Application of photocatalytic procedure combined with ozonation for treatment of industrial wastewater – a case study

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Abstract

Several kinds of industrial wastewaters contain pollutants which cannot be entirely removed by physico-chemical treatments. In this case study wastewaters of a metal-working factory were purified. The results clearly indicated that TiO$_2$-based heterogeneous photocatalysis combined with ozonation can efficiently decrease the COD value of the effluent from the cleaning plant currently applied, thus a final biological treatment ensures the required new (higher) level of purity. However, for wastewaters of large volume, which are generally mixtures of various process waters of different origins, the application of this heterogeneous photocatalysis at the end of the purification chain is not reasonable because of the high costs of investment. Insertion of the combined method into the middle of the cleaning technology, as a pre-treating stage of a heavily polluted constituent (an emulsion in this case) of the whole mixture before the biological treatment, is more cost effective. In the most economical procedure the combined method is applied for the emulsion diluted with weakly polluted wash waters. Thus, the subsequent biological treatment of the total mixture decreases the COD to 116 mg dm^{-3}.

Keywords

heterogeneous photocatalysis · titanium dioxide · ozonation · wastewater treatment · mineralization

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1 Introduction

Surface waters are polluted with considerable amounts of toxic or dangerous materials (mostly of industrial origins, which cannot be approriately removed by conventional cleaning technologies). Hence, increasing demands have been arisen to develop new procedures, which are environmentally friendly, using little or no chemical additives, economical and efficient against a wide range of organic compounds. Possible techniques may be membrane technology, vacuum evaporation, biological treatment and UV oxidation photocatalysis [1,2]. The latter two methods decompose the organic pollutants, deviating from the first two procedures, which only concentrate the contaminants. However, their costs of investment, especially in the case of the photocatalytic procedure, are relatively high, thus their applicability ought to be thoroughly examined from economic point of view.

Photocatalytic detoxification of wastewaters belongs to the Advanced Oxidation Processes (AOP) [3]. In the past decade, the purification methods utilizing UV light-driven catalytic treatment were more frequently applied in the modern environmental protecting procedures. In these photocatalytic degradation processes the oxidizing agent is oxygen and/or ozone, or solution of hydrogen peroxide, which finally became the part of the simple inorganic end-products of the mineralization (such as H_2O or CO_2). The most widely used photocatalyst applied for wastewater treatment is nanosized titanium dioxide semiconductor [4, 5]. Irradiation in the near UV range generates electron-hole pairs in the TiO_2 nanoparticles. These opposite charges may recombine or, reaching the surface of the catalyst particle, can participate in redox reactions with H_2O, HO^- or dissolved O_2, producing highly reactive species such as $HO^\bullet$ and $HO_2^\bullet$, which efficiently oxidize the organic pollutants in the bulk solution. Contaminants adsorbed on the surface of the catalyst particles can also directly react with the photochemically produced holes and electrons, promoting the processes of mineralization.

Thorough studies on TiO_2-based photocatalytic mineralization of a wide range of organic contaminants were carried out in the past decade [6–9]. Several methods developed have already

been applied in practical purification procedures [9, 10].

The combination of heterogeneous photocatalyis with ozonation can considerably increase the degradation efficiency, offering a very promising and powerful purification technique against a wide range of organic pollutants of both aliphatic [11, 12] and aromatic [13] as well as surface active [14] character. This procedure can be successfully applied for oxidative decomposition of even the most dangerous contaminants such as polycyclic aromatic hydrocarbons (PAHs) [15, 16].

The main goal of the present study was to find the most appropriate place of this combined method in the whole purification procedure applied for wastewaters of a metal-working factory, in economic and technological respects.

2 Experimental

2.1 Materials

In all experiments in this study, the titanium dioxide catalyst used was Degussa P25 (70% anatase, 30% rutile; with a surface area of 50 m^2 g^{-1}). The concentration of TiO$_2$ was 1 g dm^{-3}in all cases. Compressed air was introduced into the reaction mixtures from gas bottles both for stirring and for serving (with its O$_2$ content) as electron acceptor. Besides O$_2$, in most of the experiments, also O$_3$ produced by a LAB2B ozone generator in the same air stream functions as an oxidizer. High purity water used in this study was double distilled and then purified with a Milli-Q system.

