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Evaluation of a novel Carberry type photoreactor for the degradation of organic pollutants in water

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Abstract

The major drawback of slurry-type photoreactors is the final particle–fluid separation for the catalyst recycling. If a catalyst (e.g. TiO_2 for oxidative mineralisation of pollutants) is immobilized on a rigid support as a thin film, such problem is avoided. Unfortunately, as the reaction occurs at the liquid–solid interface, the overall rate is much lower in thin-film reactors than in the corresponding slurry systems. Our goal was to design a laboratory-scale batch photoreactor, which would combine the advantages of slurry and immobilized photocatalytic systems: (i) high ratio of illuminated immobilized catalyst surface to the volume of reaction liquid inside the reactor; (ii) high degree of mixing; (iii) possibility of installing the reactor into the compound parabolic collectors that utilize solar energy. The glass tube with the spinning basket inside (up to 12 glass slides of immobilized catalyst are positioned radially around the central axis) meets these criteria. Degussa P25 TiO_2 or sol–gel produced TiO_2 was immobilized on sodium glass support and the disappearance of 4-chlorophenol in water was monitored by HPLC analysis. Low-pressure mercury fluorescent lamps with broad maximum at 355 nm were used as a UVA radiation source. The optimal catalyst concentration in the photocatalytic experiments was 800 mg L^{-1} (regardless of the slurry or immobilized system). It was also estimated that the configuration of a novel Carberry type photoreactor with 12 fastened TiO_2 slides shows nearly 4 times (3.8 times) higher photocatalytic activity compared to the configuration with two TiO_2 slides (with the comparable surface density of immobilized TiO_2), serving as an approximation of a classic plain thin-film fixed-bed reactor. On the other hand, the activity of our novel thin-film based reactor is still almost twice (1.8 times) lower than the activity of a slurry reactor (Degussa P-25 catalyst in both cases), which is still a very promising result.

Keywords: Photocatalysis; Photoreactor; TiO_2 thin films; 4-Chlorophenol

1. Introduction

The photocatalytic behaviour of TiO_2 has been the subject of intensive studies for more than 20 years, especially when the oxidation of organic pollutants in water or in air is considered [1–3]. Compared to traditional methods, photocatalytic oxidation offers various advantages because (i) the photodegradation occurs at room temperature and atmospheric pressure, (ii) it is efficient under UVA and UVB radiation (the possibility of using solar energy as the illumination source) [4] and (iii) it destroys the molecules instead of transferring them to another form.

There are still many problems associated with the implementation of TiO_2 photocatalysis on a large-scale level. Viewed from the perspective of reactor design, three main problems arise. First, TiO_2 is mostly used in powder form in photocatalytic experiments [5], where the final particle–fluid separation for the catalyst recycling can be inconvenient, time-consuming and expensive. This problem is avoided if TiO_2 is immobilized on a rigid support as a thin (nano- or micro-scale) film. However, the second problem arises at this point because of the immobilization of the catalyst. Since, the reaction occurs at the liquid–solid interface, only a part of the catalyst is in contact with the reactant. Hence, the overall rate may be limited to mass transport of the pollutant to the catalyst surface [6]. The third issue is that besides the fact that a good contact between reactants and catalyst is required, it is also necessary to achieve efficient exposure

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Abbreviations: CTP, Carberry type photoreactor; PTFFBR, plain thin-film fixed-bed reactor; CPC, compound parabolic collector; A, surface of glass slides coated with TiO_2 layer; $t_{1/2}$, half-life of 4-chlorophenol

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Nomenclature

Carberry type photoreactor: reactor designed to perform three-phase reactions. The basket shape looks like a turbine in which the blades get trapped catalyst

Plain thin-film fixed-bed reactor: reactor where the thin film of catalyst is immobilized on a plain surface

of the catalyst to irradiation through the whole interior of the reactor [7].

