Remediation of Hydrocarbon Contaminated Soils by Microwave Continuous Irradiation

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ABSTRACT---- ***Hydrocarbon contaminated soil sample was subjected to a continuous microwave irradiation using a 30 kW microwave system. The sample was subjected to treatment using difference flow rate conditions, and the residual organics in the treated samples were extracted using Accelerated Solvent Extractor (ASE 200). By fractionation, the aromatics and aliphatic in the extracted organics were separated. A Varian CP-3800 gas chromatograph coupled to a Varian 1200 Quadrupole mass spectrometer was used to analyse the aromatic fraction to ascertain the polycyclic aromatic hydrocarbon (PAH) level in the treated samples. A thermogravimetric analyser (TGA) was also used to analyse the samples to ascertain the relationship between sample weight losses with increasing temperature. A maximum of 48% organic removal was recorded for the system. An extrapolation of results from the continuous irradiation microwave system with reference to results from batch treatment of the same soil shows the continuous irradiation system to be a more efficient treatment system.***

Keywords--- Hydrocarbons, Petroleum, Microwave irradiation, contaminated soils remediation.

1. INTRODUCTION

Hydrocarbon contamination is a common problem which is not easily resolved by any of the engineering based technique because of its wider range of contamination on ground and soils [1]. According to USEPA [2], petroleum hydrocarbons, especially PAHs are known for their high toxicity, based on their carcinogenic, mutagenic and teratogenic effects on animals. They are also known to have adverse effects on the environment, hence the need to ascertain their proportion in contaminated soils or remediate them prior sending them to disposal sites. Historically, the most common form of remediation has been to remove the contaminated soil and dispose of it in a licensed landfill site. Clean material would then be imported to replace it. There are a number of different technologies; bioremediation [3-14] chemical [15-22], thermal [23-31], and green remediation methods [32], available for land remediation. A combination of techniques can also be employed in treating hydrocarbon contaminated soils [33], e.g. Gong [34] used a combination of biostimulation and modified Fenton oxidation to treat weathered-petroleum contaminated soils. More volatile constituents of hydrocarbon contaminated soil can also be reduced by diffusion using vacuum extraction and passive venting techniques. This process might end up increasing the amount of gaseous pollutants unless the off gasses can be collected and cleaned using complex air cleaners and filters. Physical and/or chemical bond by various stabilization and solidification processes using chemicals (bitumen, cement, asphalt, polyethylene etc) [35, 36] can also render petroleum contaminants immobile. Thermal destruction technique (like oxygen enhanced incineration) which involves heating contaminated soils in incinerators is always not an accepted technique due to complexity of incinerator units and its inability to ensure acceptable emission standards [1, 36]. The use of microwave remediation technique to treat hydrocarbon contaminated soils has been on increase in recent times [37-39]. This may be attributed to its interaction with soils, efficiency and low costs involved in removing hydrocarbon contaminants from soils [38].

In this work, hydrocarbon contaminated soil (sample M) from a location in the United Kingdom (UK) were treated with continuous microwave irradiation using a 30 kW microwave treatment systems at varying flow rates. The aromatic fraction obtained after remediation was analysed to ascertain the level of organic contamination. Results from the analysis may suggest the energy requirement to treat hydrocarbon contaminated soils. Unlike conventional thermal desorption where heating is done by heating bulk of soil material using either direct fired gas stream or large volumetric flow of gas or steam, this approach is chosen because there is no need to introduce chemicals and microbes which would have required legislative permission. Also, the gases volatilised are collected, recycled or reused. This system reduces energy use as heat is concentrated at the microwave-absorbing phase within the contaminated soil. These samples have been previously studied using a batch microwave treatment systems [40]. These report will also compare results obtained on the continuous microwave radiation to the batch treatment systems.