2.2 Photochemical experiments

Photochemical experiments were performed using a laboratory-scale reactor with an effective volume of 2.5 dm^3. The heterogeneous reaction mixture (TiO$_2$ suspension) was circulated by a peristaltic pump through the reactor and the buffer vessel and by continuously bubbling air with a flow rate of 40 dm^3 h^{-1}. The photon flux of the internal light source (40W, λ_{max}= 350 nm, i.e., UVA range) was determined by potassium tris(oxalato)-ferrate(III) chemical actinometry [17, 18]. It was estimated to be 4.3×10^{-6}mol photon dm^{-3} s^{-1}.

2.3 Biological treatment

In the biological stage of the wastewater treatment in this study, a technology based on a sequencing batch reactor (SBR) was applied. SBR is a fill-draw activated sludge treatment system, in which the processes are identical to those in the conventional continuous flow activated sludge system. However, deviating from the latter procedures, SBR is a compact and time-oriented system, in which all the processes are carried out sequentially in the same tank. An operating cycle of an SBR reactor comprises five distinctive (fill, react, settle, draw and idle) phases [19]. The operational flexibility of this system allows designers to use the SBR to meet many different treatment objectives.

2.4 Analytical procedures

For analysis, 4 cm^3 samples were taken with a syringe from the reactor. The solid phase of samples, when necessary, was separated by filtration using Millipore Millex-LCR PTFE 0.45 μm filters. The pH of the aqueous phase of the reaction mixture was measured with a SEN Tix 41 electrode.

Mineralization was followed by measuring the total organic carbon (TOC) concentration, with a Thermo Electron Corporation TOC TN 1200 apparatus. The dichromate method was applied for the determination of the chemical oxygen demand (COD). The degradation of the main pollutants in the preliminary experiments was followed by gas chromatography, using a Shimadzu GC-2010 equipment. For a qualitative monitoring, absorption spectra of the reaction mixtures were also recorded with a PerkinElmer Lambda 25 spectrophotometer.

The ozone concetration was determined by iodometry, using sodium iodide as reagent and sodium thiosulfate for the titration of the iodine formed. The ozone dosage was estimated to be 3.5×10^{-4} mol dm^{-3} min^{-1}.

3 Results and Discussion

3.1 Photocatalysis of the annual average wastewater sample after physico-chemical treatments
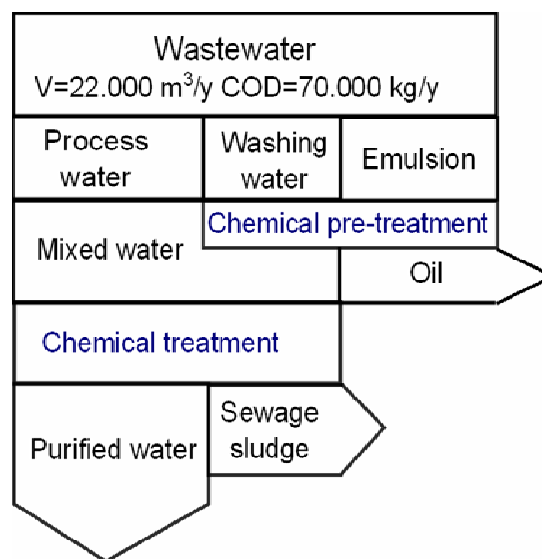
Scheme 1. Basic technology for the treatment of an industrial wastewater mixture.

