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Research Paper

Diclofenac removal by submerged MF membrane photocatalytic reactor and coupling with RO membrane

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ABSTRACT

The purpose of coating TiO_2 on microfiltration membrane in photocatalytic membrane reactor (PMR) enhances the permeate flux and effluent quality. In this study, Nitrogen doped TiO_2 (N-TiO_2) on ceramic membrane surface submerged in the photocatalytic reactor under visible irradiation was used for diclofenac (DCF) removal. Different photocatalytic processes including without (Vis/N-TiO_2 process) and with hydrogen peroxide (H_2O_2) (Vis/N-TiO_2/H_2O_2 process) were investigated. Kinetic were identified with different DCF initial concentration in bath condition for both processes. The behaviors of DCF removal by the submerged membrane photocatalytic reactor (SMPR) in combination with reverse osmosis (RO) membrane were carried out in the continuous condition in the long term. The result showed that DCF and TOC concentrations increased in the photocatalytic reactor during operation time. It was a cause of returning DCF molecules and its products to the photocatalytic reactor by the RO membrane rejection. Coupling H_2O_2 with the photocatalytic process enhanced the DCF and TOC removal by SMPR under the visible irradiation.

1. Introduction

Diclofenac (DCF) is a nonsteroidal anti-inflammatory drug (NSAIDs). It is known as a persistent compound and is difficult to removes in a wastewater treatment plant. As a result, it presents in the wastewater, surface, ground water, and drinking water. DCF had a limited acute toxicity on bacteria, algae, microcrustaceans, and fish, but higher toxic in case of chronic test (Ferrari et al., 2003). Kidney and gills of fish was not also lesion by diclofenac, but also bioaccumulation in fish (Schwaiger et al., 2004). According to Hermando et al., 2006, EC_{50} of diclofenac concentration to bacteria was less than 1 mg/L, and 1 – 10 mg/L invertebrate to algae (Hermando et al., 2006).

Natural treatment, when pollutants discharge into wetland, pollutant can absorb by wetland. However, for manmade wetland comprise the groundwater abstraction which often exceeds the actual need, the negative impact of upland drainage on neighboring lowland, and the rise of groundwater table in agricultural land (Nagy., 2001). The wetland content the Ariake clay can absorb positive charge (Du et al., 2000). Therefore, presented DCF in wetland convert to cation R-N^+ that can be absorb by wetland for removal.

Manmade treatment, advanced oxidation processes (AOPs) are known as the novel technologies for the

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removal of persistent organic compound in wastewater. Heterogeneous photocatalysis has increased the application with high efficiency for degradation (Sarasidis et al., 2014) as well as good photocatalytic activity, nontoxicity, chemical inertness, and low cost (Buscio et al., 2015). However, it has a main limitation such as the requirement for the free TiO_2 catalyst to be separated from the supernatant after ending the reaction. Thus, to solve this problem, the combination of membrane technology and the photocatalytic process as the hybrid process, known as the photocatalytic membrane reactors (PMR) was first introduced in 2000 by Molinari and his coworker (Molinari et al., 2000). Catalysts in PMRs need to be separated and reused afterwards in case of the suspension. The catalyst particles are losing in continuous processes (Chong et al., 2010). There were exiting some obstacles such as damaged organic membranes by Ultra Visible (UV) light (Molinari et al., 2002). Immobilized catalyst in/on membrane have some advantages such as without the requirement of catalyst recovery operation, reducing membrane fouling, enhance feed flux and permeate flux, enhance the effluent quality, and contaminant decomposing in the membrane surface, as well as the possibility to enhance catalyst ratio and stability in/on membrane (Baltaa et al., 2012). Submerged membrane photocatalyst can overcome the disadvantages of photocatalytic immobilized in/on membrane such as small surface area-to-volume ratio and the reduced UV light utilization efficiency (Patsios and Karabelas, 2013). High membrane fouling resistant due to the effects of catalyst particles on the membrane leads to high flux maintenance. The limitation of submerged membrane photocatalytic reactor is the reduction of photocatalyst efficiency in case of increasing the suspended turbidity due to scattering light, penetrating to the suspension (Fu et al., 2006).

Provided available sunlight on the surface of the earth is a main cause to develop the process that could be used to harvest the solar energy. Modified semiconductor by doping or gating with metals or nonmetals can improve properties and photocatalytic activity of TiO_2 in the visible light region. According to the literature review by Dong et al., (2015), the modification TiO_2 by non-metal doping is not only narrowing the band gap, but also enhancing the adsorption of contaminants and conductivity of TiO_2 (Dong et al., 2015).

