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Effect of Volatile Contaminant Types on SVE Remediation Efficiency: A Case Study of Dongxin Oil Production Plant

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ABSTRACT. An experimental model is established by simulating SVE to collect the contaminated soil samples near the wells of Dongying Dongxin oil production plant in Shandong Province as a polluted medium, ethanol, n-propanol, n-butanol as the target pollutant, the controlling variable method and gas chromatographic technique were used to investigate the effect of volatile pollutant species on the removal efficiency of SVE, found that for a single pollutant system, under the same SVE conditions, the removal rate of ethanol after 48h was up to 91.6%, n-propanol 73.5%, n-butanol 66.1%; under the same SVE conditions, the removal rate of ethanol after 48h was up to 88%, n-propanol 78% in the ethanol-n-propanol system, ethanol 84.1%, and n-propanol 64.9% in the ethanol-n-butanol system. It provides a basic reference for the remediation of contaminated soil in the field.

1 Introduction

Polycyclic aromatic hydrocarbons and other hydrocarbon pollutants in oil can be degraded by natural enzymes and the process is extremely slow [1]. There are some remediation technologies such as: Thermal desorption technology, its heating conditions, feeding methods and practicality have been significantly improved [2]-[5]. Direct photodegradation technology has developed new photocatalytic oxidation technology, high efficiency and no pollution [6]-[10]. Microbial degradation of organic pollutants, such as off-site and in situ bioremediation techniques [11]-[15]. SVE can be used to deal with volatile and certain semi volatile organic pollutants, which has become a hot research area because of its high efficiency and economy [16]-[17]. There have been SVE remediation cases in China, with notable results [18]-[20].

The purpose of the experiment was to explore the effect of different components of target pollutant and their interaction on the remediation efficiency of SVE system.

2 Experimental part

2.1 Experimental Materials

In this paper, the experimental soil is the unpolluted sand in the Dongying area, and the sampling point is located not far from the oil field in Dongxin oil production plant, where the sampling depth is 0-0.5m, and the soil sample is sealed and preserved to keep its natural characters. Because of the homogeneity and porosity of sand particles as well as the low natural organic matter, it can be used as a good experimental pollution medium [21]-[25].



2.2 Pretreatment of soil samples and determination of their physical properties

2.2.1 Particle composition. Soil samples sieved $\phi 0.25\text{mm}$, $\phi 0.50\text{mm}$, $\phi 1.00\text{mm}$ soil screening after indoor natural air drying to remove plant residues, take soil sample less than $\phi 0.25\text{mm}$, $\phi 0.25\text{mm}\sim\phi 0.50\text{mm}$, $\phi 0.50\text{mm}\sim\phi 1.0\text{mm}$ spare. The size of sand used in the experiment is shown in table 1.

Table 1. Particle size distribution of the tested soil

Particle size (mm)	$\Phi < 0.25$	$0.25 < \Phi < 0.50$	$0.50 < \Phi < 1.0$	$\Phi > 1.00$
Proportion (%)	11.45	56.63	16.85	15.07

2.2.2 Physical properties of sand. The physical and mechanical indices of the collected sand are determined according to the experimental requirements. The detailed indices of the sand for the experiment are shown in Table 2. It is shown from the following table that the water content of the sample is slightly higher (rainfall in this area when sampling), the pH value is slightly greater than 7, and the alkaline (The main saline soil in Dongying area).

