Efficiency of zinc oxide nanorods (ZnO NRs) in Real Produced Water Treatment

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Overview

Due to the rising global demand for fossil fuels for energy generation, the oil and gas industry remains the backbone of the worldwide economy. Petroleum exporting countries need to increase production to satisfy these growing demands [(7)]. However, the oil and gas reserves exploitation has not always been without environmental impacts, such as oil spills, damaged land, accidents, and fires, as well as incidences of air and water pollution. At the same time, one of the leading environmental concerns of oil production in the Sultanate of Oman is the enormous co-production of produced water. This wastewater stream contains a complex mixture of inorganic and organic compounds. It is considered the most significant toxic waste stream from the oil and gas industry [(5), (6)] and has become one of the main threats to oils and gas production companies. Sufficient treatment technologies are needed to bring these streams to a condition suitable for recycling, reuse, or discharge into the environment, as this wastewater is highly contaminated and linked with substantial health, safety, and environmental consequences [(8)]. Recently, nanotechnology-based water treatments emerged as potential treatment methods for non-conventional wastewater. They are inexpensive green technologies that do not require additional chemicals and do not produce secondary waste [(9),(1)]. Most of these techniques are based on photocatalytic degradation, which is a promising strategy as it can utilize a renewable source of energy such as solar energy. This technique depends on semiconductors that have the ability to mineralize organic matter into benign substances, such as carbon dioxide and water in the presence of light [(3)]. Developing efficient photocatalysts to degrade organic matter from produced water is vital from economic and social development viewpoints [(10)]. Even though there have recently been some major improvements, the degradation efficiency and reuse utilization are still low and cannot be used in real-world applications [(4)]. As illustrated by many studies the photocatalytic efficiency is significantly influenced by each stage of the photocatalytic process, including charge excitation, separation, transport, adsorption, and surface reaction of the semiconductor. Therefore, while applying photocatalysis in wastewater treatment some factors should be taken into account and properly tuned to enhance their efficiency, namely, the properties of water being treated, type and structure of semiconductors, reactor design and specifications, and light source and intensity.

Methodology

This study investigates the efficiency of supported zinc oxide nanorods (ZnO NRs) in the photocatalytic treatment of produced water from an oil field in the Sultanate of Oman under natural solar irradiation. A detailed analysis has been attempted on the degradation of organic contaminants in produced water under solar irradiation in the presence of ZnO NRs that were synthesized and used as a photocatalyst. ZnO NRs were prepared using a microwave-assisted hydrothermal process. Firstly, microscope glass substrates were cleaned from contaminants and used as a substrate for ZnO NRs growth. Then, the seed layer was deposited on the glass substrate using spray coating. This was done by spraying 10 mM of zinc acetate on the previously cleaned substrate at a temperature of 350 °C. After that, the nanorods' growth was maintained under microwave irradiation by mixing an equimolar amount of 40 mM of zinc nitrate and 40 mM HMTA (hexamethylenetetramine) .Finally, the prepared ZnO NRs were then annealed at 350 °C for one hour. The characteristics and properties of ZnO NRs were investigated using various techniques. On top of that, the crystallinity, phase nature, and lattice parameters were analyzed using X-ray diffraction (XRD, Rigaku MiniFlex 600, Japan). Photoluminescence Spectroscopy (PL, PerkinElmer, LS 55 fluorescence spectrometer, USA) was used to identify surface defects in the ZnO NRs. UV-Visible spectroscopy (PerkinElmer Lambda 12 UV-VIS spectrometer) was used to analyze the optical properties. A Scanning electron microscope (SEM, JSM-7600F, JEOL, Japan) was utilized to characterize the surface morphology and topography. The prepared ZnO NRs were used as a photocatalyst for the degradation of produced water under natural sunlight for 5 hours. The experiments were divided into two phases using different photocatalytic reactors (batch and continuous flow reactors). The photocatalytic degradation of produced water using ZnO NRs was determined using total organic carbon (TOC) analyzer.

Results and Discussion

Microwave-assisted hydrothermal (MAH) synthesis has been used to synthesize the ZnO NRs on glass substrates.**Fig 1** demonstrates the XRD pattern of the synthesized ZnO NRs. The diffraction peaks in