The main objective of this study is to compare two photocatalytic processes with and without H_2O_2 for DCF removal efficiency by SMPR with N-TiO_2 immobilized on the ceramic membrane under the visible irradiation. Other aspects of this work, kinetics of reaction assessed the DCF removal under various initial DCF concentrations in the bath condition. In particular, behaviors of DCF residual and TOC in the photocatalytic reactor and RO effluent in continuous condition in the long-term were investigated. Permeate flux deadline and membrane fouling were observed.

2. Materials and Methods

2.1 Chemicals and reagents

Titanium tetraisopropoxide (TTiP) (97.0%) was supplied by Sigma Aldrich Co.ltd and Diethanolamine (DEA) (98.5%) from Acros Organic. DCF was purchased from Volnac, T.O. Pharma, Co. Ltd, Thailand.

2.2 Preparation of N doped TiO_2

Sol-gel method was applied to the synthesis of N doped TiO_2 nanoparticles. First, 4.5 mL TTiP was dropped into a beaker, containing 15 mL acetic acid under vigorously stirrer. Then, 30 mL extracted chili solution was added into the beaker. Subsequently, 2.5 mL DEA was added droplet in the solution and left to stir for 30 min. The solution was poured into a ceramic dish and kept it in a hood at the room temperature. The sample was dried at 100ºC in an oven for 2 h. The sample was calcined at 500ºC in 30 min with the temperature raising 1ºC per min. Finally, N-TiO_2 was washed with ethanol and DI water five times, and dried in an oven at 105ºC in 2 h.

2.3 N-TiO_2 immobilization on MF ceramic membrane

The N-TiO_2 catalysts were immobilized on the MF ceramic membrane (Shandong Co, Ltd, China) (**Table 1**) with the total area 0.0148 m^2. The membrane was washed by ethanol several times to remove impurities on the membrane surface, and then dried it at the room temperature before doing immobilized N-TiO_2 catalyst on membrane. N-TiO_2 catalyst slurry was prepared by adding 1 g N-TiO_2 particles into a solution containing 0.05 g sodium dioctyl sulfosuccinate and 2 L of pure water under stirrer and sonication for 1 hour. MF membrane coated N-TiO_2 was prepared by carefully dipping it into the solution above and took it out. After that, the MF membrane was dried at 104 ºC in an oven, and then it was heated in a furnace with a ramp rate of 5 ºC per minute up to 500 ºC to dwell for 1 hour. This process was repeated until the desired amount of coating had been applied (Ciston et al., 2016).

Table 1. Technical parameters of tube MF ceramic membrane

Character	Parameters
Brand name	Huaci
Material	Alumina
Pore size	50 nm
Pressure strength	3.1 Mpa
Configuration	Tube
Membrane area	0.0148 m^2

2.4 Experimental set up

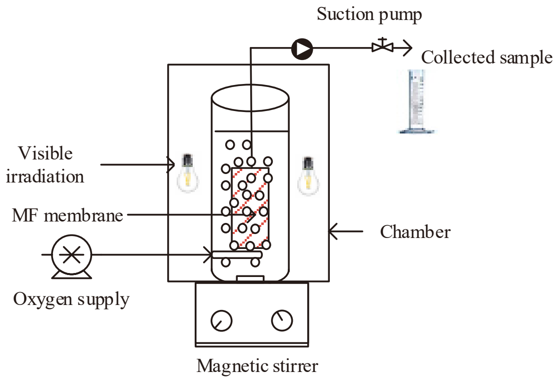

Fig. 1. Diagram of SMPR for bath condition.

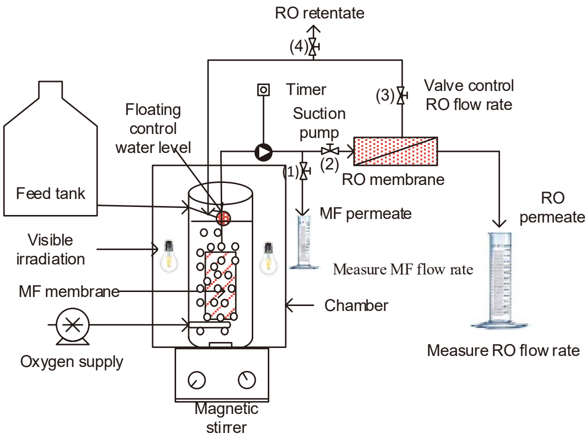

Fig. 2. Diagram of SMPR for continuous condition.

