

INTERACTION'S EFFECT OF ORGANIC MATERIAL AND AGGREGATION ON EXTRACTION EFFICIENCY OF TPHS FROM PETROLEUM CONTAMINATED SOILS WITH MAE

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Abstract

Microwave Assisted Extraction (MAE) is a type of low temperature thermal desorption process that its numerous advantages have caused a wide spread use of it. Microwave heating is a potentially attractive technique as it provides volumetric heating process to improve heating efficiencies as compared with conventional techniques. The ability to rapidly heat the sample solvent mixture is inherent to MAE and the main advantage of this technique. Presently MAE has been shown to be one of the best technologies for removing environmental pollutants specially PAHs, phenols and PCBs from soils and sediments. Five different mixtures and types of aggregation (Sand, Top soil, Kaolinite) besides three concentrations of crude oil as a contaminant (1000, 5000 and 10000 mg/L) were considered. The results indicated that regardless of aggregation, the presence of humus component in soil reduces the efficiency. Minimum and maximum efficiencies were for sandy soil (containing organic components) and kaolinite (without any organic content), respectively. According to the results of this research when some amount of humus and organic materials are available in the matrix, it causes the extraction efficiency to perform as a function of just humus materials but not aggregation. Increasing the concentration of crude oil reduced the efficiency with a sharp steep for higher concentration (5000-10000 mg/L) and less steeper for lower concentration (1000-5000 mg/L). The concentration of the contaminant, works just as an independent function with extraction time and aggregation factors. The extraction period of 10 min. can be suggested as an optimum extraction time in FMAE for PAHs contaminated soils.

Key words: Aggregation, contaminated soil, microwave, humus, petroleum hydrocarbons

INTRODUCTION

Physical process is a kind of contaminated sites remediation. Methods such as soil washing, supercritical fluid extraction, filtration (Bilstad, 1996), ultra filtration, soil vapor extraction and low temperature thermal desorption are examples of physical processes. Presently it has been shown that low temperature thermal desorption system provides numerous advantages that cause growing interest for it. In this technique, contaminated soil depending on its contaminations boiling points are heated between 90 to 320 °C. So organic pollutants are disturbed while they are removing. In addition, only the moisture, volatile organic compounds (VOCs) and semi-volatile organic compounds

(SVOCs) will be evaporated and carried to gas treatment and air pollution controlling equipments. The temperature of the bed and the retention time for matrix are carefully considered to prevent contaminants from oxidation. However, little changes may happen in the heated matrix (Naghizadeh, 2005). Petroleum hydrocarbons are kinds of hazardous wastes that might be dispersed in the environment (Dobler *et al.*, 2000 and Juhasz, 2000). Most of them are toxic and resist to biodegradation; so may leach to groundwater (Ewies *et al.*, 1998). Polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons are considered as the important kinds of hazardous wastes. These two kinds are similar in so many of their characteristics such as boiling point and etc. However, the measurement of PAHs was

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considered as an index of an environmental matrix. Polycyclic aromatic components tend to solve in lipid tissues intensely and accumulate in the body (Kastner, 2000). Also they have carcinogenic, mutagenic and teratogenic effects on human beings. Considering the high ratio of octanol-water for these components, they are very hydrophobic and tend to precipitate in soils and sediments (Reisinger *et al.*, 1994 and Juhasz, 2000). However developing the biodegradation processes or thermal desorption techniques are necessary. Using microwave energy as a low-temperature thermal desorption system is a modern way to remediate brown sites. In recent years, microwave-assisted extraction (MAE) has attracted growing interest as it allows rapid extractions of solutes from solid matrices, using small solvent volume about 10 times less than other methods with extraction efficiency comparable to that of the classical techniques (Camel, 2000; Sparr, 2000 and Appleton *et al.*, 2005). Presently MAE has been shown to be one of the best technologies for removing environmental pollution specially PAHs, phenols and PCBs from soils and sediments (Appleton *et al.*, 2005). MAE is a process of using microwave energy to heat solvents in contact with a sample in order to partition analytes from the sample matrix into the solvent. The ability to rapidly heat the sample solvent mixture is inherent to MAE and the main advantage of this technique. It may be categorized into two different systems (Camel, 2000; Sparr, 2000):

