

DEGRADATION OF ORGANIC POLLUTANTS IN PHOTOCATALYTIC REACTORS

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Titanium dioxide-mediated photocatalytic mineralization of oxalic acid and formic acid as model compounds were studied in a laboratory-scale reactor and in a pilot equipment to promote the development of procedures for wastewater treatment. Experimental results obtained by using various TiO₂ catalysts indicate that the adsorption of the pollutant substrates on the surface of the semiconductor particles is not directly correlated with the specific surface area of the adsorbent. The initial rate of the photocatalytic degradation of the model compounds is enhanced by increasing the adsorption capability of the titanium dioxide applied, but the overall mineralization efficiency is jointly determined by several factors such as the crystal structure, the mean value and the distribution of the particle size, as well as the number of the hydroxyl groups on the particle surface. The VP P90 TiO₂ proved to be the most efficient photocatalyst for degradation of both model compounds studied. Application of static mixer in the pilot equipment enhanced the rate of the photocatalytic mineralization of formic acid by about 27%. This effect can be attributed to the increased interfacial mass transfer facilitating the movement of photogenerated HO• radicals from the catalyst surface or the boundary layer to the bulk solution.

Keywords: photocatalysis, degradation, titanium dioxide, adsorption, oxalic acid, formic acid, mineralization, wastewater treatment

Introduction

Sustainable development and environmental protection warrant newer and stricter rules regarding the level of pollution. Thus, increasing attention should be paid to the viewpoints of environmental chemistry in the industrial production and agricultural activity. The best strategy, of course, is prevention, i.e., the application of environmentally friendly, pollution-free „green” technologies [1]. Nevertheless, in several cases, the use of materials having serious environmental impact, being even dangerous, moreover, toxic, cannot be avoided.

The photocatalytic detoxification of wastewaters is a typical representative of the Advanced Oxidation Processes (AOP) [2]. In the modern environmental protecting procedures, in the past decade, the techniques applying UV light-driven catalytic treatment became widespread. In such a process of degradation 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 H₂O or CO₂). Thus, the purified water does not contain any rest or trace of the oxidizing agent. The most reliable and widely used photocatalyst applied for wastewater treatment is nanosized titanium dioxide semiconductor [3, 4]. Upon irradiation in the near UV range, electron-hole pairs are formed in the TiO₂ nanoparticles. These

opposite charges may recombine or, reaching the surface of the catalyst particle, can undergo redox reactions with H₂O, HO⁻ or dissolved O₂, producing highly reactive species such as HO• and HO₂•, which efficiently oxidize the organic pollutants in the bulk solution. Besides, contaminants adsorbed on the surface of the catalyst particles can directly react with the photochemically formed holes and electrons, promoting the processes of mineralization.

Currently considerable efforts were made to thoroughly study the photomineralization of a wide range of organic contaminants on various types of TiO₂ catalysts [5-7]. Several procedures have already been applied for practical use [8, 9], thus, one of the most important requirements regarding the catalyst utilized is the highest possible efficiency. Beside the crystal structure of TiO₂ [10-12], the photoactivity of the catalyst is affected by the following parameters: the mean size [13, 14], the size distribution, and the specific surface area of the semiconductor particles [15]. These properties jointly determine the rate of the electron-hole recombination, the adsorption activity of the catalyst, and the numbers of surface hydroxyl groups [16], which significantly influence the efficiency of the degradation processes. The crystal structure of the semiconductor predominantly depends on the preparation technology.

For development of a photocatalytic treatment of a wastewater, beside the elucidation of the degradation

mechanisms of the pollutants contained, it is extremely important to design the photoreactor and to determine the limits of its applicability.

Hence, for these purposes, we have studied the degradation of formic and oxalic acids as model compounds in a laboratory-scale photoreactor as well as in a larger pilot equipment, using TiO_2 photocatalysts of different types.

Experimental

Laboratory-scale photoreactor

Irradiations of the reaction mixtures were carried out in a photoreactor of 3 dm^3 net volume (Fig. 1). The light-source was a 40-W light-tube developed for such a photocatalytic purpose. Most of its radiation energy is emitted above 300 nm (Fig. 2).

