The Coupling of Catalysis with Submerged Ceramic MF Membrane for Hybrid Water Treatment Process

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The purpose of coupling Microfiltration (MF) with the catalytic process is to separate suspended catalyst from a reaction solution. In this study, submerged ceramic membranes were used. Different operating modes of MF in combination with photocatalysis were investigated: (1) MF separation of the suspended catalyst without UV irradiation and reaction; (2) MF in connection with UV irradiation and active photocatalytic reaction, whereby the catalytic activities of TiO_2 catalytic particles were determined and the catalytic reaction rates of suspended particles were compared with that of deposited particles as a cake layer on the membrane surface.

The results of the first operating mode showed that a minimum cake layer of deposited catalytic particles on membrane surface was achieved which subsequently exhibited 10 % decline of normalized permeability by controlling the permeate flux.

The TOC degradation by the photocatalytic activity with immobilized catalyst was obtained in the range between 61 % and 82 % while with the 0.5 $g.L^{-1}$ catalytic particles in suspension the measured values was 91.2 % within a period of 2 hours irradiation in both investigated systems.

1. Introduction

Heterogeneous catalysis (e.g. UV/TiO_2) belongs to Advanced Oxidation Processes (AOPs) has emerged as a powerful technique for the degradation of complex organic compounds. Fundamentally, the catalyst can be either dispersed in suspension or immobilized on other support material (e.g. glass, membrane etc.). In case of suspension, it needs to be separated and reused such catalyst afterwards. Since the particles size becomes smaller and smaller, its post-treatment has hindered the practical application. The combination of membrane separation with catalysis process has been developed as an alternative technique for recovery catalytic particles from treated water. The driven-pressure membranes such as Microfiltration (MF) and Ultrafiltration (UF) are suitable for solid-liquid separation process involving colloids and fine particles. In comparison with UF process, MF process exhibits lower operating cost due to low operating pressure and high filtration rate. The products and by-products of decomposition are generally low molecular compounds. Conceptually, the permeate after hybrid process can be used as a feed for down-stream Nanofiltration and/or Reverse Omosis treatment (Samhaber & Nguyen, 2014).

Recently, submerged membrane filtration which has been used widely in classical membrane bioreactors shows the feasibility in mitigating particles deposition and becomes a cost-effective technique (Judd, 2008). Several recent studies investigating submerged membrane as a part of hybrid photocatalysis - membrane processes have been reported in literature (Fu et al., 2006; Chin et al., 2007; Molinari et al., 2008; Damodar et al., 2010; Damodar et al., 2012; Wang et al., 2013; Szabolcs Kertèsz, Jiří Cakl, 2013). Another further advantage of submerged membrane in combination with photocatalysis is that the degradation of organic compounds and physical separation by mean of membrane can take place simultaneously in a single unit. However, most of papers have focused on the performance of polymeric membranes as well as their stability in the photocatalytic membrane reactors (PMRs). There are only few of publications dealing with catalytic reactor equipped with ceramic membranes (Mozia et al., 2015). In comparison with polymeric membranes, ceramic membranes exhibit higher chemical and UV resistance that make them more advantageous in coupling with catalysis process.

The aim of the present work was to examine the performance of submerged ceramic MF membrane in combination with TiO_2/photocatalysis. In particular, the influence of operating conditions on membrane performance and catalytic activity of TiO_2 particles was evaluated, concentrating on (1) the effect of permeate flux on the performance of submerged MF for TiO_2 separation without UV irradiation and reaction; (2) the photocatalytic efficiency of hybrid photocatalysis – membrane process. In the latter case, the catalytic activity of TiO_2 particles was evaluated in both cases: suspended catalyst and immobilized catalyst. For the reaction, oxalic acid was chosen because it is not only the water pollutant resulting in many processes but also the intermediate of other organic compounds degradation (Franch et al., 2002). Moreover, it is easy to oxidize due to the high potential of Redox couple $E_{H2C2O4(aq)}/_{CO2(g)}$ = - 0.49 V (Herrmann et al., 1983).

