

## ULTRASOUND-ASSISTED TREATMENT OF KAOLIN ARTIFICIALLY CONTAMINATED WITH PHENANHTRENE, FLUORANTHENE AND HEXACHLOROBENZENE

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**Abstract.** Application of ultrasound in decontamination of polluted soil is a new and promising technology. The feasibility of ultrasonic treatment of clayey soil (kaolin) highly contaminated with persistent organic pollutants (POPs), such as phenanthrene (PHE), fluoranthene (FLU), hexachlorobenzene (HCB), was the main target of the work. The laboratory experiments were conducted at various conditions (moisture, power, irradiation duration and the initial concentration of contaminants) and the effects of these parameters on the process efficiency were examined. Experimental results showed that ultrasonication alone has a potential to remove POPs, although the removal efficiencies were relatively low when a short irradiation duration (1–6 hours) was adopted. Intermittent ultrasonication over longer periods (up to the total of 46 hours) increased the removal efficiencies to 45% of HCB and nearly 100% of PHE. The optimum moisture content of the slurry was found to be in the range of 50–70%. The total electric energy consumption during the experiments using the optimum operational conditions (100 W and above ultrasound irradiation power and 67% moisture content) was 1.5 kWh in comparison to 1.84 kWh during experiments utilizing minimum operational conditions.

Keywords: ultrasonication, soil remediation, persistent organic pollutants (POPs).

## 1. Introduction

Ultrasound is sound waves at frequencies greater than the upper limit of human hearing (>16 kHz) and may be utilized for diverse purposes in many different areas. The application of ultrasound may be divided broadly into two areas: i) high frequency (2–10 MHz), and ii) low frequency ultrasound (20–100 kHz), which is often used for the environmental purposes (Mason and Lorimer 1988).

When the solution is irradiated with ultrasound, tiny bubbles are formed that grow and subsequently collapse in a liquid producing local temperature up to 5000 K and pressures up to hundreds of atmospheres (Gedanken 2003). These extreme conditions may break chemical bonds by pyrolysis. In addition to thermal decomposition mechanism, ultrasonic irradiation can be an effective oxidation method for destruction of organic pollutants because of localized high concentrations of oxidizing species (Hoffmann et al. 1996). The water vapors and oxygen in the cavitation bubbles undergo thermal dissociation to yield oxygen atoms, as well as hydroxyl (HO') and hydroperoxyl (HOO') radicals. Hydrogen peroxide is formed as a consequence of hydroxyl and hydroperoxyl recombination outside the cavitation bubbles and may be used to rapidly degrade the contaminants. The formation and recombination of radicals is following (Rokhina et al. 2009):

 $H_2 O \to O H \cdot + H \cdot, \tag{1}$ 

$$OH \cdot + H \cdot \to H_2O, \qquad (2)$$

$$2OH \rightarrow H_2O + \frac{1}{2}O_2, \qquad (3)$$

$$2OH \to H_2O_2. \tag{4}$$

In general, the relative dominance of pyrolysis or radical oxidation mechanisms depends on the volatility, hydrophobicity and concentration of the contaminants and pH of the solution (Dewulf *et al.* 2001). While hydrophilic compounds are mainly oxidized by the highly reactive radicals, volatile substrates are destroyed predominantly by direct pyrolytic decomposition (Jiang *et al.* 2002). Pyrolysis is prevalent at high solute concentrations while at low solute concentrations, free radical oxidation is likely to predominate (Hoffmann *et al.* 1996).

In the past several years, there was a constant search for remediation methods that are not only able to reduce the amount of contaminants in the soil and sediments but are also technologically sound, cost and time efficient (Virkutyte *et al.* 2002). Utilization of ultrasound in environmental remediation has emerged as one of the advanced oxidation processes (AOP) for the destruction of hazardous organic compounds in aqueous solutions (Joseph *et al.* 2000). Moreover, ultrasound has been used as the pre-treatment process to improve wastewater (Blume *et al.* 2004) and saline solution disinfection (Joyce *et al.*  2003), enhance membrane filtration of wastewater (Kyllönen *et al.* 2005) and sludge stabilization (Hogan *et al.* 2004; Yin *et al.* 2004).

Ultrasonication exhibits a great potential of being an environmental friendly, clean, energy efficient, economically competitive treatment method, which does not cause a secondary contamination when compared with other technologies of organic pollutant treatment such as UV light, high voltage corona, incineration and solvent extraction (Mao *et al.* 2004).

Ultrasound irradiation is also an efficient alternative for conventional soil washing methods (Mason 2007). Ultrasonication induces high fluid-solid shear stresses, which promotes mechanical detachment and removal of contaminants (Newman *et al.* 1996; Kyllönen *et al.* 2004; Mason *et al.* 2004; Collings *et al.* 2006). Ultrasound may also be used as an enhancement method for electrokinetic treatment of heavy metals and polycyclic aromatic hydrocarbon in contaminated soils (Chung and Kamon 2005; Flores *et al.* 2007).

