

## Photocatalytic degradation of naphthalene in offshore produced water: comparison of immobilized and suspended TiO<sub>2</sub>

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### Abstract

Offshore oil and gas industry has produced and discharged a considerable amount of produced water on a daily basis. However, current treatment methods such as gravity separation are not effective in removing dissolved organic matters before discharge. As the increasing environmental awareness and stringent regulation, it is necessary to develop more effective approaches to remove dissolved organics. Photocatalysis has been introduced in water and wastewater treatment and can effectively remove organic pollutants non-selectively. However, the separation of catalysts after treatment is difficult and costly. Thus, the immobilization of catalyst could be an alternative approach that avoids any post-treatment. In this study, produced water was irradiated under UV-C (254 nm) for 12 h with the presence of catalysts. A commercial catalyst, Aeroxide® P25 was immobilized on glass plates by a heat attachment method. The P25 powder was used as a referent catalyst. Naphthalene was selected as an indicator owing to its abundance in produced water and typical chemical property of polycyclic aromatic hydrocarbons (PAHs). The results showed that the immobilized catalyst has a better enhancement to photo-oxidation. The turbidity was significantly reduced compared with suspended system.

**Keywords:** Immobilization, glass plate, naphthalene, photocatalysis, offshore produced water

### Introduction

The dramatic increase of offshore produced water (OPW) has been raising concern recently. As one of the largest treated waste streams from offshore oil and gas production, the annual generation of produced water is approximately 14 billion barrels (Hawboldt et al., 2010; Jaji, 2012). OPW is treated prior to discharge. Some toxic components such as polycyclic aromatic hydrocarbons (PAHs), heavy metals and radionuclides (Fakhru'l-Razi et al., 2009) persisted after treatment and could potentially cause chronic effects to the marine ecosystem. PAHs are among the most toxic components in OPW due to their various mutagenic and carcinogenic effects on marine biota and the resistance towards biodegradation (OGP, 2002).

Arctic Waters Pollution Prevention Act (AWPPA) has regulated that no contaminants shall be discharged into Arctic waters. A similar "Zero Discharge" policy has been also enforced by OSPAR (Oslo and Paris Conventions) commission (OSPAR, 2008). However, the conventional on-site OPW treatment technologies such as hydrocyclone, skim tank have difficulty in separating the dissolved petroleum hydrocarbons from OPW (OGP, 2002). These hydrocarbons may cause a chronic deterioration of marine ecosystem. Naphthalene (NAP) for example, who

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belongs to PAHs family, was abundant in OPW. As a result, further research and development effort in the treatment and management of OPW, are much desired.

Photocatalysis has shown a great potential as an effective and environmentally friendly option in treating organic wastewater (Melemini et al., 2009). Photocatalysis with suspended catalysts has recently been investigated for treating on-shore refinery wastewater (Saïen and Nejati, 2007; Saïen and Shahrezaei, 2012). However, such technologies require a solid-liquid separation step before analysis and discharge which in turn greatly increases the treatment time and cost of the treatment approaches (Byrne et al., 1998; Yahia Cherif et al., 2014). Immobilizing the catalysts on the substrates could be an alternative to reduce or eliminate the post-separation. Several studies have applied the immobilized TiO<sub>2</sub> on glass plates for dyes degradation (Behnajady et al., 2007; 2008; Yahia Cherif et al., 2014). These studies only focused on the photocatalysis in distilled water, the interferences of wastewater were not discussed.

In order to investigate the applicability of immobilized photocatalysis in treating OPW, this study evaluated and compared the removal effectiveness of NAP by nano-TiO<sub>2</sub> powder and immobilized TiO<sub>2</sub> on glass slides. Immobilized TiO<sub>2</sub> on glass slides was synthesized by a heat attached method and characterized by Scanning Electron Microscope (SEM) and X-Ray Fluorescence (XRF). The pre-treatment methods of NAP analysis were compared. The photocatalytic and adsorb performance were examined and compared. The findings are expected to help develop a better photocatalytic technology and potentially lead to a promising option for OPW treatment.

