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A new perspective of particle adsorption: Dispersed oil and granular materials interactions in simulated coastal environment

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ABSTRACT

This study, adsorption behaviors of dispersed oil in seawaters by granular materials were explored in simulation environment. We quantitatively demonstrated the dispersed oil adsorbed by granular materials were both dissolved petroleum hydrocarbons (DPHs) and oil droplets. Furthermore, DPHs were accounted for 42.5%, 63.4%, and 85.2% (35.5% was emulsion adsorption) in the adsorption of dispersed oil by coastal rocks, sediments, and bacterial strain particles respectively. Effects of controlling parameters, such as temperature, particle size and concentration on adsorption of petroleum hydrocarbons were described in detail. Most strikingly, adsorption concentration was followed a decreasing order of bacterial strain (0.5–2 μm) > sediments (0.005–0.625 mm) > coastal rocks (0.2–1 cm). With particle concentration or temperature increased, adsorption concentration increased for coastal rocks particle but decreased for sediments particle. Besides, particle adsorption rate of petroleum hydrocarbons (*n*-alkanes and PAHs) was different among granular materials during 60 days.

1. Introduction

Petroleum hydrocarbons as priority organic contaminants are an extremely complex assemblage of chemicals coming from various sources including drilling, manufacturing storing and transporting (Crone and Tolstoy, 2010; Griffiths, 2012). However, the petroleum hydrocarbon pollution is not only confined to the ocean, but is also extended to the beach due to tides and waves (Bejarano and Michel, 2010). Beached oil from the oil spill accidents including Torrey Canyon (1967) (Nanda, 1967), Amoco Cadiz (1978) (Chasse, 1978), Exxon Valdez (1991) (Bragg et al., 1994), Nakhodka (1998) (Kasai et al., 2001), and Prestige (2002) (Morales-Caselles et al., 2007) have caused severe damages to seacoast and required huge costs to clean up the shoreline (Pandey et al., 2009). When petroleum hydrocarbons are spilled into the ocean, floating crude oil are subject to several weathering processes, which include evaporation, dissolution, emulsification, oxidation, and biodegradation (Brandvik and Faksness, 2009; Kingston, 2002; Neff et al., 2000). On one hand, some of petroleum hydrocarbons are dissolved in seawaters; on the other hand, some of petroleum hydrocarbons are dispersed into smaller oil droplets. Oil droplets form aggregates with particles due to collision and dissolved oil partitions into particles due to capillarity and surfactant ions.

Recently, the influences of adsorption by granular materials on the transport, fate and pollution control of persistent organic pollutants in the environment have received increasingly more attention. Mesocosm experiments were used to simulate coastal environment by many researchers. Nine wave tanks were studied to investigate the behavior of chemically dispersed oil and the whole oil on a near-shore environment (Page et al., 2000). Two mesocosm experiments simulating beach and open-water conditions were conducted to study the effects of wave action on the biodegradation of Iranian light crude (Santas et al., 1999). Besides, the fate of oil-degrading bacteria for a bioremediation strategy was investigated in the simulated coastal environment (Gertler et al., 2009).

Previous studies showed that transport of petroleum hydrocarbons to granular materials was considered as important natural removal mechanism. For sediment particles, it was summarized that between 20 and 30% of the total amount petroleum hydrocarbons could be naturally submerged and transported to the seabed as clay-oil flocs (Muschenheim and Lee, 2002); the other scenario simulations went up to 65% of petroleum hydrocarbons in the aggregated form with sediments (Bandara et al., 2011). For microorganism particles, Most research focused on the factors affecting the adsorption behavior of

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bacteria, fungi or algae; the relevance of adsorption, cell polarity or the partition coefficient; the contributions of bioadsorption and biodegradation to biodissipation of dissolved and adsorbed pollutions; and the influence of continuous culture on adsorption (Chen et al., 2010; Ke et al., 2010; Chen and Ding, 2012; Ding et al., 2013). Moreover, for coastal rock particles, many studies were performed from monolayer to multilayer adsorption of petroleum hydrocarbons on rock minerals (de la Cruz et al., 2009; Shelton et al., 2014; Lashkarbolooki et al., 2014). However, most studies were considered densification and sedimentation of floating crude oil by granular materials while ignoring the dispersed petroleum hydrocarbons including DPHs and oil droplets in the seawaters. A new perspective about adsorption of dispersed oil by granular materials remains to be explored.

Therefore, in this study, a specially designed device was used to simulate the coastal environment in the mesocosm experiment. The dispersed petroleum hydrocarbon consists of two parts, one is dissolved petroleum hydrocarbon, the other is small oil droplets. Firstly, to demonstrate the dispersed petroleum hydrocarbons in the seawaters adsorbed by granular materials were both dissolved petroleum hydrocarbons and oil droplets. Secondly, to determine how much the adsorption ratios were between DPHs and oil droplets absorbed by three types of granular materials. Thirdly, to understand how particle concentrations, and temperature affected the concentration of DPHs and oil droplets in the seawaters that absorbed by granular materials. Last but not least, to analyze DPHs changes in the seawaters and particle adsorption rate of petroleum hydrocarbons for three types of granular materials.

