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## The physical-biological processes of petroleum hydrocarbons in seawater/sediments after oil spill

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**ABSTRACT:** The adsorption and desorption behaviors of dissolved petroleum hydrocarbons (DPHs) in the seawater-sediment system were investigated. The tidal flat sediment was used as the adsorbent, and crude oil was used as the adsorbate. The processes of adsorption and desorption at low concentration ( $<14.3 \text{ mg}\cdot\text{L}^{-1}$ ) were described by the first-order kinetic model. The rate of desorption was slower than that of adsorption, and about 49% DPHs remained on sediment. Therefore the potential risk of pollution would be in existence for a long time. The adsorption isotherms could be better fitted to the linear isotherm model than Freundlich and Langmuir models. The adsorption process is a physical adsorption, because  $|\Delta H|$  was  $39.0 \text{ kJ}\cdot\text{mol}^{-1}$  which less than  $42.0 \text{ kJ}\cdot\text{mol}^{-1}$ . The change of the *n*-alkanes in the process was more obvious than aromatic, the weathering loss rate was 25.56%, emulsification loss rate of dispersant was 0.65% and the microbial degradation rate was 15.46%. The results showed the degradation process of petroleum hydrocarbon in tidal flats.

**Keywords:** Petroleum hydrocarbons pollution; adsorption; kinetics; thermodynamics; biodegradation

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## 1. Introduction

Petroleum hydrocarbons are a complex mixture of components, which include hydrocarbons (such as alkanes, cycloalkanes and aromatics) and nonhydrocarbon components (such as oxygen containing compounds, sulfur containing compounds, nitrogen containing compounds, resins and asphaltenes).<sup>1</sup> Many of these components have teratogenic, carcinogenic and mutagenic effects.<sup>2</sup> With the development of petroleum industry, marine oil spill accidents happened frequently in recent years. When the crude oil was spilled into the ocean, it was subject to several weathering processes, which include evaporation, dissolution, emulsification, oxidation, biodegradation.<sup>3,4,5</sup> However, the petroleum hydrocarbons pollution is not only confined to the ocean, but also expanded to the beach due to tides and waves.<sup>6</sup>

Petroleum hydrocarbons have a very devastating effect on marine ecosystem. DPHs would certainly be harmful to the marine environment especially the near shore and estuarine areas.<sup>7</sup> The particle size of the sediment is fine. Once petroleum-contaminated seawater touches the tidal flat sediment, DPHs will be removed from the aqueous phase. Although the oil concentration in seawater decreased, the pollution is not eliminated exactly. The study of the adsorption and desorption behaviors can provide theoretic basis for the migration of DPHs in marine environment.<sup>8</sup>

Many studies have simulated the coastal environment. Nine wave tanks were used to investigate the behavior of chemically dispersed oil and the whole oil on a near-shore environment, studying the effects of wave action on the biodegradation of Iranian light crude.<sup>9</sup> Santos used two mesocosm experiments and each experiment was performed in three tanks simulating beach and open-water conditions.<sup>10</sup> Govarthanan conducted oil remediation studies used the SKK11 bacteria.<sup>11</sup> Gertler investigated the fate of oil-degrading bacteria for a bioremediation strategy in the simulated coastal environment.<sup>12</sup>

In this research, the adsorption and desorption of DPHs in the seawater-sediment system were investigated using the tidal flat sediment as the adsorbent and DPHs as

the adsorbate. The thermodynamic law and kinetic law of DPHs adsorbed on sediment were studied systematically, and the mechanism of adsorption was explored. Bioremediation agents were employed to deal with coastal weathered spill oil adsorbed on the rock of the artificial beach, petroleum hydrocarbons of the seawater, intertidal and subtidal zones.

## 2. Materials and Methods

### 2.1. Crude oil Sample

The crude oil sample was obtained from Shengli oilfield (Shandong, China). The properties of oil sample were as following, viscosity was 22.2 mPa·s at 50 °C, freezing point was 23.0 °C and density was 0.8552 g·cm<sup>-3</sup>.

### 2.2. Seawater and sediment sample

The seawater sample (salinity 32‰ and pH 7.95) was collected from the Shilaoren bathing beach, Qingdao, China (36°5'34.61"N, 120°28'13.40"W). The sample was filtered by a 0.45 µm polycarbonate filter<sup>13</sup> and sterilized by autoclave. The aim of pretreatment was to remove large particles and microorganism. The sediment sample was also obtained from the tidal flat of the Shilaoren bathing beach. The gravel and the remains of organisms were eliminated. The sediment sample was dewatered, and sieved using a mesh (224 µm) before the experiment.<sup>14</sup>

### 2.3. Bacteria and dispersant

*Strain S-1* isolated from crude oil contaminated sediment in our previous study was used for the biodegradation experiment.<sup>15,16</sup> Sequence analysis of the 16S rDNA gene, BLAST sequence comparison and phylogenetic analysis confirmed that the *Strain S-1* (GenBank IDs) was affiliated with *Bacillus cereus* (KF033125).<sup>15</sup> The *Strain S-1* can catabolize crude oil as carbon and energy source, it prefers alkanes to aromatic. In this study it was used for the biodegradation experiment.

The commercial chemical dispersant GM-2 was employed as surface active agent to increase the concentration of petroleum hydrocarbon in the water which was purchased from Qingdao Guangming Environmental Technology Co., Ltd. Its biodegradation rate was BOD<sub>5</sub>/COD(%) > 30, pH 7 ~ 7.5, and it was stored at normal temperature. GM-2 is an approved product by maritime bureau, ministry of

transportation. The main purpose of GM-2 was dispersing the crude oil into tiny particles in the waves or additional force and cannot rise anymore when oil spill occurs, then accelerate the process of microbial degradation of crude oil in the water.