2. Experimental

2.1 Materials

Aeroxide TiO_2 P90 (Evonik, Degussa) was used as photocatalyst. The suspensions were prepared by dispersion of the desired amount of TiO_2 in deionized water. In aqueous solutions with natural pH (pH 4.9 ± 0.2), it was found that TiO_2 forms aggregates with the mean size of 326 nm. Oxalic acid (> 97 %, Fluka) with concentration of 100 mg.L^{-1} was used. Two commercially ceramic membranes were employed in this study. The main properties of the membrane as given by the manufacturer are shown in Table 1.

Table 1: Properties of ceramic membranes used in the experiments

	Membran G	FSM
Referred as	**ItN 02.2**	**LT01**
Manufacturer	ItN Nanovation (Germany)	Liqtech (Denmark)
Material	α-Al_2O_3	SiC
Configuration	Flat sheet	Flat sheet
Pore size, μm	0.2	0.2
Membrane area, m^2	Approx. 0.075 m^2	Approx. 0.066 m^2

2.2 Analysis

The concentration of TiO_2 suspension was determined based on a calibration curve (concentration vs. turbidity) prepared with known concentrations. WTW-Turb 550 turbidity meter (Germany) was used to measure the turbidity of bulk suspension and permeate. The pH of the reaction mixture was measured using a digital pH meter (Knick, Portatest 655). Electrical conductivity of mixture was measured with a conductivity meter (WTW-LF95). The total organic carbon (TOC) was determined using the Multi N/C 2100 (Analytik Jena, Germany). The samples of reaction mixture were collected at regular time intervals and filtered through a CHROMAFIL® O-20/15MS filter to remove the particles before TOC analysis.

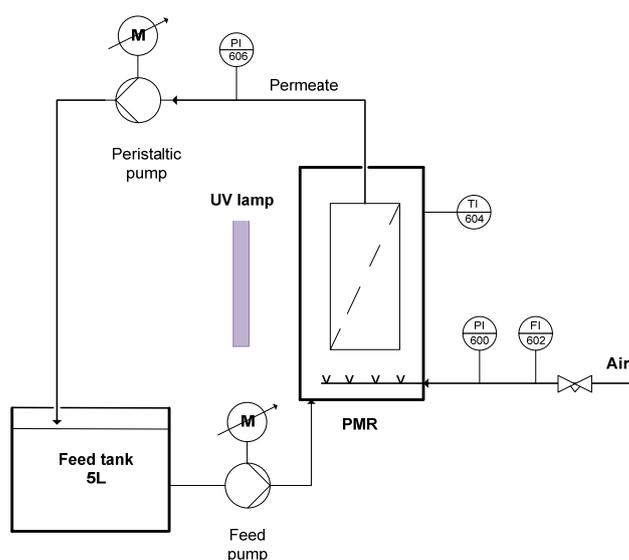### 2.3 Photocatalysis – submerged membrane system

Figure 1: Schematic diagram of photocatalysis – submerged membrane in this study

Figure 1 illustrates the schematic diagram of photocatalysis - membrane system. The flat sheet membrane was immersed in the centre of the module. Retentate compartment was directly irradiated by a 400W UV lamp (the wavelength in the range of 225 nm to 360 nm, provided by UMEX GmbH Dresden, Germany), placed at a distance of 90 mm away from the module. The experiments with suspended catalyst and immobilized catalyst were conducted in the same reactor to ensure the reproducibility of the obtained data and to be able to compare the performances accurately.

The permeate was withdrawn by a peristaltic pump (Masterflex, Easy Load head model 7518-00) with a constant flux and recycled back to the feed tank. The permeate pressure was measured by a digital vacuum gauge (DVR1, Vaccubrand) placed in the permeate line. Air was injected at the bottom of the reactor with circular nozzles.

3. Results and discussion

3.1 Submerged MF experiments for TiO$_2$ separation

The experiments were carried out for separating TiO$_2$ catalytic particles in water without UV irradiation. All experiments were conducted at constant permeate flux condition. The effect of permeate flux on pressure drop (filtration resistance) and extent of cake layer formation on membrane surface was evaluated. The transmembrane pressure (TMP) and the turbidity of bulk suspension were monitored during the filtration time. The turbidity of permeate (less than 0.2 NTU) confirmed that permeate was free of TiO$_2$ particles and MF membrane can separate completely TiO$_2$ particles from suspension. Due to the recirculation mode, the turbidity of suspension decreased during the experiments which indicated the accumulation of particles on membrane surface. On the other hand, the TMP rise (i.e. pressure drop) represents the cake resistance due to cake layer formation. The rate of pressure drop is calculated as Eq(1):

$$\frac{d(TMP)}{dt} \approx \frac{\Delta(TMP)}{\Delta t} = \frac{(TMP_t - TMP_0)}{\Delta t} \tag{1}$$

