

Study on the lifetime of photocatalyst by photocatalytic membrane reactors (PMR)

Xiaoju Yan, Junyu Li, Cong Ma, Yu Tang, Xiangji Kong and Jinfeng Lu

ABSTRACT

The continuously photocatalytic degradation of methyl orange (MO) was carried out using a photocatalytic membrane reactor (PMR). The lifetime, cause of deactivation, and regeneration of Degussa P25 titanium dioxide (TiO₂) were investigated. The photocatalyst was deactivated when the concentration of MO in the effluent of the PMR was stable. To characterize the lifetime of the photocatalyst, we applied g MO/g TiO₂. The lifetime of the photocatalyst during the photocatalytic degradation of 10 mg/L MO was 3.71 times that of 5 mg/L MO. Changing the hydraulic retention time of the PMR from 0.75 to 3 h prolonged the lifetime of the photocatalyst. Deactivation of the photocatalyst was not due to pore blocking by the reactant (MO) or intermediate products. The surface adsorption of MO and the reaction intermediates deactivated the catalyst. The spent catalysts were regenerated after washing with methanol and hydrogen peroxide (H₂O₂) and then treated with heat. H₂O₂ treatment generated the highest regeneration rate, because H₂O₂ is a strong oxidizing agent that oxidized the deposited species on the surface of the photocatalyst.

Key words | deactivation, lifetime, photocatalytic membrane reactor, regeneration

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INTRODUCTION

The superior oxidizing ability and the utilization of solar energy are the main advantages of the photocatalytic degradation process (Sun *et al.* 2003; Wang *et al.* 2019). Photocatalyst deactivation is an important reason to hinder industrial applications of the photocatalytic degradation process. The researches on photocatalyst deactivation problems mainly include: photocatalyst lifetime, deactivation mechanism and regeneration method. In fact, the mechanisms of photocatalyst deactivation and regeneration have been widely studied, organic pollutants occupying the adsorption sites of the photocatalyst are considered as the deactivation mechanism (Jing *et al.* 2004), and the regeneration methods to solve the deactivation problem include: washing, oxidation, and thermal treatment (Gandhi *et al.* 2012). However, researches on photocatalyst lifetime were rarely studied, and no researches on the factors of photocatalyst lifetime have been found.

To study photocatalyst lifetime and its factors, it is necessary to use a continuous photocatalytic reactor.

Photocatalytic membrane reactor (PMR) is a new type of continuous photocatalytic reactor. PMRs are hybrid reactors in which photocatalysis is coupled with a membrane process (Moza 2010; Yan *et al.* 2018). Membrane filtration can resolve the water/catalyst separation problem and maintain the high quality of the TiO₂ constant in the photocatalytic reactor (Shon *et al.* 2008; Boonya-atichart *et al.* 2018; Gao *et al.* 2018; Rani & Karthikeyan 2018). Photocatalyst deactivation represents a major drawback that hinders many industrial applications. Therefore, this study intends to change the photocatalytic reaction conditions in PMR to determine the effect of different reaction conditions on the lifetime of the photocatalyst. The study of the factors affecting the lifetime of the photocatalyst can optimize the photocatalytic reaction conditions and extend the lifetime of the photocatalyst, which is significant to the photocatalytic degradation process.

In this paper, the methyl orange (MO) dye was treated by PMR until the photocatalyst deactivated. The deactivation

mechanism was understood by Fourier transform infrared spectroscopy (FTIR) and Brunauer-Emmett-Teller (BET) surface area analysis. The regeneration effects of methanol cleaning, hydrogen peroxide oxidation, and calcination regeneration were investigated. In addition, the effects of reaction conditions on the lifetime of the photocatalyst were investigated by changing the concentration of TiO_2 and MO, hydraulic retention time (HRT) and UV light intensity in PMR. The effects of changing the TiO_2 concentration, MO concentration, HRT and irradiance of the UV lamp in the PMR on the lifetime of the photocatalyst were investigated.