2. EXPERIMENTAL

2.1 Microwave treatment pilot plant experimental procedure

The soil sample preparations, mass balance calculations, and the dielectric properties for this sample have been reported in [40]. The microwave continuous irradiation system (Figure 1) consists of a 30 kW microwave generator, a specially designed tunnel applicator, waveguides (WR430), an automatic tuner, gas/liquid condensation system, an extraction unit, a nitrogen supply system, solid handling system, main drive motor and gear box. The maximum microwave power input was 10 kW. Although treatment was attempted at higher powers but was unsuccessful due to the occurrence of thermal runaway. The microwave generator is a G2450/30kW4BIR model produced by IBF Electronics GmbH & Co. KG-Germany and operates at 2450 MHz. Soil samples were fed manually and directly into the conveyor belt by the inlet of the applicator. A constant bed depth of 30 mm was maintained during the tests, and the speed of the belt was adjusted according to the required soil mass flow rate. Approximately 60 L/min of hot nitrogen at about 60 ^{o}C and pressure of 10 bar was supplied directly into the applicator. While 5-10 L/min of cold nitrogen was supplied into the centre part of the microwave cavity to provide an inert (oxygen free) condition within the applicator.

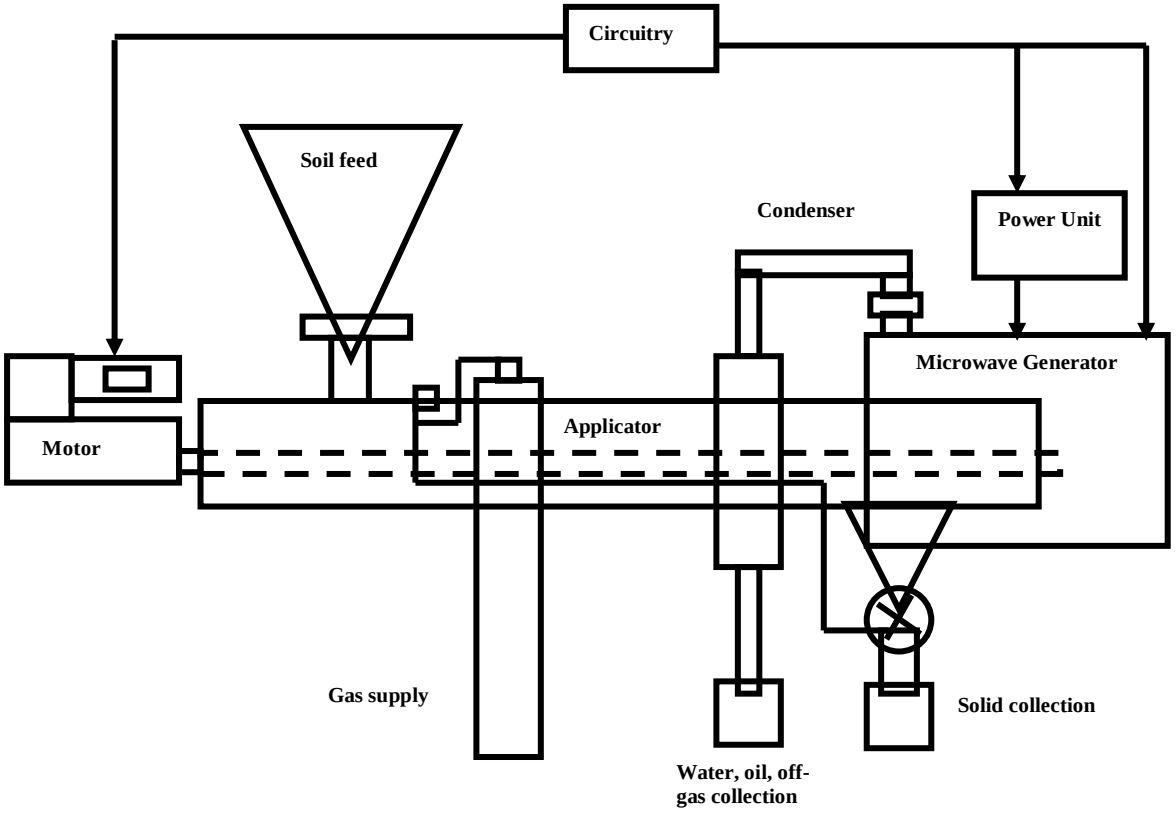

Figure 1 A schematic of the microwave continuous irradiation system

The conveyor belt carried the soil samples into the microwave cavity where the materials were heated uniformly. Water and off-gas were condensed as they passed through the condenser, while treated samples were collected at the end of the conveyor belt as they are discharged into a metal container.

After microwave treatment, the samples were weighed again to ascertain the sample mass loss. The organic contents of the treated samples were determined. After Microwave treatment, an accelerated solvent extraction - ASE 200

manufactured by Dionex Corporation California USA was used for the extraction of organics. While fractionation method was used to separate the organics. This separates the different organic solvents into two groups of compounds; aliphatics and aromatics. The third compound (polar compounds) in the sample was not separated because it was not necessary for this study.

Finally, in conjunction with a gas chromatography (GC), a mass spectrometer (MS) was used to get a precise identification of the peaks of chromatographs. The chromatographic column was a non-polar J & W DB5-MS (50 m X 0.32 mm) employing a cross-linked phenylmethylsiloxane stationary phase, and using helium as the carrier gas. GC/MS analysis was carried out on Varian CP-3000 gas chromatograph equipped with a Fisons 1200 quadrupole mass spectrometer.

3. RESULTS AND DISCUSSION

3.1 Organics removed for sample M

Results obtained showed that the organics removal increased with reduced flow rate at constant power input. This followed from the fact that at 10 kW input power, approximately 35 and 48% of organics were removed for 100 and 50 kg/h flow rates respectively (Figure 2). The higher organic removal observed in the 50 kg/h flow rate may be attributed to the fact that the sample had more residence time within the microwave cavity. Figure 2 shows the results of continuous microwave irradiation on sample M.