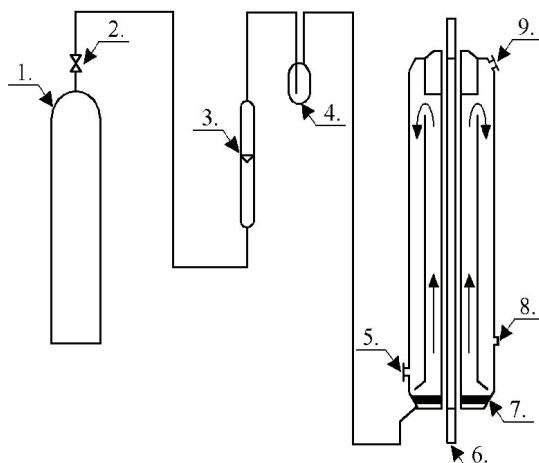


Figure 1: Simplified scheme of the laboratory-scale reactor

1. Cylinder for compressed air vessel, 2. Regulating valve,
3. Rotameter, 4. Buffer, 5. Input stump, 6. Light source,
7. Glass filter, 8. Sampling stump, 9. Gas output

In this reactor the heterogeneous reaction mixture (TiO_2 suspension) was circulated by continuously fed air with a flow rate of $40 \text{ dm}^3 \text{ h}^{-1}$. The photon flux of the internal light source was determined by potassium *tris*(oxalato)ferrate(III) chemical actinometry. It was estimated to be $4.3 \cdot 10^{-6} \text{ mol photon dm}^{-3} \text{ s}^{-1}$. The concentration of TiO_2 was 1 g dm^{-3} in all photochemical experiments. High purity water used in these experiments was double distilled and then purified with a Milli-Q system. The initial pH of the reaction mixture was adjusted using H_2SO_4 and NaOH solutions prepared by of pure reagent grade acid and hydroxide, respectively.

Pilot equipment

A SOLARDETOX[®] ACADUS-2005/2.0 movable reactor developed for investigation of photocatalytic procedures driven by solar radiation has been modified so that it can be operated by artificial light sources, too (Fig. 3). For irradiation of the reactor consisting of 24 tubes connected, three 40-W light-tubes were applied, the emission spectrum of which was similar to that used in the laboratory-scale equipment (Fig. 2).

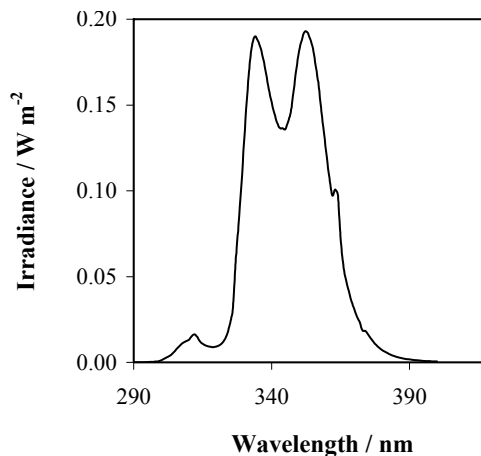


Figure 2: Emission spectrum of the light tube applied at 40 W load,
UV-B (280–315 nm): 0.15 W m^{-2}
UV-A (315–400 nm): 6.3 W m^{-2}

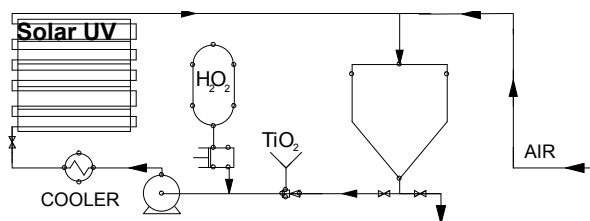


Figure 3: The simplified scheme of the photochemical reactor

For promotion of homogeneous energy transfer to the flowing reaction mixture, the stream of the fluid was modified with static mixers. An efficient photocatalytic oxidation needs the titanium dioxide powder kept in homogeneously suspended state. The static mixers in the reactor tubes promote not only the effective energy input, but they prevent the sedimentation of the catalyst powder and its deposition on the glass wall of the reactor.

Analysis

Before and during the continuous UV-A irradiation aliquot samples were taken from the reaction mixture through a septum with a syringe. TiO₂-containing samples were filtered through a Millipore Millex-LCR PTFE 0.45 µm membrane filter. The pH of the aqueous phase of the reaction mixture was measured by a SEN Tix 41 electrode.