#### 2.4. Batch static equilibrium experiments

The seawater/crude oil system was stirred at 100 rpm without phase separation and oil-water emulsions. Measured the concentration of DPHs in seawater until the same, we got the petroleum hydrocarbon saturated solution. The oil content in the aqueous phase was extracted by petroleum ether and analyzed by UV spectrophotometry.<sup>17,18</sup> The adsorption and desorption were studied using sediments as the adsorbent and DPHs as adsorbate by static immersion. The adsorption experiments were conducted in 250 mL conical flasks. 0.3 g sediment was transferred into the flask before the addition of 100 mL saturated petroleum hydrocarbons solutions. Two control experiments were conducted, the first one (sediment and clean seawater) was to eliminate the influence of dissolved substances and the second (only saturated petroleum hydrocarbons solution) was to remove the influence of evaporation. Then these conical flasks were placed in a reciprocal shaker at 25 °C, 120 rpm, and sampled at 10, 20, 30 min and 1, 2, 4, 6, 12, 24 h to determine the time-variable concentration of DPHs. The amount of adsorption  $Q_A$  ( $\text{mg} \cdot \text{g}^{-1}$ ) could be counted by the concentration of petroleum hydrocarbons.

To investigate the effect of temperature and evaluate the kinetic activation energy and thermodynamic parameters of the process, some experiments were conducted at 293K, 298K and 303K, the sediment concentrations in some experiments were 3, 5, 10 g/L, respectively.

After the adsorption equilibrium was established, the supernatant was replaced with 100 mL clean seawater. Then the conical flasks with contaminated sediment samples and clean seawater were used in the desorption experiments. The experiment condition was same with the adsorption experiment. They were sampled at 0.5, 1, 2, 6, 12, 24, 48, 54 h to determine concentrations of DPHs for calculating the amount of desorption  $Q_D$  ( $\text{mg} \cdot \text{g}^{-1}$ ).

The oil content in the aqueous phase was extracted by petroleum ether and

analyzed by UV spectrophotometry. All trials were determined in triplicate to ensure the accuracy of experiments.

## **2. 5. Column simulation experiment of crude oil migration**

Indoor simulation device was consisted of a cylindrical separatory funnel which filled with the sediment collected from different depth. Set a certain amount of crude oil on the surface of the sediment. The tidal flats simulation experiment column was connected to a peristaltic pump and it was eluted by artificial seawater at certain time. The concentration of the petroleum hydrocarbon was determined from the collected eluent every day. Experimental period was 15 days and leached 12 hours every day.

The oil content in the eluent was extracted by petroleum ether, ultrasonic extraction was used to extract the oil content in the sediment. All the extract was analyzed by UV spectrophotometry.

## **2.6. Simulation experiment of oil spill in tidal flats**

Two tanks (108 cm×42 cm×48 cm) were designed to simulate the remediation after oil spill in tidal flats. The sediments in both tanks were deep to 18 cm, and its slope was about 9.46°. Poured about 12.6 L of artificial seawater into the tanks.

In the stage I dissolved 50 g of crude oil into petroleum ether, then dumped them into tank A and B to form the oil film at the surface of the artificial seawater. A week later the petroleum ether was evaporated completely and crude oil was weathered. The oscillator was activated and the motor frequency was maintained at 0.4. In stage II poured about 15 g (30% of the crude oil) GM-2 dispersant into tank A at day 15. In stage III added 380 mL(3% of the artificial seawater) *Strain* S-1 enrichment culture to tank A and 380 mL artificial seawater to tank B at day 29. The temperature ranged from 15 to 20 °C.

The oil content in the aqueous phase was extracted by petroleum ether, ultrasonic extraction was used to extract the oil content in the sediment. All the extract was analyzed by UV spectrophotometry. At the end of each stage stored about 1 g crude oil sampled from the tank A and B. The samples were analyzed by GC-MS using a Shimadzu (Kyoto, Japan) GC-MS-QP2010. Helium was employed as a carrier gas. The details for the experimental conditions and quality control were reported

previously by Sun.<sup>19</sup>

### 3. Results and Discussion

#### 3.1. Adsorption and desorption kinetics of DPHs

The solubility of petroleum hydrocarbons was  $14.3 \text{ mg}\cdot\text{L}^{-1}$  eventually. So we discussed the low concentration ( $<14.3 \text{ mg}\cdot\text{L}^{-1}$ ) of DPHs only. According to the result of control experiment the influences of DPHs evaporation could be neglected, and the amount of petroleum hydrocarbons released from the sediment was also disregarded. Fig. 1a shows the adsorption kinetic curve of the sediment sample.  $Q_A$  increased over time until the adsorption equilibrium was established, and settled at a stable value after about 320 min. A hypothesis was proposed that the adsorption rate was proportional to the difference between the amount of equilibrium adsorption and instantaneous adsorption. The adsorption rate could be expressed:

$$dQ_A / dT = A(L_A - Q_A) \quad (1)$$

In Formula (1),  $Q_A \text{ (mg}\cdot\text{g}^{-1})$  is the amount of instantaneous adsorption;  $A \text{ (min}^{-1})$  is adsorption rate constant;  $L_A \text{ (mg}\cdot\text{g}^{-1})$  is the amount of equilibrium adsorption.

The integral transform of Formula (1) was communicated:

$$Q_A = L_A(1 - e^{-AT}) \quad (2)$$

The experimental data of adsorption were fitted with Formula (2). The correlation coefficient was about 0.965. So Formula (2) could be satisfied to describe the adsorption process. The amount of equilibrium adsorption was  $0.3955 \text{ mg}\cdot\text{g}^{-1}$  by the fitting curve analysis. Reaching 80% of the adsorption capacity needed about 69 min. Therefore, once DPHs in the seawater touched the sediment, it would be adsorbed soon. Although the DPHs concentration in the aqueous phase was decreased, the potential risk of pollution still existed.

Fig. 1b illustrates desorption kinetic curve of the sediment sample. According to the similar method of the adsorption kinetics, the process of desorption was fitted with Formula (2). The correlation coefficient was about 0.967. The amount of equilibrium desorption was  $0.2011 \text{ mg}\cdot\text{g}^{-1}$ . In view of the different units of adsorption and desorption rate constants, desorption rate was slower than adsorption rate. The DPHs

adsorbed by sediment would be released slowly with clean seawater scouring continuously. Compared with the adsorption process, the process of desorption would be time-consuming. So the pollution threat to bathing beach would exist in a long period of time.

