Journal of Hazardous Materials 170 (2009) 871–875

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Effect of ultrasound on removal of persistent organic pollutants (POPs) from different types of soils

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ARTICLE INFO

Article history:
Received 12 June 2008
Received in revised form 9 May 2009
Accepted 11 May 2009
Available online 19 May 2009

Keywords:
Ultrasonication
Soil remediation
POPs

ABSTRACT

A new and promising technology is utilization of sonochemistry on decontamination of polluted soil. The feasibility of this technology on treatment of contaminated soils (synthetic clay, natural farm clay, and kaolin) was studied by using two target persistent organic pollutants (POPs): hexachlorobenzene (HCB) and phenanthrene (PHE). The soils were highly contaminated in 500 mg/kg. The laboratory experiments were conducted with various conditions (moisture, power, and time duration). The effects of these parameters on ultrasonication (as well as the removal of contaminants) were examined. The reasonable moisture ratio of the slurry could be in range of 2:1–3:1. The process did not change pH values of soils. Experimental results showed that ultrasonication has a potential to reduce the high concentrations of these POPs.

1. Introduction

Soil contamination is a significant concern to environment due to a critical threat to health through food system and groundwater. Among soil contaminants, hydrophobic persistent organic pollutants (POPs) are of particular concern because of their long half life and toxicity. Though there are some remediation technologies, the treatment of POPs as they are adsorbed strongly in soils, still remains a problem. Therefore, more extensive researches are needed in the field.

Desorption of adsorbed POPs from soil matrix is the first task and then consequently the degradation of the pollutants. Ultrasonication associates with two important phenomenon: formation and collapse of cavitation bubbles that generates extremely high pressures and temperatures in the center of cavitation bubbles [1]. It is a new and clean field due to limitation of the available methods using no chemicals to eliminate the undesirable chemicals from contaminated matrix. A large number of studies have been reported on sonodegradation of organic pollutants in water [2,3]. Ultrasonication was used as pre-treatment process to improve wastewater [4] and saline solution disinfection [5]. Ultrasound irradiation could also enhance membrane filtration of wastewater [6] and sludge stabilization [7,8]. Ultrasonication exhibits a great potential of being environmental friendly and economically competitive treatment method [9]. On the other hand, ultrasonication was taken as method to promote the process of soil washing [10]. Water passes across the substrate on an ultrasonically shaken tray irradiation. Ultrasonication induces high fluid-solid shear stresses, which promotes mechanical detachment and removal of contaminants [11]. Two basic mechanisms for acoustically enhanced soil washing which have been suggested are abrasion of surface cleaning and leaching out of more deeply entrenched material [12]. With successful applications of high power ultrasound in mineral processing, ultrasonic leaching was investigated for the decontamination of various kinds of contaminants like heavy metals and organic compounds from different types of soils [13].

Ultrasound was also used as an enhancement method for electrokinetic treatment of heavy metals and polycyclic aromatic hydrocarbon in contaminated soils. When ultrasonic energy was applied, viscosity of fluid phase decreased, flow rate increased, sorbed contaminants mobilized, cavitation developed, porosity and permeability increased resulting in increased removal efficiency [14]. Moreover, ultrasonication not only assists the desorption of the contaminants from the soil, but also promotes the formation of the strong oxidant, OH radical [15]. Ultrasonic energy can destroy the contaminants through oxidation by free radicals and pyrolysis processes, not only transport the contaminants from one place to other place like in conventional soil washing.

Only few researches which focused on remediation of the contaminated soil were conducted by sonication. Previous studies indicated that sonication could enhance pollutant removal and the degree of enhancement could depend on a number of factors such as sonication power, water flow rate, and soil type [16]. The objective of this lab-scale study was to investigate the possibility of ultrasonic treatment on different types of clayey soils contaminated

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0304-3894/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2009.05.048

by persistent organic compounds at high concentrations. Because of their low permeability, clayey soils often are difficult mediums to treat. However, the cavitations (opening bubbles) produced in clay/silt by ultrasonication can increase its porosity and permeability [17]. Therefore, research into fundamental factors like moisture content, power, pH, time, temperature affecting ultrasound remediation of contaminated soils was conducted to understand the potential treatment process.

