Chemical Engineering Journal 351 (2018) 56–64

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Visible light photocatalytic degradation of HPAM polymer in oil produced water using supported zinc oxide nanorods

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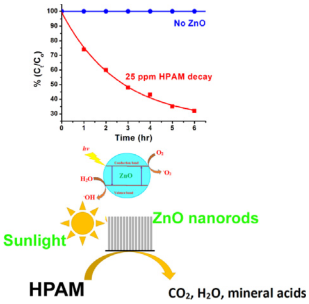
HIGHLIGHTS

- Visible light photocatalysis (VLP) of HPAM using ZnO nanorods.
- Microwave assisted hydrothermal (MAH) growth for defect engineered ZnO nanorods.
- Viscosity was dramatically reduced using ZnO nanorods in few hours.
- More than 65% reduction in HPAM (25 ppm) within 6 h of visible light irradiation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
HPAM
Enhanced oil recovery
Zinc oxide nanorods
Produced water
Solar photocatalysis

ABSTRACT

Polymer flooding displacement ability during petroleum extraction from the earth's crust plays an important role in enhanced oil recovery processes. Produced water, as a byproduct, still contain high concentrations of petroleum hydrocarbons and partially hydrolyzed polyacrylamide (HPAM) which is a serious environmental concern. Remediating produced water economically is a big challenge for meeting the permissible discharge limits leading to failure in the effectiveness of the conventional water treatment technologies. Advanced oxidation processes (AOPs) are playing increasing role in the treatment of polluted water and is receiving much attention in recent times as a green and safer water treatment technology. Here we report a new approach to use vertically aligned zinc oxide nanorods (ZnO NRs) supported on substrates engineered for improving their visible light harvesting capacity for effective solar photocatalytic degradation of HPAM. The viscosity of collected oilfield produced water containing HPAM were found to be reduced dramatically when the samples are photocatalytically degraded using ZnO nanorod catalysts irradiated with simulated solar light showing a reduction of 51% within 6 h. With high pressure liquid chromatography 68, 62, 56 and 45% removal of 25, 50, 100 and 150 ppm HPAM, respectively, was demonstrated. The pH of the solution was observed to move to acidic region due to acetamide, nitrate, propionamide and acetic acid which are

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https://doi.org/10.1016/j.cej.2018.06.071
Received 29 March 2018; Received in revised form 10 June 2018; Accepted 12 June 2018

the intermediate byproducts formed during degradation as determined by mass spectrometry. Zinc oxide nanorod coatings showed about 74% removal efficiency over 5 cycles with less than 1.2% removal of zinc ions after 6 h of light irradiation.

1. Introduction

Many technologies are commercially implemented to enhance crude oil recovery including steam injection, surfactants and polymer flooding, carbon dioxide flooding and microbial modification [1–3]. Enhanced oil recovery is improving oil production by injecting a material not usually present in the well formation [4,5]. Polymer enhanced oil recovery (PEOR) is categorized as a tertiary oil recovery method as the polymer is added to the injected water to increase the water viscosity thus reducing water mobility problems. Polymer flooding is the most used chemical EOR method since about 40 years now [6,7]. The most popularly used polymers are polyacrylamide (PAM), partially hydrolyzed polyacrylamide (HPAM) and biopolymer xanthan gum. Large increase in oil production rate has been reported with polymer flooding (HPAM concentration of 1500 ppm) in Chinese oilfields [8,9]. HPAM, as the most widely used among the others that has been proven to improve oil recovery to 45% in several polymer flooding projects [7,10]. It has notably been proven in laboratory tests that viscosities of 150–1000 cP of HPAM can improve the oil recovery as compared to normal injection of water [11]. The global produced water was estimated to be about 300 million barrels/day in 2015 [12]. In the produced water byproduct from oilfields that uses polymer flooding techniques, it has been reported that 200–600 ppm of HPAM contamination persists even after the conventional treatment of waste water [13].

Although HPAM polymer addition for enhanced oil recovery is a highly innovative development, it could seep into water bodies such as ground and surface water and subsequently has environmental impacts and affects the health of animal and plant lives if not properly treated [14]. HPAM is known to persist long with slow biodegradability [14–16]. Furthermore, the produced water will be much difficult to manage for reinjection and/or reuse when HPAM is present as it would affect the viscosity of the starting water [17]. In addition to that, the difficulties associated to separate oil from water resulting in reducing oil yield and HPAM polymeric compound behave to degrade naturally to produce highly toxic compounds of acrylamide monomers and were reported to threaten the ecosystem and identified to cause a genotoxic carcinogen [15,16,18].