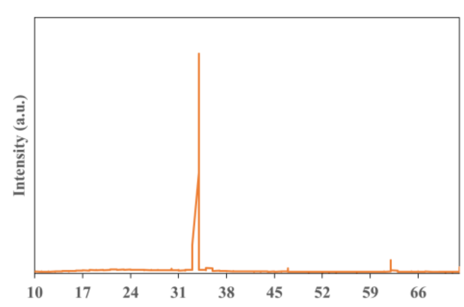

***Fig 1**: XRD pattern*

(Fig. 1) are related to the hexagonal wurtzite crystal structure of ZnO. This data was in agreement with card no JCPDS 36-1451. The strongest diffraction peak was observed at 34.3° which implies that the nanorods have a preferential c-axis orientation that is perpendicular to the substrate. The SEM results(**Fig 2**)show a high yield of homogeneous and well aligned ZnO NRs grown on the glass substrate. Moreover, the PL curve (**Fig 3**) demonstrates different peaks at 3.102 eV, 2.949 eV, 2.822eV, 2.567 eV, and 2.354 eV that are related to ZnO point defects complexes that are related to violet, blue and green emissions. The presence of these defects was found to enhance the ZnO optical properties towards the visible region and therefore, make it an effective candidate for photocatalytic degradation under natural sunlight [(5)]. Moreover, the UV-visible spectrum of the as-prepared ZnO NRs shows broad/strong absorption at ~ 375 nm as shown in (**Fig 4**). The estimated band gap of the prepared ZnO NRs is ~ 3.27 eV according to the Tauc plot demonstrated in (**Fig 4**). The ZnO NRs were used to treat real produced water in a batch reactor under natural Sunlight. The preliminary results of the prepared ZnO NRs show that ZnO is an effective photocatalyst under solar irradiation. **Error! Reference source not found.** shows the percentage of degradation of the organic contents in the produced water. As it is clear from (**Fig 5**), the concentration of organics decreases from 100% to around 70% after 5 hours of light irradiation with a removal efficiency of 30% (as shown in the green column **Fig 5**). Additionally, the degradation of organics in the absence of ZnO shows around 7% degradation which demonstrates that sunlight alone has almost no effect on organic degradation. The findings will be discussed in detail in the poster.

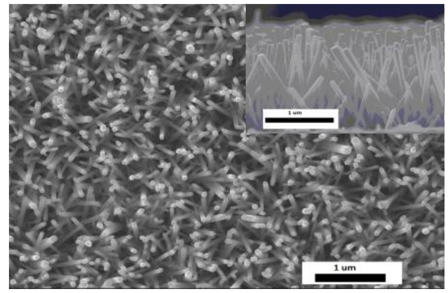

Fig 2: SEM micrograph (Top and cross-sectional view).

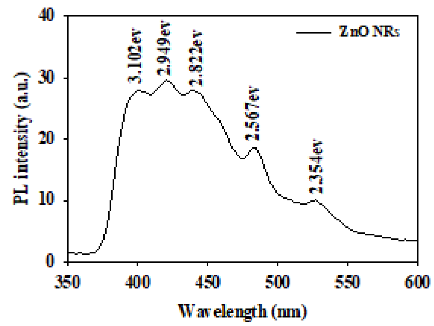

Fig 3: PL curve

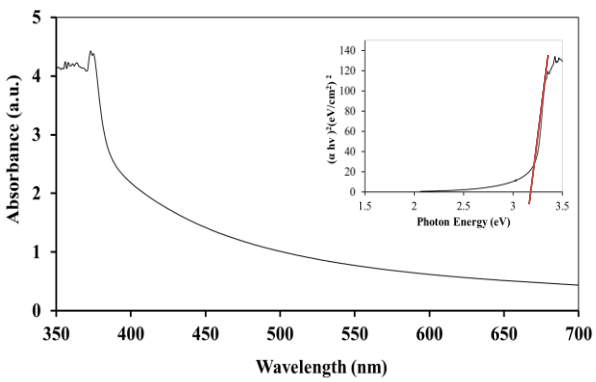

Fig 4:UV-Visible spectroscopy plot

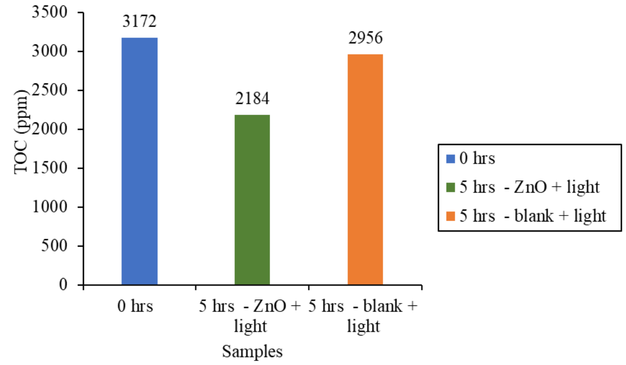

Fig 5 : The Results of TOC of the prepared ZnO NRs in a batch system

Conclusion

The current preliminary study reveals the high efficiency of ZnO NRs in organic pollutants degradation for produced water treatment. Organic matter degradation of >30% was achieved under optimal conditions showing the high potential of photocatalysis in produced water treatment.

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