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Solar Heterogeneous Photocatalytic Oxidation for Water and Wastewater Treatment: Problems and Challenges

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Abstract

Solar operation of heterogeneous photocatalytic oxidation reactors is looked at as a sustainable process for water and wastewater treatment, because it does not consume electric power and chemicals. However, there are still problems for technical-scale application. The problems addressed in this article are large area demand, water evaporation from open reactors and lack of simple photocatalyst recovery. An optimum solar reactor type is the parabolic compound collector reactor with borosilicate glass tubes. Challenges for further research are improvement in mass transfer as well as identification of novel photocatalysts which make use also of visible light, are efficient and stable, and are easy to be produced in an economically feasible way. Also the combination of photocatalysts with adsorbents is promising. Although membrane filtration processes have been successfully combined with solar photocatalytic oxidation and represent a safe barrier against spreading photocatalyst nanoparticles into the aquatic environment, more simple and less energy-consuming methods for photocatalyst recovery would be desirable.

Keywords: Mass transfer; Novel photocatalysts; Photocatalysis adsorption hybrid process; Photocatalyst recovery; Solarphotocatalytic oxidation

Introduction

Literature on photocatalysis research is exponentially growing [1] totaling in about 4000 publications in 2011 [2]. Out of these, more than 500 were related to solar photocatalysis [2]. Much attention has been attracted by heterogeneous photocatalysis, i.e. the oxidation of organic substances dissolved in water under UV irradiation in the presence of insoluble photo semiconductor particles (photocatalyst). When photons are absorbed by the photocatalyst particle, electronsare promoted from the valence to the conduction band generating mobile electrons (e^-) and positive charges (holes, h^+). Both charge carriers will either recombine within the particle (or also on the particle surface) or - after arriving at the particle surface - react with molecules attached to the photocatalyst. The holes are strong oxidants and are able to oxidize water molecules forming hydroxyl radicals, ·OH:

$$h^+ + H_2O \rightarrow .OH + H^+ \qquad (1)$$

Also organics adsorbed to the photocatalyst can be oxidized directly by the holes:

$$h^+ + organic \rightarrow organic^+ \qquad (2)$$

The electrons arriving at the surface can react with electron acceptors adsorbed to the photocatalyst such as dissolved oxygen molecules yielding superoxide anion radicals (eq. 3). However, also other oxidants such as peroxodisulfate or hydrogen peroxide can be added to the illuminated photocatalyst/(waste)water suspension. The presence of electron acceptors in the water reduces electron/hole recombination and increases efficiency of heterogeneous photocatalytic oxidation.

$$e^- + O_2 \rightarrow .O_2^- \qquad (3)$$

From the superoxide anion radical or its conjugated acid, the hydroperoxyl radical, HO_2; hydrogen peroxide is formed in different reactions [1]. H_2O_2can take up another electron from the illuminated photocatalyst particle's surface yielding one more hydroxyl radical and a hydroxide anion. Additional to the holes on photocatalyst particles, the hydroxyl radicals represent strong short-lived oxidants which oxidize organic constituents of the (waste) water rather unselectively. As the hydroxyl radicals are formed at ambient temperatures, heterogeneous photocatalytic oxidation belongs to the group of advanced oxidation processes (AOPs). An advantage of heterogeneous photocatalytic oxidation is that no long-lived oxidants are used which cause adverse effects in subsequent treatment stages such as might damage of oxidant-sensitive membranes in membrane filtration processes. AOPs offer an alternative to the ozonation process which is currently being implemented in technical scale as tertiary stage in municipal wastewater treatment plants for the removal of organic micropollutants [3].Heterogeneous photocatalytic oxidation has proved to be suitable for micropollutant removal from biologically pretreated wastewaters, e.g. from greywater pretreated in a constructed wetland [4].Pharmaceuticals were shown to be removed by this process from spiked secondary effluents [5]. Similar to other AOPs and ozonation, heterogeneous photocatalytic oxidation can be used for water disinfection [6,7]. It has to be considered that AOPs are not feasible for the treatment of wastewaters with high concentrations of organics [8]. Therefore, also heterogeneous photocatalytic oxidation is limited to pretreated wastewaters.

Heterogeneous photocatalytic oxidation utilizing UV lamps has been commercialized by the Canadian company Purifics [9]. With respect to UV lamps, Mazzarino [10] has pointed out that a “key factor limiting the feasibility of the process at a real scale” is “the short life of the UV sources that must be periodically replaced”. Additionally, operation of UV lamps means energy consumption which was estimated to account for approximately 80% of the operation cost [11]. Recently, it has been demonstrated that photocatalytic oxidation can also be powered by ultraviolet-light-emitting diodes (UV LEDs) [12-15]. The advantages of UV LEDs over UV lamps are their much longer life-time and the absence of hazardous mercury. However, purchase costs are still higher than for UV lamps. In both UV lamps and UV LEDs, the conversion of electrical to UV power is relatively low. In a study of Levine et al. [15], it was reported to be 13%.

Solar heterogeneous photocatalytic oxidation is a very promising process, because it does not depend on lamps or LEDs. The wavelength of the absorbed photons which is able to generate hydroxyl radicals and holes depends on the band gap of the photocatalyst. The most frequently investigated photocatalyst, TiO_2, exhibits a band gap of 3.0 eV for the rutile modification and of 3.2 eV for the anatase modification. So, TiO_2 can only absorb wavelengths below 400 nm.This spectral range accounts for about 5% of the solar radiation. There is a large variety of other metal chalcogenidephoto semiconductor materials with smaller and larger band gaps available, e.g. MoS_2 (1.75 eV) or ZrO_2 (5.0 eV) [1]. It was shown very early with the photocatalytic degradation of pentachlorophenol that TiO_2 was the most efficient photocatalyst among a couple of metal chalcogenide semiconductors: $TiO_2 > ZnO >> CdS >> WO_3 \approx SnO_2$ [16]. Further advantages of this material are its easy availability (it is an industrial mass product) and its photostability. Contrastingly, ZnO and CdS release divalent metal cations into the aqueous solution under illumination [1].