The initial concentration of oxalic acid was adjusted to be 10⁻³ M and of formic acid was adjusted to be 2·10⁻³ M. The concentration of the oxalic acid was determined by classical permanganometry using the aliquot of the clear

liquid sample. The mineralization of model compounds was followed by measuring the total organic carbon (TOC) concentration, utilizing a Thermo Electron Corporation TOC-TN 1200 apparatus.

Results and Discussion

The adsorption and the efficiency of the photodegradation of the model compounds, formic and oxalic acids, have been studied on catalysts of various compositions and particle sizes. The characteristic data of the individual catalysts are summarized in *Table 1*.

Table 1: Characteristic data of the catalysts applied

Catalyst	Anatase (%)	Anatase	Rutile	Specific surface area (m ² g ⁻¹)
		Particle size (mean diameter) (Å)		
VP P90	94	278	195	90
Aeroxid P25	91	275	435	50
Degussa P25	70	278	484	50
MPC 500	100	69	-	300

Adsorption measurements

For determination of the adsorption the suspension containing the catalyst was circulated in the photoreactor for 60 minutes without irradiation. The initial concentration of the investigated formic acids was adjusted to 2·10⁻³ M and oxalic acid 1·10⁻³ M. Aliquot samples were taken from suspensions after various time intervals. The samples were filtered. The measure of the amount of the substrate adsorbed on the surface of the catalyst was determined on the basis of the change in TOC in the aqueous phase. It decreased continuously until the equilibrium concentration has been achieved. After 30 minutes stirring the concentration of the model compounds was found to be constant in the homogeneous solutions.

As *Fig. 4* displays, the adsorption of formic acid on the catalyst Aeroxid P25 is surprisingly low, while it is about the same on the other semiconductors. Also in the case of reaction mixtures containing oxalic acid, the lowest adsorption was observed on Aeroxid P25 catalyst, while the highest one on Degussa P25 (*Fig. 5*). Comparing the values of the adsorption and the specific surface areas of the semiconductor, interesting relations can be noticed. It is unambiguously seen that the measure of adsorption is determined by not only the magnitude of the catalyst's specific surface area. It is valid for both substrates studied that the highest adsorption is observed not on the catalyst MPC 500 with the largest specific surface area (300 m² g⁻¹).

The adsorption on the particle surface is also affected by the anatase content of the catalyst. The catalysts Degussa P25 and Aeroxid P25 are of the same specific surface area and very similar mean particle sizes (278 Å and 274 Å, respectively), but the higher anatase content for the second TiO₂ sample (70% vs. 91%) resulted in lower adsorption (23% vs. 18.8% for oxalic acid and 19.2% vs. 4.9% for formic acid).

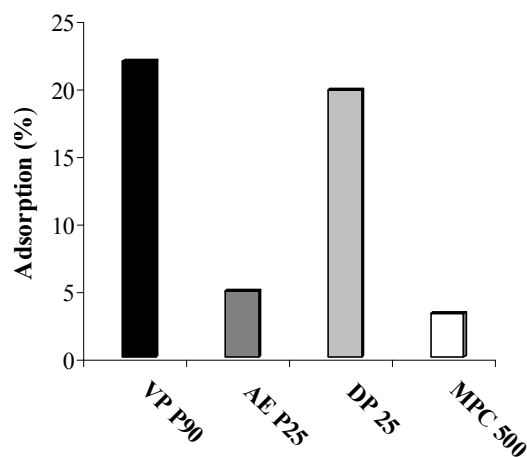


Figure 4: The surface adsorption of formic acid, C₀(formic acid) = 2·10⁻³ mol dm⁻³, 1 g dm⁻³ TiO₂