Table 2. The chemical and physical properties index statistics of the tested soil

Statistical project	Sample number	Maximum	Minimum	Mean
Water content %	6	24.8	17.9	21.4
Density / ρ	6	1.76	1.21	1.485
e	6	1.37	0.48	0.925
Sr	6	35.8	30.1	32.95
W_L	6	34.6	25.6	30.1
W_P	6	20.6	15.6	18.1
I_P	6	15.9	8.6	12.3
I_L	6	0.51	0.13	0.32
PH	6	8.12	7.56	7.83
Salt content %	6	0.48	0.32	0.39
$a_{0.1\sim 0.2}$	6	1.28	0.18	0.73

2.3 experimental device

The experiment design was shown in Figure 1, the glass column is fitted with soil samples, porous medium is placed at the top and bottom to make the pumping force evenly distributed, the top of the glass column connects suction pipe, and sequentially connected rotameter and pump, each connection is sealed with belt and daubed with vaseline or butter to ensure the relative sealing of the ventilation system. Finally, the extracted exhaust gas is connected with the activated carbon device. The glass column is arranged on the upper, middle and bottom three sampling holes, the aperture is 20mm.

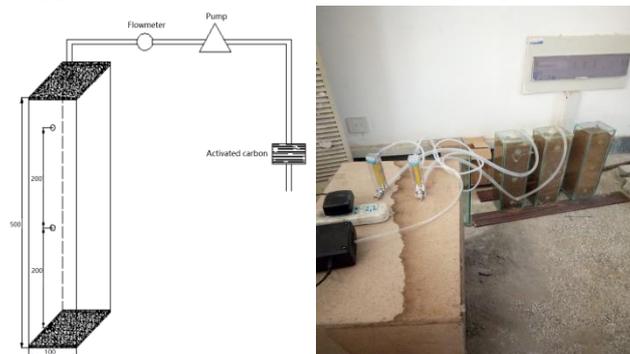


Figure 1. The experiment design drawings and photos

2.4 Experimental instruments and equipment

Plexiglass column, rotameter, vacuum pump, air pump, gas chromatography (with capillary shunt/shunt not into the injection port, can be programmed to temperature, with hydrogen flame ionization detector (FID), etc.

2.5 Experimental conditions and experimental procedures

2.5.1 Experimental condition. Using the continuous ventilation method of the top extraction, the ventilation flow 0.12L/min, the water content of each soil column is 15%, the influence of the pollutant species on the SVE remediation effect under the condition of room temperature 8°C~12°C, the influence of the experimental results under the room temperature range can be neglected [26]-[27]. The types and contents of the pollutants contained in the pillars are shown in the following table 3:

Table 3. The types and concentrations of pollutants in soil column

Number of soil column	Species and content of target pollutants
I	Ethanol 1%
II	Propanol 1%
III	N-butanol 1%
IV	Ethanol 1%; Propanol 1%
V	Ethanol 1%; N-butanol 1%

2.5.2 experiment procedure

2.5.2.1 Preparation of contaminated soil. Before the polluted soil is configured, the glass column of the loaded container is weighed and its mass is m_1 , then the soil after drying is filled in the glass column, and the mass m_2 , $m_2 - m_1$ is obtained by the total mass m of the experimental soil. According to the total mass m of the soil, the quality of the water and the target pollutant need to be added, and the components in the soil should be homogeneous.

2.5.2.2 Physical ventilation test. After filling the whole system, we closed the air inlet and outlet and kept it static for 48 hours in order to make the components of the system to mix evenly. Both of them are controlled by rotameter with a flow rate of 0.12L/min.

2.5.2.3 Sampling method and interval. After sampling, the sampling outlets should be sealed again quickly to prevent the change of air tightness of the system from affecting the experimental results. Sampling time interval should not be too long in the early stage. According to the existing research, the system components will change greatly in the early stage. Therefore, the sampling time is set to 0h, 6h, 12h, 24h, 36h, 48h when the ventilation starts. The concentration of target contaminants in each sample was calculated and charts were drawn.

2.5.2.4 Sample detection. The collected samples were determined by headspace/meteorological chromatographic method for the content of the target pollutants.