Closed System

This system is sometimes called as a pressurized microwave-assisted extraction (PMAE). In closed vessels, the solvent can be heated above its boiling point at atmospheric pressure, thus enhancing both extraction speed and efficiency. Such systems permit temperature control of the extraction process. In addition, they usually increase sample throughput if several vessels are used that allows simultaneous extractions to be performed.

Open Systems

In the so called focus microwave-assisted extraction (FMAE), extraction proceeds under atmospheric pressure. As a consequence, the maximum possible temperature is determined by

the boiling point of the solvent at that pressure. Such systems use focused microwaves, so that the heating of the sample is homogeneous and very efficient. Very recently, this system has been improved in order to allow multiple extractions. Also larger samples may be extracted in such systems than in closed vessel systems. Open vessel extractors are usually preferred when organometallic compounds are to be extracted, as the precise control of the energy delivered to the sample prevents destruction of the carbon-metal bonds.

Mechanisms of MAE

Polar molecules and ionic solutions (Usually acids) will absorb microwave energy strongly because they have a permanent dipole moment that will be affected by the microwaves. However non-polar solvents such as hexane will not heat when exposed to microwaves. The fact that different chemical substances absorb microwave energy to different extents implies that the heating imparted to the surrounding media will vary with the chemical substances used. Hence for samples with non-homogeneous structural characteristics, or that contain various chemical species with different dielectric properties dispersed into a homogeneous environment, it is possible to produce a selective heating of some areas, or components of the sample. This phenomenon is sometimes called superheating (Sparr, 2000).

This paper gives a brief presentation of the theory of microwave and extraction systems and a discussion of the effect of concentration and the interaction between organic materials with aggregation on the extraction efficiency of PAHs from petroleum contaminated soils with observed results by focused microwave-assisted extraction.

MATERIALS AND METHODS

In this research all the results were based on the FMAE methods. Crude oil from Tehran Refinery was considered for this investigation. Dichloromethane was used as a solvent and it has been suggested that anhydrous sodium sulfate can be added to soil samples to handle water during the MAE procedure. Finally five different types of aggregation, kaolinite, top soil, sand, the mixture

of sand with kaolinite (1:1) and the mixture of sand with top soil (1:1) were considered to do the research. At the first step, in an optimum excitation and emission range for crude oil, calibration curve has been drawn. Then spiked soils were sampled and MAE procedure has been performed. In order to measure the concentration of analytes according to EPA Method 3550C, November 2000, samples were taken both before the process and after it. To investigate the extraction efficiency, blank soil samples were examined in the same condition just like spiked ones. To determine the remained contamination concentration of treated samples, the observed intensity from the Ultraviolet Fluorescence (UVF) has been put in equation of equilibrium from calibration curve and the

concentration was calculated. In this research 3 concentrations of crude oil (1000, 5000 and 10000 mg/L) has been considered for studying the effect of concentration on extraction efficiency. The particle sizes of the extracted materials were in the range of 0.1-2 mm. The optimum extraction times were 10 and 20 minute. The first level of sample's moisture was 35 to 40 % and finally the used temperature was 225 °C.

RESULTS

In Fig. 1 the equation of equilibrium from calibration curve is shown. Fig. 2 shows the effect of the interaction between aggregation and organic components in soils within 10 minutes extraction time for various concentrations of TPH.

