Removal of naphthalene from offshore produced water through immobilized nano-TiO₂ aided photo-oxidation

Bo Liu, Bing Chen, Kenneth Lee, Baiyu Zhang, Yinchen Ma and Liang Jing

ABSTRACT

In order to increase the applicability of photocatalysis in treating offshore produced water (OPW), an immobilized catalyst was introduced into the UV irradiation system and its performance on the degradation of organic compounds in OPW was evaluated. Naphthalene was selected as the target pollutant owing to its abundance in produced water and its chemical property as a typical polycyclic aromatic hydrocarbon. Aeroxide® P25 nano-scale TiO₂ powder was immobilized on glass slides by a heat attachment method and its photocatalytic capacity was compared to that of the original powder in terms of naphthalene removal efficiency. The results of adsorption showed that the reduction of catalysts’ surface area by immobilization was similar to that by agglomeration. The photocatalytic reaction rate constants in the homogeneous and immobilized systems were 0.00219 min⁻¹ and 0.00305 min⁻¹, respectively, indicating that the immobilized catalyst had a better performance in photo-oxidation. The fouling of catalyst surface during the irradiation process came from the deposition of insoluble particles, organic matter, and the scaling of calcium. The immobilization of catalysts was more resistant to the substrate effects of OPW, indicating a promising alternative in treating OPW.

Key words | immobilization, naphthalene, offshore produced water, photocatalysis

INTRODUCTION

Offshore produced water (OPW) is one of the largest waste streams produced during the exploitation and production of oil and gas at sea (Jaji 2012; Zheng et al. 2016). The annual generation of OPW is approximately 14 billion barrels worldwide (Hawboldt et al. 2010; Jaji 2012). The composition of OPW is site specific and usually includes suspended solids, salt, petroleum hydrocarbons, organic acids, heavy metals, radionuclide and treating chemicals (Li et al. 2006). Without proper treatment, the discharge of OPW can cause long-term negative impacts on marine and coastal environments. OPW is usually treated on-site prior to being reinjected or disposed. The conventional on-site treatment technologies are mainly physical separation, such as hydrocyclone, skimming, and dissolved air flotation; however, they have difficulties in efficiently removing the dissolved petroleum hydrocarbons from OPW (OGP 2002; Fakhru’Razi et al. 2009). These hydrocarbons may cause severe deterioration of marine environments. Particularly, polycyclic aromatic hydrocarbons (PAHs) are among the most toxic components in OPW due to their strong mutagenic and carcinogenic effects on marine biota and the resistance towards biodegradation (OGP 2002). With the presence of insoluble particles, the removal of PAHs by membrane technologies could be more problematic because of easily jamming the membrane modules (Fu et al. 2015). Furthermore, there is a growing need for more stringent regulations when the petroleum industry is marching toward the Arctic and deep waters. For example, the ‘Zero Discharge’ policy has been required by the Arctic Waters Pollution Prevention Act in Canada, which means that no contaminants shall be discharged into Arctic waters. A similar policy has also been enforced by the Oslo and Paris...
Conventions Commission (OSPAR 2008). Therefore, further research efforts in developing more efficient methods for OPW treatment are very desirable.

Photocatalysis by TiO₂ semiconductor photocatalysts has been extensively studied and proven to be an effective and environmentally friendly option for mineralizing organic contaminants in wastewater (Shon et al. 2008; Melemeni et al. 2009). The significant reduction of organic contaminants and chemical oxygen demand in on-shore refinery wastewater was also demonstrated by applying photocatalysis (Saien & Nejati 2007; Saien & Shahrezaei 2012). Recently, the photocatalytic degradation of PAHs in oily seawater including OPW was investigated by introducing suspended TiO₂ (Liu et al. 2013, 2016). The enhancement of degradation efficiency was found compared with other photolysis studies (Ping et al. 2011; Jing et al. 2014).

In spite of the promising mineralization potential, the application of photocatalysis may raise other issues.

