Solar-photocatalysis for removal of pharmaceuticals and personal care products (PPCP) in water

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1. Introduction:

Pharmaceuticals and Personal Care Products (PPCP) have been finding their way into our environment [1].

At present about 3600 active pharmaceutical ingredients for human and veterinary medicine are licensed in Germany (see Fig. 1). So for example in 2009 nearly 68 tons of lipid regulators, nearly 102 tons of antiphlogistic drugs, 204 tons of ß-blockers and nearly 570 tons of antibiotics were prescribed [1].

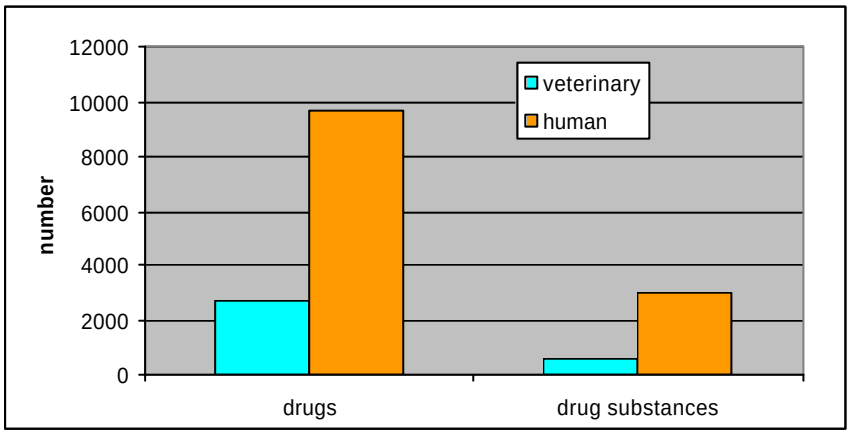

Fig.1: The situation in Germany (2006): Number of drugs and their active pharmaceutical ingredients

Different ways and sources lead to the fate of pharmaceuticals and personal care products (PPCP) in the aquatic environment (see Fig. 2), today about 150 drugs and their metabolites are detected in water of rivers and lakes. Most of the organic drugs are very stable and **non-biodegradable** compounds. Regional and international studies showed the increase of drugs in water due to the incomplete removal of these substances during passage through a sewage treatment plant.

The concentrations of persistent PPCP and some of their metabolites accumulated in water systems are very low (0,001 µg/L – 10 µg/L). But pharmaceuticals are specifically designed to elicit biological response at very low levels. Scientists are increasingly becoming aware of how medications let loose on the environment may have effects no one ever anticipated.

For that reason it is a crucial demand to develop new and energy-efficient methods for elimination of drug residues in water to protect natural resources.

