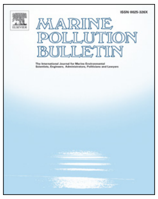
Marine Pollution Bulletin 133 (2018) 693–700

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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



Review

Classification of oil–particle interactions in aqueous environments: Aggregate types depending on state of oil and particle characteristics

Daria Boglaienko, Berrin Tansel*

Department of Civil and Environmental Engineering, Florida International University, Miami, FL, USA

ARTICLE INFO

Keywords:
Oil spills
Emulsions
Marine snow
Colloidal particles
Pickering emulsions
Aggregation

ABSTRACT

There are significant differences in the aggregation mechanisms and types of aggregates that form by oil-particle interactions in marine and laboratory environments depending on the state of oil (i.e., dissolved, emulsified, floating), size and type of particles involved (i.e., colloidal, granular, organic, inorganic), oil-particle interaction mechanisms, and settling/suspension characteristics. Distinct characteristics of oil-particle aggregates that form by interaction of granular particles with floating oil separate them from the well-known oil-colloidal particle aggregates (OcPA), which are sometimes called Pickering emulsions. Unlike OcPA, which involve emulsified oil (entrained oil droplets suspended in the water column) and colloidal particles, the oil-granular particle aggregates (OgPA) involve the floating oil and granular particles. Here, to clarify the differences and similarities between the two types of aggregates (OcPA and OgPA), we present classification of oil aggregates, drawing attention to important characteristics of OcPA, marine oil snow (MOS), and OgPA.

1. Introduction

Research activities and advancements for understanding the interactions between oil and particles in aqueous systems have intensified in the recent years with increasing environmental awareness and major oil spill incidents which received public attention (e.g., Deepwater Horizon spill in 2010). Despite the similarities in terminology used by different research groups who have addressed the fate of oil and oil-particle interactions in aqueous systems and marine environments; there are significant differences in the aggregation mechanisms and types of aggregates that form as a result of oil-particle interactions depending on the state of oil in the aqueous medium (i.e., dissolved, emulsified, floating), size and type of particles involved (i.e., colloidal, biogenic, granular, organic, inorganic), particle-oil interaction mechanisms, and sedimentation rates of the aggregates. In this study, we address the differences in the particle-oil aggregates and aggregation mechanisms, and characterize to the similarities and differences in the types of aggregates that form in aqueous environments (e.g., marine conditions, estuaries) after oil spills and laboratory studies. This clarification is necessary to consolidate the terminology into a more universally accepted notation for understanding the differences in the types of particle-oil aggregates that form in aqueous systems as well as for development of appropriate oil spill response and mitigation methods. Here, we use the term 'dispersed' to include both naturally entrained oil droplets and oil droplets generated by the addition of chemical dispersants.

We focus on three major types of oil-particle aggregates: 1) oil and suspended particulate material (SPM) aggregates, which form by collision of dispersed oil droplets and suspended colloidal particles in water column; 2) oil and suspended particulate inorganic and organic material, including plankton and bacteria (marine snow); and 3) oil and granular particle aggregates which form by direct application of particles on floating oil. Although, the three types are referred in general as aggregates, there are significant differences in their physical characteristics as well as formation mechanisms. In addition, there are inconsistencies in terminology used for the first type, and confusion between the first and third type due to the similarities in the overall composition of the oil-particle aggregates. Oil and suspended particulate material aggregates were initially referred as clay-oil flocs (Bragg and Owens, 1995; Muschenheim and Lee, 2002), and later they were often referred as oil-mineral aggregates (OMA) (Lee et al., 1998; Khelifa et al., 2002; Omotoso et al., 2002; Owens and Lee, 2003; Ajijolaiya et al., 2006; Zhang et al., 2010; Niu et al., 2011). More recently, the term oil-sediment aggregates (OSA) is found in the scientific literature (Bandara et al., 2011; Gong et al., 2014; Sun et al., 2014), as well as oil-SPM aggregates (Sørensen et al., 2014), and oil-particle aggregates (OPA) (Zhao et al., 2016). The third type is often confused with the first one, as it is also called 'oil-particle aggregates' (Boglaienko and Tansel, 2015). However, there are significant differences, and some notable variations within this type of aggregates that form by interaction of

