Thuy Duong Pham

ULTRASONIC AND ELECTROKINETIC REMEDIATION OF LOW PERMEABILITY SOIL CONTAMINATED WITH PERSISTENT ORGANIC POLLUTANTS

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Chamber Music Hall at the Mikaeli Concert and Congress Hall, Mikkeli, Finland on the 5th of November, 2014, at noon.

Acta Universitatis
Lappeenrantaensis 587
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ISSN-L 1456-4491
ISSN 1456-4491

Lappeenranta University of Technology
University Press 2014
ABSTRACT

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Ultrasonic and Electrokinetic Remediation of Low Permeability Soil Contaminated with Persistent Organic Pollutants
Lappeenranta, 2014
130 p.
Acta Universitatis Lappeenrantaensis 587
Diss. Lappeenranta University of Technology
ISSN-L 1456-4491, ISSN 1456-4491

Electrokinetics has emerged as a potential technique for in situ soil remediation and especially unique because of the ability to work in low permeability soil. In electrokinetic remediation, non-polar contaminants like most organic compounds are transported primarily by electroosmosis, thus the process is effective only if the contaminants are soluble in pore fluid. Therefore, enhancement is needed to improve mobility of these hydrophobic compounds, which tend to adsorb strongly to the soil.

On the other hand, as a novel and rapidly growing science, the applications of ultrasound in environmental technology hold a promising future. Compared to conventional methods, ultrasonication can bring several benefits such as environmental friendliness (no toxic chemical are used or produced), low cost, and compact instrumentation. It also can be applied on-site. Ultrasonic energy applied into contaminated soils can increase desorption and mobilization of contaminants and porosity and permeability of soil through developing of cavitation.
The research investigated the coupling effect of the combination of these two techniques, electrokinetics and ultrasonication, in persistent organic pollutant removal from contaminated low permeability clayey soil (with kaolin as a model medium). The preliminary study checked feasibility of ultrasonic treatment of kaolin highly contaminated by persistent organic pollutants (POPs). The laboratory experiments were conducted in various conditions (moisture, frequency, power, duration time, initial concentration) to examine the effects of these parameters on the treatment process. Experimental results showed that ultrasonication has a potential to remove POPs, although the removal efficiencies were not high with short duration time. The study also suggested intermittent ultrasonication over longer time as an effective means to increase the removal efficiencies.

Then, experiments were conducted to compare the performances among electrokinetic process alone and electrokinetic processes combined with surfactant addition and mainly with ultrasonication, in designed cylinders (with filtercloth separating central part and electrolyte parts) and in open pans. Combined electrokinetic and ultrasonic treatment did prove positive coupling effect compared to each single process alone, though the level of enhancement is not very significant. The assistance of ultrasound in electrokinetic remediation can help reduce POPs from clayey soil by improving the mobility of hydrophobic organic compounds and degrading these contaminants through pyrolysis and oxidation. Ultrasonication also sustains higher current and increases electroosmotic flow. Initial contaminant concentration is an essential input parameter that can affect the removal effectiveness.
Keywords: ultrasound, electrokinetics, soil remediation, persistent organic pollutants

UDC 502/504:628.51:504.5:54:615.917
ACKNOWLEDGEMENTS

I wish to express my sincere appreciation and heartfelt gratitude to my supervisor, Professor Mika Sillanpää, for his kind guidance and constant support, for giving me a chance to do research in Finland and for encouraging me to come back to complete my study after many years. Getting to know you is a true blessing in my life that is forever cherished.

I am greatly grateful to Dr. Reena Amatya Shrestha and Dr. Jurate Virkutyte, for their careful advices, instructions and encouragement. I would like to thank Marina Shestakova for her thorough comments that helped me improve my manuscript.

I am thankful to all my former and present colleagues at the Laboratory of Green Chemistry for their company. Special thanks to Anshy Oonnittan for her precious friendship, Heikki Särkkä and Mikko Rantalankila for their kind helps as always, and Amarendra Dhar Dwivedi for his positive discussions and encouragement. Moreover, lots of thanks and love to my wonderful girls for all the support, fun and nice times we have had together.

I acknowledge the financial support from the Maj and Tor Nessling Foundation, the Maa-ja vesitekniikan tuki organization and the Lappeenranta University of Technology.

Thank you very much Finland, the beautiful Land of Snow, for all the good memories and the nice people that I have met!

Thank you All for being my friends and a part of my life!
I also would like to take this chance to express the deepest gratitude to my beloved parents and angels for their endless support and trust in me.

Mikkeli, September 2014

Pham Thuy Duong
LIST OF PUBLICATIONS


IV. Thuy Duong Pham, Reena Amatya Shrestha, Mika Sillanpää, Electrokinetic and Ultrasonic treatment of kaoline contaminated by POPs, Separation Science and Technology 44 (2009) 2410 - 2420.


Author’s contribution in the publications

I, II  The author conducted the experiments and participated in analyzing the data and writing the manuscripts.

III, IV, VI  The author planned and conducted the experiments, analyzed the data and prepared the first draft of the manuscripts.