2. Materials and methods

2.1. Chemicals and equipments

The representative persistent organic compounds chosen in these experiments were hexachlorobenzene (HCB, 99%) and PAHs, phenanthrene (PHE, 97%). The HCB was purchased from Sigma–Aldrich, and phenanthrene, hexane, acetone from Merck. All chemicals were of analytical grade.

The ultrasonic processors used in these experiments were UP100H with operating frequency of 30 kHz, power of 100 W from Hielscher Ultrasonic Ltd. (In power series' experiments, 24 kHz frequency, power of 400 from Hielscher Ultrasonic Ltd. was also used.) The power of these ultrasonic processors could be controlled in the amplitude range of 20–100%.

2.2. Characteristics of soils

Three clayey soils were used in these experiments: white kaolin (VWR), clay (Sinooperi Ltd.), and natural soil (the farm in Ristiina, Finland). Some main characteristics of these soils are summarized in Table 1.

2.3. Experimental methodology

2.3.1. Soil preparation

Natural farm soil and synthetic clay were dried and grinded in porcelain mortar with pestle. They were then sieved in a 2-mm-sieve. Kaolin was in powder size. For contamination of soil, HCB and PHE were weighed for 500 mg/kg soil. They were dissolved in hexane and then mixed with soil. Different sample soils were soaked with solutions separately. The soil and solution were mixed well with stainless steel spoon to make homogeneous distribution of compounds in the soils. Then, the slurries were kept in flume wood for about 7 or more days to assure total evaporation of solvents [15,18,19]. In some samples, it was then washed by water and dried again at 80 °C in oven for 12 h. It gave no significant change in concentration from that of without washing. After them, no more washing was done. From this result, it was considered the PAHs were adsorbed in kaolin. The most homogeneous distribution of PAHs in the spiked soil was observed by Sawada et al. when the slurry of kaolin and acetone containing PAHs were evaporated by a rotary evaporator at 30–35 °C [20]. Before starting each experiment, the concentration of pollutants in the soils was measured.

Table 1
Some main characteristics of the three soils.

Parameters	Kaolin	Synthetic clay	Natural soil
Color	White	Brown yellow	Grey brown
pH	5.0	7.8	5.6
Dry bulk density (g/cm^3)	0.508	0.895	0.886
Moisture (%)	1.11	4.95	3.53
Particle size distribution (USDA)			
% sand	3.9	6.76	39.04
% silt	20.2	62.66	54.64
% clay	75.9	30.58	6.32

Table 2
Summary of experimental conditions.

	Test	V-water (ml)	Frequency (kHz)	Power (W)	Duration (h)
Water series	1	100	30	100	1
	2	200	30	100	1
	3	300	30	100	1
Time series	1	300	30	100	1
	2	300	30	100	2
	3	300	30	100	4
	4	300	30	100	6
Power series	1	300	~30	20	1
	2	300	~30	50	1
	3	300	~30	70	1
	4	300	~30	100	1

2.3.2. Ultrasonic irradiation

Desired amounts of soils and water were taken in glass beakers and were mixed by glass rod to get homogenous slurries. The slurries were subjected to ultrasonic waves at desired frequency and amplitude of power during a desired period of time.

The tests were conducted with three different soils, 100 g soil weight each, in three series: water series, time series and power series: (1) water series were conducted with various volume amounts of water at the same 30 kHz frequency with constant power 100 W during 1 h to find out the appropriate water ratio for ultrasonication; (2) each time-test was conducted with 300 ml water at 30 kHz frequency and power applied 100 W during 6 h to study the effects of ultrasonication on different parameters of soil mediums like temperature, pH and mainly the POPs removal efficiency along with time; (3) pH was measured by using a pH-meter (pH730 inolabWTW series). Finally, the power series investigated the effects of various power input applied during ultrasonication. Each power-test was conducted with various power applied and 300 ml water at about 30 kHz frequency during 1 h. Different conditions of the three series are summarized in Table 2.

