

Contaminant Removal Mechanisms in Microwave Heating Remediation of PAH-Contaminated Soils

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Polycyclic aromatic hydrocarbon (PAH) contamination represents a very relevant environmental problem worldwide. Due to PAH persistence, bioaccumulation and mutagenic effects on human health, restoration techniques for PAH - contaminated soils have recently attracted particular attention.

Several chemical-physical treatments have been proposed for this purpose; however, they may often be expensive or require combined-multi-step processes. On the other hand, thermal treatments were shown to be more effective, but generally requiring high fuel costs. Recently, microwave heating (MWH) has been proposed as a cost - effective thermal treatment.

The main goal of this study was to assess the potential application a microwave heating (MWH) treatment of soils contaminated with PAHs, investigating the effects of various operating conditions on contaminant removal kinetics and mechanisms. A sandy soil was artificially contaminated with PAHs and irradiated for a period of 5 – 60 min, applying powers in the range of 250 - 1000 W. Main results suggest that PAH polarity features, significantly influence the maximum temperature achievable during the MWH and the contaminant removals. Specifically, total removal was achievable only for biphenyl and fluorene, while concentrations lower than 2 mg kg⁻¹ were found for anthracene and phenanthrene. Several mechanisms, namely, thermal desorption, molecular bond breaking, selective heating and contaminant stripping took place during PAH removal. Observed mechanisms could provide basic information and be helpful in order to improve the development of novel MW based - remediation technologies.

1. Introduction

Polycyclic Aromatic Hydrocarbon (PAH) contamination represents a very relevant environmental problem worldwide. High hydrophobicity of PAHs makes their interaction with minerals and organic matter very strong. Consequently, they can be easily adsorbed onto grain surface, making soil the environmental compartment most polluted by these contaminants. PAHs are a group of organic compounds with two or more fused aromatic rings of carbons and hydrogen atoms, mainly formed by incomplete combustion or pyrolysis of organic matter, generally generated by industrial or urban activities (De Guidi et al., 2016; Falciglia et al., 2017b). Due to their persistence, bioaccumulation and mutagenic effects on human health, restoration techniques for PAH - contaminated soils are strongly required. Several chemical-physical treatments have been proposed for this purpose; however, they may often be expensive or require combined-multi-step processes. Alternatively, thermal treatments were shown to be more effective, but generally requiring high fuel costs (Falciglia et al., 2011a, 2011b).

Microwave heating (MWH) has been recently proposed as a cost-effective thermal treatment. It presents several advantages, among which a more homogeneous heating and a higher flexibility in controlling automatically the heating process (Falciglia and Vagliasindi 2014, 2015). This is mainly due to the direct interaction between the microwaves and the medium, which allows the conventional heating limitations to be overcome. MWH has been successfully proposed for contaminated soils (Falciglia et al., 2013; Robinson et al., 2009, 2012), aquifers (Falciglia et al., 2016) or wastes (Pereira et al., 2014). MWH was shown to be

effective in soil decontamination applications for a large number of organic contaminants such as nitrobenzene, PCBs, HCB and diesel-fuel (Falciglia et al., 2013).

The MWH key factor is represented by the mechanism of conversion of the MW energy into heat. This allows a temperature increase of the irradiated medium, or a contaminant selective heating in the case of high-dielectric (polar) contaminants. In both cases, organic contaminant removal processes are activated. The electric power \dot{Q} dissipated into heat per unit of volume during the MW irradiation depends on the frequency of the applied electromagnetic field and the dielectric properties of the medium. The dissipation equation is derived from Maxwell's equations (Falciglia et al., 2015, 2017c):

$$\dot{Q} = \frac{1}{2} \omega \epsilon_0 \epsilon'' |E_{\max}^2| = \omega \epsilon_0 \epsilon'' |E|^2 \quad (1)$$

