Reduction of Pharmaceutical Residues by Engineering a TiO_2/Membrane Reactor

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1 Abstract

In this project, a model reactor for degradation of pharmaceutical residues from both waste and drinking water was engineered. The degradation is based on oxidizing organic molecules in water by using TiO_2 nanoparticles as photocatalyst immobilized on polymer membranes. Since diclofenac is one of the most commonly found pharmaceuticals in most water sources, degradation of diclofenac in various concentrations and solved in different water types was tested. The reactor, with its simple design, was shown to be very effective in degrading diclofenac. The membrane acts as a carrier for the nanoparticles as the polluted solution is flowing across the membrane. In addition, no fouling of membrane occurred even after long time operation.

2 Introduction

Growing population and industrialization is a global issue and a much-discussed topic in the literature[1]. Water resources are highly affected by this, especially because of the increasing pharmaceutical residues therein.

Several processes were developed in the last years to purify both waste and drinking water. Amongst others, advanced oxidation processes (AOPs), with the ability to not just remove pollutants from water, but even to oxidize them completely to carbon dioxide and water[2] have shown great potential in water purification processes. Titanium dioxide (TiO_2), as a photocatalyst, stands out among all of the AOPs due to the low costs of TiO_2, its chemical stability[3], and its high photocatalytic activity. By applying UV light, TiO_2 will catalytically generate $^{\bullet}OH$ radicals in the presence of water, which will non-selectively oxidize organic molecules to produce carbon dioxide and water[4].

Polymer membranes are often used in water purification because of their high chemical and physical stability. In addition, they can act as a carrier material to immobilize photocatalytic active nanoparticles, such as TiO_2.

Here, non-agglomerated TiO_2 nanoparticles were synthesized *via* titanium tetraisopropoxide (TTIP) hydrolysis on a microfiltration membrane (polyethersulfone, PES)[5].

In cooperation with students of Gustav-Hertz High School in Leipzig, a model reactor to remove pharmaceutical residues (*e.g.* diclofenac, ibuprofen, and carbamazepine) by using polymer membranes immobilized with TiO_2 nanoparticles was engineered. Experiments on degrading diclofenac as one of the most spread pharmaceuticals[6] in our water sources were performed.

3 Experimental

3.1 Nanoparticle preparation

Dry polyethersulfone (PES) membrane (pore size 0.22 µm, Millipore Express Plus® membrane GPWP, Millipore, USA) was placed into a TTIP solution (3 vol% in ethanol, Fluka Chemika) for 5 min. Afterwards the membrane was air dried and then washed in ultrapure water (Milli-Q integral system, EMD Millipore, USA) for 5 min to form TiO_2 nanoparticles. After drying the membrane again, a washing step with ultrapure water (three times for 30 min) and a final air drying step were performed[5]. Amorphous TiO_2 nanoparticles were crystallized in water at 90 °C for 2 h to gain photocatalytic active anatase TiO_2.

3.2 Reactor engineering

The self-built membrane reactor consists of four borosilicate glass tubes. UV light with a wavelength of 365 nm can penetrate these tubes, as it has been confirmed by using a UV radiometer (UV radiometer, 16575, Jenoptik, Germany). Therefore, expensive quartz glass can be avoided. The tubes were provided with small obstacles to increase the circulation. The membrane in this reactor acts as a carrier material for TiO_2 and is not used in a common way (dead-end or cross-flow setup, see Fig. 1). The test solution flowed continuously through the reactor by using a membrane pump (membrane liquid pump, LIQUIPORT®, Carl Roth, Germany) with a flux range from 200-1600 mL min^{-1}. The solution fills all four tubes equally from the bottom and passes the membrane on one side. Exchange with the inner pores of the membrane can still take place. Using the membrane with such a pore size (0.22 µm) has a big advantage as it provides a high surface area and at the same time efficient exchange with the inner surface is accomplished. In contrast, small pores reduce the diffusion of the solution into the inner pores. On the other hand, a membrane with larger pores would not offer enough surface area (and thus lower photocatalytic activity). The UV light source is a UV-A LED lamp with a radiant flux density of 8-10 mW cm^{-2} (15 x 365 nm LED chips each 2 W, UV-LEDFL-

15F, UVECO, Germany). A screen covers the tubes and part of the lamp. This screen is coated inside with aluminum foil acting as a mirror, so that the light will be reflected. Samples were taken on the top right of the reactor (Fig. 1).

