

Supplementary Information

for

Carbonaceous Nano-Additives Augment Microwave-Enabled Thermal Remediation of Soils Containing Petroleum Hydrocarbons

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Biodegradation Procedure for Soils Containing Petroleum Hydrocarbons

Soil was biodegraded in a 1.5 L glass pan containing 1.25 kg of soil. Each kg of soil was dosed with 10 mL of macronutrient solution, 1 mL Trace A solution, 1 mL Trace B solution, and 1 mL vitamin mix solution for bacterial growth. The composition of these solutions was published previously ^{S1}. The soil was mixed/tilled twice weekly to oxygenate, and DI water was provided to maintain the moisture content at 60-80% of the soil water holding capacity (i.e, 15-18% w/w). Incubations were performed for 120 days at 30° C in the dark.

Extraction and Quantification of Total Petroleum Hydrocarbons from Soil

One gram of soil was dried with sodium sulfate and extracted with dichloromethane (DCM) in a Gerhardt[®] Soxtherm automatic extractor (Gerhardt Analytical System, Königswinter, Germany). The DCM extract was concentrated to 1 mL final volume, filtered through a 0.2- μ m PTFE filter, and analyzed on a GC-FID (Shimadzu GC2010, Shimadzu Corp., MD, USA) equipped with a Restek Rxi[®]-1HT column (30 m x 0.25 mm x 0.25 μ m). The GC-FID analytical method was developed according to the extractable petroleum hydrocarbons standard method ^{S2}. TPH was defined as the collective concentration of all compounds eluting from n-nonane (C₉) to n-tetracontane (C₄₀). Calibration curves were generated to obtain calibration factors using an alkane C₉-C₄₀ standard mixture (Sigma-Aldrich Co. Ltd.; St. Louis, MO) at six different concentrations between 2 and 200 mg/L. All TPH concentrations were reported per dry weight of the soil.