SMPR with immobilized N doped TiO_2 under the visible irradiation were applied for treated synthetic wastewater containing DCF. SMPR was designed by a photoreactor cylindrical tank with immerged tube MF ceramic membrane at the center of reactor and connected to a suction pump via a pipe (**Fig. 1**). The photoreactor cylindrical tank was made by stainless steel with working volume 2 L. Five visible lamps with the power of 50 W (wavelength with 520 nm) (Panassonic, Thailand) were put around outside the reactor. The photocatalytic reactor was placed in a chamber. To ensure the uniformity of DCF molecules in solution, DCF solution was mixed by a magnetic stirrer. Oxygen was supplied though the pipe, placed under the bottom of MF membrane. SMPR under Vis/N-TiO_2 and Vis/N-TiO_2/H_2O_2 processes were taken place for 180 min to investigate the DCF removal and pathways its products. In the continuous condition (**Fig. 2**), RO membrane, placed outside the reactor was combined with SMPR after MF membrane.

2.5 Analytical methods

The residual DCF concentrations were measured by UV-Vis spectrophotometer at wavelength 276 nm (A. Achilleos et al., 2010) by UV-Vis spectrophotometer with model: SENESYS 10S UV-Vis was applied. Total organic carbon (TOC) was determined by the TOC analyzer model: TOC-L CPH (Shimadzu), operating in a non-purge organic carbon mode. Calibration was achieved by injecting standards of potassium phthalate.

3. Result and discussion

3.1 Batch condition

3.1.1 Effect of DCF initial concentration

DCF concentration in the pharmaceutical wastewater treatment process is a key parameter. The investigation of the DCF concentration effect on the process performance is necessary. In this study, various initial DCF concentrations were investigated by photocatalytic processes with and without H_2O_2 in the bath condition. Initial DCF concentrations ranged from 1 to 50 mg/L for the Vis/N-TiO_2 process, whereas they were from 1 – 100 mg/L for the Vis/N-TiO_2/H_2O_2 process. The solution pH and H_2O_2 concentration were 6.5 and 15 mM, respectively. We found that it was the best operating condition for this study (not report here). **Table 1** showed the DCF and TOC removal efficiency with different initial DCF concentrations for both processes. The result indicated that increasing the initial DCF concentration reduced DCF and TOC removal efficiency in both processes. DCF at 1 mg/L was completely removed at the end of the reaction time. However, DCF residual concentrations in the reactor were high with increasing the initial DCF concentration in any process. The high initial DCF concentration was a cause of reducing DCF and TOC removal efficiency for SMPR with immobilized N-TiO_2. At the high organic pollutant concentration, TiO_2 surface is saturate, resulting in the deactivation photocatalyst due to reducing the photonic efficiency (Kashif and Ouyang, 2009). In addition, when DCF products are increasing that can adsorb on TiO_2 surface, and compete on active sites of TiO_2 surface with DCF molecules, resulting in prolonging the treatment time and reducing the process efficiency (Sarasidis et al., 2014). Increasing the DCF concentration induces the rise of the internal optical density and an inert filter effect, resulting in more impermeable solution to light irradiation (Aleboyeh et al., 2005).

The comparison at the same initial DCF concentration (20 and 50 mg/L) between two processes with and without H_2O_2 in photocatalytic processes (Vis/N-TiO_2 and Vis/N-TiO_2/H_2O_2 processes) showed that coupling H_2O_2 with the photocatlytic process under the visible irradiation enhanced the DCF removal efficiency (**Table 2**). As strong oxidant, H_2O_2 can scavenge excited electrons of TiO_2 to generate hydroxyl radical (Eq.1 and 2) (Velegraki et al. 2006). Therefore, it prevents the recombination of electron and hole, and reduces photocatalytic quantum yield (Achilleos et al. 2010). In addition, the reaction between H_2O_2 and oxygen species produces the hydroxyl radical (Eq. 3) (Irmak et al., 2004). Moreover, TiO_2 adsorption capacity is enhanced because forming peroxo complexes between H_2O_2 and Ti (Zou and Jao, 2011).

