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# Abatement of oil residues from produced water using a thermocatalytic packed bed reactor

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## ABSTRACT

Produced water is a major waste and environmental concern in the oil and gas industry, since it contains dispersed oil and dissolved compounds, which may harm the aquatic environment. Thus, focus on the offshore treatment of the produced water is required. Current methods include hydrocyclones and water clarifiers that cannot achieve full abatement of the oily contaminants. Here we propose a novel thermocatalytic degradation of the dispersed oil using a thermocatalyst, namely  $\text{Sr}_{0.85}\text{Ce}_{0.15}\text{FeO}_3$  perovskite that benefits from the thermal energy contained in the produced water, which has temperatures of 40–50 °C when reaching the cleaning phase. It is found that the oil is removed faster with higher perovskite concentrations, and the initial removal is mainly adsorption to the perovskite surface followed by catalytic degradation. Based on batch testing, a lab-scale packed bed reactor (PBR) is modelled showing that oil can be continuously removed by sufficient residence time in the reactor.

## 1. Introduction

Oil is a major resource in the modern society as it is used for, e.g., fuel, heat, and chemical synthesis. Unfortunately, offshore oil extraction activities result in large amounts of wastewater, so-called produced water [1]. The produced water contains various hydrocarbons, heavy metals, and minerals [2,3]. Further, the hydrocarbons can be divided into saturates (covering alkanes and cycloalkanes), aromatics, resins, and asphaltenes [4,5].

In the North Sea, international legislations (OSPAR agreement) demand that produced water contains less than 30 ppm dispersed oil [6]. Therefore, it is necessary to clean the produced water to avoid environmental harm. Conventional oil production uses separation by gravity, centrifugation, air flotation, and hydrocyclones to remove oil [7]. These are often followed by polishing of the produced water to minimize the oil by, e.g., carbon adsorption [6], membrane filtration [8], chemical oxidation [9], and biological treatment [10], and in some cases addition of water clarifiers to separate the remaining oil from water [11]. These processes take place offshore, thus, new technologies should consider limited space.

Among chemical oxidations, the most common is the advanced oxidation processes (AOP), which involves highly reactive radicals for the degradation of organic species. AOPs can include hydrogen peroxide

( $\text{H}_2\text{O}_2$ ) and UV light (photocatalysis), e.g., the Fenton or Photo-Fenton reactions for homogeneous processes [12], or photocatalysts such as  $\text{TiO}_2$  for heterogeneous processes [13]. These catalytic processes can be used for either specific [14] or non-specific targeting [15,16]. However, photocatalytic reactions might find setbacks in limited access to light, therefore, thermocatalysts is of interest as they are activated by heat and thus possible to use in the dark. Among thermocatalysts are perovskite oxides that has been used in degradation of organic compounds such as bisphenol A and dyes [17]. Perovskite oxides are metal oxides with the formula  $\text{ABO}_3$ , where A is a large alkaline earth or lanthanide element and B is a transition metal. The properties of perovskites can be easily altered by changing the composition. Furthermore, the synthesis parameters greatly affect the final properties and segregation of unwanted by-products [18]. The perovskite  $\text{Sr}_{0.85}\text{Ce}_{0.15}\text{FeO}_3$  (SCF) is of interest for abatement of organic compounds due to its temperature-dependence [19] and it is able to degrade water pollutants such as bisphenol A at temperatures as low as 30 °C [20], thus, a possible solution to degrade organic residues leaving the hydrocyclone at temperatures around 40–50 °C.

In this study, removal of North Sea oil from synthetic produced water by applying  $\text{Sr}_{0.85}\text{Ce}_{0.15}\text{FeO}_3$  perovskite thermocatalyst is investigated. The tests will be carried out at 50 °C to work at a real-world realistic temperature of produced water, and the oil concentration is determined

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by UV-Vis spectroscopy. A packed bed reactor will be modelled and prepared for testing of continuous oil removal from a synthetic produced water stream.