Problems Experienced with Solar Heterogeneous Photocatalytic Oxidation

In 1993, simple shallow lagoons were suggested as economically feasible solar photocatalysis reactors [11], which are filled with the TiO_2/wastewater suspension and subsequently insolated. However, open solar photocatalytic oxidation reactors will lead to considerable evaporation of water from the suspension especially at higher temperatures as experienced in photocatalytic oxidation experiments performed by the author (Figure 1).On the other hand, elevated temperatures are favorable for enhancement of reaction rate constants according to Arrhenius' equation.However, temperatures >80°C result in increased hole/electron recombination. Moreover, adsorption of organics to the photocatalyst surface decreases with increasing temperature.

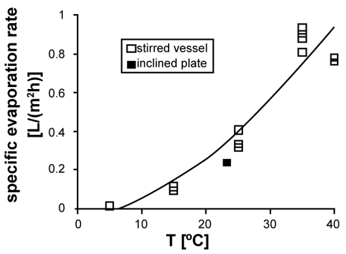

Figure 1: Specific water evaporation rate from uncovered laboratory scale stirred vessel and inclined plate photocatalytic oxidation reactors at different temperatures.

Evaporation in open reactors will become a problem particularly with very thin films of water, i.e. large specific gas/liquid interfaces. High rates of water evaporation and transfer of volatile wastewater constituents to the atmosphere have also been highlighted in a review article about design of solar photocatalytic reactors [17]. In uncovered reactors, the water is also susceptible to contamination by dust and avian excreta. Types of uncovered photocatalysis reactors comprise lagoons, inclined plate reactors, and water bell reactors (nozzles which spray the photocatalyst/wastewater suspension as an unsupported thin film) [17]. In the inclined plate reactor, the wastewater flows as a thin film over an inclined flat surface. The photocatalyst is either suspended in the water or supported on the surface of the inclined plate. The inclined plate reactor can also be covered e.g. with UV-translucent polymethyl methacrylate (Plexiglas®) in order to prevent water evaporation.

A closed reactor type for photocatalytic oxidation which utilizes concentrated sunlight is the parabolic trough reactor; the water/photocatalyst suspension is pumped through a UV translucent tube (made from Pyrex) which is in the focus of a parabolic trough focusing the sunlight on the tube. Another light-concentrating solar photocatalytic oxidation reactor is the optical fiber reactor [17]. Sunlight collected by a parabolic mirror is transferred to the reactor tank via glass fibers. Also immobilization of photocatalyst particles on the glass fibers within the reaction tank is suggested. Although there is an increase in intensity of the incoming light in light-focusing photocatalytic oxidation reactors, Braham and Harris [13] have emphasized two disadvantages of these reactors:1st they require a tracking mechanism controlling the alignment of the parabolic trough with respect to the sun which makes the reactors expensive.2nd they total quantity of photons which can be used by this reactor type is reduced because diffuse sunlight cannot be collected by parabolic concentrators. So, light-concentrating reactors are not suitable for the operation under cloudy conditions. Moreover, with increasing light intensity, electron/hole recombination is intensified leading to impaired quantum efficiencies [2].

Covered reactors which are not concentrating the light are thus a good choice. One type is the double-skin sheet reactor (DSSR) [18]. It is a flat box and consists of two parallel UV translucent Plexiglas® panes with a few centimeters distance between them. Plexiglas® strips around the double-skin encase the reactor content. Further Plexiglas® strips inside the double-skin form channels within the reactor. The water/photocatalyst suspension is pumped through this channel system during insolation. For gathering more practical experience in the field of solar photocatalytic oxidation, a 2 m^2 DSSR was tested by the author for solar PCO treatment of biologically pretreated greywater in Hamburg in summertime. However, the reactor had become brittle subsequent to a storage period of three years under dry conditions. It even showed some small cracks which were sealed by sticking small Plexiglas® sheets over the cracks. Due to the ageing of the Plexiglas® material, UV translucence was massively diminished and the mineralization rate was very low. These results were frustrating when compared to the experience of other investigators [19] with a 27.6 m^2 surface DSSR for solar photocatalytic oxidation of a pretreated industrial wastewater from car production. Those experiments were also accomplished in northern Germany and led to the optimistic assumption that the total organic carbon (TOC) concentration of 0.5 m^3 of a car production wastewater might be reduced with this reactor within one day of solar operation from 10 to 1 mg/L in Brazil.

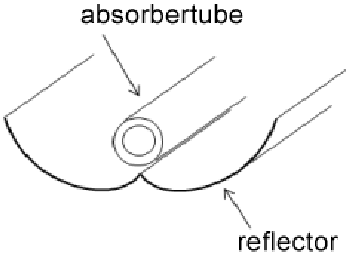

Figure 2: Cross-section of a CPC.

There is agreement among experts that the compound parabolic collector (CPC) is a good choice for solar applications [2,17]. In this type, reactor tubes made from borosilicate glass (transmissive for light with wavelengths above 285 nm) are located in the center of the compound parabolic reflector (Figure 2). CPCs are widely applied in thermal collectors. The advantage of the CPC is that by the reflector geometry also indirect light is reflected to the absorber tube. So, they make use of both direct and diffuse sunlight. A tracking system is not necessary. As reflector material, aluminum is recommended [2]. CPCs in pilot-scale have been investigated in several photocatalytic oxidation studies for the removal of organics from wastewaters [5,20] as well as for disinfection [21].