The amount of equilibrium adsorption and desorption (0.3955 and 0.2011 mg·g<sup>-1</sup>, respectively) demonstrating that the DPHs adsorbed to sediment would not be released completely. About 49% of the total adsorbed amount would be remained in the sediment. We should not forget the pollution adsorbed on sediment after oil spill or the pollution will present consistently.

### 3.2. Adsorption isotherms of DPHs

Fig. 2a and Fig. 2b illustrated the relationship between  $C_e$  and  $Q_e$ . The standard deviation (SD) of the triplicate sample was not more than 2%. In this study three adsorption models were used to fit experiment data. The first model was Langmuir isotherm model  $Q_e = Q_m C_e / (C_e + A)$  ( $Q_m$  is the saturated adsorption capacity,  $A$  is constant associated with the adsorption energy), the second was Freundlich isotherm model  $Q_e = K_F C_e^{1/n}$  ( $K_F$ ,  $1/n$  are empirical coefficients for each adsorbent pair at a given temperature), and the last was the linear isotherm model  $Q_e = K_P C_e$  ( $K_P$  is the linear distribution coefficient or Henry adsorption constant).<sup>20,21</sup> Adsorption isotherm parameters and the correlation coefficients were summarized in Table 1.

In Table 1 the correlation coefficients of the linear, Langmuir and Freundlich isotherm models were in descending order. The adsorption of DPHs on sediment at low concentration was fitted the linear isotherm model better than Freundlich isotherm model. Langmuir isotherm model had been traditionally used to quantify and contrast the performance of different bio-sorbents.<sup>22</sup> The values of saturated adsorption capacity fitted by Langmuir isotherm model were negative. They were not consistent with experimental results, so the adsorption of DPHs on sediment did not belong to this category.

Freundlich isotherm model was used to describe non-uniform and multiple substances adsorption which was not restricted to the formation of monolayer.<sup>23</sup> The value of  $1/n$  is a measure of adsorption intensity or surface heterogeneity, it ranging



between 0 and 1. Adsorption intensity or surface heterogeneity will become more heterogeneous as its value gets closer to zero.<sup>24,25</sup> But the values of  $1/n$  were in our paper slightly larger than 1 according to curve fitting analysis. It means the adsorption was closer to the linear adsorption.

The correlation coefficients fitted by the linear isotherm model were more than 0.99 at low concentration. The linear adsorption isotherm indicated that the attractive force between the adsorbate and the adsorbent was invariant, and the distribution of adsorbate was irrelevant to its initial concentration. It was usually applied to the situation where the surface coverage was far from the saturation. In the study very fine sediment was used which had many adsorption sites, and the DPHs concentration in seawater was pretty low. Therefore the adsorption of DPHs on sediment can be described by the linear adsorption model.

### 3.3. Effect factors and thermodynamic analysis of adsorption

The linear model used to interpret the adsorption equilibrium has been accepted widespread due to its lack of mathematical complexity.<sup>26</sup> Table 1 shows  $K_P$  ( $L \cdot g^{-1}$ ) were 161, 93.6 and 48.9 when sediment concentrations were 3, 5 and 10  $g \cdot L^{-1}$ , respectively.  $K_P$  decreased with increasing of sediment contents. It meant 3  $g \cdot L^{-1}$  sediment had been able to provide sufficient adsorption sites, and more sediment contents did not contribute to the adsorption process.

At the same time,  $K_P$  ( $L \cdot g^{-1}$ ) were 190, 161 and 112 when temperatures were 20, 25 and 30 °C, respectively.  $K_P$  decreased with elevating temperature. It meant the petroleum hydrocarbons were more likely to exist in the aqueous phase rather than adsorbed by sediment with increased of temperature. Therefore, if the marine oil spill accidents happened in summer, polluted degree of the beach would be lighter. For example, temperature inversely affect the crude oil uptake due to the exothermic nature of the sorption.<sup>27</sup>

The adsorption isotherms at different temperature were conducted thermodynamic analysis. Van't Hoff equation<sup>28,29</sup> was as following:

$$d \ln K_P / dT = \Delta H / RT^2 \quad (3)$$

In Formula (3),  $K_P$  is distribution coefficient;  $\Delta H$  is the heat of adsorption;  $T$

stands for temperature.  $\Delta H$  is thought to be constant in a narrow temperature range. The integral transform of Formula (3) was taken to linear regression analysis.

$$\ln K_p = -A / T + B \quad (4)$$

In Formula (4),  $A = \Delta H / R$ . According to the above method,  $\Delta H$  of DPHs on sediment could be obtained by values of  $K_p$  and  $T$  in Table 1.  $\Delta H = -39.0 \text{ kJ} \cdot \text{mol}^{-1}$ .  $\Delta H$  showed that the adsorption process was exothermic, and the increasing of temperature was not conducive to the adsorption. The adsorption belonged to physical adsorption according to  $|\Delta H| < 42 \text{ kJ} \cdot \text{mol}^{-1}$ .<sup>30</sup>

### 3.4. Crude oil migration result

Fig. 3a shows the concentration changes of hydrocarbon component in the leaching liquid. The concentration of hydrocarbon component in leaching liquid risen sharply at first. Because the water constantly scoured the sediment, at the beginning the soluble components in crude oil spread to the sediment, part of them adsorbed to sediment and others along with the water out, the concentration in the leaching liquid reached to  $142.1 \text{ mg} \cdot \text{L}^{-1}$  at day 5. The concentration of leaching liquid constantly decreased from the sixth day, and it was only  $16.8 \text{ mg} \cdot \text{L}^{-1}$  at the end of the experiment. It because as time goes on diminishing of the soluble components in crude oil lead to oil concentration of leaching liquid medium declined. At the same time the continuous leaching made adsorbed hydrocarbon component start to dissolve, and eventually reached the balance of adsorption and desorption.