## Materials and Methods

### Materials

Naphthalene-d<sub>8</sub> was purchased from Cambridge Isotopes Labs as surrogate. Acetone, ethyl alcohol, dichloromethane (DCM) and concentrated hydrofluoric acid solution were purchased from Sigma-Aldrich Canada Co. Aeroxide® P25 nano-scale TiO<sub>2</sub> (anatase: rutile is 9:1, average particle size is around 21 nm) and sodium hydroxide were obtained from Fisher Science Company. Glass microscope slides were purchased from VWR International. The key components of OPW samples were analyzed and tabulated in Table 1.

Table 1. Background information of the OPW sample

| Parameters  | Concentration (mg/L) |
|-------------|----------------------|
| Naphthalene | 0.01                 |
| Magnesium   | 83.28                |
| Calcium     | 971.08               |
| Iron        | 4.12                 |
| Chlorine    | 17197                |
| Sulfur      | 630.92               |
| pH          | 6.86                 |
| Turbidity   | 22 NTU               |

### The immobilization of catalysts

The immobilization of catalyst on glass plate was conducted by a heat attached method. 0.4 g Aeroxide® P25 was dispersed into 100 mL ethyl alcohol. The slurry solution was sonicated by Branson S-450D homogenizer with 100% amplitude for 30 minutes. Glass microscope slides were pre-treated with dilute hydrofluoric acid for 1 day, then with  $0.01 \text{ mol} \cdot \text{L}^{-1}$  sodium hydroxide solution for 2 hours to increase the amount of OH radical on the slides. The slurry solution was dipped on both sides of slides which have been washed by distilled water before using. After air drying, the glass slides were calcinated under  $450 \text{ }^\circ\text{C}$  for 2 hours. The weakly attached P25 particles on glass slides were removed by distilled water. The attaching process was duplicated to ensure the formation of P25 film. The scanning electron microscope (SEM) images and elemental analysis data of coated glass slide surface were acquired from mineral liberation analyzer (FEI MLA 650F).

## Irradiation Experiments

Five hundred millilitres of produced water samples and four coated glass slides or the equivalent amount of P25 powder were added to a 500 mL amber bottle and stirred for 30 minutes prior to irradiation in order to achieve equilibrium. The bottle, in which pen-ray light source (254 nm) covered with a quartz tube was submerged, was then irradiated for 12 hours. The aqueous suspension in the bottle was kept homogeneous by using a magnetic stirrer. Water bath was employed to keep the system at ambient temperature. Control experiments were conducted in darkness to evaluate the changes of analytes without irradiation.