The amount of deposited particles, referred as mass of cake, was calculated based on mass balance due to recirculation batch performance, as follow:

$$M_c = \frac{(C_0 - C_t).V}{A_m} \tag{2}$$

where M_c is the mass of cake, g.m^{-2}; V is the total volume, L; A_m is membrane area, m^2 and C_0, C_t are concentration of bulk suspension at the beginning and at filtration time t, respectively, g.L^{-1}.
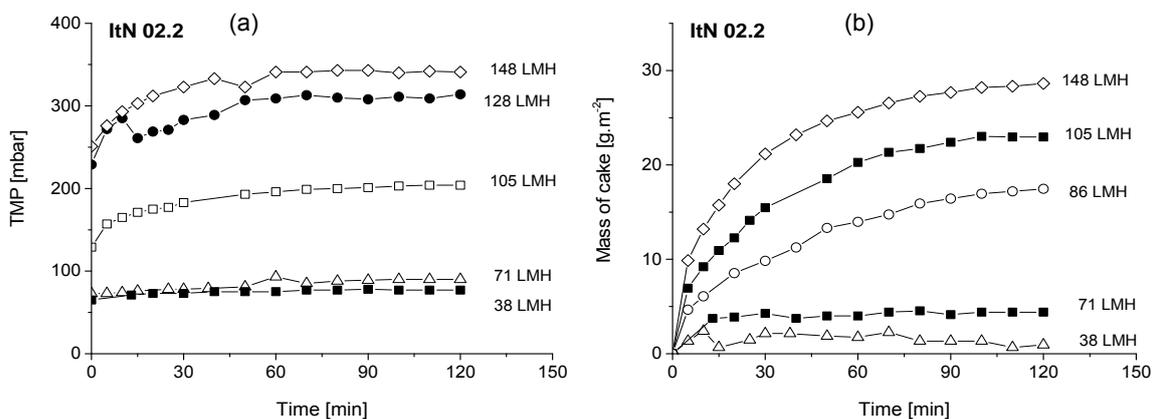
Figure 2: (a) Transmembrane pressure and (b) particles depositions on ItN membrane during filtration time at different permeate fluxes, initial C$_{TiO2}$ 0.5 g.L^{-1}, pH 4.9 and air flow rate 300 L.h^{-1}.

The results obtained in the experiments performed with ItN membrane at different permeate fluxes, with the concentration of 0.5 g.L^{-1} TiO$_2$ and air flowrate of 300 L.h^{-1} are presented in Figure 2. As we can see from Figure 2a, the TMP was very stable during the performance of ItN membrane at imposed permeate flux of 38 and 71 L.m^{-2}.h^{-1} (LMH) whereas at higher fluxes, it increased gradually at first 30 minutes of filtration and remained quite stable afterwards. The rise of TMP was in agreement with the rapid deposition of particles on membrane surface at the early period of filtration which shown in Figure 2b. The results reveal that the amount of deposited particles is more severe as permeate flux increases. Accordingly, the cake layer formation was

mitigated with lower permeate flux. Almost all particles were retained in suspension at permeate flux lower than 71 LMH and about 10% decline of normalized permeability was achieved. The steady-state permeability of membrane was about 500 $L.m^{-2}.h^{-1}.bar^{-1}$.

