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Research Article

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Treatment of oil polluted marine environment through multi-functional materials

Jianliang Xue, Linao Zheng, Hongsheng Lu, Blin Guo, Yanan Wu, Nenghu Qiao and Bingqi Yan

College of Chemical and Environmental Engineering, Shandong University of Science and Technology,Qingdao, Shandong, P. R. China

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ABSTRACT

Increasing of oil exploitation and transportation, the accidents of oil polluted marine are increasing. Owing to the oil complex components, this destroy the marine ecosystem. In order to restore the ecosystem in oil polluted marine, it introduced the function of multi-functional materials in this paper. There are two types of multi-functional materials to restore the ecosystem(e.g. Adsorption materials and dispersed material). In this paper, these two types materials were introduced and compared in detail. At finally, the paper put forward the development direction in the future..

Key words: Marine oil pollution; Adsorption materials; Dispersed material; Ecological restoration

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INTRODUCTION

In recent years, in order to solve the problem of increasing petroleum demand, petroleum exploitation has been more frequent in the sea. At the same time, about half petroleum have been transported by sea in the world. Consequently, the risk of petroleum pollution accidents are increased in the sea, such as oil spill from oil well, oil transport ships and coastal refineries [1-2]. And range from 4 to10 tons of petroleum are spilled into the ocean every year, the amount of petroleum spill is also increased rapidly. About 60 percents of petroleum spill are caused by the exploitation accidents [3-5].Thus a lot of oil are sent into the ocean due to the petroleum spill accidents occur frequently, which take great bad influence to the marine ecological environment.

In order to control marine pollution and minimize the hazards, domestic and foreign researchers have did many researches in different areas. Common treatment methods include physical method (e.g. mechanical method), chemical method (e.g. combustion and chemical dispersion) and bioremediation method. Bioremediation technology has been paid more and more attention because of its low production cost, on-the-spot disposal, security, good treatment effect and small impact on environment. The key point of the ecological restoration of polluted ocean is to research and develop bioremediation technology with high effective and low cost, which include screening of prior degradation bacteria and biological degradation pathways for petroleum, etc. However, the study on bioremediation has many limitations, such as various types of oil have complex components. Nevertheless, petroleum degrading bacteria is highly specific for degradation, the degradation effect of degrading bacteria is not ideal because the ocean environment is unpredictable, the adaptability of degrading bacteria and oil solubility of water are poor.

At present, many reports have studied the the factors for restricting the application of bioremediation technology at domestic and foreign [6-9]:

① Materials are added to increase the contact area between microbial oil and seawater, such as the surfactant materials；

② Microorganism is added which degrades petroleum effectively to increase the population quantity of microorganism；
③ N, P and other nutrition source are supplied to promote the degradation of oil by indigenous microorganism

From the above methods, in this paper the point was considered that the changes of relation among oil - water – microorganism by adding materials into the ocean environment. At the same time, the composition of oil to improve biodegradability (reducing the recombination proportion by adsorption, photocatalysis) also could change. Therefore, a micro-environment increasing the contact area of oil and degrading bacteria could be provided. The aim of this paper was to discuss this area due to little related reports had been known till at domestic.

2. COMPONENTS OF PETROLEUM AND DESTRUCTION

The main components of oil are alkanes (e.g. hexane), aromatic hydrocarbons (e.g. benzene, toluene and xylene) and polycyclic aromatic hydrocarbons (e.g. Pyrene and Phenanthrene). The typical oil composition are as follows in Figure. 1. Therefore, oil spill will have great influence to the ocean.

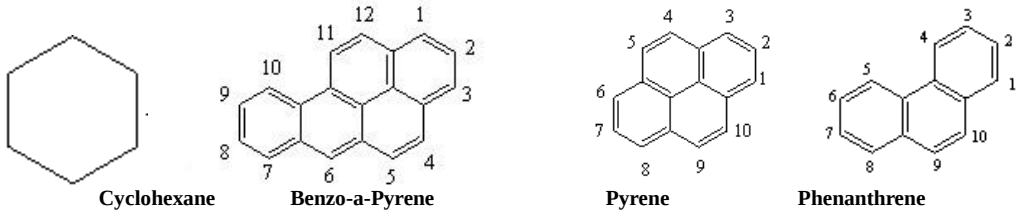

Fig. 1 The typical oil composition

Influence of marine gas phase and material exchange

After the accident, gas exchange (e.g.O_2 and CO_2) can be hindered due to the formation of oil film At the ocean surface. Thus the balance between the ocean-atmosphere circulation and materials is destructed. And what's more, the oil film also prevent sunlight to enter the ocean [10]. Moreover, the marine oil pollution will lead to weaken the circulation of ocean water evaporation process and the entire system is affected, so that the land desertification phenomenon is more serious. Global weather and climate change are also have been a significant impact [11].

The destruction of the marine ecological environment

In the accident area COD is increased, and gas exchange and photosynthesis are prevented by oil spill. Therefore, aquatics will die because of the destruction of aquatic photosynthesis and lack of oxygen. For example, the oil film could destory coastal wetland ecosystem [12].

