectives of pilot scale research. Results from photooxidation of cyanide in UV/O₂, and UV/H₂O₂/O₂ systems are presented in Fig. 10.

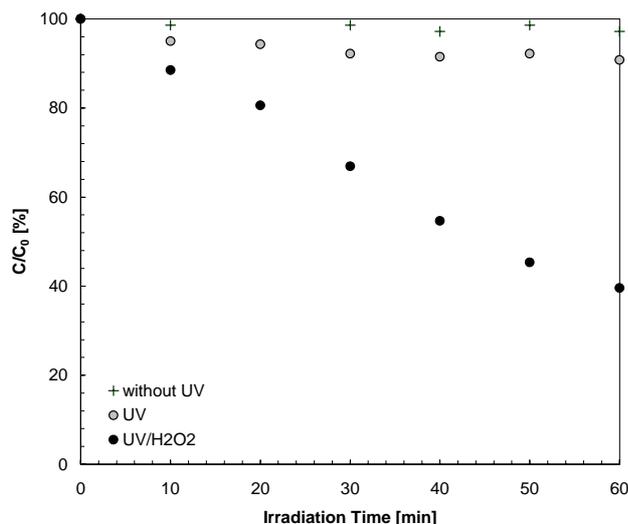


Fig. 10. Photodegradation of free cyanide solution in a homogeneous system in pilot scale ASH unit; 100 mg/dm³ initial cyanide concentration; pH = 12; 40 dm³/min air flow rate; 120 dm³/min solution flow rate, 5 mM H₂O₂ addition, temperature 30 °C

The efficiency of cyanide degradation in the investigated systems corresponds to the results obtained in laboratory scale experiments, in which the photocatalytic oxidation of cyanide in the UV/H₂O₂ system showed best efficiency. The time required for complete detoxification of cyanide is longer than for laboratory conditions. About 60 % of cyanide was oxidized in 60 minutes of irradiation with addition of 5 mM H₂O₂ in ASH unit, while complete oxidation of cyanide can be achieved in one hour for the same homogeneous system in the laboratory set-up. The different process rate reflects UV radiation power available from the lamps. While 150 W UV lamp was the source of irradiation in one liter laboratory reactor, the 2.0 kW UV lamp was used in the pilot tests. About 9 times more intense light (based on the lamps power) was available in laboratory set-up per unit time. Taking this into account it can be concluded that the scale-up of the photocatalytic system did not significantly affect the efficiency of cyanide degradation.

The influence of H₂O₂ addition on the efficiency of cyanide degradation is presented in Fig. 11. The results show that oxidation of cyanide with hydrogen peroxide can be efficient when the solution is illuminated with UV light. No

degradation of cyanide using H_2O_2 was found in “dark” conditions. Once the solution was illuminated with UV lamp, degradation of cyanide proceeded. An increase in addition of H_2O_2 from 5 mM to 20 mM to the reaction system caused an increase in cyanide degradation from 60 % to 94 %. It is also evident that additions of H_2O_2 exceeding 20 mM will promote recombination of photogenerated hydroxyl radicals, contributing less to oxidation of cyanide ions.

