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Floating Photocatalysts for Passive Solar Degradation of Naphthenic Acids in Oil Sands Process-Affected Water

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Abstract: Oil sands process-affected water (OSPW), generated from bitumen extraction in the Canadian oil sands, may require treatment to enable safe discharge to receiving watersheds, as dissolved naphthenic acids (NAs) and other acid extractable organics (AEO), identified as the primary toxic components of OSPW, are environmentally persistent and poorly biodegradable. However, conventional advanced oxidation processes (AOPs) are impractically expensive to treat the volumes of OSPW stockpiled in the Athabasca region. Here we prepared floating photocatalysts (FPCs) by immobilizing TiO₂ on glass microbubbles, such that the composite particles float at the air-water interface for passive solar photocatalysis. The FPCs were demonstrated to outperform P25 TiO₂ nanoparticles in degrading AEO in raw OSPW under natural sunlight and gentle mixing conditions. The FPCs were also found to be recyclable for multiple uses through simple flotation and skimming. This paper thus demonstrates the concept of a fully passive AOP that may be scalable to oil sands water treatment challenges, achieving efficient NA reduction solely through the energy provided by sunlight and natural mixing processes (wind and waves).

Keywords: passive; solar; photocatalysis; naphthenic acids; oil sands

1. Introduction

Bitumen extraction in Canada's oil sands uses large volumes of water, which is contaminated in the process by compounds leached from the oil sands ore, and referred to as oil sands process-affected water (OSPW). Release of OSPW to the environment is hindered by the toxicity of the water, due primarily to dissolved naphthenic acids (NAs) and other acid extractable organics (AEO) [1,2], and thus an estimated 1 billion m³ of OSPW to date has been retained in tailings ponds on site. NAs are not fully biodegradable [3,4], and their toxicity persists over decades [5], therefore a water treatment solution may be required to enable OSPW discharge.

Recently the oil sands industry has sought passive, or low energy, water treatment technologies capable of addressing large volumes of OSPW [6]. Considering the large sunlight-exposed surface area of oil sands tailings ponds, solar photocatalysis is a promising advanced oxidation process (AOP) with demonstrated capability to fully degrade OSPW AEO through hydroxyl and superoxide radical-mediated oxidative mineralization [7–9]. In contrast to other advanced oxidation processes (AOPs) that have been tested for OSPW treatment [10,11], solar photocatalysis enables complete degradation of even recalcitrant NAs, without the need for chemical amendment of the water or electrical power consumption. Nevertheless, there remain a number of key technical challenges towards application of photocatalysis for OSPW treatment. Previous research has studied

photocatalytic nanoparticles dispersed into OSPW as a slurry, and while slurries enable high treatment rates through efficient mass transfer, they require continuous mixing to remain suspended, as without mixing the photocatalyst near the water surface, the turbidity of OSPW is likely to occlude sunlight from reaching the catalyst. Indeed, our previous measurements indicated the UV light penetrates <1 cm into OSPW [7]. Since the photocatalytic reaction thus only occurs at the water surface, the bulk majority of slurried catalyst dispersed in the dark zone below the surface is not effectively utilized, resulting in unnecessary material oversupply. Furthermore, slurries present challenges for cost effective nanocatalyst recovery and reuse at a large scale.

It was hypothesized that immobilizing a photocatalyst onto a buoyant support could address the above challenges, while adapting this promising treatment technology into a passive platform enabling large-scale deployment. On floating cores, the photocatalyst is naturally concentrated without any mixing at the water surface, where sunlight intensity is greatest, and the catalyst can be easily collected by simple skimming. Thus, in this work we sought to demonstrate treatment of AEO in raw OSPW by use of floating photocatalysts under natural sunlight. While buoyant photocatalysts have been synthesized previously [12–14], this report represents the first demonstration of such materials as a passive treatment for OSPW remediation.