Many different types of photoreactors have already been designed and evaluated for photocatalytic degradation of organic molecules in aqueous media. Examples of these reactors (either with suspended or immobilized photocatalyst) include optical fiber reactor [8], rotating disk photocatalytic reactor [9,10], corrugated plate photocatalytic reactor [11], fountain photocatalytic reactor [12], cylindrical photoreactor [13], Taylor Vortex photocatalytic reactor [14], fluidized photoreactors [15], the spinning disc reactor [16], labyrinth flow photoreactor [17], etc. However, it is still necessary to improve the current photocatalytic reactors or develop new types of such reactors with the objective of increasing their efficiency, which would end up in commercialization of this technology. To achieve this goal, it is also very important to utilize solar energy as a source of UV radiation. Compound parabolic collectors (CPCs) have shown that they could be efficient for solar photocatalytic detoxification [18]. TiO_2 slurries were usually tested in CPCs, whereas supported catalysts have not been efficiently applied in such systems yet.

Organic pollutants present in water include pesticides, pharmaceuticals, dyes, personal care products, surfactants, different other organic compounds from chemical industry, etc. Many of them are chemically, photochemically and/or microbiologically stable and have been found in wastewaters all around the world [19]. TiO_2 photocatalysis is one of the possible processes, able to eliminate such emerging contaminants from the wastewater. The removal of 4-chlorophenol (intermediates in dyestuffs and in the manufacture of higher chlorinated phenols) by TiO_2 photocatalytic oxidation has been studied in details [20–22], therefore 4-chlorophenol was chosen as a model organic compound in our photocatalytic experiments.

The aim of the present work was first to design the laboratory-scale batch reactor with: (i) no problems with particle–fluid separation; (ii) high ratio of illuminated immobilized catalyst surface to the volume of reaction liquid inside the reactor; (iii) mixing of the pollutant solution; (iv) possibility of installing such reactor into the CPC (utilizing solar energy). Next, the efficiency of the reactor for the degradation of 4-chlorophenol in water was evaluated by Degussa P-25 TiO_2 slurry and two types of immobilized TiO_2 films.

2. Experimental

2.1. Immobilization of the catalyst

2.1.1. Immobilization of Degussa P-25 catalyst

The commercially available Degussa P-25 TiO_2 was used as a test photocatalyst. The immobilized particulate TiO_2 layers were prepared on glass slides (175 mm × 12.5 mm × 2 mm) by sedimentation from aqueous suspension of TiO_2 P-25 ($10\,g\,L^{-1}$) for different periods of time, with additional drying and annealing at 500 °C for 15 min [23]. The sedimentation was also repeated on the other side of the glass slide. The amount of immobilized TiO_2 was determined by weighing and the results are given in Table 1 (samples F–M).

2.1.2. Sol–gel derived TiO_2 films

In contrast with opaque P-25 films, transparent TiO_2–anatase films deposited on both sides of SiO_2-precoated soda-lime

Table 1
Characteristics of different photocatalytic systems and calculated half-lives of 4-chlorophenol for each configuration

Configuration	Catalyst	Number of glass slides	Average amount of TiO_2 on each slide (mg)	The total surface area covered with TiO_2 (cm^2)	Weight concentration of TiO_2 in the solution of pollutant ($mg\,L^{-1}$)	Half-life of 4-chlorophenol (min)
A	P-25	0	Slurry	Slurry	148	3.5
B	P-25	0	Slurry	Slurry	300	2.9
C	P-25	0	Slurry	Slurry	720	2.5
D	P-25	0	Slurry	Slurry	1000	2.4
E	P-25	0	Slurry	Slurry	1440	2.3
F	P-25	6	5.3	262	160	13.5
G	P-25	6	9.2	262	275	8.5
H	P-25	6	26.3	262	790	6.6
I	P-25	6	36.5	262	1095	6.9
J	P-25	6	52.5	262	1575	6.7
K	P-25	2	71	87	710	16.9
L	P-25	1	148	44	740	24.9
M	P-25	12	35	524	2100	4.4
N	Sol–gel	6	1.8	262	55	52.8
O	Sol–gel	6	11.1	262	333	29.7
P	Sol–gel	6	18.3	262	550	23.4
R	Sol–gel	6	25.5	262	764	24.7
S	Blank	6	0	262	0	245

glass slides (175 mm × 12.5 mm × 2 mm) were produced by the sol–gel processing route described in detail already in our previous publications [24–26].

2.1.2.1. SiO_2 sol. Tetraethoxysilane (Acros Organics) (15.0 g) was dissolved in ethanol (Riedel-de Haen) (22.0 g). Separately 11.5% solution of nitric(V) acid was prepared by dissolving concentrated (65%) nitric(V) acid (Acros Organics) (1.85 g) in water (10.5 g). After 10 min both solutions were mixed together and the resultant sol was used after being aged at room temperature for 2 h.

