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Microwave-Assisted Thermal Remediation of Diesel Contaminated Soil

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Abstract. Leakage of petroleum products, gasoline and diesel, at gas station had become one of major soil contamination sources in Taiwan. Total number of 154 petroleum contaminated gas stations was successively ascertained since the implementation of Soil and Groundwater Remediation Act in 2002. One of the contaminated gas stations, mainly diesel polluted, was studied for the feasibility of microwave-assisted thermal remediation. The average of total petroleum hydrocarbons (TPH_t) in hotspot of this site was 2,845 mg/kg exceeding regulatory limit (1,000 mg/kg). According to the groundwater condition in the site, soil samples treated by microwave radiation with and without water as saturation and vadose zones were respectively tested in laboratory. The results show that a 12-min microwave energy can heat soil with water to reach 235 °C and degrade its TPH_t to 934 mg/kg; additionally, a 5-min microwave energy can heat soil without water to reach 220 °C and degrade its TPH_t to 520 mg/kg. Both soil samples passed TPH_t regulatory limit and microwave remediation with fast and effective advantages for petroleum products contaminated soil was also verified.

Keywords: Petroleum, diesel, gas station, remediation, total petroleum hydrocarbons.

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1. Introduction

All of gas stations in Taiwan belonged to government-owned company (Chinese Petroleum Corporation, CPC) before July, 1987. After the open policy of gas station, total number of gas stations from around 500 rapidly increased to 2,667 in 2008. However, high competition and oil leakages successively happened in some older gas stations make the total number of gas station decreasing to 2,490 in the middle of 2015 [1].

Soil and Groundwater Remediation Act (SGRA) was promulgated in 2002. According to the act, contaminated sites can be classified into two kinds of sites: (1) contamination control site: a site in which its soil and/or groundwater quality exceeding regulatory monitoring standard; therefore, this kind of site needed to be controlled; (2) contamination remediation site: a site having serious contamination in soil and/or groundwater; thus, site remediation is necessary. Total number of 154 gas station contaminated sites, including contamination control and remediation sites, was successively ascertained since the implementation of SGRA [2].

According to the regulatory soil contamination control standard, the usually used soil contamination identification items and their regulatory limits are as follows: total petroleum hydrocarbons (TPH_t)(1,000 mg/kg), benzene (5 mg/kg), toluene (500 mg/kg), ethylene (250 mg/kg), and xylene (500 mg/kg) [3]. Among these often used items, TPH_t is mostly used because of more precise in both of sampling and analysis.

Physical, chemical, and biological remediation technologies and remediation train, combining different remediation technologies as a train, can be applied to petroleum products contaminated sites [4−5]. However, suitable remediation technologies or train must consider lots of aspects such as technology availability, soil texture, geological structure, groundwater condition, contaminant property and concentration, second pollution and treatment, operation & maintenance, cleanup time, and overall cost [4−7]. The most available technologies used in petroleum contaminated soil are *in-situ* soil vapor extraction (SVE), *in-situ* and *ex-situ* thermal treatments, *in-situ* oxidation, *ex-situ* surfactant washing, and *ex-situ* bioremediation [4−7].

Microwave with high frequency, normally 2.45 GHz, can create non-ionizing electromagnetic radiation and let polar molecules such as water rotate extremely (i.e., dipole rotation or dipolar polarization) and rapidly raise material temperature. Consequently, microwave accompanied with strong acid is often applied to decompose metal-organics in sludge, soil and sediment digestion [8−12]. Therefore, microwave with quick thermal decomposition characteristics can be employed for rapidly treating organic contaminant and this new remediation method have been studying at laboratories for developing a future practical technology [13]. In this paper, a petroleum products contaminated soil sampled from a gas station was studied for evaluating the feasibility of microwave remediation.