2.6 Determination of test methods

2.6.1 Headspace/meteorological chromatography. According to the standard of determination of volatile organic compounds in soil and sediments, which was introduced by Ministry of Environmental Protection on July 1, 2015, the concentration of target pollutant in simulated polluted soil was determined by headspace/gas chromatography. At a certain temperature, the volatile organic

compounds in the top empty bottle evaporates to the liquid space, after the gas-liquid-solid has reached thermodynamic dynamic equilibrium, volatile organic compounds in meteorology are separated by gas chromatography, detected by flame ionization detector, to retain the time qualitative, and the external standard method is quantitative [28]-[29].

3 Results and discussion

As shown in Table 4, the component concentration of each sampling port in each time system was calculated and charts were drawn to analyze its potential law.

Table 4. Concentration changes in the sampling port at different times

Contaminant types and concentrations	Concentration sampling port(mg/kg)	Time (h)					
		0	6	12	24	36	48
Ethanol 1%	I-1	8235	4342	1825	1059	853	695
	I-2	8459	4516	2117	1325	928	756
	I-3	8592	4859	2459	1542	1029	867
N-propanol1%	II-1	8325	5236	3085	2556	2335	2202
	II-2	8482	5641	3217	2713	2559	2417
	II-3	8739	5884	3424	2959	2868	2685
N-butanol 1%	III-1	8265	5762	3842	3216	3059	2805
	III-2	8862	6434	4456	3665	3386	3142
	III-3	9206	6958	5025	4018	3824	3573
Ethanol 1%	IV-1	8342	4853	2359	1436	1206	1003
	IV-2	8556	5015	2532	1560	1385	1236
	IV-3	8662	5352	2681	1702	1498	1402
N-propanol1%	IV-1	8328	4835	2736	2103	1956	1831
	IV-2	8503	5023	2901	2359	2185	2059
	IV-3	8865	5462	3205	2602	2362	2193
Ethanol 1%	V-1	8528	5136	2564	1603	1465	1352
	V-2	8603	5260	2701	1859	1685	1465
	V-3	8865	5357	2835	2002	1865	1626
N-butanol 1%	V-1	8153	5456	4102	3019	2859	2619
	V-2	8436	6206	4763	3429	3242	2905
	V-3	8978	6612	5384	3906	3617	3210

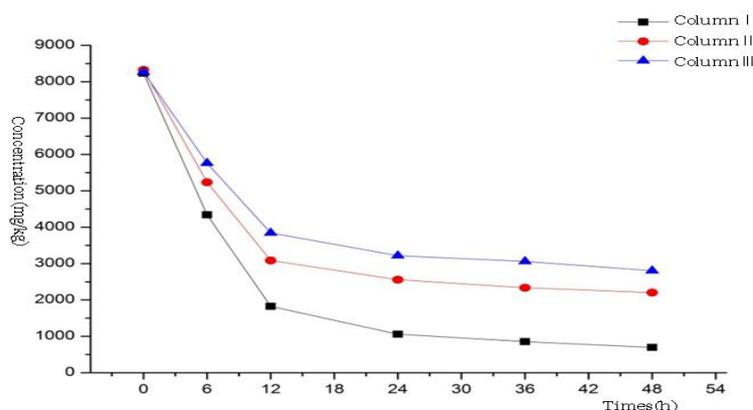


Figure 2. The change of different concentrations of one component at with time

As shown in Figure 2, the removal rate of ethanol in the prophase of ventilation is obviously better than that of n-propanol and n-butyl alcohol in the final removal effect, and it is the first to reach the "trailing period". The removal rates of ethanol, n-propanol and n-butanol were 87.1%, 69.3%, 61.1% at the 24h, The reason for this phenomenon is that with the increase of the number of carbon atoms in the main chain of organic compounds, the molecular weight of organic compounds increases, which leads to the electrostatic attraction, van der Waals force and hydrogen bond of the mixed organic matter in the soil particles on the adsorption of volatile organic compounds are further strengthened.