---

* Corresponding author at: 10555 W. Flagler Street, Florida International University, EC 3676, Miami, FL 33174, USA.
E-mail address: tanselb@fiu.edu (B. Tansel).

https://doi.org/10.1016/j.marpolbul.2018.06.037
Received 6 November 2017; Received in revised form 30 May 2018; Accepted 11 June 2018

floating oil with larger particles. Depending on the interaction mechanisms, different type of aggregates form and they have been referred as raft, slurry, bowl, and rope formation (Abkarian et al., 2013; Boglaienko and Tansel, 2016; Boglaienko and Tansel, 2017). Here, we call OPA, belonging to the first type, that is 'oil-colloidal particle aggregates' (OcPA), taking into account the colloidal particles and micro scale of the aggregation process, and the third type as 'oil-granular particles aggregates' (OgPA) because they are formed by granular particles and the size of the aggregates can reach up to several centimeters.

The purpose of this study is to clarify the major differences among the different types of aggregates that form by particle-oil interactions in aqueous systems, bring attention to the effect of particle size and state of oil on the characteristics of the aggregates forming, include the OgPA type aggregates in the classification, bring clarification to the use of terminology, and address the differences in characteristics of the aggregates in view of their formation conditions, oil-particle interaction times, stabilization characteristics, and settling rates.

2. Collision and aggregation

2.1. Oil-colloidal particle aggregates (OcPA)

When dispersed in water column, oil droplets and suspended particulate material (SPM) collide and aggregate (or flocculate). Fine mineral particles, generally $< 5\,\mu m$ (Sun and Zheng, 2009; Gong et al., 2014) adhere to oil droplets ($< 50\,\mu m$), preventing their coalescence, hence, form relatively stable oil-in-water emulsions (i.e., oil droplets suspended in water) while contributing to dispersion of oil and natural cleansing of shorelines (Bragg and Owens, 1995; Stoffyn-Egli and Lee, 2002; Khelifa et al., 2005). Here, we use of the term emulsified oil to imply entrained oil droplets suspended in the water column or oil-in-water emulsions. In the literature the term emulsified oil is also used to designate water-in-oil emulsions, commonly referred to as mousse.

The oil-droplet-particle aggregation can occur through different mechanisms and our understanding of the interactions between particles, oil droplets, and other particles has evolved since the earlier depiction provided by Bragg and Owens (1995). Fig. 1 presents some of the possible mechanisms for oil-particle and oil-particle-liquid interactions which may occur with particles. The size of the oil droplets and entrapment of particles, liquid, molecule within the emulsified oil droplets, arrangement of other particles and molecules around the emulsified oil droplets can result in different forms of emulsions. The subsequent coalescence of the emulsified oil droplets produce aggregates with different physical, chemical and biogenic characteristics.

The attraction of SPM to oil phase occurs due to electrostatic forces. Mineral particles possess electrically charged surfaces, and crude oil droplets create surface charge by aligning the polar fractions at the oil-water interface (e.g., positively charged asphaltenes and negatively charged clay particles) (Guyomarch et al., 2002), or negatively charged resins and positively charged calcium carbonate (Bassioni and Taqvi, 2015). Oil droplets in water that are stabilized by fine solids are called Pickering emulsions (Aveyard et al., 2003) and oil droplets coated by SPM belong to this category. However, there are differences in the types of OcPA, such as droplet, solid, and flake forms (Stoffyn-Egli and Lee, 2002) as shown in Fig. 2. The particles with oil attached and exposed to the surrounding water are generally less stable depending on the particle size and density (Zhao et al., 2016).

