Proceedings of the 9th World Congress on New Technologies (NewTech'23)
Brunel University, London, United Kingdom - August 09-11, 2023
Paper No. ICEPR 114
DOI: 10.11159/icepr23.114

Coupling Leaching-Bioremediation for Petroleum-Contaminated Soile

Bing Qin[1], Fanbin Meng[1], Liming Ren[1], Jianlin Jiang[1,*], He Gong[1]
[1] SINOPEC Research Institute of Petroleum Processing Co., Ltd
Beijing, PR China
qinbing.ripp@sinopec.com;mengfanbin.ripp@sinopec.com; renliming.ripp@sinopec.com; jiangjianlin.ripp@sinopec.com;
gonghe.ripp@sinopec.com;

Abstract - Petroleum-contaminated soils are difficult to remediate due to a wide range of point/nonpoint sources of pollution and complex components. Here, the optimizations of the leaching process and process parameters were carried out based on the selection of conventional eluting agents and the development of oligomers, modified bio-based surfactants and synergists. Furthermore, a new and efficient leaching system was constructed. Moreover, based on the characteristics of the soil after leaching and its flora structure, the best degradation flora was selected and optimized. The proposed leaching-bioremediation coupling treatment process could make the petroleum hydrocarbon content of the contaminated soil less than 0.45%. The field validation was also conducted for petroleum hydrocarbon-contaminated soil with a mass of 12 000 t. Finally, the economic and environmentally friendly remediation technology and process for oil-contaminated soil are established. This approach can provide technical support for the environmental protection of sudden oil pollution and other historical problems in oil areas.

***Keywords*:** leaching, bioremediation, soil remediation, petroleum pollution

1. Introduction

Petroleum hydrocarbons (PHs) can pollute the soil ecosystem via different pathways during exploitation, transportation and storage. This adversely affects the soil's physical and chemical properties, microbial community structure, the growth of multicellular organisms and human health [1-3]. Some dominant characteristics of petroleum-contaminated soil (PCS) are point and nonpoint pollution sources, complex composition, high viscosity and difficulty decomposing[4]. Steam extraction, high-temperature treatment, leaching, microbial degradation and phytoremediation are the common remediation technologies for PCS [5-9]. Among them, leaching and bioremediation technology are preferred technology for environmentally friendly remediation.

The chemical leaching method is a more intensive, faster, and more efficient method to remove high concentrations of hydrophobic organic pollutants in soil [10]. Meanwhile, the soil leaching equipment is simple and flexible, and the investment is relatively small. Thus, it is suitable for rapid remediation of high-concentration organic contaminated sites.

On the other hand, bioremediation exhibits low cost, simple operation and environment-friendly processes, widely used in ex-situ remediation of low-concentration contaminated soil with high removal efficiency. Especially for the pond bottom sludge, modified sludge and contaminated soil with low oil content, it is preferred to deal with such pollutants due to its unique advantages [11-13].

Bioremediation technology combined with other technologies such as leaching, ultrasonic and chemical oxidation has the potential to improve soil remediation. For instance, leaching technology can be used to reduce the oil content in soil to a level suitable for bioremediation, while enhanced bioremediation can be used to make the oil content meet the relevant environmental standards. Combining two or more techniques will be important for solving not only sudden oil pollution but also different leftover environmental problems and establishing economic and environmentally friendly remediation technology and process.

However，the conventional chemical leaching has poor removal ability and low removal efficiency for heavy oil pollution in contaminated soil, and conventional leaching agents cause secondary pollution to the environment. Also, the existing microbial remediation agents have poor soil saline-alkali resistance and low degradation rate of petroleum hydrocarbons, which are difficult to meet the actual site remediation needs. Moreover, the conventional leaching agent may inhibit the activity of microbial remediation agent, so the compatibility between them is poor. Therefore, the contsrtuction of coupling leaching-bioremediation are limited by the above-mentioned problems.

The object of this research was to contsrtuct of the coupling leaching-bioremediation for the efficient and low cost remediation of complex oil-contaminated soil. Hence, a new type of leaching agent system was constructed through the selection of conventional leaching agents, the development of oligomers and modified bio-based surface surfactants, and the addition of ion regulators and synergists. Meanwhile, the microbial degradation system for the leached soil was constructed through the breeding and research of high-efficiency degradation bacteria and the optimization of nutrient formula and technological process. Moreover, the developed coupling leaching-bioremediation technology realized the large-scale and efficient remediation of the actual contaminated soil in an oil field, which shows extensive prospect of application in the field remediation of petroleum contaminated soil.