Soil contamination is a critical issue because of its significance as a threat to human and animal health through food system and ground water and may finally result in the loss of entire ecosystems (Virkutyte and Sillanpää 2007). Among soil contaminants, persistent organic pollutants (POPs), such as hydrophobic organic compounds, are of particular concern because of their long life-time and toxicity. Their solubility in pure water is low, usually less than  $10^{-4}$  M and they are strongly adsorbed in soils, especially onto terrestrial colloids (McKay et al. 2002). POPs adsorption onto soils strongly limits the efficiency of remediation techniques (Petitgirard et al. 2009). Although many remediation technologies are currently available, the treatment of these organic pollutants, especially in low permeable clayey soils, still remains a problem.

In general, the potential of ultrasound in soil remediation has not been much studied yet. Therefore, the objective of this laboratory-scale study was to investigate the effect of ultrasound and various experimental conditions on clayey soils contaminated with three persistent organic compounds: hexachlorobenzene (HCB), phenanthrene (PHE) and fluoranthene (FLU). Because of their low permeability, clayey soils are often very difficult media to treat. Therefore, cavitation produced in clay by ultrasonication was assumed to increase its porosity and permeability (Kim 2000) and, thus, aid the remediation process.

## 2. Methods

The representative persistent organic compounds were hexachlorobenzene (HCB, 99%), a typical polychlorinated hydrocarbon and two polycyclic aromatic hydrocarbons (PAHs): phenanthrene (PHE, 97%) and fluoranthene (FLU, 98%) purchased from Sigma-Aldrich, Germany. N-hexane, acetone and other chemicals were from Merck, Germany. Chemicals were of analytical grade and used without further purification. All the solutions were prepared using high purity deionized water (0.055  $\mu$ S, 18 m $\Omega$ ,  $T = 22 \pm 1^{\circ}$ C, pH 7.1). Laboratory scale experiments were performed in triplicates in a closed Pyrex glass reactor  $(0.004 \text{ m}^3)$  with no head-space, equipped with a temperature controller and ultrasonic transducers with 0–100% duty cycles UP 100 and UP 200 (Dr. Hielscher, Germany) with a horn-type sonotrodes (titanium, tip diameter 22 mm), capable of operating either continuously or in a pulse mode at a fixed frequency of 24 to 30 kHz and a maximum electric power output of 200 and 100 W, respectively.

When indicated, an immersion circulator unit (Mo 1112A, VWR, UK) was used to maintain a constant temperature throughout experiments. The actual ultrasonic power dissipated in the reactor (85 and 160 W, respectively) was determined according to Hageson and Doraiswamy (1998).

White kaolin (VWR, Finland) was used as a model clayey soil throughout the tests. Main characteristics of kaolin are summarized in Table 1. The pH of the soil was measured by mixing 10 g of dry sample and 25 ml 1 M KCl as reported by Alshawabkeh and Sarahney (2005). Organic matter content was measured by loss of ignition at 550 °C for 1 h as suggested by Nystroem *et al.* (2005). The cation exchange capacity of air dried sample was determined with 1 M ammonium acetate diffusion at pH 7 according to Koivula *et al.* (2009).

Table 1. Main characteristics of kaolin

pH	4.8
Dry bulk density (g $\text{cm}^{-3}$ )	0.508
Moisture (%)	1.03
Electrical conductivity ( $\mu$ S cm <sup>-1</sup> )	448
Cation exchange capacity (cmol kg <sup>-1</sup> )	3.1
Organic content (%)	0
Particle size distribution:	
% sand ( > 0.05 mm)	3.9
% silt (0.05–0.002 mm)	20.2
% clay ( < 0.002 mm)	75.9

POPs removal efficiency from artificially contaminated kaolin was calculated:

Removal efficiency = 
$$\frac{(c_0 - c) \times 100}{c_n}$$
, (i)

where  $c_0$  was the initial and c was the final POPs concentration (mg kg<sup>-1</sup>).

Kaolin was artificially contaminated with HCB, PHE and FLU at target concentrations of 500 mg kg<sup>-1</sup> (Phase 1 – high initial concentration, continuous ultrasonication) and 100 mg kg<sup>-1</sup> (Phase 2 – low initial concentration, intermittent ultrasonication) as may be seen in Table 2.

Because of the low solubility in water, n-hexane was used as a solvent to dissolve POPs required to yield the target concentrations (Saichek and Reddy 2003). Kaolin was stirred well to obtain homogeneous contamination. The mixtures were kept in a fume-hood nearly a week for solvents to evaporate entirely. Un-sonicated samples spiked with appropriate levels of contaminants showed no evaporation, degradation or sorption of contaminants to the container during the course of the contamination process.