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2(h^+) + {}^\bullet OH + OH^- \quad (1)$$

$$H_2O_2 + e^-_{CB} \rightarrow {}^\bullet OH + OH^- \quad (2)$$

$$H_2O_2 + {}^\bullet O^-_2 \rightarrow {}^\bullet OH + OH^- + O_2 \quad (3)$$

The total organic carbons (TOCs) at end point of experiments (at 180 min) were measured to determine the DCF mineralization. The results showed that the TOC removal efficiency was reduced with increasing the initial DCF concentration in both processes. The TOC removal efficiency in the photoctalytic process coupling with H_2O_2 was increased to compare with the solely photocatlytic process. Thus, coupling H_2O_2 with the photocatalytic process not only enhances the DCF removal efficiency, but also enhances the removal of its products. In comparison between the DCF and TOC removal efficiencies, it showed that the TOC removal efficiencies were less than the DCF at the end point (**Table 2**). It indicated that the DCF intermediates firstly formed after oxidation process, and incomplete mineralization of DCF to the end product (formed CO_2).

Figure 3 showed the fate of H_2O_2 versus various initial DCF concentrations. The results indicated that the initial DCF concentration has effect on the fate of H_2O_2 in reactor, lower DCF concentration as faster H_2O_2 degradation. Maximum and minimum H_2O_2 degradation at low and highest DCF were 33.57 and 16.78%, respectively after 180 operation time by SMPR. As above explanation, H_2O_2 can directly react with N-TiO_2 to form hydroxyl radical by react with electron of N-TiO_2 or electron of conduction band that may be main reason for H_2O_2 degradation in photocatalytic reactor.

Table 2. Effect of initial DCF concentration on DCF and TOC removal

DCF (mg/L)	Process			
	Vis/N-TiO_2		Vis/N-TiO_2/H_2O_2	
	DCF removal (%)	TOC removal (%)	DCF removal (%)	TOC removal (%)
1	100	56.18	100	67.18
5	51.23	29.68	-	-
10	42.23	19.53	-	-
20	31.10	12.5	48.99	26.56
50	5.70	4.06	23.10	8.93
100	-	-	7.46	2.18

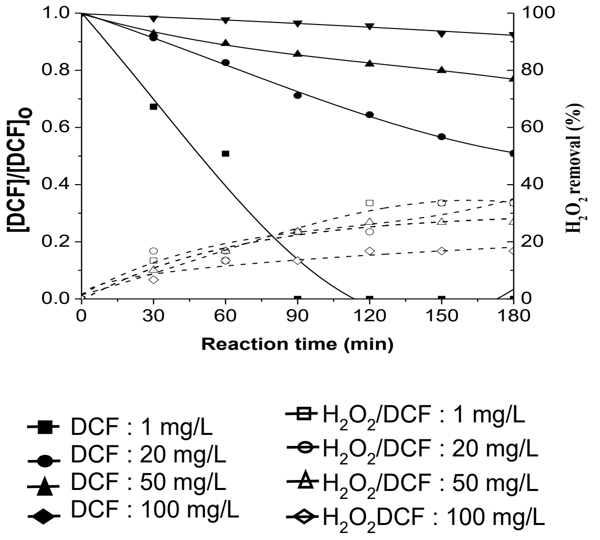

Fig. 3. Different DCF initial concentration removal versus H_2O_2 fate

H_2O_2 fate was lower degradation after 120 min for SMPR with immobilized N-TiO_2. Higher concentration of organic pollutant may be a cause of saturate the TiO_2 surface that lead to reduce the photonic efficiency, as result the deactivation of photocatalyst. Moreover, more organic intermediates may compete for active sites of TiO_2 surface with DCF that is a reason for prolonging the treatment time and reducing process efficiency (Sarasidis et al., 2014). Increasing DCF concentrations induce the rise of internal optical density and an inert filter effect leading to lower forming hydroxyl radical concentration (Muruganandham and Swaminathan, 2004). In addition, the lower initial organic concentration is more significant effect on organic degradation rate and permeate flux than higher initial organic concentration in term of membrane photocatalytic reactor (Chin et al., 2007, Kertèsz et al., 2014).

