A Photocatalytic Membrane
For Treatment of Pharmaceuticals in Wastewater

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A Photocatalytic Membrane
For treatment of pharmaceuticals in waste water

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Abstract

Toxic organics, pharmaceuticals and antibiotics are currently only partially or not at all removed from wastewater, as today’s wastewater treatment will only partly degrade those substances. Therefore, those substances will be found in the effluent from wastewater treatment plants and this can be a threat to both human health and aquatic species.

Photocatalytic membranes show great promise as a method to combat the challenge of toxic organics in wastewater. The novel photocatalytic membrane developed in the project was shown to photocatalytically decompose organic compounds such as pharmaceutical residues and dyes in both tap water and treated effluent from a membrane bioreactor (MBR) wastewater treatment process. Several parameters affecting the affinity of the pharmaceuticals to the membrane surface, such as the hydrophobicity and pKa of the pharmaceuticals and the pH of the water, were shown to affect the efficacy of the removal.

Finally, when irradiated with UV light the photocatalytic membrane showed promise of keeping high flux and reducing downtime by lengthening the cleaning cycle.

Key words: Water, residue, organic, pharmaceutical, water, health, membrane, cleaning, photocatalyst
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Executive Summary

A new photocatalytic membrane filter has been produced in lab scale. It has been tested for its ability to decompose pharmaceutical residues in spiked tap waterer and spiked MBR effluent. In this report we show the results from tests using both dead-end and cross-flow filtration.

The results show that the membrane filter with photocatalysts in combination with UV irradiation is promising for keeping high flux and reducing the downtime of the filtration unit by lengthening the cleaning cycle. Photocatalysis also decomposes organics such as pharmaceutical residues and dyes in both tap water and effluent from the MBR. The hydrophobicity and charge of the pharmaceuticals are important parameters for the degradation efficiency.
1 Photocatalysis and Photocatalytic Degradation of Organics

For photocatalysis TiO$_2$ is often used due to its low toxicity, chemical stability and low cost [1]. TiO$_2$ is a native n-type semiconductor having a wide band-gap (E$_g$) of 3.2 eV for its anatase form and 3.0 eV for its rutile form. In this semiconductor material, a light energy absorption $h\nu \geq E_g$ (E$_g$ of anatase TiO$_2$ = 3.2 eV which corresponds to a wavelength below 380 nm) generates an electron/hole ($e^-/h^+$) pair. Thus, when TiO$_2$ nanoparticles are irradiated with a suitable wavelength black light fluorescent lamp, for example, it generates an electron/hole pair.

![Figure 1 Light spectrum with the zone of action of TiO$_2$](image)

The photocatalytic decomposition of organic molecules is illustrated in Figure 2. It is clearly shown that formation of reactive oxygen species (ROS) is the main reason for the photodegradation of organic species at the surface of TiO$_2$ photocatalysts. A generated electron in the conduction band is transferred to oxygen as the acceptor, while the hole in the valence band of TiO$_2$ receives an electron from the targeted organic molecule that acts as the donor, resulting in decomposition of the organic molecule.

The anatase form of TiO$_2$ is more effective for producing ROS than the rutile form. The size and shape of the anatase TiO$_2$ is also important as the reaction kinetics of TiO$_2$ photocatalysis depends on the fast recombination of $e^-$ and $h^+$. For a small TiO$_2$ particle size of a few nanometers, the surface recombination dominates, while smaller particle size also lowers the volume recombination of $e^-$ and $h^+$ and thus enhances interfacial charge carrier transfer [2, 3].
Photodegradation of dyes of different charge were studied using anatase TiO$_2$-loaded microporous PVDF membranes. Dye adsorption on the solid catalyst is required for efficient dye degradation by the active species formed on the catalyst. Without adsorption, the dyes are solely degraded via the soluble oxidant species (e.g. hydroxyl radicals) photogenerated by the oxidation of water molecules on the anatase TiO$_2$ particles under UV irradiation. When dyes are also adsorbed onto the photocatalyst, dye molecules are photodegraded both directly and via these soluble oxidant species. For photodegradation of both single dyes and dye mixtures the dye degradation rate increased according to the sequence of dye adsorption on the membrane [5].

For adsorption of charged compounds, the surface charge of TiO$_2$ and thus the pH of the solution are important to keep in mind. Anatase TiO$_2$ in water has a point of zero charge (pH$_{pzc}$) of about pH 6.0 [6]. At low pH (pH < pH$_{pzc}$), TiO$_2$ particles possess positive charge while a negative charge is expected at higher pH (pH > pH$_{pzc}$) [7].