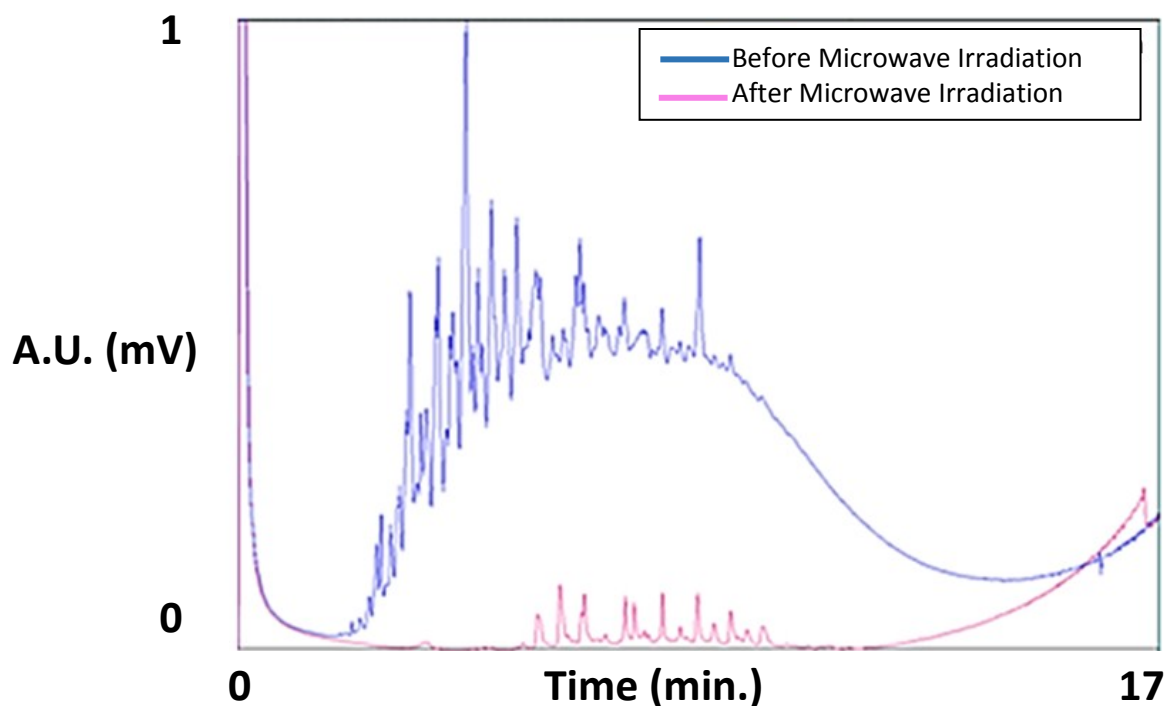


Figure S1. Chromatograms of soils containing petroleum hydrocarbons before and after 15 minute microwave irradiation enhanced with granular activated carbon. Microwave treatment of soils using granular activated carbons as additives: two grams of contaminated soil (containing 14,000 mg/kg TPH, 12.5% soil moisture) were placed into a 40 ml borosilicate VOA vial. Calgon granular activated carbon (10% w/w) was added to the soil matrix and manually mixed to ensure sample homogeneity. The vials were placed on a rotator disk in a household Hamilton Beach (Glen Allen, VA; Model No: P100N30ALS3B, 2.45 GHz, 1000-W output) microwave oven in a laboratory hood and set to 15 minutes. Residual TPH chromatograms were generated in-house using SRI 8610C Gas Chromatograph with Restek MXT-1HT SimDist column (10m, 0.53 mmID, 0.21 μ m df). Temperature programming was: 40-380 °C at 20 °C/min (total 17

minute run time) with gas flow rates of helium carrier 10 ml/min, hydrogen 20 ml/min, and air 230 ml/min.