where ω is the angular frequency ($\omega = 2\pi f$), ϵ_0 is the permittivity of free space ($8.85 \cdot 10^{-12} \text{ F m}^{-1}$), ϵ'' is the dielectric loss factor, E_{\max} is the electromagnetic field peak value (V m^{-1}) and E is electromagnetic field effective value (V m^{-1}). For hydrocarbon-polluted soil remediation by MW heating, the time dependent-temperature increase ($\Delta T \Delta t^{-1}$, $^{\circ}\text{C min}^{-1}$) can be expressed by Eq. 2 as follows (Falciglia et al., 2017a):

$$\frac{\Delta T}{\Delta t} = \frac{\omega \cdot \epsilon_0 \cdot \epsilon'' |E|^2}{c_p \cdot \rho} \quad (2)$$

where c_p is the heat capacity of the matrix ($\text{KJ kg}^{-1} \text{ } ^{\circ}\text{C}^{-1}$) and ρ is its density (kg m^{-3}). ϵ'' represents the ability of a material penetrated by a MW electric field to convert its energy into heat.

The main goal of this study was the application of a bench-scale MWH treatment of soils contaminated with PAHs, investigating the effects of various operating conditions on contaminant removal kinetics and mechanisms.

2. Materials and methods

2.1 Experiments

A model sandy soil (Table 1) was artificially contaminated with PAHs in order to achieve a homogeneous and typical contamination level. The contamination procedure was carried out by mixing a solution containing nine selected PAHs (Bph, Flu, Phe, Ant, Flt, Pyr, BaA, Chr and Per) in dichloromethane (DCM) with the soil. The soil was mixed for 1 hour using a rotavapor system, and then the solvent was entirely separated from soil by means of the same rotavapor system. The contaminated soil samples were stored for six months before extraction and HPLC analysis procedure for initial contaminant content (C_0) or MW irradiation experiments. Analysis revealed an average C_0 value as total PAHs of 226.9 mg kg^{-1} .

A MW decontamination treatment was simulated using a MW cavity apparatus, which mainly consists of a 1.0 kW MW generator (2.45 GHz) connected to cavity by means of a WR340 waveguide. The cavity was connected to a volatile organic compound (VOC) capture system made up of a condensing unit, an activated carbon filter and a vacuum pump. PAH - contaminated soil samples (20 g) were placed in the centre - section of the cavity and irradiated for treatment times (t) in the range 5 - 60 min, applying power (P) values from 250 to 1000 W. The soil sample temperature (T) was measured with a type - k thermocouple system.

After MWH treatments, contaminant residual concentration (C) was obtained for each selected P . The condensate liquid and activated carbons were also collected for PAH and by-product content.

Table 1: Properties and characteristics of selected soils

Parameter	Method	Value
Soil mineral		Silica sand (75-200 μm)
pH	ASTM D4972-13	8.72
Bulk density (g cm^{-3})	ASTM D7263-09	1.36
Porosity (%)	ASTM D4404-10	32.5
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	EGME	3.45
Organic matter (g kg^{-1})	UV-VIS	3.55
Moisture content (%)	ASTM D2216-10	0.0; 10.0
Dielectric constant (ϵ')	cavity perturbation	6.98 (0%); 7.08 (10%)
Loss factor (ϵ'')	cavity perturbation	0.68 (0%); 0.72 (10%)