Another problem arising with heterogeneous oxidation is the recovery of the photocatalyst when nano-sized semiconductor particles are used as photocatalyst without being supported on larger carriers. This problem will be addressed in a particular chapter below.

Overall, insolation on the earth's surface is limited and shows large geographical and seasonal variation. Average data for Hamburg, Germany, are approximately 0.5 kWh $m^{-2}d^{-1}$ in winter and about 5 kWh m^{-2} d^{-1} in summer. It has to be considered that only about 5% of this is represented by UV light which can be utilized by TiO_2photocatalysts. Of course, insolation is significantly larger closer to the equator, for example in Acapulco, Mexico (5.2 kWh $m^{-2}d^{-1}$ in December and 7.4 kWh $m^{-2}d^{-1}$ in April on an average). For different pretreated wastewaters from different origins, areas were calculated that are required for decreasing the TOC of 1 m^3 wastewater to 2 mg L^{-1} by solar heterogeneous photocatalytic oxidation in the presence of 2 g L^{-1} TiO_2 within one day when the insolation is 3.9 kWh $m^{-2}d^{1}$ [22]. These data were based on photocatalytic oxidation experiments with UV-A lamps. For a secondary municipal effluent, the required light collecting area for a purification target of 2 mg TOC $L^{-1}$was 70 m^2, for biologically pretreated greywater even 350 m^2. For an extremely saline biologically pretreated wastewater from chemical industry, more than 1000 m^2 were calculated to treat one m^3 within one day, while for the treatment of pretreated wastewater from a lubricating oil refinery only 19 m^2 were required. These results show that it has to be carefully investigated whether a wastewater is suitable for solar heterogeneous photocatalytic oxidation or not. It has been stated that the large area demand makes solar "photocatalytic processes... currently infeasible to treat large volumes of wastewater" [17]. Large land area is one reason that solar heterogeneous photocatalytic oxidation shows worse results in life cycle assessment than the solar photo-Fenton process, another solar driven AOP [23].

It was shown that the area required for a particular purification target was decreasing with alkalinity of the pretreated wastewaters. The reason for this finding is that a great deal of waters' and wastewaters' alkalinity is represented by dissolved CO_2, hydrogen carbonate or carbonate (depending on the water's pH). These carbon dioxide species are radical scavengers, i.e. they react with hydroxyl radicals forming carbonate radicals ($\cdot CO_3^-$ or $\cdot HCO_3$) which are more stable than the OH radical. This means that rate constants for reactions of these radicals are commonly significantly lower than with hydroxyl radicals. Accordingly, the lubricating oil wastewater with low area requirement for solar photocatalytic oxidation exhibited the lowest alkalinity (75 mg $CaCO_3$ L^{-1}) among the tested wastewaters [22]. However, the matrix does not only impact the efficiency by its radical scavenger concentration, but also by other inorganic cations and anions [24-27].

Two conclusions can be drawn from the stated problems: 1st Real wastewaters should be used for testing photocatalytic oxidation equipment and conditions instead of pure solutions of model organics in deionized water. 2nd Future research should focus on maximizing process efficiency. Improving mass transfer, tailoring photocatalysts for expanding the spectral range of their absorption toward visible light wavelengths as well as combining photocatalysts with adsorbents bear a great potential for reducing area demand for solar heterogeneous photocatalytic oxidation. Also robust and economically feasible photocatalyst recovery is an important area of future research in this field.

Mass Transfer

As heterogeneous photocatalytic oxidation takes place in heterogeneous systems, solid/liquid mass transfer is of eminent relevance in solar reactors. Therefore, non-agitated solar lagoons [11] are far away from being efficient photocatalytic reactors. Diffusionally controlled kinetics in heterogeneous photocatalytic oxidation is discussed in Halmann [28]. It was demonstrated that rate constants for heterogeneous photocatalytic oxidation of benzoic acid increased with Reynolds numbers [29]. The efficiency of photocatalytic oxidation of biologically pretreated greywater in a stirred vessel reactor could be markedly enhanced with increasing velocity gradient [30].

Dionysiou et al. [31] have pointed out that also the gas/liquid mass transfer of oxygen is essential for increased photocatalytic rates. The reason is that dissolved oxygen acts as an electron acceptor which suppresses electron/hole recombination and provides additional hydroxyl radicals as explained in the introduction. In open 1 L stirred vessel reactors for photocatalytic phenol degradation in the presence of 2.5 g L^{-1} TiO_2 which were agitated with magnetic stirring bars at 300 min^{-1}, dissolved oxygen concentrations above 5.3 mg L^{-1} were steadily maintained [32]. However, optimizing gas/liquid mass transfer will also increase water evaporation as discussed above as a problem in uncovered reactors for heterogeneous photocatalytic oxidation. For minimizing evaporation during oxygen transfer, thin silicone rubber tubes can be used which have been investigated for oxygen supply of reactors for aerobic biological regeneration of activated carbon loaded with volatile chlorinated hydrocarbons such as dichloromethane [33].

Maximized mass transfer between photocatalyst and reactor fluid is realized in inclined plate collectors [17] which can also be operated with UV-translucent covers for reducing water evaporation. A variation of this type with intensified mass transfer was the "coated-mat reactor" [34]. In this reactor a mat woven from glass fibers is located on an inclined plate. The glass fibers are coated with immobilized TiO_2 particles and the wastewater is recirculated over the inclined plate.