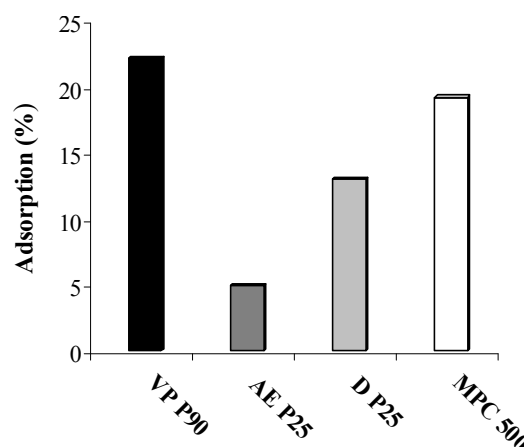


Figure 5: The surface adsorption of oxalic acid; in the case of the MPC 500 (300 m² g⁻¹) catalyst consisting of pure anatase, only 19.2% of oxalic acid is adsorbed on the surface, this is significantly lower than that observed for Degussa P25, C₀(oxalic acid) = 10⁻³ mol dm⁻³, 1 g dm⁻³ TiO₂

Photodegradation of the model compounds in the laboratory-scale reactor

The efficiency of the photocatalytic degradation was followed by measuring the total organic carbon content (TOC), before and after the removal of the suspended TiO_2 and the pH of the reaction mixture (Fig. 6).

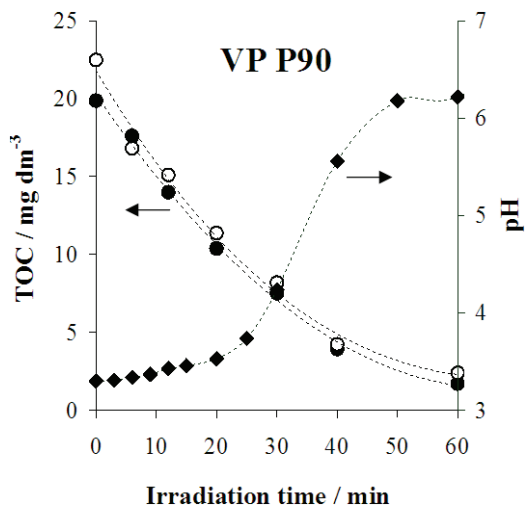


Figure 6: Photodegradation of formic acid, $C_0(\text{formic acid}) = 2 \cdot 10^{-3} \text{ mol dm}^{-3}$, $1 \text{ g dm}^{-3} \text{ TiO}_2$; TOC measured before (o) and after (●) filtration

The decrease of TOC indicates that the substrate is mineralized, i.e., hydrogen carbonate or carbon dioxide is formed during the process. Although hydrogen carbonate is dissolved, but it is protonated at about pH 5. If the pH of the reaction mixture is ca. 5, bubbling ($40 \text{ dm}^3 \text{ h}^{-1}$ air) removes carbon dioxide from the system, thus the total inorganic carbon (carbonate) content (TIC) of the photocatalysed samples is practically zero. In solutions of higher pH TIC increases to some extent, and the difference between the total carbon content (TC) and TIC gives the actual value of TOC. On the VP 90 catalyst, 40 min irradiation significantly decreased the TOC of the reaction mixture, along with the increase of pH (Fig. 6).

The initial rate of the photocatalytic degradation was determined by a simple procedure of fitting polynomial on the TOC vs. irradiation time plots (Fig. 7). The experimental results clearly indicate the strong correlation between the adsorption of the substrate to be mineralized and the initial degradation rate (Figs. 4 and 7). Both the most efficient absorption and the highest initial degradation rate for formic acid were observed on the VP P90 catalyst. Besides, the measurement data suggest that other factors also affects the degradation rate of the substrates studied. The lowest adsorption was measured on the Aeroxid P25 catalyst, while the initial mineralization rate on it is significant.

The lowest degradation rate was observed in the case of the MPC 500 catalyst consisting of 100% anatase and having the highest specific surface area. Apparently pure anatase is not advantageous from the viewpoint of the reaction rate, and there is an optimum for the magnitude of the specific surface area above which an increase is not favourable.