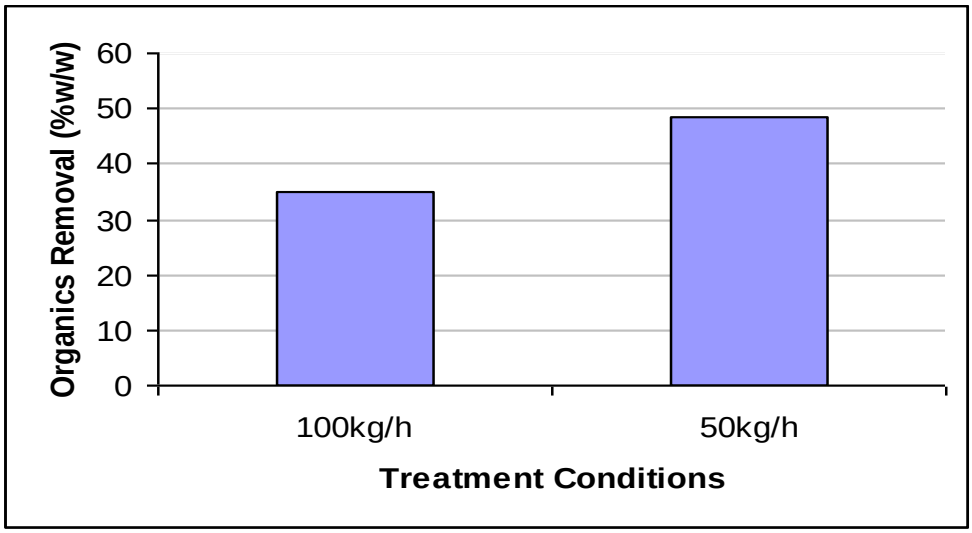

Figure 2 Influence of flow rate on organics removed for M

3.2 PAH removal for sample M

The total PAH level reduced by approximately 77% and 87% of its original level at flow rates of 150 and 50 kg/h respectively (Figure 3). This result was not good enough for regulatory reasons as the total residual PAH levels (2623 and 1450 ppm) obtained after remediation were above the permitted limits (< 100 ppm) in soils [41]. The total residual PAH in the treated samples also increases as the molecular weight of the hydrocarbons increases (Figure 4). Low molecular weight (from 128 to 178) PAHs were totally removed for the 50 and 100 kg/h flow rates. As molecular weight increased from 202 to 278, heavier molecules remained within the sample. Also, as the flow rate increased from 50 to 100kg/h, the molecular weights of the respective residual PAH also increased, showing the effect of less residence time of samples within the microwave cavity