3.1.2 Kinetic of photooxidation of DCF under batch conditions of SMPR with immobilized N-TiO₂ under visible irradiation

Data analysis revealed that the DCF initial concentrations significantly influenced on the photodegradation kinetic rate. The pseudo-first-order equation (Eq. 4) was applied to calculate the initial rate (r) and kinetic constant (k_{obs}). **Table 3** showed the values of kinetic parameter for SMPR with immobilized N-TiO₂ on the MF membrane under the Vis/N-TiO₂ and Vis/N-TiO₂/H₂O₂ processes.

$$\mathrm{Ln}\ \frac{[\mathrm{DCF}]_{T,t}}{[\mathrm{DCF}]_{T,o}} = k_{obs}t \qquad (4)$$

Where: k_{obs} was pseudo-first-order kinetic constant, $[DCF]_T$ was total concentration of DCF. For each experiment k_{obs} was determined from the slope of the linear time course plot of $Ln([DCF]_{T,t}/[DCF]_{T,o})$.

Table 3. Values of kinetic parameters for DCF removal by SMPR with immobilized N-TiO₂ under visible irradiation, and coupling with H_2O_2.

	Vis/N-TiO₂			**Vis/N-TiO₂/H₂O₂**		
DCF (ppm)	r (mg L^{-1} min^{-1})	k_{obs} (min^{-1})	R^2	r (mg L^{-1} min^{-1})	k_{obs} (min^{-1})	R^2
1	0.0005	0.0056	0.9492	0.0016	0.0113	0.9970
5	0.0013	0.0040	0.9982	-	-	-
10	0.0015	0.0030	0.9872	-	-	-
20	0.014	0.0021	0.9811	0.0025	0.0037	0.9770
50	0.0003	0.0003	0.9702	0.0012	0.0015	0.9729
100	-	-	-	0.0004	0.0004	0.9673

Figure 3 showed the plot of straight-line relationship of $Ln([DCF]_t/[DCF]_o)$ versus irradiation time, t, under varying DCF initial concentration, **Fig. 4** for Vis/N-TiO₂ process and **Fig. 5** for Vis/N-TiO₂/H₂O₂ processes. The kinetic constants (k_{obs}) were reduced with the increasing DCF initial concentration in all different processes. The highest reaction rates of the DCF removal were 10 mg/L for the Vis/N-TiO₂ process and 20 mg/L for the Vis/N-TiO₂/H₂O₂ process, respectively. Increasing the initial DCF concentration from 10 to 50 mg/L for the Vis/N-TiO₂ process, and from 20 to 100 mg/L for the Vis/N-TiO₂/H₂O₂ process, the reaction rate reduced. As discussion above, increasing the organic pollutant reduces the deactivation photocatalyst. In contrary, the reaction rate was low at DCF 1 mg/L to compare with optimum the initial DCF concentration. Low DCF concentration gives less opportunity for DCF adsorption on the TiO₂ surface.

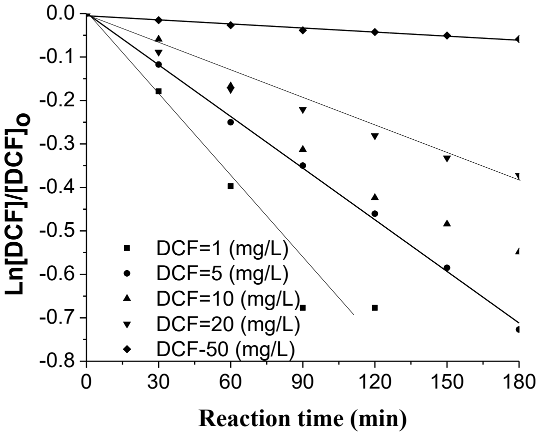

Fig. 4. Pseudo-first-order kinetic plot of DCF Photocatalytic oxidation by SMPR with N-TiO₂ immobilization on membrane under varying DCF initial concentration for Vis/N-TiO₂ process. Experimental conditions: pH 6.5, $[H_2O_2]$ = 15 mM.

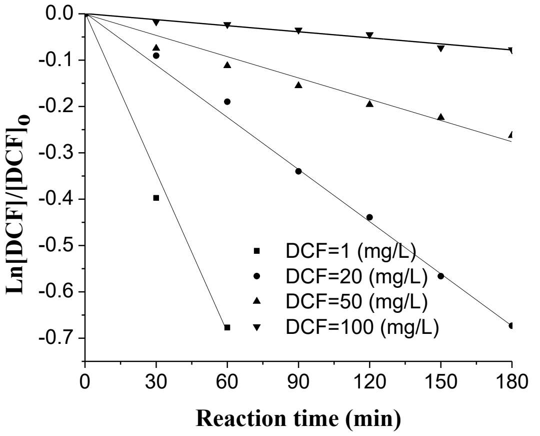

Fig. 5. Pseudo-first-order kinetic plot of DCF Photocatalytic oxidation by SMPR with N-TiO₂ immobilization on membrane under varying DCF initial concentration for Vis/N-TiO₂/H₂O₂ process. Experimental conditions: pH 6.5, $[H_2O_2]$ = 15 mM.

