Photooxidation in Combination with Nanotechnologies - Principles, Developments and R&D Approaches of an Advanced Technology for Water and Air Treatment - *Uviblox*®

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Abstract:
Many organic and oxidizable inorganic substances are main targets for oxidation and destruction during treatment, purification and disinfection of contaminated ground water, waste water, air, soil and waste gas and odor. *Uviblox*® technology uses the effects of photooxidation and photocatalytical processes by middle and low pressure UV lamps for technical systems. There are many possibilities for combination and optimisation of photooxidation with other technologies like nanotechnologies. Degradation processes can be enforced by nano structures of photocatalysts significantly. Different approaches are strongly pursued in research & development projects like NanoAqua, Fe-NANOSIT and *nanoblox*. These projects search for different ways of applying and handling the photocatalytical nano particles like TiO_2 and ZnO. Biological surface layers, magnetite, transparent and reflecting materials are tested for suspending nano particle solids as well as for coating fixtures. Research results are very promising and economic application of nano photocatalysts in water and gas phase for purification seems likely. Any presumed ecotoxicity was not found for the examined nanoparticles so far.

Introduction

Photooxidation can be used as water treatment technology which is well known for disinfection of potable water. Also the application as an AOP-technique (Advanced Oxidation Process) for elimination of contaminants in the water phase is often documented. Experiences in this field did not show good results with the available techniques in the past (1). The old systems were expensive due to high operational costs and often were not efficient. Sometimes problems with forming of undesired byproducts occurred. So in former times this technique did not win a lot recognition in a wide field of application. Meanwhile UV-photooxidation processes have been continuously developed during the last years. Today effective systems for water or gas phase treatment are in great demand. Beside low invest and operational costs a technique should be characterised by small requirements to installation spaces and high process stability. Flexible adjustment of the system with respect to future capacity increase or on the other hand process integrated reduction of emission are favored. The new developed technology of photooxidation *uviblox*® shows the ability to fill the bill.

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Rigorous regulations like e.g. the EU-VOC (Volatile Organic Compounds) directive have caused the need for development of waste air treatment technologies for remediation and industry processes. On the other hand the traditional treatment techniques like thermic oxidation for gas treatment or activated carbon adsorption for water treatment are very expensive. This brought much attention and investment in the area of Advanced Oxidation Processes (AOP), specially the UV-photooxidation (1). UV-technology is an established technology for the disinfection of drinking water. On the contrary the degradation of contaminants with UV-irradiation has never been a market for mass products, because every case of waste gas and water is different and needs intelligent adapted techniques for purification. But time passed with many developments in this area in the last 5-10 years and the developments are still on-going (energy supply, lamp efficiency, reactor geometry, etc.).

UV-photooxidation technology is based on the main rules in oxidation processes by producing highly reactive radicals for oxidizing pollutants. They can be produced with H_2O, H_2O_2, O_2 activated by special VUV light (vacuum-ultra-violet). Furthermore VUV light can charge organic compounds directly by photolysis. Many organic and oxidizable inorganic substances are the main targets for oxidizing and further destruction in treatment, purification and disinfection of contaminated water, wastewater, air, waste-gas and odor by this UV-technology. There are a lot of possibilities for combination with other technologies like e.g. bioengineering and nanotechnologies. Toxic substances can be metabolized by VUV so that they will become available for microorganisms and thus for biological degradation processes.

Materials and Methods

Photooxidation

Light is a radiation and its energy content is correlated directly with its wavelength. UV radiation is a powerful radiation and can be used for the technical degradation of contaminants. UV-light can be divided into UV-A, UV-B, UV-C and VUV. VUV (vacuum UV) is defined as radiation with wavelengths below 200 nm. Within UV-light VUV shows the highest energy density (2). This radiation can be measured precisely only in a vacuum space system, cause this radiation would be absorbed by air molecules.

A typical UV lamp emits light with different wavelengths (Figure 1). For the destruction of a contaminant by UV-light the contaminant has to absorb the emitted energy from the lamp that means the maximum of emission of the light should be close to the maximum of the specific absorption of the molecule. This process of destruction is called photolysis. Absorption maxima of molecules are depending on the type and number of their chemical bonds and are known for nearly all substances (2).