2. The development of leaching-bioremediation for petroleum-contaminated soil

2.1. Characteristic analysis of contaminated soil

On-site sampling and analysis of 8 production and operation units such as the oilfield production well site, joint station and decommissioning well site, was performed. The results showed that the typical oil-contaminated soils were floor oil sludge, tank (pool) sediment, modified sludge and mild oil contaminated-soil.

The basic properties of five different types of PCS are listed in Table 1. Properties of oily soil varied; the oil content of ground oily sludge and tank bottom sludge was higher, and the oil content of modified sludge and oily soil was lower. On the other hand, the water content and clay particle content of different types of PCS were irregular, depending on their sources and occurrence states.

Table 1 Basic properties of different types of petroleum-contaminated soil.

Contaminated soil type	Moisture content/%	Clay particles/%	Oil content/%
Ground oil sludge	30.3~45.5	13~24	3.8~14.3
Tank (pool) bottom sludge/polymer-bearing oil sludge	45.2~55.4	16~25	10.1~25.3
	40.3~52.9	15~21	7.7~22.5
	55.1~65.3	36~52	6.4~15.8
Modified sludge	43.2~49.7	21~28	2.5~4.9
Lightly oiled soil	21.4~35.6	22~29	3.7~5.1
	12.0~20.7	14~19	0.6~3.3

2.2. Structure of indigenous flora

Alcanivorax, Marinobacter, Pseudidiomarina and Pseudoalteromonas were the dominant taxa among microbial communities in the PCS of the well site (Figure 1). On the other hand, Alcanivorax, Mycobacterium, Pseudomonas and Thalassospira were the main indigenous flora in the tank bottom mud (Fig. 2). Alkanophagous bacteria have the ability to degrade alkane organic matter.

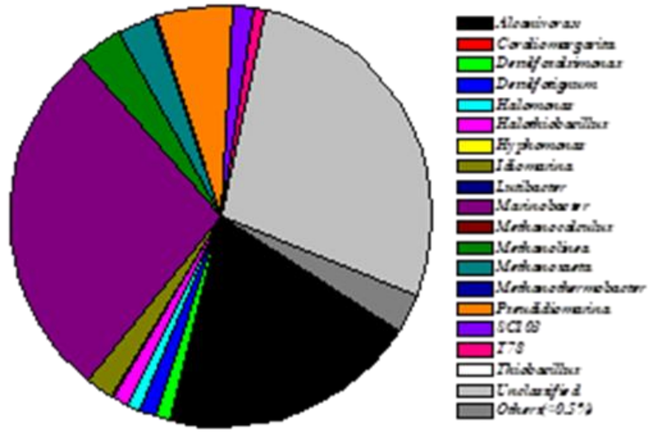

Fig. 1: Community structure of indigenous microorganisms in ground oil sludge

The above strains have the function of degrading PHs or polycyclic aromatic hydrocarbons reported. This implies that the hydrocarbon-loving microbial communities—capable of degrading petroleum pollution—have been formed in the contaminated soil. However, these communities are usually formed under anoxic/suboxic conditions and low nutrient contents such as nitrogen and phosphorus; the microorganisms cannot effectively degrade petroleum pollutants.