Figure 3 illustrates the pressure drop rate as function of permeate flux and the mass of cake for both ItN and Liqtech membranes. From Figure 3a, the data indicate that the rise of TMP was noticeably low up to a certain flux level beyond which a substantial increase in pressure drop occurs. Likewise, it was shown in Figure 3b that a significant increase of pressure drop was detected when the mass of cake was higher than 17.5 $g.m^{-2}$ for ItN membrane and 24 $g.m^{-2}$ for Liqtech membrane. In this study, it was found that the performance of submerged membrane at a moderate permeate flux (lower than 71 LMH) could maintain very low pressure drop and minimize the particles deposition. Similar results regarding the effect of permeate flux on submerged polymeric membrane performance were also reported by Chin et al. (2007) and Damodar et al. (2010).
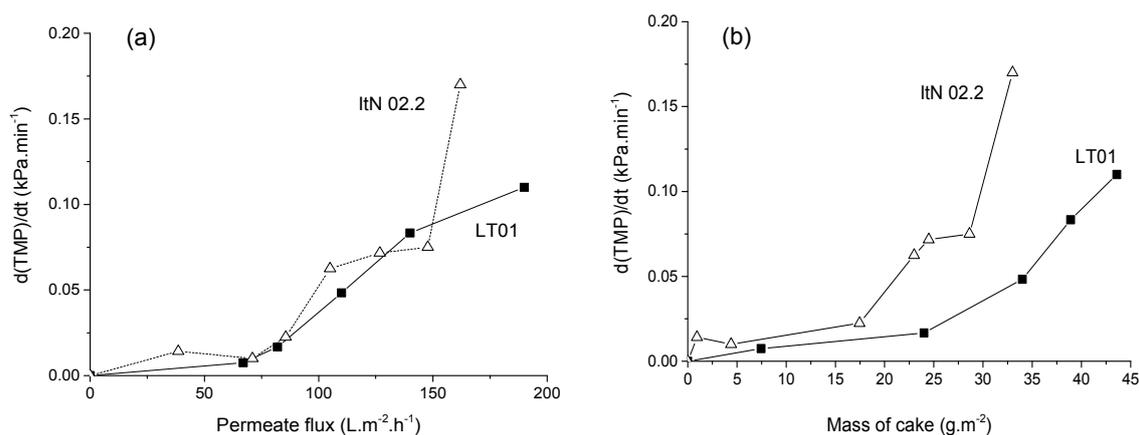

Figure 3: The pressure drop rate versus permeate flux (a) and mass of cake after 2 hours filtration (b) at initial C_{TiO2} 0.5 $g.L^{-1}$, pH 4.9 and air flow rate 300 $L.h^{-1}$.

3.2 The performance of photocatalysis - membrane system

Figure 4 shows the effect of UV irradiation on the TMP of ItN membrane at TiO_2 concentration of 0.5 $g.L^{-1}$. The similar amount of particles deposition on membrane surface was observed (data not shown here). Interestingly, the TMP was stable even slightly decreased when membrane was exposed by UV irradiation. The photocatalysis – membrane process was obtained with 25 % – 33 % higher permeability compared to process of MF alone. The results are in agreement with the findings of Mozia et al. (2015) which showed no permeate flux decline regardless of cake layer formation in case of using tubular ceramic membranes. According to the authors, the abrasion of membrane skin layer by catalytic TiO_2 particles could be a reason of enhanced permeate flux.
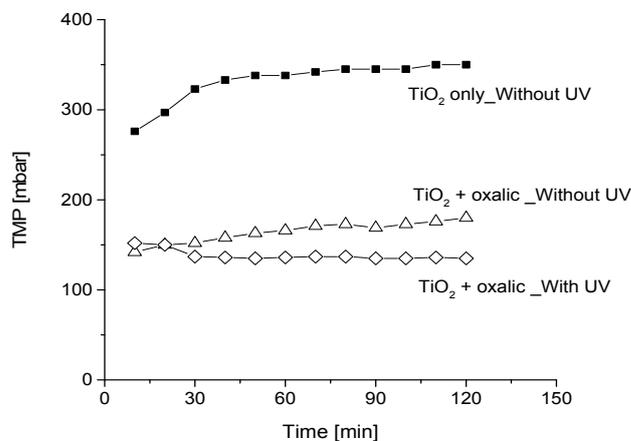

Figure 4: Effect of UV irradiation on TMP (ItN membrane at C_{TiO2} 0.5 $g.L^{-1}$, permeate flux of 140 LMH)

In order to evaluate TiO_2 catalytic activity in photocatalysis – membrane system, photocatalytic experiments were examined. With the aim of retaining catalyst within the photocatalytic reactor, the activity of TiO_2 catalyst in suspension was compared with TiO_2 particles in cake layer as immobilized catalyst. A certain cake layer was deposited physically on membrane surface at controlled conditions.