2. Experimental

2.1. Materials

OSPW collected on 17 March 2014 was provided by Shell Canada (Calgary, AB, Canada), and stored in sealed polyethylene containers in the dark at 4 °C. The OSPW was homogenized by stirring before each use, herein referred to as raw OSPW. The OSPW was characterized previously to have a conductivity of 1.695 mS/cm, 1450 mg/L total dissolved solids (TDS), 49.5 mg/L total suspended solids (TSS), and a turbidity >200 NTU [7]. The AEO concentration was measured by the FTIR method (Fourier-transform infrared spectroscopy, PerkinElmer, Waltham, MA, USA) below to be 26.3 mg/L.

A commercial mixture of naphthenic acids (technical grade, carbon numbers 6–20, z-classes 0 to –4, as characterized by Damasceno et al. [15]), dichloromethane (DCM, ≥99.9%, HPLC grade) NaOH (≥98%, ACS grade) and nitric acid (70%, ACS grade) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Sulfuric acid (95–98%, ACS grade, Fisher, Hampton, NH, USA) and titanium dioxide nanoparticles (Aeroxide P25, ~10–50 nm particle diameter, 55 m² g^{−1} surface area, Acros, Geel, Belgium) were used as received. Glass microbubbles (3M iM30k, Maplewood, MN, USA, soda-lime-borosilicate glass, ~10–30 µm diameter, 0.6 g/cm³ density) were washed by 1 mol/L HNO₃ and 0.1 mol/L NaOH before use (at 125 g/L microbubbles), rinsing thrice with deionized (DI) water after each wash, then drying at 120 °C in air.

2.2. Floating Photocatalyst Synthesis and Characterization

TiO₂ nanoparticle powder was dispersed at 60 g/L into DI water by probe sonication, after which 0.1 mol/L HNO₃ was added to a concentration of 1 mmol/L, thereby adjusting the suspension to a nominal pH of ~3. This TiO₂ suspension was then added to microbubble powder (17.75 mL per g microbubbles), and the mixture was stirred at 500 rpm for 2 h, before transferring to a separatory funnel. The floating layer was collected after 1 h, vacuum filtered to form a cake, dried and crushed to a powder, which was then calcined for 4 h at 500 °C in air (5 °C/min ramp rate) to form the floating photocatalysts (FPCs).

Particle morphology was analysed by SEM (Zeiss Merlin FESEM, Oberkochen, Germany), and elemental composition was measured by EDX (EDAX, Zeiss, Oberkochen, Germany). Crystal phase was assessed by powder XRD (Bruker D8-Advance, Vântec-1 detector, 1.5405 Å Cu-Kα radiation, Billerica, MA, USA).

2.3. Photocatalysis Experiments

Outdoor solar photocatalytic experiments were performed between 22 and 28 August 2015 at the University of Waterloo (Waterloo, ON, Canada). 1 g of FPC powder (or 0.5 g of P25 TiO₂) was stirred into 500 mL of raw OSPW in a borosilicate glass beaker (90 mm O.D.). Beakers were sealed from above with polyethylene film (Glad, measured to be UV transparent by spectrophotometry) to prevent evaporation during the experiments, and wrapped around the sides with Al foil. The beakers were then placed on a rooftop outdoors (43°28'17.9" N 80°32'32.2" W) and exposed to sunlight while stirring at 130 rpm, where a control included OSPW exposed to sunlight in the absence of TiO₂. The stirring Reynolds number was calculated according to the formula $Re = fr^2v^{-1}$, where f is the rotational frequency (130 rpm), r is the radius of the stir bar (1.905 cm) and v is the kinematic viscosity of water [16]. Following solar treatment, the photocatalyst was separated from the OSPW by flotation or centrifugation, retaining the water for analysis (stored at 4 °C in the dark).

Weather data was obtained from the University of Waterloo Weather Station archives [17]. Cumulative insolation was calculated by integrating the incoming shortwave radiation (measured by the weather station using a Kipp & Zonen CM11 pyranometer (Delft, Netherlands), spectral range 285 to 2800 nm) over the duration of the experiment (Figure S1). Cumulative UV exposure was estimated on the basis of the ASTM G173-03 global tilt solar spectrum as 4.72% of the cumulative insolation.