2.3.3. Extraction and analysis

After ultrasonic irradiation, the temperatures and pH of slurries were measured. The slurries were dried in an oven at 80 °C overnight. The dried slurries were pulverized for analysis. pH values of the dried and pulverized soil samples were also measured by pH-meter in 2 h after stirring 10 mg soil in 10 ml double distilled water. One gram of each dried and pulverized sample were mixed with 5 ml hexane in glass tube and was put into ultrasonication bath for 30 min to get the organic compounds extracted from the soil mediums into hexane solvent. The glass tubes were centrifuged at 5000 rpm for 10 min. The supernatants were then taken into small glass vials for GC–MS analysis to get the concentrations of those model organic compounds remained in the soils. This method was taken instead of the traditional approach, Soxhlet extraction because it gives nearly identical results that came from traditional method and is fast and less organic solvent required [21,22].

3. Results and discussion

3.1. Water series

The oxidation of organic compounds by sonocation highly depends on the energetic hydroxyl radicals' formation during the process [23]. Therefore, amount of water (fluid) is an important factor. The remediation efficiency corresponded with different water soil ratios are shown in Fig. 1. With increase in ratio of water and soil, the efficiency increased. At 1:1 ratio, 12.2 mg/kg of HCB and 67.5 mg/kg of PHE was removed in 1 h whereas 25.1 mg/kg of HCB and 97.5 mg/kg of PHE at 3:1 ratio of water and soil was removed

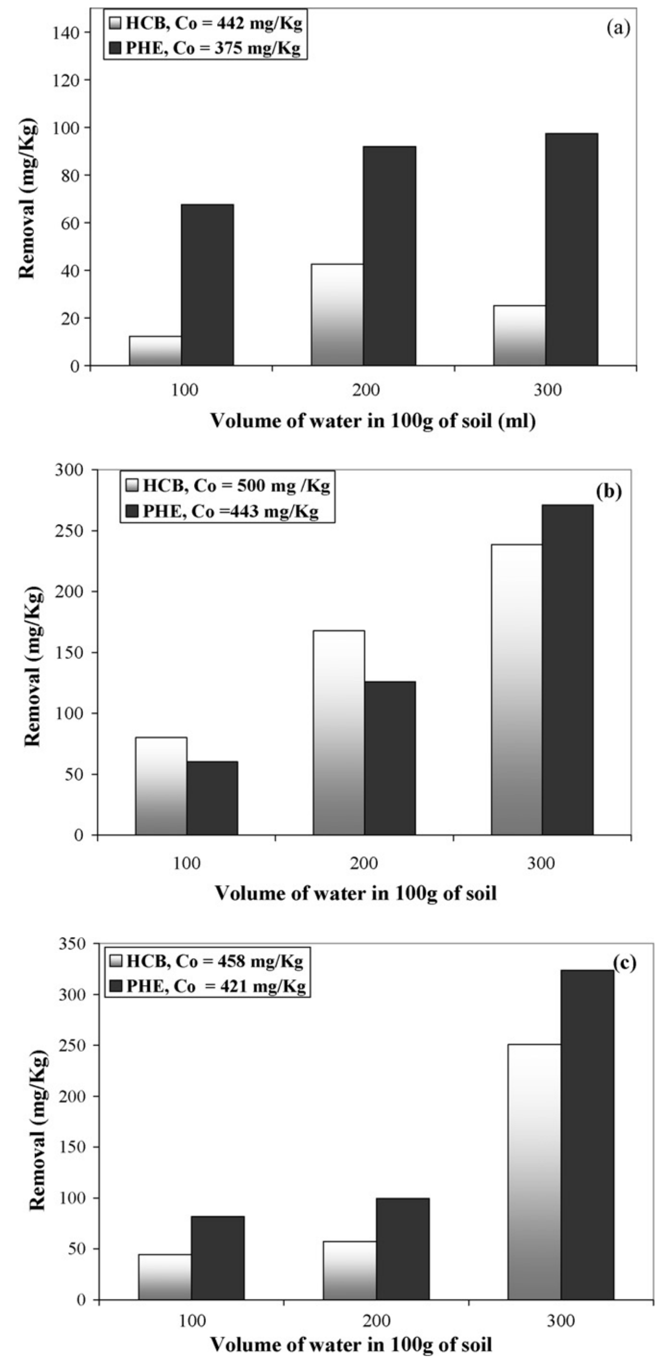

Fig. 1. Removal of POPs in soil medium with different water ratio: (a) kaolin, (b) synthetic clay, and (c) natural farm soil.