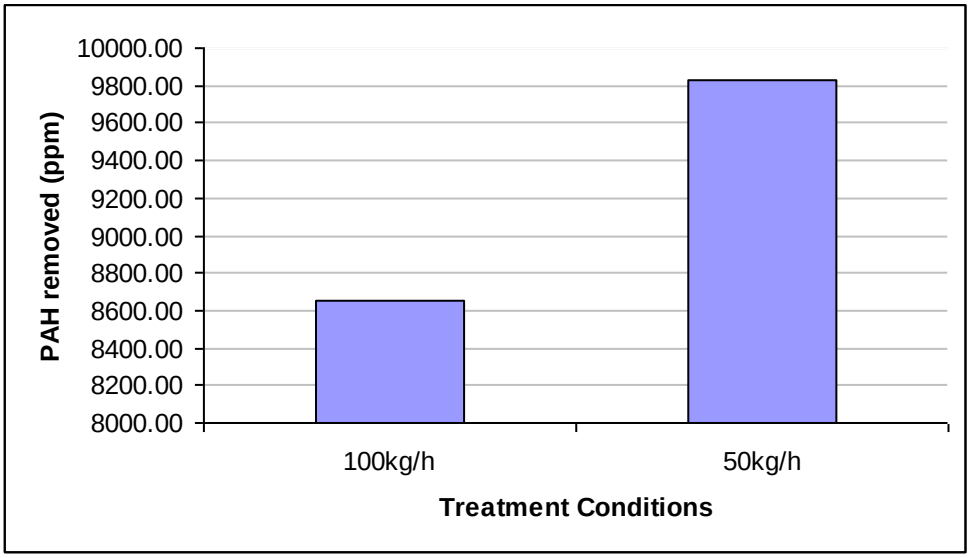

Figure 3 Total PAH removal from sample M for different treatment conditions

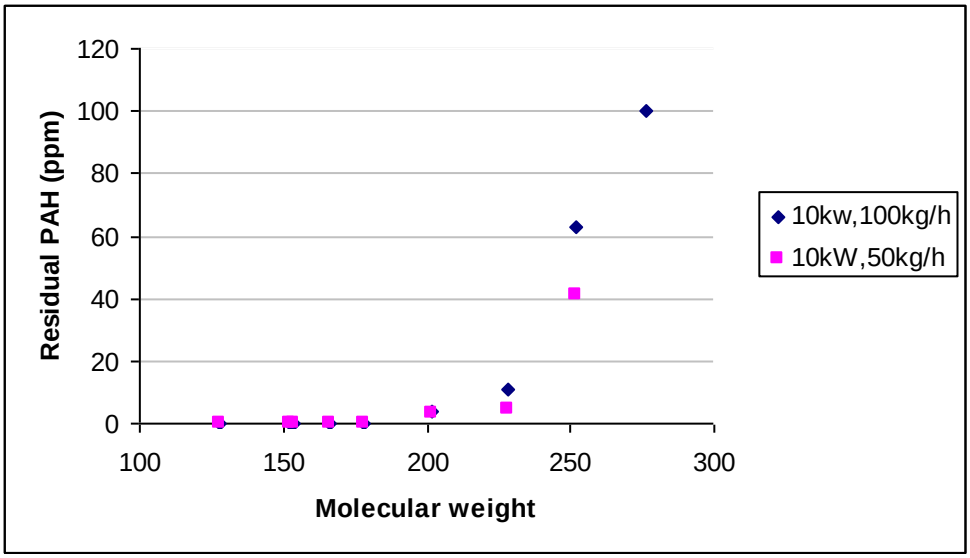

Figure 4 Residual PAH within sample M for different treatment conditions

3.2 Comparison between the batch and continuous trial microwave treatments

Comparison was made for treatment of sample M using a 15 kW microwave batch system (see Ogbuka et al. [40]) and the continuous microwave irradiation system (reported in this work). The results presented in Figure 4 and Figure 6 are representative of the average values obtained from the TGA analyses. Figure 4 shows the TGA profile for the M sample using the continuous irradiation microwave system, while Figure 6 shows the TGA profile for the M sample using the 15 kW microwave batch system.

From Figure 5, it can be seen that the initial weight loss for the 10kW-50 kg/h and 10 kW-100 kg/h treatment conditions were zero and 10% respectively at about 100 ^{o}C compared to 27% weight loss obtained for the fresh sample at the same temperature. This is because most organics have been removed during the microwave treatment. Since this initial weight loss was recorded at about 100 ^{o}C (boiling point of water), it gives an indication that organic removal at this temperature is as a result of entrainment of water molecules. Between 100 ^{o}C and 450 ^{o}C, about 78, 87 and 93% weight loss were observed for the 10 kW-50 kg/h, 10 kW-100 kg/h and the fresh sample respectively.