## 2. Experimental

### 2.1. Perovskite synthesis and characterization

$\text{Sr}_{0.85}\text{Ce}_{0.15}\text{FeO}_3$  perovskite was synthesized by solution-combustion method, calcined, and washed as described elsewhere [21]. The crystal structure of the synthesized perovskite was verified by X-ray diffraction by comparing to the diffraction pattern to the one in the International Centre for Diffraction Data (ICDD) database.

### 2.2. Batch degradation experiments

Removal of oil was tested in batches (200 mL) containing 100 ppm crude oil (mixture from different wells in the North Sea), and 5 ppm dispersant. The dispersant was a mixture of Tween 80 (Sigma Aldrich) and lecithin (TCI) with ratio 40/60 w/w% in ethanol (60/40 w/w% dispersant/ethanol) as reported in Ref. [22]. The SCF concentration was studied in the range 0.5–2 mg mL<sup>-1</sup>. The dispersant was dissolved in water followed by crude oil under vigorous stirring. The temperature during experiment was 50 °C. The perovskite was added when the target temperature was reached. Samples for analyses were taken continuously to follow the decrease in oil concentration.

The oil removal was analyzed by UV-Vis using a Cary 50 Biospectrophotometer (Varian). The absorbance between 200 and 500 nm was measured, and the oil concentration was determined based on peaks around 226 and 256 nm [23] from a standard curve. The samples were diluted 1:1 in 2-propanol prior to UV-Vis measurements. To verify the UV-Vis measurements, total organic carbon (TOC) and total inorganic carbon (TIC) was determined for a batch experiment using a LCK380 test kit (Hach Lange). Oil adsorption to the perovskite was investigated by ATR-FT-IR using a Tensor II spectrometer (Bruker). Samples of the pure dispersant and oil as well as perovskites used for oil removal were analyzed.

### 2.3. Packed bed operation

The reaction kinetics obtained from batch experiments were used to model the amount of catalyst needed to reach a target outlet concentration of oil in a PBR. The mass of catalyst [g] was determined using Eq. (1), where  $Q$  is the flow rate [L s<sup>-1</sup>],  $C_{A0}$  is the initial concentration [ppm],  $X$  is the conversion factor [-], and  $k$  is the reaction rate constant [L g<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>] assuming first order reaction kinetics.

$$\frac{m_{\text{cat}}}{C_{A0}} = -\frac{Q \cdot C_{A0} \cdot \ln\left(\frac{f_0}{f_1}\right)(X-1)}{k} \quad (1)$$

The lab-scale packed bed reactor was made using a perovskite-filled syringe (maximum dimensions  $\varnothing = 1.2$  cm and length = 5.5 cm filled with 2 g of SCF, and exit of syringe has  $\varnothing = 0.3$  cm) connected to synthetic produced water (concentrations as in batch tests) that is pumped through the reactor using a Masterflex easy-load II peristaltic pump (Cole Parmer). The flow through the reactor was measured continuously during experiments to 0.0167 L min<sup>-1</sup> and 0.0075 L min<sup>-1</sup>. The produced water was heated to a temperature of 50 °C while the reactor was submerged in a water bath at 50 °C to ensure a constant temperature in the reactor. Samples were collected at reactor outlet at different durations to follow the oil concentration.