2. Materials and methods

2.1. Device set up

To study the adsorption of different granular materials, one tidal device was used in this research (Fig. S1). The tank size was 108 cm × 42 cm × 48 cm, which was made by Polyethylene plastics (PE). The device equipped with a computer-controlled electrical machine, which could make the rectangular container to do reciprocating motion. The electrical machine could control the tidal range and cycles.

2.2. Adsorbate of crude oil

A crude oil sample was obtained from Shengli oilfield (Shandong, China). The properties of the oil sample were as follows: the viscosity was 23.2 mPa s at 50 °C, the freezing point was 23.0 °C and the density was 0.8552 g cm^{-3} at 20 °C. 20 g crude oil was used in this study.

2.3. Adsorbents of granular materials

Granular materials including coastal rocks, sediments, and bacterial strain were used in this study (Table 1). Sediment sample and coastal rocks sample were obtained from the tidal flats of the Shilaoren bathing beach. The gravel and the remains of organisms were eliminated. All samples were dewatered. Bacterial strain sample were collected from laboratory-preserved bacteria. Bacterium N1, N2, N3 and N4 were isolated from petroleum-contaminated seawater and mud from Qingdao port. Sequence analysis of the 16S rRNA gene, BLAST sequence comparison and the phylogenetic analysis confirmed that the bacterial strain N1, N2, N3 and N4 were affiliated with *Ochrobactrum sp.* N1, *Brevibacillus parabrevis* N2, *B. parabrevis* N3 and *B. parabrevis* N4 respectively.

2.4. Seawaters

A seawater sample (salinity of 32.57 and pH of 7.85) was also collected from the Shilaoren bathing beach, Qingdao, China (36°5′34.61″N, 120°28′13.40″W). The sample was filtered with a 0.45 μm polycarbonate filter and sterilized using an autoclave. The aim of the pretreatment was to remove large particles and microorganisms. 50 L seawater was filled into every tank in this study.

2.5. Experimental set up and Samples collected

50 L seawater was filled into the tanks, 20 g of crude oil was dispersed in petroleum ether, then dumped into tanks, all the granular materials initial mass was 2 Kg including coastal rocks, sediments, and bacterial strain (wet weight) were added into tanks together, and then the granular materials and oils were mixed in the tank by the device equipped with a computer-controlled electrical machine. The rock and sediment particles should be sterilized so that it would not bring unwanted bacteria into the system. The temperature of the experimental operation of the tank was consistent with ambient temperature. When we explored how particle concentrations, size affected the concentration of DPHs and oil droplets in the seawaters that absorbed by granular materials. Granular particles of each size (0.5 kg) was initially added to the tank and tried to sieve the different sizes after the interaction via different filters (various μm nominal pore size). When we considered the effect of temperature on adsorption for three types of granular materials, simulation experiment was carried out in three months of June, July and August, and temperature was selected to be 25 °C, 30 °C, and 35 °C respectively.

50 mL seawater samples were taken from the tank and sampling depth was just below the water surface. The tank was sampled at times:1, 3, 7, 12, 18, 25, 33, 42, 52, 60 days. Control tank without crude oil was incubated in the same conditions to serve as reference. All seawater samples were immediately stored at 4 °C.

20 g granular materials samples including coastal rocks, sediments, and bacterial strain taken from the tank and samples were collected after 1, 3, 7, 12, 18, 25, 33, 42, 52, 60 days for analysis. Control tank without crude oil was incubated in the same conditions to serve as reference. All granular materials samples were immediately stored at 4 °C.

2.6. Measurement of the concentration of petroleum hydrocarbons

In order to separate the dissolved petroleum hydrocarbons (DPHs) and the oil droplets as two different phases, we detected the signal that DPHs form were nominally < 0.7 μm (Bianchi et al., 2014). Therefore, two different phases could be gravity filtered through filters (47 mm diameter and 0.7 μm nominal pore size).

For DPHs in seawaters, all samples were immediately filtered through filters (47 mm diameter and 0.7 μm nominal pore size), extracted by petroleum ether and then measured the absorbance at 225 nm by ultraviolet spectrophotometry (Gong et al., 2014). As showed in Fig. S3, the quadratic function of standard curve of petroleum hydrocarbons concentration was: $Y = 0.01635X + 0.04282$ ($R^2 = 0.9994$). All tests were done in duplicates. $\mathbf{C_0}$ (mg L^{-1}) represented this concentration of DPHs in the seawaters.

For granular materials, all samples were collected by centrifugation (6000 rpm for 5 min at 4 °C) and washed three times with ddH_2O and filtered through filters (47 mm diameter and 0.7 μm nominal pore size). The filtered liquid was extracted by petroleum ether and stored immediately at 4 °C. Crude oil absorbed onto the filters was not analyzed. All samples (filtered liquid) were immediately extracted by petroleum ether and analyzed the absorbance at 225 nm by ultraviolet spectrophotometry (Fig. S3). $\mathbf{C_2}$ (mg g^{-1}) represented this concentration of DPHs absorbed by granular materials. After this process, granular materials were washed another three times with petroleum ether. The washed solutions and throttle liquid were collected, extracted by petroleum ether and then stored immediately at 4 °C (Chen et al., 2010; Binks and Lumsdon, 2000). All samples (washed solutions and throttle liquid) were analyzed the absorbance at 225 nm by ultraviolet spectrophotometry (Fig. S3). $\mathbf{C_3}$ (mg g^{-1}) represented this concentration of