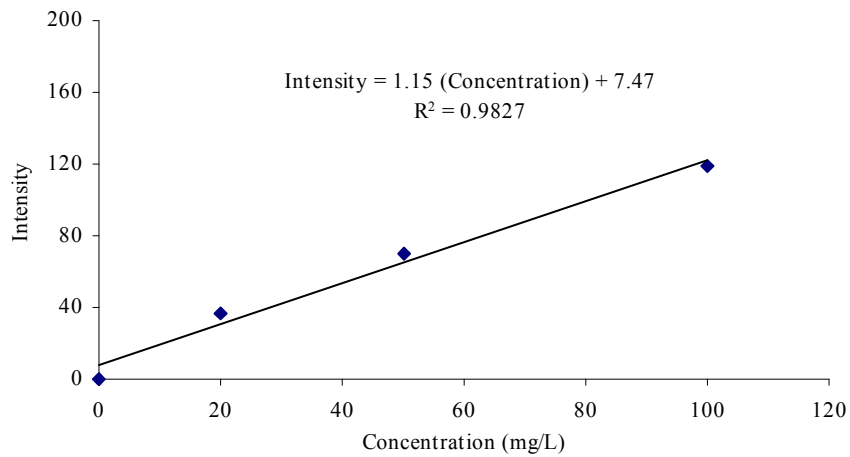


Fig. 1: The calibration curve for crude oil in UVF

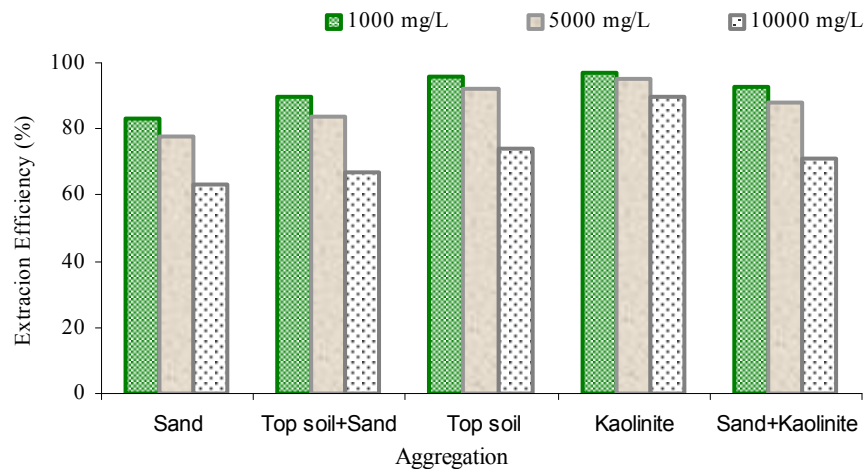


Fig. 2: Interaction of organic components with aggregation in soils (10 min)

The maximum removal efficiency for various concentrations in 10 minutes process belonged to Kaolinite sample and the minimum was for Sandy soil.

Fig. 3 shows the results of the same conditions like Fig. 2 during 20 minutes extraction time for various concentrations of TPH.

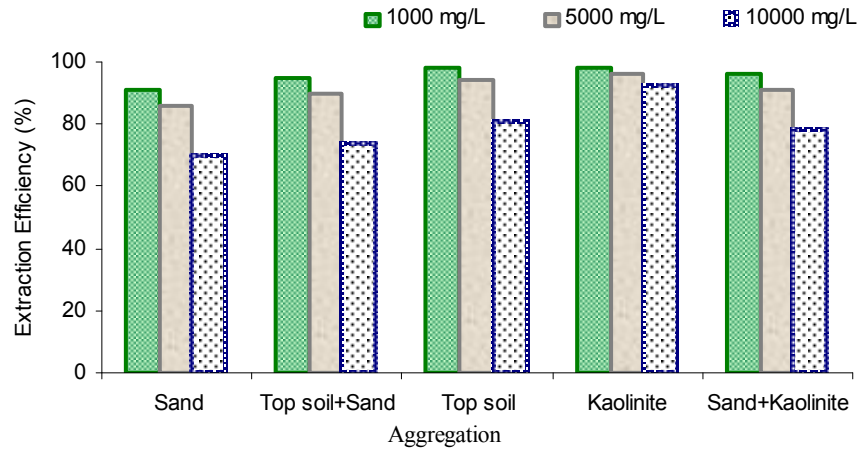


Fig. 3: Interaction of organic components with aggregation in soils (20 min)

Table 1 shows the result of experiments for studying the effect of the interaction between the presence of soil organic components and

aggregation in different concentrations by 10 and 20 minutes detention times on extraction efficiency.