2.2 PAH extraction and analytical methods

Contaminant residual concentration (C) was assessed by means of Soxhlet solvent extraction (EPA method 3540C). Briefly, the weighed soil sample was placed in a thimble and PAHs were extracted for 24 h with 300 mL of DCM, light was excluded by aluminium foil and oxygen was removed by gently purging nitrogen. Most of the solvent was removed from the extract by dry inert gas. The extract was re-dissolved to a final volume (2 mL) with DCM by ultrasonic agitation in a warm (35 °C) bath for 10 min, filtered through a membrane (250/60 g, Albet) and finally clarified using a PTFE syringe filter (0.2 μm , Millipore). Then, the samples were transferred to a silica SPE cartridge for solid-phase extraction (Florisil, Varian), and eluted with 3 mL of hexane. The eluate was dried under a stream of nitrogen, and the residue was re-dissolved in MeOH. Aliquots of 20 μL were removed from the sample for further analysis by HPLC. Thus samples or standards (20 μL) were injected onto a reverse-phase C18 column (Lichrosphere; 4.6 mm x 250 mm). The HPLC analyses of samples were performed on a Hewlett-Packard 1100 chromatograph equipped with on-line diode array detector (DAD), ESA model 5100A electrochemical detector (ECD) and a Kontron SFM fluorescence detector (FLD). Typically, chromatograms were obtained using a diode array (DAD) and a fluorimetric detector (FLD). A linear gradient of water and methanol (MeOH; v/v) was used to elute the compounds at a flow rate of 1 ml/min as follows: 0-16 min, a linear gradient from 75 to 85% MeOH; 16-27 min, MeOH hold at 85%, 27-55 min, a linear gradient from 85 to 90% MeOH, finally, 55-60 min, back to 75% MeOH. Two separate chromatographic runs were used to resolve the changing excitation/emission wavelengths of the PAHs in the fluorescence detector. The first run was monitored at 265/389 ($\lambda_{\text{exc/em}}$) nm from 0 to 60 min (for Bph, Flu, Phe, Ant, Pyr, BaA and Chr). Then, the second run (for Flt and Per) was monitored at 280/410 nm from 0 to 60 min.

3. Results and discussion

3.1 Soil temperature variation during MWH

Temperature (T) profiles with time (t) (Figure 1) showed a general increase in T with P and t increasing. Specifically, T increased quickly at the beginning of the irradiation process and it tended to stabilise after 18 min. In the case of PAH-moisturised soils the maximum T value (208 °C) was reached, when the 1000 W power was applied for 60 min.

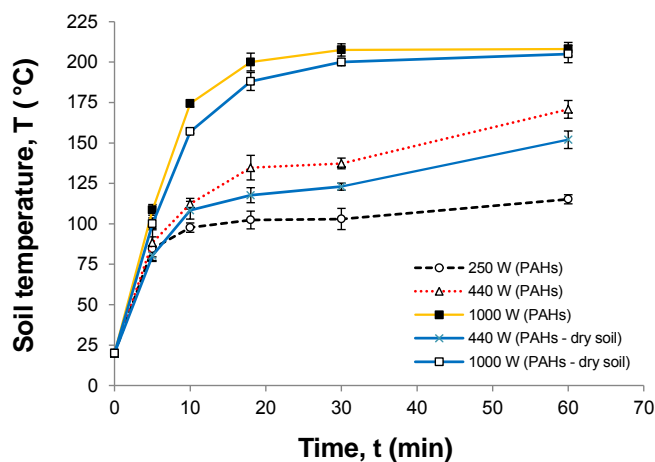


Figure 1: Soil temperature (T) variation with time (t) during MWH tests.

Overall, the specific temperature trend observed depended on the reduction of the ability of the soil to convert the electromagnetic energy into heat. It was shown (Robinson et al., 2012) that during soil MW irradiation, ϵ'' decreased with time, consequently resulting in constant values of soil temperature. The observed temperature profiles are in the same range observed in our previous works (Falciglia and Vagliasindi, 2015, 2016), where we investigated the thermal effects of a MW treatment of the same sandy soil used in this work but contaminated with diesel fuel at about 1900 mg kg^{-1} . The final temperature values of the irradiated diesel polluted-soil were 10, 14 or 52 °C higher than those of the PAH-polluted soil (this work) for the applied power of 250, 440 or 1000 W, respectively. This is probably due to the presence of a higher hydrocarbon concentration in the case of diesel contamination vs. a low PAH concentration (1916 vs. 227 mg kg^{-1}).

(Robinson et al., 2009). However, the difference of temperature values observed between diesel and PAH - contaminated soils was limited due to the presence of a higher polar fraction of PAHs compared to diesel fuel, and this was able to balance the final soil temperature reduction (Robinson et al., 2009). Lower T values were observed for dry soils respect to the moisturised ones when irradiated at the same operating conditions, due to the lower dielectric constant observed (Table 1).