MATERIALS AND METHODS

PMR

The cylindrical PMR had a volume of 2.16 L and a $33 \mu\text{W}/\text{cm}^2$ UV lamp with a wavelength of 254 nm. The schematic diagram of the PMR setup is shown in Figure 1. A hollow microfiltration (MF) membrane module was immersed in the PMR. Polyethylene (PE) MF membranes (Mitsubishi, Japan) had a pore size of $0.1 \mu\text{m}$, an inner diameter of 0.27 mm, an outer diameter of 0.41 mm and an effective filtering area of 0.06 m^2 . Titanium dioxide (P25 TiO_2 , Degussa, Germany) was the photocatalyst, and it was suspended in the PMR. The influent was mixed with the photocatalyst in the PMR and continuously filtered by a suction pump. The water level of the PMR was maintained with a level sensor that controlled the influent pump and valve. Air was pumped through a gas diffuser placed at the bottom of the reactor to provide dissolved oxygen, prevent the accumulation of TiO_2 particles on the membrane surface, and mix the dye and photocatalyst. In order to obtain the MO concentration in the effluent of the PMR, we measured the absorbance value of the effluent with the

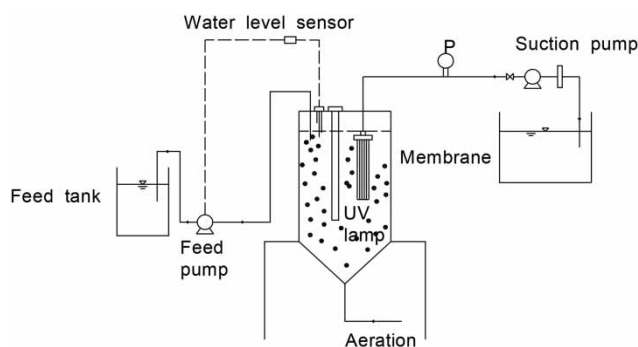


Figure 1 | The schematic diagram of the PMR setup.

UV spectrophotometer at the wavelength of 465 nm, using distilled water as the background.

Regeneration methods

The spent TiO_2 was collected from the PMR after the photocatalyst was completely deactivated by sedimentation and filtration and then dried at 50°C . The spent TiO_2 catalysts were regenerated via three methods. The spent catalyst was washed with methanol (0.1 g of catalyst per 10 ml of solution) and then dried at 50°C in a vacuum drying oven for 2 h; this sample was designated as ST_W . After oxidation using 30% H_2O_2 solution (0.1 g of catalyst per 1 ml of solution), the spent catalyst was dried at 100°C in a vacuum drying oven for 20 min; this sample was designated as ST_O . Lastly, the spent catalyst was calcinated in air at 420°C for 3 h in a muffle furnace, this sample was designated as ST_C .

The regenerated photocatalysts were transferred into the photocatalytic batch reactor for the regeneration performance test. A $33 \mu\text{W}/\text{cm}^2$ UV lamp with a wavelength of 254 nm was placed inside the reactor. The photocatalytic batch reactor was equipped with 2.16 L of 10 mg/L MO solution and an air diffuser, which provided oxygen for the photocatalytic reaction. The concentration of the TiO_2 catalyst was 0.5 g/L.

Characterization of the fresh, spent, and regenerated TiO_2 catalysts

All samples were characterized by FTIR, and BET surface area analysis. To identify any changes in the surface functional groups, FTIR was performed using a spectrometer (BRUKER, TENSOR27). The samples were mixed with KBr powder at a ratio of 1:100, evenly ground in an agate mortar with a pestle, and then pressed for measurement. The infrared band used for determination was $400\text{--}4,000 \text{ cm}^{-1}$. The surface area of the sample was measured using a BET specific surface area tester (Micromeritics Instrument Corp., Tristar II 3020, USA).

RESULTS AND DISCUSSION

Deactivation and regeneration of the photocatalyst

Regeneration performance

The continuous photocatalytic degradation of MO was carried out in a PMR. The concentration of MO in the effluent

of the PMR increased with the increase in the volume of treated MO. The photocatalyst was deactivated when the concentration of MO in the effluent of the PMR was stable (Yan *et al.* 2016). To characterize the lifetime of the photocatalyst, we applied g MO/g TiO₂. Approximately 1.12 g of MO was destroyed in the presence of 2.16 g of photocatalyst before complete catalyst deactivation. The lifetime of the photocatalyst was 0.52 g MO/g TiO₂. The concentrations of TiO₂, and MO were 1 g/L and 10 mg/L, respectively. The HRT was 0.75 h.