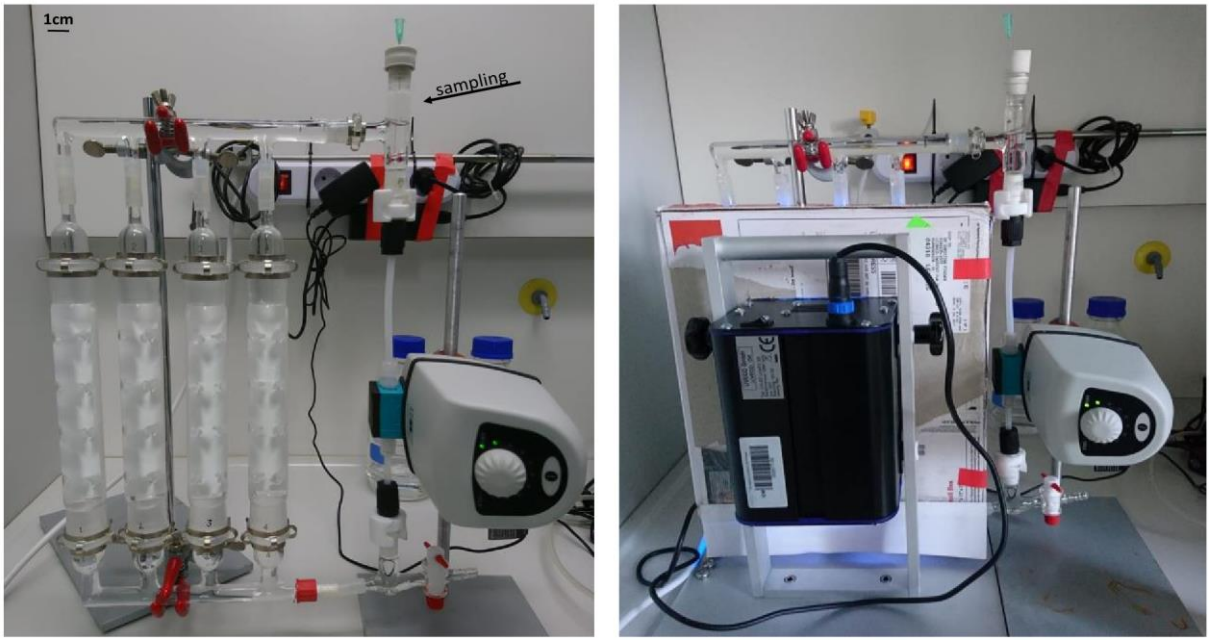

Fig. 1: Photographic images of the reactor, equipped with TiO_2 immobilized membranes within the glass tubes (**left**), and in operation with UV lamp and screen (**right**).

3.3 Characterization

The photocatalytic activity was tested by degrading diclofenac (25 or 100 mg L^{-1}, Cayman chemical) in ultrapure water, and wastewater filtrate (household wastewater filtered through ultrafiltration membranes) as shown in table 1. Membranes were cut into rectangles (5 x 10 cm) and placed at the back of the inner glass tubes (two pieces in each tube). The reactor was filled with diclofenac solution (700 mL) and left for 15 min for total dark adsorption. The UV lamp was turned on to start the photocatalytic reaction. The absorbance was measured periodically with a UV/Vis spectrometer (Infinite M200, Tecan Group Ltd., Switzerland) at 276 nm.

Table 1. Varied parameters in degradation experiments.

name	**diclofenac (mg L^{-1})**	**solvent**	**flux (mL min^{-1})**	**mirror**	**reloading**
T1	25	water	400	no	no
T2	25	water	400	yes	no
T3	25	water	800	yes	yes
T4	100	water	800	yes	yes
T5	100	filtrate	800	yes	no

4 Results and Discussion

A simple reactor design is presented here, which can be easily upscaled for cleaning large amounts of water. In contrast to other membrane reactors, the membrane here is not used in a common way (filtration in dead-end or cross-flow mode). This brings major advantages as the energy consumption will be decreased by avoiding high pressure and the overall buildup is simplified.

Reflecting the light with an aluminum foil showed an positive impact on the photocatalytic degradation velocity of diclofenac (Fig. 2). After 15 hours 66% was degraded with and 50% without an aluminum foil. The photocatalytic degradation was improved by increasing the flux from 400 to 800 mL min^{-1} (Fig. 2). Comparing the degradation of a lower and higher concentrated diclofenac solution showed that the degradation is slower at a higher concentration of diclofenac (Fig. 4).