3.2 PAH removal kinetics and mechanisms

Contaminant removals (R) of treated PAH - contaminated soil samples calculated from C values for all t and P are shown in Table 2. The best performance in contaminant removal was obtained with the highest power of 1000 W. After about 18 min MW treatment, the energy is great enough to allow a significant reduction of the contaminants adsorbed onto the soil. Except for BaA and Chr, the same removal order, which follows a criterion based on the molecular structure, the boiling point and the polarity of any single compound, was found. Similarly to conventional thermal desorption, higher removals took place with the higher soil temperatures and with the lower molecular weights that have the lower boiling point values and, consequently, require lower heat of vaporisation. Furthermore, saturated vapour pressure of organic matter increases with temperature rising, resulting in a most effective formation of volatile organic compounds (VOCs), which are transferred from the soil to the gas phase. The different behavior of the four rings compounds, BaA and Chr, is probable due to these compounds are more resistant to thermal decomposition being more thermally stable than the other PAH compounds. This is also confirmed by Robinson et al. (2009) who showed similar findings.

Table 2: PAH removals (%) achievable by MW treatment for the different powers and times investigated

t (min)	P(W)	Bph	Flu	Ant	Phe	Flt	Pyr	BaA	Chr	Per
5	250	90.56	74.72	9.81	51.21	7.52	1.59	12.23	16.30	19.03
5	440 - dry	88.74	77.54	15.18	46.89	14.14	14.68	13.12	15.02	25.27
5	440	91.16	80.15	18.41	58.03	14.38	17.63	13.43	14.97	31.49
5	1000	97.49	93.05	58.86	78.64	51.51	47.52	38.08	39.18	53.58
10	250	97.04	86.10	20.70	60.66	18.61	25.40	22.14	23.52	39.80
10	440 - dry	96.63	87.23	50.87	55.48	30.88	30.60	25.47	28.74	45.00
10	440	96.71	92.05	52.09	72.54	37.29	33.35	29.10	30.36	50.31
10	1000	98.58	97.16	76.87	87.02	60.86	57.98	46.49	47.43	69.82
18	250	97.83	91.23	33.58	74.99	35.76	39.98	34.18	41.85	55.62
18	440 - dry	97.05	93.12	66.67	80.40	44.37	40.85	33.58	30.8	57.7
18	440	97.69	93.36	70.49	82.98	48.58	46.66	34.29	35.46	60.06
18	1000	98.69	100.0	86.95	89.81	68.02	64.00	47.55	48.95	74.38
30	250	98.05	94.01	49.10	75.25	43.28	47.08	43.73	39.86	57.42
30	440 - dry	97.65	93.44	69.69	84.11	48.59	46.66	32.08	30.87	62.26
30	440	98.47	96.81	73.41	85.47	50.10	47.25	32.09	33.29	64.64
30	1000	100.0	100.0	89.04	92.44	69.11	69.48	49.25	50.15	77.03
60	250	98.35	95.59	51.31	76.23	44.16	62.61	45.48	44.14	62.06
60	440 - dry	97.77	96.63	82.01	81.87	66.36	67.55	48.00	49.56	75.22
60	440	98.74	97.07	85.80	92.11	69.59	68.80	49.03	49.93	75.83
60	1000	100.0	100.0	89.40	94.24	70.36	79.40	50.86	51.73	80.08

The fate of removed PAHs was also assessed by means of the analysis of the stripped PAH and their derivatives in the condensate liquid and activated carbon samples (440 W, $t = 60$ min). Analysis showed that all investigated PAHs were detected in the condensed phase after remediation in a range 15 – 25 % of the total PAHs removed from soil samples (Table 2), with a percentage for each PAH decreasing with increasing its boiling point. In the analysed condensed liquid some compounds were identified as fragments (degradation products) of the starting compounds. This phenomenon is frequently observed for example in UVA irradiated PAHs (Librando et al., 2014) or PAH derivatives (Rafael and Morel, 2013). For example, the photochemical degradation of Ant and BaA leads mainly to oxygenated photoproducts such as PAH-hydroxides, as well as ring opening and fragmentation and/or photodimerization, depending on the polarity of the environment (Librando et al., 2014). In the case of nitro aromatic PAHs, the main photoreaction of in the presence of molecular oxygen is frequently the loss of nitro groups and formation of oxygenated derivatives similarly to what happen for PAHs (Holloway et al., 1987).