2.1.2.2. TiO_2 sol. The 17.02 g of titanium(IV) isopropoxide (Acros Organics) was added to 8.12 g of ethyl acetoacetate (Riedel-de Haen) during constant stirring. After 5 min the prepared solution was dissolved in 62.53 g of 2-methoxyethanol (Fluka). Then 9.4 g of the triblock copolymer Pluronic F-127 (Sigma) was dissolved in the sol. The resultant alkoxide solution was stirred for solvolysis and condensation reactions at room temperature for at least 3 h before the deposition of the films.

The SiO_2 films were first deposited on clean glass slides using the dip-coating technique with the withdrawal speed of 10 cm min^{-1}. The substrates coated with gel films were left in air at room temperature for 30 min and then they were calcined at 500 °C for 30 min. Then the TiO_2 films were deposited on the SiO_2 protective layer as described above. The thicknesses of the TiO_2 films were increased by repeating the dipping and heat-treatment cycles. The amount of the catalyst on a glass slide was determined by weighing and the results are given in Table 1 (samples N–R).

2.2. Photocatalytic cell and photoreactor

The photocatalytic cell consists of a DURAN glass tube (240 mm, inner diameter 40 mm), which is closed on the lower side with a glass frit and the valve for purging with gas (Fig. 1A). The effective volume of the glass tube is 250 mL.

The spinning basket is made exclusively of Teflon (Fig. 1B) and fits into the photocatalytic cell. Up to 12 glass slides with immobilized catalyst were fastened around the axis (10 mm in diameter, Fig. 1C) with the help of two holders. The glass slides and the axis are not joined together, there is a gap of 1.5 mm in between to enable homogeneous mixing of the solution in all segments of the cell. The spinning basket with the immobilized TiO_2 placed in the glass tube can freely rotate around its axis.

The photocatalytic activity of the as-prepared films were evaluated in a tailor-made chamber photoreactor using six low-pressure mercury fluorescent lamps as a UVA radiation source (CLEO 20 W, 438 mm × 26 mm, Philips; broad maximum at 355 nm). The lamps in the periphery of the photoreactor are positioned on a circular line and the reflective surface of polished aluminium is placed behind them. The photocatalytic cell is put in the center of the circle. The motor on the top of the reactor rotates the spinning basket with variable speeds (between 0 and 300 rpm).

2.3. Photocatalytic experiments

Aqueous solution (200 mL) of 4-chlorophenol (15 mg L^{-1}) was used as a photodegradation medium in the evaluation experiments of the novel reactor. 4-Chlorophenol (Aldrich) was used as received.

The photocatalytic degradations were performed with: (i) the P-25 TiO_2 slurries; (ii) 1, 2, 6 or 12 glass slides with immobilized P-25 TiO_2; (iii) six glass slides with immobilized sol–gel derived TiO_2. Blank experiments were performed in the same way, but without TiO_2 on the glass plates. At least two repetitions with each configuration were performed to evaluate the reproducibility of measurements.

During the irradiation, the solution was constantly purged with oxygen (1.0 L min^{-1}), keeping the solution saturated with dissolved oxygen the whole irradiation time. The effect of rotation on photocatalytic activities was also evaluated. The temperature was kept constant at 35 °C during the experiment. The photon flux in the cell was evaluated by potassium ferrioxalate actinometry [27], and determined to be 4.2×10^{-5} einstein L^{-1} s^{-1}.

The solution of organic pollutant was left rotating and purging with oxygen 30 min in the dark prior to irradiation. Samples of 2 mL were taken from the cell at different times during the irradiation and analyzed by HPLC. Except the samples taken from TiO_2 slurry (these samples were centrifuged at 13,200 rpm for 15 min and then the supernatant was collected for chromatographic analysis), they were analysed without additional