Mass transfer in tubular reactors can be enhanced by static mixers [35]. Introduction of static mixers into tubes which act as photochemical reactors has been patented [36]. Borosilicate glass tubes with integrated static mixers might be used in CPCs for solar heterogeneous photocatalytic oxidation.

It has to be considered that enhancing mass transfer by turbulences requires mechanical energy input. Solar photocatalytic reactors are expected to be operated in a sustainable way, i.e. without consumption of chemicals (because the catalyst is ideally reused infinitely) and without electric power consumption. It would be desirable to drive the mechanical agitation also by the sun. There is large experience about photovoltaic water pumping [37], and even reverse osmosis modules can be solar-driven [38]. Therefore, it would be reasonable to use photovoltaics also for the operation of heterogeneous photocatalytic oxidation reactors. The problem of power storage does not exist for solar photocatalytic oxidation, because the pumps only need to be operated during the time of the day when the sun is shining. Solar operation of pumps in solar heterogeneous photocatalytic oxidation will significantly improve results of life cycle assessment of this process in the categories global warming potential, ozone depletion potential, photochemical oxidant formation potential, acidification potential and non-renewable energy consumption [23].

When selecting pumps for the reactors, it has to be considered that they have to resist abrasion by the photocatalyst in case of pumping wastewater/photocatalyst suspensions. In solar experiments with a DSSR for mineralization of Acid Orange 7 [39], a centrifugal pump was used. After several months of experiments, the rotating impeller of the pump was destroyed by the abrasive photocatalyst TiO_2"P25".

Photocatalysts Utilizing Visible Light

A vast amount of very optimistic studies have been recently published about photocatalysts which are able to utilize visible light and thus might exploit broader spectral ranges of the sunlight making solar photocatalytic oxidation more efficient. Most of these novel photocatalysts are based on TiO_2 which has been modified targeting to extend the spectral range of TiO_2 into the visible region [40,41]. Luan et al. [42] gave an overview over TiO_2modification procedures for the preparation of tailored titanium dioxide photocatalysts. However, there are also types of novel heterogeneous photocatalysts which are not TiO_2-based, e.g. zinc ferrite, $ZnFe_2O_4$, [43], Bi_2WO_6 [44] or $CaBi_2O_4$ [45], which catalyze visible-light-induced degradation of organics.Unfortunately, most of the novel photocatalysts were tested by using aqueous solutions of pure organic compounds not containing any inorganics. Therefore, most of these studies do not reflect problems arising with real wastewaters.

Modification of TiO_2 can be done by doping with metals and with nonmetals [41]. These features are also termed "cation doping" and "anion doping", respectively [40]. A third possibility is coupling of semiconductor photocatalysts with different energy levels [40].

The following drawbacks of cations doping of TiO_2 were mentioned by Daghrir et al. [40] and by Zhang et al. [46].

Under UV irradiation, photocatalytic activity is usually impaired in comparison to pure TiO_2.

Metal-doping of TiO_2 can lead to thermal instability.

The metal centers in the catalyst particle lead to hole/electron recombination.

They conclude that band gap narrowing of TiO_2 will be better achieved by anionic dopants, i.e. by nonmetal doping. Moreover, it was stated that transition metal-doped TiO_2photocatalysts"suffer from... possible photo-corrosion and harmful nature of the dopants" [47].

Stability of photocatalysts and thus the possibility of their reuse are essential for application in practice. Unfortunately, testing stability of novel photocatalysts is rare [46]. Results of some exceptional studies with respect to stability of synthesized photocatalysts active in the visible spectral range are e.g. the following ones: NB-co-doped TiO_2 showed a small decrease of catalyst activity after four cycles of use [48]. The degradation of Acid Red B with visible light catalyzed by Ag-AgBr-TiO_2 was reported to be not significantly diminished after eight successive cycles of catalyst use [49].

Experiments of the author with modified TiO_2 catalysts which utilize visible light were not successful. When biologically treated greywater was irradiated with visible light in the presence of a $ZnFe_2O_4/TiO_2$ composite catalyst synthesized according to [50], TOC elimination was very small, and the catalyst disintegrated forming a fine suspension. Moreover, a small amount of zinc was dissolved into the wastewater: The background concentration in the biologically pretreated greywater was 12 µg L^{-1}, while subsequent to photocatalytic oxidation the zinc concentration was 19 µgL^{-1}. An S-doped TiO_2 catalyst prepared according to [51] did not show any activity when suspended in biologically pretreated greywater and irradiated with visible light for 4 days. Moreover, the pale yellow colour of the photocatalyst faded more and more during the irradiation experiment. It cannot be concluded by the results whether photocatalyst production conditions (molar ratios of raw materials and calcination temperature) were not in the optimum or whether the catalyst was in general unsuitable for greywaterphotocatalytic oxidation.

Due to the unmanageable diversity of "visible light photocatalysts", comparative studies with respect to stability and photocatalytic efficiency are urgently needed in order to identify the most promising candidates. From an economic point of view, even those novel catalysts which proved to be stable will be hardly competitive with the industrial mass product TiO_2 (which is known to be very stable), because the catalysts exploiting visible light have to be especially produced in more or less complicated processes and require special expertise.

Photocatalyst hybridization with adsorbents

Already in 1988, Matthews has investigated the regeneration of loaded activated carbon by TiO_2based photocatalytic oxidation [52]. The hybrid process of activated carbon adsorption/heterogeneous photocatalytic oxidation attracted a lot of attention since then. Investigations were either carried out with simple mixtures of activated carbon (or other adsorbents) and photocatalysts [32,53-63] or with TiO_2(or other semiconductor photocatalysts)coated on activated carbon [64-77].