PAHs and fragmented by-products found suggested the following removal mechanisms: contaminant thermal vaporization due to the surpassing of the heat of vaporisation threshold and molecular bond breaking, producing PAH-derivatives or other smaller molecules (Figure 2).

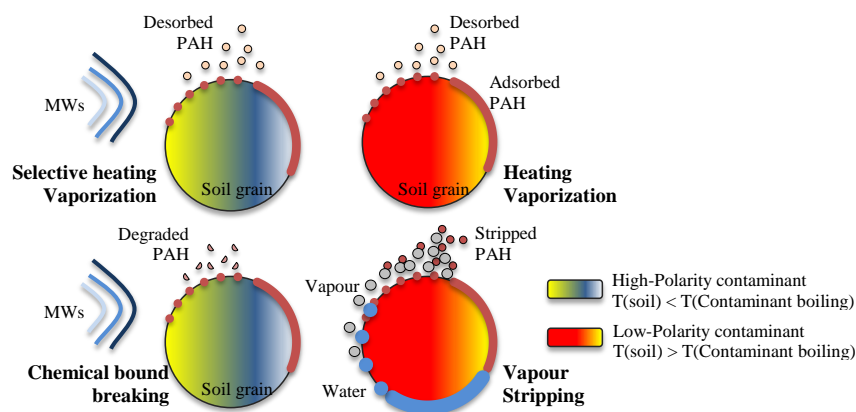


Figure 2: Schematic of PAH removal mechanisms from soil.

PAH removals and related temperature profiles observed for each investigated treatment of dry and moisturized soil samples (Table 2, Figure 1) also suggested selective heating as further removal mechanism (Figure 2). A “selective heating” occurs when a soil and adsorbed contaminant convert the absorbed MW energy into heat following different rates due to their different dielectric properties. Specifically, higher dielectric properties of PAHs respect to the soil led to a higher localized temperature of the adsorbed contaminants which was shown to be not directly measurable (Chien, 2012). Therefore, a selective heating takes place when, as in this work, a significant contaminant removal occurs at a soil temperature significantly lower than the contaminant boiling point. **In general**, it was found that the higher the difference between the boiling point of the contaminant and the soil temperature recorded, the higher the influence of the contaminant polarity in terms of selective heating on the contaminant removal efficiency (Kawala and Atamańczuk, 1998). As a final point, the higher removal efficiencies found for the moisturized (10%) soil samples respect to the dry ones, showed that the presence of water significantly contributed to increase the effectiveness of treatment due to distillation and subsequent contaminant stripping phenomena (Figure 2). In addition, water solubility of organic compounds generally increases with the temperature increasing. At the same time, the existence of water vapour can modify the soil structure, also increasing its porosity, which is favourable to contaminant mass transfer.

4. Conclusions

MWH for removal PAH from contaminated soil was shown to be efficient. PAHs removal rates were observed in the 70 - 100 % range when MWH was applied at 1000 W for remediation times higher than 10 min. Findings also revealed that PAH properties, especially polarity, significantly influence the temperature achievable during the MWH and the removal kinetics. Overall, PAH removal could be due to four different mechanisms: (i) thermal desorption vaporization; (ii) molecular bond breaking; (iii) selective heating vaporization; (iv) contaminant stripping due to steam distillation processes. The obtained kinetics could be useful for studying the future removal process or predicting the response of the remediation activities, as well as for guiding the design and the scale-up of MWH systems. Observed PAH removal mechanism can also represent the basis for the development of novel MWH based-remediation technologies.

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