Table 2. Summary of experimental conditions for ultrasound-
assisted tests during Phase 1 and Phase 2

	High initial POPs concentration					
	<b>Short time, continuous ultrasonication</b> 100 g kaolin/test					
	Test	V-water	Frequency	Power	Duration	
PHASE 1	Test	(ml)	(kHz)	(W)	( <i>h</i> )	
	W1	100	30	100	1	
	W2	200	30	100	1	
Water	W3	300	30	100	1	
content	W4	400	30	100	1	
	T1	300	30	100	6	
Time	T2	300	24	100	6	
	P11	200	30	20	1	
	P12	200	30	40	1	
	P13	200	30	60	1	
	P14	200	30	80	1	
	P15	200	30	100	1	
	P21	200	24	40	1	
	P22	200	24	60	1	
	P23	200	24	80	1	
	P24	200	24	100	1	
	P25	200	24	140	1	
Power	P26	200	24	200	1	
	Low initial POPs concentration Long time, intermittent ultrasonication					
PHASE 2	500 g kaolin/test					
	Pulse		Frequency	Power	Total hours	
Experiments	mode	(ml)	(kHz)	(W)	<i>(h)</i>	
1. Minimum						
conditions	0.5	500	24	40	46	
2. Optimum						
conditions	1	1000	24	100	15	

The amount of kaolin used for each test was about 100 g in Phase 1 and 500 g in Phase 2. Experimental conditions are summarized in Table 2. Prior experiments, kaolin was mixed with deionized water to make slurry as proposed by Pham *et al.* (2009). The slurry was subjected to ultrasound irradiation at the desired frequency and power amplitude during a designated period of time. The ultrasound-assisted slurry treatment reactor is sketched in Fig. 1.

During Phase 1, initial concentrations of  $500 \text{ mg kg}^{-1}$  to investigate the effect of water ratio, irradiation duration and power were used. First, experiments were conducted using various volumes of water at the same (30 kHz) frequency and (100 W) power applied for 1 hour, to determine the optimum moisture content.

Second, experiments were conducted with 300 ml water per 100 g kaolin at both, 30 kHz and 24 kHz frequencies and 100 W for 6 hours to study the effects of ultrasound irradiation on temperature in the medium and the POPs removal efficiencies. Samples were analyzed after 1, 2, 4 and 6 hours of experiments for residual POPs concentrations.



**Fig. 1.** Ultrasound-assisted slurry treatment reactor: 1) ultrasonic processor, 2) power amplitude control, 3) pulse mode control, 4) reactor, 5) ultrasonic horn submerged in slurry, 6) holder

During Phase 2, experiments were conducted: at (1) minimum and (2) optimum operational conditions. In each experiment, 500 g kaolin contaminated with HCB and PHE at initial concentration of 100 mg kg<sup>-1</sup> were used. Samples were intermittently ultrasonicated for 1–4 hours per day, for 15–30 days.

Evaporation was monitored and water was added during experiments to keep the same moisture content as initial experimental conditions. Control test showed that no significant HCB or PHE evaporation (the loss of HCB and PHE was in the range of 5-7%) was observed when artificially contaminated kaolin was left uncovered for 30 days to ensure that POPs removal during the ultrasonication process may be attributed to the effect of ultrasound and not to the natural evaporation of contaminants. The first test of the second phase was carried out at the lowest power amplitude (20%) applying 24 kHz frequency and 40 W (as stated by the manufacturer not calorimetric values) and in a 0.5 pulse mode for 30 days.

During the first 4 days, kaolin was irradiated for 4 hours per day, then 2 hours per day for the next 4 days, and finally 1 h per day for the subsequent 22 days of the experiment. Samples were analyzed after 10, 20, 30 days, corresponding to total 26, 36, 46 hours of ultrasound irradiation duration. During the second test, experimental slurry was irradiated at a 1 pulse mode applying 24 kHz frequency and 100 W (as stated by the manufacturer, not calorimetric values), and intermittently 1 h per day for 15 days. Samples were analyzed after 15 days, corresponding to the total of 15 hours of ultrasound irradiation duration.

After experiments, the slurry samples were dried in the oven at 80 °C for 24 hours and pulverized for analysis. Samples were analyzed in duplicates for the quality assurance. 1 g of the sample was mixed with 5 ml n-hexane/acetone (3:1) mixture and contaminants were extracted according to Guerin (1999). The glass tubes containing samples were then centrifuged at 5000 rpm for 10 minutes (Yuan *et al.* 2006). The supernatants were transferred into 2 ml glass vials for GC–MS analysis (Agilent 5975 with inert XL mass selective spectrometer, equipped with HP–5 column (Agilent, 5% phenyl methyl siloxane, capillary 30.0 m × 320  $\mu$ m × 0.25  $\mu$ m nominal). Carrier gas was helium argon (99.999% at 1.0 mL min<sup>-1</sup>) with the flow of 1.2 ml min<sup>-1</sup>.