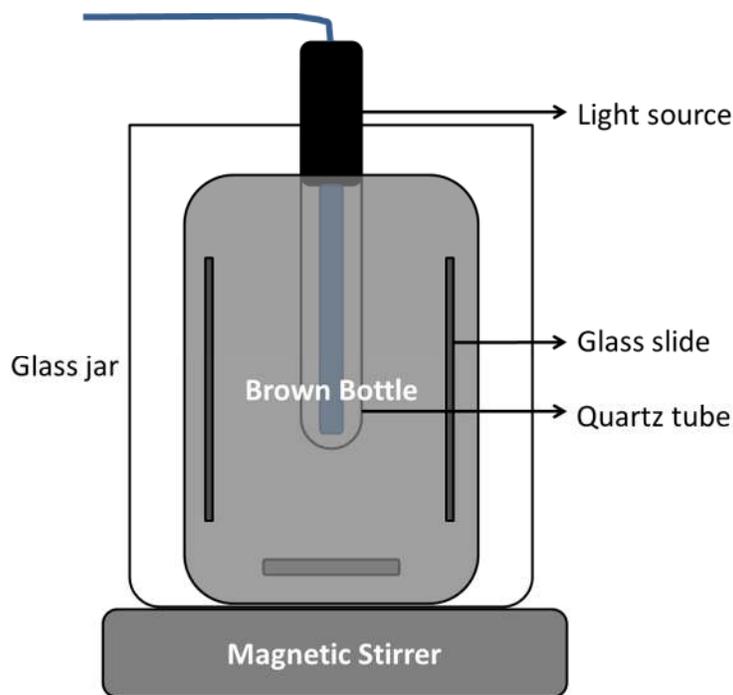


Figure 1. Scheme of the photocatalytic reactor

## Analytical Methods

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Liquid-liquid micro-extraction (LLME) method used in this paper was modified from Zheng et al. method (2012). For the water samples from the immobilized system, 10 mL water samples were spiked with  $20 \mu\text{g}\cdot\text{mL}^{-1}$  Naphthalene- $\text{d}_8$  solution and 250  $\mu\text{L}$  DCM were sequentially added and vortexed for 10 seconds and 1 minute, respectively. The mixture was centrifuged at 1,500 rpm for 5 minutes to completely separate water and organic phases. 100  $\mu\text{L}$  extract was transferred into a 150  $\mu\text{L}$  micro-vial.

For the water samples from the suspended system, 10 mL water samples were centrifuged at 3,000 rpm for 15 minutes. 5 mL supernatant was filtered with a 0.2  $\mu\text{m}$  syringe (Whatman<sup>®</sup> Spartan<sup>®</sup> RC) to remove any catalyst particle.  $10 \mu\text{g}\cdot\text{mL}^{-1}$  Naphthalene- $\text{d}_8$  solution was added and the solution was vortexed for 10 seconds. 250  $\mu\text{L}$  DCM was added and further vortexed for 1 minute. The mixture was centrifuge at 1,500 rpm for 5 minutes to completely separate the phases. 100  $\mu\text{L}$  extract was filled into a 150  $\mu\text{L}$  micro-vial.

Instrumental analysis was performed using an Agilent 7890A/5975C gas chromatograph – mass spectrometer (GC-MS) equipped with an Agilent 7693 autosampler. The analytes were separated by a  $30 \text{ m} \times 0.25 \text{ mm id} \times 0.25 \mu\text{m}$  DB-5MS UI fused silica capillary columns. The injected mode was splitless at 300 °C. A temperature ramp was set as follows: the temperature was held at 65 °C for 1 minute, programmed at the rate of  $4 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  to 110 °C which was held isothermally for 5 minutes, and then to 300 °C at the rate of  $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . The analytic processes were triplicated. The relative standard deviations for NAP were 6% without filtration and 4.7% with filtration.

## Results and Discussion

### Characterization of immobilized catalyst on glass slide

The surface morphology of immobilized catalyst was illustrated by SEM and XRF in Figure 2. It can be seen that a P25 film was formed on the surface of glass slides. However, the thickness of film was not uniform and some of scratches were observed. By XRF, the textures of red and green were presented as Titanium (Ti) and Silicon (Si) respectively. The non-uniformed red texture occurred during the drying step. Due to the uneven evaporation, some of P25 moved from the area with high solvent evaporation rate and accumulated into the area with low evaporation rate, forming a catalytic film with uneven thickness. The black spots indicated no P25 coverage which was caused by the scratch after the immobilization. The semi-quantization of different elements was performed. The response rate of Si and Ti was 57: 32, indicating a thin P25 film was formed on the glass slides.

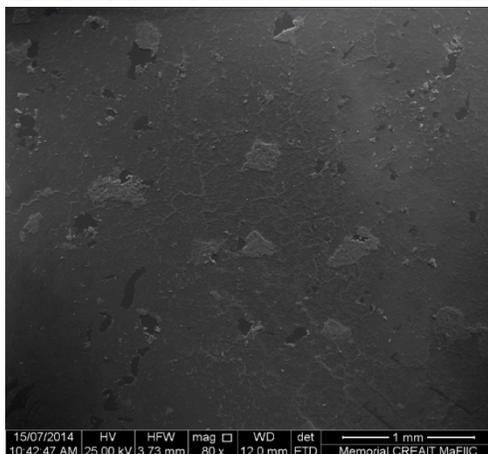
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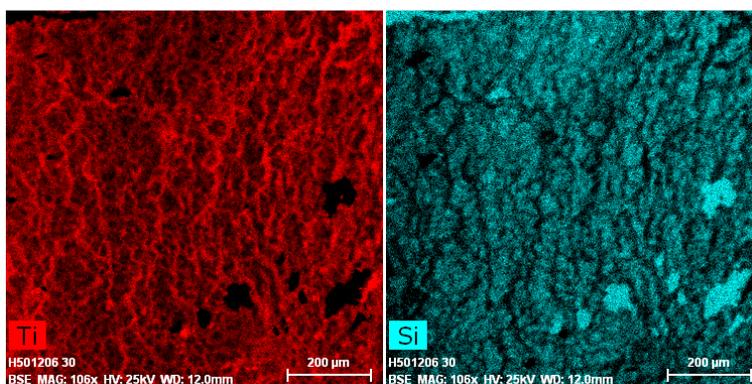
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(a)