The industrial wastewater dealt with in this work resulted from a factory specialized in metal-work and galvanization. It was a mixture of several polluted waters of various origins, such as process water, washing water, and emulsion as well. The typical components of this mixture were various lubricants (oil, grease), ethoxylates of unsaturated fatty alcohols, fatty acid amids as well as benzyl and methyl ethers of fatty alcohols. The different polluted waters inflowing into the cleaning plant underwent individual pre-treatments and also a common purification procedure (Scheme 1). However, at the end of this procedure the value of the chemical oxygen demand (COD) of the effluent was one order of magnitude higher than the officially allowed value
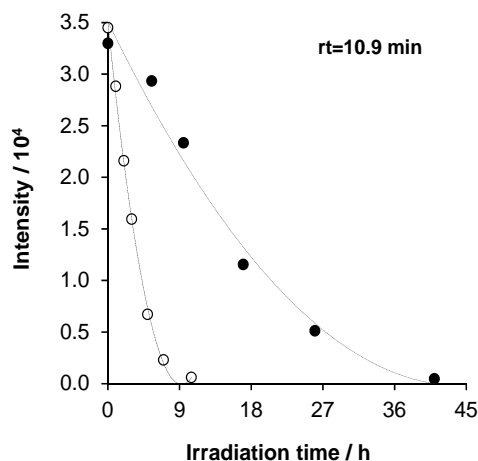
Fig. 1. The decay of the predominant pollutant in mixture (at 10.9 min retention time) followed by GC during the treatment with photocatalysis (•) and combined method (o).

Fig. 2. The decrease of TOC during the treatment with photocatalysis (•) and combined method (o).

(150 mg dm^{3-}). Hence a post-treatment seemed to be a possible solution. For this purpose, application of both photochemical and biological methods were reasonable because both result in the mineralization of the pollutants, deviating from other techniques which just separate them. Thus we tested the effect of the photocatalytic treatment before and after the biological stage.

The aim of our first series of experiments was the comparison between the effiency of the heterogeneous photocatalysis and that of its combination with ozonation. The progress of the degradation was followed by both GC-monitoring of the decay of the predominant pollutant (ethoxylate of a fatty alcohol) (Fig. 1) and measuring the total organic carbon content (TOC) in the mixture treated (Fig. 2).

As Fig. 1 indicates, the conversion of the main pollutant (with retention time of 10.9 min) is about 4.8 times faster with the combined procedure than in the case of the photocatalysis alone. The difference between the inital rates of mineralization (i.e., TOC decrease) is somewhat smaller because during the conversion of pollutants, especially in the first period of the treatments, intermediates are formed, the TOC contribution of which is very significant. Hence, the ratio of the initial mineralization rates is about 2.8 as the data of Table 1 show.

These results unambiguously prove that the combined method is significantly more efficient than the heterogeneous photocatalysis alone. Moreover, independent studies indicated that in this combination a synergistic effect enhances the resulting efficiency compared to the sum of the efficiencies of the individual methods.

Tab. 1. Initial rates of degradation (main pollutant) and mineralization (TOC) at treatments with photocatalysis and its combination with ozonation.

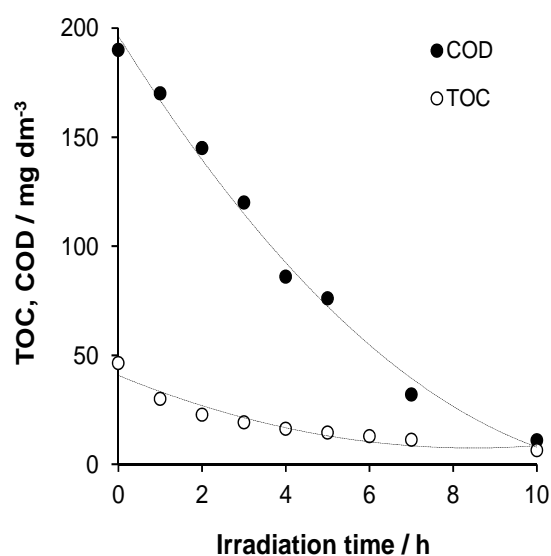| Type of experiment	Initial rate	
	Main pollutant (GC intensity)	TOC (mg dm^{-3}min^{-1})
Air + TiO$_2$+ UV	1590	0.11
O$_3$+ TiO$_2$+ UV	7630	0.31
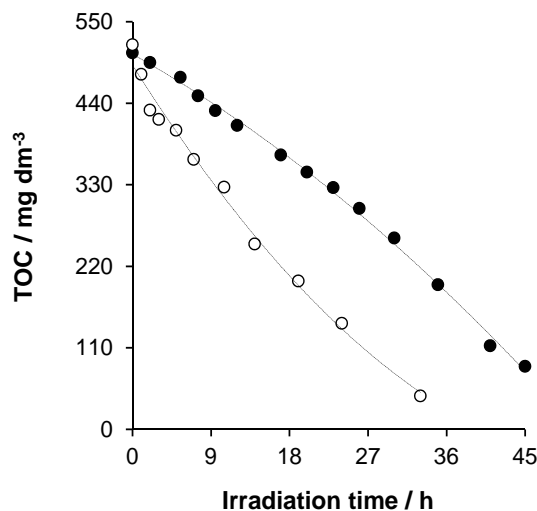
Fig. 3. The decrease of COD and TOC during the treatment of the effluent with the combined procedure after the biological stage.