The following chromatographic conditions were adopted: the temperature was from 80 °C (1 min) to 150 °C at 15 °C min<sup>-1</sup>, then from 150 °C to 200 °C at 5 °C min<sup>-1</sup>, and finally from 200 °C to 300 °C at 10 °C min<sup>-1</sup>. The injector temperature was set at 250 °C and 1  $\mu$ L solution was injected in splitless mode. The electron impact energy was 70 eV, and the ion source and quadruple temperatures were set at 280 °C and 230 °C, respectively.

#### 3. Results and discussion

## 3.1. Effect of water content

Ultrasound irradiation of water produces hydroxyl radicals that are responsible for the degradation of many toxic organic compounds, thus, sonochemical oxidation can only happen in aqueous solution (Adewuyi 2001). Since kaolin has a high water absorption capacity, the tests were initiated at 50% moisture content. Fig. 2 shows POPs removal rates at various added water amounts.



**Fig. 2.** POPs residual concentration (%) in kaolin at various initial moisture contents after 1 hour of ultrasound irradiation at 30 kHz and 100 W

Although it is beneficial to have high water ratio since more hydroxyl radicals can be produced and thus higher degradation efficiencies can be achieved (Mason 2007), the too high water content might impair practical application of the process, especially in the field-scale. The results showed that there was no significant difference in removal efficiencies of a single contaminant when various amounts of water were added to the kaolin samples (Fig. 2).

However, FLU exhibited the highest removal efficiency of 40%, followed by PHE (up to 30%) and HCB (up to 15%) when 200 ml and/or 300 ml was added to 100 g of kaolin. Therefore, the 67% moisture content

(200 ml added to 100 g kaolin) was chosen for the subsequent 1 hour – power series and 75% moisture content (300 ml added to 100 g kaolin) was chosen for 2–6 hours experiments series.

# **3.2. Effect of ultrasound irradiation duration and temperature**

It was observed that at above 100 W and when no cooling was employed in an open reactor, kaolin slurries eventually dried out. Therefore, ultrasound irradiation experiments should not be carried out continuously over a very long time. Moreover, when considering efficient energy expenditure, it is important to choose the optimal reactor operation time.

Since ultrasound irradiation induces high concentration of energy, one of its physical effects is heating, i.e. the increasing temperature of the bulk solution (Suslick 2001). Fig. 3 shows the variation in experimental medium temperature during ultrasonication without the cooling used. In general, the temperature of slurries around the sonotrode increased significantly (up to 80 °C), in comparison to up to 60 °C in the bulk slurries. Moreover, the increase in temperature remained constant until the termination of the experiments.



Fig. 3. Variation in temperature in kaolin slurries during ultrasound irradiation process

Therefore, in order to maintain sufficient moisture conditions and ensure the efficient degradation of contaminants, cooling must be employed. The use of a recycled flow of slurry through the reactor in addition to the external cooling from the immersion circulator would ensure the constant low temperature throughout the experiments and would aid the ultrasound-assisted remediation of the soil slurry.

## 3.3. POPs degradation

Degradation of organic compounds in aqueous phase or slurries in the presence of ultrasound occurs through complex mechanisms involving thermal decomposition (pyrolysis) and oxidation by the formed hydroxyl radicals. Selected POPs have a very low solubility in water, therefore it is expected that target contaminants will be adsorbed on to the kaolin surfaces. Since the white kaolin does not contain organic matter (Table 1), the binding of POPs to kaolin surface is expected to be weak. This is in a good agreement with the work performed by Thangavadivel and co-workers (2009) who researched the ultrasound-assisted removal of DDT from artificially contaminated sand.

Differences in ultrasound irradiation frequency (and power) will consequently result in various wavelenghts, formed bubble size and its life time, which in turn will affect the effective mass transfer to the bubbles and subsequent energy release, hydrolysis of water and contaminants' degradation mechanisms (Thangavadivel *et al.* 2009). According to Keck and co-authors (2002), the applied ultrasound irradiation will induce cavitation on the kaolin particles surface as well as in the liquid.

Moreover, higher frequency ultrasound has lower wave length and less intensity than lower frequency ultrasound hence, attenuation is proportional to the square of frequency. In slurry treatment, with increase in frequency and slurry percentage the attenuation energy increases, which produce the intense cavitation at the slurry surface (Keck *et al.* 2002). Thus, due to very severe localized energy and temperature changes, the adsorbed POPs will be subjected to to chemical and physical processes that induce their desorption and decomposition via pyrolysis and/or radical mechanism (Adewuyi 2001).