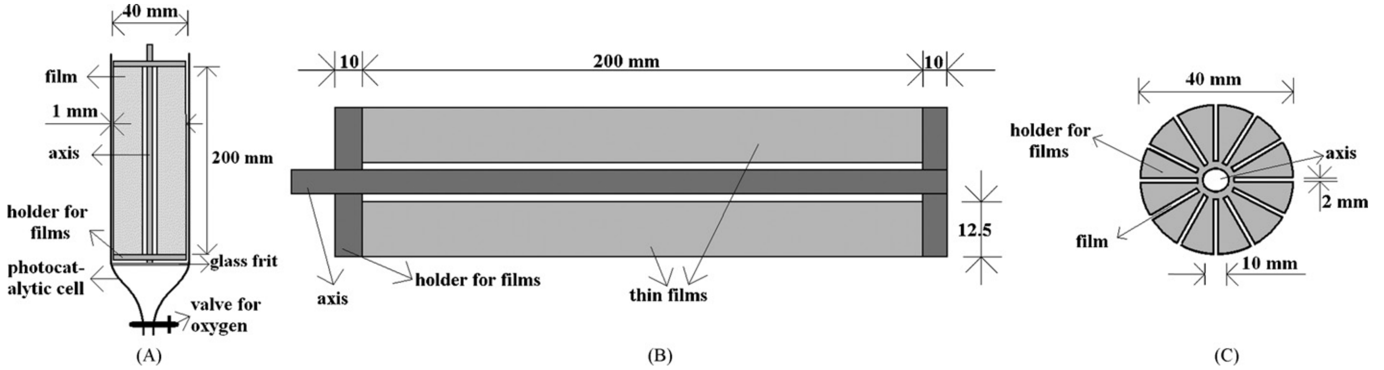

Fig. 1. The photocatalytic cell with the spinning basket inside: (A) the spinning basket is placed into the tube with an inner diameter of 40 mm; (B) longitudinal section of the spinning basket; (C) cross-section of the spinning basket.

filtration, extraction or centrifugation. All disappearance curves indicate first-order kinetics, therefore they were fitted as first-order reactions.

The TiO_2-coated slides and the photocatalytic cell were washed with deionised water after the experiment. Before starting the next one, the cell was washed and filled with the new solution of 4-chlorophenol.

2.4. Analytical procedures

The HPLC equipment consists of a HP 1100 Series chromatograph, coupled with a DAD detector. The chromatographic separations were run on a C18 Hypersil ODS column (Supelco, 150 mm × 4.6 mm, 5 μm) using a 70:30 mixture of 10 mM aqueous NH_4OOCCH_3 (Merck) solution and acetonitrile (J.T. Baker) as the eluent in the first 5 min, then it was changed into a 45:55 mixture by applying a linear gradient between 5 and 10 min. The eluent flow rate was 1.0 mL min^{-1}. Injection volume was 30 μL. The compound elutions were monitored by the DAD detector at 226 nm.

3. Results and discussion

3.1. Photocatalytic degradation with different configurations of the catalyst

When considering solar photocatalytic pilot plants, two different types of reactors are mostly used: CPC reactors with TiO_2 slurries or plain thin-film fixed-bed reactors (PTFFBR) [28]. We combined the advantages of both systems, i.e. compact and convenient compound parabolic collectors with glass tubes and turbulent flow from CPC reactors, and immobilized catalysts from fixed-bed reactors. The tube with the central axis through it, on which long slides of immobilized catalyst are positioned radially, meets the above criteria. To our knowledge, there is only one scientific publication discussing the use of the principle of the spinning basket with immobilized TiO_2 for photocatalytic reactor (a Carberry type photoreactor = CTP) [29]. That photoreactor, however, is not intended for CPCs and aqueous solutions.

In our photocatalytic cell, the irradiated area of TiO_2 film is 15 cm^2/1 cm of tube length, when six glass slides are used. If we take into account the fact that the aperture of a standard compound parabolic collector is 9.25 cm [30] and if we presume that the tube is placed in the standard CPC, we are able to irradiate a 1.62 times higher surface area of the catalyst in a novel photocatalytic reactor than in a fixed-bed reactor on the same projected area. The magnification is even higher when more glass slides with immobilized catalyst are positioned into the cell.