Damage of the polymer membrane by TiO_2 photocatalysis is a big issue. The SEM images of the membrane in Fig. 3 showed small holes and cracks in the membrane after photocatalytic reaction took place for seven days. The polymer of the membrane has been degraded by TiO_2. Further experiments showed that damaging the membrane can be avoided by increasing the diclofenac concentration, or raising the overall amount of molecules in water using a wastewater filtrate as solution. The amount of diclofenac was raised to 100 mg L^{-1} and the reactor was reloaded with diclofenac after about 70% degradation of diclofenac. The SEM image in Fig. 3 (middle image) shows except for a few cracks, nearly any decomposition of the membrane. Additionally, the membrane surface did not foul (Fig. 3) compared to membranes used in dead-end photocatalytic filtration experiments. TiO_2 nanoparticles are not blocked and are still highly active after seven days of testing. Furthermore, repeated degradation of diclofenac using the same membrane has been proven (Fig. 5). Investigation of diclofenac reduction in wastewater filtrate showed the same effect (Fig. 6). The membrane was not destroyed by TiO_2 during photocatalytic degradation (Fig. 3, right image). The velocity of reducing diclofenac slowed down in the wastewater filtrate, mostly due to lower light transmittance and large amount of other organic molecules next to diclofenac (Fig. 6).

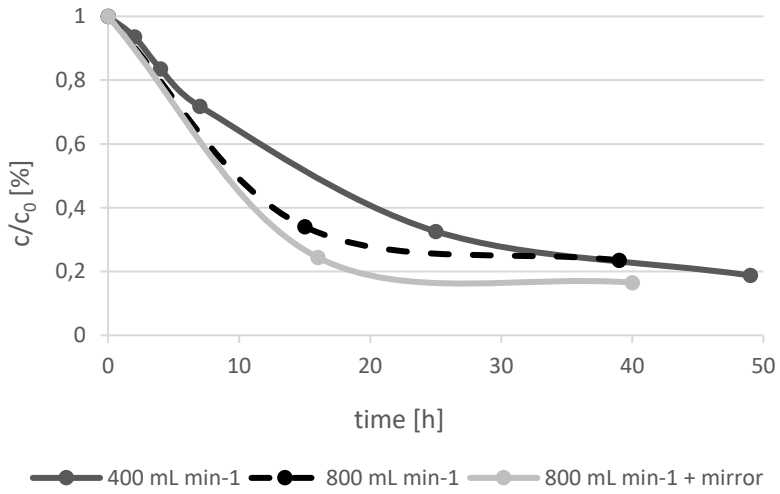

Fig. 2: Degradation of diclofenac (25 mg L^{-1}) in water over time.

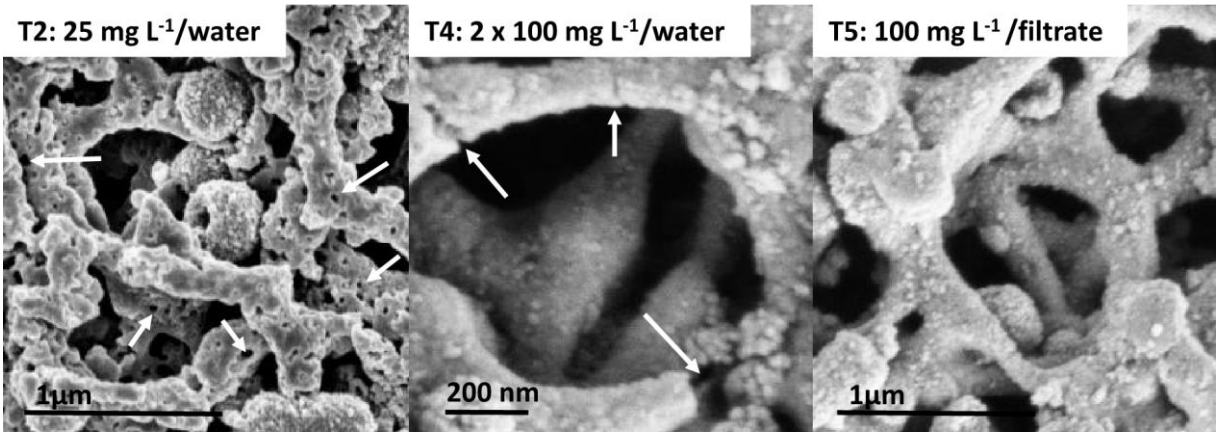

Fig. 3: SEM images of PES membranes immobilized with TiO_2 nanoparticles after 7 days of running tests: T2 (Fig. 2, black dashed line), T4 (Fig. 5), T5 (Fig. 6, black dotted line), the white arrows show membrane damage by TiO_2 photocatalysis.