Hence, in the further experiments exclusively the combination of heterogeneous photocatalysis and ozonation was applied. The 24-hour treatment with the combined method decreased the COD value of the effluent sample from 1470 to 229 mg dm^{-3}. The wastewater treated in this way was of suitably high purity approaching the quality required for the output. The subsequent biological stage easily diminished its COD value below 150 mg dm^{-5}. However, for a practical application, due to the large volume of wastewater load of the UV oxidation stage (21718 m^3/year, ca. 60 m^3/day), the costs of investment would be extremely high.

Application of the photochemical and biological steps in a reversed order provided similar results. After a 2-week biological treatment the COD value decreased to about 200 mg dm^{-3}. A subsequent (final) combined photochemical procedure resulted in an extremely low COD value (11 mg dm^{-3}, Fig. 3), almost the quality of drinking water, much better than the required limit for

the output. However, similarly to the previous case, the costs of investment would be enormous because of the large volume of wastewater input into this stage (43118 m³/year, ca. 120 m³/day).
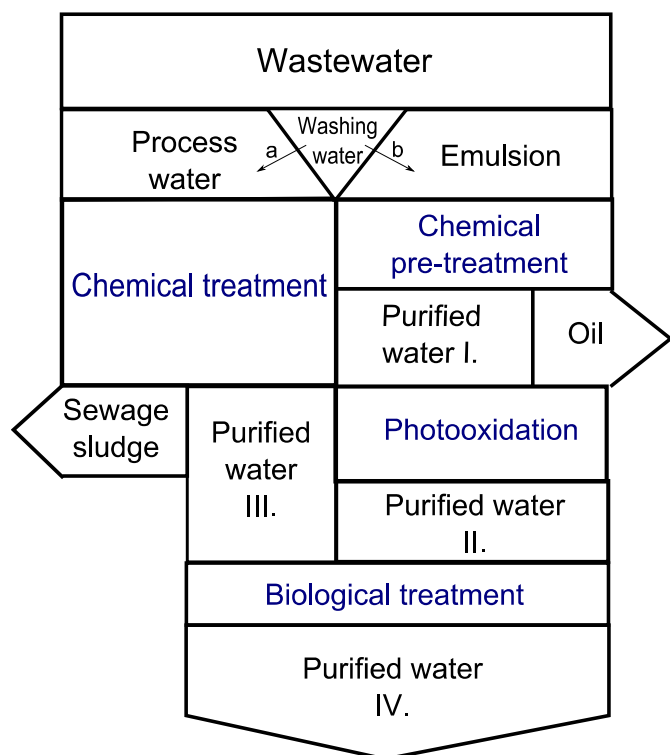
Scheme 2. Purification technology with the combined (photooxidation) stage applied for the highly polluted emulsion before the biological treatment of the entire (merged) effluent; a) fivefold dilution with outer water source, b) dilution with weakly contaminated washing water.

