

## Biological Treatment Technology of Oily Sludge

Long Wenyu, Zou Linlin, Shao Luhua

Liaoning Shihua University, Fushun, Liaoning, China

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**Abstract:-** In petroleum refining and wastewater treatment process, petrochemical enterprises produce a large amount of oily sludge which mainly comes from the oil separator, flotation pool, biological activated sludge, the tank of crude oil dehydration, oil tank and slop tank etc. Therefore oily sludge can be divided into sludge from oil tank, scum mud and landing mud. The sludge composition is so complex because of containing hydrocarbons, benzene, phenol, anthracene and other substances with the odor and toxicity. It's generally made up of the oil in water, water in oil and suspended solids. And it has features of full emulsification, larger viscosity and solid hardly completely settling. With the continuous expansion of the scale of production equipment, these enterprises face also more environmental pressure when they make economic benefits. The resource utilization and harmlessness of solid waste is the important content for the construction of saving society. According to the new regulations and standards, it is difficult to meet the requirements for many enterprises in disposal of oily sludge, which results in increased enterprise pollution burden and highlighted environmental pollution problems. In this paper, the research status and development of oil sludge biological treatment technology were reviewed including bioreactor method, bioaugmentation method, biological land tillage method, biological flotation method and so on. All these methods were compared and commented before the future research suggestion were presented.

**Keywords:-** Biodegradation, Oily sludge, Lab experiment, Oil removal rate, Harmless, soil

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### I. INTRODUCTION

Oily sludge is a kind of oily solid waste in the process of oil transportation, exploitation, refining, and oily wastewater treatment, and it is colloid system composed of petroleum hydrocarbons, colloid, asphaltene, sand, inorganic flocs, organic flocs, water and so on. Oily sludge contains hundreds of toxic compounds in which some as benzene, polycyclic aromatic hydrocarbons are carcinogenesis, teratogenesis and mutagenicity. The United States Environmental Protection Agency listed oily sludge as Priority Pollutants. And China also regards oily sludge as the national hazardous waste. Harmless, reduction, resource treatment processing of oily sludge have attract more attentions, such as demulsification method, profile control method, flotation method, solidify method, chemical cleaning method, burning method, extraction method, pyrolysis method, biological method and so on. Besides, the biological method is simple, low cost and low energy consumption. In this paper, biological treatment technology were introduced, including bioreactor, biological flotation and so on. Moreover, future development direction of biological treatment method of oily sludge was put forward, which will provide references to related research.

### II. STUDY ON BIOLOGICAL TREATMENT TECHNOLOGY OF OILY SLUDGE

The main mechanism of biological treatment method is that microbe assimilates with petroleum hydrocarbons as carbon source to complete mineralization. Then petroleum hydrocarbons are transformed into friendly inorganic substances such as CO<sub>2</sub> and H<sub>2</sub>O. More and more scholars pay attention to it in recent years.

### III. BIOREACTOR METHOD

Bioreactor is a kind of muddy container with oily sludge added to the nutrient medium. An institute in Spain <sup>[1]</sup> treated the soil polluted by diesel oil with bioreactor. The bioreactor (40 cm long × 25 cm wide × 3 cm high) was a borosilicate glass container and temperature was controlled in the range of 15 - 25 °C. The results showed that after 45 days, the degradation rate could reach more than 90%. Northeast Forestry University in china <sup>[2]</sup> invented a new type of bioreactor and initially applied microbial-electric coupling technique to the treatment of oily sludge. Then field test was conducted in Daqing Oil Field. The results showed that when vertical electric field (electric field strength 3V/cm) was chose and bacterium were added, oil removal efficiency was greatly improved. The oil removal rate of skin layer reached 74.07% and the oil removal rate of underlayer reached 85.60%.

Also, Institute of Applied Ecology, Chinese Academy of Sciences <sup>[3]</sup> has done much research. The experiment samples are shown in table 1.

**Table 1.** Experiment samples

Label	A	B	C	D	E
				Ventilation	
			Ventilation		
Treatment	Contrast	Ventilation	Agent	Agent	Agent,salt ,fertilizer
		Agent	Fertilizer	Fertilizer,inorganic	
				Salt	

Note: ventilation time were 30 minutes four times a day at  $0.7 \text{ mmmmmmmL}\cdot\text{min}^{-1}$ . The adding amount of microbial inoculum and fertilizer were 5% and 10%. Inorganic salt was  $\text{NH}_4\text{NO}_3$ ,  $\text{CH}_3\text{COONH}_4$  and  $\text{KH}_2\text{PO}_4$ .  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N and  $\text{PO}_3^{4-}$ -P content of alien-soil were 40, 20 and 20  $\text{mg}\cdot\text{kg}^{-1}$ .