As discussed above (section 3.1), in order to keep TiO_2 well-dispersed in suspension, the performance of ItN membrane was carried out at 52 $L.m^{-2}.h^{-1}$ with the presence of aeration (air flow rate of 64 $L.h^{-1}$). The catalyst concentration was 0.5 $g.L^{-1}$ and the amount of TiO_2 immobilized on the membrane was 23 $g.m^{-2}$. The results are presented in Figure 5a. After 2 hours of UV irradiation, the highest decomposition of oxalic acid (88.5 %) was obtained for slurry system with membrane permeation, while for slurry system without membrane (as photoreactor) it was 75.6 %. In case of immobilized catalyst, the degree of decomposition was 58.3 %. The TOC analysis showed that the TOC degradation was 91.2 % and 67 % at the end of process in slurry and immobilized system, respectively.
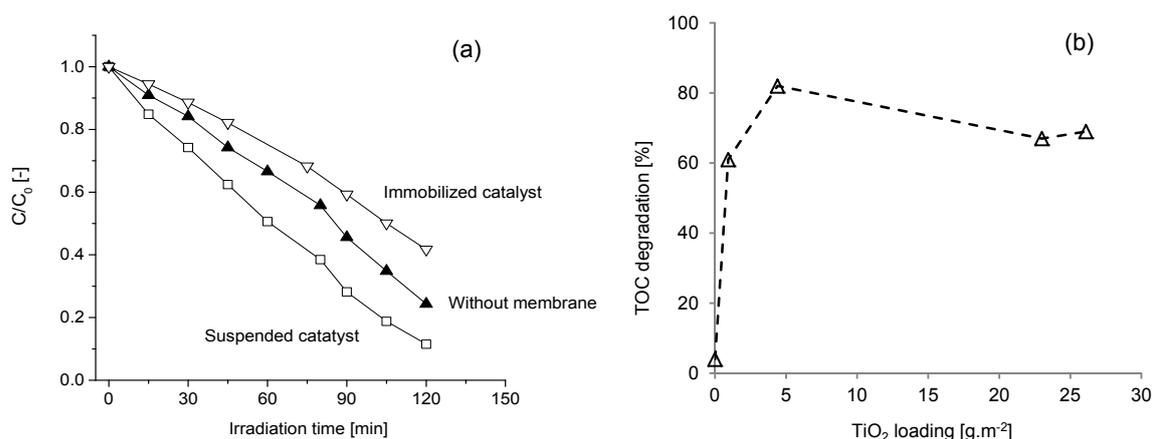

Figure 5: (a) The change of electrical conductivity as C/C_0 during the photocatalytic process and (b) the TOC degradation with immobilized catalyst on ItN membrane after 2 hours of UV irradiation.

Figure 5b illustrates the TOC degradation obtained in the immobilized system. In the range of deposited TiO_2 amounts in this study, the TOC degradation was from 61 % to 82 % and exhibited a maximum at the TiO_2 loading of 4.4 $g.m^{-2}$. The decrease of reaction rate at the higher deposited TiO_2 loading might be due to the decrease of UV penetration in the cake layer. As a consequence, the particles on the top of the layer could take part in the reaction whereas the particles closed to the membrane surface could not be active. In case of using deposited TiO_2 in cake layer as immobilized catalyst, it may have advantage for certain application due to the applicability of control catalyst amount. In addition, there is no effect on membrane structure either.

4. Conclusions

In this study, the performance of submerged ceramic MF membrane in combination with photocatalysis process was investigated and discussed. The following conclusions can be drawn:

1. Increasing permeate flux led to an increase of pressure drop due to the increase in the amount of deposited particles on membrane surface. It was found that with TiO_2 concentration of 0.5 $g.L^{-1}$ a minimal cake layer was obtained at a permeate flux of 500 $L.m^{-2}.h^{-1}.bar^{-1}$.

2. Under UV irradiation, the deposited TiO_2 particles in cake layer were active to degrade the organic compounds. However, the reaction rate increased up to an optimum catalyst loading of 4.4 $g.m^{-2}$ and decreased again beyond this optimum value. The maximum TOC degradation with the optimum TiO_2 loading was 82 % whereas the TOC degradation of 0.5 $g.L^{-1}$ suspended catalyst was 91.2 %.

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