As we do not have a CPC pilot plant yet, all our experiments were performed in the chamber photoreactor, where the photocatalytic cell is placed in the center of irradiation in order to equally irradiate the tube from all sides (approximation to CPC). First we compared the rate of disappearance of 4-chlorophenol catalyzed by different configurations of immobilized Degussa P-25 TiO_2 films, while keeping the amount of TiO_2 the same in all cases (Fig. 2). Degussa P-25 was chosen for evaluation purposes of the novel photoreactor for two reasons. Firstly, it is used worldwide as a standard TiO_2 photocatalyst and its characteristics are known. Secondly, since we were able to prepare pure Degussa P-25 films, a direct comparison between the photocatalytic activity of a slurry and immobilized system could easily be evaluated. It should be stressed that films prepared by the procedure described above could not be used in industrial applications because of low physical adhesion of the catalyst. In our experiments, they only served as model films for comparison of photocatalytic activities between slurry and immobilized systems.

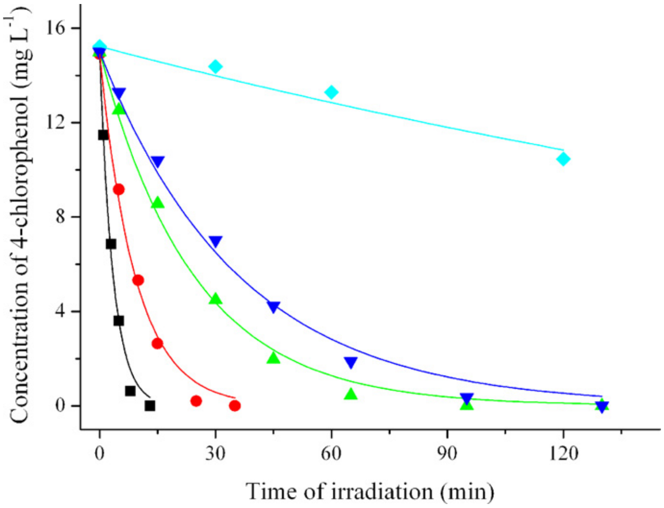

Fig. 2. Photocatalytic degradation of 4-chlorophenol; spinning rate 100 rpm; configurations from Table 1: (■) C; (●) H; (▲) K; (▼) L; (◆) S.

When working with Degussa P-25 films, the problem of losing the catalyst from the films has to be evaluated. About 2 ± 1 mg of TiO_2 was lost from the first to the second experiment when six TiO_2 films were used (configuration H). The differences between the calculated half-lives of the first three repetitions using the same films were lower than 5% in all configurations. After using the films constantly for some days (20 repetitions or more), the layers of TiO_2 (not powder) were detached from the surface and fell to the bottom of the cell. Nevertheless, the novel CTP worked as an immobilized system and not as a slurry one. At the end of the experiment, only up to 3 mg of suspended TiO_2 was measured in the solution, which represents a maximal concentration of 15 mg L^{-1} of TiO_2 in the solution at the end of the experiment, i.e. 10 times lower than in the configuration A. The beginning of the experiment was however always devoid of suspended TiO_2 as 3 mg of TiO_2 were found exclusively at the end of the experiment. Most of detached TiO_2 was not even in the form of milky suspension, since the catalyst detached in form of bigger aggregates with a low surface area to volume ratio. The solution of the pollutant under investigation was always clear (not turbid) with new films (first five repetitions). When changing the spinning rate, no increase in photocatalytic activity was measured. If the system had worked as a slurry one, the increased spinning (300 rpm) would certainly have resulted in higher degradation because of the more pronounced detachment of the catalyst.

No measurable dark adsorption of the parent molecules on TiO_2 particles was noticed before the irradiation. The photodegradation of 4-chlorophenol in the absence of TiO_2 (curve S in Fig. 2) was much slower than in photocatalytic experiments, where four different photocatalytic systems were used to evaluate the photoreactor (C, H, K, L in Fig. 2 and Table 1).

The disappearance rate was highest when TiO_2 slurry instead of thin films was used (curve C in Fig. 2). This is because in a slurry system the transport processes are facilitated by the high liquid–solid interface between the TiO_2 particles and the pollutant solution. The disappearance rate of 4-chlorophenol during the run with the system in the configuration H, with six glass slides and 790 mg of TiO_2, is ca. 2.6 times higher than that of the system in configuration K, two slides and 710 mg of TiO_2 (see Fig. 2). The magnification of the disappearance rate should ideally have been 3 (instead 2.6), since the surface area was three times higher in H than in K. The difference between the real and the ideal system is expected due to the effect of additional shading in the configuration where six instead of two slides are used. Despite this, the result is very promising and was additionally improved by placing 12 slides with immobilized TiO_2 in the cell (Section 3.4).