Matos et al. [55] found enhanced reaction rate constants of TiO_2-based photocatalytic phenol oxidation when powdered activated carbon was added. The ratio of photocatalytic oxidation rate constant in the presence of activated carbon to the rate constant in the absence of activated carbon was termed synergy factor. Except for phenol degradation, synergy factors above 1 have also been recorded in photocatalysis/adsorption experiments with 4-chlorophenol [56], 2,4-dichlorophenol [73], caffeic acid [63], Direct Blue 53 [58], clofibric acid [60], and cytarabine [62]. The increase of heterogeneous photocatalytic oxidation reaction rate constants was not expected, because the addition of activated carbon reduces light transmission of the suspension.

It was hypothesized that photocatalyst particles in simple slurries of TiO_2/powdered activated carbon mixtures are attached to the activated carbon surface (similar as in photocatalyst/activated carbon composites) and thus diffusion pathways of organic molecules from activated carbon adsorption sites to the surface of the illuminated photocatalyst surface are very short [55]. Lim et al. [78] have optimistically stated that "this overcomes the perceived shortcoming of heterogeneous photocatalysis (i.e. mass transfer limitation and low photonic efficiency) that has been limiting its applications in water treatment". Asenjo et al. [79] have contradicted the hypothesis of decreased diffusion pathways in activated carbon/photocatalyst conglomerates being responsible for increased rate constants. They argued that the desorption path (from the activated carbon) cannot contribute significantly to the global reaction rate because the desorption rate constant based on data of Matos et al. [55] was much lower than the reaction rate constant.

A further hypothesis for causes of increased photocatalytic rate constants by addition of activated carbon is that TiO_2 and activated carbon form surface nano-aggregates (as shown by electron microscopy [80]) and that Ti centers on the photocatalyst surface coordinatively interact with particular surface groups on the activated carbon surface [80] (as concluded from the disappearance of signals for cyclic ether groups in the infrared absorption spectrum of activated carbon when TiO_2 was added [61]). This coordination is assumed to enable the transfer of charge carriers between photocatalyst and activated carbon [80,81]. The transfer of electrons from the illuminated photocatalyst particle into the adjacent activated carbon particle is suggested to suppress electron/hole recombination and thus to increase photocatalytic efficiency. The increase of photocatalytic oxidation rate constants has only been observed with particular kinds of activated carbon while others did not show this phenomenon designated as synergy [32,80,82] (see also Figure 4). Different impact of particular activated carbons on synergy was explained by different functional surface groups present on different kinds of activated carbon [80].

Another feature discussed to be involved in photocatalysis/activated carbon adsorption synergy is the regularity of graphene layers in the graphite microcrystallites forming the activated carbon [78]. The higher the order of the graphene layers in the activated carbon is, the more similar the activated carbon becomes to graphite and the higher is the electric conductivity of the microcrystallites. A larger conductivity in the activated carbon will increase its ability to transport the charge carriers injected from the illuminated photocatalyst particle attached to the activated carbon grain thus decreasing electron/hole recombination in the photocatalyst.

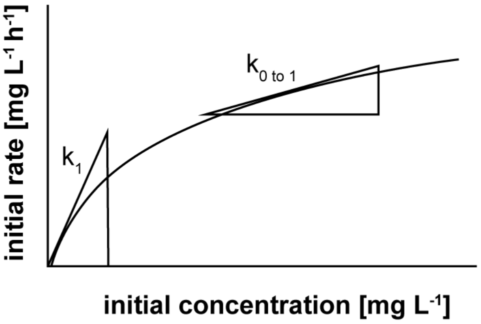

Figure 3: Schematic of Langmuir-Hinshelwood kinetics.

Explaining the synergy phenomenon in photocatalyst/activated carbon hybrid systems remains hypothetical in spite of a great deal of research in this area. Recently, it has been claimed that the synergy observed for photocatalytic oxidation of phenol was based on a misinterpretation of kinetic data [79]. It is widely accepted that heterogeneous photocatalytic oxidation follows Langmuir-Hinshelwood kinetics (Figure 3). For very low concentrations of the organic in the liquid phase, an apparent first order kinetics is observed, i.e. equation 4 describes the dependence of the reaction rate on the initial concentration of the organic molecules in the aqueous solution, c_L. The apparent first order rate constant is designated as k_1 (index 1 for 1st order) in this context.

$$\text{rate} = k_1 \cdot c_L \quad (4)$$

When the initial concentration of the organic in the liquid phase is increased, the kinetic regime is no longer first order. At very high concentrations, the rate does no longer depend on the concentration in the liquid phase and the graph approximates a horizontal line describing zeroth order kinetics. So, there is a large concentration range where the reaction order is between 0 and 1. When for this range first order kinetics are erroneously assumed, smaller rate constants will be determined under the wrong premise of differentiating equation 4 resulting in equation 5.

$$d(\text{rate})/dc_L = k \quad (5)$$

So, it is obvious that rate constants determined under the wrong assumption of an apparent first order kinetics regime will increase when the organic concentration in the liquid phase is decreasing due to addition of activated carbon (compare k_{0to1} to k_1 in Figure 3).