2. Materials and Methods

2.1. Sampling and Analysis of Contaminated Soil

The petroleum products (gasoline and diesel) leaked gas station built in 1980 is located in the middle of Taiwan. Because gasoline and diesel tanks and pipelines in this station is old-style design, two sampled soils exceeding TPH_t limit of 1,000 mg/kg were detected in 2011. Thus, this gas station was announced by the government as a contamination remediation site (M site). After a series of pollution investigation on M site, the geological, hydraulic, and contaminated conditions were examined [14]. Therefore, several 5 m depth of serious contaminated soils in the hotspot were sampled by a percussion hammer mounted on vehicle. The contaminated soils marked each sampling depth were carried to our laboratory, wrapped up in a black plastic bag and stored in a 4 °C refrigerator. According to the soil profile of the site, each different depth, 0−2.0 m (vadose zone), 2.0−3.7 m (middle zone) and 3.7−5.0 m (bottom zone), of contaminated soil was took out and quickly mixed respectively. Some of soils were picked out for physico-chemical property analysis including TPH_g, TPH_d, and TPH_t (in accordance of TW EPA standard method of S703.62B), and the others were stored again for experimental study.

2.2. Microwave Remediation of Contaminated Soil

After TPH measurements of three different depths of contaminated soils, the soil TPH_t of vadose zone was below the regulatory limit of 1,000 mg/kg and the soil TPH_t of middle zone and bottom zone were similar. Therefore, the remediation of vadose zone soil was not necessary and the middle zone and bottom zone soils were quickly mixed as the study contaminated soil and its TPH was examined again. A microwave oven, Panasonic NN-ST651 with 355 x 365 x 251 mm dimensions and maximum output power of 1,000 W, was used for the experiment of microwave remediation. Because the actual contaminated soils were two kinds of soils: soil with groundwater and soil without groundwater, thus two stage experiments were then designed and carried out.

The first stage experiment: a 50 g contaminated soil was put into a crucible, with cap or without cap, and moved into microwave oven, with water or without water. Different microwave time was set at medium output power mode and then started microwave remediation test. Once the set time reached, soil temperature was immediately detected by a digital thermocouple. Therefore, soil temperature affected by soil conditions (capped or uncapped; with or without water) and microwave remediation time was recorded.

The second stage experiment: the results of first stage experiment were evaluated firstly. According to energy consumption, higher energy consumption (capped soil with water) and lower energy consumption (capped soil without water) operational conditions were selected for second stage remediation experiment.

In the second experiment, a 50 g contaminated soil was put into a capped crucible and moved into microwave oven, with or without water. Different microwave remediation time was set, also at medium output power mode, and started the remediation experiment. After that, soil was moved out, cooled down at room temperature and then filled into a brown glass bottle for analysis.

3. Results and Discussion

3.1. Contaminated Site Investigation

The TPH_t contour in contaminated site was shown in Fig. 1. Major contamination in which TPH_t concentration exceeding 1,000 mg/kg covered two-third of the gas station area and had moved outside of the gas station. Moreover, two major pollution plumes and their sources were found as follows: (1) northeastern plume: four gasoline and diesel underground tanks located at the north part may be the major pollution source, and plume moving toward northeast reveals that groundwater moves toward the northeast or east. (2) southeastern plume: this plume may be caused by pipeline leakages in the three fuel islands; especially, a heavy leakage near the eastern fuel island was found. Thus, the contaminated soils in the heavy leakage area (i.e., hotspot) were sampled for study in this paper.

