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Degradation Kinetics of Petroleum Contaminants in Soil-Water Systems

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Abstract On the basis of site investigation and sample collection of petroleum contaminants in the soil-water-crop system in the Shenyang-Fushun sewage irrigation area, the physical-chemical-biological compositions of the unsaturated zone is analyzed systematically in this paper. At the same time, the degradation kinetics of residual and aqueous oils is determined through biodegradation tests. The studies show that dominant microorganisms have been formed in the soils after long-term sewage irrigation. The microorganisms mainly include bacteria, and a few of fungus and actinomycetes. After a 110-days' biodegradation test, the degradation rate of residual oil is 9.74%–10.63%, while the degradation rate of aqueous oil reaches 62.43%. This indicates that the degradation rate of low-carbon aqueous oil is higher than that of high-carbon residual oil. In addition, although microbial degradation of petroleum contaminants in soils is suitable to the first-order kinetics equation, the half-lives of aqueous oil, No. 20 heavy diesel and residual oil in the surface soils (L2-1, S1-1 and X1-1) are 1732 h, 3465 h and 17325 h, respectively.

Key words: dominant microorganisms, soil residual oil, aqueous oil, biodegradation rate

1 Introduction

Petroleum hydrocarbons contain many kinds of toxic substances, and their toxicity increases in a sequence of alkenes, cycloalkanes and aromatic hydrocarbon. It is acknowledged that many carcinogenic, teratogenic and mutagenic chemical substances come from petroleum contaminants, such as 3, 4-benzo-pyrene, benzanthrene and so on. The aqueous petroleum in soils can be concentrated in the roots, stalks, leaves and seeds of crops under the wastewater irrigation, which result in the reduction of grain quality. In addition, the excessive adsorption of petroleum on the soil surface may influence the soil permeability and change the growth environment of crops. What needs to be pointed out is that petroleum hydrocarbon can solve cell membranes, disturb the enzyme system and result in the pathological changes of the viscera like kidney and liver after entering the human body (Han et al., 1988).

The initial knowledge on the relation between petroleum and microorganisms commenced in the 1940s. At that time, the interest was concentrated on the relationship of microorganism and petroleum formation. In the 1950s and 1960s, the basic theory and application of hydrocarbon degradation became a new research field. Since the sinking of the super oil tanker, *TORRY CANYON* in 1967, many microbiologists began to study petroleum contamination ecology, and did some research on the fate and influence of petroleum contaminants (Huang et al., 1991; Lu, 2004). Alexander (1977) identified more than 30 kinds of hydrocarbons degrading microorganisms, which can live in surface water, soil and groundwater. Atlas (1981) analyzed water samples from 12 petroleum-contaminated aquifers, which shows that there are about 100 bacteria per milliliter water.

In addition, Kincannon (1977) applied land farming to treat the petroleum-contaminated soil. As a result, alkenes reduced to 80%–82% after 18 months' degradation. Therefore, they think the method can be used to treat petroleum contaminants in the surface layer. Raymond and Hudson (1976) and Jobson (1974) added 6 types of oil products to soils and then planted rutabaga and broad bean in the east, middle and west districts of the USA. The research results showed that the average concentration of various oils was reduced by 48.5%–90% after one year's degradation.

In the 1970s and 1980s, Liu et al. (1981) and Liu and Yang (1984) studied the microbial ecology and degradation in the Shenyang-Fushun sewage irrigation area, which indicated that there was not evident petroleum accumulation due to the formation of endemic microorganisms and their degradation after 40–50 years petroleum sewage irrigation. In addition, through the column planigraphy test, Zhang and Li (2002) pointed out there was a sequence of degradation rate for three petroleum hydrocarbons: aromatic > aliphatic > resins.

Considering the soil properties, microbial community and the type of petroleum contaminants in the Shenyang-Fushun irrigation area, the kinetics of residual oil, No.20

heavy diesel and aqueous oil in different layer are determined in this paper.

2 Physical Composition and Microbial Characteristics of Test Soils

All the soil samples are collected from the Shenyang-Fushun sewage irrigation area. Considering the history of petroleum contamination and the constitution of unsaturated zone, three sampling sites are selected in Lishizhai, Sifangtai and Xingnong respectively. In addition, the soil profiles are re-divided into the top layer and bottom layer due to the discrepancy of soil properties. The mechanical composition and main characteristics for the soil samples are shown in Table 1.

The microbial isolation and identification show that endemic oilphilic microorganisms have occurred in the irrigation area after a long-term petroleum sewage. Bacteria are the majority endemic microorganisms, which mainly includes *Pseudomonas*, *Xanthomonas*, *Plesiomonas*, *Acinetobacter*, and *Brevibacterium*. In addition, there are a few of fungus and actinomycetes, which mainly includes *Penicillium* and *Aspergillus* (see Table 2).

3 Petroleum Degradation Test

3.1 Methods

Since the composition of the residual oil in soil is different from that of petroleum product and aqueous oil, their degradation tests are conducted separately.

