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The enhanced stability and biodegradation of dispersed crude oil droplets by Xanthan Gum as an additive of chemical dispersant

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It is necessary for chemical dispersant to disperse oil effectively and maintain the stability of oil droplets. In this work, Xanthan Gum (XG) was used as an environmentally friendly additive in oil dispersant formulation to enhance the stability and biodegradation of dispersed crude oil droplets. When XG was used together with chemical dispersant 9500A, the dispersion effectiveness of crude oil in artificial sea water (ASW) and the oil droplet stability were both greatly enhanced. In the presence of XG, lower concentration of 9500A was needed to achieve the effective dispersion and stabilization. In addition to the enhancement of dispersion and stabilization, it was found that the biodegradation rate of crude oil by bacteria was dramatically enhanced when a mixture of 9500A and XG was used as a dispersant. Because of the low environmental impact of XG, this would be a potential way to formulate the dispersant with lower toxicity.

1. Introduction

The accidental release of crude oil into marine environments during oil drilling or shipping is becoming a serious environmental problem for the marine ecosystem (Etkin, 2001), such as the recent Deepwater Horizon event in the Gulf of Mexico in 2010. When oil spills occur, different response measures are adopted to minimize their adverse effects. With the goal of dispersing crude oil and stimulating oil biodegradation, the application of dispersant plays an important role. In the presence of dispersants, the surface oil slick would be emulsified into small oil droplets by wind shear and the action of the sea waves (Lewis et al., 1985). Effective oil emulsification increases dissolved oil concentrations and reduces oil delivery to shorelines. The emulsification makes oil more bioavailable for biodegradation, because microbial attack is at the oil-water interface and the dispersion of oil dramatically increases the area available for microbial colonization (Board, 2005). Although the application of dispersant is a feasible response to oil spill accidents, biodegradation is the eventual fate of the spilled oil (Hazen et al., 2016). To stimulate biodegradation of oil, some studies have been reported based on the formulation of a dispersant. For example, lecithin had been added in some dispersant formulations to enhance the biodegradation rate of dispersed oil, because the phosphorus and nitrogen in the lecithin accelerated the growth of bacteria (Nyankson et al., 2015). Dispersants are usually consisted of different surfactants dissolved in a solvent (Kujawinski et al., 2011). A promising dispersant should have the following properties: (i) environmentally friendly; (ii) efficient dispersion; (iii) inhibiting the coalescence of dispersed droplets; and (iiii) stimulating rapid biodegradation of oil in marine environment (Brochu et al., 1987; Lunel, 1993). EPA-approved Corexit 9500A is one of the most commonly used dispersants for oil spill dispersion. Corexit 9500A contains nonionic surfactants, anionic surfactants and a solvent medium (George-Ares and Clark, 2000). Recent studies demonstrated that Corexit 9500A is an efficient chemical dispersant in dispersing various types of crude oil due to the significant decrease of interfacial tension between oil and water (Mukherjee and Wrenn, 2011). Although Corexit 9500A is effective in dispersing crude oil, it has been shown that oil droplets created by Corexit 9500A rapidly coalesce (Sterling et al., 2004). Therefore, it is necessary to improve the stability of dispersed oil droplets when Corexit 9500A is used as a dispersant. Environmental impact of Corexit 9500A is also an important constraint for their wide applications due to the increased environmental awareness and strict legislation (Makkar and Cameotra, 2002). Accordingly, some studies have been conducted to find environmentally friendly oil spill dispersants (Athas et al., 2014; Nyankson et al., 2016).

To enhance the stability and biodegradation of oil in the treatment of marine oil spills, this study proposes a new idea where natural biopolymer Xanthan gum (XG) is used together with chemical dispersants. The synergistic interactions between XG and chemical dispersants are expected to enhance not only the stability of the dispersed oil droplets but also the biodegradation of the dispersed oil. Additionally, the presence of a more environmentally friendly biopolymer is expected to potentially reduce the amount of chemical dispersant needed for effective dispersion and stabilization of crude oil (Venkataraman et al., 2013). XG,

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as a high molecular weight polysaccharide, is a well-known natural thickeners in food and cosmetic industries (Prajapati et al., 2013; Becker et al., 1998; Katzbauer, 1998). It is a semi-rigid rod-like molecule produced by a fermentation process. XG is an efficient stabilizer for suspensions and emulsions due to the formation of three-dimensional network by the associated chains (Chivero et al., 2015). Above a certain concentration, XG alone can stabilize emulsions by increasing the viscosity of aqueous phase and impeding the coalescence of oil droplets (Desplanques et al., 2012). To the best of our knowledge, this is the first study on the application of XG in the treatment of marine oil spills. The application of chemical dispersant is necessary for creation of small crude oil droplets by reducing the oil-water interfacial tension. The presence of XG can improve the stability of dispersed oil droplets by modifying the flow properties of emulsions. The size and stability of crude oil droplets are important to their eventual microbial degradation in the marine environment. It is worth noting that the biodegradation of crude oil droplets dispersed by a mixture of XG and chemical dispersants is remarkably enhanced in our study. Experimental results show that a dispersant formulation like this not only disperses the crude oil efficiently, but also accelerates the biodegradation of the dispersed oil by bacteria. Due to the presence of XG, the amount of chemical dispersants needed to apply to an oil spill pollution would be potentially reduced.