The results indicated that the removal of POPs did not differ significantly after 1 hour and 6 hours (except for PHE, when 24 kHz, 200 W was applied) ultrasound irradiation. This could be explained by the fact that these recalcitrant hydrocarbons were present in very high initial concentrations (approximately 500 mg/kg as target concentration with variation less than 10%) mimicking industrially contaminated sites and thus maximum 6 h of irradiation did not result in a significant formation of oxidative species (hydrogen peroxide and hydroxyl radicals) that were responsible for the POPs degradation.

Indeed, Rehorek *et al.* (2004) reported that e.g. the rate of OH• radicals formation was only 14.9  $\mu$ M min<sup>-1</sup>, 4  $\mu$ M min<sup>-1</sup>, and 0.1  $\mu$ M min<sup>-1</sup> at 120 W, 90 W and 60 W, respectively, of applied ultrasound irradiation under air atmosphere. Therefore, a rather low degradation of POPs may be attributed to the lack of formed radicals during ultrasound irradiation when no additional oxidation agents were employed. Fig. 4 presents the removal of POPs after 6 hours of ultrasound irradiation.



Fig. 4. POPs remaining (%) in kaolin after ultrasound irradiation process

According to Fig. 4, the lower frequency (24 kHz) but higher power (200 W) resulted in approximately 5–15% higher POPs reduction. Moreover, lower frequency and higher power ultrasound produces more violent cavitation, leading to higher localized temperatures and pressures that favor the thermal decomposition of organic compounds; on the other hand, higher frequency may lead to higher reaction rates because of increased free radicals in the system (Adewuyi 2001). Based on the nature of POPs and the reaction conditions, degradation favored the pyrolytic mechanism rather than the free radical oxidation. Among the three compounds, PHE had the highest removal efficiencies (15–50%), followed by HCB (5–20%) and FLU (5–15%) after 6 hours of continuous ultrasound irradiation.

Relatively low POPs removal efficiencies may also be attributed to the attenuation of ultrasound phenomenon when high slurry densities are used for the remediation as suggested by Thangavadivel and co-workers (2009). Thus, to overcome such drawback it is advisable to use lower slurry densities.

## 3.4. Intermittent ultrasound irradiation treatment

Due to the heating effect, especially when there is an open experimental system employed, ultrasound irradiation cannot be continuously carried out over a very long operation time. However, longer times may be achieved through intermittent operation of the system, e.g. 1 to 4 hours of ultrasound irradiation per day for a designated number of days. During the intermittent ultrasound irradiation process, experiments using 500 g kaolin contaminated with only HCB and PHE (100 mg kg<sup>-1</sup>) were conducted.

First, experiments were carried out to examine the feasibility of ultrasound irradiation to remove selected POPs using minimum operational conditions: 40 W ultrasonic intensity (20% amplitude), 0.5 pulse mode and 50% moisture content. The amounts of POPs remained in kaolin after 10, 20, 30 days corresponding to the total 26, 36, 46 hours of ultrasound irradiation are presented in Fig. 5. It may be observed that nearly 100% removal efficiency of PHE was achieved after 46 hours of the experiments. However, the highest HCB removal was only 31%.



**Fig. 5.** HCB and PHE residuous concentrations in kaolin with increasing intermittent ultrasound irradiation duration

Then experiments were carried out to determine the optimum operational conditions utilizing higher ultrasound power intensity (above 100 W), higher water ratio (67%) and a full pulse mode (1). These conditions provided significantly higher removal efficiencies for HCB (45%) and a complete PHE removal with 3-times shorter ultrasound irradiation time (15 hours). The total electric energy consumption applying optimum conditions (1.5 kWh) was lower than using the minimum operational conditions (1.84 kWh).

## 4. Conclusions

Ultrasound proved to have a high potential in environmental applications, however, its science and technology is still in the developing stage. Most existing information available is mainly on the laboratory scale, and little processing on the pilot and/or industrial-scale is being carried out (Gogate and Pandit 2004).

The number of studies on applications of ultrasound in soil remediation is even fewer. Although the present laboratory-scale study showed that ultrasonic irradiation may be used to remove selected POPs from soils, future research is highly warranted considering current limitations, especially the formation of reactive species when no other oxidative agents are present and the reactor design. Therefore:

1. Ultrasound irradiation has a potential to reduce the high concentrations of persistent organic compounds in soils. However, for the complete removal, the application of ultrasound should not be considered a single treatment process but rather as an enhancement for appropriate technique. Moreover, ultrasound irradiation treatment was found to be more effective to polycyclic aromatics hydrocarbon than polychlorinated hydrocarbon like hexachlorobenzene, which may be attributed to the different chemical composition of these contaminants.