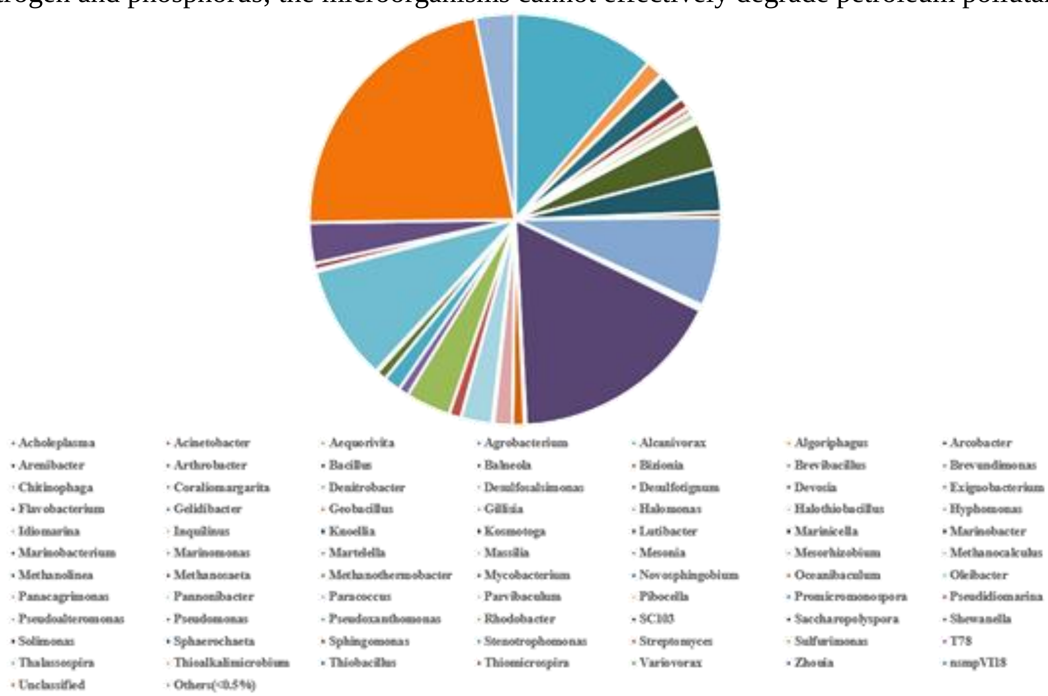

Fig. 2: Community structure of indigenous microorganisms in tank bottom sludge

2.3. Development and Evaluation of New Eluent

2.3.1 Development of oligomeric surfactant

A benzene ring was used as a reaction site, and carbonyl and imino functional groups and substituted benzene were subjected to polycondensation reaction through catalysis to construct a molecular skeleton structure of the oligomeric surfactant. A branched structure could be formed by adding dialdehyde with double reaction sites and then a hydrophilic group was introduced into the reaction site on the benzene ring. For example, phenolic hydroxyl and ethylene oxide/propylene oxide were introduced into a hydrophilic end of polyether. The synthetic route can be found in Fig. 3.

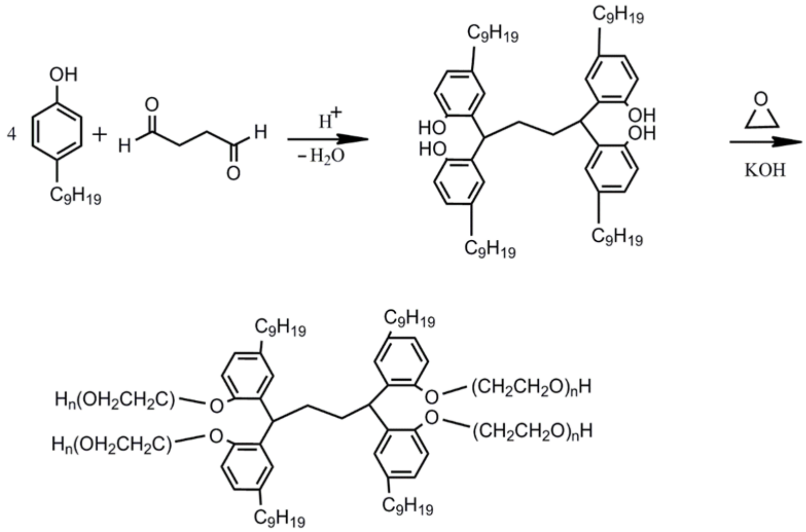

Fig. 3: Design route of oligomeric surfactant

All raw materials required by an oligomeric surfactant (RPOS) are easy to obtain in the process. Compared with the traditional single-chain surfactant, the dimeric and oligomeric surfactants can form self-aggregate to realize various functions of the surfactant under reducing dosage by one to several orders of magnitude. Thus, the dimeric and oligomeric surfactants have the potential advantage of high effectiveness with reduced dosage.

2.3.2 Development of modified sophorolipid

The sulfonated modified sophorolipid was preferably prepared by the following method: (1) lactone sophorolipid was added into an organic solvent, which was further heated and stirred to obtain the lactone sophorolipids solution; and (2) sulfonating agent was added into the solution of the lactone Sophoroilpids to obtain the sulfonated modified Sophorolipids via sulfonation reaction.

2.3.3 Performance evaluation of the new leaching agent

According to the elution results (Table 2), the removal rate of petroleum in highly PCS by conventional eluent sodium dodecyl sulfate (SDS) was only 9.1%. The oil removal rates of the newly developed eluent RPOS, sulfonated modified sophorolipids, and methyl esterified modified sophorolipids were 21.5%, 15.9% and 18.7%, respectively, which could effectively increase the oil removal rate by more than 200%.