3.2. The influence of spinning on photocatalytic activity

The intense spinning of the TiO_2 films should provide better (more turbulent) mixing of the solution of 4-chlorophenol and consequently better transportation of molecules to the surface of the catalyst. Interestingly, when performing the experiment with configuration H (Table 1), no differences in disappearance rates were noticed at different spinning rates. Even in the absence of rotation, the disappearance rate was the same. It seems that purging with oxygen from the bottom of the cell through the glass frit generates a degree of mixing which is high enough for the reaction not to be diffusion-controlled. In order to confirm this hypothesis, two experiments were carried out by bubbling oxygen for 10 s every 5 min; the first one maintaining the slides in rotation and the second one with the system working as a fixed bed (Fig. 3). In the last case the disappearance rate was 1.25 times slower than in the case of continuous spinning. The same effect was also noticed with the configuration K (two TiO_2 films).

As it can be seen from Fig. 3, the disappearance rate of the 4-chlorophenol in a system, where purging with oxygen for 10 s each 5 min was applied together with continuous rotation was only slightly slower than in the system with continuous purging with oxygen. It can be concluded from this result that the flow rate of oxygen was unnecessarily high in configuration H, since 1 min of purging led to almost the same result as 30 min of puring with the same oxygen flow rate in the configuration H. Lowering of the oxygen flow rate for 50 times while purging through the whole experiment would still be enough for the solution to remain saturated with the oxygen during the experiment. But in this case the spinning of the solution would become necessary, otherwise the kinetic-controlled regime would turn into the diffusion-controlled one.

When studying the possibility of installing a novel CTP type into CPC system, it must be stressed that the CPCs generally work in total recirculation configuration and the flow inside the tubes is highly turbulent. In such case the spinning of the films would not be necessary. But another characteristic of CPCs is that the tube is irradiated from all sides, not only from the top or bottom. Therefore, we find such configuration of TiO_2 slides, which is used in our novel CTP reactor, convenient and promising for the application in the CPCs, as a very large surface of immobilized TiO_2 could be efficiently irradiated.

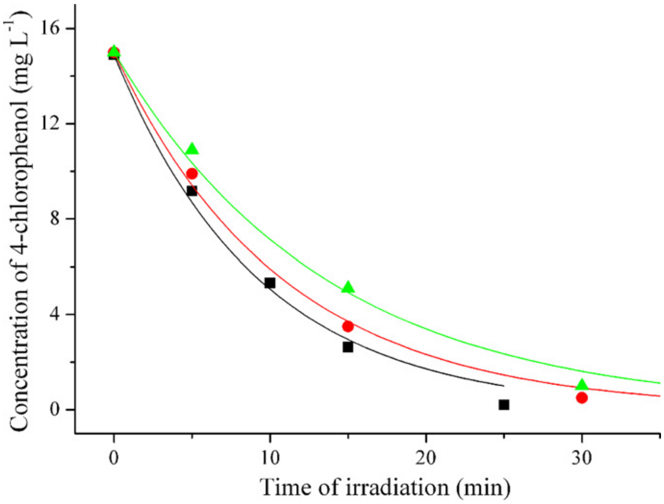

Fig. 3. Photocatalytic degradation of 4-chlorophenol; configuration H from Table 1: (■) constant purging with O_2 during the irradiation, spinning rate 100 rpm; (●) purging with O_2 for 10 s every 5 min, spinning rate 100 rpm; (▲) purging with O_2 for 10 s every 5 min, no rotation.

3.3. The effect of the amount of TiO_2 in slurry and in immobilized system on photocatalytic activity

In slurry and in immobilized photocatalytic processes, the amount of photocatalyst is an important parameter which can affect the disappearance rate of organic compounds. The optimal catalyst concentrations reported in literature for TiO_2 Degussa P-25 range from 100 to 5000 mg L^{-1}, depending on the nature of the compounds and the photoreactor geometry [31].