2. The efficient treatment of soil by ultrasound requires a certain amount of water. The moisture content was the most effective in the range of 50-70%.

3. Despite the use of various ultrasound irradiation intensities (20–200 W), the removal efficiencies were only 5–20% for HCB, 15–50% for PHE and 5–15% for FLU after 6 hours of the experiment. Thus, to achieve higher removal efficiencies, longer ultrasound irradiation duration or the addition of oxidative agents should be applied.

4. Because of the intense localized heating, ultrasonication should not be carried out over a very long time. Therefore, intermittent ultrasound irradiation as an effective means to increase the removal efficiencies may be adopted. It was found that with intermittent ultrasonication 45% of HCB and 100% of PHE may be removed.

## References

- Adewuyi, Y. G. 2001. Sonochemistry: environmental science and engineering applications, *Industrial and Engineering Chemistry Research* 40: 4681–4715. doi:10.1021/ie0100961
- Alshawabkeh, A. N.; Sarahney, H. 2005. Effect of current density on enhanced transformation of naphthalene, *Envi*ronmental Science and Technology 39: 5837–5843. doi:10.1021/es049645f

- Blume, T.; Neis, U. 2004. Improved wastewater disinfection by ultrasonic pre-treatment, *Ultrasonics Sonochemistry* 11: 333–336. doi:10.1016/S1350-4177(03)00156-1
- Chung, H. I.; Kamon, M. 2005. Ultrasonically enhanced electrokinetic remediation for removal of Pb and phenanthrene in contaminated soils, *Engineering Geology* 77: 233–242. doi:10.1016/j.enggeo.2004.07.014
- Collings, A. F.; Farmer, A. D.; Gwan, P. B.; Sosa, P. A. P.; Leo, C. J. 2006. Processing contaminated soils and sediments by high power ultrasound, *Minerals Engineering* 19: 450–453. doi:10.1016/j.mineng.2005.07.014
- Dewulf, J.; Langehove, H. V.; Visscher, A. A.; Sabbe, S. 2001. Ultrasonic degradation of trichloroethylene and chlorobenzene at micromolar concentration: Kinetics and modeling, *Ultrasonics Sonochemistry* 8: 143–150. doi:10.1016/S1350-4177(00)00031-6
- Flores, R.; Blass, G.; Dominguez, V. 2007. Soil remediation by an advanced oxidative method assisted with ultrasonic energy, *Journal of Hazardous Materials* 140: 399–402. doi:10.1016/j.jhazmat.2006.09.044
- Gedanken, A. 2003. Sonochemistry and its application to nanochemistry, *Current Science* 85: 1720.
- Gogate, P. R.; Pandit, A. B. 2004. Sonochemical reactors: scale up aspects, *Ultrasonics Sonochemistry* 11: 105–117. doi:10.1016/j.ultsonch.2004.01.005
- Guerin, T. F. 1999. The extraction of aged polycyclic aromatic hydrocarbon (PAH) residues from a clay soil using sonication and a Soxhlet procedure: a comparative study, *Journal of Environmental Monitoring* 1: 63–67. doi:10.1039/a807307d
- Hagenson, L. C.; Doraiswamy, L. K. 1998. Comparison of the effects of ultrasound and mechanical agitation on a reacting solid-liquid system, *Chemical Engineering Science* 53: 131–148. doi:10.1016/S0009-2509(97)00193-0
- Hoffmann, M. R.; Hua, I.; Höchemer, R. 1996. Application of ultrasonic irradiation for the degradation of chemical contaminants in water, *Ultrasonics Sonochemistry* 3: S163– S172. doi:10.1016/S1350-4177(96)00022-3
- Hogan, F.; Mormede, S.; Clark, P.; Crane, M. 2004. Ultrasonic sludge treatment for enhanced anaerobic digestion, *Water Science and Technology* 50: 25–32.
- Jiang, Y.; Petrier, C.; Waite, T. D. 2002. Effect of pH on the ultrasonic degradation of ionic aromatic compounds in aqueous solution, *Ultrasonics Sonochemistry* 9: 163–168. doi:10.1016/S1350-4177(01)00114-6
- Jiang, Y.; Petrier, C.; Waite, T. D. 2002. Kinetics and mechanisms of ultrasonic degradation of volatile chlorinated aromatics in aqueous solution, *Ultrasonics Sonochemistry* 9: 317–323. doi:10.1016/S1350-4177(02)00085-8
- Joseph, J. M.; Destaillats, H.; Hung, H.; Hoffmann, M. R. 2000. The sonochemical degradation of azobenxene and related azo dyes: Rate enhancement via Fenton's reactions, *Journal of Physical Chemistry A* 104: 301–307. doi:10.1021/jp992354m
- Joyce, E.; Mason, T. J.; Phull, S. S.; Lorimer, J. P. 2003. The development and evaluation of electrolysis in conjunction with power ultrasound for the disinfection of bacterial suspension, *Ultrasonics Sonochemistry* 10: 231–234. doi:10.1016/S1350-4177(03)00109-3
- Keck, A.; Gilbert, E.; Koster, R. 2002. Influence of particles on sonochemical reactions in aqueous solutions, *Ultrasonics* 40: 661–665. doi:10.1016/S0041-624X(02)00195-6
- Kim, Y. U. 2000. Effect of sonication on removal of petroleum hydrocarbon from contaminated soils by soil flushing me-