Therefore, the target pollutants are more easily adsorbed by the soil and difficult to desorb and remove by ventilation. In addition, with the addition of a $-CH_2$ in the main chain of alcohols, the physical properties of ethanol are different. The boiling point of ethanol is $78^{\circ}C$, the boiling point of n-propanol is $97.4^{\circ}C$, and the saturated vapor pressure of ethanol is $117.7^{\circ}C$. The saturated vapor pressure of ethanol is higher than that of n-propanol and n-butanol. The different physical and chemical properties of the target pollutants eventually lead to the different removal efficiency of the target pollutants.

From the change of different pollutant concentrations of a single group, we have a preliminary understanding of the different types of pollutants to the system removal effect, in order to further explore the interaction between different types of pollutants, we collate and draw the same pollutant in different systems of the concentration of the contrast diagram and analysis as Figure 3.

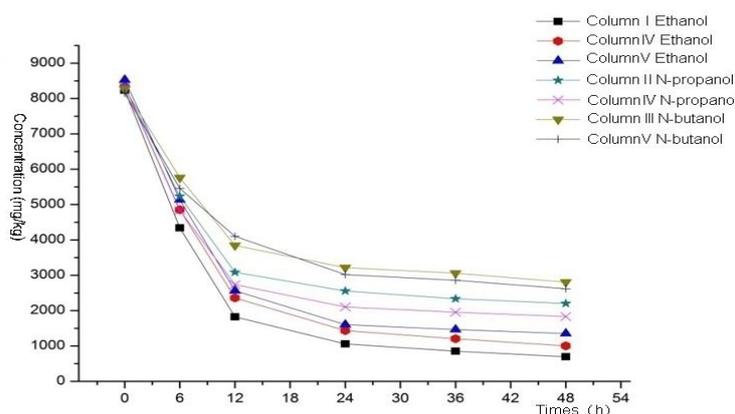


Figure 3. Comparison of concentrations of single component and mixed component

Table 5. Statistical table of variation of system components before and after ventilation of soil columns

Number of soil column	Target pollutant	Starting concentration(mg/kg)	End concentration (mg/kg)	Removal rate %
I	Ethanol	8235	695	91.6
II	N-propanol	8325	2202	73.5
III	N-butanol	8265	2805	66.1
IV	Ethanol	8342	1003	88.0
IV	N-propanol	8328	1831	78.0
V	Ethanol	8528	1352	84.1
V	N-butanol	8153	2619	67.9

From Figure 3, we found that the removal rate of the target pollutants at column I is 87.1% after ventilation for 24 hours, while the removal rates of ethanol at column IV and column V were 82.8% and 81.2% respectively, both of which are lower than the removal rates of ethanol in single component system, and the removal rates of n-propanol and n-butanol in the mixture are higher than those in single component system; according to Table 5, it is known that the system components change before and after ventilation in each soil pillar, the removal rate of ethanol reaches 91.6%, the removal rate of n-butanol is at least 66.1%. This phenomenon occurs because the lower saturated vapor pressure of organic compounds is, the harder it is to evaporate, and the target pollutant is mixed evenly after adding to the soil, in fact, the whole system is in a state of mutual encircling, so that the Van der Waals force exists between their molecules is strong. Therefore, the organic compounds with higher saturated vapor pressure have a certain effect on the organic compounds with lower saturated vapor pressure, in other words, the organic compounds with lower saturated vapor pressure has a certain "hindrance" effect on the removal of organic compounds with higher saturated vapor pressure. Because of the lowest saturated vapor pressure of n-butanol, the ethanol removal rate is the lowest in the internal system.

4. Conclusion

The types and properties of volatile organic compounds are important factors affecting the effect of soil vapor extraction experiments.

For the low boiling point, small molecular weight, high saturated vapor pressure, volatile organic compounds in the system are more easily removed through soil vapor extraction, removal rate: ethanol>n-butyl>n-butanol and the difference is about 20%.

The higher the volatile components in the soil mixed system, organic compounds with higher volatility have a certain promotion effect on the relatively lower when they are repaired by soil vapor extraction.

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