from contaminated kaolin. Thus, the removal efficiency was almost double. There is not much difference in 2:1 and 3:1 ratios in remediation. In case of synthetic clay, 1:1, 2:1 and 3:1 ratios increased in remediation as 1:2:4. The 3:1 ratio in natural soil gave the best remediation. Kaolin was found in almost homogenous mixture with water whereas in cases of synthetic clay and natural soil, the clay materials settled down at the bottom and created several kinds of solid layers during experiments. As kaolin has low percentage of sand and slit and high percentage of clay materials (Table 1), for desorption and oxidation, more water may be needed. Sonocation worked best in natural soil in 3:1 ratio due to the presence of high percentage of sand and slit and low clay material. It was found that removal of DDT and PCD was effective in sand using 1:1 water and sand ratio and frequency of 20 kHz [12]. Though high water amount gives better results, the too high ratio can make the slurry into solution that is not practical in field scale.

3.2. Time series

One physical effect of applying ultrasonication is heating or increasing temperature of the bulk solution [24]. Fig. 2 shows the variation of soil media's temperature during ultrasonication. The temperature of bulk slurries increased up to a certain value and remained the same during ultrasonication. When duration time was long enough, water started evaporating, slurries getting dried and returned to solid phase. This may be due to effects of cavitation. The increase in temperature also depends on the type of soils, which was proved by Fig. 2. In case of kaolin, the temperature increased from 20 °C to 56 °C in first 1 h, then slowly increased to 63 °C. Then, it remained constant. The temperature increased from 20 °C to 52 °C in first 1 h in synthetic clay. Then, it remained almost same in increase the time. In case of natural soil, temperature increased slowly with time of irradiation. This difference may be due to presence of different percentage of sand. The sand can accumulate heat more than other materials.

pH did not change much along the time and remained almost the same (Fig. 2). This confirmed the fact that there was no formation of ions H^+ or OH^- during ultrasonication. It can be concluded that pH value is not affected by ultrasonication, thus, can be neglected. The pH values of synthetic clay stayed in the range of 7.6–8.1. The pH values of natural clay slightly fluctuated in the range of 5.6–5.8. And the pH values of kaolin were in the range of 4.8–5.0.

Sonolysis of organic compounds in aqueous phase (slurries) occurs through complex mechanisms involving thermal decomposition and hydroxyl radical oxidation. The removal efficiencies are shown through the concentrations of POPs remained in soil mediums during ultrasonication in Fig. 3; the lower the concentration of model compound was the higher the removal efficiency. In general, the concentrations of model compounds reduced gradually with time. However, there were not very big differences between the concentrations after 1 h and 6 h. This is important for choosing the optimal duration operation time when considering energy cost-effective. Between the two models, PHE always had the lower concentrations remained. This can be explained by the fact that PHE has the lower molecular weight and is not as stable chemically as HCB. Therefore, may be in synthetic and natural clay cases, the free radical oxidation mechanism is dominant while in kaolin case, the pyrolysis is dominant for organics breakdown.

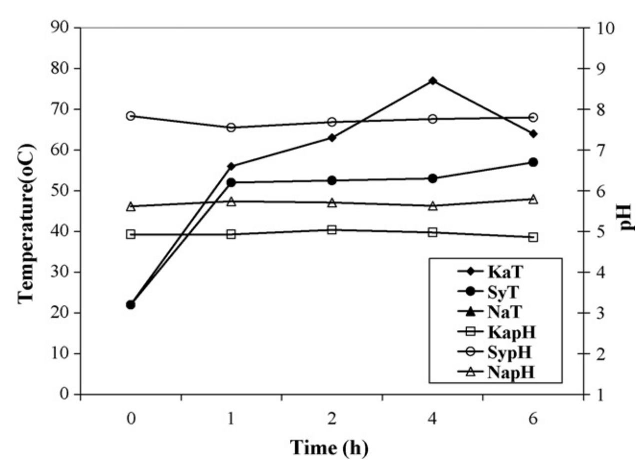

Fig. 2. Temperature (*T*) and pH of the soil mediums during ultrasonication (Ka, kaolin; Sy, synthetic clay; Na, natural soil).