## 3. Results and discussion

### 3.1. Batch degradation experiments

The concentration of perovskite affects the degree of oil removal (Fig. 1). Within the first 5–10 min, a rapid decrease in oil concentration is seen followed by a slow continuous removal. By increasing the perovskite concentration from 0.5 mg mL<sup>-1</sup> to 2 mg mL<sup>-1</sup>, the oil concentration drops from 33% to 9% after 10 min, and after 45 min, all the oil is removed for a perovskite concentration of 2 mg mL<sup>-1</sup>. In contrast, 12% of the oil is remaining after 90 min when using 0.5 mg mL<sup>-1</sup> SCF. The initial removal of oil is caused by adsorption of oil to SCF confirmed by ATR-FT-IR (Fig. 2). The higher perovskite concentration gives a larger surface area for adsorption explaining the higher rate of initial removal. After 10–15 min, the kinetics of abatement significantly decreases due to full adsorption and the degradation of oil becomes the major cause of oil removal, like for photocatalytic studies [24]. As SCF degrades the adsorbed oil to minor carbohydrate compounds, and finally full mineralization to CO<sub>2</sub> and water, more oil can be adsorbed to the surface of SCF particles as free surface area occur. As seen in Fig. 2, the IR spectrum of the SCF used as catalyst only shows absorption bands corresponding to the oil and not dispersant, seen by comparing to the spectra of the pure compounds (inset of Fig. 2). Additionally, a SrCO<sub>3</sub> band occur which is due to the SCF being in contact with water and used as catalyst, which is caused by the reaction of Sr-O sites of SCF with dissolved CO<sub>2</sub> and carbonate species in the water [21], similar carbonate formation is found on non-doped SrFeO<sub>3</sub> [25]. The increasing presence of CO<sub>2</sub> is validated by TIC that increases to  $c/c_0 = 3.3$  after 1 min followed by a small decrease to  $c/c_0 = 2.6$  after 10 min, due to the removal of CO<sub>2</sub> from the water to the surrounding atmosphere. In contrast, TOC decreases and follows the trends observed by UV-Vis experiments, though, TOC shows a minimum of  $c/c_0 = 0.2$ , which is slightly higher than that shown by UV-Vis experiments. This suggests that at least parts of the oil underwent a full mineralization.

As the initial drop in oil concentration plausibly is caused by adsorption, a cyclic experiment was prepared to verify whether oil degradation occur or the oil removal is purely caused by adsorption (Fig. 3). The first cycle is performed as in Fig. 2, where 100 ppm oil and 5 ppm dispersant is dispersed in water followed by addition of SCF. Here, the oil concentration shows a rapid drop within 10 min as previously shown followed by a slow decrease in concentration up to 90 min. After 90 min 100 ppm oil and 5 ppm dispersant is added, and the second cycle is started. It can be seen that the concentration increases within the first 10 min where the concentration reaches a maximum (Fig. 3a). This is caused by a certain equilibration time it takes for the oil to be

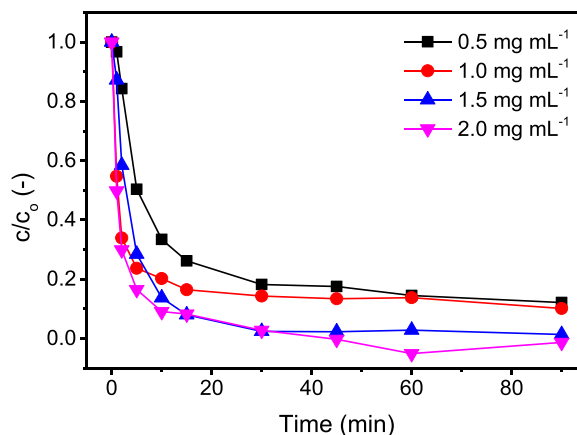


Fig. 1. Removal of oil with varying the SCF perovskite concentration from 0.5 to 2 mg mL<sup>-1</sup>. The initial oil and dispersant concentrations are 100 ppm and 5 ppm, respectively.

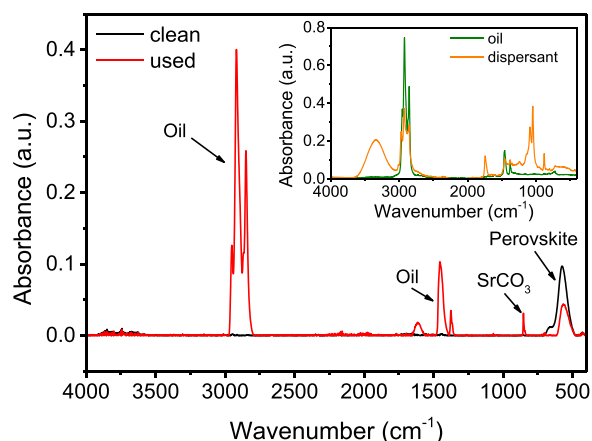


Fig. 2. ATR-FT-IR spectra of clean as-prepared SCF perovskite catalyst and a catalyst used for oil degradation. Inset shows ATR-FT-IR spectra of the pure crude oil and dispersant mixture.