Methylene blue (MB) is positively charged (Figure 3) and should thus be attracted to the photocatalytic membrane at pH values above 6.

2 Development of the Membrane

In order to be able to develop photocatalyst-coated membranes, it is necessary to develop membranes that can be used for wastewater treatment. For this reason, a poly(vinylidene fluoride) (PVDF) membrane was modified.

2.1 Phase Inversion Method

PVDF membranes have been developed by a phase inversion method. PVDF, N,N-Dimethylacetamide (DMA) and water or ethanol are used as polymer, solvent and anti-solvents/coagulants in the development of PVDF membranes by the phase inversion method. The typical membrane casting process is shown in Figure 4.
2.2 Casting of Membrane Films

A K-coater was used for film casting on the PP support (approx. A4 size), see Figure 5. The support is fastened to the glass support with tape. The films were cast with an applicator at low speed and very carefully placed immediately into a water bath while still attached to the glass. They were kept in the water for one minute, and then extracted from the water. The glass was then dried with soft paper to remove the excess water and the membrane on the membrane support media was placed carefully on a double layer of drying paper and left to dry overnight at ambient temperature.

The TiO$_2$ particles are well distributed in the membrane, as seen in Figure 6. The production was optimized for a membrane thickness of 100 micrometer. When using the 500 µm wet film applicator the membrane thickness was 90-100 µm, see Figure 7, whereas when using the 750 µm the membrane thickness was 150-160 µm.
2.3 Photoactivity of the Membranes

2.3.1 Evaluation of Absorption/Adsorption of Dye by the Membrane

In order to omit the effects of absorption and adsorption of MB, the photodegradation studies were performed on membranes that had been saturated with MB. Saturation and evaluation of the amount of MB absorbed/adsorbed by the filter was accomplished by the following procedure:

1. The MB solution is poured into a vessel with the membrane to be tested on the bottom and secured with a ring, see Figure 8. The vessel is covered with paraffin film and then with aluminum foil, placed in a dark room and left there for 17-18 hours (overnight).
2. The next day, this solution is removed from the vessel and analyzed with UV-VIS spectrophotometry. After 17-18 hours, some MB will be absorbed/adsorbed by the porous membrane and the absorbance of the solution will be lower than the absorbance of the initial MB solution.
3. The MB solution is replaced with a fresh batch of MB solution and the absorbance is measured immediately. If the absorbance has the same value as the original MB solution, the UV irradiation experiment can start.

This way, it will be possible to evaluate the effect of the UV irradiation omitting the effect of MB absorption/adsorption of the membrane, as it is assumed that the membrane is already saturated with MB when the UV test starts. The absorbance is around 13% of the initial MB in the solution.

The photocatalytic degradation test was performed in the glass vessels shown in Figure 8 and it is schematically shown in Figure 9. 60 mL of the $10^{-5}$ M MB solution and a membrane circle with a diameter of 9.0 cm were irradiated with UV light for 3 hours. The photocatalytic membrane was very effective, achieving 80-90% reduction, while non-photocatalytic membranes showed only an average reduction in UV absorbance of 2.9% in the same test.

In summary the photocatalytic membrane has high efficacy, but the UV light does not degrade MB significantly without the presence of the photocatalytic membrane.
3 Dead-End Filtration

3.1 Design of a Dead-End Membrane Reactor

A dead-end membrane reactor has been constructed and put in use, see Figure 10. The equipment consists of a UV-lamp with a peak wavelength of 365 nm, which is close to the absorption maximum for the photocatalyst (4 lamps LL-UVP40, total power 160 W) fitted at the top of a black box. The membrane filtration unit is placed below the lamp and a lid is placed in front of the box during its use.

3.2 Flux vs Vacuum

The flux was tested as a function of the amount of vacuum used, and observed to be linearly dependent on the vacuum, Figure 11. However, when taking a reading every 5 minutes there is a variation around the mean, see Figure 12, due to variability in timing, sampling and vacuum level.
3.3 UV Absorption of Residual Organics in the MBR Effluent

It is important that for the photocatalytic reaction that the UV light is not absorbed by organics present in the effluent wastewater. The absorbance spectrum of the MBR effluent was therefore measured. It can be observed from Figure 13 that the organics do absorb UV, mainly below 240 nm (UV-C region). Therefore, the UV absorption by these organics should not affect the efficacy of the photocatalytic reaction where photocatalytic process occurs mainly in UV-A region, 315-400nm.