As for the degradation test of residual oil, 20 g of soil samples in the top layer (L2-1, S1-1 and X1-1) with the natural moisture (about 25%) are added into a small aluminum box in 20 replicate. And then, they are cultivated in an incubator at 20°C. The oil contents in soils are measured on the days of 0, 2, 4, 8, 15, 25, 40, 60, 110 (see Table 3).

The No. 20 heavy diesel is solved into ligroine for the degradation tests of oil product, and their mixture is added to the soil samples (L2-1, L2-2, S1-1, S1-2, X1-1, X1-2) according to the addition of oil in Table 3. And then, they are cultivated in an incubator at 20°C and with a water content 25% after 24 hours' volatilization at the ambient temperature.

As for the aqueous oil degradation test, 100 g of soil sample is added into 1000 ml tap water supersaturated with petroleum, in which the ratio of carbon, nitrogen and phosphor (C: N: P) is 100:10:1. After 30 days' inoculation, the inoculated petroleum-saturated solution is added into a kind of clean sandy clay at 25% soil moisture. And then, the samples are cultivated in incubator at the 20°C. The oil contents are also determined periodically. The results are listed in the Table 3.

Based on the tests mentioned above, the results can be drawn as follows:

(1) The degradation rate of residual oil accumulated in the soils is about 10% after 110 days' cultivation, which is the lower than that of the No. 20 heavy diesel and the soluble oil;

(2) The degradability of the No. 20 heavy diesel is higher; its degradation rate can reach above 45%. There are the background oil contents in the top soils of L2-1, S1-1 and X1-1, so in the soil it is the mixture oil after the addition of No. 20 heavy diesel into the soil. Therefore, their degradation rate is between the rate of residual oil and the rate of No. 20 heavy diesel;

(3) The degradation rate of the aqueous oil is the highest (62.43%).

3.2 Kinetics characteristic of oil degradation

Based on the test results in Table 3, the petroleum content in the soil decreases with the time of degradation. And the relationship can be expressed as follows:

$$C = C_0 e^{-\lambda} \quad (1)$$

Table 1 Mechanical composition and main characteristic of soil samples

Sample site	Layer	Sample code	Soil mechanical composition							pH	Organic content (g/kg)	Total porosity (%)	Density (g/cm^3)	Soil texture
			Sample depth (cm)	<0.001 (mm)	0.001–0.005 (mm)	0.005–0.01 (mm)	0.01–0.05 (mm)	0.05–0.25 (mm)	>0.25 (mm)					
Lishizhai	top layer	L2-1	0–30	7.80	8.40	6.40	33.88	23.60	20.92	6.25	40.81	47. 9	1.38	loam
	bottom layer	L2-2	30–130	3.24	4.06	2.23	13.17	42.33	34.97	6.95	4.87	43.8	1.49	sandy loam
Sifangtai	top layer	S1-1	0–25	11.78	13.43	9.92	50.23	9.56	5.08	5.55	74.02	50.2	1.32	silty clay
	bottom layer	S1-2	25–130	10.10	10.09	7.21	50.48	18.70	3.42	6.30	11.4	43.0	1.51	silty clay
Xingnong	top layer	X1-1	0–35	8.93	14.74	7.06	56.89	11.07	1.31	5.25	21.66	49.8	1.38	silty clay
	bottom layer	X1-2	35–130	8.95	15.81	10.19	48.69	16.07	0.29	6.45	7.01	46..8	1.41	silty clay

Table 2 Dominant microorganisms in the petroleum contamination area*

Soil sample	Bacteria	Fungi
HCA top layer	*Bacillus*	*Penicillium freguentan w.*
	Plesiomonas	*Penicillium citrinum*
	Pseudomonas	*Penicillium roqueforti*
	Acinetobacter	*Aspergillus versicolor*
	Kurthia	*Penicillium patulum*
	Brevibacterium	*Cladosporium herbarum*
bottom layer	*Bacillus*	*Penicillium chrysogenum*
	Plesiomonas	*Penicillium veimiculatum*
	Arthrobacter	*Aspergillus niger*
	Xanthomonas	*Aspergillus versicolor*
	Acinetobacter	
	Pseudomonas	
MCA top layer	*Bacillus*	*Penicillium chrysogenum*
	Arthrobacter	*Penicillium italicum*
	Plesimonas	*Penicillium implicatum*
	Staphylococcus	
bottom layer	*Bacillus*	*Aspergillus terreus*
	Plesimonas	*Aspergillus versicolor*
	Pseudomonas	*Penicillum chrysogenum*
	Kurthia	*Penicillum italicum*
	Enterobactiaceae	*Alternaria*
		Penicillum roqueforti
LCA toplayer	*Bacillus*	*Penicillium veimiculatum*
	Pseudomonas	*Penicillium funienlosum*
	Xanthomonas	*Penicillum italicum*
	Flavobactcriium	*Aspergillus wentii*
	Arthrobacter	*Cladosporium herbarum*
	Enterobactiaceae	
bottom layer	*Bacillus*	*Paecicomyces varioti*
	Plesimonas	*Penicillium citrinum*
	Arthrobacter	*Aspergillus candidus*
	Xanthomonas	*Aspergillus wentii*
	Staphylococcus	*Aspergillus versicolor*

* HAC: heavy contaminated area; MCA: medium-contaminated area; LCA: slightly contaminated area.

where C_0 is the initial oil concentration in the used soil or water, C is the instantaneous oil concentration in the soil or water and λ is the degradation constant.