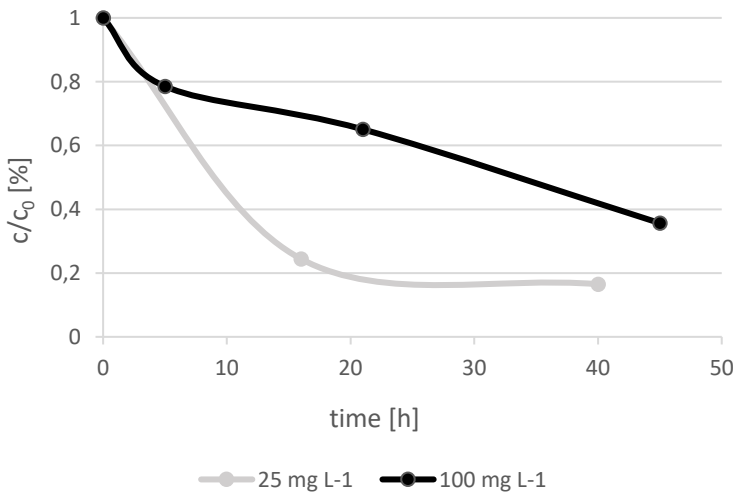

Fig. 4: Degradation of two different concentrations of diclofenac in water over time, 25 mg L^{-1} (T3), and 100 mg L^{-1} (T4).

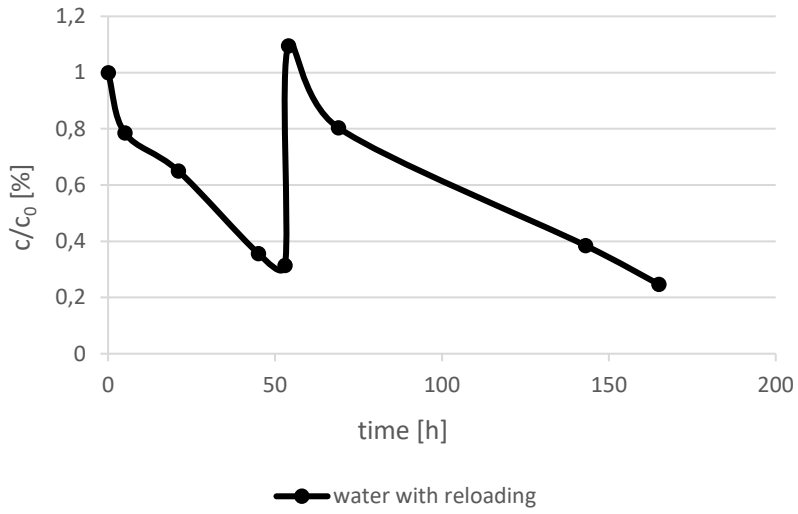

Fig. 5: Degradation of diclofenac (100 mg L^{-1}) in water (T4) with reloading of diclofenac after 50 h.

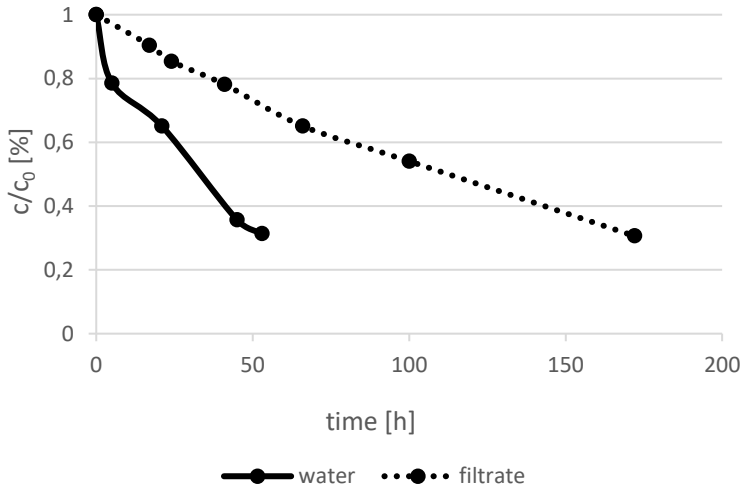

Fig. 6: Degradation of diclofenac (100 mg L^{-1}) in water (T4) and in wastewater filtrate (T5) over time.

5 Conclusion

Facing the issue of water purification concerning pharmaceutical residues, this model reactor proved itself as a good template for real purification systems due to its simple design and its easy application. By using the membrane as a carrier for TiO_2 nanoparticles, a large surface area was provided and a high efficiency in the reduction of diclofenac was achieved, even after refilling diclofenac and using real wastewater. Up to 70-80% of diclofenac has been degraded. In addition, fouling of the membrane surface could be avoided. Finally, the usage of higher amounts of organic molecules, like in pre-cleaned wastewater, prevents the TiO_2 nanoparticles attacking and decomposing the polymer membrane.

6 References

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