3.4 Experimental

The test consisted of four runs that were performed over three days using the same photocatalytic microfilter in all runs. Between runs 2 and 3 the membrane was cleaned by running it with the UV on and deionized water feed for 83 min.
Table 1 Overview of test runs

<table>
<thead>
<tr>
<th>Run</th>
<th>Date</th>
<th>Water</th>
<th>UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (DI water flux test)</td>
<td>2015-11-24</td>
<td>Deionized water</td>
<td>Off</td>
</tr>
<tr>
<td>1</td>
<td>2015-11-24</td>
<td>Spiked MBR effluent</td>
<td>On</td>
</tr>
<tr>
<td>2</td>
<td>2015-11-24</td>
<td>Spiked MBR effluent</td>
<td>Off</td>
</tr>
<tr>
<td>2.5 (Cleaning)</td>
<td>2015-11-25</td>
<td>Deionized water</td>
<td>On</td>
</tr>
<tr>
<td>3</td>
<td>2015-11-25</td>
<td>Spiked tap water</td>
<td>On</td>
</tr>
<tr>
<td>4</td>
<td>2015-11-26</td>
<td>Spiked tap water</td>
<td>Off</td>
</tr>
</tbody>
</table>

The MBR effluent was taken from frozen samples collected in plastic 1 L bottles from the membrane permeate of Line 1 at Hammarby Sjöstadsverk. It was spiked with a standard solution (Faix 42; 1000 ng/mL) containing 42 pharmaceuticals, each at 1000 ng/mL concentration, to increase the concentration of each pharmaceutical by 500 ng/L. 24 of these pharmaceuticals were measured during the tests.

Tap water was taken from an often used tap in one of the labs, which was kept flowing for 5 min before sampling in order to flush out any contamination. It was spiked with pharmaceuticals in the same way as the MBR effluent, using the same batch of pharmaceutical standard solution to reach 500 ng/L concentrations.

The water temperatures varied between 19.2 and 22.9 °C (mainly due to fluctuations in room temperature), the only exception being run 3, which started at 17 °C since the sample had been stored in a fridge overnight. Due to practical limitations in the equipment the extent of UV heating was not measured. The pH was between 8.6 and 8.8 in the MBR effluent and between 8.0 and 8.3 in the tap water.

The membrane was activated by placing it in 99.5% ethanol for 10 min and then washed with deionized water for 10 min right before the start of the test. A vacuum of ~0.2 bar (gauge) was used during the whole test.

Table 2 Analysis results for a 24 h flow proportional composite sample of MBR effluent with sampling start at 8:00 20150602.

<table>
<thead>
<tr>
<th>COD (mg/L)</th>
<th>NH4-N (mg/L)</th>
<th>NO3-N (mg/L)</th>
<th>T-N (mg/L)</th>
<th>PO4-P (mg/L)</th>
<th>Color (m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>0.010</td>
<td>3.6</td>
<td>4.3</td>
<td>0.22</td>
<td>1.1</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>TOC (mg/L)</td>
<td>BOD7 (mg/L)</td>
<td>Filt. PO4-P (mg/L)</td>
<td>T-P (mg/L)</td>
<td>Fe (mg/L)</td>
</tr>
<tr>
<td>&lt;0.70</td>
<td>7.7</td>
<td>&lt;2</td>
<td>0.17</td>
<td>0.21</td>
<td>0.086</td>
</tr>
</tbody>
</table>

Table 3 Analysis results for a 7 day flow proportional composite sample of MBR effluent with sampling start at 8:00 20150601.

<table>
<thead>
<tr>
<th>TOC (mg/L)</th>
<th>NH4-N (mg/L)</th>
<th>NO3-N+NO2-N (mg/L)</th>
<th>T-N (mg/L)</th>
<th>T-P (mg/L)</th>
<th>Fe (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.9</td>
<td>0.130</td>
<td>2.7</td>
<td>3.3</td>
<td>0.28</td>
<td>0.100</td>
</tr>
</tbody>
</table>
3.5 Results

3.5.1 Flux
As seen in Figure 14 using water spiked with pharmaceuticals (Table 1) runs 2, 3 and 4 and the flux test generally show an initial decrease in flow rate over time as expected, and the runs also show the expected stabilization of the flow rate after 30 – 90 min, similar to earlier tests (not shown). As in the earlier tests, the runs with UV show a markedly higher flow rate than their counterparts without UV.