In addition, a first-order kinetics equation of biodegradation can be derived from the Eq. (1). It can be expressed as:

$$dC / dt = -\lambda C \quad (2)$$

At the same time, the half life ($t_{1/2}$) of oil degradation in soil water can be derived from the Eq. (2), and it can be expressed as:

$$t_{1/2} = 0.693/\lambda \quad (3)$$

The degradation rate can be reflected from the λ and $t_{1/2}$. The bigger the value of λ (or the smaller the value of the $t_{1/2}$), the faster the degradation reaction.

The kinetic equations and eigenwerts of oil degradation in soil and water can be drawn from the numerical calculation (see Table 4). The results indicate that the half-lives of the aqueous oil, the No. 20 heavy diesel and the residual oil in the topsoil (L2-1, S1-1 and X1-1) are 1732 h, 3465 h and 17325 h respectively.

4 Conclusions

On the basis of the up-to-date researches and petroleum contamination problems of soil-water-crop system in the Shenyang-Fushun sewage irrigation area, the physical-chemical-biological compositions of unsaturated zone have been analyzed systematically in this paper. At the same time the kinetics characteristic of residual oil and the soluble oil in the soil are studied. According to the intensive tests stated above, the following conclusions can be derived:

(1) The studies show that there are dominant microbial populations in the soils after long-term sewage irrigation. Among the dominant microorganisms, the bacteria are the major species, and the fungus and the actinomycetes are the

Table 3 Residual oil content in the soil water

Sample	oil content (mg/l)	Oil content in the soil water (mg/l)										degradation rate (%)
		0 d	2 d	4 d	8 d	15 d	25 d	40 d	60 d	80 d	110 d	
L2-1	0	676.3	671.5	652.1	638.9	632.4	631.7	622.4	618.0	609.0	604.4	10.63
	272	931.0	911.4	876.0	841.1	838.2	822.3	799.1	764.5	731.9	716.0	23.09
S1-1	0	1404.7	1396.1	1389.2	1342.1	1326.2	1311.3	1301.4	1281.7	1269.2	1267.9	9.74
	272	1710.1	1711.2	1678.9	1644.1	1590.0	1521.1	1485.0	1445.8	1421.7	1420.9	16.91
X1-1	0	171.4	174.4	168.9	162.1	160.0	159.1	157.1	154.0	156.2	153.5	10.53
	136	313.2	302.9	284.0	262.2	240.1	230.4	210.1	197.0	189.2	192.1	38.70
S1-2	68	97.9	92.3	89.2	78.2	70.4	61.7	58.3	55.6	56.1	53.7	45.15
X1-2	68	98.1	91.4	85.1	72.4	67.3	61.4	59.0	56.4	56.7	51.3	47.71
L2-2	68	94.4	89.7	82.7	78.5	71.6	66.4	57.1	52.6	53.1	51.9	45.02
Aqueous oil	18.1	18.1	16.9	15.2	14.3	12.6	11.3	9.6	8.8	7.9	6.8	62.43

Table 4 Kinetics characteristic of petroleum degradation

Soil sample	Oil content (mg/l)	Kinetics equation	Coefficient	degradation constant (l/h)	half live (h)
L2-1	0	$y=654.8e^{-0.00004x}$	0.7358	0.00004	17325
	272	$y=885.1e^{-0.00009x}$	0.8973	0.00009	7700
S1-1	0	$y=1369e^{-0.00004x}$	0.7715	0.00004	17325
	272	$y=1649.1e^{-0.00007x}$	0.8192	0.00007	9900
X1-1	0	$y=167.05e^{-0.00005x}$	0.6675	0.00004	17325
	136	$y=277.69e^{-0.0002x}$	0.7871	0.0002	3465
S1-2	68	$y=82.23e^{-0.0002x}$	0.7008	0.0002	3465
X1-2	68	$y=81.23e^{-0.0002x}$	0.7227	0.0002	3465
soluble oil	18.1	$y=17.209e^{-0.0004x}$	0.968	0.0004	1732

minors.

(2) According to the degradation tests, the residual oil degradation rate may reach 9.74%–10.63%, while the degradation rate of aqueous oil is as high as 62.43%.

(3) Although microbial degradation of petroleum contaminants in the soils is suitable to first-order kinetics equation, the half-lives of aqueous oil, No. 20 heavy diesel and residual oil in the surface soils (L2-1, S1-1 and X1-1) are 1732 h, 3465 h and 17325 h, respectively.

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