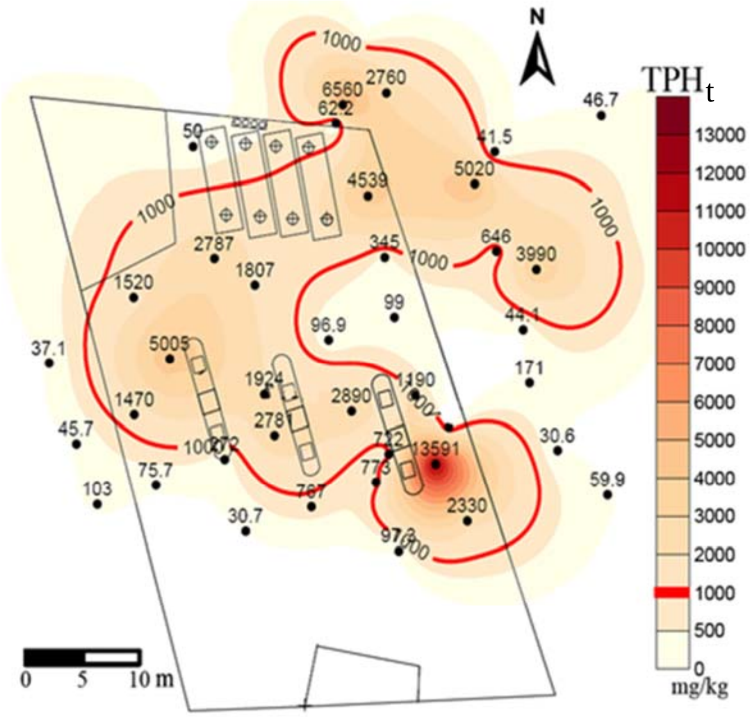

Fig. 1. TPH_t contour in the petroleum products contaminated gas station [14].

According to the geological investigation of the contaminated site, soil profile and contaminated conditions were shown in Fig. 2. Three different zones were vadose zone (0–2.0 m), middle zone (2.0–3.7 m) and bottom zone (3.7–5.0 m), respectively. The TPH measurements illustrate that soil TPH_t in vadose zone was below regulatory limit, revealing that highest possible contaminant in this zone was gasoline, lighter and easier vaporized petroleum product, and most of contaminant had vaporized because a SVE remediation had been done in this station several years ago. Next, both of the soil TPH_t in middle and bottom zones was similar and exceeded regulatory limit. Therefore, both soils of middle and bottom zones were mixed and the measurement of mixed soil TPH_t was 2,845 mg/kg.

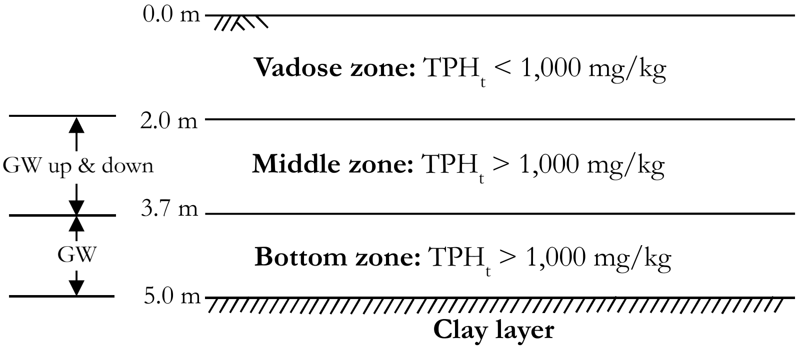

Fig. 2. Soil profile and TPH_t condition in contaminated site.

3.2. Microwave Remediation of Contaminated Soil

The first stage experimental results of microwave remediation time vs. soil temperature were shown in Table 1. Obviously, soil temperatures of soils with water as groundwater in the environment, no matter whether the soil was capped or uncapped in crucible, were lower than those of soils without water. The major reason is water, a polar molecule, can rapidly initiate dipole rotation under microwave radiation and exhausted most of energy. Moreover, temperatures of uncapped soils were higher than those of capped soils, indicating that soil in crucible without cap can be directly excited with microwave radiation.

Table 1. The first stage experimental results of microwave remediation time vs. soil temperature.

		Microwave remediation time (min)												
		0.5	**1.0**	**2.0**	**3.0**	**4.0**	**4.5**	**5.0**	**6.0**	**7.0**	**8.0**	**10**	**11**	**12**
Temp. (°C)	Capped soil (w/ water)	–	–	–	96	115	–	133	–	150	160	160	166	235
	Uncapped soil (w/ water)	–	–	88	80	157	144	171	175	–	–	–	–	–
	Capped soil (w/o water)	92	96	113	159	212	–	220	–	–	–	–	–	–

–: without detection

The temperature of soil without water increased very quickly comparing with that of soil with water. At the same of soil capped condition, temperature of 220 °C could be easily reached for soil without water after a 5-min microwave remediation. Comparatively, soil with water needed about 11.5 min as shown in Fig. 3. For the convenience of comparison, the best and worst soil temperature operational conditions were adopted for soil remediation in the second stage experiment.