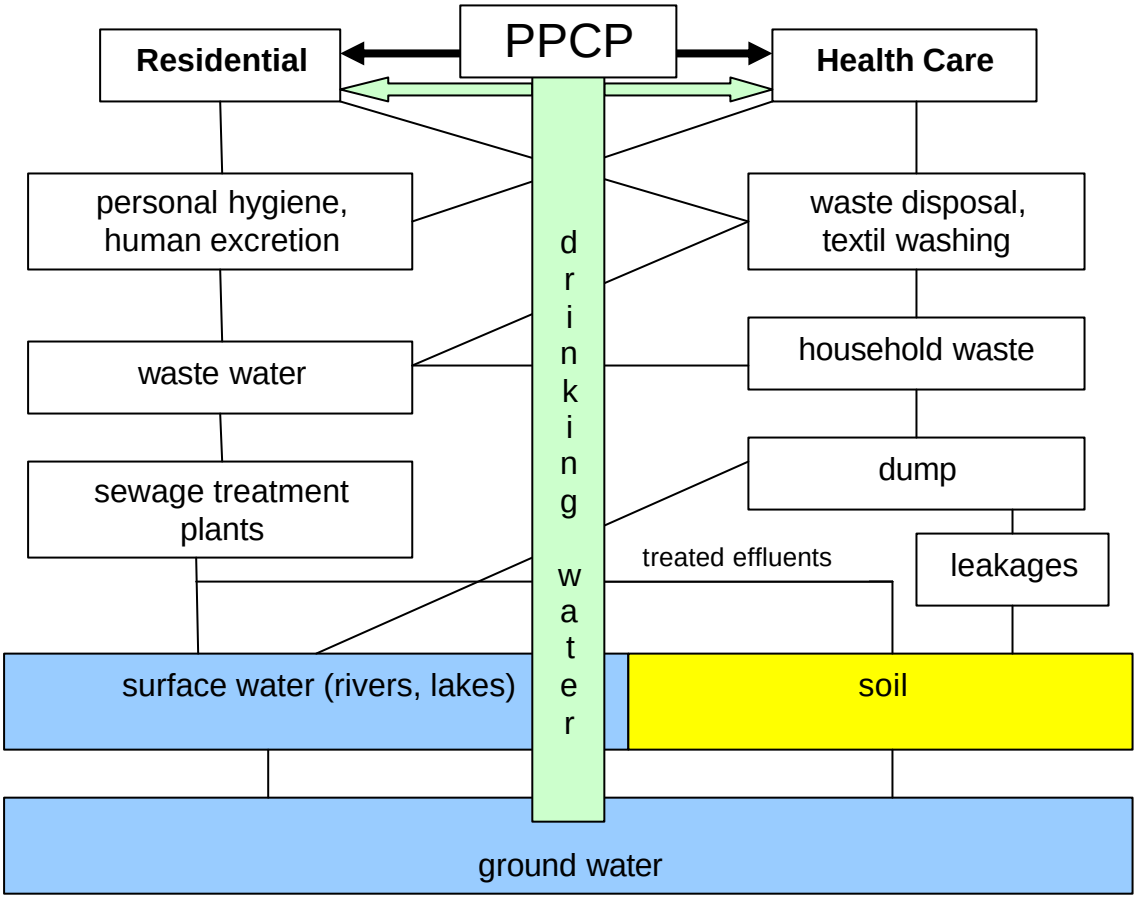

Figure 2: PPCP flow from homes and health care facilities [2]

Important groups of substances (PPCP) as micropollutants are shown in Tab.1 and Tab.2.

Tab. 1: Pharmaceuticals
antibiotics
steroids and hormones
antiphlogistics
psycholeptics
lipid regulators

Tab. 2: Personal Care Products	
cosmetics	uv-filter substances (sun protectors), fragrance compounds, dental care substances, emulsifying agents
household chemicals	surfactants (tensides), oils, solvents, antidegradants
material protectors	emulsifying agents, stabilizers, flame retardents, polymer plasticisers,
cleaning products	bactericides, oils, solvents, fragrance compounds, antidegradants

2. Solar-Photocatalysis

The solar-photocatalysis is an alternative and energy efficient technology for degradation of organic pollutants in water:

- oxygen in air as natural and simple oxidant agent
- degradation of organic pollutants (OP) like pharmaceuticals or personal care products in water at very low concentrations
- low energy technology without use of lamps (sun light) or with the use of low energy lamps by artificial visible light emission
- combination with other technologies (nanofiltration or biological treatment)
- many fields of application in water treatment (drinking water, ground water, process water)

The catalyst is a semiconductor which absorbed visible light (320 - 750 nm) preferred and transformed energy of photons into charge carriers.