Experimental data from studies on the hybrid process with phenol [83] (Figure 4a) and 4-chlorophenol [82] (Figure 4b) testing different activated carbons support this view. H-type (activated at high temperature) and L-type (prepared by low temperature chemical activation) activated carbons were tested. In the experiments always the same amounts of activated carbon and TiO_2 in phenol solutions were agitated for 80 min (Figure 4a) or 60 min (Figure 4b), respectively, in order to establish adsorption equilibrium. Then UV irradiation was switched on. Apparent first order rate constants obtained during UV irradiation of mixed activated carbon/TiO_2 suspensions were either divided by rate constants for photocatalysis without activated carbon [83] or by the sum of rate constants for photocatalysis in the absence of adsorbent and for photolysis (UV irradiation in the presence of activated carbon but without photocatalyst) [82] for calculating synergy factors. Although there is some data variation in Figure 4a, it can be generalized that higher synergy factors were obtained when more of the phenol was adsorbed. The data in Figure 4b shows a larger extent of variation. However, when only the H-type activated carbons are considered, the same trend is visible for the experiments with 4-chlorophenol. In another synergy study [32] the activated carbon showing a synergy was the better adsorbent for phenol than the activated carbon which did not exhibit a synergy. This data can be interpreted as follows: The more of the phenol is adsorbed, the lower is its concentration in the aqueous solution and the larger is the slope of the Langmuir-Hinshelwood curve in Figure 3. This might be misinterpreted as a "synergy effect".

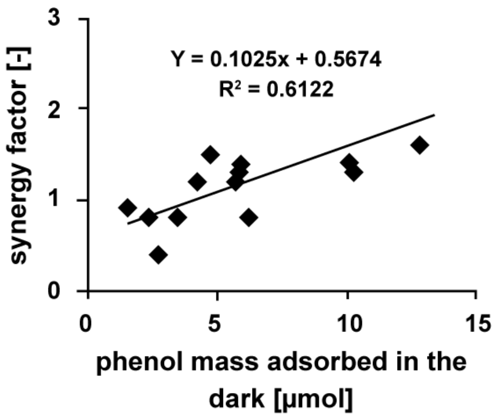

Figure 4a: Synergy factors from a study using phenol and different activated carbons (data from [83]).

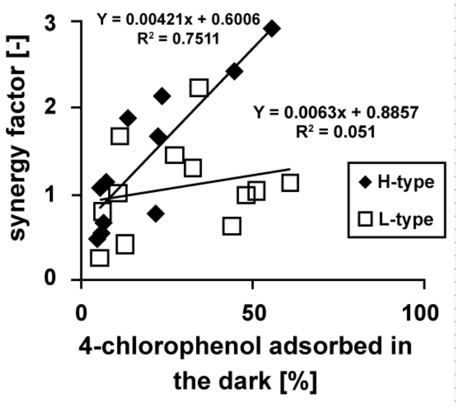

Figure 4b: Synergy factors from another study using 4-chlorophenol (data from [82]).

Irrespective of the question whether the claimed synergy in the photocatalysis/activated carbon adsorption hybrid process is a myth or not, the following conclusion can be drawn: The combination process is a promising hybrid technology for advanced treatment of waters and wastewaters leading to safe reduction of organics. When biologically pretreated greywater was UV-irradiated in the presence of powdered activated carbon and TiO_2, a TOC concentration below 2 mg/L was achieved even after reusing the photocatalyst/activated carbon mixture several times [59] although no synergy was observed. It was estimated that the combination process requires only about 1/7 of the area which is necessary for solar photocatalytic oxidation in the absence of activated carbon. Increased TOC concentrations subsequent to greywater irradiation with progressing reuse of the photocatalyst/activated carbon mixture however clearly indicated that the in situ regeneration of the activated carbon was not complete. Photocatalytic regeneration of activated carbon has been modeled for a photocatalyst/activated carbon composite [84].

Another adsorbent which has recently been tested in the adsorbent/photocatalyst hybrid process by the author is the anion exchange resin Lewatit MP 500. Anion exchange resins are suitable for the adsorption of anionic organics such as humic or fulvic acid anions and also dyes (e.g. Reactive Blue 4). Unfortunately, consecutive reuse of Lewatit MP 500/TiO_2 mixtures for photocatalytic oxidation with fresh batches of biologically pretreated greywater led to decreasing removal of the organics from reuse cycle to reuse cycle. The same was observed with aqueous Reactive Blue 4 solutions. This may be explained by progressing oxidative damage of the organic anion exchange resin during photocatalytic oxidation.

Photocatalyst Recovery

Because of their larger photocatalytic efficiency, nano-sized photocatalyst particles are superior to micro-photocatalyst particles [85-87]. Unfortunately, TiO_2 nanoparticles are toxic contrasting to larger TiO_2 particles which are even used as food additives or abrasives in tooth paste. Nanoparticles cannot only enter cells but also mitochondria and nuclei. They interact with cytoskeletal proteins affecting a variety of cell functions [88]. Concentrations of TiO_2 particles with about 100 nm diameter as low as 2 mg L^{-1} led to immobilization of Daphnia magna, while 200 nm TiO_2 particles were less toxic [89]. It has to be considered that municipal treatment plants do not represent a safe barrier against spreading of nanoparticles into the aqueous environment [90]. From this point of view, safe photocatalyst nanoparticle retention in photocatalytic oxidation reactors is of eminent importance.

Sedimentation is usually not feasible for recovery of suspended photocatalyst particles. Sometimes it is even difficult to separate the photocatalyst by centrifugation. Depending on the wastewater matrix, the photocatalyst nano-particles can agglomerate [91]. However, the influence of wastewater constituents on photocatalyst flocculation is extremely complex [92]. Sand filtration was able to remove TiO_2 nanoparticles when they flocculated but not under conditions where no flocculation took place [93]. Hydrocyclones were suitable for photocatalyst recovery when the particle size was in a range of 1 to 100 µm diameter [94].

