

## **Study of Photocatalytic Treatment of Produced Water from Oil Fields Using Zinc Oxide Nanorods**

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### **Abstract**

Produced water from oil fields is considered as the largest liquid waste globally from oil and gas exploration and operation activities. This study explores the use of zinc oxide (ZnO) nanorods coatings on glass substrates in degrading toxic contaminants using visible light irradiation (sunlight). The constituents present in produced water are complex and vary from one site to another. In the beginning, samples of produced water from oil fields were analyzed and the contaminants were determined using analytical chromatographic techniques. In previous studies, produced water was reported to mainly contain aliphatic and aromatic hydrocarbons, phenolic compounds, dissolved gases and polymeric materials, amongst others. Several conventional water treatment methods are available in the market that have been industrially implemented in production processes in oil and gas fields. Examples are membrane filtration, chlorination, air flotation, reverse osmosis, centrifugation and ion exchange methods. No single method can remove all the contaminants and usually a mixture of techniques are employed to remove harmful materials from produced water before releasing it to the environment. Oman is one of the oil producing countries with daily production of 5 million barrels of produced water associated with crude oil extraction. Produced water is usually re-injected to deep aquifers after treating it that also has a potential to re-use for other industrial and non-industrial purposes. The cost of treating produced water to meet the environmental requirements is increasing over time and with increasing quantity of produced water for every liter of oil or gas extracted due to shale oil and gas explorations and aging of oil wells. Finding innovative methods for treating produced water capable to reduce the capital and operational costs, area of operation and meeting stringent safety and environmental legislations are urgent. Advanced oxidation processes (AOPs) received attention as a possible solution to meeting these requirements offering vital solutions to the critical problems. However, classical AOPs require the use of oxidizing chemicals which add to the cost and increase carbon credits for oil and gas producers. Photocatalysis, which is a modified AOP utilizes the generation of electrons and holes in semiconductors that have the possibility of inducing redox reactions utilizing the sunlight as the energy source for the formation of excitons. Zinc oxide being a wide band gap semiconductor (band gap=3.37 eV) is a suitable photocatalyst material. As photocatalysis is a surface driven process, higher surface areas make the processes more efficient. Hence nanoparticles are often used in photocatalytic degradation, which is not very practical for industrial applications since they have to be removed post cure prior to release of water to the environment. Supported catalysts are thus the materials of choice for application of this process. ZnO nanorods (ZnO NRs) further leads to an enhancement of surface area compared to nanoparticulate coatings and can be grown on a variety of substrates like, glass, paper, polymer membranes, steel, ceramics, wood, etc. The supported ZnO NRS on the glass substrates got much attention and follow up.

ZnO nanorods produce electrons and highly reactive oxygen species (ROS), when irradiated with a light source, that subsequently react with the toxic contaminants resulting in degrading them into harmless products such as carbon dioxide, water and mineral acids either through oxidation or reduction processes. Zinc oxide nanorods were engineered by annealing at temperatures of 100 and 350 °C to create defects (sub- stoichiometry) that improves visible light absorption. For example, ZnO nanorods, annealed at 100 and 350 °C, were able to degrade 20% and 72% of phenol, respectively. The best photocatalytic material in this dissertation (ZnO nanorods annealed at 350 °C) was used for degrading petroleum hydrocarbons, partially hydrolyzed polyacrylamide (HPAM), benzene, toluene, ethylbenzene and xylene showing promising results. The intermediate byproducts of phenol and HPAM were studied to understand the degradation mechanism throughout the photocatalytic process. ZnO-based continuous cross-flow photocatalysis was carried out for the removal of phenol and it was observed that more than 2 folds (60% in 2 hours) improvement could be achieved compared to the batch type photocatalytic degradation of phenols. The cross-flow reactor system was then tested for degrading organic compounds present in the refinery wastewater and the produced water. The removal rate was 29 % and 19 %, respectively, within 5 hours, under simulated sunlight irradiation. The original produced water sample was then diluted with equal amount of water and the pH was adjusted to 7 (neutral) resulted in a 63% removal of the total organic content. Photo-dissolution of ZnO was tested and only trace amounts could be observed in treated water over different conditions of pH, salinity and flow rates. In conclusion, this work shows that supported ZnO NRs can be a good choice for treating produced water and can be tested as an accompanying technology along with the currently used produced water treatment methods.