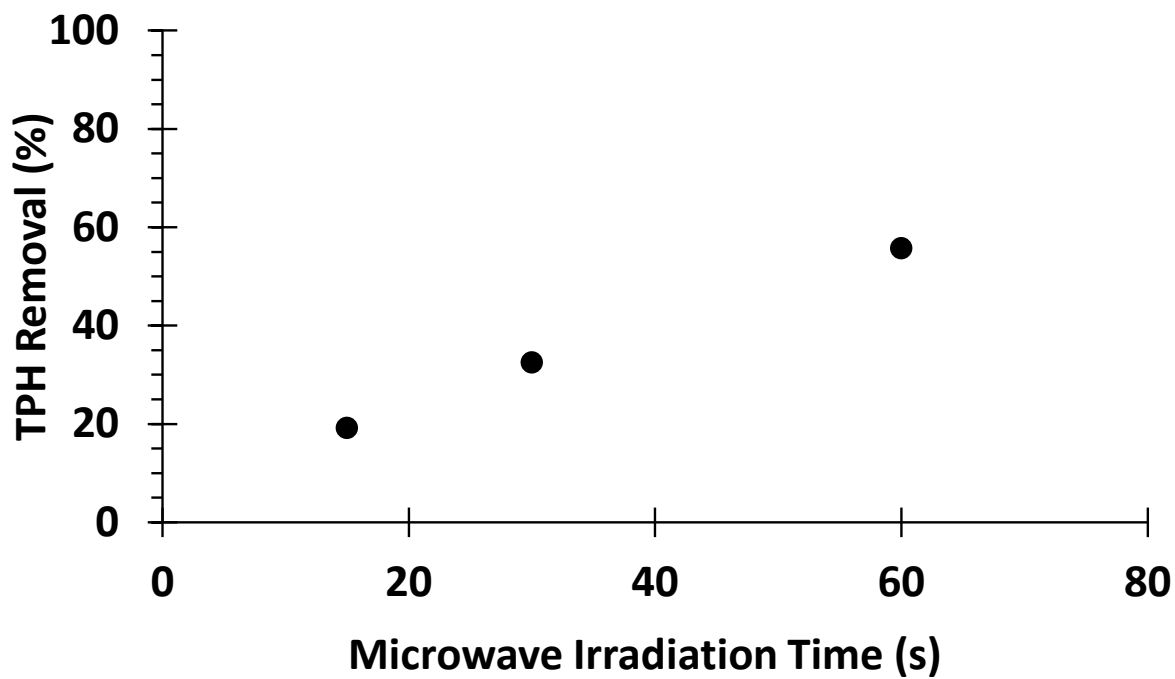


Figure S2. Effect of microwave irradiation time on TPH removal using MWCNT-1 (1% w/w) as dielectric additive.

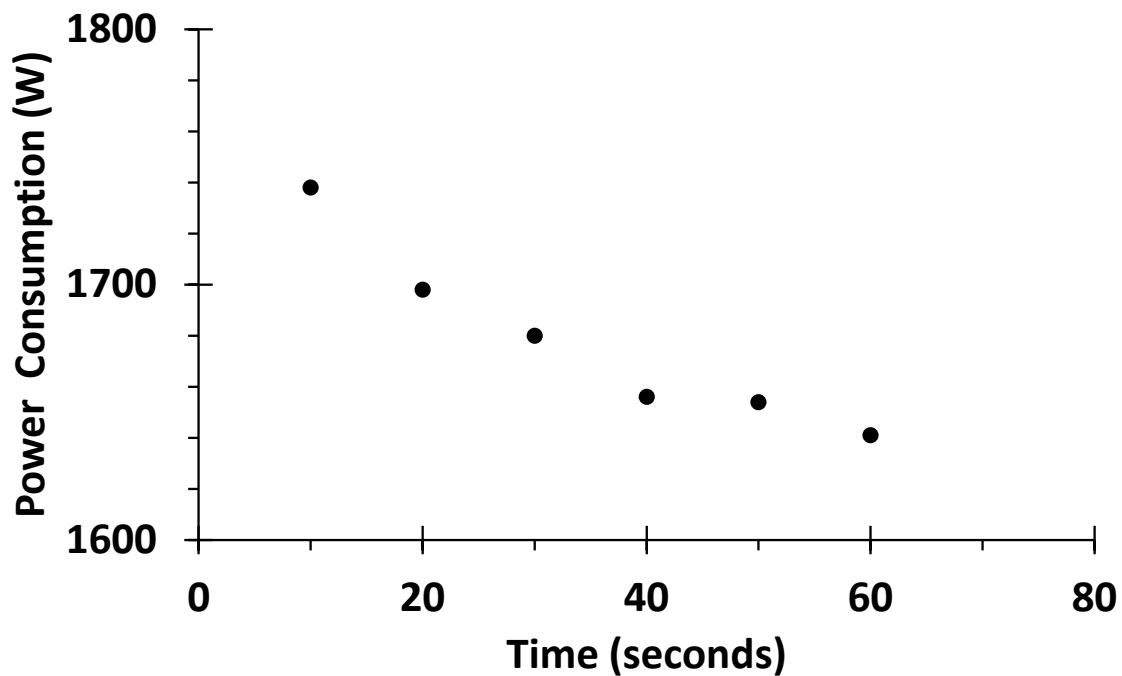


Figure S3. The online power measurements of the microwave oven when it was set to run for 60-seconds with no power adjustment.