Direct photolysis is also used for the disinfection of water or air. In this case cells, proteins, nucleic acids with their maximum of absorption near 254 nm correspond to the main emitting line of so-called low pressure (LP) UV-lamps. When these substances can be cracked, the microorganisms will be inactivated and loose their ability for growth or reproduction.

Direct photolysis with VUV is not the only effect for degradation. During homolysis of water and peroxide OH-radicals are formed. Oxygen can be ozonolyzed and the ozone will generate ozone radicals. Both kinds of radicals will cause chain reactions with the organic contaminants. There are further possibilities of combining these processes with photocatalysis and integration of catalysts online or in series (3).

<u>Photolysis</u>

Direct photolysis of organics:

$$R\text{-}R + h\nu \rightarrow R^{\bullet} + R^{\bullet} \rightarrow n\,CO_2 + m\,H_2O \quad (1)$$

<u>Ozonolysis</u>

Activation of oxygen:

$$O_2 + h\nu \rightarrow O_3 \quad (2)$$

Photolysis/homolysis of ozone:

$$O_3 + h\nu \rightarrow O^{\bullet} \quad (3)$$

<u>Homolysis</u>

Photolysis/homolysis of water:

$$H_2O + h\nu \rightarrow OH^{\bullet} \quad (4)$$

Photolysis/homolysis of peroxide (water):

$$H_2O_2 + h\nu \rightarrow 2\,OH^{\bullet} \quad (5)$$

In technical solutions UV-lamps are equipped with power supplies and are integrated in special reactors. A typical UV-lamp is constructed as a glass tube closed on both ends after filling with a mixture of noble gases under pressure, doted with mercury and other metals. By connecting a certain voltage with special frequency a plasma between the electrodes will be fired. This plasma emits a spectrum of light with different wavelengths. Depending on the filling pressure two main types of lamps can be differed, low pressure lamps (LP) and middle pressure lamps (MP). Low pressure lamps (LP) have a filling pressure < 1bar and show two emission lines at 185 nm and 254 nm. These lamps are used for water disinfection all over the world and are mass products. Low pressure lamps can be built with power outputs ranging from 10 to 400 W.

The filling pressure of middle or high pressure lamps (MP) varies from 1 to 10 bar. Lamps with 1.000 to 32.000 W with nearly continuous emission spectra can be produced (Figure 1). Because an optimum of emission has to be found for each individual application these lamps are custom products. The advantages of UV MP-lamps are high power density, middle to high recovery of UV-C and VUV, long life time, polychromatic emission, bowlength up to 2 m, few loss of energy at the power supply and low operational costs.

In former days the supply of these MP-lamps with electrical power was realized by conventional magnetic power supplies. They were large and heavy and had a high loss of energy. The UV-emission and lamp power of MP-lamps were waving and toddling. Starting of MP-lamps with conventional power supplies caused high peaks of power consumption which led to low life time cycles. Today special adapted electronic power supplies (EVGs) are used, which are small, light and allow gentle operation of the lamps by stepless control. EVGs can be operated with normal or high voltage frequency.

By installing lamps in rows or serial integration of lamp row modules all sizes of reactors can be realized for the optimal design of the flow dynamics. The main

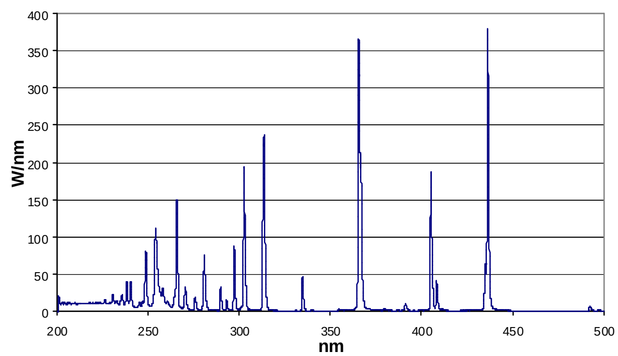

Figure 1. Emission spectra of a typical MP-UV-lamp (10kW).

challenge for a custom made solution lies in the optimal combination of lamp, EVG, reactor and combined processes. Special attention has to put on the parameters of operation which are different for the various composition and type of organic contaminants.