The aim of the experiments was to determine the optimal amount of the catalyst used in our photocatalytic cell. The photocatalytic efficiencies of the suspended as well as of the immobilized catalyst through the whole range of TiO_2 concentrations were evaluated and compared. The spinning rate was 100 rpm and the solution was purged with oxygen during the whole experiment. Fig. 4A shows a plot of the half-lives (min) of 4-chlorophenol as a function of the Degussa P-25 concentration. It is observed that the initial disappearance rate increases with TiO_2 concentration both for slurry or immobilized system until it reaches a plateau, indicating a progressive saturation of the photonic absorption by the catalyst for a given incident radiation flux. The initial rate of oxidation of 4-chlorophenol is not affected above 900 mg L^{-1} of TiO_2. This phenomenon may be due to the aggregation of catalyst particles at high concentrations, causing a decrease in the number of surface-active sites and higher hole–electron recombination rates. The increase of the disappearance rate between 100 and 800 mg L^{-1} of TiO_2 is

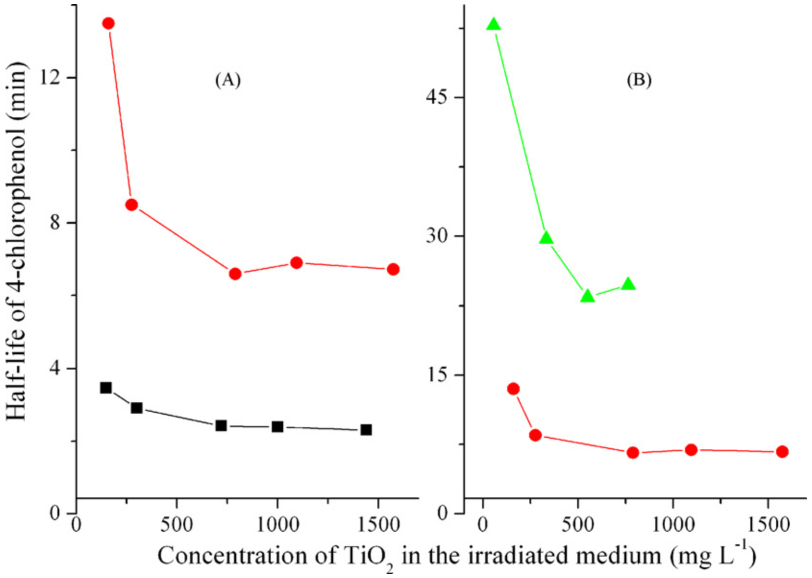

Fig. 4. The influence of the amount of the irradiated catalyst on half-life of 4-chlorophenol: (A) half-life in the range 0–14 min; (B) half-life in the range 0–50 min. (■) The configurations from A to E in Table 1; (●) the configurations from F to J in Table 1; (▲) the configurations from N to R in Table 1.

more pronounced in an immobilized system. The reason could be the penetration of the radiation through the solution and higher absorption of UV radiation by thicker films. In a slurry system, the outer layer of the suspended catalyst absorbs the majority of photons and the core of the tube is actually non-irradiated yet at low concentrations of catalyst. An additional amount of TiO_2 therefore does not improve the photocatalytic activity. On the contrary, the radiation can penetrate all the way to the center of the tube in case of immobilized TiO_2 catalyst.

3.4. Optimizing the configuration of the photocatalytic system

The optimal configuration of our photocatalytic system was determined on the basis of the results, obtained in experiments described in the previous subchapters. The spinning rate was 100 rpm and the solution was purged with oxygen during the whole experiment. The average amount of TiO_2 on each slide was around 36 mg. Lower amounts would have resulted in lower photocatalytic efficiencies while higher amounts would not have brought any significant benefits to the improved photocatalysis. Fig. 2 shows that more slides with immobilized catalyst resulted in higher efficiencies and that the plateau (maximal disappearance rate with immobilized TiO_2) has still not been reached with six TiO_2 films. Therefore, another six slides with immobilized catalyst were incorporated in the photocatalytic cell, which increased the surface area of the slides by a factor of 2 (configuration M from Table 1).

The configuration M was compared to configuration I, which had six TiO_2 slides with the TiO_2 amount on one slide similar to that in configuration M. As a third reference, a slurry system with the highest photoactivity was chosen (configuration D). Indeed, the disappearance of 4-chlorophenol was 1.45 times faster when 12 glass slides (half-life, 4.4 min) were used instead of six (half-life, 6.9 min) (Table 1). Our optimized photocatalytic system with the immobilized catalyst was in this way only 1.8 times slower than the slurry system (half-life, 2.4 min). A difference between slurry and immobilized systems was expected, but it is known from the literature [32] that usually the kinetics of immobilized TiO_2 systems is more than 10 times slower than the kinetics of comparable slurry systems. Moreover, our results are comparable to the most efficient laboratory scale reactors with immobilized TiO_2 [11,13,14].