dissolved in the water and, therefore, the concentration continuously increases towards this equilibration occur. After 10 min of the second cycle the oil concentration drops. As approx. 10% of the oil is remaining from the first cycle, the surface of SCF must be fully occupied and no more adsorption can take place. Therefore, the decreasing oil concentration must be related to degradation. After another 90 min, 100 ppm of oil and 5 ppm of dispersant is added again. The third cycle is similar to the second one. Note that  $c_0$  is the first measurement after addition of new oil, and the total oil concentration is higher in cycle 3 compared to cycle 2 even though  $c/c_0$  is higher in cycle 2 than cycle 3. This is due to the 100 ppm oil and 5 ppm dispersant is based on the initial amount used in the first cycle.

The reaction kinetics are calculated for all three cycles (Fig. 3b). The kinetic constant is calculated with time = 10 min as starting point due to the equilibration time in the second and third cycle, and the fact that the majority of oil removal in the first cycle is caused by adsorption. The oil is slowly removed from the water phase in the first cycle. In comparison, the oil is removed significantly faster in second and third cycle (almost 8 times faster). The higher kinetic constants in the second and third cycles compared to the first cycle suggests degradation to occur, as the removal were to be slower if only adsorption took place. This is due to the adsorption being dependant on the number of adsorption sites or available surface area in order to remove the oil, and the entire surface should be covered after first or at least second cycle, thus, no oil could be removed in the third cycle if no degradation occurred.

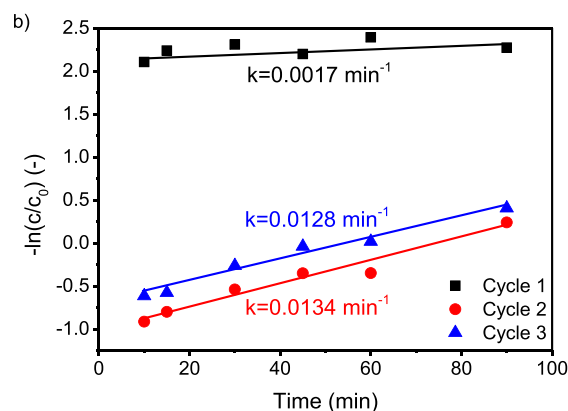
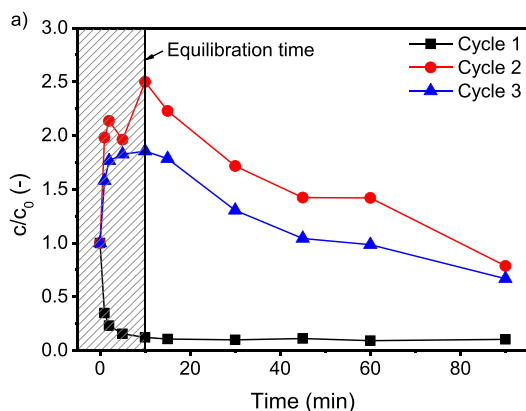


Fig. 3. Repeated tests on same perovskite catalyst by addition of 100 ppm oil and 5 ppm dispersant every 90 min. The perovskite concentration was 1 mg mL<sup>-1</sup>. a) the change in oil concentration with time for three consecutive cycles, and b) determination of the kinetic constants after 10 min for the three cycles.  $k$ -values are the kinetic constants determined for first order reaction.

### 3.2. Packed bed reactor

A packed bed reactor (PBR) was dimensioned to remove 80% of the oil from the feed water at 0.0167 L min<sup>-1</sup>, thus, reaching an outlet oil concentration of maximum 20 ppm in this study. The amount of SCF for this experiment was calculated based on Eq. 1 using the kinetic constant found in Fig. 3b. For calculations, the kinetic constant of 0.0134 min<sup>-1</sup> is used as the kinetic constants for the second and third cycles are similar. The kinetic constant is recalculated to 2.233·10<sup>-4</sup> L g<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>. The value for the third cycle is used as it is assumed that the perovskite surface is saturated with oil and the decrease in oil concentration is, therefore, caused by degradation and not adsorption as seen in the first cycle.