Nano Catalytic Particles and Nano Photocatalytic Particles

Today there are many research & development activities in the field of nanotechnologies, where the application for UV is a great spot of interest. The development of catalysts based on nano particles is in progress. Nano catalysts combined with photocatalytic substances can support VUV oxidation processes with high efficiency.

Nanotechnology, sometimes shortened to "Nanotech", refers to a world of atomic and molecular scale. Generally nanotechnology deals with structures of 100 nanometers or smaller and involves developing materials or devices within that size.

Nanotechnology is applied or developed in many areas. New materials like Fullerenes or Carbon-Nanotubes are already used in a wide range of daily application.

Nanotechnology is also in the focus of present R&D projects related to the purification of water and gas phases, for which the main task is to develop nanoparticles from oxidizing compounds like nano-iron or nano- catalysts (4).

A promising option for the production of efficient photocatalytic layers is the use of semi-conductor photocatalysts like nano based TiO_2- or ZnO in flatbed reactors. However, disadvantages of this technology are caused by the small depth of penetration by light which allows only the treatment of thin films in flat beds. To reach the required volume rates for waste water treatment large scale areas have to be considered. Similar problems arise with the development of fall film reactors.

One possibility for improvement of photocatalytic processes regarding efficiency and simplifying is the application of suspensions of nanoparticles. Due to the favorable relation between surface and volume, nanoparticles show high catalytical activity.

A problem that may arise by using nanoparticles is their potential toxicity. Hence, immobilization is essential to guarantee a reliable particle displacement, to ensure their recovery and to avoid entry to the environment. A solution for this problem is the deposition of nanoparticles on microscale particles which can be separated or sedimented. These composite structures allow to retain a large surface area and effective separation from the water phase for recovery and re-use.

Disadvantageously by using suspensions of nano particles is straying of light at high particle concentration which leads to high reduction of irradiation of the particles and in the end low photocatalytic activity. One approach to overcome this problem is the application of transparent or UV light reflecting micro particles which would help to reach a higher light permeation in the water. The combination with magnetized materials will enable the separation of the catalysts.

R&D Projects (Results and Discussions)

NanoAqua

At present, the project NanoAqua, a cooperation with the Helmholtz Centre Dresden-Rossendorf HZDR explores biotechnological potentials (biocomposite) of nanotechnology (5). The concept considers three main aspects. Self organizing bacterial surface proteins are able to fix metal oxides (Figure 2). TiO_2- exp. ZnO-nano particles are immobilized by this effect. Surface proteins themselves can be fixed on carrier materials.

Surface proteins or surface layer (S-layer) represent the biological and technological basis. These self organizing proteins generate the outer surface of many bacteria and protect against environmental influences. After isolation these proteins generate very regular lattice structures with different symmetries like shown in Figure 2. They form monolayers with 10 nm thickness and are applicable for coating of different materials. Furthermore these S-layers are able to bind anorganic nano particles (Figure 3).

To reach highest permeation of irradiation transparent (glass, quartz sand) and/or reflecting (mica, bariumsulphate, aluminium flitter) micro particles have to be used. As photocatalysts TiO_2 or ZnO-nanoparticles were chosen, also with doping materials with a size of 14-18 nm (Figure 3).

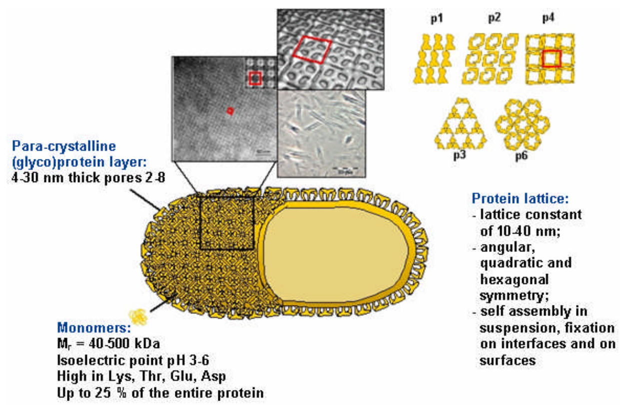

Figure 2. Structure of the bacteria of surface proteins (S-layer) (5).