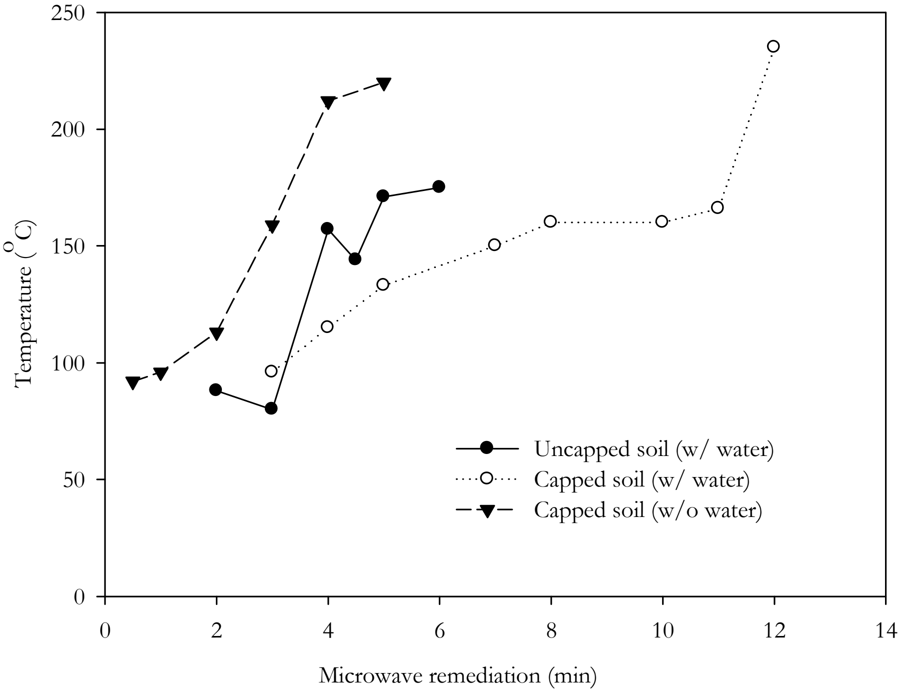

Fig. 3. Soil temperature varied with different microwave remediation time.

The second stage experimental results of microwave remediation time vs. soil TPH were shown in Table 2. The TPH_t of soil with water increased from 2,845 to 3,425 mg/kg after 3 min microwave remediation; moreover, TPH_g decreased from 25 to 5 mg/kg and TPH_d decreased from 2,845 to 3,425 mg/kg. The soil temperature of 3 min microwave remediation for capped soil with water was 96 °C as shown in Table 1. Therefore, TPH_g (C6−C9 compounds, e.g., BTEX) decreased because of evaporation; unfortunately, TPH_d increased. Theoretically, TPH_d includes C10−C28 compounds but GC/FID measurement of TPH_d includes C10−C40 compounds. Once the soil temperature increased, some denser compounds (e.g., C28−C40) even only few content in diesel would decompose and become lighter compounds; thus, the TPH_d increased. Figures of 4(a) and 4(b) show the evidence of gas chromatogram variations in GC/FID measurements.

Table 2. The second stage experimental results of microwave remediation time vs. soil TPH.

	$TPH_{g, d, or t}$ (mg/kg)	**Microwave remediation time (min)**					
		0	**1**	**3**	**5**	**7**	**12**
Capped soil (w/ water)	TPH_g	25	–	5	–	9	14
	TPH_d	2,820	–	3,420	–	2,170	920
	TPH_t	2,845	–	3,425	–	2,179	934
Capped soil (w/o water)	TPH_g	25	7	9	6	–	–
	TPH_d	2,820	4,280	1,860	514	–	–
	TPH_t	2,845	4,287	1,869	520	–	–

