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A practical review on photooxidation of crude oil: Laboratory lamp setup and factors affecting it



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ABSTRACT

After an oil spill, crude oil in the marine environment is affected by a variety of processes collectively called weathering. Photooxidation induced by ultraviolet (UV) light from the sun is one of the most significant processes of long-term weathering that changes the chemical nature of oil. Experimental studies on photooxidation in the natural environment are generally not practicable due to the variability of factors that are more readily controlled in a laboratory. The emission spectra and irradiance of artificial lamps are critical factors for simulating sunlight, and the process of acceleration should be differentiated from simulation. We present a comprehensive review of the exposure conditions affecting *in vitro* photooxidation studies, including the types of lamps, their spectra and irradiance levels and maintenance conditions. The importance of xenon arc, metal halide along with mercury–xenon, high-pressure mercury lamps and other lamps with respect to their spectral characteristics is discussed and the selection guide is provided. A brief discussion on other factors affecting photooxidation rates and outcomes, such as photosensitisers, photodegraders, solvents and the synergistic effects of compounds is also given.

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Abbreviations: AM, Air mass; ASTM, American society for testing and materials; CIE, International commission on illumination; HP Hg, High pressure mercury; IR, Infrared; LP Hg, Low pressure mercury; MP Hg, Medium pressure mercury; OECD, Organisation for economic co-operation and development; PAHs, Polycyclic aromatic hydrocarbons; PAR, Photosynthetically active radiation; WAF, Water-accommodated fraction; WSF, Water-soluble fraction; UV, Ultraviolet.

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1. Introduction

Crude oil, a complex mixture composed of hydrocarbons and compounds containing heteroelements like nitrogen, sulphur, oxygen and also metals in traces poses a wide range of risks when released into the environment (NRC, 1985). More than 1 million tonnes of crude oil enter the marine environment every year through numerous sources, including natural seeps, petroleum extraction, petroleum transportation, petroleum consumption and accidental spills (GESAMP, 2007). As a result of tanker spills, ~5.74 million tonnes of oil were released between 1970 and 2012 (ITOPF, 2013). Two recent oil spills, the *Hebei Spirit* oil spill in Korea in 2007, and the *Deep Water Horizon* oil spill in the United States in 2010, released 10,900 tonnes (12,547 kL) and ~672,360 tonnes (780,000 kL) of crude oil, respectively (McNutt et al., 2011; Yim et al., 2012).

Spilled oil begins to spread immediately after a spill, increasing the exposure area and subsequent weathering processes, such as evaporation, dispersion, emulsification, dissolution, photooxidation, sedimentation and biodegradation (NRC, 2003). Weathering processes together with the chemical nature of the spilled oil determine the fate and rate of degradation. Weathering under natural conditions is complicated and may have varying effects on different oil components. Therefore, understanding the fate of weathering oil is essential for cleanup, remediation and environmental risk assessment (Garrett et al., 1998; Wang and Fingas, 1995).

Photooxidation is an important factor in the transformation of crude oil after its release into the environment (Garrett et al., 1998). Chromophores in the oil absorb sunlight and initiate a chain of photochemical reactions resulting in a wide range of products (D'Auria et al., 2008). Photooxidation occurs by two principal mechanisms: direct photolysis and reaction with reactive oxygen species produced by solar radiation acting on a variety of photosensitisers in natural

waters (OECD, 2008). The primary action spectrum includes the ultraviolet (UV) region of solar radiation, consisting of 5% UV-B (280–315 nm) and 95% UV-A (315–400 nm) (Lee, 2003). Certain compounds of crude oil can also absorb and photooxidise in the visible region (400–700 nm) (Mallakin et al., 2000; Yu, 2002). Photooxidation changes the physicochemical properties of oil and its related components, with the oxygenated forms being more polar, increasing the dispersibility and toxicity of the oil (Wang and Fingas, 2003).

The extent of photooxidation depends on the spectrum and irradiance of the incident light, the optical properties of the surface water and the hydrocarbons themselves and on the presence of photosensitisers and photodegraders (NRC, 1985). Most of the previous studies tried to reproduce sunlight for photooxidation study of petroleum hydrocarbons using artificial lamp, but they did not discriminate the concept of simulation from acceleration. Simulation is defined as “the imitation of the operation of a real-world process or system over time” (Banks, 2001), whereas acceleration could be defined as the intensification of the operation of specific processes in a limited period of time. The act of simulating something first requires the development of a model which represents the key characteristics of the selected physical process or system (Robinson, 2004). In case of sunlight, the key characteristics to be modelled for photooxidation process are spectrum and irradiance, and its simulation should mimic these characteristics in controlled conditions over time. When the rate of reaction is increased, photooxidation process would be accelerated. Acceleration could be achieved by two ways: firstly by increasing the intensity of the artificial light and secondly by using artificial lamp with a limited range of solar spectrum and high intensity. Recognizing differences between simulation and acceleration is critical when choosing a lamp for photooxidation studies.

Lamps and other experimental setups used for photooxidation by several researchers have been inconsistent from

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