The Fig. 3b shows that hydrocarbon component of oil content at 3 cm can be up to  $500 \text{ mg} \cdot \text{g}^{-1}$  after water leaching. Because the sediment block the infiltration of hydrocarbon component,<sup>31</sup> the adsorbed hydrocarbon component decreased gradually with sediment depth increasing, hydrocarbon component of oil content was  $18.69 \text{ mg} \cdot \text{g}^{-1}$  at 9 cm deep, and hydrocarbon component of oil content gradually stabilized. Just as the finding that the spilled hydrocarbons had remained predominantly in the organic surface horizons of the soil where spillage occurred.<sup>32</sup> Thus the concentration of the hydrocarbon component of oil on the beach sediment in vertical direction was reduced constantly and oil pollution mainly concentrated in the surface layer of beach sediment in the marine offshore after oil spill. It is same with Bejarano's investigation

that tidal flats had the more high-risk samples at the surface than the bottom.<sup>6</sup> Therefore remediation process of the surface sea sand within 10 cm should be strengthened at oil spill pollution area.

### 3.5. The oil content changes in seawater

Petroleum hydrocarbon content changes in seawater phase shows in Fig. 4.

In stage I the first 14 days, petroleum hydrocarbon contented in the seawater phase of the tank A and B presented a tendency of increasing. The maximum DPHs concentration was  $3.107 \text{ mg}\cdot\text{L}^{-1}$ . In this stage crude oil was dissolved under the external force, but the function of oscillator was weaker than stirrer, the concentration was lower than section 2.4.

In stage II from day 15 to 28, oil concentration in the tank A at 15 d reached the highest value of  $4.875 \text{ mg}\cdot\text{L}^{-1}$ , it was mainly due to the scatter and emulsification of dispersant GM-2 which increased the solubility of petroleum hydrocarbon. However, the emulsified crude oil-seawater system cannot be stable for long-term. The increase of hydrocarbons can be due to the presence of oil droplets in emulsion or increased dissolution of hydrocarbons from the surfaces of the numerous droplets (surface area effects).<sup>33</sup> It was consistent with the Zhao's study that the dispersant was much more effective in solubilizing more hydrophobic PAHs.<sup>34</sup>

In stage III from day 29 to 48, oil concentration in the tank A decreased while in the tank B increased. At 48 d, oil concentration in the tank A reduced to  $2.28 \text{ mg}\cdot\text{L}^{-1}$ , which means *Strain S-1* catabolized crude oil as carbon and energy source so it made the DPHs content reduce.<sup>35,36</sup> The degradation removal percentage of DPHs was about 33.72%, including physical and chemical degradation such as weathering and catabolizing.

### 3.6. The oil content changes in sediment

Petroleum hydrocarbon content in sedimentary phase decreased with the depth. Oil contented in surface sediment 0 ~ 1.7 cm was greater than in sediment 1.7 ~ 3.3 cm and 3.3 ~ 5.0 cm. The result was similar with the migration result in section 3.4, crude oil entered the surface sediment through many paths, and then entered deep layer as the result of hydrodynamic and infiltration, but the surface had the higher

concentration than other depths all the time. The DPHs and suspended oil directly contacted to the interface of seawater and sediment, leading to the DPHs adsorbed to sediment consistently.

Fig. 5a shows that the oil content of intertidal sediments in the experimental group presented the downward trend after rose, the change of the diagram is the same with Fig. 4. In the presence of dispersant the strong sorption of the dispersant on sediments and the weak solubilizing of phenanthrene made its uptake enhance.<sup>37</sup> Similarly the dispersant can enhance the sorption of crude oil. In this study because the emulsification of GM-2 caused DPHs to increase, the crude oil in sediment peaked at 21 d, it is consistent with that the dispersant enhanced the sorption extent.<sup>35</sup> Dispersants made crude oil down from the wall at the same time, it may increase oil pollution in tidal flat. Fig. 5b shows that the oil content of intertidal sediments in control group also fell after rising, but the change lagged in the experimental group. It means the dispersant can accelerate the dissolution of crude oil but cannot change its property. The oil content of surface sediment achieved the maximum.

Fig. 5c shows that the oil content of supratidal zone 0 ~ 1.7 cm increased gradually as time goes on in the experimental group. Because fine sediment particles accumulated to supratidal zone due to the scouring of the waves, the small size particles can easily adsorb the oil,<sup>38</sup> so the petroleum hydrocarbon accumulated on the sediment. At 28 d, the oil content of sediment in 1.7 ~ 3.3 cm is slightly greater than in 0 ~ 1.7 cm. It may be due to the lateral migration of petroleum hydrocarbon at the interface between high water line and supratidal zone. As shown in Fig. 5d, in tank B the oil content of the supratidal zone emerged the rising trend, and also reached maximum at 33 d.

### 3.7. Hydrocarbon components change in seawater

Fig. 6 shows the change of hydrocarbon components in seawater, Table 2 and Table 3 shows the loss rate of *n*-alkanes and aromatics. We can see the loss of hydrocarbon components C<sub>10</sub> ~ C<sub>26</sub> was bigger than other *n*-alkanes at 14 d through Fig. 6a, it indicated natural weathering has little effect on heavy hydrocarbon component after C<sub>26</sub> because long chain alkanes have a complex structure and difficult

to evaporation but the short chain alkanes evaporate easily. Table 2 and Table 3 shows natural weathering total loss rate of *n*-alkanes was 26.56%. We can speculate that the loss of *n*-alkanes was not only because of its low boiling point but also because of its large solubility that caused *n*-alkanes migration into the surrounding environment. Fig. 6b describes several typical aromatics content changes, naphthalene was strongly influenced by natural weathering, the loss rate of naphthalene was biggest and reached 71.89% but the loss rate of other aromatic was low. Just as the finding that removal was more effective for short-chain alkanes and low ring-number PAHs.<sup>39</sup> All in all the *n*-alkanes was removal more than aromatic hydrocarbon, and light component of hydrocarbons were greatly influenced by weathering. The initial crude oil diagnosis ratio parameters of pristane / phytane (Pr/Ph) was 1.35 (> 1), the data shows that the environment of the crude oil was brackish water oxidation environment, and the crude oil belongs to the mature crude oil.