Oil spill is also harmful to aquatic animal, birds and other rare animals [13]. For example, fat - soluble substances such as PAHs and other persistent organic pollutants are easy to be cumulatived in the Fat visceral and other organs, so spawns, juvenile fish and the ecosystem survival will be at risk. At the same time, birds may lose power of fly due to be direct exposure to oil and also be harmed by eating polluted fish. Birds are dead because liver, lung, kidney and other organs will be damaged and the number of white blood cells will reduce due to pollutant intake.

Economic losses and human health

Oil pollution directly or indirectly restricts the sustainable development of human society and the environment. Human health will be damaged due to oil pollution influence the development of marine aquaculture and fishing industry [14-15].

3. THE TYPES AND MECHANISM OF THE MATERIALS TO DEAL WITH OIL POLLUTION

Recently, in the marine oil polluted area, corresponding materials are used as a pretreatment method to improve the environment of polluted marine area. Materials can be used to deal with oil spill are divided into several categories according to their different functions: oil absorbent and dispersant.

Among them, absorbent materials contain natural inorganic oil absorption material, natural organic oil absorption material and chemical synthetic oil absorption material. The common materials include activated carbon, zeolite, perlite, clay, silica gel, graphite, rice husk, cellulose, cotton and polyurethane, etc. Bentonite consist of montmorillonite is the clay rock, and montmorillonite is composed of two layers of silicon oxygen tetrahedron cliping a layer of alumina octahedral composition of 2:1 type clay minerals content. Due to the mineral surface adsorption, the interlayer cation exchange action, the filtering effect of channel and special effects of two-dimensional structure, bentonite has been paid attentions widely in environmental pollution control and restoration [16-19].

Natural organic oil absorption materials and inorganic mineral materials have a wide range of sources. Synthetic organic materials is the most common oil spill absorption material due to the better oil absorbing ability now, but these materials are difficult to be biodegraded.

Dispersant is composed of surfactant, solvent and a small amount of additives (wetting agent and stabilizer, etc.). According to the classification, dispersant can be divided into the chemical surfactants and the biosurfactant.

3.1 Adsorption material

The repair mechanism of adsorption material is taking advantage of the porosity of solid materials, and the adsorption materials make the wastewater pollutants attach to its surface. So the adsorption materials which can be chosen have the similar characteristics [20].

(1)The characteristics of natural materials can be shown as follows. Inorganic materials with high oil absorption speed are cheap and accessible, and which are mainly granular or have a porous structure. Therefore, the disadvantages of the natural material are as follows: oil-water poor selectivity, low saturated oil absorption capacity, poor suspension property and difficult regeneration, etc.

(2) The characteristics of the composite materials can be shown as follows. The synthesis can be changed with the characteristics of different oil composition, which have the better Oil-wet hydrophobic and high oil absorption capacity. But the biodegradability is poor.

3.1.1 Natural adsorption material

Many reports study adsorption materials which are as the key pretreatment technology to repair the marine oil spill because of the wide range of source. The natural absorption material are researched and the natural oil absorption materials such as milkweed, cotton, wool and cotton have been investigated systematically [21].

In Japan Hokkaido forest site thinning wood and old cardboard are used to make oil absorption materials, and the heavy oil absorption ratio is range from 13.4 to 13.4 g/g. The woody oil absorption materials are easy to be produced and the oil absorption material can be recycled [22]. Natural oil absorption materials have advantages such as strong oil absorption ability, easy to receive, a wide range of materials possible and environmentally friendly. Nevertheless, there are also several faults, such as poor oil and water selective capacity, which restrict its application in treating marine oil spill.

In addition, many experts and scholars improved modification process of the natural adsorption materials and obtained the better oil absorption effect. For example, in order to improve the oil absorption capacity and oil-water selectivity, common natural oil absorption materials are needed to be modified. After acid treatment on the surface of graphite, the expanded graphite has the high oil absorption performance for three kinds of heavy oil, the largest oil absorption ratio can reach 80 g/g, and the ability of oil absorption is much better than activated carbon and soil [23].

3.1.2 Chemical synthetic material

Chemical synthetic materials have been paid more attention because of poor adsorption performance characteristics of natural materials. Chemical synthetic oil absorbing materials has been a hotspot in the oil-absorbing materials with good selectivity and absorption capacity. Nowadays, the most widely study on chemical synthetic oil-absorbing materials are polyurethane foam, polyurethane and Organic polymer microfiber, etc.

For example, high polyurethane foam has a good selectivity between oil and water with high oil adsorping and oil protection abilities. This is mainly due to polyurethane foam is a high polymer materials consisit of lipophilic monomer and cross-linkers. Polyurethane foam has a good suction properties which contains a three-dimensional mesh and porous structure inside. Polyurethane foam uses the lipophilic segment present in the molecule, and solvent effect gradually occurs into the porous structure of the polyurethane foam under both oil molecules and lipophilic group of the oil molecules reaction, finally unsaturated polymer chain segment starts slowly to retract after the suction reached equilibrium [24].