Table 2 Removal effect of new eluent on petroleum

Type of eluent	**Removal rate of petroleum/%**
SDS	9.1
RPOS	21.5
Sulfonated modified sophorolipid	15.9
Methylated modified sophorolipid	18.7

2.3.4 Intensification study of the leaching system

In this study, elution conditions such as elution temperature, elution time, and solid-liquid ratio were investigated and optimized, and ion regulators and synergists were selected. The removal of petroleum in the contaminated sites was carried out based on the optimized conditions of the above study. An optimized leaching system significantly improves the removal rate of petroleum in highly contaminated PCS, with a removal rate of up to 92.1% (Table 3). The technique has strong petroleum removal capability for the leaching pretreatment of heavily oil-polluted soil.

Table 3 Test results of petroleum removal rate in highly petroleum-contaminated soil

Case NO.	Content of petroleum in soil after leaching/ (mg/kg)	Removal rate of petroleum/%
1	31 689	70.1
2	25 773	75.7
3	13 774	87.0
4	8 421	92.1
5	21 156	80.0
6	27 627	73.9
7	9 828	90.7
8	73 215	30.9
9	89 178	15.9
10	75 114	29.1
11	47 375	55.3

2.4. Development and Evaluation of New Eluent

2.4.1 Isolation and screening of hydrocarbon-degrading bacteria

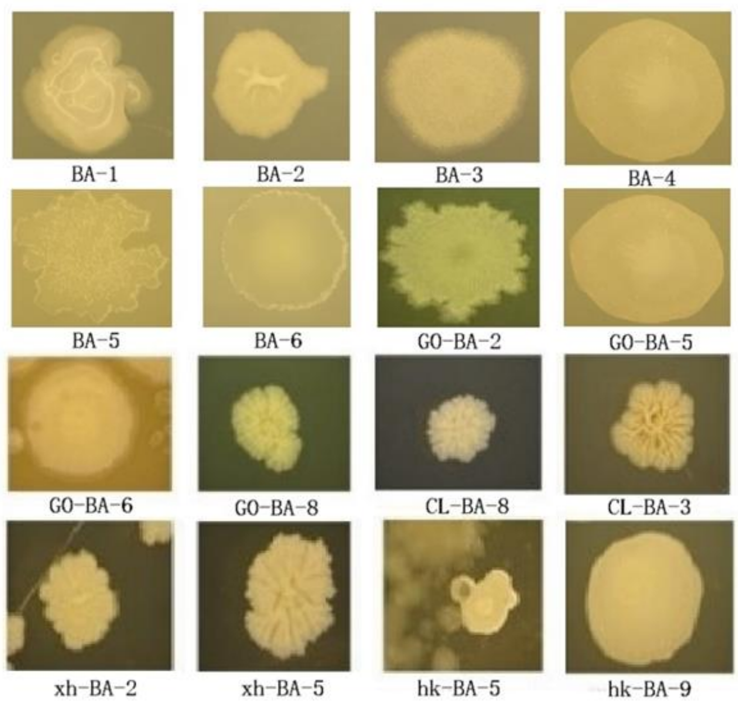

Fig. 4: Community structure of screened strains

Total of 16 strains of hydrocarbon-loving microorganisms were obtained through isolation and screening (Fig. 4). The strains were identified as Pseudomonas, Bacillus, Microbacterium, Arthrobacter and Micrococcus. These microorganisms are commonly found in soil and have the ability to degrade PHs. It was found that GO-BA-6, CL-BA-3 and xh-BA-2 were the three strains with an outstanding ability to metabolize crude oil by optimizing hydrocarbon-loving bacteria.

2.4.2 Optimization and enhancement of microbial degradation system

The microbial degradation system was optimized by controlling soil nutrients and optimizing the filler. The microbial degradation ability of petroleum pollutants was further enhanced by combining the aforementioned results with the optimization of bio-friendly oligomeric surfactant and the study on the compatibility of sulfonated modified sophorolipids with exogenous hydrocarbon-loving bacteria GO-BA-6, CL-BA-3 and xh-BA-2.