Recently, a sheet-like ZnO assembly has been synthesized exhibiting a particle size of 10 µm [95]. Combining these particles with silver particles in a mass ratio of 1% resulted in good photocatalytic activity. For recovery, the particles were separated by centrifugation. They were reused 5 times for methyl orange photocatalytic oxidation showing less loss of activity than TiO_2"P25" in the reuse experiments. Also a porous titanium-niobium mixed oxide photocatalyst with good settling properties was described [96].

Immobilization of photocatalyst nanoparticles on larger and thus settleable particles is a means for simple sedimentative photocatalyst recovery. Composites made from photocatalyst nanoparticles and adsorbents [66-77,84] combine this with the advantages described in the previous chapter. Wet chemical impregnation methods for preparing TiO_2/adsorbent nanocomposites were reviewed in [47].For magnet photocatalyst recovery; photocatalysts can be coated on magnetic carrier particles [97]. Another possibility is the coating of photocatalyst nanoparticles on particles with a lower density than water which can be separated by flotation. Support materials for these "buoyant"photocatalysts can be polypropylene granules [98], polypropylene fabric [99], or hollow glass spheres [100,101]. Hollow glass spheres are not mechanically stable. Thus, they should not be applied when the composite/water mixture is agitated by pumping.

Vinu and Madras [1] have listed the following supports for the immobilization of TiO_2: glass beads, flexible fiber glass cloth, glass tubes, cotton, PTFE mesh sheets, polystyrene beads, perlite, and porous lava. Further supports are activated carbon (as mentioned above), vermiculite and volcanic ash [102]. Alsosteel [103], paper [104] and concrete [105]were tested as support materials.

Coating photocatalyst nanoparticles as films is a good option for photocatalyst retention in the photocatalytic reactor as long as the photocatalyst is stably fixed on the support. The "thin-film fixed-bed reactor" [19] and TiO_2 coated to tubes which are used in CPCs [106] are examples for reactors with immobilized photocatalyst films.

Similar to preparation of novel visible-light catalysts, the production of composite catalysts and photocatalysts supported as films requires special expertise. Moreover, the stability of the composites and films is decisive for their application. Doll and Frimmel [107] have tested techniques for immobilizing TiO_2 films on glass with photocatalytic oxidation experiments in mini flow-through reactors. They stated that the investigated techniques resulted in good photocatalytic activities with good long-term stabilities. However, coating of photocatalysts to supports does not always lead to stable films or composites. There is some concern about this. Kodom et al. [104] emphasized that coating of TiO_2 to non-woven paper requires several times washing in order to remove non-bound particles. Experience of the author with a TiO_2/Zn_2O_4/activated carbon composite photocatalyst prepared by himself according to [50] was similarly unsatisfying as with the unsupported TiO_2/Zn_2O_4 photocatalyst described in the section about "photocatalysts utilizing visible light". After the composite was recovered by sedimentation subsequent to the first cycle of photocatalytic oxidation of a biologically pretreated greywater sample, it was only poorly efficient and showed only a reduced adsorption capacity for the greywater organics. Moreover, within the first reuse cycle, the catalyst developed a green colour. It is assumed, that this catalyst is not sufficiently stable for being used several times.Additional to problems with stability, a common drawback is that photocatalysts coated to supports were frequently found to be less efficient than slurries of non-supported photocatalysts [21,108 -110].

Membrane filtration - in most cases microfiltration - was intensely investigated for photocatalyst recovery [109,111]. However, also ultrafiltration and nanofiltration were combined with heterogeneous photocatalytic oxidation [112]. Also submerged microfiltration modules (as widely used in commercially available membrane bioreactors) were investigated in photocatalytic membrane reactors [113]. It was early recognized that efficient particle filters for photocatalyst retention add to the cost and complexity of solar photocatalytic oxidation systems [110]. Membrane filtration will significantly increase power consumption of heterogeneous photocatalytic oxidation. A sustainable option might be powering membrane filtration by photovoltaics as discussed above for intensification of mass transfer.

The membranes are either used for retaining the photocatalyst applied as slurry or they serve as support for photocatalyst immobilization [112]. In the latter case – referred to as "photocatalytic membranes" [109], the membranes have to be illuminated. When organic polymer membranes are coated with photocatalysts and irradiated, this might lead to damage of the membrane either by UV light or by oxidative attacks of hydroxyl radicals [112]. On the other hand, mass transfer of organics to photocatalyst particles is enhanced in photocatalytic membranes [109]. Decreased membrane fouling is another advantage of photocatalytic membrane reactors with photocatalysts immobilized on or in the membrane [112]. Xiao et al. [114] have recently reviewed in depth two categories of photocatalytic membranes: TiO_2-entrapped membranes and TiO_2-deposited membranes.

The most often investigated photocatalytic membrane reactors apply microfiltration or ultrafiltration membranes which are not coated by photocatalyst, but are used for retention of photocatalyst suspended in the feed solution [112]. However, low permeate fluxes and massive membrane fouling were observed in this reactor type [111,112]. Especially when removal of organics by photocatalytic oxidation is incomplete, interaction of residual organics and suspended photocatalyst particles lead to dense cake layers at the membrane surface resulting in membrane fouling and permeate flux decline [111]. However, Huang et al. [115] found that photocatalytic oxidation is effective in controlling membrane fouling in drinking water treatment, because the "natural organic matter" (NOM) contained in raw drinking water is subjected to changes in molecular weight. Predominantly, large hydrophobic NOM compounds which play a role in membrane fouling are removed by heterogeneous photocatalytic oxidation. The photocatalyst concentration in TiO_2 slurry photocatalytic membrane reactors is influencing the flux decline in a complex way as discussed by Mozia [112]. Increasing cross flow velocity of the feed in the membrane module as recommended in [112] will increase electric power consumption of the photocatalytic oxidation reactor, however.