The spent TiO₂ catalyst was recovered from the PMR by sedimentation and filtration. Subsequently, it was regenerated by washing with methanol and treating with H₂O₂ and heat and reused for the photocatalytic degradation of MO as shown in Figure 2. The spent TiO₂, which was regenerated by washing with methanol (ST_W) and treating with heat (ST_C), degraded slowly, resulting in an MO degradation of 12.44% and 17.50% after 120 min, respectively. Compared to the washed spent catalyst (ST_W) and the heat-treated catalyst (ST_C), the regenerated photocatalyst treated with H₂O₂ (ST_O) showed slightly faster removal of MO, resulting in an MO degradation of 57.12% after 120 min. These results indicate that the catalyst could be regenerated to some extent by H₂O₂ treatment, which may have been due to the fact that H₂O₂, a strong oxidizing agent, provided plenty of ·OH radicals. The organic species adsorbed in the spent photocatalyst were oxidized by ·OH radicals into CO₂ and H₂O, thereby freeing all the surface active sites (Gandhi *et al.* 2012).

The regeneration recovery rate is defined as the ratio of the MO removal rate after 120 min by the regenerated photocatalyst and the MO removal rate after 120 min by the fresh photocatalyst. The regeneration recovery rates were 13.16%, 18.52%, and 60.43% for the ST_W catalyst,

ST_C catalyst, and ST_O catalyst, respectively, indicating that the photocatalyst could not be completely regenerated by washing with solvents or treating with H₂O₂ or heat.

Characterization of fresh TiO₂, spent TiO₂, and regenerated TiO₂

Fresh TiO₂ is a white powder, whereas spent TiO₂ is a light yellow powder. Furthermore, the ST_O catalyst turned white, and the ST_W and ST_C catalysts remained light yellow. The fresh, spent and regenerated TiO₂ catalysts were characterized by BET surface area analysis and FTIR.

The BET surface areas of the fresh TiO₂, spent and regenerated TiO₂ by washing, heat treatment, and H₂O₂ treatment were 59.86 m²/g, 58.87 m²/g, 59.66 m²/g, 60.19 m²/g, 58.40 m²/g, respectively. Compared to the fresh catalyst, no significant change was observed in the BET surface area of the spent catalyst, revealing that photocatalyst deactivation was not due to pore blocking by the reactant (MO) or intermediate products. Gandhi *et al.* (2012) obtained similar results when the spent photocatalyst for the degradation of phthalic acid was regenerated by washing and treating with H₂O₂ and heat.

The FTIR spectra of the fresh, spent, and regenerated TiO₂ are shown in Figure 3. In the spent TiO₂ spectrum, a new peak with strong intensity appeared at 1,262 cm⁻¹, which assigned the C–O stretch in –C–OH. These results were consistent with those of Kaewgun & Lee (2010), who evaluated the deactivation of polymorphic brookite titania by observing the photocatalytic degradation of MO. FTIR peaks, which can be assigned for the C–O stretch in –C–O–C– and –C–OH, were identified, and their relative intensities increased with the increase in the reaction cycle

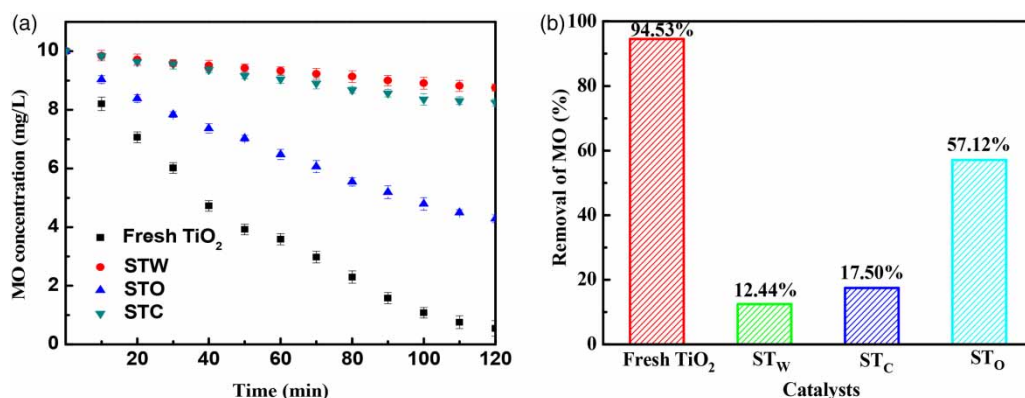


Figure 2 | (a) Variation of MO concentration with time during photocatalytic degradation using fresh TiO₂ catalyst, spent TiO₂ regenerated by washing with methanol (ST_W), treating with heat (ST_C) and treating with H₂O₂ (ST_O). (b) Removal of MO after 120 min with fresh TiO₂, ST_W, ST_C and ST_O.