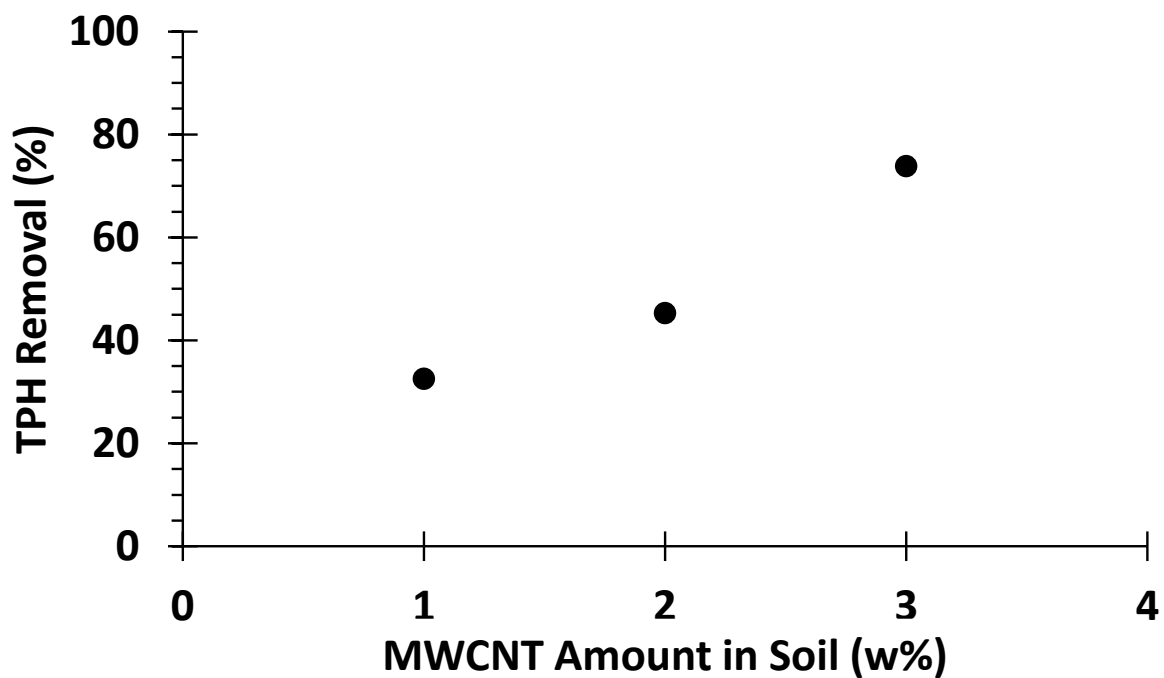


Figure S4. Effect of dielectric additive (MWCNT-1) amount on TPH removal. Thirty-second microwave irradiation was applied to all samples.