![Figure 14 Flow rates over the entire run time of the membrane during the test (pauses not included). The red bars mark the starting points of the different runs.](image)

3.5.1.1 Dissolved Oxygen
The dissolved oxygen concentration in the water (DO) is important as it can facilitate the photocatalytic process. The DO of the sample is consistently lower than in the reservoir, see Table 4, a behavior that was also seen in earlier tests (not shown) and attributed to degassing due to a combination of heating and vacuum pressure. However, the differences observed are small.

Sample DO values are similar but slightly lower for the UV runs, which indicates that the vacuum is the dominant mechanism of DO reduction, with temperature playing a smaller but measureable part. Comparing membrane DO values for runs 3 and 4, there is a noticeable reduction in DO already at the membrane for run 3 and little or no reduction for run 4. This indicates that the UV, through heating and/or reactions, can cause a significant DO reduction in the membrane chamber. However, the final DO value still seems to be mostly determined by the vacuum.

Table 4 DO values during the test.

<table>
<thead>
<tr>
<th>Run</th>
<th>Reservoir (mg DO/L)</th>
<th>Membrane (mg DO/L)</th>
<th>Sample (mg DO/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (UV/MBR effluent)</td>
<td>6.5 - 7.2</td>
<td>-</td>
<td>5.7</td>
</tr>
<tr>
<td>2 (MBR effluent)</td>
<td>7.2</td>
<td>-</td>
<td>6.0</td>
</tr>
<tr>
<td>3 (UV/tap water)</td>
<td>7.4 - 7.5</td>
<td>6.6</td>
<td>5.8</td>
</tr>
<tr>
<td>4 (Tap water)</td>
<td>7.5 - 8.0</td>
<td>7.5</td>
<td>6.2</td>
</tr>
</tbody>
</table>
3.5.1.2 Absorbance/Transmission
Changes in absorbance are small but consistent and behave as expected, see Table 5. The absorbance is greater for the MBR effluent than for the tap water, sample absorbance is always lower than initial absorbance and the reduction is several times larger for the UV runs. Concentrations at the membrane are slightly higher during run 3 and 4, which might indicate that substances are being concentrated in the membrane chamber, probably due to retention by the membrane.

Table 5 Values for adjusted absorbance during the test.

<table>
<thead>
<tr>
<th>Run</th>
<th>Reservoir at test start</th>
<th>Membrane at test end</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.199</td>
<td>-</td>
<td>0.185</td>
</tr>
<tr>
<td>2</td>
<td>0.200</td>
<td>0.200</td>
<td>0.195</td>
</tr>
<tr>
<td>3</td>
<td>0.121</td>
<td>0.124</td>
<td>0.113</td>
</tr>
<tr>
<td>4</td>
<td>0.122</td>
<td>0.127</td>
<td>0.119</td>
</tr>
</tbody>
</table>

3.5.2 Pharmaceutical Concentrations
As seen in Figure 15 and Figure 16, the different pharmaceuticals show greatly varying behavior; Citalopram, Sertralin, Fluoxetine and Risperidone are removed to a large degree in all runs, Ramipril and Warfarin seem to increase in concentration (this is caused by measurement technicalities as will be discussed in the discussion section) and Carbamazepine is barely affected. It is expected that the different substances will show differences in their degree of removal due to the large variations in chemical structure between the different substances, which affects affinity for the membrane and photocatalyst surfaces, as well as ease of degradation.

In Figure 15 and Figure 16 it is shown that bases (Table 7) with high K<sub>ow</sub> (high partitioning in octanol compared to water) and high log D (D is the ratio of solubility of the ionized species) show good reduction in dead-end filtration even without UV irradiation. The following bases have Log K<sub>ow</sub> > 2.5 and log D<sub>pH7.4</sub> ≥ 1.27: Citalopram, Fluoxetine, Sertralin, Risperidone and Amlodipine. They all contain one or more F or Cl functionalities.

Comparing the results of the runs using the same water (Runs 1 and 2 using spiked MBR effluent and runs 3 and 4 using spiked tap water) in Figure 17, the runs using UV show a higher reduction of pharmaceutical concentrations in almost all cases.

The effect of UV is visibly greater for the tap water runs. This can be explained by dissolved organic matter (DOM) present in the MBR water, which will adsorb pharmaceuticals with neutral and basic properties and also consume reactive species that would otherwise have degraded pharmaceutical compounds. As discussed in section 3.3, the effect of direct UV absorption by the DOM is of minor consequence.
Figure 15 Removal efficacy in % for the investigated pharmaceuticals in spiked tap water with and without UV treatment using dead-end filtration. The warfarin columns extend beyond the scale used.