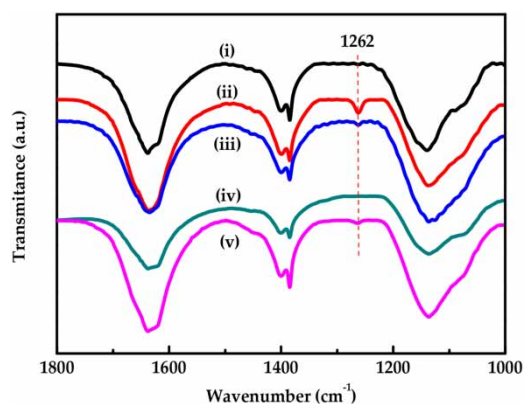


Figure 3 | FTIR spectra of the TiO_2 catalysts. (i. fresh TiO_2 , ii. spent TiO_2 , iii. ST_W , iv. ST_O , and v. ST_C).

number. In a study by *Li et al. (2012a)*, product formation of MO was measured by liquid chromatography mass/spectrometry (LC/MS); the results indicate $-\text{C}-\text{OH}$ existing in the products. These results indicate that the deactivation of TiO_2 was due to the deposition of the decomposed MO products on the TiO_2 .

From the FTIR spectra of the regenerated catalyst, the intensity of the FTIR peak at $1,262\text{ cm}^{-1}$ decreased, and it completely disappeared in the ST_O photocatalyst. The decrease in the intensity of the peak was consistent with the regeneration recovery rate by different regeneration methods. ST_W and ST_C photocatalysts exhibited a lower regeneration rate, which was due to deposited species that could not be removed by washing or treating with heat. However, H_2O_2 oxidized the species on the surface of the photocatalyst, so the ST_O photocatalyst exhibited a higher regeneration rate.

Factors affecting the lifetime of TiO_2

When the initial concentration of organic pollutants is small, the Langmuir-Hinshelwood equation can be simplified as a quasi first-order kinetic equation. The effects of TiO_2 , MO concentration and light intensity on the photocatalytic degradation process were analyzed based on quasi first-order reaction kinetics. At the same time, the effect of the above factors on lifetime was investigated through the dynamic reaction in the PMR.

Effect of the TiO_2 concentration

The concentration of TiO_2 is important in treatment. The TiO_2 concentration is directly proportional to the reaction rate (*Feilizadeh et al. 2015; Hosseini et al. 2016*). The effect of the photocatalyst concentration on the photocatalytic degradation of MO was investigated as shown in *Figure 4(a)*. Before the suspension concentration of TiO_2 increased to 3 g/L , the photocatalytic degradation rate increased with the increase in the concentration of TiO_2 . The reason was that the number of active sites increased with the increase in the dosages of TiO_2 , while the photocatalytic degradation slightly decreased when the suspension concentration of TiO_2 was 4 g/L . It is well known that the rate of photon uptake by TiO_2 should depend on the amount of light transmitted to the suspension, which can be influenced by the concentration of TiO_2 (*Huang et al. 2008*). This attributed that the high TiO_2 concentration led to the increased light shielding and scattering as well as the loss in surface area occasioned, which was caused by TiO_2 particle agglomeration (*Kaneco et al. 2009*).