Based on the given information, the amount of SCF is calculated to 2.01 g for 80% oil removal at the PBR outlet. However, as shown in Fig. 4, the removal rate of at least 80% only occur within the first 30 min, after which the concentration increases at the outlet of the PBR. After 120 min, the concentration of oil in the outlet equals that in the inlet, hence, no oil is removed. This indicates that the residence time in the reactor is only sufficient for adsorption and not degradation of the oil. The kinetic rate constant determined in the batch experiments is, therefore, not sufficient for any reaction in the PBR. In order to enhance the residence time, thus, time for reaction, the flow through the PBR was reduced, while keeping the amount of SCF constant. After decreasing the flow rate to 0.0075 L min<sup>-1</sup>, the oil removal is higher than 80% during 120 min of operation. After 120 min, the removal of oil is 86%. This should be compared to the oil removal after 55 min for the high flow (same volume of produced water has then passed through the PBR),

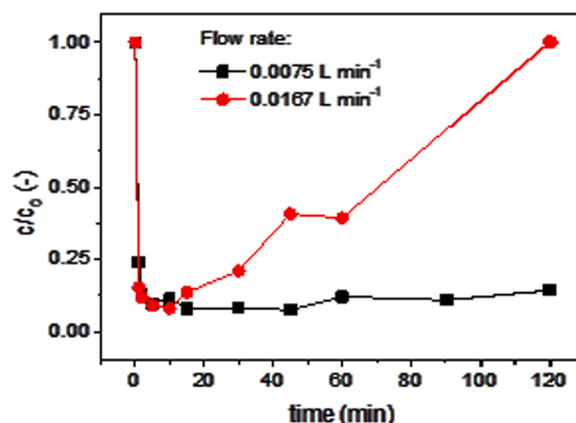


Fig. 4. Development of oil concentration in the outlet of the PBR with different flow rates.

which is 61% (after 60 min). Thus, the prolonged residence time in the PBR significantly increases the removal of oil from the synthetic produced water.

Although the lab-scale dimensioned reactor did not provide sufficient time for oil degradation plausibly due to difference in the kinetic constant obtained from the cyclic batch experiment to the PBR, it is shown that oil can be continuously removed by enhancing the residence time (decreasing the flow). The important step is that the time of degradation of oil adsorbed to the surface of the catalyst needs to be faster than the residence time as this will allow free adsorption sites for oil that passes through the PBR. Therefore, this suggests that a thermocatalytic PBR is a possible way to remove and degrade oil from produced water in the future without spending energy for heating or electricity. Future studies should aim at four subjects: (1) improving the kinetics of the oil degradation by optimization of the thermocatalyst, (2) understanding which components in the crude oil that is degraded, (3) investigating if the degraded materials undergo a full mineralization or if more environmental harmful compounds are created, and (4) examining the effect of salinity and heavy metals that occur in produced water, e.g., regarding adsorption of ions to active sites of the catalyst decreasing the efficiency.

#### 4. Conclusion

$\text{Sr}_{0.85}\text{Ce}_{0.15}\text{FeO}_3$  (SCF) can be used as catalyst to degrade oil to reach a concentration <30 ppm in produced water that is discharged to the sea. The high temperature of produced water (40–50 °C) promotes the removal of oil by using SCF without any input of energy to the process. A packed bed reactor (PBR) was modelled based on initial batch tests, followed by preparing a lab-scale PBR for continuous oil removal experiments. The oil removal did not follow the modelled degree of removal. However, by reducing the flow and thereby increasing the residence time in the reactor, >85% of the oil is removed. By improving the kinetics of degradation, the process shows great potential for future use in offshore treatment of produced water.

#### CRediT authorship contribution statement

**Martin B. Østergaard:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Visualization, Funding acquisition. **Azeem B. Strunck:** Validation, Investigation, Writing – review & editing. **Vittorio Boffa:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Mads K. Jørgensen:** Conceptualization, Methodology, Formal analysis, Resources, Writing – review & editing, Supervision, Funding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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