Figure 16 Removal efficacy in % for the investigated pharmaceuticals in spiked MBR water with and without UV treatment using dead-end filtration. The Simvastatin column extends beyond the scale used.
The difference (in percentile units) between percentage removal for runs with and without UV. In order to calculate the results, values below the detection limit were set to the detection limit, which should lead to a slight underestimation of the degree of removal. Increases > 100% are assumed to be erroneous and are not shown in order to preserve the scale of the graph.

4 Cross-Flow Filtration

4.1 Experimental

A crossflow membrane setup was constructed, see Figure 18 and Figure 19, and tests performed using MBR effluent from the same process as in the dead-end filtration tests spiked to a concentration of around 20 µg/L with the 24 investigated pharmaceuticals (Table 7). The lamp used was a 30 W UV FL30BLB Blacklight Blue Tube F30WT8/BLB from International lamps, UK (UVA, 315 – 400 nm).

Figure 17 The difference (in percentile units) between percentage removal for runs with and without UV. In order to calculate the results, values below the detection limit were set to the detection limit, which should lead to a slight underestimation of the degree of removal. Increases > 100% are assumed to be erroneous and are not shown in order to preserve the scale of the graph.

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Figure 18 Cross-flow membrane chamber.  
Figure 19 Schematic of cross-flow set-up.
4.2 Results

The flux was tested both with and without UV light. It was clear that the UV light increased the flux, see Figure 20. After the measurement, the membrane was left standing soaked in water, and then cleaned with a dilute P-3 Ultrasil 11 solution. The flux after the Ultrasil cleaning was similar to the flux at the beginning of the tests.

![Figure 20](image)

Figure 20 Flux as a function of test time and use of UV light. There was an overnight pause after 525 minutes.

After use the membrane reactor was dismantled (see Figure 21) and the membrane was analyzed. There was some easily removable contamination on the membrane. A very slight stroke could push the residue aside. SEM-EDX analysis showed that there were some inorganic contaminants on the membrane (< 2 atom%), see Table 6.

Table 6 Inorganic material (atom%, SEM-EDX, 5kV) on the membrane after initial flushing with dilute Ultrasil solution.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>V</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>0.04</td>
<td>0.23</td>
<td>0.07</td>
<td>0.4</td>
<td>0.01</td>
<td>0.12</td>
<td>0.04</td>
<td>0.02</td>
<td>0.66</td>
<td>0.23</td>
<td>0.2</td>
<td>0.42</td>
</tr>
<tr>
<td>Min</td>
<td>0.04</td>
<td>0.13</td>
<td>0.07</td>
<td>0.17</td>
<td>0.01</td>
<td>0.07</td>
<td>0.04</td>
<td>0.02</td>
<td>0.19</td>
<td>0.23</td>
<td>0.17</td>
<td>0.42</td>
</tr>
</tbody>
</table>

4.2.1 Assessment of Membrane Ageing

Some parts of the used membrane were washed by gentle brushing with a soft brush in MilliQ-deionized water or by soaking in an Ultrasil solution (pH 10.7) at 35 °C for 12 minutes. The SEM micrographs before use and the ones after use and Ultrasil soaking look fairly similar, as seen in Figure 22 and Figure 23. Furthermore, EDX analysis (15 kV) showed that the Ti/F ratio was similar for the two membranes, demonstrating that there is no great loss of TiO₂ (if any). Thus there is no obvious change from the use and cleaning of the membrane in these respects.
Figure 21 The membrane after use. The dark spot is dirt pushed together using gentle force.

Figure 22 SEM micrographs of unused membrane.

Figure 23 SEM micrograph after use and Ultrasil soaking.
4.3 Photocatalysis Efficacy on Methylene Blue

An assessment of the efficacy of the membranes before and after use was performed by testing their photodegradation capacity on a $10^{-5}$ M MB solution comparing the used filters with an unused filter. All filters were left for absorption of the MB dye for 17.5 h after which the test of photocatalytic degradation of a new dye solution was performed.

The visual results are shown in Figure 24, where it is observed that the membranes with pre-absorbed/adsorbed MB are bluer than when the same filters have been exposed to a new solution of MB and UV light for 3 hours. This indicates that in addition to degradation of the MB in solution, some of the pre-absorbed MB has been degraded.

The conclusion of the comparison between used and new membranes is that the efficacy of the degradation was only slightly lower for the used membranes compared to the unused, see Figure 25.

Figure 24 Left: Filters after absorption of Methylene blue. Right: Filters after absorption and photocatalysis. Samples: 1 & 2 are unused photocatalytic membranes, 3 & 4 are used membranes after water cleaning, 5 & 6 are used membranes after an P-3 Ultrasil wash at pH 11.