Photocatalyst recyclability experiments were performed under in a custom photoreactor enclosure, consisting of an array of UVA fluorescent bulbs (Philips F20T12/BL, Amsterdam, Netherlands, peak emission ~350 nm) suspended above the samples [9]. The UV intensity was measured to be ~40 W/m² with a UVA/B light meter (Sper Scientific, Scottsdale, AZ, USA, NIST certified calibration), which is similar to the UV content of the solar spectrum (ASTM G173-03 global tilt). Following UV exposure, the photocatalyst was separated from the OSPW by flotation, and then directly redispersed into a fresh sample of OSPW for another round of photocatalytic testing.

2.4. Analysis

The concentration of AEO was measured by Fourier transform infrared spectroscopy (FTIR, PerkinElmer, Waltham, MA, United States) according to the standard method [18,19] with minor modifications (*viz.*, the acidified samples were extracted thrice with DCM in a 1:12.5 solvent to sample volumetric ratio, with $80 \pm 4\%$ total recovery), using the commercial NA mixture to prepare the calibration curve. AEO is a composite measure of classical NAs, oxy-NAs (C_nH_{2n+z}O_x, where $x > 2$), and other organic acids [20]. Samples were filtered prior to the analysis (Whatman 934-AH glass fiber filter, Little Chalfont, Buckinghamshire, UK). Pseudo-first order rate constants were calculated on the basis of cumulative incoming solar shortwave insolation (285–2800 nm).

3. Results and Discussion

Photocatalysts were immobilized on the outer surface of buoyant microspheres, such that the composite particles would passively float at the air-water interface and degrade aqueous organic contaminants under sunlight illumination (Figure 1a). A heterocoagulation and sintering process was used to adhere photocatalytic TiO₂ nanoparticles to a high strength glass microbubble (GMB) core, wherein the TiO₂ and GMBs were mixed together at a pH between their respective isoelectric points to induce electrostatic attraction, followed by high temperature calcination to fix the nanoparticles in place. Thermal sintering has been previously demonstrated to promote strong adhesion of immobilized TiO₂ to glass supports [21–23], although reducing specific surface area of the TiO₂ in the process [24]. Floating photocatalysts synthesized previously have used plastic supports susceptible to photocatalytic degradation [25–30], or fragile materials such as perlite [31–33], which sink upon breaking. The floating photocatalyst (FPC) composites prepared herein are entirely inorganic and resistant to photodissolution, and thus more suitable towards long term emplacement in a passive treatment system. The synthesized particles were observed to readily float at the water surface as intended (Figure 1b).

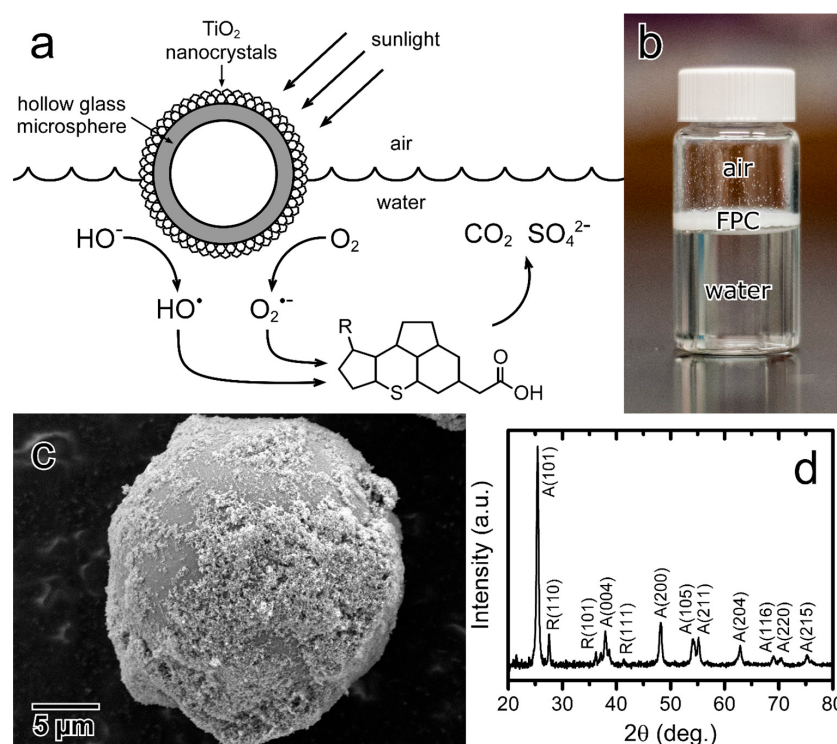


Figure 1. (a) Schematic of the floating photocatalyst (FPC) structure and mechanism of solar water treatment for naphthenic acid mineralization (not to scale), (b) photograph of the FPCs added to water, (c) SEM image of a single FPC particle, and (d) XRD pattern of the FPC powder.