3.2 Photocatalysis and ozonation of the emulsion part of the wastewater mixture
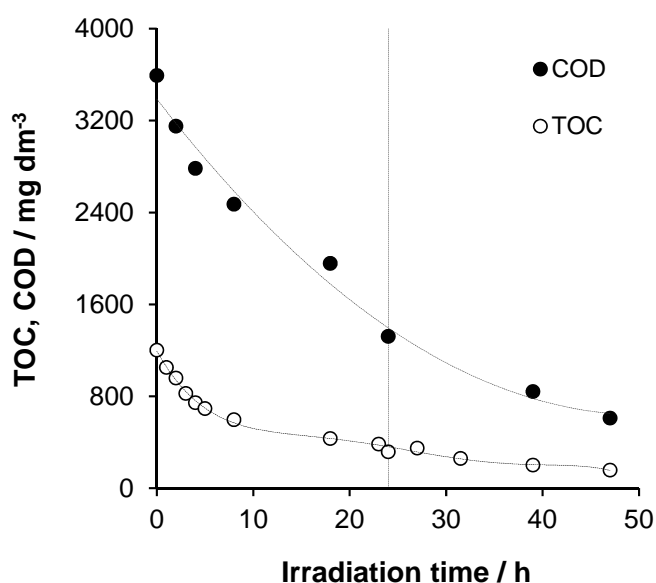

Fig. 4. The decrease of COD and TOC during the combined procedure applied for the aqueous part of the pre-treated emulsion after a fivefold dilution. (The vertical dashed line designates the 24-hour period.)

For diminishing the costs of investment and operation of the photochemical stage, this relatively expensive method is more reasonable to be applied for a much smaller but extremely heavily polluted part of the wastewater mixture. This very contaminated contribution is an emulsion, the COD value of the aqueous part of which was as high as 13592 mg dm⁻³ even after the physico-chemical pre-treatment (decomposition) (Scheme 2).

Since this COD value was much too high for an efficient photochemical treatment, a fivefold dilution of the sample had to be made before the combined stage. As Fig. 4 indicates, a 24-hour treatment with the combined method diminished the COD value of the diluted sample from 3300 to 1320 mg dm⁻³. This more than 60% COD decrease was accompanied by a considerable increase of the acidity of the sample treated.
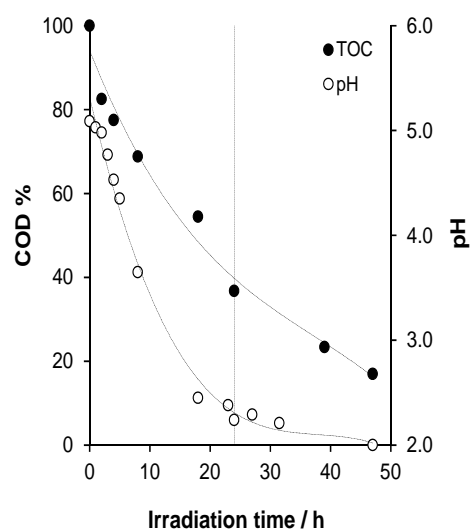

Fig. 5. The decrease of COD (in %) and pH during the combined procedure applied for the aqueous part of the pre-treated emulsion after a fivefold dilution. (The vertical dashed line designates the 24-hour period.)

The initial value of pH (ca. 5) decreased to about 2.3 within the irradiation period, and to 2.0 after a 48-hour irradiation as shown in Fig. 5. Such an increase of the hydrogen ion concentration during the photooxidation of this kind of wastewater is a general phenomenon due to the formation of simple organic and inorganic acids. Also in this respect is advantageous to apply this method only for a part of the wastewater mixture in the middle of the whole purification technology. Thus, after the photochemical treatment, mixing this part with the other constituents of the total effluent undergoing the biological stage considerably increases the final pH towards the neutrality.

The final biological purification of the pre-treated mixture diminished its COD to 127 mg dm⁻³ (much below the prescribed limit of 150 mg dm⁻³). Since the volume of the input into the combined stage in this technological arrangement is considerably low (520 m³/year, i.e., 1,4 m³/day), this procedure may be realized at relatively low costs of investment and operation.
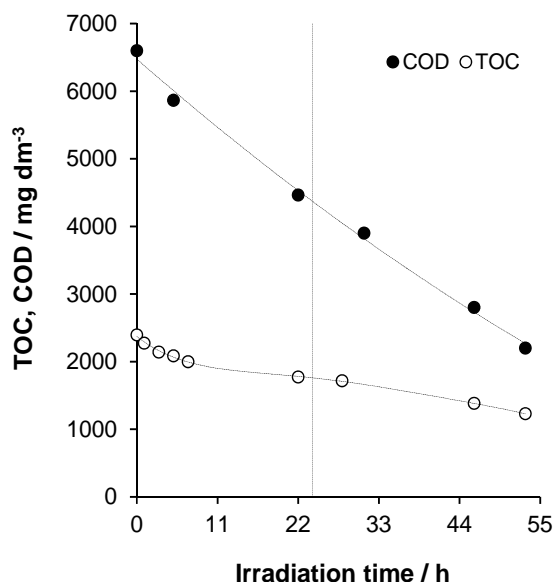
Fig. 6. The decrease of COD and TOC during the combined procedure applied for the pre-treated emulsion diluted with weakly polluted washing water. (The vertical dashed line designates the 24-hour period.)