Figure 25 Reduction of total amount of MB [%] in the solution after 3 h photocatalysis.
5 Discussion

5.1 Observed Negative Removal During Treatment

During estimation of the removal efficacy some of the 24 pharmaceuticals exhibited a negative reduction during treatment (Figure 15 and Figure 16). Similar results have been reported for sewage treatment of pharmaceuticals in peer-reviewed literature [8-10]. An explanation to the phenomenon is that some pharmaceuticals in influent wastewater are in a conjugated state, i.e., in order to enhance the urine excretion of a pharmaceutical from the human body the liver has added a polar group to the molecule structure (Phase I and phase II metabolism of anthropogenic chemicals (R) in the liver).

Thus when a pharmaceutical in a conjugated state reaches the sewage treatment plant (STP), bacteria present within the treatment process cleave (deconjugate) the energy-rich bond between the conjugate and the pharmaceutical molecule and it returns to its original structure. This means that if we do not have access to the conjugated state of the investigated pharmaceutical as an analytical standard, which is usually not available for purchase, and add it during evaluation a selective analytical measurement will perceive the concentration of the parent pharmaceutical as increasing from influent to effluent wastewater [9].

In a study by Magnér et al. [11] it was investigated if deconjugation could be an explanation to observed negative reduction of selected pharmaceuticals. They concluded that contribution from deconjugation to the observed phenomenon was insignificant. However, they also studied if the recovery during sample preparation of influent and effluent wastewater could explain the observed increase, i.e. if the more complex matrix of influent wastewater could affect and hamper the recovery of selected pharmaceuticals compared to the less complex effluent wastewater. In addition, they investigated the differences in ion-suppression during instrumental analysis between
influent wastewater extracts and effluent wastewater extract. Ion-suppression occurs during analysis when the analytes of interest (investigated pharmaceuticals) compete with co-eluting dissolved organic matter present in the sample extract for the ionization energy in the ion-source of the mass-spectrometer. This would mean that the influent wastewater, which contains a higher amount of residues of dissolved organic matter compared to the effluent wastewater, should exhibit a higher degree of ion-suppression, which would be perceived as though a negative reduction of selected pharmaceuticals would have occurred from influent to effluent wastewater.

The result of the study showed that ion-suppression was the dominant factor for the observed negative reduction of selected pharmaceuticals during sample treatment. Ion-suppression accounted for an average of 49% of the reduction in analytical signal in the influent wastewater extract compared to an average of 38% of the reduction in analytical signal in the effluent wastewater extract (Magnér et al., 2016). Ion-suppression is probably the explanation for the observed negative reduction for some of the pharmaceuticals in our study (Figure 15 and Figure 16), especially considering that more pharmaceuticals exhibit negative reduction and to a higher extent in the more complex MBR effluent than in the relatively clean spiked tap water (Figure 15, Figure 16).

The fact that we observe a negative reduction for some pharmaceuticals in tap water is probably due to bleeding of polymeric material from the solid-phase extraction (SPE) columns used during sample extraction, which allows for ion-suppression to occur and contributes to uncertainties in the analysis. It is possible to compensate for losses in both recovery and ion-suppression during sample preparation and analysis by the addition of isotope-labeled standards for every pharmaceutical investigated before the start of the sample preparation. However, the problem is that isotope-labeled standards are not commercially available for all the pharmaceuticals investigated.

5.2 Removal Efficacy of Pharmaceuticals During Treatment

Pharmaceuticals with neutral and basic properties (Table 7, Atenolol to Terbutaline, except Paracetamol and Ketoprofen) exhibit a generally higher removal efficacy compared to pharmaceuticals with acidic properties (Diclofenac to Warfarin as well as Paracetamol and Ketoprofen) in both dead-end (Figure 15, Figure 16) and cross-flow filtration experiments (cross-flow results not shown).

An explanation could be that the surface of the photocatalytic membrane has an isoelectric point of ~6.2 and the water matrix a pH of ~7, which will give the surface an overall negative net charge that could repel acidic molecules with negative charge. In a previous study by Zhang et al. [12] the solution media was adjusted to pH values between 3.0 and 7.0. The degradation rate of the four investigated pharmaceuticals was the highest when the pH value was set to 6.0. The results were explained in terms of electrostatic attraction/repulsion between the photocatalyst surface and the pharmaceuticals. The isoelectric point of the P25-TiO2/TEOS membrane studied was 6.66. The four pharmaceuticals represented weak acids with pKa values of 2.98, 4.15, 4.50 and 5.20 for salicylic acid, naproxen, diclofenac and ibuprofen, respectively. The result showed that:
At pH values below the isoelectric point, the catalyst particles are protonated and become positively charged.