Research on photocatalytic oxidation membrane reactors is usually done in laboratory scale and the investigations are not run on a long term. Therefore, the question arises whether organic polymer membranes are damaged by abrasion due to photocatalyst particles when they are used for a long period. Doll and Frimmel [116] found organic polymer membranes susceptible to abrasion and therefore selected a ceramic single channel microfiltration membrane made from α-aluminum oxide for their investigations. Also the commercially available Purifics process is equipped with ceramic membranes [9].

A low-cost filtration technology for photocatalyst recovery might be pre-coat filtration of TiO_2 nanoparticles by means of powdered activated carbon with simple fabrics. Nonwoven polypropylene fabrics did not reject the nanoparticles when no powdered activated carbon was added. However, preliminary tests revealed that around 90% of the entire particulate material can be retained on the fabric filter when 2 gL^{-1} of powdered activated carbon are added to 1 gL^{-1} TiO_2 suspension [92]. In that study, TiO_2/powdered activated carbon suspensions were filtered over small fabric pieces by means of vacuum. Unfortunately, the particle concentration in the filtrate was varying to a high extent. In order to evaluate which percentage of the particles in the filtrate was represented by photocatalyst particles, further experiments with varying TiO_2 concentrations, but a constant powdered activated carbon concentration (2 gL^{-1}) suspended in deionized water were performed by the author in a similar way. The ash content of the particles in the filtrate was gravimetrically analyzed after glowing at 550°C. The ash content determined in the filtrate was increasing with increasing TiO_2concentration in the original suspension (Figure 5).This increase was caused by TiO_2 particles which escaped with the filtrate. Total solids concentration in the filtrate varied between 10 and 200 mg L^{-1}.

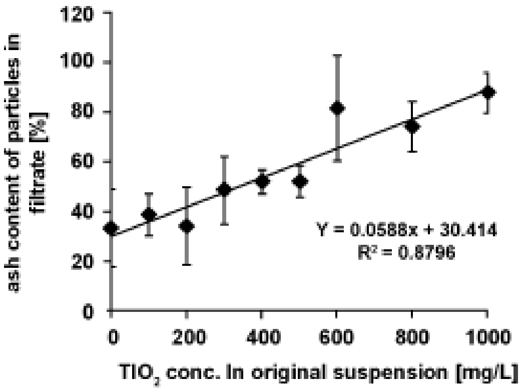

Figure 5: Ash content of particles in the filtrate after filtering powdered activated carbon suspensions (2 gL^{-1}) in deionized water containing different concentrations of TiO_2.

So, this low-cost alternative to membrane processes does not act as a safe barrier. Filtering a 20 mg L^{-1} TiO_2 suspension in deionized water over a 30 cm deep layer of granular activated carbon resulted in a clear filtrate as examined by the author. It might serve as a final TiO_2 retention stage subsequent to precoat filtration. However, breakthrough curves for processing larger volumes were not yet recorded for this technique. The disadvantage of an additional activated carbon filter is that this has to be periodically backwashed. The research on this low-cost option for photocatalyst recovery by precoat filtration using powdered activated carbon will be continued, because it has been shown that mixing adsorbents with photocatalyst is advantageous in photocatalytic oxidation (see previous chapter). Precoat filtration might be feasible as a pretreatment for membrane filtration [92] and alleviate problems like flux reduction and fouling which was observed in photocatalytic membrane reactors.

Conclusions

A couple of problems are known to hinder technical scale application of solar heterogeneous photocatalytic oxidation. The main obstacle is the large land area demand for the solar process. To overcome this problem is a challenge for researchers in this field. Strategies which have been investigated are increase of mass transfer, synthesis of innovative photocatalysts which are able to utilize also photons with wavelengths in the visible range and combining photocatalysts with adsorbents. It is inevitable that innovative photocatalysts and also photocatalyst/adsorbent composites are tested for their long-term stability. This has not yet been done with all novel products described in literature. Besides the availability of reproducible preparation methods for visible-light photocatalysts and photocatalyst/adsorbent composites, comparative studies on their stability and efficiency are required. It is recommended that such studies are done with real raw waters or (pretreated) wastewaters rather than with aqueous model solutions of pure organic compounds in order to include also impacts of the water matrix on the stability and efficiency of the catalysts. It is assumed that special sophisticated methods as well as particular chemicals for the synthesis of novel photocatalysts will lead to costs which are not competitive with expenses for the industrial mass product TiO_2. The combination of TiO_2 with suitable activated carbons still has high chances for technical application with respect to photocatalyst stability and economic issues. For solar application, closed reactors (preventing water evaporation) with compound parabolic collectors are presently favored by many researchers in this field. Another challenge for technical application is photocatalyst recovery. As many composites with high settling velocity have not yet been investigated for long-term stability, the use of ceramic membranes which will resist to abrasion by suspended photocatalysts may be an option in the future. However, similar to mass transfer intensification, membrane processes require electric power. Therefore, it is recommended to combine solar heterogeneous photocatalytic oxidation with photovoltaics. In order to reduce fouling problems in photocatalytic membrane reactors, another photocatalyst removal stage such as sedimentation or precoat filtration prior to membrane filtration might be advantageous, especially when solar photocatalytic oxidation is operated in batch mode.

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