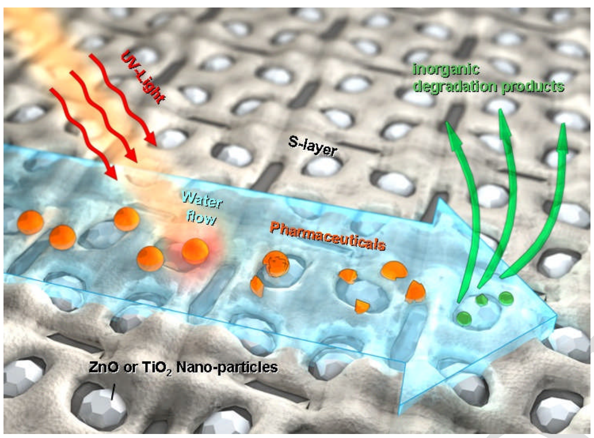

Figure 3. Technological concept of photocatalytical layers with S-Layer and photocatalytical nano particles (5).

This technology concept was tested for the degradation of well known substances such as toluene (Figure 4) as well as pharmaceutical substances, e.g. diclofenac (Figure 5). Figure 4 shows the high reactivity of ZnO fixed on different S-layers generated under different temperature conditions (methods 1-3) for the degradation of toluene.

S-layers from different bacteria were fixed with polyelectrolyte layer on suspended carriers (aluminium flitter). It is obvious that the type of bacterial S-layers and the methods of generation have a significant influence on the efficacy of photooxidation.

First tests were performed with a low pressure UV-lamp (20W, 300nm). For further specified examination middle pressure UV-lamps were designed and produced which showed an emission spectrum such as shown in Figure 1. These lamps not only generate UV-A emission for activation of ZnO or TiO_2 (photocatalysis) but also UV-C and VUV for direct photolysis, ozonolysis and homolysis. Therefore they promise much higher synergetic effects for degradation.

For the performance of further tests pilot systems were designed and built (Figure 6).

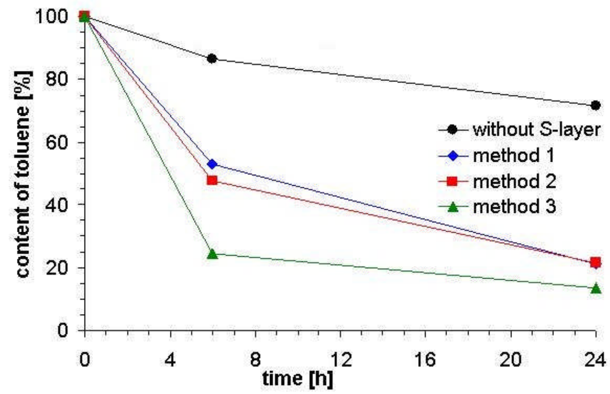

Figure 4. Degradation of toluene under UV-light with ZnO on S-layer of Lysinibacillus sphaericus JG-A12. (methods 1-3: different production temperatures) (5).

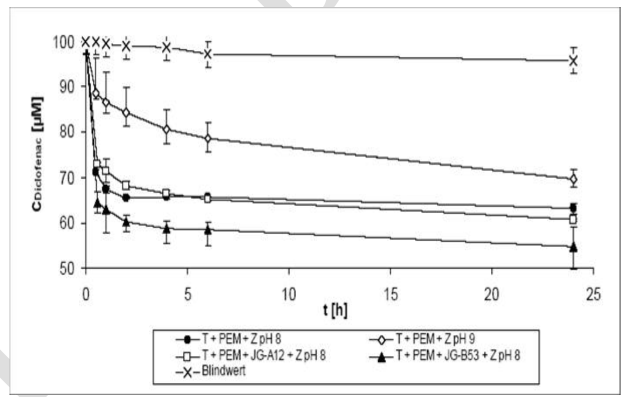

Figure 5. Degradation of diclofenac under UV-light with ZnO on S-layer/polyelectrolyte layer/carrier and different pH values. (T = carrier: aluminium flitter, PEM = polyeletrolyte layer, Z = ZnO, JG-A12/JG-B53 = different bacteria strains) (5).