3.2 Continuous condition

3.2.1 Permeate quality of MF and RO membranes long-term operation

An examination of the long-term continuous operating performance of the Vis/N-TiO_2 and Vis/N-TiO_2/H_2O_2 processes for SMPR with immobilized N-TiO_2 was carried out with the solution pH 6.5, and DCF concentration 20 mg/L. The RO permeate was kept at 2.4 L/h which was equivalent to the hydraulic retention time (HRT) of 4 hours. DCF solution was continuously fed into the photocatalytic reactor from the feed tank. H_2O_2 was added in the feed tank and mixed with the DCF solution in the case of the Vis/N-TiO_2/H_2O_2 process. To control membrane fouling, SMPR systems were operated with an intermittent membrane filtration, controlled by a timer with a cycle at 5 min operation (ON) and 1 min pause (OFF). The samples were collected at MF and RO permeates at a regular interval of time to measure the residual DCF and TOC (**Fig. 1**). The RO permeate flux was measured after 4 hours to control the HRT. MF permeate flux deadline was measured by the measured output of the MF membrane regularly after 4 hours. **Fig. 6** showed the DCF concentrations in reactors and RO permeates under the Vis/N-TiO_2 and Vis/N-TiO_2/H_2O_2 processes by SMPR with immobilized N-TiO_2 to combine with the RO membrane during the operation time. The results showed that the trends of the DCF concentration in the photocatalytic reactor reduced at the early 2 hours for both processes, and regularly increased after 4 hours later up to the end of the operation time. Increasing DCF concentration in photocatalytic reactor illustrated that DCF molecular returned the photocatalytic reactor by RO rejection. Increasing DCF in the photoctalytic rector lead to overload of SMPR treated capacity. The DCF removal under the Vis/N-TiO_2 process was lower than the Vis/N-TiO_2/H_2O_2 process.

Most DCF molecular passed though MF membrane, whereas RO permeates showed the high effluent quality. They were steady less than 2 mg/L DCF during the operation time. It indicated that the RO membrane was very high potential to reject the DCF molecular. In the work of Kimura et al., 2003, they also find that RO membranes can negatively reject charged DCF up to 95% (Kimura et al., 2013). Good effluent quality after treatment by SMPR systems can be applied for discharging into the resources. The Photocatalytic membrane reactor using UF membrane in PMR in combination with the RO membrane not only prevented RO membrane from fouling, but also gave the higher effluent quality (Ollis, 2003). In this study, coupling the SMPR with the RO membrane had some advantages such as less TOC and small molecular weight (DCF products) at effluent. High molecular weights of DCF intermediates were rejected by the RO membrane to return the photocatalytic reactor for a more degradation to become less molecular weight. However, it brought a big problem such as increasing very high DCF concentration in the photoreactor that leads to the overload of treatment capacity of the SMPR system.

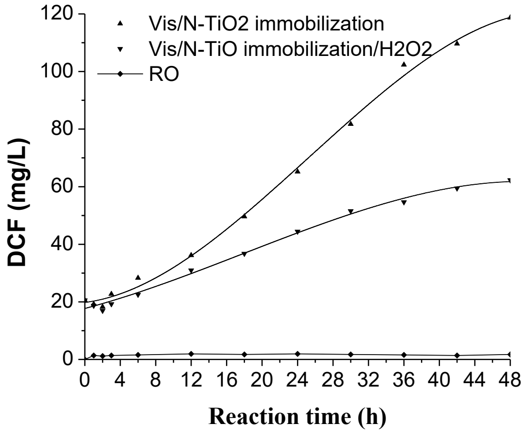

Fig. 6. Temporal variation of DCF degradation during long term condition for SMPR systems operation combination with RO membrane. Experiment conditions: pH = 6.5; initial DCF 20; [H_2O_2] = 15 mM for Vis/N-TiO_2/H_2O_2 process; intermittent membrane filtration 5 min ON and 1 min OFF.