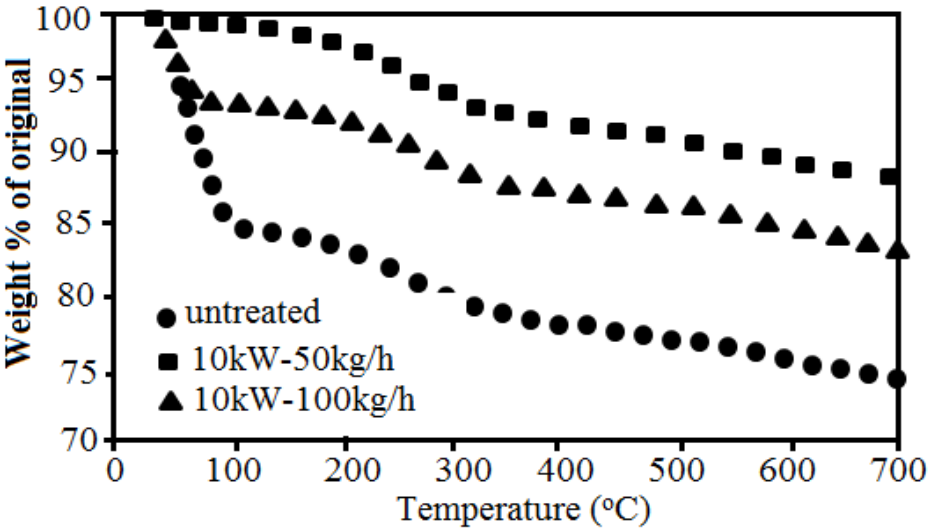

Figure 5 TGA result for sample M in the continuous trial microwave system

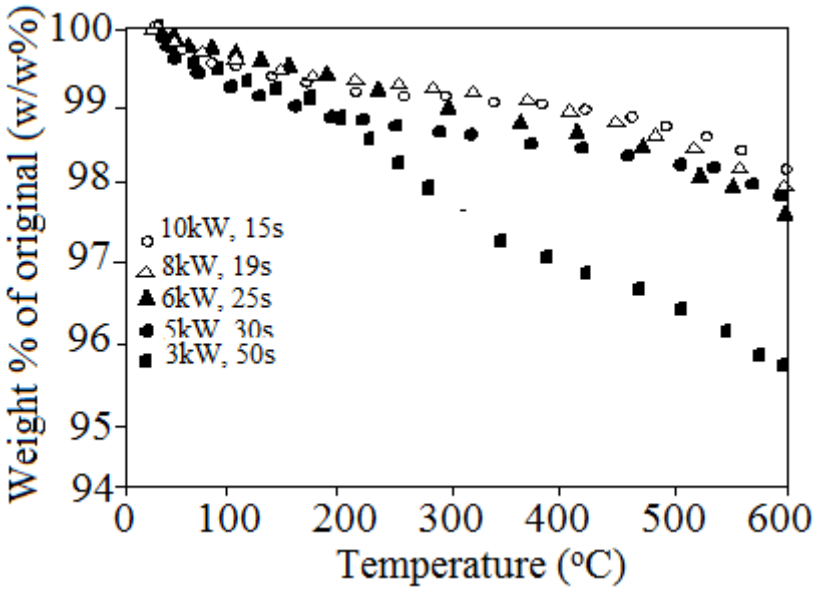

Figure 6 TGA profile for M in the 15 kW microwave system

In contrast to the weight loss profile obtained in Figure 5, the TGA profile for the 15 kW microwave system shows that the proportion of weight loss observed between 100 and 450 ^{o}C increased from about 53% to 98% as power input was increased from 3 kW to 10 kW. Weight loss at higher power resulting from high energy input may be attributed to the pyrolysis of the contaminants. Above 450 ^{o}C, weight loss reduces at a slower rate (low desorption) for both profiles (Figure 5 and Figure 6). This suggest that residual species are either transparent to microwave irradiation or energy input is not sufficient enough to cause further desorption of contaminants. Also, the high volatiles observed at higher temperatures in both profiles suggest that thermal desorption is responsible for removing heavy hydrocarbon molecules from contaminated soils.

The same weight loss trend was reported by Lee et al. [42] from analysed results obtained in treating petroleum contaminated soil by fluidized thermal desorption using a Temperature Programmed Desorption (TPD), at 10 ^{o}Cmin^{-1} heating rate, 20 to 900 ^{o}C and 500 ccmin^{-1} nitrogen flow conditions. Four stages of weight loss which correlates with stages of weight loss discussed in this work were reported. The first steep stage according to their result represents release of volatile organic compounds and water. The second stage represents slower