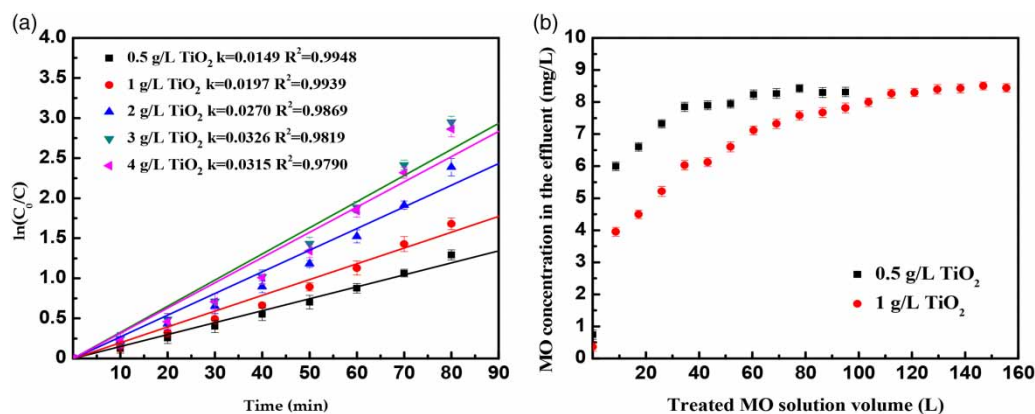


Figure 4 | Effect of the TiO_2 concentration on the lifetime of photocatalyst. (a) Effect of the TiO_2 concentration on the removal efficiency in batch reactor. (b) MO concentration changes in the effluents of the PMR (experimental conditions: TiO_2 , 0.5 g/L and 1 g/L ; MO, 10 mg/L ; HRT, 0.75 h ; light intensity, $33\text{ }\mu\text{W/cm}^2$).

The effect of the TiO_2 concentration on the photocatalyst lifetime was investigated using the PMR, as shown in Figure 4(b). The MO concentration in the effluent of the PMR was stable after treating with 57.6 L of a 10 mg/L MO solution with a TiO_2 concentration of 0.5 g/L. The lifetime of the photocatalyst was 0.53 g MO/g TiO_2 . The MO concentration in the effluent of the PMR was stable after treating with 112.3 L of a 10 mg/L MO solution with a TiO_2 concentration of 1 g/L. The lifetime of the photocatalyst was 0.52 g MO/g TiO_2 . These results show that the lifetime of the photocatalyst was similar under different photocatalyst concentrations, indicating that the concentration of the photocatalyst had few effects on the lifetime of the photocatalyst.

Effect of the initial MO concentration

The effect of the initial MO concentration on the photocatalytic degradation rate was investigated over a concentration range of 5–20 mg/L of MO. Figure 5(a) shows that the degradation rate decreased with the increase in the initial MO concentration. There may be two reasons: firstly, when the dosage of photocatalyst is fixed, its specific surface area is also fixed. The increased occupation of TiO_2 active sites by contaminants hindered generation of the oxidants, such as $\cdot\text{OH}$, $\cdot\text{O}_2^-$, which led to the reduction of the degradation rate. Secondly, more photons were absorbed, resulting from a higher concentration of MO, which caused the number of effective photons reaching the surface of TiO_2 to be reduced, and then the reaction rate is reduced (Niu & Hao 2013).

We used the PMR to investigate the effect of initial MO concentration on the lifetime of the photocatalyst as shown

in Figure 5(b). The MO concentration in the effluent of the PMR was stable after treating with 60.5 L of a 5 mg/L MO solution, and the lifetime of the photocatalyst was 0.14 g MO/g TiO_2 . The MO concentration in the effluent of the PMR was stable after treating with 112.3 L of a 10 mg/L MO solution, and the lifetime of the photocatalyst was 0.52 g MO/g TiO_2 . The lifetime of the photocatalyst after treatment with 10 mg/L MO was 3.71 times that of 5 mg/L MO, indicating that increasing concentrations of MO can markedly increase the lifetime of the photocatalyst. It maybe attributed that the efficiency of the photocatalyst per unit mass was enhanced under high concentrations of MO.

Effect of the irradiance

The irradiance has a direct impact on the photocatalytic degradation rate. Figure 6(a) shows that the degradation rate increased linearly within a light intensity of 10–72 $\mu\text{W}/\text{cm}^2$, which was consistent with the view that the rate of degradation typically changes linearly with the intensity up to a certain value beyond which the reaction shows a square root dependency on the intensity (Gogate & Pandit 2004). Since the TiO_2 particles were suspended in a stirred solution, the degree of absorption of light by the TiO_2 particle surface increased with the increase of light intensity (Kaneco et al. 2009). This is because the number and rate of photons supplied to the semiconductor surface will be higher when the irradiation intensity of light was higher (Julson & Ollis 2006).