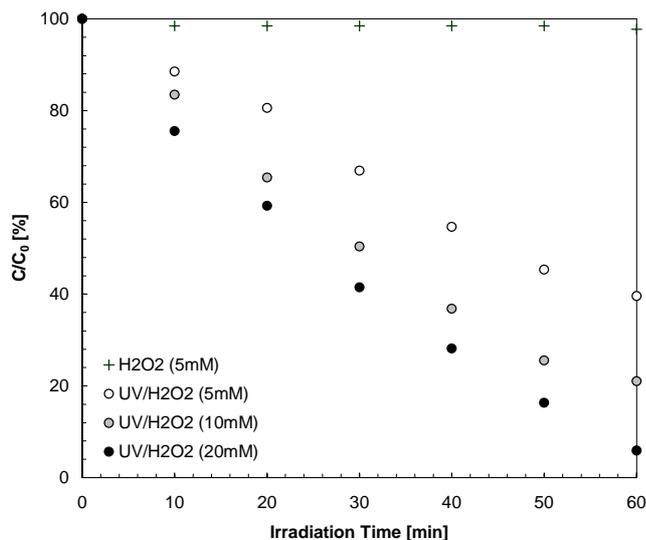


Fig. 11. The influence of H_2O_2 addition on the kinetics of cyanide elimination; 100 mg/dm^3 initial cyanide concentration; $\text{pH} = 12$; 80 dm^3/min air flow rate; 120 dm^3/min solution flow rate; temperature 30 °C

The influence of air flow rate on the efficiency of degradation of cyanide was also the subject of investigations and the results are presented in Fig. 12. The data shows that there is no dependence between the amount of air sparged into the system and the efficiency of cyanide degradation within the range of investigated air flowrates. It confirms data obtained in laboratory experiments (see Fig. 5) which shows similar pattern for elimination of cyanide vs. time for different gas flow rates. From the industrial point of view it means that the demand for the gas phase does not exceed 80 dm^3/min and the impact on the process efficiency can be neglected compared to the importance of UV illumination.

The influence of solution flow rate on the efficiency of cyanide photodegradation is presented in Fig 13. The data shows that the flow rate of the liquid phase has significant effect on the efficiency of cyanide degradation using the Air-Sparged Hydrocyclone unit. An increase in the solution flow rate from 30 dm^3/min to 180 dm^3/min resulted in an increase in the efficiency of cyanide degradation from 15 % to 60 %. Partially it is related to the number of passes through the illuminated area in the reactor but major factor in this case is the linear velocity of the liquid phase entering the cyclone header.

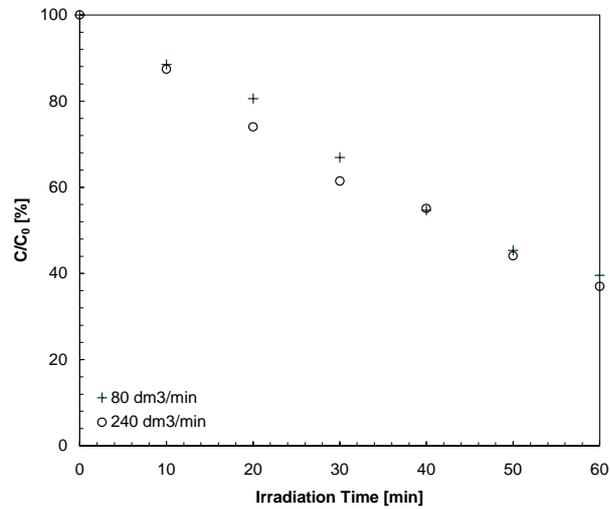


Fig. 12. The influence of air flow rate on the kinetics of cyanide elimination in UV/H₂O₂ system; 100 mg/dm³ initial cyanide concentration; pH = 12; 120 dm³/min solution flow rate; 5 mM H₂O₂, temperature 30 °C

In the experimental system used, 30 dm³/min, 120 dm³/min, and 180 dm³/min flowrates correspond to linear velocity of 1 m/s, 4 m/s, and 6 m/s respectively. It means that linear velocity of at least 4 m/s was necessary for efficient operation of the ASH unit.