release of oil with temperature increase. In the third stage, weight loss became faster with further increase in temperature. Suggested reason was as a result of the pyrolysis of petroleum products in soils. While the final stage reported was a very slow weight loss which results attributed to release of all volatile matters.

The energy input for the batch treatment tests were based on kWh/t while the flow rate is the main variable for characterising the continuous irradiation treatment system. In order to compare the efficiencies of organic removal of

these systems, their energy input must be expressed in the same unit. Therefore converting flow rate (kg/h) to energy input (kWh/t) can be achieved as described below

$$50kg/h = \frac{1h \times 10kW \times 1000kg}{50kg \times t} = 200kWh/t \quad \text{..... (1) and}$$

$$100kg/h = \frac{1h \times 10kW \times 1000kg}{100kg \times t} = 100kWh/t \quad \text{..... (2)}$$

Where *kg* represents kilogramme, *h* is hour, *kW* represents kiloWatt, and *t* is tonne. Since high higher energy treatment conditions could not be undertaken due to the occurrence of thermal runaway, the calculation of theoretical energy input from recorded results became necessary. Theoretical results were interpolated using equation (3) and results obtained are shown in Table 1.

$$y = 0.13x + 22 \quad \text{..... (3)}$$

Table 1 Results obtained from the extrapolation of energy input and organic removal for sample M treatment

Microwave system	Energy input (kWh/t)	Organics removed (%w/w)
Batch system	891	55
	2107	98
	2003	98
	100	35
Continuous system	200	48
	254	55
	585	98