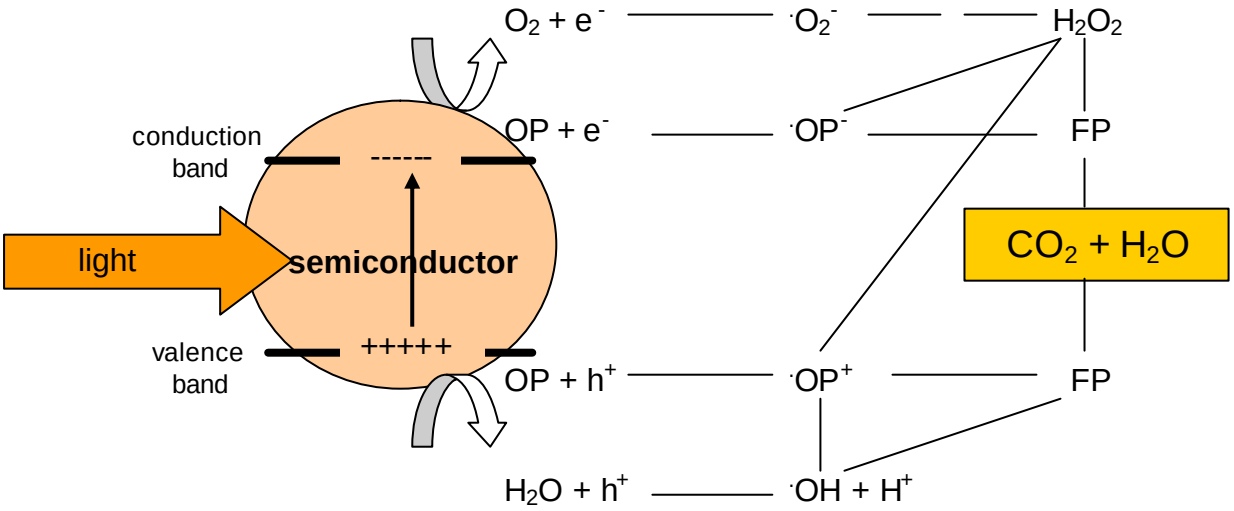

Fig. 3: Principle of photocatalysis for degradation of organic pollutants (OP) in water via fragmentation products (FP)

The formed electrons (e^-) and positive holes (h^+) diffuse on the surfaces of the semi-conductor particles and react with water, oxygen and organic pollutants (OP) in water (see Fig. 3).
As result of these initial reactions and the following oxidation and hydroxylation reactions by OH-radicals the degradation of organic pollutants via fragmentation products (FP) and finally to CO_2 and water can be expected.

A number of authors reported about the use of doped semiconductors [3] for visible light photocatalysis in suspensions or hydrosols. Also the use of nanoparticles can increase the photo activity of the semiconductors [4-5]. But, efficient water treatment is only possible using well-prepared catalysts on solid supports [6].

3. Preparation of catalysts

Granular clay materials with high porosities are used as carrier systems for photocatalytic materials. The advantages of this material can be summarized:

- natural products with constant quality
- chemical inertness
- containing iron (Fe)
- mechanical hardness
- particle sizes (2-4 mm) ideal for fixed bed reactors [6].

On these supports nanoparticles of ZnO or TiO_2 are deposited by:

- fluid bed technology and
- dip coating technique

After drying and calcination we produced coated clay materials with thin and stable photocatalytic layers (see Fig. 4)[4-6].

Fig. 4a: ZnO-coated mineral support during the process of drying

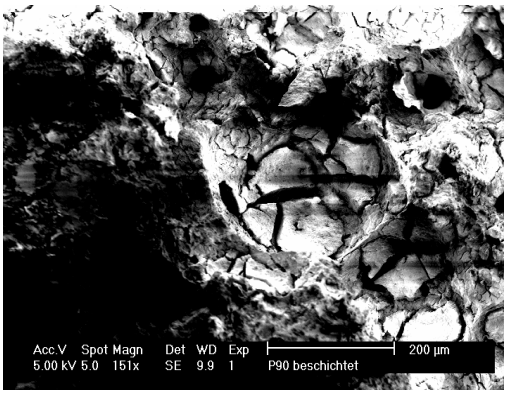

Fig. 4b: REM-picture of a supported photocatalyst

The mass of photoactive coating of the semiconductor materials (see Fig. 4b) is nearly 100- 150 mg per gram granulate [6]. So it can be used such granulates for fixed bed applications to remove micropollutants in water by sunlight (see Fig. 5).

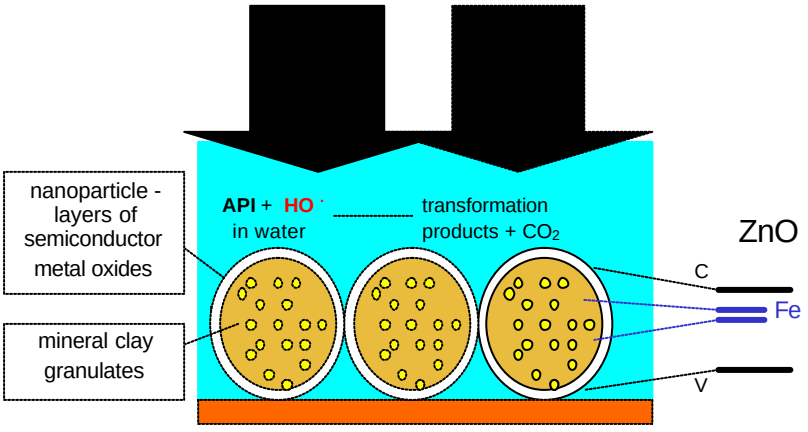

Fig.5: Photocatalytic granulate for water purification by sunlight.