Each treatment reactor was added 600 g substrate. Substrate included Liaohe oily sludge and special soil of ratio 1:1. Special soil, screened by 2mm, comprised 5% crude oil (thin oil and thickened oil was 1:1). At the same time, the proportion of water and soil was 1:1, and treatment temperature was at 25°C

Then TPH residue was determined every 15 days. The results showed that TPH degradation rate at aerobic condition was more than that at anaerobic condition in bioslurry reactor. Reactor D treatment effect was the best at aerobic condition. After 75d treatment, TPH decreased from  $43.39 \text{ g}\cdot\text{kg}^{-1}$  to  $0.72 \text{ g}\cdot\text{kg}^{-1}$ , and removal rate was 98.3%.

In a word, Bioreactor method can accelerate biodegradation of hydrocarbons by controlling temperature, oxygen, nutrients and so on.

#### IV. BIOAUGMENTATION METHOD

Bioaugmentation method is a method of adding efficient microbial inoculants into oily sludge, so as to accelerate the biodegradation of petroleum hydrocarbons. It is divided into single bacteria strengthening and bacterial consortium strengthening.

#### V. SINGLE BACTERIA STRENGTHENING

At present, Xi'an University of Architecture and Technology<sup>[4]</sup> has done much research. The lab experiment is as follows. (1) the preparation of *Pseudomonas aeruginosa* NY3 bacterial suspension: NY3 were inoculated on broth peptone medium at 30°C and 160 r/min, aerobic oscillation 24h and  $\text{OD}_{600 \text{ nm}} 1.52\pm 0.08$ . (2) Degradation experiments of oily sludge: 10mL bacterial suspension of NY3 was inoculated on oil sludge medium at 30°C and 160r/min. There were two sample groups: germ-free, adding cofactor I, purified rhamnolipid and cofactor II; without NY3, cofactor I, purified rhamnolipid and cofactor II. It was necessary to sample at regular time. The results showed that the optimum degradation temperature of NY3 was 30°C and the optimum pH value was 7.2-7.5. At suitable ventilation and oxygen supplied, the removal rate of petroleum hydrocarbons could be up to 82% after 168h of degradation.

TERI University<sup>[5]</sup> repaired contaminated soil by acidic oily sludge. In the process, *Candida digboiensis* TERI ASN6 was used. The results showed that when pH was low, the bacteria were capable to degrade petroleum hydrocarbon. TPH decreased from 184.06 g/kg to 7.96g/kg. Indian Institute of Technology Roorkee<sup>[6]</sup> isolated and purified a strain from the soil samples of Ankleshwar. The strain was identified as *Bacillus subtilis* DSVP23 by 16SRNA technology. Meanwhile, its oil removal characteristic was researched. The results showed that the long chain alkane (C12-C30) and aromatic hydrocarbons were effectively degraded. National Environmental Engineering Research Institute (NEERI) in India<sup>[7]</sup> obtained two strains of hydrocarbon degradation bacterias (Chry2 and Chry3) from the oily sludge in Gujarat refinery of India. Then the oil removal characteristics were researched. The results showed that oil removal rate were 15% and 17% respectively.

#### VI. BACTERIAL CONSORTIUM STRENGTHENING

At present, northwest university in china<sup>[8]</sup> has done more research. The lab experiment is as follows. Composed flora Flo.2 bacteria cultured from the bottom tank sludge of Changqing Oil Field, which comprised of PB2 (*Baeillus* sp.), PB1 (*Baeillus* sp.), SY-3 (*Pseudomonas* s sp.) and SY-8 (*Pseudomonas* s sp.). Flo.2 flora strains were inoculated on seed culture medium to culture 36h. Then concentrations of PB2, PB1, SY-3 and SY-8 in the incubation fluid were  $1.51 \times 10^7$  /ml,  $1.34 \times 10^7$  /ml,  $1.23 \times 10^7$  /ml and  $1.42 \times 10^7$  /ml. Flora strengthening test had four groups. Every group needed a lot of tapered flask, and every tapered flask contained 80g tank bottom sludge of Changqing Oil Field. In group I, inoculation bacteria ,according to L9 (34) orthogonal experiment, was inoculated in tapered flask with 80mL fresh seed culture medium. And bacteria were cultured 24h and centrifuged 3 times and then added in the tapered flask containing 80g sludge and 80ml inorganic salt medium. Group II was contrast one. Group III was without inoculated bacteria and inorganic salt

medium. Group IV was added flora Flo.2 bacteria without inorganic salt. Oil content of bottom tank sludge sample was determined every two days and then oil degradation rate was calculated. The results showed that adding bacteria and inorganic nutrients could improve the oily sludge biological biodegradation, and petroleum hydrocarbon degradation rate reached 71.4%. University of Belgrade in Serbia <sup>[9]</sup> isolated a bacterial consortium from a petroleum sludge sample. The bacterial consortium which was able to efficiently degrade petroleum hydrocarbon was made up of strains from the genera *Pseudomonas*, *Bacillus* *Achromobacter* and *Micromonospora*. In addition, two groups of experiments were carried out. The results showed that the Oil removal rate was up to 82 – 88% in oily sludge experiment and the oil removal rate was up to 86 – 91% in oily sludge-contaminated soil experiment. Tata Energy Research Institute in New Delhi <sup>[10]</sup> performed four experiments by bacterial consortium strengthening method. The results showed that under the condition of adding a bacterial consortium (1kg carrier-based bacterial consortium/10 m<sup>2</sup> area) and nutrients, the degradation rate of TPH was up to 90.2% in 120 days. School of Environment at Beijing Normal University <sup>[11]</sup> introduced "Rhoder" inocula from the Moscow State University to treat oily sludge. The inocula contained two kinds of high activity strains which were isolated from petroleum. Besides three groups of experiments were performed in order to obtain the optimum processing parameters in oily sludge treatment and the experiments were showed in table 2. The results showed that when inocula and sawdust were added, oil content of sludge decreased from 24% to 11% after 45d and the removal rate was up to 54%.