Fig. 6c shows that C<sub>22</sub> ~ C<sub>37</sub> components of *n*-alkanes in the tank A had greater degradation than the tank B, but other hydrocarbons showed an opposite phenomenon. It showed GM-2 had an impact on high molecular weight hydrocarbons, it can dissolve more C<sub>22</sub> ~ C<sub>37</sub> components of *n*-alkanes into the water and accelerate their degradation. Fig. 4 also shows an increasing trend in stage II tank A, combined with Fig. 4 we can know that dispersant lowered the crude oil–seawater interfacial tension, oil slicks was broke into fine droplets and dispersed into the water column, thereby the degradation was higher than tank B.<sup>40</sup> We can see from Table 3 excluding the natural weathering loss rate in the tank B, the loss rate of *n*-alkanes was 0.65% in the tank A. In this stage GM-2 immediate directional adsorbed on the oil-water interface, hydrophilic group dispersed into the water and hydrophobic group dispersed into oil, it made the oil film emulsify into small droplets and turn into water under the action of external force. So the crude oil was degradation more easily in tank A than in tank B. Sauret also investigated the changes of hydrocarbon composition in crude oil, our study was same with the investigation that addition of emulsifier resulted in a more rapid and more efficient removal of hydrocarbon.<sup>41</sup> Fig. 6d shows the dispersants had little effect on aromatic hydrocarbon component of oil. It because on the one hand the

structure of aromatics was more complex and stable than *n*-alkanes, on the other hand aromatics was more difficult to dissolve than *n*-alkanes.

Fig. 6e shows that oil content of  $C_{11} \sim C_{26}$  in tank A was smaller than tank B, which suggested that short chain alkanes were more likely to be used by *Strain* S-1 than long chain alkanes. It illustrated *Strain* S-1 had special hydrocarbon oxidase which can degrade oil content of  $C_{11} \sim C_{26}$  and the long chain alkanes was difficult to degrade because of its rigid structure. Total biodegradation rate of *n*-alkanes reached 15.46% and the biodegradation rate of  $C_{11} \sim C_{14}$  could reach 81.24% ~ 100% if excluding the influence of weathering. It was due to the effect of dispersant, when used in the right amount and circumstances, the application of chemical dispersants may promote biodegradation of oil in the water column and eliminate or reduce the impacts of oil on sensitive shorelines and habitats significantly.<sup>42</sup> We used the dispersant before added the *strain* S-1, the dispersant made the crude oil dissolve into the seawater so the *strain* S-1 can degrade it easily and the biodegradation rate of alkanes was high. We can see from Fig. 6f the *strain* S-1 had no obvious effect on typical PAHs. It is mainly because the selected *Strain* S-1 is degradation bacterium for alkane, its utilization for aromatic hydrocarbon is poorer.

#### 4. Conclusion

The thermodynamic parameters and the adsorption kinetic of DPHs at low concentration were studied systematically. At low concentration the adsorption and desorption processes were fitting to the first-order kinetic model, the linear isotherm model could be used to describe the adsorption isotherms well, and the adsorption belonged to physical adsorption according to the thermodynamic analysis. Tidal flats remediation should focus on the sediment surface at a depth of 0 -10 cm. The DPHs concentration in seawater was about  $4.875 \text{ mg} \cdot \text{L}^{-1}$ . The oil content of intertidal zone is higher than the supratidal zone. The total loss ratio of *n*-alkanes in the three stages was 25.56%, 16.56% and 19.40%, respectively, the loss rate caused by dispersant was 0.65%, the microbial degradation rate was 15.46%, crude oil was more sensitive to natural weathering and microbial degradation than dispersant after oil spill. Future

research should focus on the effect of other chemicals on adsorption such as surface active agent and microbial, because these chemicals may affect the concentration of crude oil, maybe we can get a different law of adsorption and desorption.

### Acknowledgements

This research was founded by grants from “The National Natural Science Foundation of China” (41376084); the “Program for New Century Excellent Talents in University” (NCET-11-0464); the “Program for Innovative Research Team in University” (IRT1289); “the Open Foundation of Key Laboratory of Marine Spill Oil Identification and Damage Assessment Technology of SOA” (201402). This is MCTL Contribution No. 98.

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**Table Captions**

**Table 1** Adsorption isotherm models of DPHs on sediment

**Table 2** The related parameters of petroleum hydrocarbons

**Table 3** The loss ratios of petroleum hydrocarbons in the inoculated tank

**Table 1** Adsorption isotherm models of DPHs on sediment

Effect factors	Para-meters	Langumir isotherm model			Freundlich isotherm model			Linear isotherm model	
		$Q^0(\text{mg}\cdot\text{L}^{-1})$	$A(\text{mg}\cdot\text{L}^{-1})$	$R^2$	$K_F(\text{mg}^{1-n}\cdot\text{g}^{-1}\cdot\text{L}^n)$	$n^{-1}$	$R^2$	$K_P(\text{L}\cdot\text{g}^{-1})$	$R^2$
Sediment content ( $\text{g}\cdot\text{L}^{-1}$ )	3	-1.58	-11.8	0.983	0.145	1.13	0.976	161	0.993
	5	-0.886	-11.5	0.975	0.085	1.08	0.926	93.0	0.992
	10	-0.571	-13.6	0.974	0.046	1.09	0.967	48.9	0.992
	20	-2.40	-14.4	0.982	0.179	1.08	0.968	190	0.994
Temperature ( $^{\circ}\text{C}$ )	25	-1.58	-11.8	0.983	0.145	1.13	0.976	161	0.993
	30	-3.27	-31.7	0.987	0.107	1.05	0.975	112	0.996