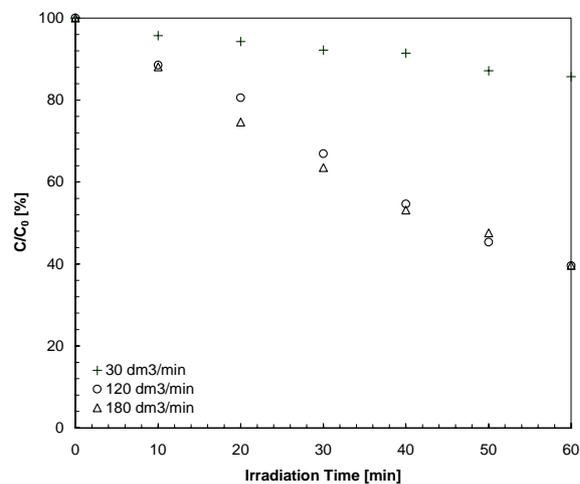


Fig. 13. The influence of solution flow rate on the kinetics of cyanide elimination in UV/H₂O₂ system; 100 mg/dm³ initial cyanide concentration; pH = 12; 80 dm³/min air flow rate; 5 mM H₂O₂, temperature 30 °C

SUMMARY

Cyanide photodegradation can be accomplished by irradiation of the treated solution only, but the presence of TiO_2 as a catalyst in the UV/ O_2 reaction system allowed to increase twice the degradation rate of free cyanides. The reaction order with respect to free cyanide concentration changes, depending on the initial cyanide concentration. The initial cyanide concentration affected the rate of oxidation in the UV/ TiO_2 / O_2 system, but the first order kinetics followed for higher cyanide concentration. The increase of the processing temperature from 20 °C to 35 °C did not influence cyanides degradation efficiency.

The degree of cyanide elimination was not dependent on the air or oxygen flow rate of 20 dm³/h, which means that for such flow rates saturation of the solution with oxygen is greater than the oxygen demand. However, results obtained for deoxygenated system revealed the necessity of the presence of dissolved oxygen in the reaction environment.

The efficiency of cyanide photodegradation dropped about 25 % when not suspended but “supported”. However, easiness of the catalyst separation from the aqueous phase for recycle overweighs the drop of degradation efficiency. TiO_2 attached to the hollow glass microspheres can be recovered and reused. Because of the low density of such catalyst it can be dispersed on the surface of contaminated water and will be exposed to the sunlight. Microspheres could be easily separated, if necessary, and reused.

Degradation of cyanide in the UV/ H_2O_2 system is enhanced when compared to the heterogeneous system. Therefore the application of hydrogen peroxide could be suitable where fast and clean detoxification of cyanide is necessary.

The presence of copper ions in the reaction environment has a positive effect on the efficiency of cyanide degradation. Therefore it can be expected that treatment of cyanide in industrial effluent is more effective than cyanide degradation in synthetic solutions.

It was found that complete degradation of cyanide can be expected in an ASH reactor. As anticipated, the best results of cyanide photooxidation in the ASH reactor were obtained for the UV/ H_2O_2 system and 20 mM initial concentration of hydrogen peroxide. The influence of the gas phase flowrate was found to be insignificant, while maintaining the aqueous phase flowrate above 4 m/s linear velocity assures best hydrodynamic conditions within the ASH reactor, thus enhancing photooxidation of cyanide ions.

During all experiments, despite changing processing conditions, practically no HCN was released to the surroundings, which is essential for safety reasons.

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W pracy badano efektywność procesu degradacji cyjanków stosując odpowiednie metody utleniania. Roztwory modelowe cyjnków zawierające TiO₂ i H₂O₂ były poddane fotodegradacji przy różnych warunkach pH, temperaturze, przy różnym składzie fazy gazowej i w obecności różnych katalizatorów. Doświadczenia laboratoryjne nad fotodegradacją cyjanków zostały wykonane w układzie homogenym UV/H₂O₂ i układzie heterogenym UV/TiO₂ przy zastosowaniu różnych form katalizatora. Po raz pierwszy badano degradację cyjanków przy zastosowaniu jako katalizatora TiO₂, który został naniesiony na szklane mirokulki. Fotodegradacja cyjanków wzrasta po dodaniu do układu nadtlenu wodoru i jonów miedzi. Prawie 20% wzrost w efektywności utlenienia cyjanków był zaobserwowany dla fotodegradacji cyjankowych kompleksów miedzi. Dodatkowo badano fotodegradację w specjalnym hydrocyklonie (air sarged hydrocyclone-ASH).