The concerns originate mainly from the introduction of catalyst slurry in photocatalysis. One of the major disadvantages is that the aqueous suspension of catalyst in treated effluent needs to go through a solid-liquid separation step before discharge, which, in turn, greatly increases treatment time and cost (Byrne et al. 1998; Yahia-Cherif et al. 2014). Further, the suspended catalysts are more susceptible to water matrix. The immobilization of TiO₂ on different substrates has then been studied to control the dispersion of catalysts in treated effluent (Behnajady et al. 2008; Chong et al. 2010). Some studies compared suspended TiO₂ with immobilized TiO₂ regarding the performance of photocatalysis and indicated that the immobilization of catalyst reduced its surface active sites and limited its mass transfer potential (Matthews 1987; Mascolo et al. 2007). However, these studies were conducted without considering the matrix effects of water media. Limited research has been conducted to compare the performance of different catalysts in wastewater treatment (Pozzo et al. 1997; Mascolo et al. 2007). To date, the research on photocatalytic treatment of OPW by immobilized catalysts has not been well studied.

It has been proved that the matrix effect of OPW significantly deteriorated the performance of photocatalysis (Liu et al. 2013, 2016). As a surface sensitive reaction, the activity of catalyst surface plays an important role in photocatalysis (Hidaka et al. 2003, 2006). The surface change of catalysts could be vulnerable to the complex inorganic and organic composition of wastewater, which results in the reduction of reactivity (Pablos et al. 2012). The presence of inhibitory ions (Mg²⁺, Ca²⁺, SO₄²⁻, CO₃²⁻, etc.) could significantly reduce the effectiveness of a catalyst, especially for a suspended one, by blocking the active sites and/or forcing the agglomeration of the catalyst (Armanious et al. 2011; Fard et al. 2013). On the other hand, the high concentration of organic substrates saturate the TiO₂ surface, reducing the photonic reactivity of the catalyst (Chong et al. 2010). The complex composition of OPW includes many inorganics and organics that could affect the performance of photocatalysis. To improve the performance of photocatalysis and reduce matrix effects, it is important to evaluate the surface changes by investigating the adsorption kinetics and catalyst fouling in OPW.

In order to investigate the applicability of immobilized photocatalysis in treating OPW, immobilized and suspended TiO₂ have been used as catalysts to evaluate their photocatalytic and adsorptive performance in the presence of OPW substrate. The catalysts were immobilized by a heat-attached method and further characterized by scanning electron microscope (SEM) and energy-dispersive x-ray spectroscopy (EDS). Naphthalene was selected as the target contaminant due to its abundance in OPW. The removal of naphthalene and other organic substrates in OPW was examined. The effects of OPW substrates were discussed. The findings are expected to help develop better photocatalytic technology to improve its efficiency in treating OPW and reduce adverse effects caused by the OPW matrix.

MATERIALS AND METHODS

Materials

Naphthalene-d₈ was purchased from Cambridge Isotopes Laboratories (USA) and used as surrogate. Acetone, ethyl alcohol, dichloromethane (DCM), and concentrated hydrofluoric acid solution were purchased from Sigma-Aldrich Canada Co. Aeroxide® P25 nano-scale TiO₂ (anatase:rutile is 9:1, average particle size is around 21 nm) and sodium hydroxide were obtained from Fisher Scientific, Canada. All the chemicals were of analytical grade. Glass
microscope slides (75 × 25 mm²) were purchased from VWR International, Canada. The OPW was provided by a local oil and gas industry.

**Immobilization of catalysts**

The immobilization of catalysts on glass slides was conducted using a heat-attached method (Yahia-Cherif et al. 2014). First, 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 (0.1 mol·L⁻¹) for 1 day and 0.01 mol·L⁻¹ sodium hydroxide solution for 2 hours, successively, to increase the amount of OH group on the slides. After washing with distilled water, both sides of the slides were dipped into the slurry solution and then dried at ambient temperature. After drying, the glass slides were calcinated in a muffle furnace (Thermolyne™) under 450 °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 estimated concentration of P25 on the glass surface was around 0.8 g m⁻². SEM images and EDS spectrum of coated glass slide surfaces were acquired from MLA 650F (FEI™). The surface fouling of used slides was examined by Fourier transform infrared spectroscopy (FT-IR, Bruker Corporation) and EDS.