Fe-NANOSIT

Within the project Fe-NANOSIT, a cooperation with the Helmholtz Centre for Environmental Research Leipzig (UFZ), catalytic and phototcatalytic nanoparticles will be fixed on iron-based microparticles (6). The resulting nanocomposite structures can be used for treatment of contaminated groundwater and waste water.

The aim is to develop first iron/carbon-composites (carbo iron) as in situ agents for the treatment of groundwater. By variation of particle size, modification of surface charge, hydrophobicity and the use of different additives such as carbon, catalyst or specially developed coatings the properties of these nanoparticles will be improved and optimized for the technical application.

Furthermore magnetic nanocatalysts will be applied for the selective reductive AOX-elimination (Pd/magnetite) and for photooxidation of contaminants (ferrite/TiO_2/ZnO) in waste water (Figure 6). Magnetite

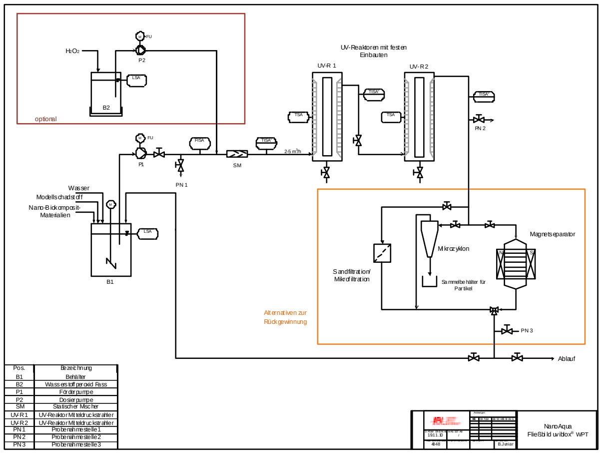

Figure 6. Pilot system for NanoAqua.

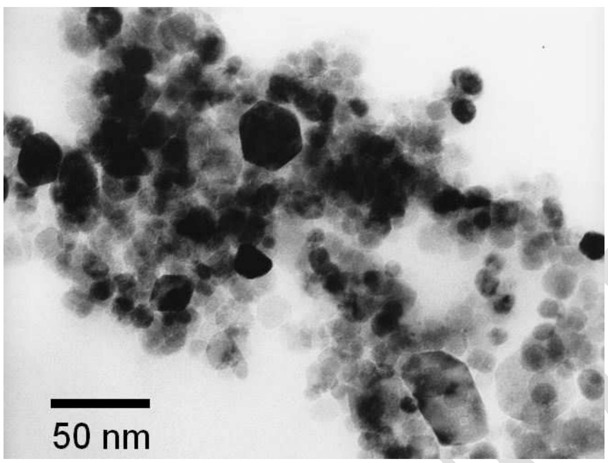

Figure 7. Pd/magnetite nanocatalysts (6).

appears to be capable not only as a carrier, but also as a promising catalyst for heterogeneous Fenton reaction because of its specific properties. It contains Fe(II). The octahedral binding site in the Magnetite structure is able to absorb Fe(II) and Fe(III). The isostructural substitution of Fe can be varied by other metals like Cu, Mn, Co or Ni (formation of ferrites). Ferrites as well as magnetites are ferromagnetic and can be separated by magnetoseparators. This concept allows a reliable removal and recovery of nanoparticles from the water (Figure 8).

Degradation tests with Pd/magnetite under reductive conditions were performed e.g. for monochlorobenzene (MCB) and trichloroethene (TCE). They showed high activities A_{Pd}. of the catalyst (Figure 9).