**Table 2** The related parameters of petroleum hydrocarbons

number	group	<i>n</i> -alkanes ( $\mu\text{g}\cdot\text{g}^{-1}$ )	aromatic ( $\mu\text{g}\cdot\text{g}^{-1}$ )	biomaker ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Pr/Ph
1	0d experimental group	501 793	53 510	39 376	1.35
2	14d experimental group	368 512	106 602	42 587	1.32
3	28d experimental group	307 481	68 007	33 053	1.33
4	28d control group	309 890	42 970	42 121	1.29
5	48d experimental group	247 835	59 103	48 790	1.12
6	48d control group	297 792	85 611	34 448	1.29

**Table 3** The loss ratios of petroleum hydrocarbons in the inoculated tank

test	<i>n</i> -alkanes		aromatic	
stage	total loss rate (%)	net loss rate (%)	total loss rate (%)	net loss rate (%)
I	26.56	26.56	-	-
II	16.56	0.65	36.20	-
III	19.40	15.46	13.09	-

Ps: Total loss rate is hydrocarbon components total loss rate in experiment group; Net loss rate is deducted the weathering loss in control group; “-” represent negative value.

**Figure Captions**

**Fig. 1** Adsorption (a) and desorption (b) kinetics of DPHs on sediment.

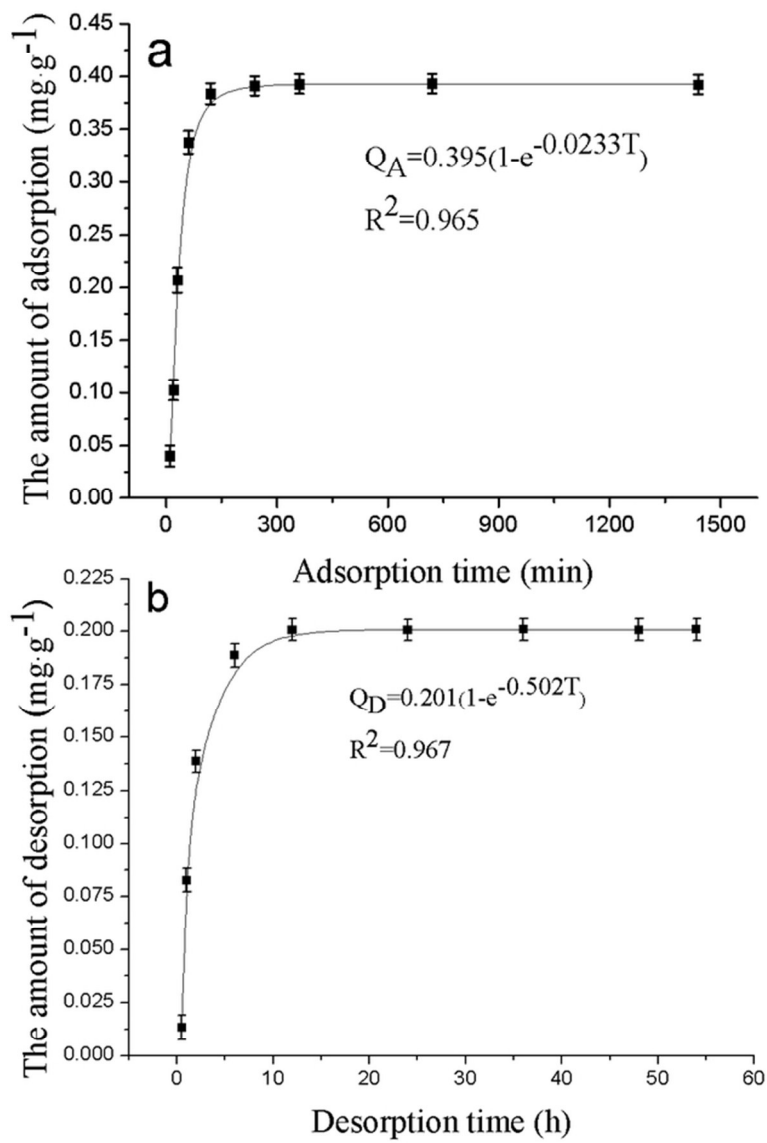
**Fig. 2** Adsorption isotherms of DPHs at different sediment concentration (a) and different temperature (b).

**Fig. 3** Change of oil concentration in effluent seawater (a) and vertical distribution of crude oil in the sediment (b).

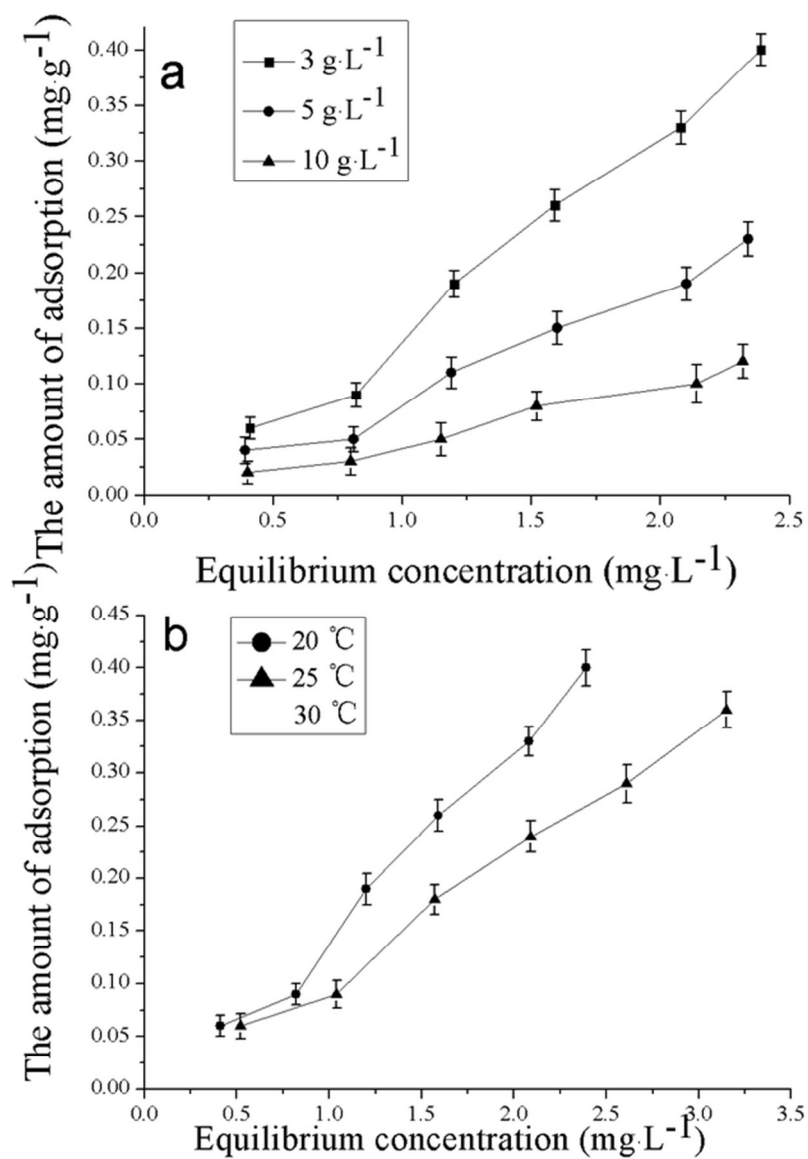
**Fig. 4** Oil concentration changes in the aqueous phase.