**Irradiation experiments**

The irradiation experiments were conducted in a photocatalytic reactor (Figure 1). Five hundred milliliters of produced water sample were filled into a 500 mL amber bottle. Four coated glass slides with an equivalent amount of P25 powder were hung in the middle of the amber bottle and the mixture was stirred for 30 minutes prior to irradiation in order to achieve equilibrium. The systems with coated glass slides and P25 powder represented the immobilized and suspended systems, respectively. Pen-ray light source (UVP® 11SC-1, peak wavelength at 254 nm, irradiance of 4.4 mw/cm²) covered with a quartz tube was then submerged in the bottle for 12 hours’ irradiation. A water bath was used to keep the system at ambient temperature. Water samples were collected at 0, 0.5, 1, 1.5, 2, 3, 6, and 12 hours, respectively. The mixture was kept homogeneous by using a magnetic stirring. Adsorption experiments were conducted using the same apparatus as stated above. The sampling times for adsorption were 0, 0.25, 0.5, 1, 1.5, 2, 3, 6, and 12 hours, respectively.

**Analytical methods**

The liquid–liquid micro-extraction (LLME) method was modified from the extraction methods developed by Zheng et al. (2015) and Jing et al. (2014). For the OPW samples from the immobilized system, 10 mL water sample was first spiked with 20 μL of 1 μg mL⁻¹ naphthalene-d₈ solution and vortexed for 10 seconds and then extracted by 250 μL DCM for 1 minute. The mixture was centrifuged at 1,500 rpm for 5 minutes to completely separate water from organic phase. After centrifugation, 100 μL extract was transferred into a 150 μL micro-vial.

For the OPW samples collected from the suspended system, 10 mL water sample was centrifuged at 3,000 rpm for 15 minutes. 5 mL of supernatant was withdrawn and forced through a 0.2 μm syringe filter (Whatman® Spartan® RC) with low organic retention to remove any catalyst residue. Then, 10 μL 1 μg mL⁻¹ naphthalene-d₈ solution was added and the solution was vortexed for 10 seconds. After that, 250 μL DCM was added and further vortexed for 1 minute. The mixture was finally centrifuged at 1,500 rpm...
for 5 minutes to complete the phase separation. The extract with volume of 100 μL was transferred into a 150 μL microvial.

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 m × 0.25 mm id 0.25 μm DB-5MS UI fused silica capillary column. The injected mode was splitless at 300 °C. A temperature ramp was set as follows: held at 65 °C for 1 minute, then raised at the rate of 4 °C min⁻¹ to 110 °C and held for 5 minutes; and finally raised to 300 °C at the rate of 20 °C min⁻¹. Total ion current chromatogram was acquired to examine the changes of organic components in OPW. The analysis of naphthalene and its surrogate was carried out in a selected-ion monitoring chromatogram. The analytical processes were triplicated. The relative standard deviations for naphthalene in the immobilized system and suspended system were 6% and 4%, respectively.

Other parameters of OPW, such as inorganic composition, pH, and turbidity were quantified by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer ELAN® DRCII), pH meter (EL20, Mettler Toledo®), and turbidity meter (VWR Scientific®, USA), respectively.