Beside the chemical and technical topics also ecotoxicological aspects of the used nano particles are examined in this project. Potential acute and long-term effects on aquatic organisms and the mechanism of action are investigated using fish (*Danio rerio*),

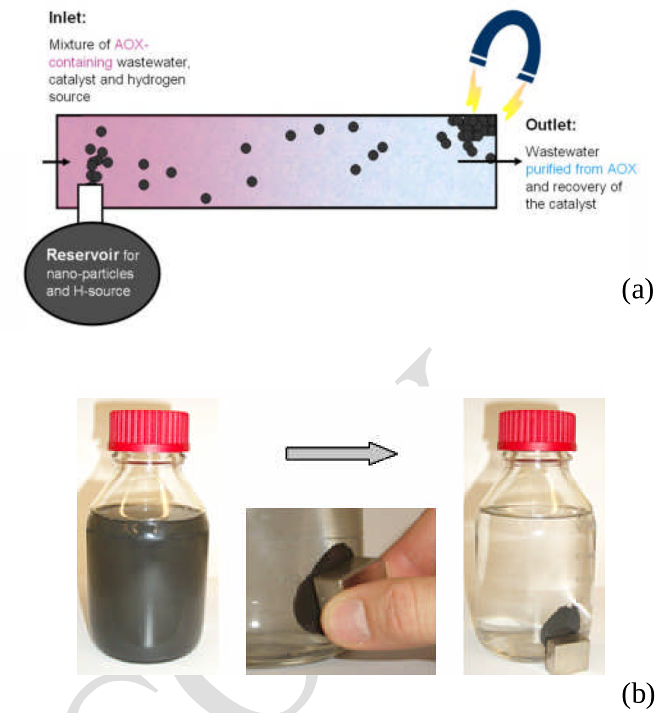

Figure 8. (a+b) Separation of magnetic nano/micro-particles from waste water (6).

daphnids, (*Hyallela sp.*) and algae as model organisms. Furthermore, interactive effects with contaminants are investigated. Preliminary data indicate only a very weak ecotoxicity of the tested nanocomposite structures.

Nanoblox

For the application of nanotechnology for degradation of VOC (Volatile Organic Compounds) emission and odors in air treatment processes other technical requirements are essential. Rather than transmission of media the homogeneous input of high energy intensities of UV light in high and very high flow rates are limiting here. In the R&D project *nanoblox* in cooperation with the Institute of Energy and Environmental Technology IUTA in Duisburg the development of nanobased photocatalysis modules is in progress despite new problems in application (7-8).

The main challenge in the construction of the reactor is to create a sufficient area with an active surface of the photocatalyst which can be reached with the UV lamps. At the same time the carrier structures should avoid any increase of pressure in the treatment system. The easiest approach is to coat the inner surface of the reactor directly with nanoscale TiO_2 (Figure 12) or to use porous structures (like metal foams or mats) for fixing the nanoparticles.

Irrespective of the carrier structure the photo-catalyst has to be fixed to the carrier in a permanent

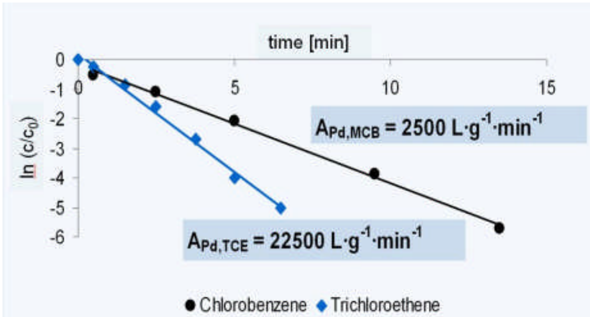

Figure 9. High catalytic activities with nano-Pd/Magnetite (V_{H2O}= 200 mL, catalyst contains 0.15 wt% Pd, MCB: $c_{catalyst}$ 0,15 wt% Pd= 150 mg/L, $c_{0\ MCB}$ = 10 ppm; TCE: $c_{catalyst}$, 0,15 wt% Pd = 25 mg/L, $c_{0\ TCE}$ = 1 ppm) (6).

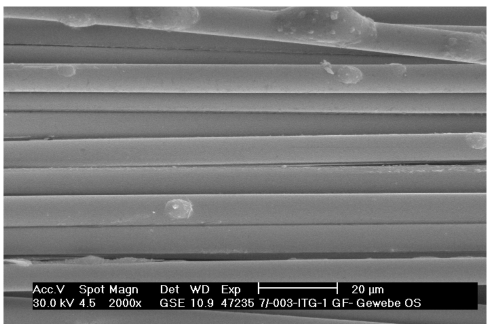

Figure 10. Glass fibre mat primed and impregnated with TiO_2 (8).