The experimental results showed that the optimized microbial degradation system could effectively improve the degradation rate of PHs and shorten the treatment cycle. The best performing group can reduce the content of petroleum hydrocarbons to 4.3 mg/g within 30 days, meeting the Chinese screening value standard for Class II construction land (PHs < 4. 5 mg/g). In the control group, the content of TPH was 8. 5 mg/g on the 30th day, and the degradation rate of TPH was significantly lower than that in the accelerator group. Meanwhile, the modified sophorolipids had good compatibility with the above exogenous hydrocarbon-loving bacteria. It had a slight bacteriostatic effect under the mass content of modified sophorolipids > 3%, while under other conditions, the exogenous bacteria could grow well with an abundance of > 10^8/mL.

2.5. Study on the establishment of a new leaching-bioremediation process system and its field application effect

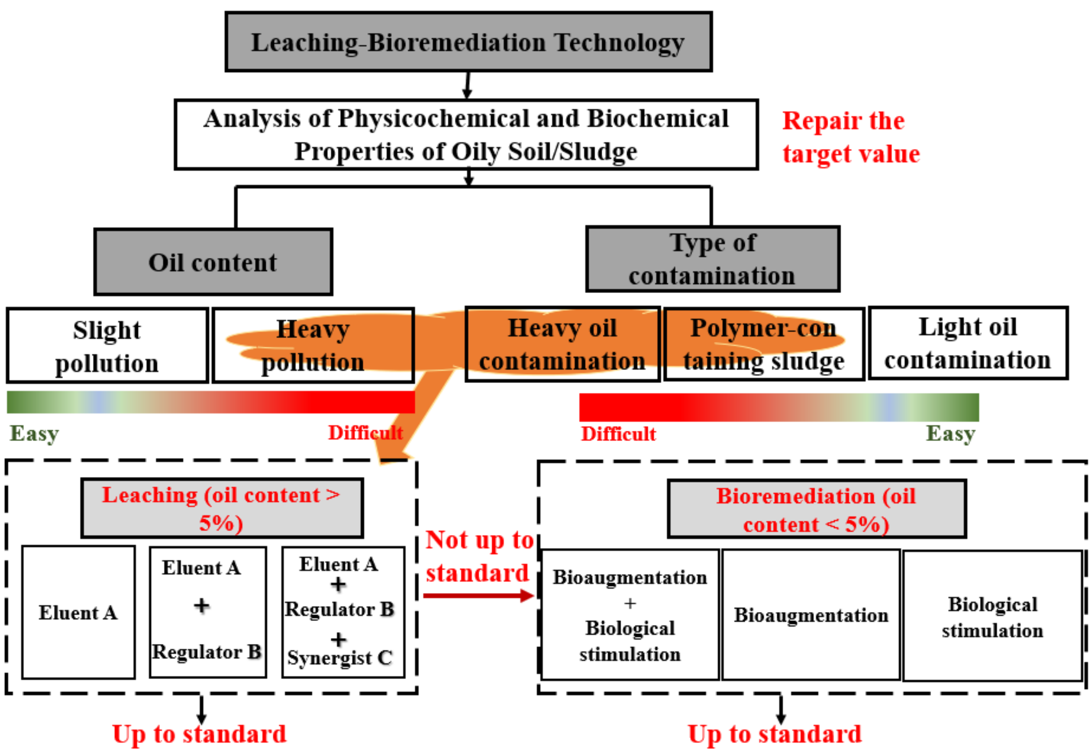

Fig. 5: The new leaching-bioprocess remediation system

Based on the prior studies, we have sorted out and established a complete set of process flow and technical systems (Figure 5), which started with determining the repair target value. Furthermore, the physicochemical and biochemical properties of oil-contaminated soil/oil sludge sand were analyzed. According to the oil content, pollution can be divided into two major categories; slight pollution and heavy pollution. The soil with heavy pollution needs to be pretreated by a new leaching process, followed by bioremediation if the quality (after the prior treatment) is below standard. For the leaching process, the combination of leaching agent, regulator and synergist was used (from easy to difficult) to achieve high oil removal effectiveness. The soil with slight pollution or leached soil could conduct the bioremediation process until reaching the standard. For the bioremediation process, the combination of biostimulation and bioaugmentation was also used to achieve the targeted bioremediation.

Fig. 6: The remediation process and site construction of the ground oil sludge treated with the leaching-bioprocess remediation

Based on the lab-established framework for bioremediation, the ex-situ remediation was carried out for 12000 t of ground oil sludge in the field (Figure.6). According to the previous test results, the oil content was between 5.7% and 9.6% (Figure.7a). According to the disposal ideas of different types of PCS, the "leaching -biological" process was used for treatment. The results showed that, as expected, the oil removal efficiency of leaching could be more than 60%.