Table 1: Extraction efficiency of MAE affected by the interaction between soil organic materials and aggregation for different concentrations by 10 and 20 min.

Detention Time (min)	Conc. (mg/L)	Sand	Top soil + Sand	Top soil	Kaolinite +Sand	Kaolinite
10	1000	83%	90%	96%	92%	97%
10	5000	78%	84%	92%	88%	95%
10	10000	62%	67%	74%	71%	90%
20	1000	91%	95%	98%	96%	98%
20	5000	86%	90%	94%	91%	96%
20	10000	70%	74%	81%	78%	92%

In Table 2 the results of the observations for the blank soil samples has been shown. Fig. 4 and Fig. 5 show the effect of concentration on the

extraction efficiency of TPHs within 10 and 20 minute in MAE process.

Table 2: Extraction efficiency of MAE for blank soil samples

µg/ml	Kaolinite	Top soil	Sand + Top soil	Sand + Kaolinite	Sand
C ₀	0	0	6	4	16
C _f	0	0	6	4	16

C₀: Primary concentration of soil samples before MAE
 C_f: Final concentration of soil samples after MAE

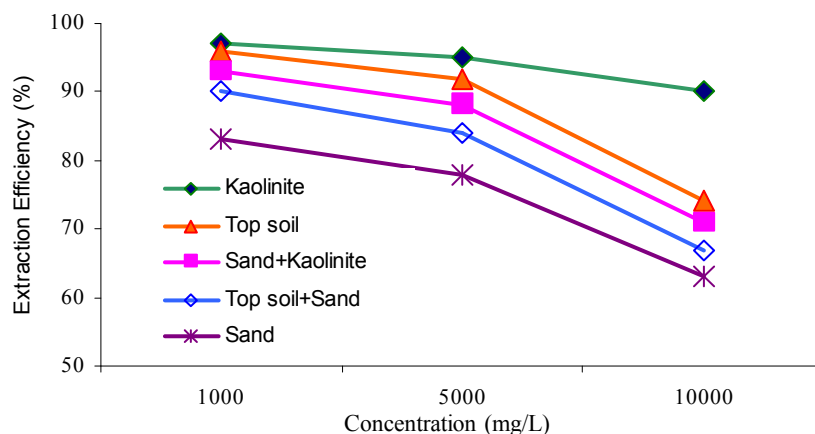


Fig. 4: The effect of concentration on the extraction efficiency of TPHs within 10 min in MAE

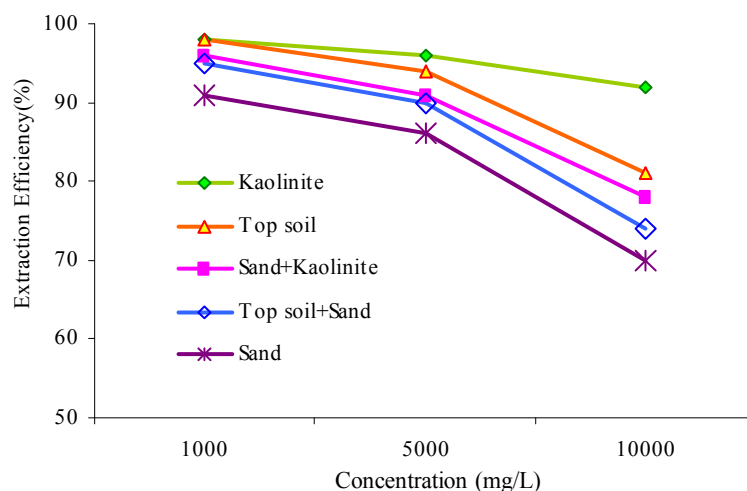


Fig. 5: The effect of concentration on the extraction efficiency of TPHs within 20 min in MAE