At pH values above the isoelectric point, the catalyst particles are deprotonated and become negatively charged.

At pH less than 6.66 and above the pKa values of the four pharmaceuticals, the surface of TiO$_2$ becomes positively charged and the pharmaceuticals become negatively charged and are electrostatically attracted to the TiO$_2$ surface leading to improved degradation.

At pH above 6.66, the surface of TiO$_2$ and the four pharmaceuticals become negatively charged, resulting in an electrostatic repulsion between them which can reduce their sorption to the TiO$_2$ surface and thus decreases their rate of degradation.

Table 7 Chemical and physical properties of the 24 investigated pharmaceuticals.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mode of action</th>
<th>Chemical properties</th>
<th>Acid/Base</th>
<th>Log $K_{ow}$</th>
<th>Log $D_{pH7.4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diclofenac</td>
<td>Anti-inflammatory</td>
<td>Acid</td>
<td>4.06</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>Furosemide</td>
<td>Diuretics</td>
<td>Acid</td>
<td>3.10</td>
<td>-0.78</td>
<td></td>
</tr>
<tr>
<td>Hydrochlorothiazide</td>
<td>Anti-inflammatories</td>
<td>Acid</td>
<td>-0.07</td>
<td>-0.01</td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>Anti-inflammatory</td>
<td>Acid</td>
<td>3.72</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>Naproxen</td>
<td>Anti-inflammatory</td>
<td>Acid</td>
<td>3.00</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>Ramipril</td>
<td>Antihypertensives</td>
<td>Acid</td>
<td>3.41</td>
<td>-0.13</td>
<td></td>
</tr>
<tr>
<td>Warfarin</td>
<td>Anticoagulants</td>
<td>Acid</td>
<td>3.42</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>Atenolol</td>
<td>Antihypertensives</td>
<td>Base</td>
<td>0.10</td>
<td>-1.85</td>
<td></td>
</tr>
<tr>
<td>Amlopidine</td>
<td>Antihypertensives</td>
<td>Base</td>
<td>4.16</td>
<td>1.91</td>
<td></td>
</tr>
<tr>
<td>Bisoprolol</td>
<td>Antihypertensives</td>
<td>Base</td>
<td>2.14</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Caffeine</td>
<td>Stimulant</td>
<td>Neutral</td>
<td>-0.13</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>Sedatives</td>
<td>Neutral</td>
<td>2.67</td>
<td>2.28</td>
<td></td>
</tr>
<tr>
<td>Citalopram</td>
<td>Antidepressants</td>
<td>Base</td>
<td>2.51</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>Fluoxetine</td>
<td>Antidepressants</td>
<td>Base</td>
<td>4.09</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>Anti-inflammatory</td>
<td>Acid</td>
<td>2.81</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Metoprolol</td>
<td>Antihypertensives</td>
<td>Base</td>
<td>1.79</td>
<td>-0.25</td>
<td></td>
</tr>
<tr>
<td>Oxazepam</td>
<td>Sedatives</td>
<td>Neutral</td>
<td>2.31</td>
<td>2.06</td>
<td></td>
</tr>
<tr>
<td>Paracetamol</td>
<td>Anti-inflammatory</td>
<td>Acid</td>
<td>1.08</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Propranolol</td>
<td>Antihypertensives</td>
<td>Base</td>
<td>3.10</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>Ranitidine</td>
<td>Antulcers</td>
<td>Base</td>
<td>1.23</td>
<td>-0.63</td>
<td></td>
</tr>
<tr>
<td>Risperidone</td>
<td>Antipsychotic</td>
<td>Base</td>
<td>2.88</td>
<td>1.81</td>
<td></td>
</tr>
<tr>
<td>Sertraline</td>
<td>Antidepressants</td>
<td>Base</td>
<td>4.81</td>
<td>3.14</td>
<td></td>
</tr>
<tr>
<td>Simvastatin</td>
<td>Lipid-regulating</td>
<td>Neutral</td>
<td>4.41</td>
<td>4.60</td>
<td></td>
</tr>
<tr>
<td>Terbutaline</td>
<td>Asthma medication</td>
<td>Base</td>
<td>0.48</td>
<td>-1.61</td>
<td></td>
</tr>
</tbody>
</table>

$D$ is the ratio of solubility of the ionized species, and $K_{ow}$ partitioning in octanol compared to water.