As shown in Figure 6(b), we investigated the effect of light intensity on the lifetime of the photocatalyst in the PMR. The MO concentration in the effluent of the PMR was stable after treating with 25.9 L MO solution under

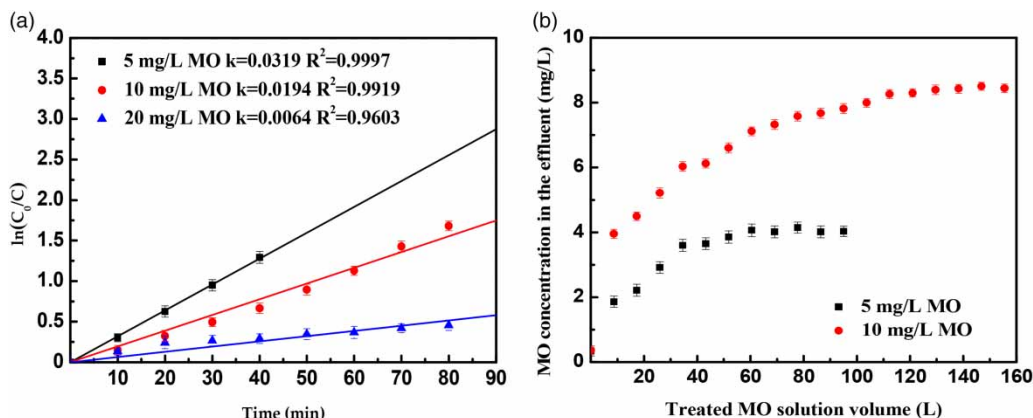


Figure 5 | Effect of the initial MO concentration on the lifetime of the photocatalyst. (a) Effect of the initial MO concentration on the removal efficiency in batch reactor. (b) MO concentration changes in the effluents of the PMR (experimental conditions: TiO_2 , 1 g/L; MO, 5 mg/L and 10 mg/L; HRT, 0.75 h; light intensity, 33 $\mu\text{W}/\text{cm}^2$).

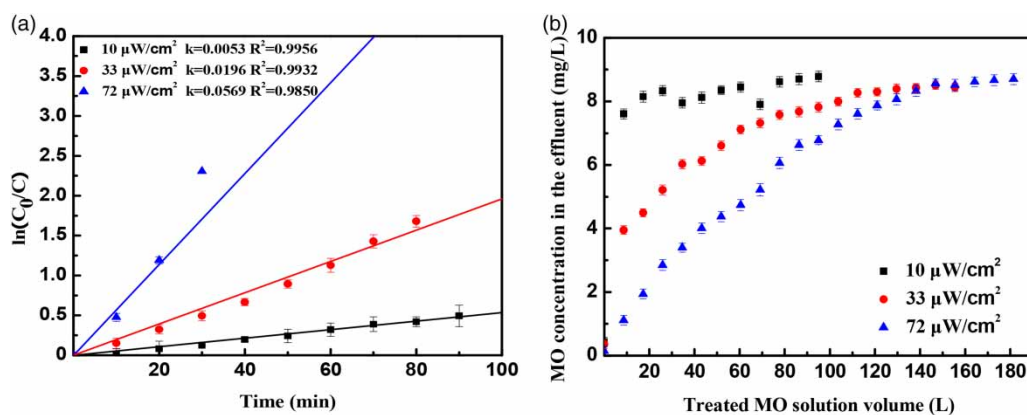


Figure 6 | Effect of the light intensity on the lifetime of the photocatalyst. (a) Effect of the light intensity on the removal efficiency in batch reactor. (b) MO concentration changes in the effluents of the PMR (experimental conditions: TiO_2 , 1 g/L; MO, 10 mg/L; HRT, 0.75 h; light intensity, 10, 33 and 72 $\mu\text{W}/\text{cm}^2$).

the 10 $\mu\text{W}/\text{cm}^2$ light intensity, and the lifetime of the photocatalyst was 0.12 g MO/g TiO_2 . The MO concentration in the effluent of the PMR was stable after treating with 112.3 L MO solution under the 33 $\mu\text{W}/\text{cm}^2$ light intensity, and the lifetime of the photocatalyst was 0.52 g MO/g TiO_2 . The MO concentration in the effluent of the PMR was stable after treating with 164.2 L MO solution under the 72 $\mu\text{W}/\text{cm}^2$ light intensity, and the lifetime of the photocatalyst was 0.76 g MO/g TiO_2 . The lifetime of the photocatalyst after treatment under 72 $\mu\text{W}/\text{cm}^2$ light intensity was 1.46 and 6.33 times that under 33 and 10 $\mu\text{W}/\text{cm}^2$ light intensity. It is thus clear that the effect of light intensity on the lifetime of the photocatalyst is very significant.