DISCUSSION

Aggregation is one of factors which strongly affects the extraction efficiency of TPHs with MAE from soils and sediments (Camel, 2000; Sparr, 2000). It can be said that as the aggregation content of the contaminated matrix becomes finer (Loam and Clay), the removal efficiency of contaminants decreases. The higher specific surface of the finer materials leads to increase contamination adsorption to the matrix. In addition, as the CEC capacity of clay soil is high, it's contaminants strongly bind to the matrix, making the extraction process difficult and reducing the overall efficiency (Bhandari *et al.*, 2001).

Based on the results shown in Fig. 2, 3 and Table 1, it can be seen that the different types of matrices in various concentrations rank in the order of decreasing efficiencies as follows; Kaolinite, top soil, sand+kaolinite, sand+top soil and finally sandy soil.

Increasing heating (detention) time from 10 minutes to 20 minutes does not appear to have a considerable effect on the extraction efficiency. Accordingly, the extraction period of 10 min. can be suggested as an optimum extraction time in FMAE for PAHs contaminated soils.

Table 3 shows some applications and extraction efficiency of MAE for TPHs.

Table 3: Applications and extraction efficiency of MAE for TPHs

Matrix	System	Extraction conditions	Recovery (%)
VEGETALS			
Pollen and spruce needles	Closed vessel system (CEM MES 1000)	5 g dried matrix, 50 ml hexane-acetone 3:2, 140°C, 20 min	Pollen: 119-192 Needles: 92-171 (vs. sonication)
SOILS AND SEDIMENTS			
Spiked soil	Closed vessel system (CEM MES 1000)	5 g soil, 30 ml hexane-acetone 1:1, 115°C, 1000 W, 10 min	47-116
Certified sediment (NIST 1941a)	Closed vessel system (CEM MES 1000)	10 g soil, 30 ml CH ₂ Cl ₂ , 115°C, 1000 W, 10 min	48.5-129
Marine sediments (certified and real samples)	Closed vessel system (CEM MES 1000)	5 g sediment, 30 ml hexane-acetone 1:1, 115°C, 500 W, 5 min	73.5-136.8
Contaminated soils	Closed vessel system (CEM MES 1000)	2 g soil, 40 ml acetone, 120°C, 300 W, 20 min	-
Spiked soil	Open vessel system (Prolabo)	10 g soil, 50 ml CH ₂ Cl ₂ , 30 W, 10 min	63.9-112
Native, contaminated soils	Open vessel system (Prolabo, Soxwave 100)	2 g soil, 70 ml CH ₂ Cl ₂ , 297 W, 20 min	64-125.6 (vs. Soxhlet)
Native, contaminated soils	Closed vessel system (CEM MES 1000)	2 g soil, 40 ml acetone, 120°C, 300 W, 20 min	70.5-106.1 (vs. Soxhlet)
Certified soils, sediments and particulate matter	Open vessel system (Prolabo, Maxidigest MX 350)	1-5 g sample, 30 ml CH ₂ Cl ₂ , 30 W, 10 min	66-109 (vs. certified)
Marine sediments (certified SRM 1941a, and real samples)	Open vessel system (Prolabo Soxwave 100)	0.3-10 g sediment, 30% moisture, 30 ml CH ₂ Cl ₂ , 30 W, 10 min	89 (vs. certified)
Contaminated soil	Open vessel system (Prolabo Soxwave 100)	5 g soil, 40 ml acetone-CH ₂ Cl ₂ 1:1, 30 W, 10 min	36-200 (vs. Soxhlet)
Certified soils and sediments	Closed vessel system (CEM MES 1000)	5 g soil, 30 ml hexane-acetone 1:1, 115°C, 475 W, 10 min	70.8-128.1 (vs. Soxhlet)
Sediments	Domestic oven (closed vessels)	2-10 g sediment, 6-30 ml toluene, 1 ml water, 660 W, 6 min	49-150 (vs. certified)
Soil, sediment and wet sludge	Closed vessel system (CEM MDS 2100)	3-6 g sample, 22 ml NMP, 130°C, 60 min	99-107 (vs. Soxhlet)
Real contaminated matrices (diesel contaminated soil, cokery soil) and certified materials (soil, urban dust)	Closed vessel system (CEM MES 1000)	0.1-2 g soil, 10 ml hexane-acetone 1:1, 115°C, 950 W, 20 min	116.7 (vs. Soxhlet)
Certified soil (ERA soil) and marine sediment (NIST 1941a)	Closed vessel system (CEM MES 1000)	5 or 10 g sample, 30 ml hexane-acetone 1:1, 115°C, 950 W, 10 min	76-132.2 (vs. certified)
Spiked soil	Open vessel system (Prolabo Microdigest 301)	7 g soil placed in a cellulose cartridge, 1 ml water, 30 ml CH ₂ Cl ₂ , 15 s/cycle, 100 W, 10 cycles	26-114
WATER SAMPLES			
Spiked tap water, sea water	Closed vessel system (CEM MES 1000)	Sample pre-extracted onto a C ₁₈ disk, 10 ml acetone, 100°C, 475 W, 7 min	94-108 (vs. Soxhlet)