Fig. 7. The change of the COD/TOC ratio and pH during the combined procedure applied for the pre-treated emulsion diluted with weakly polluted washing water. (The vertical dashed line designates the 24-hour period.)
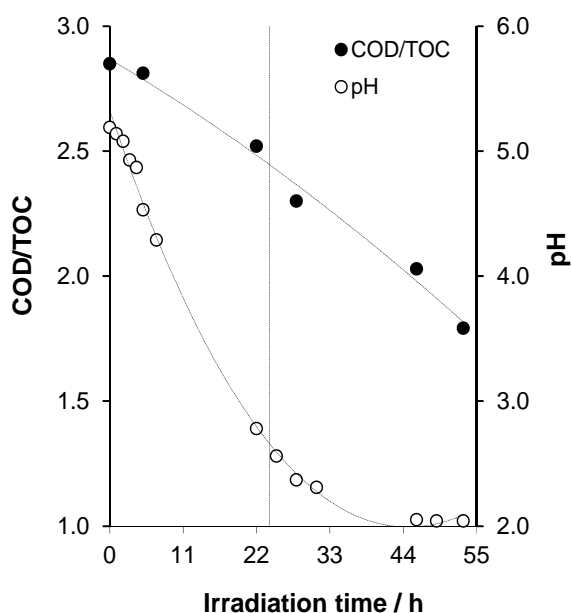
3.3 Photocatalysis and ozonation of the emulsion mixed with weakly polluted washing water

Although the results of the previous compilation of purification steps seemed to be favourable, the dilution of the heavily polluted aqueous part of the pre-treated emulsion with an outer source of clean water is not reasonable or maybe even prohibited. Thus, improving the technology in this respect, in a much more reasonable solution a weakly contaminated input constituent of the wastewater was applied for the dilution of the emulsion. The collection of various wash waters (designated as „washing water") was utilized for this purpose as indicated in Scheme 2 (arrow with „b"). Although the COD value of the pre-treated emulsion was still rather high in this case (6600 mg dm^{-3}), it was diminished to 4460 mg dm^{-3} by a 24-hour combined procedure, while 2200 mg dm^{3-} was reached after a 48-hour treatment (Fig. 6).

Also in this case a significant decrease of pH was observed during the irradiation (Fig. 7) because oxidation resulted in the formation of various acids. In accordance with this explanation, COD decreased considerably faster than TOC did, indicating that oxygenation of the pollutants led to the formation of acidic intermediates. In such processes the oxidation state of all the oxygenated carbon atoms increases, while their number just moderately changes. Only the terminal carbon atoms can be mineralized, forming carbonate or its protonated derivatives, which results in TOC decrease.

The final biological purification of the pre-treated mixture, following the 24-hour combined stage, reached a COD value of 116 mg dm^{-3}, reliably satisfying the official requirement. Hence, this technological arrangement unambiguously proved to be the most reasonable one to put into practice as a consequence of the fairly low load at the photochemical stage (840 m^3/year, 2,3 m^3/day).

4 Conclusions

Although the heterogeneous photocatalysis is an effective procedure for wastewater treatment, its application at the end of the purification technology is not reasonable because of the high costs of investment and operation – also in the case of combination with ozonation. Application of the combined method is more cost effective as a pre-treating stage for the purification of a heavily polluted part of the wastewater mixture, an emulsion in this case, before the biological treatment. In the most economical arrangement of the individual purification steps, the combined method was applied for the emulsion diluted with moderately polluted washing water, before the final biological purification.

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