2. Materials and methods

2.1. Materials

Polyoxyethylene Sorbitan Fatty Acid Esters 80 (Tween 80) and bis (2-ethylhexyl) sulfosuccinate sodium salt (AOT) were purchased from Sigma-Aldrich. 1-(2-butoxy-1-methylethoxy) propanol was purchased from Aladdin Industrial Corporation. In this study, a mixture of Tween 80 (48%), AOT (35%) and 1-(2-butoxy-1-methylethoxy) propanol (17%) is prepared and used as a substitute for chemical dispersants Corexit 9500A. XG was purchased from Beijing Solarbio Science &Technology Company. The artificial sea water (ASW) consisted of (g/L): NaCl 26.726, $MgCl_2$ 2.260, $MgSO_4$ 3.248, $NaHCO_3$ 0.198, KCl 0.721, $CaCl_2$ 1.153, according to the formula of Lyman and Fleming (1940). The pH of ASW was 7.9. Crude oil was provided by Shengli Oil field, China. The characteristics of crude oil are as follows: viscosity 72.9 Pa/s (25 °C, 3 r/min), freezing point 23.0 °C, and density 0.8552 g/cm^3.

2.2. Preparation of emulsions

The emulsions were prepared by mixing crude oil with chemical dispersants, followed by the addition of ASW. The aqueous solution of XG was prepared in advance. Then, a specific volume of the aqueous solution of XG was added to the vial. (Venkataraman et al., 2013; Athas et al., 2014) Since the presence of light hydrocarbon distillates as a solvent allows dispersant solubility in the oil phase, the dispersant was first introduced into the oil phase before mixing with water. If the dispersants were applied to oil slick floating on the seawater, the stable emulsions also were obtained after the surfactants in the dispersants partitioned to the oil-water interface. The oil-to-water volume ratio was maintained at 0.01. Different amounts of 9500A did not indicate a significant difference in the oil-to-water volume ratio, because the volume of dispersants added was far lower than the volume of oil used. Therefore, different samples were considered to have similar oil-to-water volume ratio because of the neglected dispersant volume. After mixing, the sample was stirred at 11000 rpm for 30s with an IKA homogenizer instrument. Then, the emulsions were visualized by optical microscope (Leica DM1000 LED, Leica, Germany). The average oil droplets size was estimated by Nano Measurer software according to the optical images.

2.3. Emulsions stability

To determine the stability of the dispersed oil, the turbidity of an emulsion was measured as a function of time at a wavelength of 425 nm using an Alpha-1860 ultraviolet spectrophotometer (Shanghai Lab-spectrum Instruments Co. Ltd., China) (Zattoni et al., 2003). The stability of an emulsion was also determined by light scattering measurements using a vertical scan analyzer (Turbiscan LAB, France). The samples were scanned by the instrument along the sample tube. A number of profiles of back-scattering (BS) percentages were given as a function of time and tube length (Pan et al., 2002). Then, Turbiscan Stability Index (TSI) was calculated according to the primitive data of BS, as shown in Eq. (1). All processes taking place in the sample are taken into account by this TSI parameter.

$$TSI = \sqrt{\frac{\sum_{i=1}^{n}(xi - xBS)^2}{n-1}} \quad (1)$$

where x_i is the average BS for each minute of measurement, x_{BS} is the average of x_i, and n is the number of scans. The value of TSI reflects the change of emulsion concentration and its particle size throughout the whole standing time. The higher TSI value implies the less stable emulsion (Kang et al., 2011).

2.4. Baffled flask test

Dispersion effectiveness of a dispersant was evaluated by using the modified baffled flask test (Sorial et al., 2004). 0.1 g of crude oil was added to a baffled flask containing 100 mL of ASW. Certain volume of dispersants (9500A, XG and a mixture of 9500A and XG) was added directly on top of the oil. Then, the baffled flask was placed on a rotary shaker at 120 rpm for 12 h. 25 mL of the aqueous media with dispersed oil was drawn and then the dispersed oil was extracted with 25 mL petroleum ether (PE) and quantified with an Alpha-1860 ultraviolet spectrophotometer at an absorbance of 225 nm (Nyankson et al., 2015). All experiments were conducted in at least triplicate.

2.5. Rheology

The flow behavior and viscoelastic properties of emulsions were measured using a HAAKE MARS III (ThermoFisher, Germany) at a fixed temperature of 25 ± 0.1 °C with a parallel plate (35 mm diameter). The shear viscosity (η) of the samples was obtained from steady shear measurements with the shear rate ranging from 1 to 1000 s^{-1}. Dynamic oscillatory measurements were performed to determine the storage modulus (G') and loss modulus (G'') of an emulsion for frequencies (f) ranging from 0.1 to 100 Hz at a given stress of 0.1 Pa, which was confirmed to be in the linear viscoelastic range.

2.6. Interfacial tension

Interfacial tension between aqueous solution of dispersant and crude oil was measured using the spinning drop method (TX-500D Full Range Interfacial Tensiometer, USA). Approximately 0.001 cm^3 of crude oil was injected into the capillary filled with dispersant aqueous solution to form a small drop. Then, the capillary tube was sealed and rotated at a velocity range of 5000–6000 rpm. Three independent measurements were used to calculate the average interfacial tension of each sample.

2.7. Biodegradability of dispersed crude oil droplets

Biodegradability of the dispersed crude oil droplets was evaluated in Erlenmeyer flasks. Petroleum hydrocarbon degrading bacteria, *Bacillus cereus* S-1, was isolated from oil-polluted seafloor sediment. A detailed

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