Biological treatment of mineral oil in a salty environment

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Abstract  Mineral oil may be spilled into the marine or coastal environment through the discharges of ballast and bilge water, dry docking activities and tanker and non-tanker accidents to contaminate both of the seawater and coastline, especially in harbors. The unsuitable storage and disposal of wasted mineral oil may also contaminate saltified soil or brackish groundwater that have been polluted by salty wastes or intruded by seawater in coastal areas. In order to clean those contaminated sites, the mineral oil must be removed from the salty environment. In this study, a lab-scale aerobic biofilter-biotrickling tower system packed with particulate plastic media (1.5 cm, hexagon in shape) was used to treat the salty artificial wastewater polluted by mineral oil (diesel fuel) mixed with chemical dispersant (CPC OD-10 and inorganic nutrients. The volatile organic compounds (VOCs) escaped from the biofilter due to aeration was then treated by the biotrickling tower of the treatment system. According to the experimental results, the optimal removal efficiencies of the emulsified diesel in this salty water was found to be 95% controlled under concentrations as high as 1000 mg TOC/L of diesel in the influent and volumetric loading rate of 1.5 kg TOC/m³-day. The biodegradation rate constant (k) was measured to be 0.169 hr⁻¹ for a first-order reaction assumed. As to the removal efficiency for VOCs, a low percentage of 68.2% was measured due to short hydraulic retention time (10 seconds) applied to the tower. However, only a small fraction (7.9%) of total amounts of diesel was measured as VOCs. The chemical dispersant used in this study was biodegradable, which could be used as a surfactant to emulsify the mineral oil into seawater for biological treatment. Due to short HRT applied to this aerobic biofilter-biotrickling tower treatment system, both the surface area and reactor volume required to build this treatment equipment are thus decreased to make it more easily set up in a mobile ship or truck. Thus, we may treat the mineral oil in marine or any other salty environment more conveniently.

Keywords  Mineral oil spills; marine and coastal environment; saltified soil; brackish groundwater; biofilter; biotrickling tower; diesel; VOCs; bilge; ballast; dock wastewater

Introduction

Since petroleum and its refined products were used widely in industry as an energy source and raw materials, oil pollution has become a major problem in marine, coastal and other salty environments. A significant amount of oil comes into the ocean from operational discharges of ships (tankers and non-tankers), such as ballast and bilge water, as well as from incidents such as explosion, collision, groundings and contacts (Doerffer, 1992a). The activities of offshore exploration and exploitation of oil also pose an increased threat of oil pollution to the marine environment (Liukkonen et al., 1995). Besides, all ships require periodic dry docking for servicing, repairs, and cleaning the hull. To avoid the risk of explosion during running these activities, all oil is removed from the ships, and thus the oily docking wastewater may be generated at the ship repair yards to contaminate the seawater of harbours (Clark, 1992). In addition, the unsuitable storage and disposal of wasted mineral oil may also contaminate saltified soil or brackish groundwater that have been polluted by salty wastes or intruded by seawater in coastal areas.

There are many ways to deal with the oil spill and pollution in marine and salty environments. Most commonly, the mechanical recovery methods by using floating booms, skimmers and oil-water separator are the most favorable oil spill combating methods in the marine environment. Use of sorbents is also a popular physical way to clean up the oil spill in both the oceanic areas and coastal zones. For some situations, chemical dispersants,
which are kinds of surfactants (surface-active agents), are used to emulsify the oil slick. The drop sizes of the emulsified oil tend to be smaller to help in removing oil from the seawater surface and increasing the oil biodegradation rates. However, using chemical dispersants can let more amount oil enter the seawater, which may cause an impact to the biota in both seawater column and seabed (Doerffer, 1992b).