4. Results of laboratory studies

For testing the photoactivity of the supported catalysts ***a screening system*** with a fluorescent lamp for *warm white light* (OSRAM DuluxeS, 11 W) and for *blue light* (NARVA BLUE 018, 15 W) was developed. Solutions of 10 or 20 mg/L of drug substances or active substances from personal care products (PPCP) in deionized water (50 mL) was shaken in glass bottles under irradiation light for a time of 240 min. A second series was shaken under exclusion of light. The mass of supported catalyst was 6 g.
The solutions of test substances in water were analysed by a HPLC- system (HP 1050) equipped with a UV detector (200 nm) and an EC 250/3 Nucleosil 100-5 C18 column.

4.1. Stability of substances in water

We investigated the chemical behaviour of the pure test substances (PPCP) in water (hydrolysis) and in the darkness (no photolytic reactions). In the most of cases the PPCP are stable in water under exclusion of light.

4.2. Adsorption and light stability of substances in water

All test substances (PPCP) were irradiated by different illuminates (uv-A, artificial day light, blue light) and the reduction of concentration were analysed by HPLC.

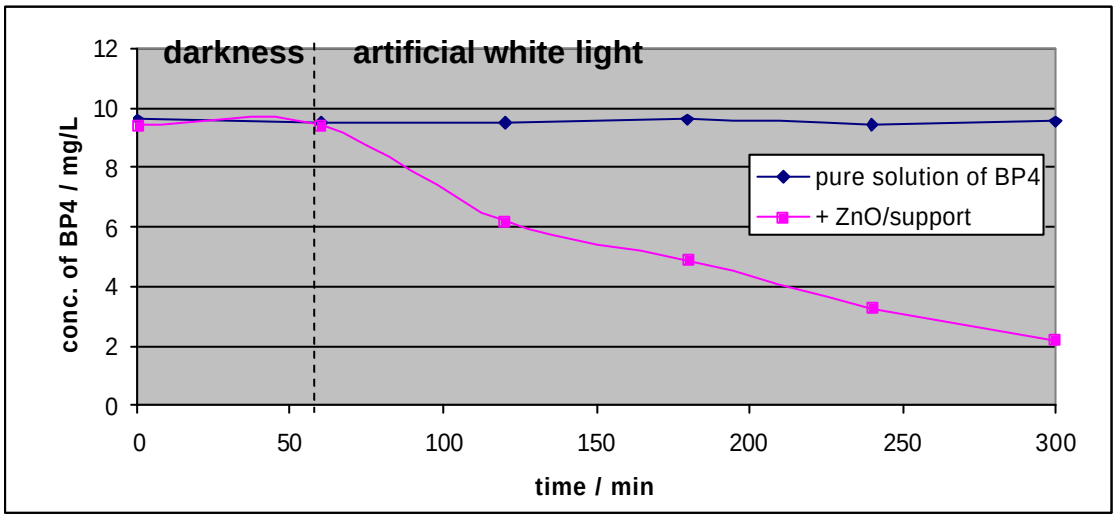

Fig. 6: Photocatalytic degradation of uv-filter-substance benzophenone-4 (BP4) in pure solution and with a supported nano-ZnO-catalyst by artificial visible light

The uv-filter substance **benzophenone4 (BP4)** in water is very stable during irradiation by artificial white light (see Fig. 6). But in the present of a supported nano-ZnO-catalyst it can be seen the decrease of concentration of BP4 because of photocatalytic degradation reactions.
The tests started at the first 60 min with the exclusion of any light. Here it coluld be observed the adsorption behaviour of the PPCP on the supported catalyst. In our case the adsorption rate of BP4 is less than 10%.