(b)

Figure 2. Characteristic of coated glass slide by SEM (a) and XRF (b)

## Comparison of different analytical methods

Two sets of LLME methods were developed for the samples from the immobilized and the suspended systems respectively. The catalytic particles in immobilized system were extremely less than that in suspended system. In this case, the separation of catalyst from OPW samples was not necessary before the extraction steps. Since the labour-intensive and time-consuming steps of centrifuge and filtration in the separation steps were not used, the sample extraction for immobilized system was shortened.

The mass spectra from different samples were illustrated in Figure 3. The abundance decreased after the filtration, which was due to the retention of organics by using syringe filter. Furthermore, some of the organic components in OPW, especially those with higher molecular weight hydrocarbons, were separated from water samples before extraction. These hydrocarbons had lower solubility and were more intent to adhere on the insoluble particles in OPW (Ukiwe et al., 2013), resulting in the difficulty of the particles passing through the filter.

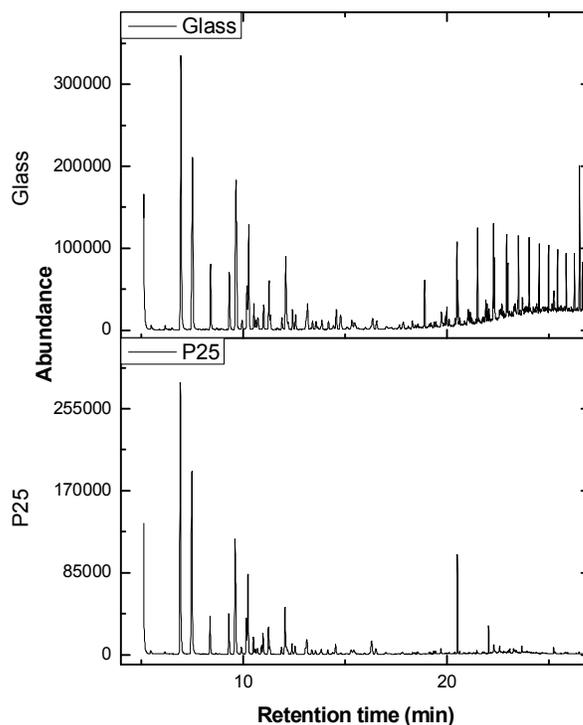


Figure 3. The mass spectra of OPW samples from immobilized system and suspended system

### Evaluation of photocatalysis and adsorption

The photocatalytic process was simulated with an apparent-first-order kinetics (Xu et al., 2013)

$$Rate = \frac{c_t}{c_0} = e^{-kt}$$

where  $t$  is the reaction time;  $k$  is the first-order reaction rate constant;  $c_t$  is the determined concentration of the reactant at time  $t$ ; and  $c_0$  is the initial concentration of the reactant.