SEM was used to confirm the presence of immobilized TiO₂ on the surface of the GMBs, observed as a rough particulate coating (Figure 1c), with a particle diameter of ~25 nm, similar to the diameter of the TiO₂ nanocrystals used (Figure S2). SEM images of the uncoated GMBs are presented in Figure S3. EDX analysis further confirmed the presence of Ti, and the TiO₂ content of the composite particles was estimated to be 36.6 ± 4.1 wt % (Figure S4, Table S1). TiO₂ nanocrystals are known to partially sinter at the temperatures applied during the synthesis [24], which is proposed to be the mechanism of TiO₂ adhesion [34,35]. XRD revealed the presence of anatase and rutile phases in the FPCs, characteristic of the mixed-phase TiO₂ nanocrystals used [36], confirming that the calcination step did not significantly affect the crystal phase of the particles. In fact, mild calcination at the temperatures applied herein has been reported to enhance the photocatalytic activity of TiO₂ nanoparticles [24].

The photocatalytic activity of the FPC particles was assessed under natural sunlight for the degradation of AEO in raw OSPW under gentle mixing conditions (Figure 2). The FPC particles degraded >80% of the AEO within 22 h of sunlight exposure (~33.4 kJ L⁻¹ cumulative solar UV), from a starting concentration of ~30 mg L⁻¹ down to 4 mg L⁻¹. The oxidized intermediate compounds produced during photocatalytic AEO degradation have been thoroughly characterized in our previous work, where photocatalysis was demonstrated to result in nearly complete mineralization of organic carbon [7,9]. The kinetics were apparently first order, as observed previously [7], and the pseudo-first order rate constant for the FPCs was $3.46 \pm 0.20 \times 10^{-8}$ m² J⁻¹. The FPCs compared favourably to P25 TiO₂ as a benchmark photocatalyst, which had a pseudo-first order rate constant of $4.15 \pm 0.34 \times 10^{-8}$ m² J⁻¹, where the measured rate constants were indistinguishable from each other ($p > 0.1$). However, normalized on a TiO₂ mass basis, the FPCs outperformed the P25 TiO₂, with a rate constant of 9.45×10^{-8} m² J⁻¹ g⁻¹ compared to 8.30×10^{-8} m² J⁻¹ g⁻¹, respectively. Conventionally, nanoparticle slurries would be expected to outperform immobilized photocatalysts, such as the FPCs, due to enhanced contaminant mass transfer and higher accessible catalyst surface area [37,38]. However, in the low mixing regimes studied herein, the advantages provided by the FPCs

of concentrating the photocatalyst at the water surface where sunlight intensity is highest apparently outweighed the typical disadvantages of immobilized systems. Thus the FPCs exceeded the activity of a known excellent photocatalyst formulation while enabling a convenient means of recycling through their buoyant properties.

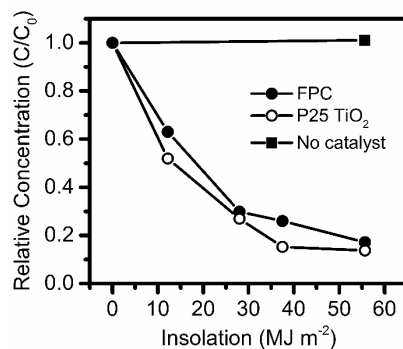


Figure 2. Photocatalytic degradation of AEO in raw OSPW under natural sunlight, where C and C_0 are the concentration and initial concentration of AEO, respectively.