–: without detection

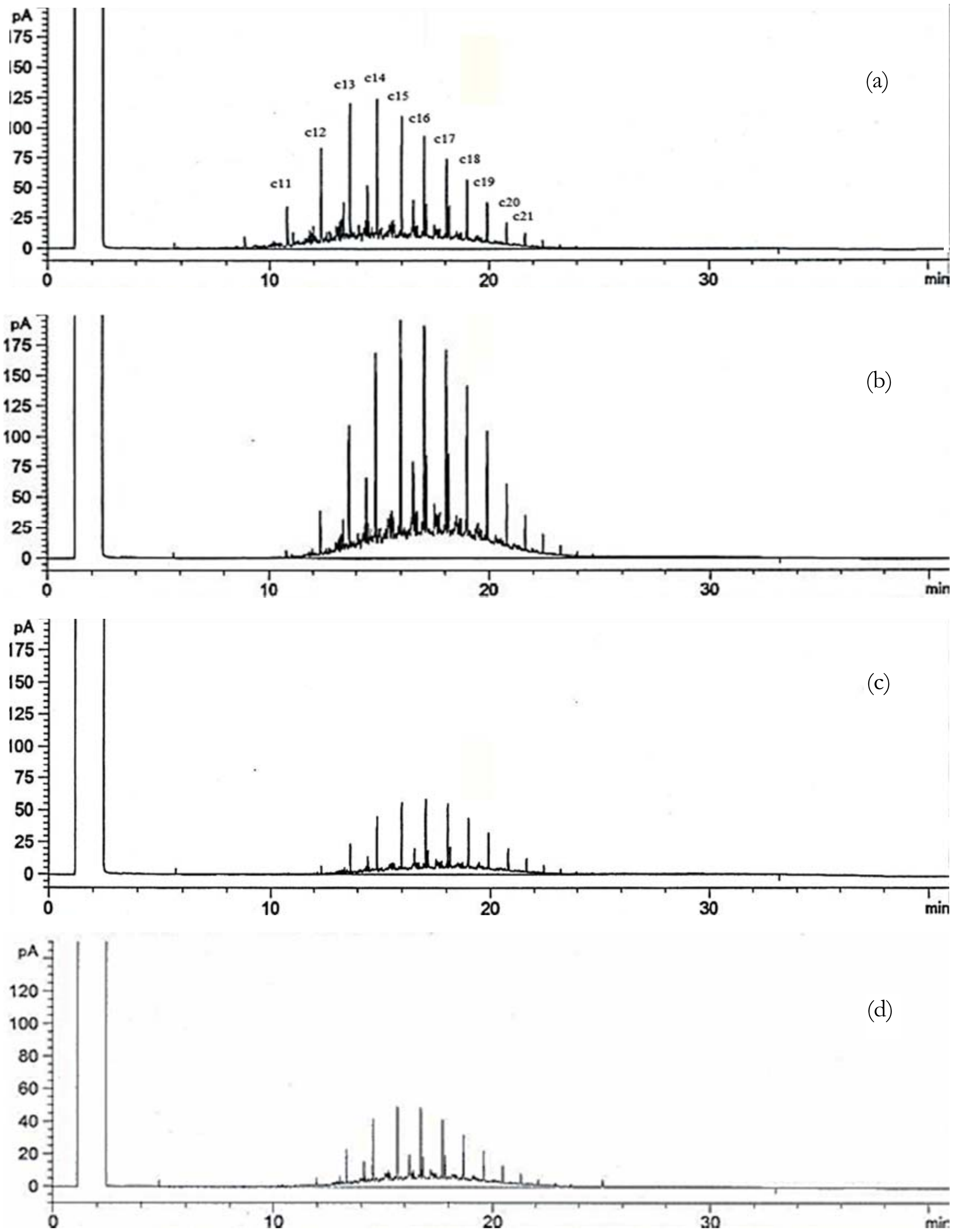

Fig. 4. Gas chromatograms in GC/FID measurements: (a) original soil, (b) 3 min microwave remediation of capped soil with water, (c) 12 min microwave remediation of capped soil with water, (d) 5 min microwave remediation of capped soil without water.