Table 8 Removal efficacy in % in dead-end tests with respect to treatment technique and water matrix.

<table>
<thead>
<tr>
<th>Type of treatment</th>
<th>Average</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>All</td>
<td>Without Warfarin &amp; Simvastatin</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>With UV, Tap water</td>
<td>29</td>
<td>45</td>
</tr>
<tr>
<td>Without UV, Tap water</td>
<td>14</td>
<td>24</td>
</tr>
<tr>
<td>With UV, MBR water</td>
<td>36</td>
<td>38</td>
</tr>
<tr>
<td>Without UV, MBR water</td>
<td>2.1</td>
<td>11</td>
</tr>
</tbody>
</table>
In the dead-end filter tests the removal efficacy of the investigated pharmaceuticals was shown to be slightly higher with UV light in tap water (average removal 45%, Table 8) compared to MBR effluent with UV light (average removal 38%, Table 8), if Warfarin and Simvastatin were excluded from the calculations. Warfarin and Simvastatin were excluded as they demonstrated values which for unknown reasons differ greatly from the overall measurements (Figure 15 and Figure 16). The chromatogram and calculations have been thoroughly examined and the vast differences for Warfarin and Simvastatin can’t be explained with more than that something seems to interfere during analysis of two the substances. That the removal efficacy of the investigated pharmaceuticals proved to be slightly higher with tap water as matrix compared to MBR effluent as matrix can be due to the tap water having a much lower content of DOM, which will compete with the pharmaceuticals for the photocatalytic degradation at the surface of the membrane in the MBR effluent.

In the dead-end filter tests UV treatment enhanced the average removal of the investigated pharmaceuticals both in tap water and MBR effluent, as expected (Table 8). However, the difference in removal with or without UV light is slightly greater with MBR effluent as the matrix, which indicates that DOM present in the MBR effluent is retained at the surface of the filter and will enhance the adsorption of pharmaceuticals with neutral and basic properties. Pharmaceuticals with neutral properties are in average more hydrophobic than compounds with ionic properties at natural pH, allowing neutral pharmaceuticals to distribute to a greater extent to organic matter [13]. In addition, the net charge of organic matter is slightly negative [14], which makes basic pharmaceuticals with a positive charge adsorb to the organic materials [15].

6 Conclusions

The project has shown that a photocatalytic membrane filter is promising for keeping high flux and reducing the downtime by lengthening the cleaning cycle.

Photocatalysis also degrades organics such as pharmaceutical residues and dyes in both tap water and effluent from an MBR treatment process. Several parameters affect the efficacy, including the hydrophobicity and pKa of the pharmaceutical, the pH of the water and the presence of dissolved organic matter, and of course the running conditions:
• Bases with high $K_{ow}$ and high log D show good reduction in dead-end filtration even without UV irradiation. The following bases have $\log K_{ow} > 2.5$ and $\log D_{pH \text{7.4}} \geq 1.27$: Citalopram, Fluoxetine, Sertralin, Risperidone and Amlodipine. They all contained one or more F or Cl functionalities.

• The pH of the aqueous phase is also an important factor in the removal. The alkaline and neutral drug residues were broken down at natural pH, while it has previously been shown that at acidic pH acidic drug residues will also be degraded [12]. The underlying reason is that effective degradation is achieved when the drug is in close vicinity to or adsorbed on the photocatalyst.

It was also shown in our study that the dissolved organic matter present in the MBR effluent absorbs UV light with shorter wavelengths (UV-C region, to be more precise), thus, they do not interfere with the degradation of organic by the UV light-induced photocatalytic reaction. However, the dissolved organic matter may adsorb the pharmaceutical residues, preferably positively charged bases, and reduce the photocatalytic efficacy in this way.

The results of the study show that our reduction levels are minimum reduction levels, due to technicalities in the analysis method: ion-suppression in the LC/MS/MS analysis of the pharmaceuticals affected the analysis of the concentration of the pharmaceuticals in the influent and effluent. It is possible and recommended for future work to compensate for losses in both recovery and ion-suppression during sample preparation and analysis by addition of isotope-labeled standards for every pharmaceutical investigated before the start of the sample preparation. However, a problem is that commercial isotope-labeled standards are not available for all the pharmaceuticals investigated.

The tests of the membrane before and after 15 hours use in cross-flow filtration of MBR effluent showed no significant deterioration in terms of appearance (SEM) or loss of TiO$_2$, (Ti/F ratio, XPS) or efficacy of photocatalysis of dye.

7 Acknowledgement

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8 References


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