**Fig. 5** Oil concentration changes of the intertidal (a, b) and supratidal (c, d) sediments in the experimental (a, c) tank and in the control (b, d) tank.

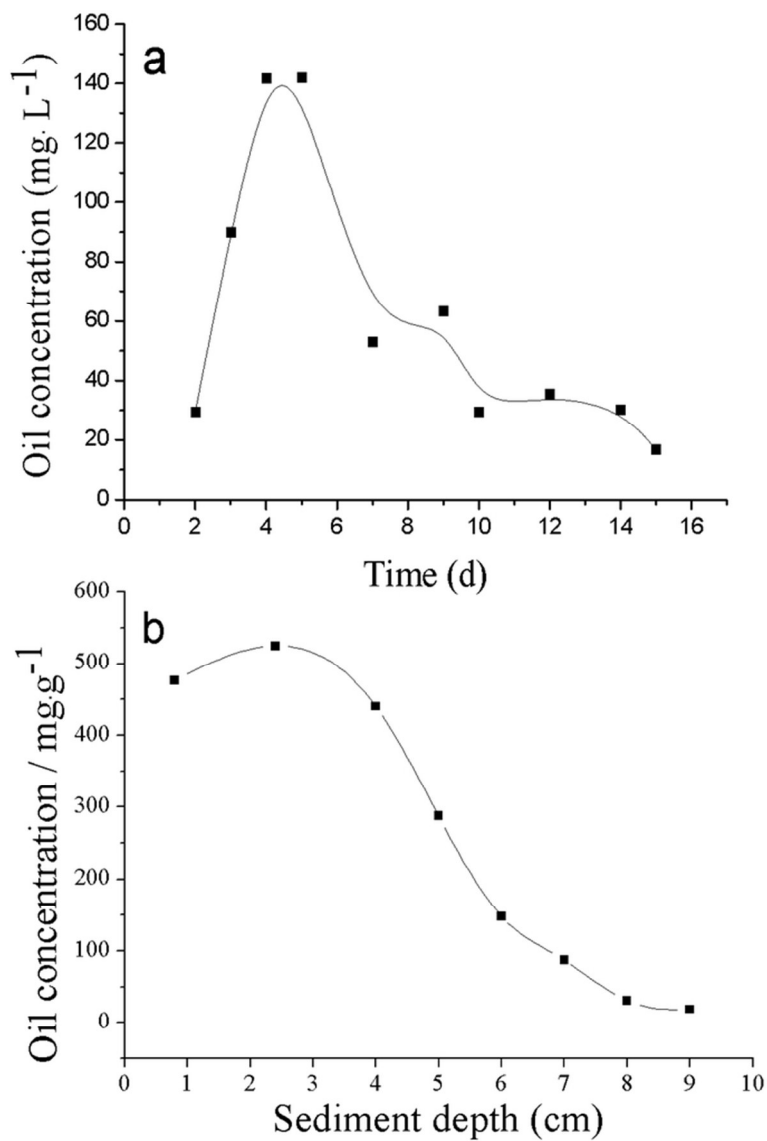
**Fig. 6** Concentration changes of *n*-alkanes (a, c, and e) and aromatics (b, d, and f) at the 14 d (a, b) 28 d (c, d) 48 d (e, f) day.



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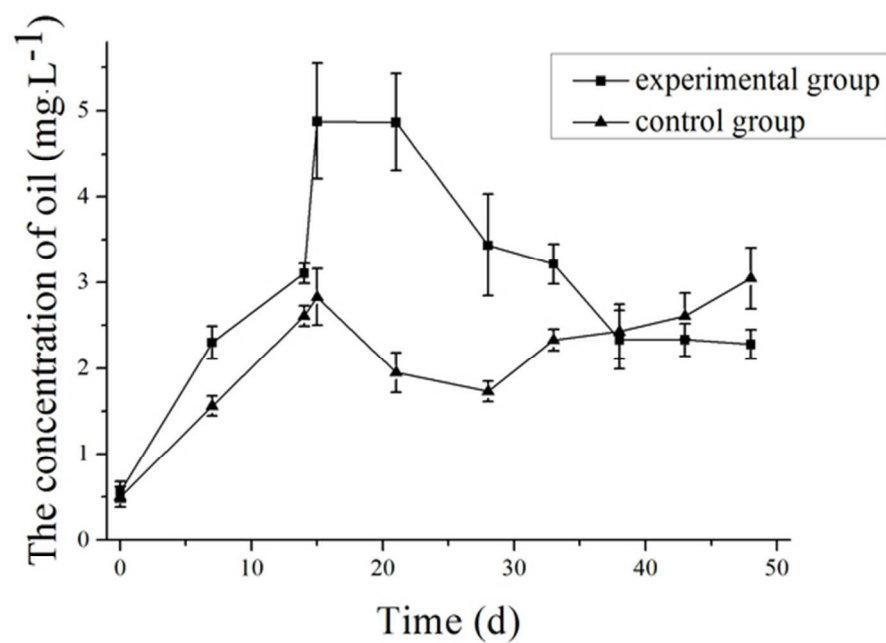