**Table 2. Experiment**

Serial number	Type	Gross weight /g	Rate of water content /%	Added substance	Fertilizer
1	Control experiment	1050	50.5	--	--
2	Inocula	1130	55.4	Inocula	KNO <sub>3</sub> 2.9g, K <sub>2</sub> HPO <sub>4</sub> ·3H <sub>2</sub> O 0.5g
3	Inocula+ Sawdust	1190	55.4	Inocula+ Sawdust	KNO <sub>3</sub> 2.9g, K <sub>2</sub> HPO <sub>4</sub> ·3H <sub>2</sub> O 0.5g

## VII. BIOLOGIC FLOTATION METHOD

Biologic flotation method is a new treatment method of oily sludge. In the process, most oil was removed through microorganism producing gas.

At present, Chengdu Institute, Chinese Academy of Sciences <sup>[12]</sup> has done much research. The lab experiment is as follows.

Medium (1L): NaNO<sub>3</sub> 3g, KH<sub>2</sub>PO<sub>4</sub> 1g, MgSO<sub>4</sub>·7H<sub>2</sub>O 0.5g, KCl 0.5g, FeSO<sub>4</sub>·7H<sub>2</sub>O 0.01g, glucose 3g, corn steep liquor 4g. Medium was fixed on the bottom of air flotation equipment. Then the strain was inoculated at culture medium. Air flotation equipment was placed in the temperature control flume to keep constant temperature. The results showed that the biological flotation optimal operation parameters were temperature 40 °C, dilution rate of 98%, adding 3.75% bacteria quantity, adding 0.25% sugar, in which the removal rate of the crude oil was up to 95%. Therefore, the use of mixed strains for biological flotation was beneficial to the improvement of the recycled oil content. Faculty of Science of Alexandria University in Egypt <sup>[13]</sup> researched biological flotation technology and mainly studied whether microorganism was immobilized affected on Petroleum hydrocarbon degradation efficiency. As a result, in the treatment of oily sludge of high concentration petroleum hydrocarbons, 90% of the hydrocarbons in the oily sludge could be degraded by immobilized *Candida parapsilosis* within three weeks, while only 27.5% was degraded by free *Candida parapsilosis* in the same period. Besides, the structure and characterization of oily sludge were studied. The result was shown in table 3 and table 4.

**Table 3. Structure and characterization of oily sludge**

	Water content/%	Ash content/% dry wt	Hydrocarbon content/% dry wt	Extractable material/% dry substance	pH value
Minimum	15	60	3	3	6.5
Maximum	70	92	30	32	7.5
Frequent	35-70	70-85	5-15	6-15	6.5-7.5

**Table 4.** Comparison of oily sludge biological treatment method

serial number	treatment method	Oil removal rate	degradation rate	occupied area	oil retrieval	inoculation	nutrient	Investment and operation cost	secondary pollution
1	Compost method	80%	Slow	big	No	Yes	Yes	Low	No
2	Bioreactor method	98%	Relatively fast	Small	Part	Yes	Yes	Low	No
3	Single bacteria strengthening	82%	Slow	Small	No	Yes	Yes	Low	No
4	Bacterial consortium strengthening	86-91%	Slow	Small	No	Yes	Yes	Low	No
5	Landfarming method	83%	Slow	Relatively big	No	No	No	Low	Possible
6	Phytoremediation method	85%	Slow	Relatively big	No	Yes	No	Low	No
7	Biologic flotation method	95%	Slow	Small	No	Yes	No	Low	No

## VIII. CONCLUSIONS

With the rapid development of petrochemical industry, how to handle reasonably oily sludge has become a bottleneck for the development of enterprises. The harmless treatment of oily sludge will be the development direction of research. Biological method is a promising technology in harmless treatment technology. Generally, biological treatment of oily sludge are mainly divided into two categories including putting microorganisms that can degrade efficiently petroleum hydrocarbon in oil sludge such as *Bacillus* and adding nitrogen and phosphorus nutrients to stimulate petroleum hydrocarbon biodegradation activity of indigenous microorganisms in oily sludge. The author suggests that in the future the following works should be done including screening the new strain that can high efficiently decompose petroleum hydrocarbons, the improvement of traditional technology, optimizing operating conditions and shortening the processing cycle.

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