Several treatment technologies have been implemented to remove residual HPAM from produced water like iron and ethylene diamine tetra acetic acid (EDTA) lead to 66% removal in 8 h, while activated sludge, in biological system spent 40 h to remove 81% of HPAM [19] followed the chemical treatment. It was reported when gas flotation with biological treatments could remove almost 96% [20]. A reported study revealed that oxidants such as hydrogen peroxide (H_2O_2) and peroxydisulfate ion ($S_2O_8{}^{-2}$), high temperature, presence of hydroquinone and cations accelerated HPAM degradation [21]. Magnetic nanoparticles have also been utilized for removing HPAM from oilfield produced water [17]. Clay reportedly reduce chemical oxygen demand (COD) by about 36% in the simulated water with HPAM and minerals while organo clays reduced the COD further by about 60% used for HPAM removal [22].

Advanced oxidation processes (AOPs) are effective green treatment technologies for degrading toxic organic compounds and have received appreciable attention in recent times for treating polluted water. It could co-play an important role for reducing toxic compounds into harmless products such as mineral acids, carbon dioxide and water, and can compete with other conventional treatment technologies. It is a process that uses reactive oxygen species (ROS) such as highly reactive oxidizing and/or reducing radicals such as hydroxyl ions ($OH^{\cdot}$) and superoxide ions ($^{\cdot}O_2{}^{-}$) to degrade organic contaminants present in solution through the choice of an appropriate chemical reactant.

Photocatalysis is one such advanced oxidation processes that is potentially viable for solving environmental problems as it does not require additional chemicals during the process [23,24]. Nanostructured wide band gap metal oxide semiconductors are generally used as photocatalysts and the photo-generated e-h pair upon exposure to light, also producing $O_2{}^{-}$, $OH^{\cdot}$ or other radicals [25]. The degradation of contaminants in water can occur through direct transfer of the photo-generated electrons or holes from the catalyst surface to the contaminant molecules or through oxidation or reduction via the radicals. Metal oxide nanostructures like titanium dioxide (TiO_2), zinc oxide (ZnO), tin dioxide (SnO_2), tungsten oxide (WO_3), strontium titanate ($SrTiO_3$) etc. are known to be good photocatalyst materials [26–29]. Metal oxides are usually wide bandgap semiconductors which normally absorb light in the UV region of the solar spectrum. However, the use of high energy UV light sources to excite the catalysts is not a cost effective solution in most of the cases. Zinc oxide (ZnO), is a direct wide band gap (3.37 eV) semiconductor [30,31] with a large exciton binding energy of 60 meV [32]. It has been utilized for large-scale wastewater treatments [33] and is often considered to be show better photocatalytic efficiency compared to TiO_2 [34–36]. Zinc oxide semiconductor has been proven to be an acceptable photocatalyst with visible light irradiation and showed promising results to degrade organic contaminants present in water [37,38]. The thermal modification (called self-doping) of ZnO, by creating surface crystal defects, often leads to a better visible light absorptivity and subsequently faster degradation of contaminants [39,40]. The crystal defects that contribute to the photocatalytic degradation was previously studied using photoluminescence (PL) and favorable surface defects were found to occur upon annealing the nanorods at 350 °C [37,39]. X-ray photoemission spectroscopy (XPS) and photoluminescence spectroscopy was used to correlate the surface defects where the binding energies could be related to the zinc and oxygen orbitals [39,41,42]. These defects trap electrons reducing the probability of electron-hole recombination leading to holes (vacancies) which upon interaction with moisture (OH^{-}) leads to the formation of hydroxyl radicals (OH^{*}) (Redox potential = +2.81 V versus standard hydrogen electrode, SHE). Furthermore, the electrons/holes trapped in the surface defects can transfer charge to adsorbed oxygen and hydroxyl species, thus forming $O_2{}^{-}$, $OH^{\cdot}$ and other oxygenated radical species which induces redox reactions with contaminants [43,44].

Few reports on the photocatalytic degradation of HPAM under UV light irradiation have been published using titanium dioxide nanoparticles (TiO_2 NPs) [21,45–48], W/Mo co-doped $BiVO_4$ particles [49] and ZnO nanoparticles [50]. UV light sources are not practical for any field application as they are expensive, increases operation costs and has maintenance issues. Furthermore, use of nanoparticles require additional treatments after the photocatalysis process for safer disposal or further usage. To the best of our knowledge, this is the first study using supported ZnO nanorods for photocatalytic degradation of HPAM under visible light irradiation. In this work, we have studied the photocatalytic efficiency of supported ZnO nanorods on different HPAM aqueous solutions (concentrations of 25, 50, 100 and 150 ppm) and also studied the viscosity changes over time. In addition to that, degradation of higher concentrations (250 ppm, 500 ppm and 1000 ppm) of HPAM in aqueous solutions were also examined. The intermediate byproducts were determined using triple MS and compared with previous relevant studies [51]. The change in pH with time for a typical HPAM solution (150 ppm) was recorded to confirm the observations of the acidic byproducts formation during the photocatalysis process.