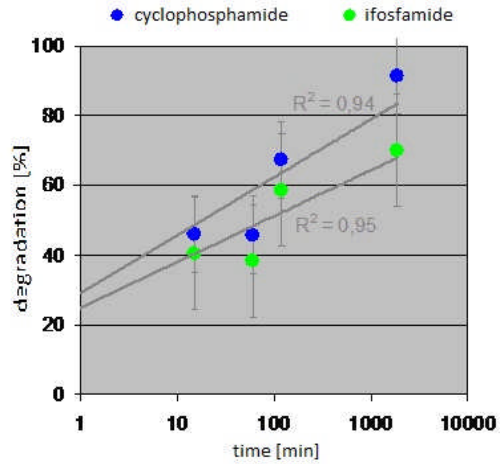

Figure 11. Influence of irradiation time on degradation of cyclophosphamide and ifosfamide (catalyst composite structural material with TiO_2) (8).

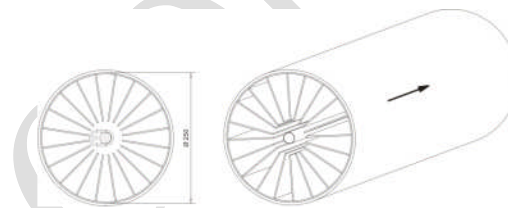

Figure 12. Lamellas impregnated with nano-TiO_2.

and secure fashion. Any adaptation of established methods to attach the catalyst must take into account the specific characteristics of the exhaust air purification plant (Temperature of exhaust air, shearing forces in the stream, etc.). Special attention needs to be devoted to the surface of the nano-sized photocatalyst which needs to be preserved and should avoid covering by the fixing material.

Catalyst materials for elimination of hazardous materials have been developed and tested successfully in particular for the elimination of cytostatics in the exhaust stream of safety cabinets. The degree to which catalytical photooxidation can eliminate critical substances largely depends on the characteristics of the carrier material, the technical process of coating and fixing as well as the catalyst material. A combination of fibre glass with a nanoscale TiO_2 coating has proven to be particularly effective directly painted from a dispersion (Figure 10).

The methods proposed have achieved promising degradation rates after droplets with dissolved cytostatics were exposed to UV-light (Figure 11). Existing analyses did not document any toxic oxidation by-product in the exhaust air. Up to now the preliminary industrial applications of photooxidation systems used for VOC- and odor-elimination in exhaust air streams have been moderately successful.

Further optimization and development are based on the construction of the reactor for maximal fixation of nano particles like e.g. shown in Figure 13. The main objective lies in the optimization of the geometric projection surface for optimal reaction conditions with respect to pressure drop. Results will be reported.

Conclusions

In this report the *uviblox*® technology was explained basically. Based on modified Vacuum-UV-medium pressure lamps this technology as an AOP technology for degradation and elimination of organic substances respectively as well as numerous inorganics has reached a much higher degree of efficiency than related technologies. Applied in water or air treatment systems the technique provides a high capability for a wide range of substances in the area of water, waste-water, air, waste-gas, and odor elimination, treatment and disinfection.

Nano photocatalysis processes can support VUV irradiation with high efficiency. These approaches are strongly pursued in different research & development projects for water and air treatment. Different R&D works with the aim to enforce photooxidation processes by photocatalytical nano structures were presented. First results in these projects show that the effiacy of photooxidation can be increased significantly as shown in laboratory scale tests. Different approaches for preparation of nanoparticles are followed as suspended solids on (magnetic) micro particles or special coatings on fixed surfaces. Surface layer structures from special bacteria show a high capability to concentrate photo-catalysts as well as organic contaminants at their surface layer and thereby increase the effiacy of degradation. In the same way reductive catalytic processes were tested successfully with nanostructures.

Only small effects of ecotoxicity at very high concentrations of nano particles were found so far. The impact of these nano-particle applications to nature seems to be not critical. Further investigations on this topic are in progress.

Technical designs and adaptions for up-scaling were made. Pilot tests onsite under real and longterm conditions will follow and results will be reported.

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