Absorbing foam is made of lipophilicity of polyester, polyether polyol and diisocyanate, and which can be used to absorb heavy oil, light oil and other toxic organic pollutants by adjusting the cell diameter. Shimizu etal use polymeric polyhydric alcohols and diphenylmethane diisocyanate as the raw material to prepare polyurethane, and the influence of density airflow and the pore structure on the lipophilicity property of polyurethane are studied [25]. The common materials and their properties of the oil absorption are listed in Table. 1.

Table.1 Collection properties of oil collection agent

adsorbing material	The types of adsorption oil	Collection Properties	References
activated carbon fibre	Refinery emissions of naphthenic acid wastewater	0. 65~ 0. 72 g/g	[26]
	PCBs	0.007 g/g	[27]
graphite	diesel	37 g/g	[28]
	crude oil	80 g/g	[29]
perlite	crude oil	5g/g	[30]
rice husk	crude oil	5.15g/g	[31]
	gasoline	3.7g/g	
polyurethane	diesel	14 g/g	[32]
	gasoline	3.9 g/g	
polypropylene	light crude	10 g/g	[33]

3.2 dispersant material

In 1960s, dispersant which can change the adhesion strength between the oil and water was applied in oil polluted water. Among them, the surfactant belonging to dispersant is composed of hydrophilic radical and lipophilic group, and which plays a main role in dispersing agent. The effect of solvent is to dilute oil, reduce the freezing point of oil and viscosity of surface active agent, eventually to facilitate emulsification. So the dispersing agent can connect the oil and water through pro-oil base group and hydrophilic group, oil-in-water emulsion particles formed are as water natural movement spread in the water through mechanical agitation or wave action. The most of surfactant used in dispersing agent are ionic surfactant and there is few anionic surfactant. The main advantages of dispersant are as follows:

The harms to sediments, biological and shore line will be abated becacse the oil viscosity can be reduced [34]. Dispersant can be used in harsh weather conditions and dispose rapidly in large area [35-36]. Moles etal. [37] compared the fresh and weathered 20 % of Alaska north slope oil dispersion effect under 10 ℃ using dispersant Corexit 9527 and 9520. The results showed that spraying the same amount of dispersant, fresh oil minimum dispersion rate is higher than 30% of weathered oil. But it is generally considered dispersants are not suitable to be used because of the highly viscous, the diffusion oil and paraffin oil.

However, chemical dispersants may bring secondary pollution. After the oil be dispersed, more aquatic organisms will be exposed to dissolve or disperse state oil and suffer damage. Much of dispersants can exist for several days in water and cause acute and subacute toxicity by Wells[38]. Biosurfactant is an important bioremediation preprocessing techniques to restore sea overflow oil.

Table.2 Examples of onsite usage of dispersants

pollutant	dispersant	dosage	effect	references
anthracene	SDS	----	250 ug/mL→199.2 ug/m	[41]
	biosurfactant	----	250 ug/mL→114.8 uIg/mL	
heavy fuel oil	Corexit 9500	dispersant：oil=（6-10）×10^4	The worst oil spill in the history of Singapore cleared within 3 weeks	[42]
Kuwait oil	biosurfactant	--	By adding the nutrition or oxygen to stimulate the growth of indigenous microorganisms to produce large amounts of biological surface active agent, and at the same time promote the degradation of petroleum hydrocarbons.	[43]
Intermediate without sulfur crude oil	Corexit 9527	Dispersant:oil=11400	Treatment effect is obvious	[42]
16 alkanes, 14 alkanes, basking shark alkane and other hydrocarbons	Biosurfactants produced by Pseudomonas aeruginosa	--	All hydrocarbon degradation rate is greatly increased	[44]

In recently, in order to produce some certain surface activity, microorganism are used and hydrophilic group and hydrophobic group are set within a molecular structure of amphiphilic compounds. The biosurfactant not only have the same properties with the chemical surfactants, such as the lower surface tension, penetrability and dispersion, but also has the salt tolerance, high temperature resistant, simple production process and raw material sources, etc. The development of the biosurfactant expands the material selection scope and dispersant application. Biosurfactant can stimulate the degradation of crude oil. Wu etal. screened four types of bacteria which can use diesel as the sole carbon source from soil of oil wastewater pollution. The diesel degradation rate can reach 62% in 32℃ after 28 d. And in the same conditions, the diesel degradation rate increased 26% after adding biosurfactant rhamnolipid diesel

[39]. Mai etal. found that crude oil could be degraded 72% by petroleum hydrocarbon degrading bacteria, but which could be degraded 78% by liquid surfactant [40]. Several kinds of dispersants and the effect are listed Table 2.

4. Prospect

Multifunctional material play an important role in the degradation of marine oil pollution. At present, although these materials have obvious advantages, there are also a larger defects. So the research emphasis is developing more efficient and cheaper materials in the future.

For example, the development of oil absorption materials consist of oil absorption, oil absorption speed and good oil-water selective is a hotspot in the field of current environmental research. In addition, biosurfactant has already been successfully used to handle the ocean oil spill events, but application of biosurfactant is limited by production cost because the biosurfactant production cost is higher than the production cost of chemical surfactants.

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