The Reynolds number of mixing during the test was calculated to be 786, characteristic of a gentle laminar flow regime. The OSPW cap layer in oil sands tailings ponds is known to be well mixed by wind and waves [39–41], and NAs are furthermore constantly replenished to the interface by methanogenic bubbling in a similar process to dissolved gas flotation (estimated flux of $12 \text{ g CH}_4 \text{ m}^{-2} \text{ day}^{-1}$) [42]. Thus, as the above photocatalytic results were observed under gentle mixing conditions, it is anticipated that the natural mixing processes provided in the tailings ponds could be sufficient for OSPW treatment, although this question will be the topic of future studies. These results suggest the possibility for photocatalysis to serve as a truly passive AOP process with no electrical power input, where energy is provided solely by sunlight and wind.

Finally, the recyclability of the FPC particles for treating multiple batches of raw OSPW was tested under controlled illumination conditions (Figure 3), simply separating the catalyst by flotation. The catalyst was found to be reusable with equivalent activity for at least 3 cycles. Some deterioration in treatment performance was observed after the third cycle, possibly due to experimental difficulties in transferring 100% of the FPC material between cycles with small sample volumes, or alternatively due to progressive surface fouling of the catalyst. Effects of long term FPC exposure to raw OSPW is the topic of ongoing investigations in our laboratory.

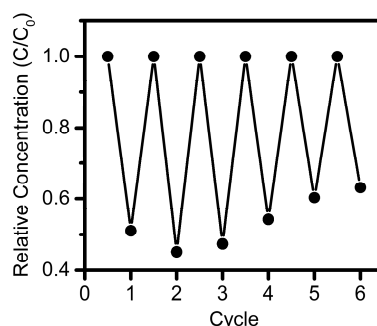


Figure 3. Recyclability of a single batch of FPC particles to degrade AEO in raw OSPW, where C and C_0 are the concentration and initial concentration of AEO, respectively.

4. Conclusions

A floating photocatalyst composite was demonstrated to match the photocatalytic activity of P25 TiO₂ in raw OSPW under natural sunlight. This is a significant finding, since photocatalytic activity was not sacrificed through this immobilization strategy, while the following advantages were gained:

- Due to their buoyancy, FPCs naturally concentrate at the air-water interface where sunlight intensity and dissolved oxygen concentrations are highest (i.e., the optimal treatment zone);
- Substantially less photocatalyst material is needed to achieve the same treatment rate as slurry deployment, since TiO₂ comprises only a minority of the buoyant composite mass, while in photocatalytic slurries, the vast majority of particles suspended below the illuminated air-water interface do not participate in the treatment process;
- NAs are naturally enriched at the air-water interface due to their surfactant properties, and are replenished to the surface from deeper OSPW in tailings ponds by methane bubbling, and through natural mixing provided by wind and waves;
- FPCs can be easily contained and collected by skimming from the surface, compared with the significant technical challenges of collecting colloidal nanoparticles from a slurry.

The use of sunlight and low energy mixing suggests the possibility that photocatalysis could serve as a truly passive water treatment process amenable to large scale deployment in the oil sands.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/10/2/202/s1>, Figure S1: Solar irradiance measured throughout the duration of the photocatalytic experiment of Figure 2. Figure S2: SEM image of TiO₂ nanostructures on the surface of a FPC particle. Figure S3: SEM images of uncoated glass microbubbles (GMBs) at (a) 500× and (b) 3000× magnification. GMBs were sputtered with Au prior to imaging. Figure S4: (a–c) SEM regions used for EDX elemental analysis and (d) typical EDX spectrum, as obtained from region (b). Table S1: Results of EDX analysis, referring to SEM regions in Figure S4.

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Author Contributions: T.L. conceived and designed the experiments; T.L. and H.K. synthesized the floating photocatalysts; H.K. and D.d.O.L. performed the experiments; T.L. analyzed the data and wrote the paper; F.G. supervised the project, contributed reagents, materials, analysis tools, and critically reviewed the paper.

Conflicts of Interest: The following authors, T.L. and F.G., declare involvement as co-founders (with stock ownership) in H2nanO Inc., an organization with a financial interest in the subject matter and materials discussed in this manuscript. The following authors, H.K. and D.d.O.L., declare no competing financial interest. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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