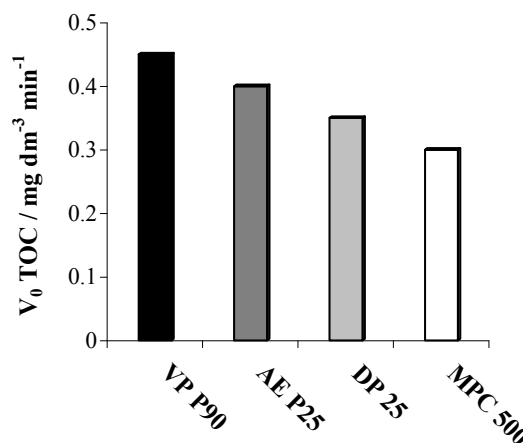


Figure 7: The initial degradation rate of formic acid on the catalysts applied

The photocatalytic mineralization of oxalic acid was studied in reaction mixtures of $10^{-3} \text{ mol dm}^{-3}$ concentration. The tendencies in this system were similar to those observed in the case of formic acid. The mineralization was followed by measuring the actual concentration of the oxalic acid and the TOC in the reaction mixture. Since the value of TOC measured in the reaction mixture and that calculated from the actual concentration of the starting material agreed within the measurement error (3–5%), the model compound was mineralized practically without formation of any longer-lived intermediate. Fig. 8 displays the results regarding the suspension containing Degussa P25 catalyst. Fig. 9 shows the comparison of the initial degradation rates measured on different catalysts applied.

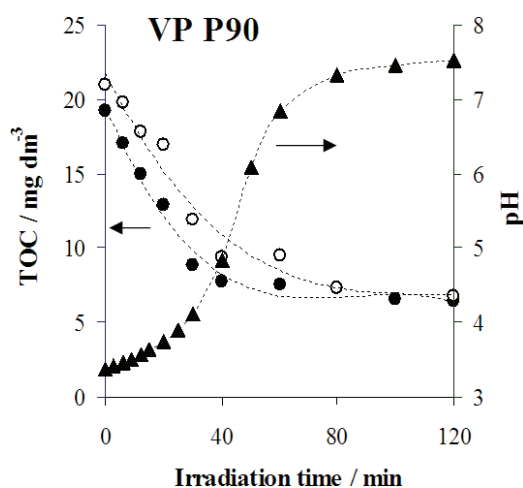


Figure 8: Photocatalytic degradation of oxalic acid on Degussa P25 catalyst, $C_0(\text{oxalic acid}) = 10^{-3} \text{ mol dm}^{-3}$, $1 \text{ g dm}^{-3} \text{ TiO}_2$; TOC measured before (o) and after (●) filtration

Similarly to the case of formic acid the most efficient adsorption of oxalic acid was observed on the surface of VP P90 (Fig. 5), also the initial mineralization rate of the substrate was the highest in the suspensions containing this catalyst (Fig. 9).

According to our observations, VP P90 proved to be the most efficient photocatalyst for degradation of both model compounds studied, while the mineralization

processes of these substrates were found to be the slowest on M-PC 500. Notably, the photoactivities of the Degussa P25 and Aeroxide P25 catalysts were quite similar despite of their significantly different anatase contents (Degussa P25 – 70%, Aeroxide P25 – 94%). Similarly to our observations, no direct relationship was found between the degradation rate and the specific surface area in the case of photocatalytic oxidation of phenol and 3-nitrobenzenesulfonic acid on various types of TiO₂ catalysts [17].

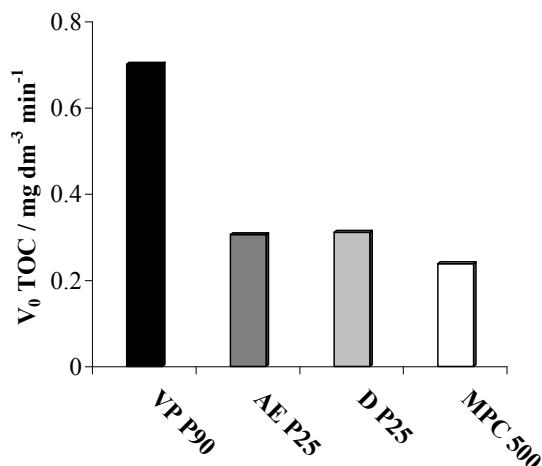


Figure 9: Initial degradation rates of oxalic acid on different catalysts

Photodegradation of formic acid in the pilot equipment

In order to investigate the effect of static mixer on the rate of the photocatalytic degradation of pollutants $7 \cdot 10^{-3}$ M solution of formic acid was irradiated in the presence of Degussa P25 catalyst (1 g dm^{-3}) in the pilot equipment. As Fig. 10 shows, application of static mixer appreciably enhanced the mineralization rate of formic acid in this photoreactor.