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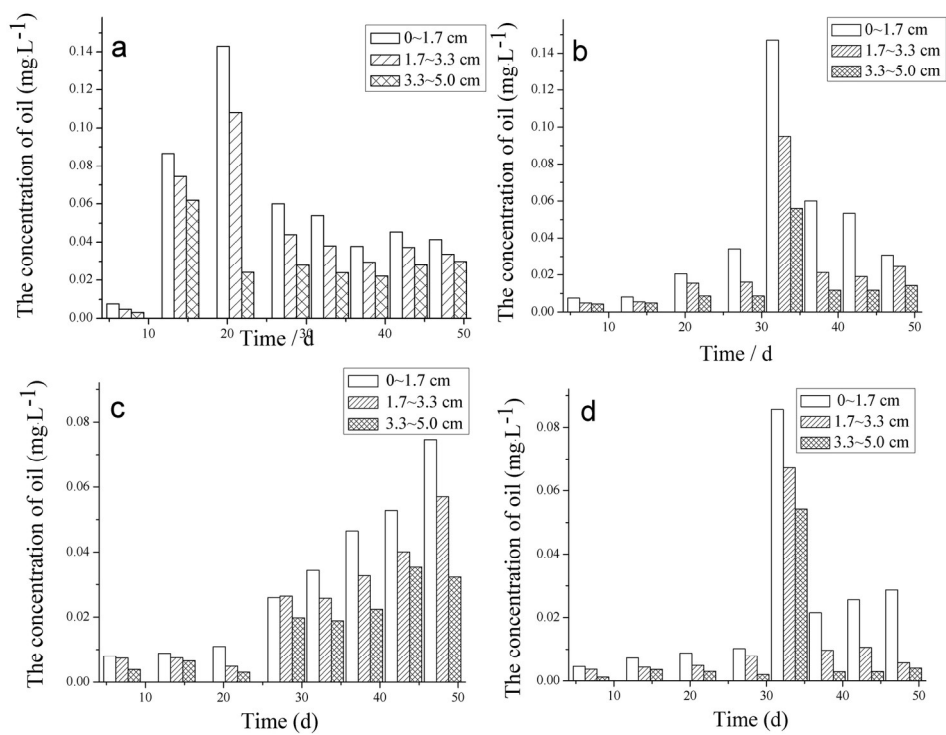


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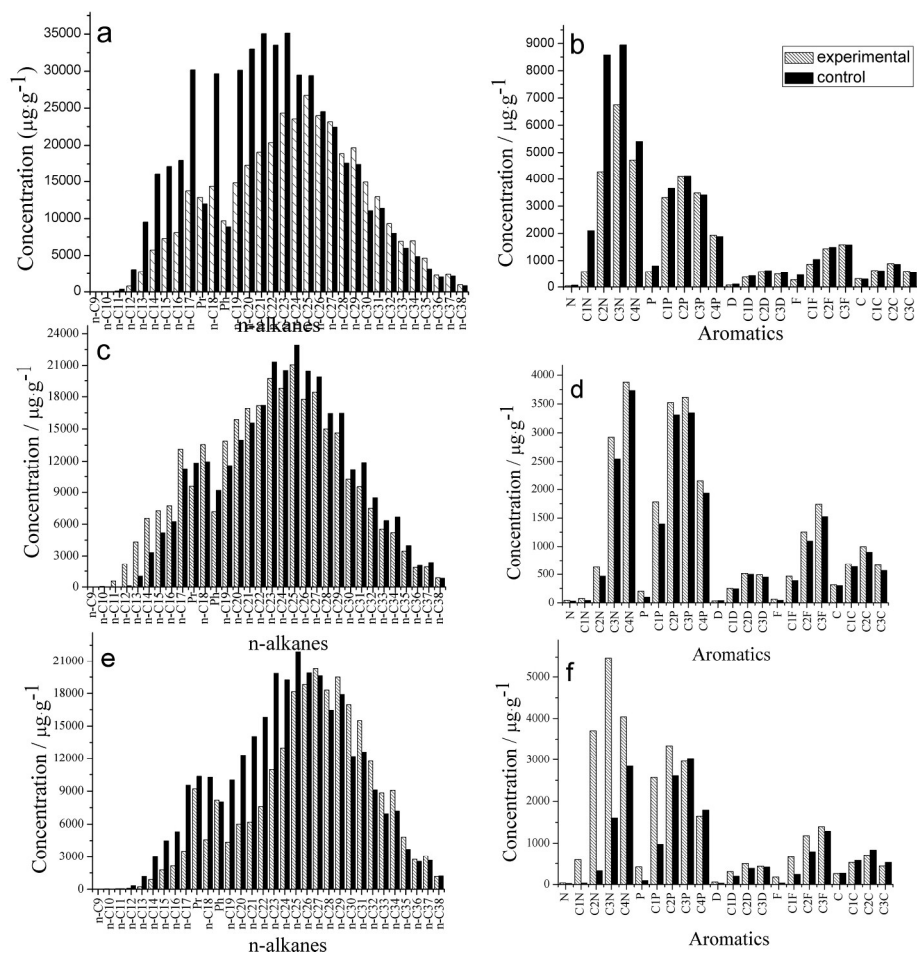




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222x216mm (300 x 300 DPI)

Physical adsorption and biodegradation process of crude oil in seawater-sediment system.