Table 4 showed the rejected DCF molecular by the RO membrane. DCF concentration of MF permeate was the feed concentration for the RO membrane. RO concentrate, rejected DCF molecular by the RO membrane was the returned photocatalytic reactor. The RO permeate quality was the effluent quality of SMPR systems. The results showed that rejected DCF by the RO membrane was around 95%. There are many factors effect on solute rejected by RO membrane such as membrane properties, feed composition and operating conditions (Bellona et al., 2005), and three mechanism (electrical, Donnan) and physico-chemical interactions between solute, solvent and membrane (Radjenovic et al., 2008) that can be rejected solute by RO membrane include size exclusion (sieving, steric effect), charge exclusion.

In this study, DCF (pK_a = 4.15) is negative charge and reduces the hydrophobicity under experimental condition (pH=6.5), resulting increasing solubility. Therefore, it refers to the negative charge of the RO membrane for a better rejection base on Donnan theory because of the prevention of the DCF adsorption and diffusion though the RO membrane. The pore sizes of the MF membrane was 50 nm or a molecular weight cut off (MWCO) of greater than 1,000,000 Daltons. The pore size of the RO membrane ranges from 0.0001 – 0.001 μm (MWCO □ 100 Dalton). Molecular weight, length, width, depth of

DCF are 296.2 (g/mol), 1.13 (nm), 0.91(nm) and 0.45 (nm), respectively. Molecular weight is the most used parameter for prediction of the removal efficiency by the filtration process (Verliefde et al., 2007). The molecular weight more than 200 g/mol can be removed by the RO membrane (Lipp et al, 2010). Thus, DCF with molecular weight 296.2 g/mol can pass though the MF membrane, but can be rejected by the RO membrane due to the bigger size than the pore size of the RO membrane.

Table 4. DCF Feed and removal by RO membrane rejection

SMPR process	MF permeate = RO feed (mg/L)	RO permeate (mg/L)	RO rejection (%)
Vis/N-TiO_2	56.04±32.89	1.85±0.20	95.43±2.39
Vis/N-TiO_2/H_2O_2	36.51±15.01	1.35±0.13	95.60±1.89

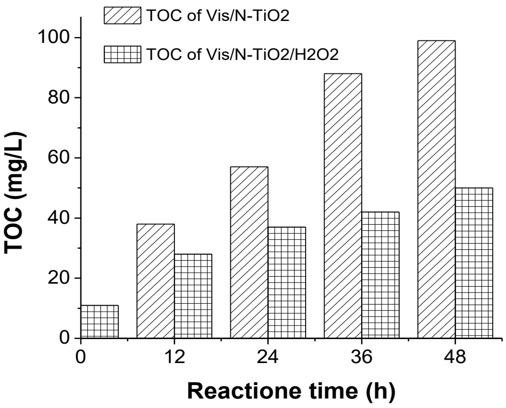

Fig. 7. Temporal variation of DCF mineralization during long term condition, (a) TOC of MF permeate and (b) TOC of RO permeate. Experiment conditions: pH = 6.5; initial DCF 20 mg/L; [H_2O_2] = 15 mM; and intermittent membrane filtration 5 min ON and 1 min OFF.

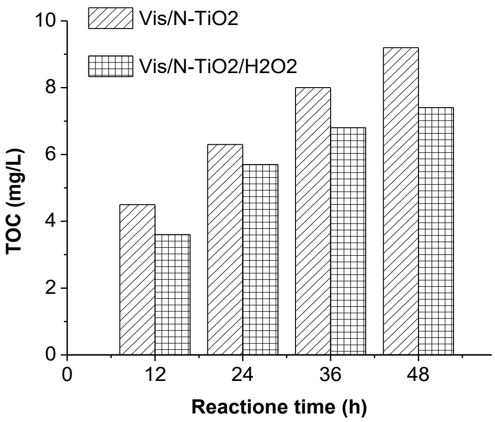

Fig. 8. Temporal variation of DCF mineralization during long term condition, (a) TOC of MF permeate and (b) TOC of RO permeate. Experiment conditions: pH = 6.5; initial DCF 20 mg/L; [H_2O_2] = 15 mM; and intermittent membrane filtration 5 min ON and 1 min OFF.

Figure 7 and 8 showed TOC removal efficiency of MF permeates (TOC in reactor) (**Fig. 7**), and RO permeate (TOC in effluent) (**Fig. 8**) during 48 hours photocatalytic oxidation. The results showed that TOC in reactor of SMPR under Vis/N-TiO_2 process was increasing faster than Vis/N-TiO_2/H_2O_2 process. TOC concentrations of RO permeate also increased from 12 to 48 hours for both processes. Increasing TOC concentration in reactor related to the retuned DCF molecular and its intermediates (high molecular weight) to reactor by RO rejection. However, increasing TOC concentration of RO permeates linked to smaller molecular weight cut-off (MWCO) of intermediates that can passed through the pores of RO membrane. It demonstrated that RO membrane played an important role to reject not only DCF, but also its products to retune to photocatalytic reactor for more mineralization.