Effect of the hydraulic retention time

The HRT, an important parameter of the PMR (Moradi & Nasrollahpour 2017), was changed by altering the membrane flux. Figure 7 shows the effect of the HRT on the lifetime of the photocatalyst.

At an HRT of 0.75 h, the photocatalyst was deactivated after treating with 119.5 L of an MO solution, and the MO concentration in effluent was 8.30 mg/L. At an HRT of 3 h, the MO concentration in effluent was less than 2 mg/L; after treating with 119.5 L of the MO solution, it increased slowly. The experiment was terminated after treating with 220 L of MO solution due to the slow increase, and the lifetime of the photocatalyst was not calculated. Furthermore, changing the HRT from 0.75 to 3 h prolonged the lifetime of the photocatalyst, which may have been due to the complete photodegradation of MO and the intermediate products, which could prevent photocatalyst deactivation. Meng *et al.* (2005) reported that organic carbon could be

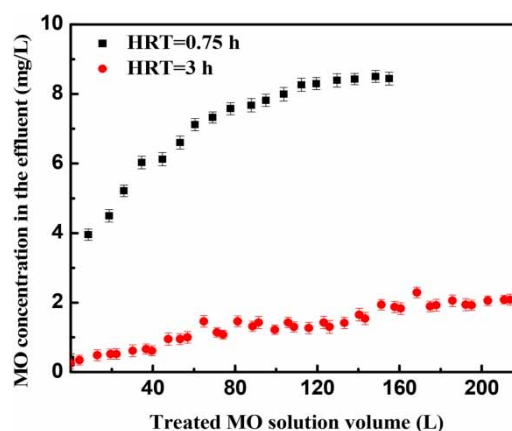


Figure 7 | MO concentration changes in the effluents of the PMR (experimental conditions: TiO_2 , 1 g/L; MO, 10 mg/L; HRT, 0.75 and 3 h; light intensity, 33 $\mu\text{W}/\text{cm}^2$).

totally mineralized as long as a relatively longer HRT was applied in the PMR.

CONCLUSIONS

The deactivation of TiO_2 was caused by the deposition of MO products but not by the blocking of pores by the reactant (MO) or intermediate products. H_2O_2 treatment yielded the highest regeneration rate over washing with methanol and treating with heat, because H_2O_2 oxidized the deposited species on the surface of the photocatalyst. The MO concentration, the irradiance of the UV lamp and the HRT of the PMR were found to affect the lifetime of the photocatalyst more significantly than the TiO_2 concentration. This may have been due to the fact that when the HRT was long, the MO and intermediate products adsorbed

on the surface of the photocatalyst were thoroughly photo-degraded, which prevented photocatalyst deactivation.