Corresponding to the Table 2, the sandy matrices contained some primary organic contents (16 mg/L) and fine matrices don't have any organic load before doing MAE process. Based on the observed results, when some amount of humus and organic materials are available in the matrix, it caused the extraction efficiency to decrease and perform as a function of just humus materials but not aggregation. So it can be suggested that the

presence of organic materials in the matrix has overcome the effect of aggregation factor on the extraction efficiency in a way that the sandy soil with some primary organic contents has the minimum removal efficiency but the kaolinite and top soils matrices without any organic material contents have the maximum removal efficiencies (Sparr, 2000; Bhandari *et al.*, 2001 and Ali, 2004). It is understood that the more humus materials

the matrix contains, the less removal efficiency obtains. Concentration is the other important factor on the removal efficiency of TPHs by MAE procedure (Beck *et al.*, 1995). The more contaminants the matrix contains, the less decrease in removal efficiency is obtained. Because when the concentration of contaminants is increased, the penetration potential into the soil's pores and also adsorption factor will strongly develop (Roberts, 1991; Beck *et al.*, 1995; Pennington *et al.*, 1995 and Schlebaum *et al.*, 1998). It means that the amount of adsorption for petroleum hydrocarbons depends on their concentrations in the matrix either can affect the extraction efficiency. Also the increase of adsorbed contaminants into the soil matrix, cause it to obtain sharper slope for higher concentration of crude oil in the experiments (Boethling, 1979 and Alexander *et al.*, 1995). The more crude oil in the matrix is, the more amount of contaminants will adsorbed into the matrix and the more decrease in removal efficiency occurs.

Considering Fig. 4 and 5, regardless of the aggregation of the matrix, the highest removal efficiencies were obtained from the sample with 1000 mg/L crude oil contents. Soils with 5000 and 10000 mg/L concentrations of crude oil were in the next levels in condition that the extraction times were both 10 and 20 minutes. In addition, the slopes of curves in lower concentrations of crude oil were sharper than the same condition for higher concentrations.

The concentration of the contaminant, works just as an independent function with extraction time and aggregation factors.

Obviously, the average removal efficiency for the sandy soils which are categorized as samples with minimum extraction efficiency in this research was about 74% and that was about 94% for kaolinite samples with the maximum removal efficiency. These observations are comparable with other results which are reported during recent years by scientist all over the world. For example reports show that the percentage of recovery for the spiked soils using FMAE with dichloromethane as a solvent within 10 minutes extraction time was obtained 63.9-112. In another case, the recovery was ranged between 64-125.6 for native

contaminated soils using the same conditions as it is mentioned above but in 20 minutes. For marine sediments in an open vessel system within 10 minutes detention time using dichloromethane, the removal efficiency was 89% (Camel, 2000).