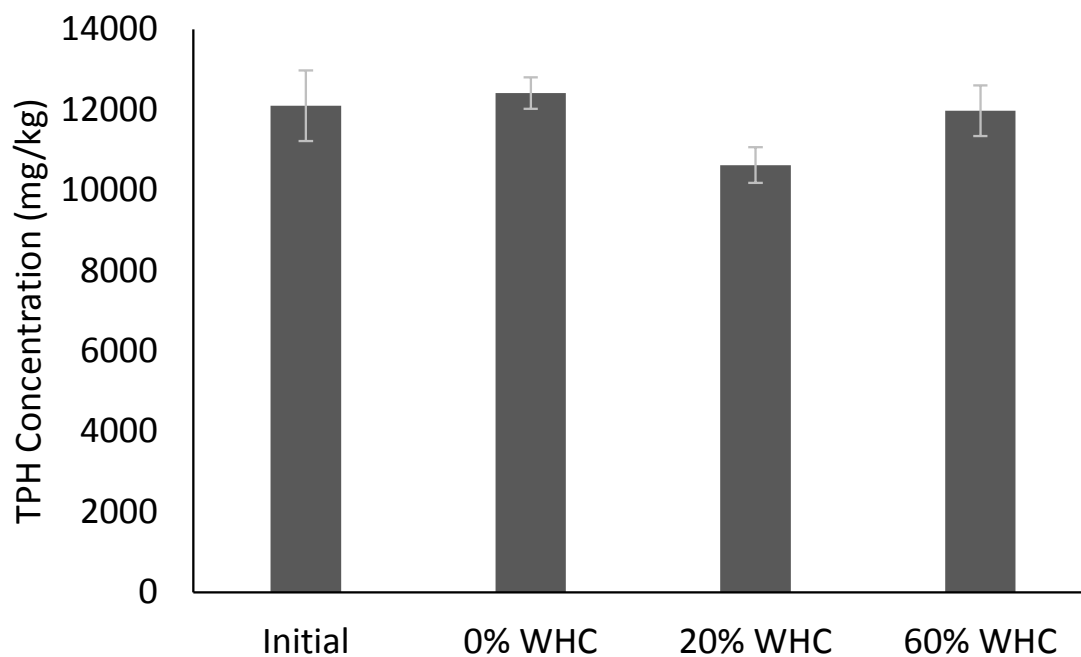


Figure S5. Effect of moisture content, reported as soil water holding capacity (WHC), on TPH removal after 60 second microwave irradiation with MWCNT-2 as the additive. Error bars indicate standard deviation of triplicate experiments.

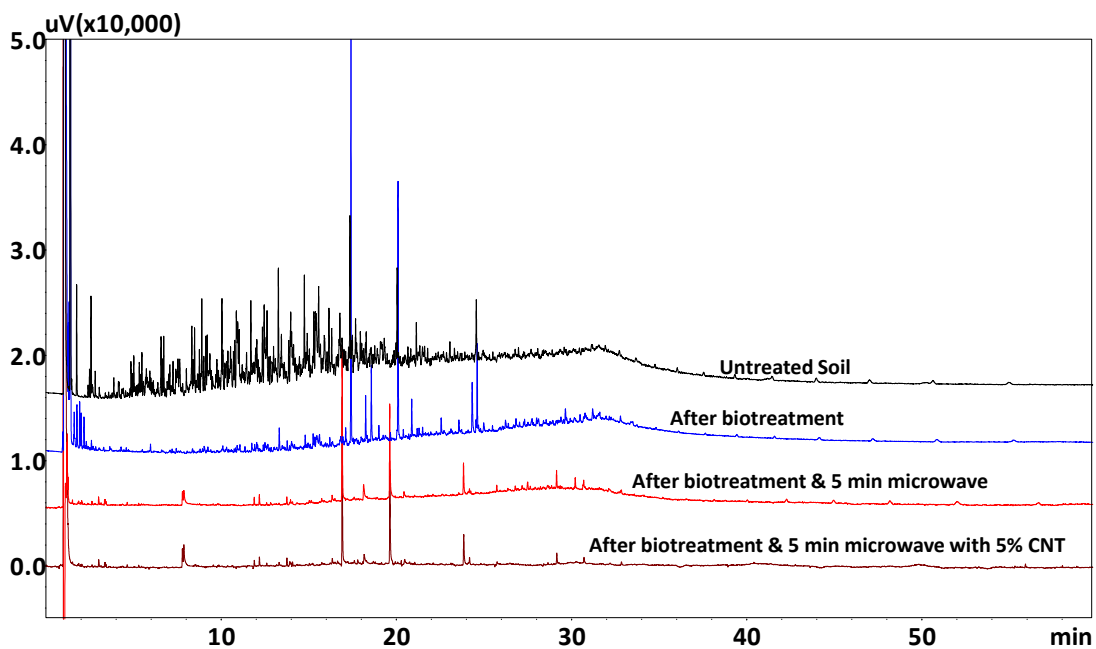


Figure S6. Chromatograms of TPH-containing soils after biotreatment and consecutive microwave treatment with and without carbon nanotubes. The baseline is shifted along the y-axis to allow better visual comparison.

REFERENCES

- S1- A.G. Delgado, D. Fajardo-Williams, S.C. Popat, C.I. Torres, R. Krajmalnik-Brown. Successful operation of continuous reactors at short retention times results in high-density, fast-rate *Dehalococcoides* dechlorinating cultures. *Appl. Microbiol. Biotechnol.*, 2014, 98, 2729-2737.
- S2- MADEP (Massachusetts Department of Environmental Protection) Method for the Determination of Extractable Petroleum Hydrocarbons (EPH). May 2004.