3.2.2 *Permeate flux of MF and RO membrane during operation time*

In the long-term operation, permeate flux of MF membranes was investigated by measuring the flow rate of MF after 4 hours. The Permeate flux of the MF membrane reduced also leaded to reducing the RO permeate flux. Thus, the RO permeate had to adjust by the RO flow rate control valve to maintain the RO flow rate at 2.4 L/h (see in **Figure 1b**). **Fig. 9** showed the changing permeate flux of SMPR under different processes (Vis/N-TiO_2 and Vis/N-TiO_2/H_2O_2). The results showed that permeate flux of SMPR was steady at beginning and lightly reducing later after 8 h. The permeate flux of SMPR under the Vis/N-TiO_2 process reduced faster than the Vis/N-TiO_2/H_2O_2 process.

Reducing the permeate flux is a phenomena of membrane fouling. There are many causes of membrane fouling such as pore blocking, formed cake layer on the membrane surface, narrowed pore size or blocked membrane pores by foulants (Zhang et al., 2016). Increasing DCF and its products concentrations in the photocatalytic reactor during the operation time were reducing the permeate flux due to stick on the MF membrane surface. At the high concentration in the solution increases membrane fouling (Lin et al., 2012). As observation of the MF membrane surface with naked eyes at the end experiment, a cake layer was formed on the MF membrane. It was a cause of the mixture ò DCF and N-TiO_2 particles immobilized on membrane to become denser, which lead to reducing the permeation. At the high organic concentration, the cake layer of TiO_2 with organic became denser (Wang et al., 2013).

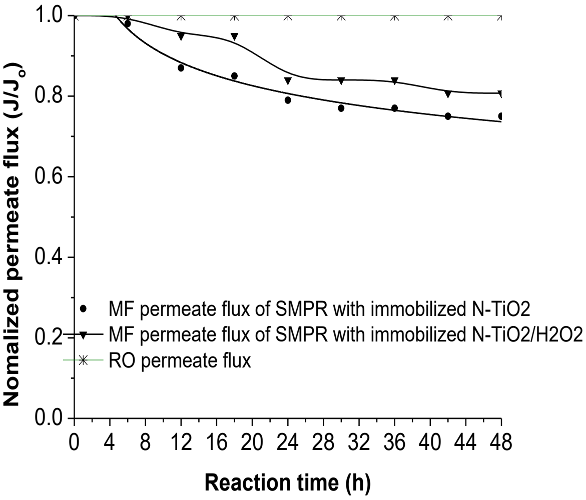

Fig. 9. MF and RO permeate flux change under continuous condition. Experiment conditions: pH = 6.5; initial DCF = 20 mg/L, [H_2O_2] = 15 mM for Vis/N-TiO_2/H_2O_2 process; and intermittent membrane filtration 5 min ON and 1 min OFF.

4. Conclusion

In this study, DCF removed by SMPR with immobilized N-TiO_2 under visible irradiation with two different processes with and without H_2O_2 in bath and long-term continuous condition. It was investigated and discussed as following:

1/ Coupling H_2O_2 with photocatalyst process under visible was enhancement DCF removal by SMPR with immobilized N-TiO_2.

2/ Coupling H_2O_2 with photocatalytic process enhanced membrane fouling resistant to compare with solely photocatalytic process.

3/ The kinetic of DCF removal by SMPR followed pseudo-first-order. Optimum DCF concentration increased reaction rate; 10 mg/L for Vis/N-TiO_2 process and 20 mg/L for Vis/N-TiO_2/H_2O_2 process.

4/ DCF concentrations in reactor were increasing during reaction time because of rejection by RO membrane. It may be a cause of overload SMPR capacity for DCF removal.

5/ TOC in RO permeate (effluent) was increasing during reaction time due to rejection of DCF and its products by RO membrane. It indicates that DCF can be more degradation to become smaller molecular, less toxic than DCF.

6/ Layer cake of organics was formed on MF membrane surface after treatment time that is the main cause of membrane fouling.

7/ Permeate fluxes of MF membrane reduced during reaction time due to membrane fouling.

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