thod. PhD dissertation. Department of Civil and Environmental Engineering, Pennsylvania State University, USA.

- Koivula, M. P.; Kujala, K.; Rönkkömäki, H.; Mäkelä, M. 2009. Sorption of Pb(II), Cr(III), Cu(II), As(III) to peat, and utilization of the sorption properties in industrial waste landfill hydraulic barrier layers, *Journal of Hazardous Materials* 164: 345–352. doi:10.1016/j.jhazmat.2008.08.008
- Kyllönen, H.; Pirkonen, P.; Hintikka, V.; Parvinen, P.; Grönroos, A.; Sekki, H. 2004. Ultrasonically aided mineral processing technique for remediation of soil contaminated by heavy metals, *Ultrasonics Sonochemistry* 11: 211–216. doi:10.1016/j.ultsonch.2004.01.024
- Kyllönen, H.; Prikonen, P.; Nyström, M. 2005. Membrane filtration enhanced by ultrasound: a review, *Desalination* 181: 319–335. doi:10.1016/j.desal.2005.06.003
- Mao, T.; Hong, S. Y.; Show, K. Y.; Tay, J. H.; Lee, D. J. 2004. A comparison of ultrasound treatment on primary and secondary sludges, *Water Science and Technology* 50: 91– 97.
- Mason, T. J.; Collings, A.; Sumel, A. 2004. Sonic and ultrasonic removal of chemical contaminants from soil in the laboratory and on a large scale, *Ultrasonics Sonochemistry* 11: 205–210. doi:10.1016/j.ultsonch.2004.01.025
- Mason, T. J. 2007. Sonochemistry and the environment Providing a "green" link between chemistry, physics and engineering, *Ultrasonics Sonochemistry* 14: 476–483. doi:10.1016/j.ultsonch.2006.10.008
- Mason, T. J.; Lorimer, J. P. 1988. Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry. Ellis Horwood Ltd., New York, USA.
- McKay, D.; Shiu, W. Y.; Ma, K. C. 2002. *Illustrated Handbook* of *Physical-Chemical Properties and Environmental Fate* for Organic Chemicals. Lewis Publishers, U.S.
- Newman, A. P.; Lorimer, J. P.; Mason, T. J.; Hutt, K. R. 1996. An investigation into the ultrasonic treatment of polluted solids, *Ultrasonics Sonochemistry* 4: 153–156. doi:10.1016/S1350-4177(97)00020-5
- Nystroem, G. M.; Ottosen, L. M.; Villumsen, A. 2005. Electrodialytic removal of Cu, Zn, Pb and Cd from harbor sediment: influence of changing experimental conditions, *Environmental Science and Technology* 39: 2906–2911. doi:10.1021/es048930w
- Petitgirard, A.; Djehiche, M.; Persello, J.; Fievet, P.; Fatin-Rouge, N. 2009. PAH contaminated soil remediation by

reusing an aqueous solution of cyclodextrins, *Chemosphere* 75: 714–718. doi:10.1016/j.chemosphere.2009.01.072