**RESULTS AND DISCUSSION**

**Characterization of immobilized catalyst on glass slides**

The surface morphology of the immobilized catalyst is illustrated in Figure 2. Figure 2(a) depicts the formation of a P25 film on the surface of glass slides. It also illustrates the non-uniformed texture on the film with different gray levels at different locations. The brighter level indicates a thicker coating, whereas the darker level indicates the thinner coating. By using EDS analysis, the density of the Ti element and its relative proportion in one area can be identified. Overall, the relative proportion of Ti was 36% on the depicted surface, indicating that a considerable amount of TiO₂ has been coated onto the slides. The density of Ti element in the scan area is shown in Figure 2(b). The higher brightness refers to a larger amount of Ti atoms in a specific area. The black indicates the absence of Ti element. It gave a clearer illustration of TiO₂ texture. This non-uniform texture was formed by the uneven evaporation of solvent during the drying step of immobilization. A higher solvent evaporation rate in some areas caused the drift of P25 in other areas with a low evaporation rate, forming a catalytic film with an uneven thickness.

**Effect of filtration on sample analysis**

The LLME methods were modified differently to pre-treat the samples obtained from the immobilized and suspended
systems. For the suspended system, the use of centrifuge and filtration significantly increased the pre-treatment time (around 15 minutes), whereas the immobilized system did not need these separation steps. This was because a negligible amount of dispersive catalytic particles was found compared with the suspended system. Without filtration, the overall time for sample pre-treatment was significantly shortened.

The mass spectra of analytic samples in the different systems are further compared in Figure 3. The decrease of abundance was observed after filtration, which can refer to the retention of organics by using a syringe filter. Furthermore, some of the organic components in OPW, especially those hydrocarbons with longer retention time, ‘disappeared’ in the spectrum after filtration. These hydrocarbons with higher hydrophobicity were more attracted to the insoluble particles and other insoluble organic matters in OPW (Luo et al. 2009; Ukiwe et al. 2013), which was consequently deposited during centrifugation and retained by the filtration membrane.

**Evaluation of adsorption and photocatalysis**

The adsorption of naphthalene onto TiO$_2$ particles is dependent upon the hydrophobicity, the surface of catalyst, and solution conditions (Xue et al. 2011). The concentration of naphthalene in the solution was monitored for over 12 hours with the absence of UV light (Figure 4(a)).

The kinetics of naphthalene adsorption onto TiO$_2$ were fitted into the pseudo first-order Lagergren equation (Gimeno et al. 2007):

\[
\frac{dq_t}{dt} = K_{ads}(q_e - q_t)
\]

where $q_e$ is the amount of naphthalene adsorbed per unit mass of adsorbent at equilibrium (mg/g); $q_t$ is the amount
of naphthalene adsorbed per unit mass of adsorbent at different time (mg/g); and $K_{ads}$ is the adsorption constant $(g/mg\cdot min^{-1})$.

The unstable changes of naphthalene occurred in the first 90 minutes in both systems. The introduction of catalysts may break the homogenous condition of OPW. The inconstant dispersion of insoluble particles during sampling steps could further intensify the fluctuation. It can be proved that there is a greater fluctuation in naphthalene concentration in OPW by introducing the suspended catalyst to the system, which was highly dispersed in the sample. The steady decrease of naphthalene concentration was found after 90 minutes. It was indicated that naphthalene was adsorbed on the catalyst during this period. Therefore, the initial adsorption of naphthalene was assumed to commence after 90 minutes. The fitting curve of adsorption kinetics was then plotted.

The adsorption kinetics results are tabulated in Table 1. The $K_{ads}$ value (0.0254 g/mg·min$^{-1}$) in the suspended system (P25) was much higher than that (0.00367 g/mg·min$^{-1}$) in the immobilized system (slide), which indicated a higher mass transfer rate of P25 powder than that of the coated glass slides. However, the similar adsorption equilibriums of 0.00353 mg/g for slide and 0.00320 mg/g for P25 showed a negligible difference of surface area between the P25 powder and the coated glass slides. It further demonstrated the similar numbers of activated sites on both catalysts. This result was inconsistent with the statement that the immobilization of catalyst would significantly reduce its surface area (Mascolo et al. 2007). 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). In our study, the agglomeration of TiO$_2$ had a similar effect to the reduction of available specific surface area. Limited dispersion of catalyst was less influenced by alkaline-earth cations. In this case, the immobilized catalysts had more resistance to the negative effects caused by OPW substrate.