Use of floating booms and skimmers sometimes cannot remove the oil spill completely from the seawater surface, and the wastewater discharged from the oil-water separators usually still contains small amounts of oil. The residual oil after being treated by those physical ways may still be accumulated to threaten the seawater quality of harbours. It has been found that many microorganisms possess the enzymatic capability to degrade petroleum hydrocarbons, such as alkanes, paraffinics and aromatics (Atlas, 1981; Leahy and Colwell, 1990; Atlas and Bartha, 1992; Atlas, 1995). Hence, biological ways may be regarded as an alternative to solve the oil spill problems, especially for considering both the economical and ecological factors. However, Bartha and Altas (1987) also indicated that the natural degradation rates of oil spill in marine environment were low and limited by several environmental factors, such as molecular oxygen, phosphate and nitrogenous nutrients (ammonium, nitrate and organic nitrogen). Therefore, to efficiently treat the oil spill in both marine and coastal environments, those abiotic environmental factors should be provided. In addition, pump and treat is usually the way applied for groundwater pollution on sites.

For treatment of the seawater or salty groundwater polluted by oil spills and the wastewater generated in dry docking activities, the biological treatment facilities controlled under the environmental conditions mentioned previously may thus be used. In this study, a lab-scale aerobic biofilter-biotricking tower system was used to treat the seawater polluted by mineral oil (diesel) mixed with biodegradable chemical dispersant and inorganic nutrients. The dispersant was used to emulsify the oil to increase its solubility in the seawater and to prevent the biofilm from being covered by the oil. The low molecular weight parts of diesel might come out of the reactor as volatile organic compounds (VOCs) due to aeration, which would pass through a biotrickling tower of the system for further treatment. The purpose of this research was to study the removal efficiencies of diesel from seawater by using this lab-scale aerobic biofilter-biotricking tower system.

Materials and methods

Sampling and seeding of sludge
The sludge seeded into the biofilter of this study was sampled from the sediments in the estuary area of Cheng-Jenn River, which flowed into Kaohsiung Harbor. The microbes living in the sediments were believed to be endurable to salts and be able to degrade mineral oil due to the oil polluted seawater flowing back and forth between the harbor and river in the estuary along with the tidal activities. The sampled sludge was then poured into the biofiltering reactor and cultured on a batch basis first. When the sludge biomass was increased to form significant biofilm on the surface of the media inside the biofilter, the culture was then changed to a chemostat pattern to grow more sludge on the media.

Preparation of artificial wastewater
In this study, artificial wastewater was used as the influent of the treatment system, which was composed of artificial brackish water with salinity of 20‰, nutrient solution and emulsified diesel solution. The receipt of artificial wastewater with salinity of 20‰ was as follows: NaCl 18 g, MgSO$_4$ · 7H$_2$O 6 g, NaHCO$_3$ 0.05 g and deionized (DI) water 1 L, while the nutrient solution was composed of (NH$_4$)$_2$SO$_4$, KH$_2$PO$_4$, FeCl$_3$ and CuSO$_4$ with concentrations of 50, 10, 2 and 1 mg/L, respectively. As to the emulsified diesel solution, it was prepared by adding diesel to the artificial seawater mixed with the chemical dispersant.
made by China Petroleum Company mentioned previously. In this study, the concentrations of diesel in the solution were controlled at 300 and 1000 mg TOC/L as low and high levels test runs, respectively.

Experimental equipment and operation
A schematic diagram of the experimental equipment is shown in Figure 1. As seen in this figure, the main parts of the equipment were two 4-L columns (diameter 12 cm, length 40 cm), both of which were filled with plastic particular media in the shape of a hexagram with a size of 1 cm in diameter and 1 cm in height. The characteristics of the media included the density of 1130 kg/m³, porosity of 0.83, and specific surface area of 576 m²/m³. The whole system was operated in a close pattern. The effluent discharged from the aerated biofilter continuously flowed into the biotrickling tower for further treatment and to keep the tower moisture, while the VOCs generated during aeration in the biofilter were entering the biotrickling tower from bottom for treatment before they were discharged out of the system. The other monitoring equipment included pH meter, DO meter and ORP meter set up in this lab-scale aerated biofilter-biotrickling tower treatment system as shown in Figure 1.