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REFERENCES

- Boonya-atichart, A., Boontanon, S. K. & Boontanon, N. 2018 Study of hybrid membrane filtration and photocatalysis for removal of perfluorooctanoic acid (PFOA) in groundwater. *Water Science and Technology* **2017** (2), 561–569.
- Feilizadeh, M., Alemzadeh, I., Delparish, A., Karimi Estahbanati, M. R., Soleimani, M., Jangiou, Y. & Vosoughi, A. 2015 Optimization of operating parameters for efficient photocatalytic inactivation of *Escherichia coli* based on a statistical design of experiments. *Water Science and Technology* **71** (6), 823–831.
- Gandhi, V. G., Mishra, M. K. & Joshi, P. A. 2012 A study on deactivation and regeneration of titanium dioxide during photocatalytic degradation of phthalic acid. *Journal of Industrial and Engineering Chemistry* **18** (6), 1902–1907.
- Gao, B., Chen, W. P., Liu, J. D., An, J. J., Wang, L., Zhu, Y. & Sillanpaa, M. 2018 Continuous removal of tetracycline in a photocatalytic membrane reactor (PMR) with ZnIn₂S₄ as adsorption and photocatalytic coating layer on PVDF membrane. *Journal of Photochemistry and Photobiology A-Chemistry* **364**, 732–739.
- Gogate, P. R. & Pandit, A. B. 2004 Sonophotocatalytic reactors for wastewater treatment: a critical review. *AIChE Journal* **50** (5), 1051–1079.
- Hosseini, S. M. B., Fallah, N. & Royaei, S. J. 2016 Optimization of photocatalytic degradation of real textile dye house wastewater by response surface methodology. *Water Science and Technology* **74** (9), 1999–2009.
- Huang, X., Leal, M. & Li, Q. 2008 Degradation of natural organic matter by TiO₂ photocatalytic oxidation and its effect on fouling of low-pressure membranes. *Water Research* **42** (4), 1142–1150.
- Jing, L., Xin, B., Yuan, F., Wang, B., Shi, K., Cai, W. & Fu, H. 2004 Deactivation and regeneration of ZnO and TiO₂ nanoparticles in the gas phase photocatalytic oxidation of n-C₇H₁₆ or SO₂. *Applied Catalysis A: General* **275** (1), 49–54.
- Julson, A. J. & Ollis, D. F. 2006 Kinetics of dye decolorization in an air–solid system. *Applied Catalysis B: Environmental* **65** (3), 315–325.
- Kaewgun, S. & Lee, B. I. 2010 Deactivation and regeneration of visible light active brookite titania in photocatalytic degradation of organic dye. *Journal of Photochemistry and Photobiology A-Chemistry* **210** (2–3), 162–167.
- Kaneco, S., Li, N., Itoh, K.-k., Katsumata, H., Suzuki, T. & Ohta, K. 2009 Titanium dioxide mediated solar photocatalytic degradation of thiram in aqueous solution: kinetics and mineralization. *Chemical Engineering Journal* **148** (1), 50–56.
- Li, W., Li, D., Lin, Y., Wang, P., Chen, W., Fu, X. & Shao, Y. 2012a Evidence for the active species involved in the photodegradation process of methyl orange on TiO₂. *Journal of Physical Chemistry C* **116** (5), 3552–3560.
- Meng, Y. B., Huang, X., Yang, Q. H., Qian, Y., Kubota, N. & Fukunaga, S. 2005 Treatment of polluted river water with a photocatalytic slurry reactor using low-pressure mercury lamps coupled with a membrane. *Desalination* **181** (1–3), 121–133.
- Moradi, S. E. & Nasrollahpour, A. 2017 Competitive adsorption and photodegradation of Methyl orange and Rhodamine B by TiO₂ modified mesoporous carbon photo-catalyst on UV irradiation. *Materials Technology* **32** (12), 716–723.
- Moziat, S. 2010 Photocatalytic membrane reactors (PMRs) in water and wastewater treatment. A review. *Separation and Purification Technology* **73** (2), 71–91.
- Niu, P. & Hao, J. 2013 Photocatalytic degradation of methyl orange by titanium dioxide-decatungstate nanocomposite films supported on glass slides. *Colloids and Surfaces A-Physicochemical and Engineering Aspects* **431**, 127–132.
- Rani, C. N. & Karthikeyan, S. 2018 Performance of an indigenous integrated slurry photocatalytic membrane reactor (PMR) on the removal of aqueous phenanthrene (PHE). *Water Science and Technology* **77** (11), 2642–2656.
- Shon, H. K., Phuntsho, S. & Vigneswaran, S. 2008 Effect of photocatalysis on the membrane hybrid system for wastewater treatment. *Desalination* **225** (1–3), 235–248.
- Sun, R.-D., Nakajima, A., Watanabe, T. & Hashimoto, K. 2003 Decomposition of gas-phase octamethyltrisiloxane on TiO₂ thin film photocatalysts – catalytic activity, deactivation, and regeneration. *Journal of Photochemistry and Photobiology A - Chemistry* **154** (2), 203–209.
- Wang, H., Liu, Q. & You, C. 2019 Regeneration of sulfur-deactivated TiO₂ photocatalysts. *Applied Catalysis A: General* **572**, 15–23.
- Yan, X., Xu, X., Liu, J., Bao, R. & Li, L. 2016 Regeneration of photocatalysts by in situ UV irradiation in photocatalytic membrane reactor. *Russian Journal of Applied Chemistry* **89** (1), 94–98.
- Yan, X. J., Tang, Y., Ma, C., Liu, Y. & Xu, J. 2018 Deactivation and regeneration of photocatalysts: a review. *Desalination and Water Treatment* **124**, 160–176.

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