The photocatalytic process was conducted under UV irradiation for 12 hours and the experimental results were then fitted with an apparent first-order kinetics (Xu et al. 2015):

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

where $t$ is the reaction time (min); $k$ is the first-order reaction rate constant $(\text{min}^{-1})$; $c_t$ is the determined concentration of the reactant at time $t$ $(\mu g/L)$; and $c_0$ is the initial concentration of the reactant $(\mu g/L)$.

The photocatalytic experimental results and the fitting curves of degradation kinetics are shown in Figure 4(b). For the immobilized system, the regression coefficient ($R^2$) between the fitting curves and experimental results was higher than 0.99, indicating a good fit. In the suspended system, the regression coefficient was therefore decreased to 0.95. The reduction of $R^2$ could result from the inhomogeneous dispersion of suspended catalysts in the early stage. The $k$ values for immobilized and suspended systems were 0.00305 min$^{-1}$ and 0.00219 min$^{-1}$, respectively. The results showed a higher removal effectiveness of naphthalene by the immobilized system. The attenuation of UV light caused by the increase of turbidity significantly affected the photocatalytic efficiency as light intensity is a critical factor in photocatalysis (Jing et al. 2014). The turbidity of OPW was not changed after introducing the immobilized catalyst. Contrastingly, it was increased to 100 NTU by applying P25 powder. The increase of turbidity promoted the attenuation of UV-C, and thus reduced the overall intensity of irradiation.

**Table 1** The comparison of different catalysts on the adsorption and photocatalysis of naphthalene

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$K_{ads}$ (g/mg·min$^{-1}$)</th>
<th>$q_e$ (mg/g)</th>
<th>Regression ($R^2$)</th>
<th>$K$ (min$^{-1}$)</th>
<th>Regression ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate</td>
<td>0.00367</td>
<td>0.00353</td>
<td>0.979</td>
<td>0.00305</td>
<td>0.995</td>
</tr>
<tr>
<td>P25</td>
<td>0.02543</td>
<td>0.00520</td>
<td>0.825</td>
<td>0.00219</td>
<td>0.949</td>
</tr>
</tbody>
</table>
Degradation of organic substrate in OPW

The degradation efficiency of different organic compounds in OPW was varied. As seen from the GC chromatogram shown in Figure 5, the major organic components in the spectra were phenols and their alkyl congeners, aromatic hydrocarbons and aliphatic hydrocarbons. The peaks with retention time less than 15 minutes generally refer to phenols, their alkyl homologues and some of the aliphatic hydrocarbons with lower molecular weights. Most of the higher molecular weight aliphatic hydrocarbons were eluted after 15 minutes. After irradiation, most of the peaks before 15 minutes disappeared from the chromatogram, indicating an effective photo-degradation of phenols and those hydrocarbons with lower molecular weights. However, the peaks after 15 minutes showed insignificant changes. It indicated that aliphatic hydrocarbons were much more inert than aromatic hydrocarbons in photocatalysis. There could be two reasons: (1) aliphatic hydrocarbons were UV-transparent in the wavelength of 254 nm, limiting their photo-degradation (Dolinová et al. 2006; D’Auria et al. 2009); (2) the hydroxyl radical addition to aromatic organics in photocatalysis reacts faster than the H-abstraction of aliphatic organics (Dionysiou et al. 2016). Therefore, the presence of aliphatic hydrocarbons had limited influence on competing the UV adsorption and the radical oxidation with NAP. The negative impact of organic substrate to the photocatalytic oxidation of NAP was mainly from the aromatic organics such as phenols in OPW. It was also observed that the depletion of all the organic matter was achieved after photocatalysis and filtration, suggesting great potential in treating and/or reclaiming OPW.