The photocatalytic experimental results and the simulated curves are illustrated in Figure 4. In the immobilized system, the regression coefficient between the simulated model and experimental data was 0.99, indicating a good fit. In the suspended system, an odd concentration of NAP at the beginning of irradiation was noticed, causing a decrease of regression coefficient to 0.95. It could be caused by the adsorption of NAP on the suspended P25 powder. The  $k$  values for immobilized system and suspended system were 0.00305 and 0.00219 respectively. The results showed a higher removal effectiveness of NAP by immobilized system. It could be due to an agglomerating effect of OPW substrate to suspended  $TiO_2$ . The significant amount of alkaline-earth cations ( $Ca^{2+}$  and  $Mg^{2+}$ ) could compress the electro static barrier of  $TiO_2$  forcing the agglomeration of  $TiO_2$  (Armanious et al., 2011). As a result, the photocatalytic effectiveness of suspended catalysts decreased. Limited dispersion of catalyst was less influenced by alkaline-earth cations. Therefore, the immobilized catalysts were more resistant to the negative effects

caused by the OPW substrate. On the other hand, the turbidity of OPW was increased to 100 NTU by adding suspended P25. The increase of turbidity reduced the penetration of UV-C light, thus the overall intensity of irradiation.

The adsorption of NAP in different systems was also evaluated. As shown in Figure 4, unstable changes of NAP occurred in the first 90 minutes in both systems. It could result from the addition of catalysts. The addition of P25 in OPW generated larger fluctuation amplitude of NAP than the coated glass slides, implying the higher dispersive rate of P25. The adsorption rate of suspended system indicated a higher surface area of P25 powder compared with coated glass plates. Higher adsorption of NAP could also result in the lower photo-degradation rate due to lower intensity of irradiation.

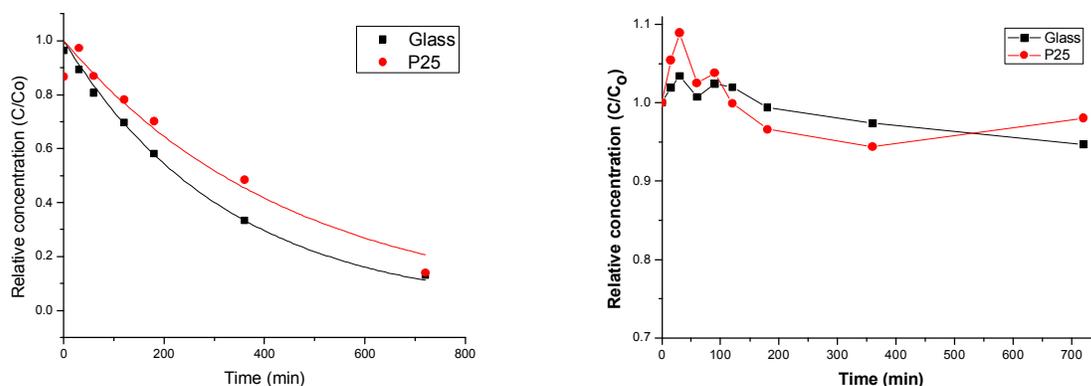


Figure 4. The comparison of different catalysts/systems: photocatalysis with simulated curve (left) and adsorption (right)

## Conclusions

This study focused on the comparison of photocatalytic effectiveness via immobilized and suspended TiO<sub>2</sub>. The glass slides were coated with aerioxide® P25 by a heat attached method. The coating steps were performed twice and a P25 film was formed on the glass surface. Water samples from immobilized system required no filtration thus reduced the difficulty of extraction. The results from OPW extract showed that the abundance of organic components in OPW were higher without filtration. Filtration could further retain almost all larger aliphatic hydrocarbon due to their low solubility and high affinity to the insoluble particles. The results of photocatalysis showed that the degradation of NAP followed apparent-first-order kinetics and the reaction rate constant of immobilized system were higher than that of suspended system. It was demonstrated that immobilized catalyst was more resistant to the negative effect of OPW substrate. The fluctuation of NAP was monitored in which the suspended system had larger amplitude. These results are expected to provide a more promising photocatalytic alternative in treating OPW.