Experimental procedure and analytical methods
After a three-month culturing period, the biofilm was formed significantly on the surface of the media. The tests were started by controlling the diesel concentration of 250 mg TOC/L in the influent of the treatment system, and by increasing the concentration up to 400 mg TOC/L during a period of 30 days for the low-level test run. During the test run, we took liquid samples from influent, liquor in the aerated biofilter, and effluent from the biotrickling tower, respectively for each day. The gaseous samples were also taken from the biotrickling tower for VOCs testing by several times during the test run. The concentration of diesel in the influent was then increased up to 1000 mg TOC/L in the high-level test run. Both of the liquid and gaseous samples and the chemical dispersant used in this study were then analyzed quantitatively by a TOC analyzer (SHIMADZU, Model TOC-5000A), while the qualitative analysis was achieved by using a GC-FID analyzer (VARIAN, GC-3600) with a capillary column (SUPELCO, DB-1, 0.25mm). The operating conditions of GC-FID were as the followed: initial temperature 50°C, temperature increasing rate 5°C/min, final temperature 300°C for column, and 320°C for FID.

Figure 1  Schematic diagram of the biological treatment system

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Results and discussion
Low diesel level test

The experimental results of the low diesel test are shown in Figures 2 and 3. According to Figure 2, we found that the concentrations of diesel in the effluent were decreased below 50 mg TOC/L during the 30-day’s test run with a low level of 300 mg TOC/L for diesel concentration in the influent. The TOC removal efficiency could reach 95% after 9-day’s test run, and the average was 92% for all of the test run. It was inferred that the attached-growth microbes inside the biofilter were cultured well to adapt the environment filled with mineral oil (diesel) and salts even under a short hydraulic retention time (HRT) of 18 hours. Hence, an aerobic biofiltering system can treat the emulsified mineral oil polluted seawater efficiently even operated under a short HRT only if the supplement of oxygen and nutrients are sufficient in this biological treatment system. In addition, according to Figure 2, we also found that the concentrations of diesel in the liquor of the biofilter were similar to those in the effluent coming from the biotrickling tower. Thus, it was concluded that most of the diesel would be biodegraded in the aerobic biofiltering process rather than in the biotrickling process. The reason might be that most of the straight-chain aliphatic hydrocarbons in diesel had been biodegraded in the biofilter making the residual parts of polyaromatic hydrocarbons (PAHs) left in the effluent difficult to be biodegraded further even in the biotrickling tower. This was also the reason why the final removal efficiency could only reach to about 92% and never went up further during the test run.

![Figure 2](image1.png)

*Figure 2* The variations of mineral oil of diesel with time in low level test run. (OI: original influent, BE: effluent from biofilter, TE: effluent from trickling filter)

![Figure 3](image2.png)

*Figure 3* The GC-FID chromatogram for the mineral oil of diesel in low level test run
As to the qualitative analysis, according to the GC-FID chromatogram shown in the Figure 3, we observed that most of the peaks existing in the influent were decreased or disappeared significantly in both the liquor in the biofilter and effluent coming from the biotrickling tower. Therefore, it was elucidated again that the aerobic biofilter-biotrickling tower system could be used to treat the mineral oil (diesel) polluted seawater efficiently. Besides, due to short HRT applied to the system, both of the surface area and reactor volume required to build this treatment equipment are thus decreased to make the treatment system easily set up in a mobile scenario, such as a ship or truck. Hence, we may treat the oil spills in marine and coastal environments more conveniently. The average daily amounts of diesel removed per unit volume of reactor in this test run were calculated to be 0.4 kg /m³-day as TOC, which was equal to about 1.0 kg BOD/m³-day. Assuming that the reaction kinetics followed the first order (i.e. \( \frac{C_{\text{eff}}}{C_{\text{inf}}} = e^{-kt} \)), we could measure the diesel biodegradation rate constant \( (k) \) equal to 0.128 hr⁻¹ by substituting the values of HRT of 18 hours and average diesel concentrations of 320 and 32 mg TOC/L in the influent and effluent, respectively into the above equation.