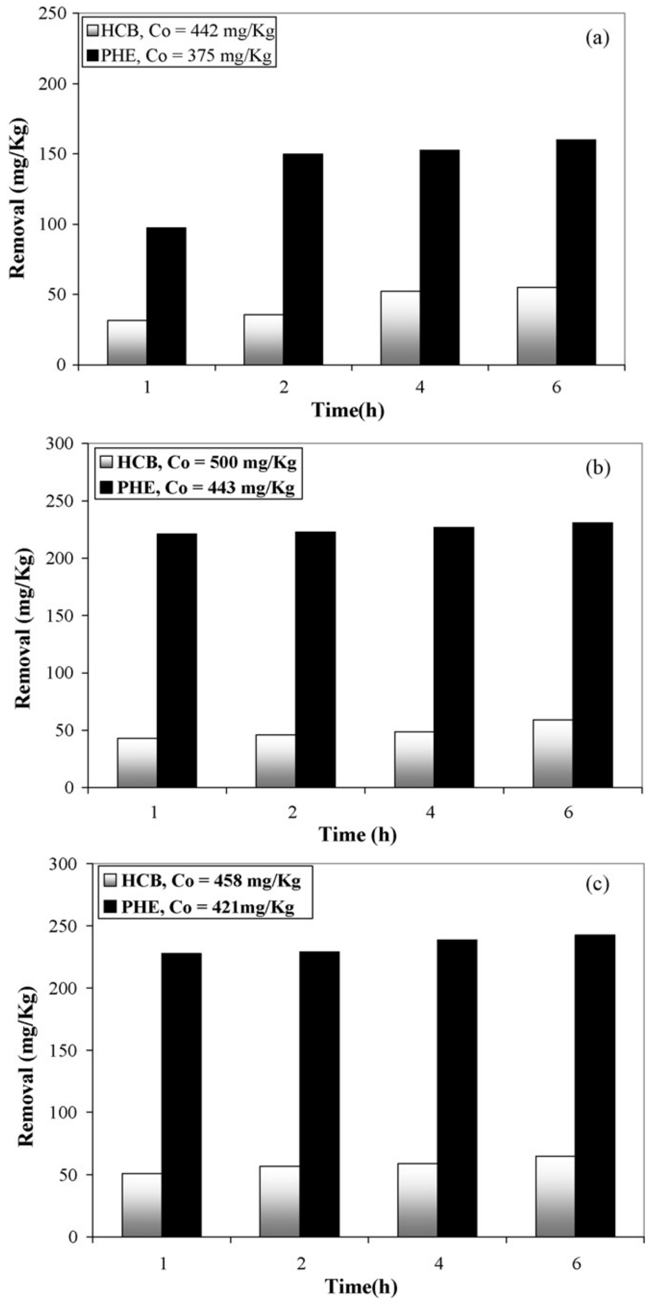

Fig. 3. Concentrations of POPs remained in soil mediums during ultrasonication: (a) kaolin, (b) synthetic clay, and (c) natural farm clay.