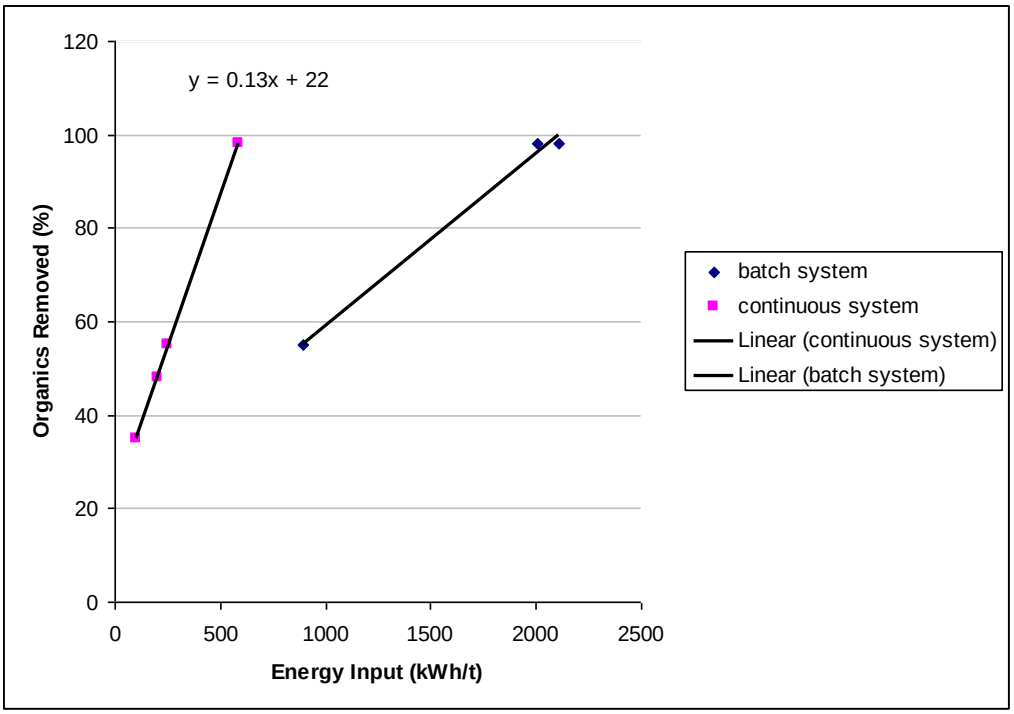

Figure 7 Comparison between energy input and organic removal for sample M treatment using the batch and continuous irradiation treatment systems

From Figure 7, it can be seen that 55% and 98% organic removal were obtained using 891 and 2107 kWh/t respectively for the batch system. The theoretical energy input needed to obtain the same amount of organic removal was calculated to be 254 and 565 kWh/t respectively for the continuous irradiation treatment system. This shows the continuous treatment system to be a more efficient system than the batch system. These theoretical results suggest that if energy input is increased to 600kWh/t, complete remediation may be achieved. This also indicates that a dedicate continuous irradiation microwave treatment system would require lower energy input for complete remediation of hydrocarbon contaminated soils, compared to that which would be needed by a batch microwave treatment system.

Studies by Mediero [43] on microwave treatment of contaminated soils using continuous and batch treatment systems agrees with results obtained in this study. At similar energy input of approximately 100kWh/t, 24 and 35% organic removal was recorded for the batch and continuous irradiation systems respectively.

4. CONCLUSION

The remediation of hydrocarbon contaminated soil using continuous microwave irradiation has been investigated in this study. Microwave treatment has proven to be an effective and efficient way to reduce the organics and PAH levels of soils investigated to considerable limits. The continuous treatment system recorded a maximum organic removal of 48% at 200 kWh/t energy input. The continuous microwave irradiation system performed better than the batch treatment system when results were extrapolated.

5. ACKNOWLEDGMENTS

The authors wish to acknowledge the financial support from the British Council and the University of Nottingham in undertaking this research.

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