4.3. Photocatalytic activity of catalysts

We studied the behaviour of test substances and mixtures of substances by light and in the present of supported catalysts (see Fig.6 and 7).

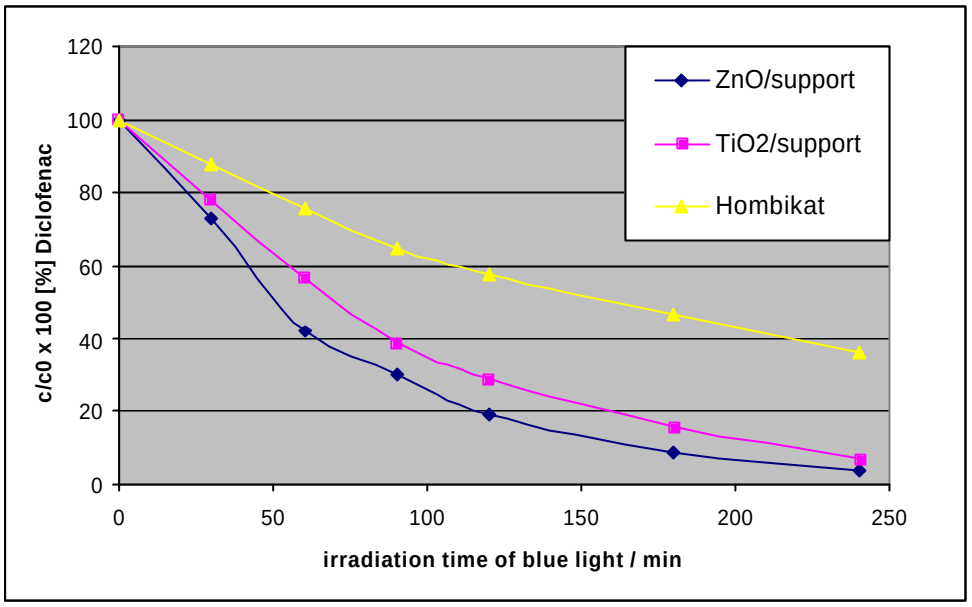

Fig.7: Photocatalytic degradation of diclofenac with supported catalysts by blue light

The comparison of the elimination rates of the non steroidal antiphlogistic drug **diclofenac** have clearly demonstrated, that nano-ZnO on support degrades the drug more efficiently than nano-TiO_2 and the non nano product Hombicat (TiO_2).

4.4. The service life of the used catalysts

In Fig.8 the concentrations of **BP4** in water before and after irradiation with uv-A light about 90 min are shown by using one and the same catalyst. In all 6 experiments (sequently cycles) the end concentrations of BP4 were under 1 mg/L. The reason of the differences between cycle 1 and 2 could be the abrasion of photocatalytic material from the clay carrier during the first reaction cycle.