- Pham, T. D.; Shrestha, R. A.; Virkutytė, J.; Sillanpää, M. 2009. Combined ultrasonication and electrokinetic remediation for persistent organic removal from contaminated kaolin, *Electrochimica Acta* 54: 1403–1407. doi:10.1016/j.electacta.2008.09.015
- Rehorek, A.; Tauber, M.; Gübitz, G. 2004. Application of power ultrasound for azo dye degradation, *Ultrasonics Sonochemistry* 11: 177–182. doi:10.1016/j.ultsonch.2004.01.030
- Rokhina, E. V.; Lahtinen, M.; Nolte, M. C. M.; Virkutyte, J. 2009. The influence of ultrasound on the RuI<sub>3</sub>-catalyzed oxidation of phenol: catalyst study and experimental design, *Applied Catalysis B: Environmental* 87: 162–170. doi:10.1016/j.apcatb.2008.09.006
- Saichek, R. E.; Reddy, K. R. 2003. Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil, *Chemosphere* 51: 273–287. doi:10.1016/S0045-6535(02)00849-4
- Suslick, K. S. 2001. Sonoluminescence and Sonochemistry. Encyclopedia of Physical Science and Technology. 3<sup>rd</sup> Ed. Meyers R. A. (Ed.). Academic Press, USA.
- Thangavadivel, K.; Megharaj, M.; Smart, R. S. C.; Lesniewski, P. J.; Naidu, R. 2009. Application of high frequency ultrasound in the destruction of DDT in contaminated sand and water, *Journal of Hazardous Materials* (in press). doi:10.1016/j.jhazmat.2009.03.024
- Virkutytė, J.; Sillanpää, M. 2007. The hindering effect of experimental strategies on advancement of alkaline front and electroosmotic flow during electrokinetic lake sediment treatment, *Journal of Hazardous Materials* 143: 673–681. doi:10.1016/j.jhazmat.2007.01.014
- Virkutytė, J.; Sillanpää, M.; Latostenmaa, P. 2002. Electrokinetic soil remediation – the critical overview, *Science of the Total Environment* 289: 97–121. doi:10.1016/S0048-9697(01)01027-0
- Yin, X.; Han, P.; Lu, X. P.; Wang, Y. 2004. A review on the dewaterability of biosludge and ultrasound pretreatment, *Ultrasonics Sonochemistry* 11: 337–348.
- Yuan, S.; Tian, M.; Lu, X. 2006. Electrokinetic movement of hexachlorobenzene in clayed soils enhanced by tween 80 and β-cyclodextrin, *Journal of Hazardous Materials* 137: 1218–1225. doi:10.1016/j.jhazmat.2006.04.014

## DIRBTINAI FENANTRENU, FLUORANTENU IR HEKSACHLOROBENZENU UŽTERŠTO KAOLINO VALYMAS ULTRAGARSU

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Santrauka

Ultragarsinės radiacijos taikymas dirvai valyti yra nauja, tačiau sparčiai plėtojama technologija. Pagrindinis šio darbo tikslas buvo įvertinti ultragarso poveikį atsparių organinių teršalų, tokių kaip: heksachlorobenzenas (HCB), fenantrenas (PHE) ir fluorantenas (FLU), – degradavimui dirbtinai užterštame kaoline. Laboratoriniai eksperimentai atlikti pasirenkant įvairų dirvos drėgnumą, ultragarso intensyvumą, stiprumą, radiacijos trukmę ir pradines organinių teršalų koncentracijas bei įvertinant jų poveikį kaolino valymo efektyvumui. Rezultatai įrodė, kad ultragarsas gali būti taikomas dirvai valyti, tačiau efektyvumas nebuvo itin didelis kaoliną švitinant nuo 1 iki 6 valandų. Taikant kintamą radiaciją (iki 46 valandų), HCB šalinimas pagerėjo iki 45 %, o PHE – net iki 100 %. Valant organinius teršalus optimali kaolino drėgmė buvo 50–70 %. Taikant optimalias reakcijos sąlygas (100 W ir daugiau, 67 % drėgmės), elektros energijos sunaudota mažiau (1.5 kWh) nei kai reakcijos sąlygos minimalios (1,84 kWh).

Reikšminiai žodžiai: ultragarsas, dirvos valymas, atsparūs organiniai teršalai.

## ОЧИСТКА УЛЬТРАЗВУКОМ КАОЛИНА, ИСКУССТВЕННО ЗАГРЯЗНЕННОГО ФЕНАНТРЕНОМ, ФЛУОРАНТЕНОМ И ГЕКСАХЛОРОБЕНЗЕНОМ

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Резюме

Применение ультразвуковой радиации для очистки почв является новой, быстро развивающейся технологией. Основной целью работы было оценить воздействие ультразвука на деградацию устойчивых органических загрязняющих веществ, таких, как гексахлоробензен, фенантрен и флуорантен, в искусственно загрязненном каолине. Лабораторные исследования проводились при разной влажности почвы, интенсивности ультразвука, его мощности, длительности радиации и начальных концентрациях органических соединений, а также при учете их воздействия на эффективность очистки каолина. Результаты показали, что ультразвук может применяться для очистки почв, однако эффективность не была высокой при воздействии излучением в течение от одного до шести часов. При применении меняющейся радиации (до 46 часов) эффективность очистки от гексахлоробензена увеличилась до 45%, а от фенантрена даже до 100%. Оптимальной для очистки от органических соединений оказалась 50– 70%-ая влажность каолина. Потребление электроэнергии при оптимальных условиях реакции (100 W и больше, 67%-ая влажность) было меньшим, чем при минимальных условиях реакции (1.84 kWh).

Ключевые слова: ультразвук, очистка почв, устойчивые органические соединения.

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