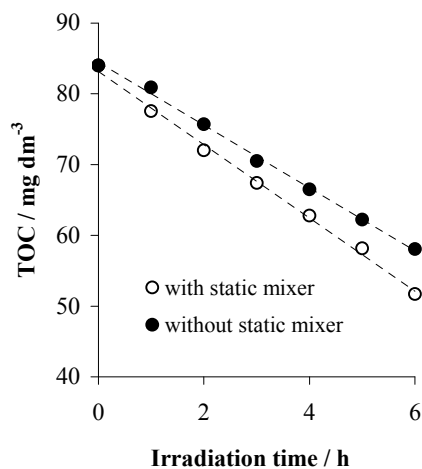


Figure 10: Photocatalytic degradation of formic acid on Degussa P25 catalyst in the pilot equipment with and without static mixer, $C_0(\text{formic acid}) = 10^{-3} \text{ mol dm}^{-3}$, $1 \text{ g dm}^{-3} \text{ TiO}_2$

The relative increase of the rate, compared to that measured under the same conditions but without static mixer, is 27% (at $16.7 \text{ dm}^3 \text{ min}^{-1}$ flow rate), which is in good agreement with the results quite recently published on the photocatalytic degradation of phenol in a similar system (16.4% at $2.2 \text{ dm}^3 \text{ min}^{-1}$ flow rate) [18]. Considering that the flow rate in our case was about one order of magnitude higher than that applied in ref. 18, and the relative effect of the static mixer significantly decreases upon increasing the flow rate, our result is quite promising.

The effect of the static mixer enhancing the mineralization rate organic pollutants can be attributed predominantly to the increased interfacial mass transfer as a consequence of the intense mixing [19]. Since the reactive radicals playing key roles in the oxidation mechanism are generated mostly on the surface of the catalysts particles, and then diffuse to the boundary layer and also into the bulk solution, intensification of mixing significantly enhances their mobility, promoting the latter steps, and, thus, increasing their overall reaction rate. Nevertheless, oxidation of the adsorbed substrate by the photogenerated holes play also considerable role in the mechanism of the photocatalytic degradation, but this type of process can be influenced by the static mixer to a much lesser extent.

Preliminary experiments were also carried out by utilization of solar radiation. Apart from the light source, the experimental conditions (materials, concentrations, flow rate, etc.) were the same as in the case of irradiation with light tubes. The application of static mixer considerably increased the degradation rate of formic acid under these circumstances, too. The magnitude of the relative enhancement was somewhat lower (ca 17%) than for the photocatalysis with artificial light. This difference suggests that the effect of the static mixer may depend on the light intensity.

Conclusions and outlook

The determining steps of a semiconductor-mediated photocatalytic oxidation, beside the primary electron-transfer processes, can be the reactions of the substrate with the superoxide radical anion formed via electron scavenging, and with the hydroxyl radical formed via hole scavenging. The reactivity of a semiconductor photocatalyst, such as TiO₂, depends on, beside its crystal structure, the mean value and the distribution of the particle size, and the specific surface area. These measurable properties jointly determine the rate of the electron-hole recombination, the number of the hydroxyl groups on the particle surface, and the adsorption capability of the catalyst. The crystal structure as well as the adsorption features of the nanoparticles predominantly depend on the preparation technology. Thus, catalysts of different structure and particle size were studied by application of two model compounds from the viewpoints of adsorption and photodegradation. The results of our experiments with various TiO₂ catalysts support that the adsorption of the model compounds significantly influence

their degradation rate, and also confirm that the efficiency of a photocatalyst is collectively determined by several factors. Accordingly, for a photochemical treatment the catalyst ought to be chosen by considering the composition of the wastewater to be cleaned.

Application of a static mixer in the pilot equipment appreciably increased the rate of the photocatalytic mineralization of formic acid. This effect can be explained by the enhanced interfacial mass transfer promoting the movement of photogenerated HO[•] radicals from the catalyst surface or the boundary layer to the bulk solution.

Our further investigation, continuing the successful preliminary experiments, is focused on the application of natural light source, i.e., on the utilization of solar energy in the photocatalytic wastewater treatment.

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