TPH_t of soil with water significantly decreased to 934 mg/kg, below the regulatory limit of TPH_t, after 12 min microwave remediation. The soil temperature of 12 min microwave remediation for capped soil with water was 235 °C as shown in Table 1. Because the boiling point of diesel is around 350 °C, therefore, most of TPH_d compounds were decomposed and weak signals in gas chromatogram were shown in Fig. 4(c). In the capped soil without water, soil TPH_t increased to 4,287 mg/kg after 1 min microwave remediation as shown in Fig. 5 because the soil temperature was only 96 °C. However, TPH_g decreased with the increase of microwave remediation time. After 5 min microwave remediation, soil temperature around 220 °C, TPH_t rapidly dropped to 520 mg/kg and passed the regulatory limit. Its gas chromatogram signals weaker than that of Fig. 4 (c) was shown in Fig. 4(d). In conclusion, microwave radiation can quickly raise soil temperature, especially for those soils without groundwater. Although diesel boiling point is around 350 °C, soil temperature reaching to 220−235 °C by microwave radiation can dramatically decompose most of diesel compounds for soil with or without groundwater.

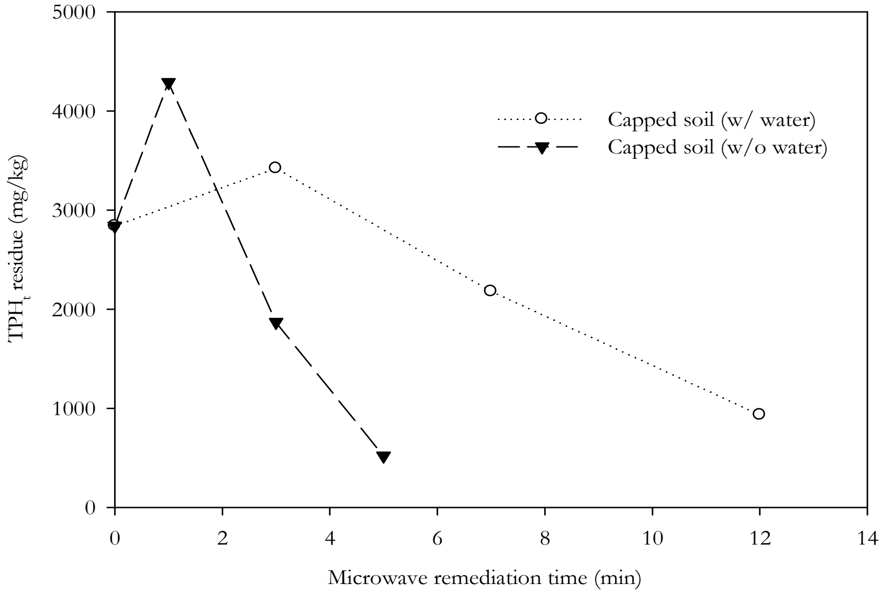

Fig. 5. TPH_t residue in contaminated soil after different microwave remediation time.

4. Conclusions

The petroleum products leaked gas station was investigated and two-third area of soil TPH_t exceeding was ascertained. Contaminated soils sampled from the hotspot were studied, and soil TPH measurements of three soil zones show that vadose zone was below TPH_t regulatory limit; in contrast, the TPH_t of other two zones were similar and higher than regulatory limit. Thereafter, these two zone soils were quickly mixed and its TPH_t is 2,845 mg/kg. The first stage experiment of microwave remediation time vs. soil temperature show that capped soil with water as groundwater exhausted much microwave energy and took much remediation time; in contrast, soil without water could be directly excited with microwave and soil temperature quickly raised. The second stage experiment of microwave remediation time vs. TPH_t residue in soil show that capped soil with water took 12 min to reduce soil TPH_t to 934 mg/kg; comparatively, capped soil without water only took 5 min to reduce soil TPH_t to 520 mg/kg. Gas chromatograms in TPH measurement provide clear evidence in signal variation and the feasibility of microwave remediation as a new technology was verified.

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