The collision (and loss) of oil droplets with SPM based on material balance for oil and SPM is described by the following equation (Payne et al., 1987):

$$\frac{dn_o}{dt} = -\alpha F = -1.3\alpha\left[\frac{\varepsilon}{\nu}\right]^{\frac{1}{2}}(r_o + r_p)^3 n_o n_p \tag{1}$$

where F is the collision frequency; α is coalescence/coagulation efficiency between oil droplet and a particle, and it is a dimensionless number from 0 (collision without adherence) to 1 (collision and coagulation), (defined in Zhao et al., 2016); ε is the turbulent energy dissipation (mass per time); ν is the kinematic viscosity of water; r_o is radius of an oil droplet; r_p is radius of a particle; n_o is the number concentration of oil droplets; and n_p is the number concentration of SPM. The term $\left[\frac{\varepsilon}{\nu}\right]^{1/2}$ is the collision frequency in turbulent shear. When more commonly measured mass/volume concentrations (mg/L) of oil droplets and particulates (N_o and N_p, respectively) are used instead of their number concentrations, Eq. (1) can be represented as follows (Payne et al., 2003):

$$\frac{dN_o}{dt} = -1.3\alpha\left[\frac{\varepsilon}{\nu}\right]^{\frac{1}{2}} N_o N_p \tag{2}$$

Using the oil droplet and SPM diameters (d_o and d_p respectively), the Eq. (1) can be written as (Hill et al., 2002):

$$\frac{dn_o}{dt} = -0.16\alpha\left[\frac{\varepsilon}{\nu}\right]^{\frac{1}{2}}(d_o + d_p)^3 n_o n_p \tag{3}$$

These equations consider only fluid shear and satisfy conditions in a well-mixed turbulent environment (e.g., near shore) with irreversible interactions occurring between oil droplets (mean oil droplet diameter up to $150\,\mu m$) and very fine SPM (mean diameters $< 5\,\mu m$) (Hill et al., 2002).

The collision frequency can also be affected by Brownian motion (F_B) and differential settling (F_{ds}) and is defined by β_B and β_{ds}, Eqs. (4) and (5) (Ernest et al., 1995; Zhao et al., 2016). Here, we use symbol F to be consistent with the Eq. (1), which is the collision frequency due to turbulent shear.

$$F_B = \beta_B = \frac{2kT}{3\mu}\left(\frac{1}{d_o} + \frac{1}{d_p}\right)(d_o + d_p) \tag{4}$$

$$F_{ds} = \beta_{ds} = \frac{\pi}{4}(d_o + d_p)^2(u_o - u_p) \tag{5}$$

where k is Boltzman's constant; T is absolute temperature; μ is dynamic viscosity of the medium; u_o is the settling velocity of the oil droplet; and u_p is the settling velocity of the particle.

However, the consideration of collision frequencies for the turbulent shear, Brownian motion, and differential settling simultaneously is not reasonable, because during well-mixed conditions Brownian motion is negligible, and differential settling becomes significant for large particles at low shear conditions (Ernest et al., 1995). Thus, taking into account only turbulent conditions, the time for OcPA formation is given by Hill et al. (2002) as follows:

$$t = -\frac{\ln\left(1 - \frac{2\pi}{\sqrt{3}}\left(\frac{d_o}{d_p}\right)^2\left(\frac{n_o}{n_p(0)}\right)\right)}{0.16\alpha\left[\frac{\varepsilon}{\nu}\right]^{\frac{1}{2}}(d_o + d_p)^3 n_o} \tag{6}$$

where $n_p(0)$ is the SPM number concentration at $t = 0$.

Using Eq. (6), the formation times of stable OcPA were calculated by Hill et al. (2002) and summarized in Table 1. In most cases (almost half of the calculated times, which corresponds to typical natural sediment concentrations) OcPA formation occurred within minutes and hours. One tenth of the times took < 30 s to form as a stable aggregate; small fraction of cases (8%) took more than one day; and almost a quarter of times fail to form stable aggregates.

Formation, or stabilization, time depends mainly on sediment concentration, the variable that can be controlled and employed as an oil spill countermeasure (Bragg and Owens, 1995; Bragg and Yang, 1996; Hill et al., 2002).