High diesel level test

The experimental results of high diesel test are shown in Figures 4 and 5. According to Figure 4, we found that when the concentrations of diesel in the influent was increased up to a level of 1000 mg TOC/L, the system was still operated well maintaining low concentrations of diesel in the effluent ranging from 45 to 60 mg TOC/L. As seen in the same figure, although the concentrations of diesel in the effluent of this test run were higher than those in the low level test run (30~50 mg TOC/L), the TOC removal efficiencies were increased up to an average value of 95%. Under the same HRT of 18 hours controlled in the system, we measured that the biodegradation rate constant \( (k) \) and average TOC removed per unit volume of reactor and time were equal to 0.166 hr⁻¹ and 1.4 kg TOC/m³ (3.74 kg BOD/m³-day). These numbers were higher than those measured in the low level test run, which meant that bacteria cultured in the aerobic biofilter-biotrickling tower treatment system were able to handle well the diesel polluted seawater in concentration as high as 1000 mg TOC/L. Certainly, the supplement of oxygen and nutrients must be sure to be sufficient in this biological treatment system. In addition, as for the results in the low level test run, according to Figure 4, we found that the concentrations of diesel in the liquor of the biofilter were still similar to those in the effluent coming out of the biotrickling tower. Thus, we also concluded that most of the diesel would be biodegraded in the aerobic biofiltering process rather than in the biotrickling process even though the diesel concentration was increased

Figure 4  The variations of mineral oil of diesel with time in high level test run. (OI: original influent, BE: effluent from biofilter, TE: effluent from trickling filter)
up to 1000 mg TOC/L in the influent. The reason still might be that the residual parts of PAHs in diesel left in the effluent from the biofilter were difficult to be biodegraded further in the biotrickling tower.

Figure 5 shows the results of qualitative analysis expressed as GC-FID chromatogram in the high level test run. According to this figure, we also observed that most of the peaks originally existing in the influent were decreased or disappeared significantly in both the liquor in the biofilter and effluent coming out of the biotrickling tower. However, as seen in the Figure 5, since the diesel loading rates to the biofilter were increased, the analytical results of liquor in the biofilter (i.e. influent to the biotrickling tower) by GC-FID showed some more significant peaks than those in the effluent discharged from the biotrickling tower. However, those small amounts of residual hydrocarbons were biodegraded further in the biotrickling tower.

VOCs removal test
It was assumed that volatile organic compounds (VOCs) in the diesel fuel could be partially volatilized in the presence of diffusive aeration without being first biodegraded by the
immobilized bacterial consortia in the biofilter. To ensure that volatilized VOCs were captured prior to their discharge into the atmosphere, the biofilter was sealed at its top to create a headspace where the exhaust gas was collected and diverted to the trickling filter for further treatment. The biodegradation of VOCs in the trickling filter was accomplished by counter-current flow of the gas and liquid phases through the media bed. The empty bed detention time of the exhaust gas in the trickling filter was approximately 10 seconds. The experimental results run by GC-FID indicate that volatilized VOCs, expressed in terms of total petroleum hydrocarbon (TPH), accounted for approximately 5 and 7% of the feed diesel fuel in the low- and high-level experiments, respectively. These low values could be a result of a better partitioning of diesel fuel in the water phase accomplished by emulsification. Moreover, it also was observed that flow paths through the media bed were tortuous which prevented the rapid ascendance of air bubbles. Consequently, volatilization of VOCs could be retarded accordingly. As would be expected, volatilized VOCs were primarily short-chain aliphatic hydrocarbons. The data illustrated in Figure 6 indicate that the trickling filter was highly effective in removing VOCs. At an empty bed retention time of only 10 seconds, approximately 68.2% of feed VOCs was removed (i.e., 4.5 mg/L versus 1.5 mg/L).

Conclusions
In order to keep the harbors clean and maintain safe shipping, the spilled oil must be removed from the seawater in harbors. In this study, we found that the aerobic biofilter-biotrickling tower treatment system performed well to treat the seawater contaminated by diesel with concentration as high as 1000 mg TOC/L only if the supplement of oxygen and nutrients are sufficient in this biological treatment system. The average removal rate of diesel could reach 1.4 kg TOC/m³-day (or 3.74 kg BOD/m³-day) by this biological treatment system even under a short HRT of 18 hours. In addition, due to large amounts of biomass accumulated in this attached-growth biological treatment system, the biodegradation rate constant was calculated equal to 0.166 hr⁻¹ by assuming the first-order reaction for diesel biodegradation, which was much higher than that in natural marine environment. Due to short HRT applied to this aerobic biofilter-biotrickling tower treatment system, both the surface area and reactor volume required to build this treatment equipment are thus decreased to make it more easily set up in a mobile ship or truck. Thus, we may treat the oil spills in marine and coastal environment more conveniently.

References