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## References

- Armanious, A., Özkan, A., Sohmen, U. & Gulyas, H. (2011). Inorganic greywater substrate impact on photocatalytic oxidation: does flocculation of TiO<sub>2</sub> nanoparticles impair process efficiency? *Water Science and Technology*, 63(12), 2808-2813.
- Behnajady, M. A., Modirshahla, N., Daneshvar, N., & Rabbani, M. (2007). Photocatalytic degradation of an azo dye in a tubular continuous-flow photoreactor with immobilized TiO<sub>2</sub> on glass plates. *Chemical Engineering Journal*, 127(1), 167-176.
- Behnajady, M. A., Modirshahla, N., Mirzamohammady, M., Vahid, B., & Behnajady, B. (2008). Increasing photoactivity of titanium dioxide immobilized on glass plate with optimization of heat attachment method parameters. *Journal of Hazardous Materials*, 160(2), 508-513.
- Byrne, J.A., Eggins, B.R., Brown, N.M.D., Mckinney, B., & Rouse, M. (1998). Immobilisation of TiO<sub>2</sub> powder for the treatment of polluted water. *Applied Catalysis B: Environmental*, 17(1-2), 25-36.
- Dolinová, J., Ruzicka, R., Kurková, R., Klánová, J., & Klán, P. (2006). Oxidation of aromatic and aliphatic hydrocarbons by OH radicals photochemically generated from H<sub>2</sub>O<sub>2</sub> in ice. *Environmental Science & Technology*, 40(24), 7668-7674.
- Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., & Abidin, Z. Z. (2009). Review of technologies for oil and gas produced water treatment. *Journal of Hazardous Materials*, 170(2), 530-551.
- Hawboldt, K., Chen, B., Thanyamanta, W., Egli, S., & Gryshchenko, A. (2010). Review of produced water management and challenges in harsh/arctic environments. Submitted to the American Bureau of Shipping (ABS), August, 2010.
- Jaji, K.T. (2012). Treatment of oilfield produced water with dissolved air floatation. Master thesis, Dalhousie University, Halifax, Canada.
- OGP (International Association of Oil and Gas Producers) (2002). *Aromatics in Produced Water: Occurrence, Fate & Effects and treatment*. Report OGP No. 1.20/324, London, United Kingdom.
- OSPAR Commission (2008). *Discharges, spills and emissions from offshore oil and gas installations in 2008* [http://qsr2010.ospar.org/media/assessments/p00452\\_offshore\\_report\\_2007\\_with\\_assessment.pdf](http://qsr2010.ospar.org/media/assessments/p00452_offshore_report_2007_with_assessment.pdf).
- Saien, J., & Nejati, H. (2007). Enhanced photocatalytic degradation of pollutants in petroleum refinery wastewater under mild conditions. *Journal of hazardous materials*, 148(1), 491-495.
- Saien, J., & Shahrezaei, F. (2012). Organic pollutants removal from petroleum refinery wastewater with nanotitania photocatalyst and UV light emission. *International Journal of Photoenergy*, 2012.
- Ukiwe, L. N., Egereonu, U. U., Njoku, P. C., Nwoko, C. I., & Allinor, J. I. (2013). Polycyclic Aromatic Hydrocarbons Degradation Techniques: A Review. *International Journal of Chemistry*, 5(4), 43-55.
- Xu, J., Xiao, X., Stepanov, A. L., Ren, F., Wu, W., Cai, G., & Jiang, C. (2013). Efficiency enhancements in Ag nanoparticles-SiO<sub>2</sub>-TiO<sub>2</sub> sandwiched structure via plasmonic effect-enhanced light capturing. *Nanoscale research letters*, 8(1), 1-5.
- Yahia Cherif, L., Yahiaoui, I., Aissani-Benissad, F., Madi, K., Benmehdi, N., Fourcade, F., & Amrane, A. (2014). Heat attachment method for the immobilization of TiO<sub>2</sub> on glass plates: application to photodegradation of basic yellow dye and optimization of operating parameters, using response surface methodology. *Industrial & Engineering Chemistry Research*, 53(10), 3813-3819.
- Zheng, J.S., Liu, B., Ping, J., Zhang, B.Y. & Chen, B. (2012). Feasibility analysis of two analytical methods with GC/MS for real-time monitoring PAHs in oil contaminated seawater. Proceedings of 35<sup>th</sup> AMOP technical seminar on Environmental Contamination and Response, Vancouver, British Columbia, Canada, June 5 to 7.