These results suggest that more than 12 glass slides would still enhance the disappearance rate, but it is physically almost impossible to fasten more 2 mm thick glass slides onto the holder. However, it remains a challenge for us to further improve the configuration of the photocatalytic system by increasing the illuminated surface of the immobilized catalyst.

3.5. Comparison of photocatalytic activities between Degussa P-25 and sol–gel thin films

Sol–gel films, prepared in our laboratory, have already been characterized and the results were published elsewhere [24–26]. Their photocatalytic efficiency was at that time monitored only as a rate of decolourisation of a Plasmocorinth B (an azo dye) in a small tailor-made reactor. The comparison between our films and the standard material has not been performed yet either. A set of experiments with a novel photoreactor was therefore performed in order to obtain additional information on our sol–gel films. The configuration with six glass supports was used for this purpose. The TiO_2 films were deposited on both sides and the amount of TiO_2 was regulated by the number of dipping–heating cycles. Fig. 4B shows that our sol–gel films have considerably lower activity than Degussa P-25 TiO_2 films.

Besides the physical and chemical differences in TiO_2 crystallites, one of the main reasons for the remarkable difference could again be the solid–liquid interface between the TiO_2 particles and the aqueous solution. The P-25 films consisted of very slightly physically adsorbed TiO_2 aggregates (0.1 μm in diameter; the BET surface area of these aggregates is $55 \pm 12\,m^2\,g^{-1}$) on glass surface. This is not a dense, adhesive structure, but rather a structure with a large surface area of TiO_2. Sol–gel deposited film probably had a much denser structure, individual crystallites were connected and consequently the contact area between the TiO_2 and the solution was lower. Therefore, fewer holes and electrons reached the surface and the disappearance rate was slower. It was also observed that the disappearance rate increased only up to TiO_2 concentration of $550\,mg\,L^{-1}$ in sol–gel immobilized system, while in Degussa system the plateau was reached at approximately $800\,mg\,L^{-1}$. The holes and electrons, formed in deeper layers of the sol–gel prepared films were caught in the crystal lattice defects and they recombined before reaching the surface of the catalyst. This also lowered the photocatalytic activity of the catalyst. But the advantage of presented sol–gel films in comparison with Degussa films is their better adhesion to the substrate. They are not detached from the substrate during the photocatalytic experiments (spinning, washing and irradiating) and they did not lose their photocatalytic activity within our experimental period.

Highly mesoporous sol–gel deposited anatase–TiO_2 films would probably yield better results because of higher solid–liquid interface. More work is planned in the preparation of mesoordered porous films and in evaluation of such films for photocatalysis, because very photo-efficient and transparent TiO_2 films have a broader area of application than opaque coatings.

4. Conclusions

A novel CTP for photocatalytic degradation of organic molecules in water has been constructed and evaluated for the photocatalytic degradation of aqueous solutions of organic pollutants. The more glass slides (up to 12 in our experiments) with immobilized TiO_2 were incorporated in the cell, the faster was the photocatalysis (keeping all other parameters the same). The advantage of such a system compared to a classic fixed-bed system is its compactness. A very large surface of immobilized TiO_2 could be efficiently irradiated in a unit of projected area. Another advantage is that such a reactor could probably be suitable for the installation in the CPCs, which are at the moment mostly reserved for TiO_2 slurries. We compared both systems (immobilized and slurry TiO_2) and when 12 slides of immobilized TiO_2 were used, the reaction rate was only 1.8 times slower than in the slurry system, which is a very promising result. We believe that with some additional improvements we can achieve a similar photocatalytic activity as it is achieved with the TiO_2 slurries.

The thin sol–gel transparent films were also applied within the novel photoreactor. The comparison with standard Degussa P-25 immobilized films showed lower photocatalytic activity of sol–gel prepared films. The possible answer of how to prepare better sol–gel based TiO_2 films is higher mesoporosity or depositing TiO_2 on substrates with a large surface area. On the other hand, diminishing of the hole–electron recombinations is beneficial for higher photocatalytic activity.

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