As it is obvious in Table 3, MAE is capable to remediate a wide range of matrices such as vegetals, soils and sediments, marine sediments, spiked or native contaminated soils, wet sludge and also water samples with considerable efficiency.

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REFERENCES

- Alexander, M., (1995). How toxic are toxic chemicals in soil. *Env. Sci. Tech.*, **29**, 2713-2717.
- Ali, H., (2004). Remediation of petroleum contaminated soils with soil washing. M. Sc. Project, Environmental Engineering Division of Civil Engineering Department, Tarbiat Modares University, Tehran, Iran
- Appleton, T.J., Colder, R.L., Kingman, S.W., Lowndes, I.S., (2005). Microwave technology for energy-efficient processing of waste. *Applied Energy*, **819**, 85-113.
- Beck, A.J., Wilson, S.C., Alcock, R.E., Jones, K.C., (1995). Kinetic restraints on the loss of organic-chemicals from contaminated soils- implication for soil-quality limit. critical reviews in *Env. Sci. Tech.*, **25**, 1- 43.
- Bhandari A., Novak, J.T., Dove, D.C., (2001). Effect of soil washing on petroleum hydrocarbon distribution on sand surface. *Hazardous Substance Research*, **67**, 148-161.
- Bilstad, T. and Espedal, E., (1996). Membrane separation of produced water, *Wat. Sci. Tech.*, **34** (9), 239-246.
- Boethling, R.S., Alexander, M., (1979). Effect of concentration of organic chemicals on their biodegradation by natural microbial communities. *Applied and Environmental Microbiology*, **37**, 1211-1216.
- Camel V., (2000). Microwave-assisted solvent extraction of environmental samples. *Trends in Analytical Chemistry*, **19** (4).
- Dobler, R., Saner, R., Bachofen, M., (2000). Population changes of soil microbial communities induced by hydrocarbon and heavy metal contamination. *Bioremediation*, **4** (1), 41-56.
- Ewies J.B., Ergas, S.J., Chang, D.P.Y., Schroeder, E.D., (1998). *Bioremediation principles*, mcgraw-hill. inc.
- Juhasz, A.L. and Naidu, R., (2000). Bioremediation of high

- molecular weight polycyclic aromatic hydrocarbons: A review of the microbial degradation of benzo[a]pyrene. *International Biodeterioration and Biodegradation*, **45**, 57-88.
- Kastner M., Rehm H., Reed J., Wiley-Vch. G., (2000). Degradation of aromatic and polyaromatic compounds. *Biotechnology Environmental Processes*, 2nd Ed, , Germany, 211-271.
- Naghizadeh, Gh., (2005). Remediation of petroleum contaminated soils with low-temperature thermal desorption. M. Sc. Project, Environmental Engineering Division of Civil Engineering Department, Tarbiat Modarres University, Tehran, Iran
- Pennington, J.C., Hayes, CA., Myers, KF., Ochman, M., Gunnison, D., Felt, DR., McCormick, EF., (1995). Fate of 2,4,6-trinitrotoluene in a simulated compost system. *Chemosphere.*, **30**, 429- 438.
- Reisinger H.J., Johnstone, EF., Hubbard, JP., (1994). Cost effective & feasibility comparison of bioventings vs. conventional soil venting. *Hydrocarbon Bioremediation*, Lewis, USA, 447-557.
- Roberts, P.V., Ball, W.P., (1991). Long-term sorption of halogenated organic chemicals by aquifer material : Equilibrium. *Env. Sci. Tech.*, **20**, 1223-1235.
- Schlebaum W., Badora, A., Schraa, G., Riemsdijk, WHV., (1998). Interactions between a hydrophobic organic chemical & natural organic matter: Equilibrium & kinetic studies. *Env. Sci. . Tech.*, **32**, 2273- 2277.
- Sparr, E. C., Bjorklund, E., (2000). Analytical-scale microwave-assisted extraction. *Chromatography A*, **902**, 227-250.