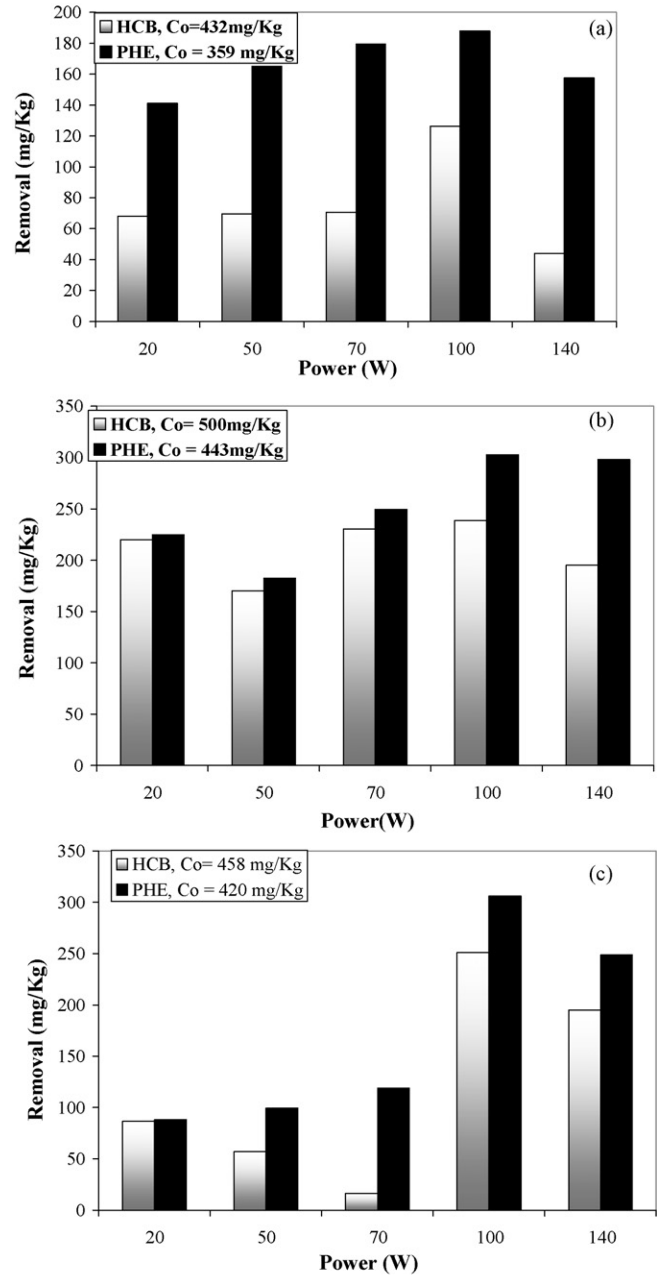

Fig. 4. POPs removed in soil mediums after ultrasonication with various power input applications: (a) kaolin, (b) synthetic clay, and (c) natural soil.

3.3. Power series

Fig. 4 shows the effects of various power input applied during ultrasonication on the reduction of POPs concentration. In the case of kaolin, there was not so big difference among the results of all the tests. The efficiency of removal of POPs decreased at 140 W. In the case of synthetic clay, the two tests at 70 W and 100 W gave the highest reduction, while the test at 140 W gave lower remediation than 100 W. However, in the case of natural farm clay, the two tests at 100 W showed the highest POPs concentration removed then decreased at 140 W. The drop in contaminant removal beyond about 100 W can be attributed to the effect of cavitation. When cavitation occurs, the sound pressure level at a distance drops because cavitation takes power away from the field. Therefore, cavitation can reduce the effective sonication power in the soil [16,25]. May be optimal level of power depends on frequency used and type of medium matrix. Rate of removal of contaminants totally depends on type of soils and contaminants. And again, the experiments confirmed that PHE concentrations remained always the lower.

4. Conclusions

On a small scale, laboratory studies proved successful and the costs are quite reasonable but the industrial adoption of ultrasonic soil remediation needs considering the economics of scale-up [10]. Ultrasonication has a potential to reduce the high concentrations of persistent organic compounds like phenanthrene and hexachlorobenzene in soils. The treatment of soil by ultrasonication requires some amount of water for sonochemistry effects to perform. The reasonable moisture ratio of the slurry could be from 2:1 to 3:1 water and soil, the higher the better, particularly kaolin needed more water amount than other clays to perform well. The removal efficiency increased but not very much after long ultrasonication time. Considering energy cost and efficiency, 1–2 h was enough for duration time application. pH values of the slurries did not change much or nearly stayed the same before and after experiments. Thus, it can be concluded that ultrasonication did not affect the pH values of slurries. The heating and irritated noise problems of ultrasonication should be considered carefully in larger scale applications. The removal rates of POPs in soils vary with soil type, power and frequency of the ultrasound applied. Of PHE and HCB, PHE was the easier one to treat; it always showed the higher reduction.

Acknowledgements

The authors wish to thank Academy of Finland (212649) and the Maj and Tor Nessling Foundation, Helsinki, Finland, for the financial support in this research.

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