Substrate effects of OPW on coating surface

The substrate of OPW was determined by ICP-MS and GC-MS. The results showed that the OPW contained high salinity, high concentration of bivalent cations, and a large number of organic components (phenols, PAHs, aliphatic hydrocarbons, etc.). The turbidity was around 22 NTU (Table 2), indicating a large amount of insoluble particulate matter in the OPW.

The significant decrease of photocatalytic degradation performance with suspended catalysts was found in OPW. The presence of bivalent cations (such as Ca$^{2+}$, Mg$^{2+}$) would force the agglomeration of catalysts (Armanious et al. 2011). Therefore, the activated sites on catalyst surface were reduced, lowering the photocatalytic rate of analytes.

The surface of coated glass slides changed from white to pale yellow during adsorption and photocatalysis processes.

Table 2 | Background information of the OPW sample

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>0.01 mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>83.28 mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>971.08 mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>4.12 mg/L</td>
</tr>
<tr>
<td>Silicon</td>
<td>20.38 mg/L</td>
</tr>
<tr>
<td>Chlorine</td>
<td>17,197 mg/L</td>
</tr>
<tr>
<td>Sulfur</td>
<td>630.92 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>6.86</td>
</tr>
<tr>
<td>Turbidity</td>
<td>22 NTU</td>
</tr>
</tbody>
</table>

Figure 5 | Degradation of organic components in OPW by different catalysts/systems.
This pale yellow color was similar to that in OPW, suggesting that the fouling of slide was due to the deposit of OPW substrate. The decrease of turbidity of OPW from 22 NTU to 16.5 NTU after applying the coated glass slides reflected the deposition of insoluble particles that occurred during the experiments. The results from EDS did not show the presence of iron, which usually appears in yellow. However, the Ca/Si ratio increased from 0.234 to 0.276 after irradiation, suggesting that a slight amount of calcium was deposited on the TiO2 film. The scaling of calcium could be attributed to the increase of temperature during irradiation. The hydrophobic organic matter could also precipitate on the catalyst surface, which resulted in the reduction of the number of activated sites. Six peaks were shown in the FT-IR spectra (Figure 6). The peaks at 2,920 cm⁻¹ and 2,850 cm⁻¹ refer to alkyl groups; while the peaks at 3,391 cm⁻¹, 1,632 cm⁻¹, 1,453 cm⁻¹, and 1,106 cm⁻¹ refer to the O-H bond in -COOH function groups, unsaturated C = C bond, alkanes and C-O bond, respectively. Therefore, the organic substrate on the fouled glass slides included acid, alkanol, alkane, and aromatic organics.

CONCLUSIONS

This study compared the removal of naphthalene by photocatalysis using suspended TiO2 and immobilized TiO2 in OPW. The adsorption of naphthalene on the surface of TiO2 and the photo-degradation of naphthalene have been evaluated. Hydrocarbons with higher molecular weight were not observed in the GC spectra after filtration. This was probably caused by their relatively high affinity to the insoluble matters which were removed by centrifugation and membrane filtration. The negligible difference of adsorbed naphthalene at equilibrium indicated that the immobilized TiO2 had a similar activated surface area as that of the suspended TiO2 in OPW. The photodegradation efficiency of naphthalene was enhanced by immobilized TiO2 because of the significant reduction of turbidity compared with TiO2 powder. The degradation of other major hydrocarbons (phenols and aliphatic hydrocarbons) suggested that the abundance of aromatic organics was more likely to affect the naphthalene degradation. The fouling on the catalyst surface was observed as the color changed from white to pale yellow. The reduction of turbidity in OPW, the increase of calcium element, and the identification of various organic functional groups on the coated glass slides reflected that the components on the fouling surface were insoluble particles, scaling and organic matters in OPW.

To provide a more promising alternative in treating OPW, ongoing research is focusing on the identification of the key compounds in OPW affecting the fouling and the color change of catalysts. The prevention of fouling is also being investigated.

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