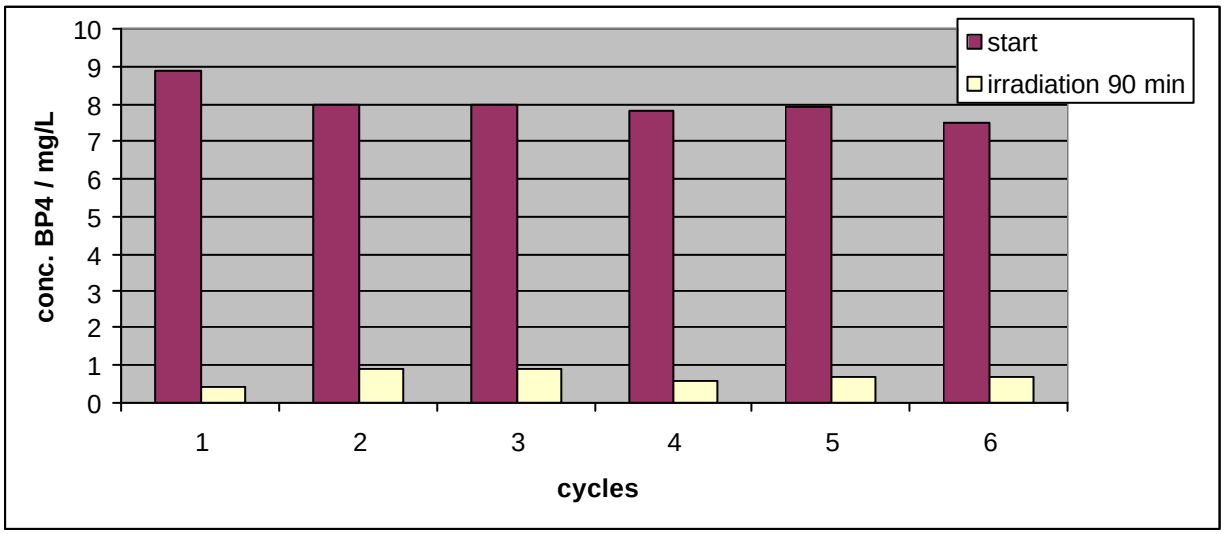

Fig. 8 Long time stability (service life) of nano-ZnO-catalyst during six reaction cycles (irradiation of BP4 in water by uv-A-light)

5. Photocatalysis in fixed bed reactors

The supported ZnO-photocatalyst was used in a fixed bed reactor (10 L) with a catalyst bed of 0.2 m^2 area [8]. The mass of the supported catalyst was 400 g and the water flow was regulated of 0.7 L / min. At the pictures it can be seen the dry fixed bed with the coated granulates (Fig. 9a) and the whole installation of the reactor (Fig. 9b).

a.)

b.)

Fig. 9a + 9b: Fixed bed reactor for photocatalytic degradation of PPCP in water by day-light irradiation

A sample solution of 20 mg/L diclofenac in trap water was irradiated by sunlight from 10 a.m. to 3 p.m at a summer day in germany. The water tank was covered by a reflector film to inhibit the pure photolytic degradation of diclofenac. Fig. 10 showed the results of the removal of TOC and diclofenac during 5 hours.

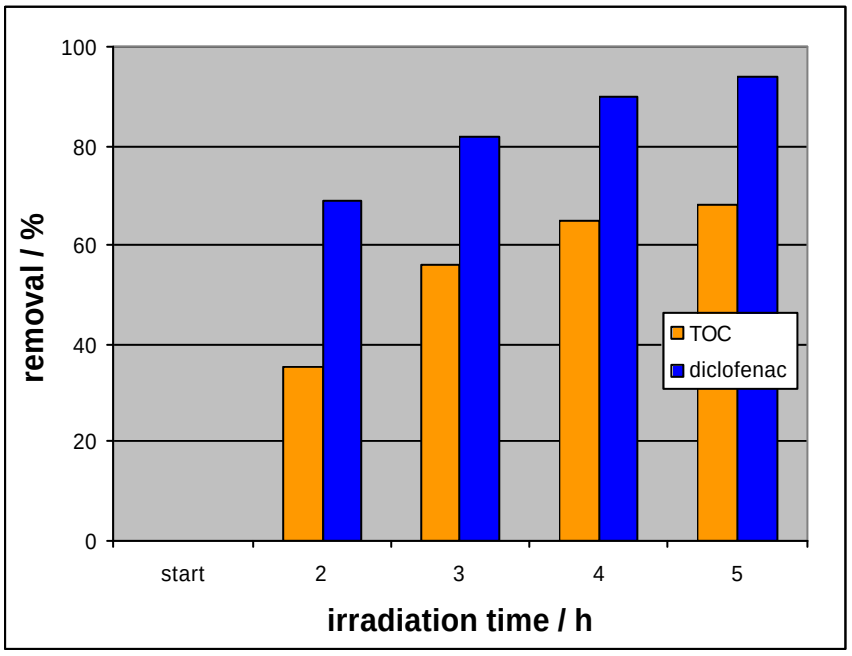

Fig.10: Removal of TOC and diclofenac by photocatalytic treatment in the fixed bed reactor

After sunlight irradiation of 5h the elimination of diclofenac was 94%, the decrease of TOC-value was only 68%. The photostability of some fragmentation products (FPs) is one reason of a incompletely degradation by photocatalysis.

6. Summery:

With a fixed bed reactor loaded with ZnO-coated granulates it will be possible to eliminate PPCPs of special cleaning or process water by using the natural sunlight. The combination of such reactor with biological treatment methods or electrolysis should be realised for complete removal PPCP in small sewage works.

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