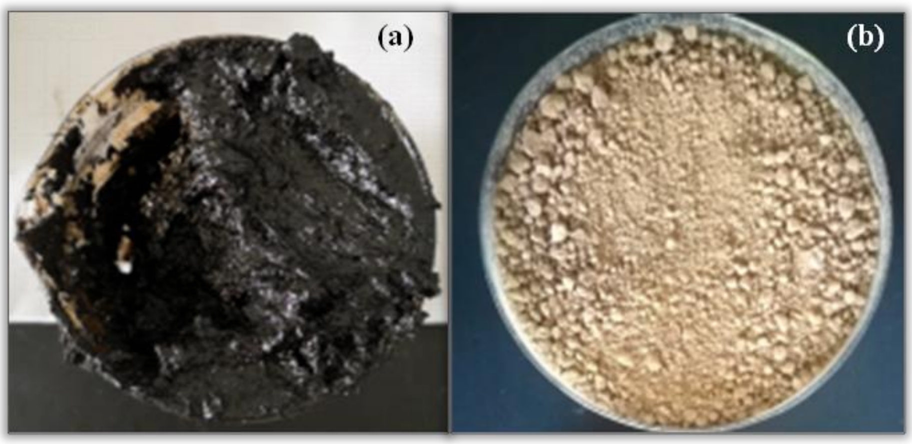

Fig. 7: The morphology of the ground oil sludge before (a) and after treated with the leaching-bioprocess remediation

Field remediation tests were carried out for various types of PCS produced by petrochemical enterprises, including ground oily sludge, tank bottom sludge, modified sludge, polymer-bearing oily sludge and decommissioned well sites by using the developed leaching-biological coupling remediation system.

The ex-situ remediation showed that the oil removal efficiency of leaching could be > 60%, which meets the expected requirements. Moreover, the oil mass fraction of the ground oil sludge could be reduced to less than 0.45% after bioremediation for 6 to 9 months (Figure.7b). The oil content of the modified sludge was reduced to less than 5% after leaching treatment. In comparison, the oil content of the leached modified sludge residual sand was reduced to less than 0.42% after ectopic biological disposal (within 6 to 8 months of remediation).

After the polymer-containing oil sludge subjected to oxidation gel break and leaching, the mass fraction of the oil reduced to less than 3%. Moreover, the mass fraction of the oil was reduced to be less than 0.38% after the leached residual sand treated by a bioremediation technology. The treatment period for remediation was 5-6 months.

The preliminary investigation and sampling analysis for the in-situ remediation test of five decommissioned well sites (2,000 m^2), it was found that the oil content of the soil in the well site was between 2.6% and 4.3%, which could be directly treated by the biological method. The oil content was less than 0. 45% after implementation.

The field remediation test shows that the PCS produced in the process from upstream mining to downstream refining in petrochemical enterprises can effectively meet the requirements of environmental protection standards while restoring the normal function of the soil after being treated by the developed leaching-biological coupling process. This has the advantages of a short remediation cycle and low cost.

3. Conclusion

In this study, a new leaching agent system was developed and synthesized, including oligomers, to construct the leaching process and optimize the soil leaching process parameters. The new agent has improved skeleton structure, green bio-based surfactant molecules, and synergists. Based on the characteristics of the leaching soil and its flora structure, more than 60 strains of petroleum degradation bacteria were isolated and screened. Furthermore, suitable bacteria for degradation were cultivated, the nutritional formula and process flow were optimized, and the microbial agent formula for heavy oil, polycyclic aromatic hydrocarbons and other pollutants were established.

According to the physical characteristics of different types of oily sludge and soil, an economical and efficient remediation technology system and supporting implementation process were established, and finally, a "leaching-bioremediation" coupling treatment process was formed. The PHs content of the actual contaminated soil after the treatment was lower than 0.45%, and 12,000 t of PHs contaminated soil was remediated. Through the study of the elution-bioremediation process, the establishment of economical and environmentally friendly remediation technology and the process will improve our knowledge to solve the sudden oil pollution in contaminated areas and the environmental protection solution of historical problems.

Acknowledgements

The research was supported by the National Natural Science Foundation of China [grant number 42207083].

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