V  The author participated in conducting the experiments.
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ABBREVIATIONS

2,4-D 2,4-Dichlorophenoxyacetic acid
AC Alternating Current
ARB Acid Red B
BTEX Benzene, Toluene, Ethylene and Xylene
CEEK Circulation-Enhanced Electrokinetic process
CHR Chrysene
CP Chlorophenol
COD Chemical Oxygen Demand
DC Direct Current
DCP Dichlorophenol
DDT Dichloro-Diphenyl-Trichloroethane
ECGO Electro-Chemical-Geo-Oxidation
ECRTs ElectroChemical Remediation Technologies
EDTA Ethylenediaminetetraacetic acid
EK Electrokinetics (Electrokinetic Remediation)
EEK+SF Surfactant-assisted Electrokinetics
EK+US Ultrasound-assisted Electrokinetics
FLU Fluoranthene
HCB Hexachlorobenzene
HPCD 2-Hydroxylpropyl-β-Cyclodextrin
IP Induced Polarization
PAH Polycyclic Aromatic Hydrocarbon
PAP p-Aminophenol
PCB Polychlorinated Biphenyl
PCP Pentachlorophenol
PCE Perchloroethylene
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>PHE</td>
<td>Phenanthrene</td>
</tr>
<tr>
<td>POP</td>
<td>Persistent Organic Pollutant</td>
</tr>
<tr>
<td>PRB</td>
<td>Permeable Reactive Barriers</td>
</tr>
<tr>
<td>PZC</td>
<td>Point of Zero Charge</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium Dodecylbenzene Sulfonate</td>
</tr>
<tr>
<td>TBT</td>
<td>Tributyltin</td>
</tr>
<tr>
<td>TCE</td>
<td>Trichloroethylene</td>
</tr>
<tr>
<td>TCP</td>
<td>Trichlorophenol</td>
</tr>
<tr>
<td>UESR</td>
<td>Upward Electrokinetic Soil Remediation</td>
</tr>
<tr>
<td>US</td>
<td>Ultrasonic/Ultrasound/Ultrasonication</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet irradiation</td>
</tr>
<tr>
<td>UV-C</td>
<td>Ultraviolet germicidal irradiation</td>
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<tr>
<td>ZVM</td>
<td>Zero-Valent Metal</td>
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</table>
1. INTRODUCTION

As a key component of the environment, soil is often a receptor of accumulated contamination from industrial, agricultural, urban and maritime activities. Since everything is interconnected in the natural cycles and in the web of life, soil contamination can lead to water and air pollution and vice versa. Any hazardous substance present in a soil matrix can be a potential threat to public health and ground water. Moreover, as soil is a ground that produces food for most living beings, soil contamination is critical because of its vital effects on biological resources, and eventually, on human health [1].

There are various kinds of pollutants found in soil and sediments, such as nutrients like phosphorous and nitrogen compounds, bulk organics like oil and grease, halogenated hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), metals, etc. Among these contaminants, the persistent organic pollutants (POPs) are of particular concern because of their long life span and toxicity.

1.1 Persistent Organic Pollutants

POPs are toxic organic compounds with highly stable chemical structures that can last for exceptionally long periods of time and travel long distance through air and water. Highly persistent and hydrophobic, these compounds often accumulate in the fatty tissues of living organisms, where their concentrations become biomagnified, resulting in higher concentrations at higher levels throughout the food chain [2, 3, 4].
POPs originate mainly from anthropogenic processes. They can be produced intentionally as synthetic chemicals in pesticides, electronic devices, dyes, plastics, or unintentionally as by-products during the manufacture of certain chemicals and during incomplete combustions in industrial processes, heating, cooking, urban vehicle exhaust, waste incineration etc. [3, 4, 5, 6, 7]

Due to their various sources and persistence, POPs are now widely dispersed and can be found around the world. Exposure to POPs can lead to potential risk of adverse health effects including cancer, allergies, reproductive disorder, endocrine and immune system disruption, obesity, diabetes etc. [2, 3, 7, 8, 9] Therefore, remediation of POPs contaminated soils is crucial for a healthy environment.

1.2 Soil Remediation of Organic Contamination

Selection of proper soil remediation strategies and technologies requires consideration of site conditions, contaminant types, contaminant sources and potential impacts of the possible methods. No single technology is appropriate for all types of contaminants and various site-specific conditions [10]. In reality, different methods are often combined simultaneously or sequentially, as assistance or enhancement of each other for optimum remediation.
There are several remediation technologies for organic decontamination from soils. These methods are generally divided into two main categories, biological treatment and physicochemical treatment (including thermal treatment) or more specifically, into four groups of biological, physical, chemical and thermal based measures as described in Fig. 1.

Biological treatment uses living organisms such as microorganisms (bioremediation), plants (phytoremediation) and earthworms (vermiremediation) for organic decontamination. Bioremediation uses aerobic and anaerobic microorganism such as bacteria [11, 12] and fungi [13, 14] to digest and transform organic contaminants, even some persistent ones such as PAHs. Bioremediation is used in many applications such as land farming, composting (biopile, bioheaps, biocells), bioslurry and bioventing. While land farming involves spreading a thin layer of excavated
contaminated soils on the ground, composting involves piling contaminated soils into piles or heaps and in both processes, aerobic microbial activities are stimulated through aeration or nutrients addition. On the other hand, to stimulate biodegradation, in bioslurry, the excavated contaminated soil is combined with water and other additives while in bioventing, bioremediation is assisted with air injection (soil venting) and circulation. Phytoremediation uses plants and grass to uptake contaminants from soil (phytoextraction), degrading or detoxifying contaminants through enzyme transformation or through plant enhancement of microbial activity in the root zone (rhizoremediation). Phytoremediation has proved to be effective to some toxic such as halogenated and nitroaromatic compounds [15, 16]. Vermiremediation uses earthworms to accelerate soil remediation through both their digestion and their digging activities which improve soil aeration. Studies indicated that earthworms can be resilient even in some persistent organic contamination when the degree of contamination is not too high [17, 18]. Among various remedial technologies, biological treatment perhaps is the most natural and ecofriendly one though it is limited to certain degree of contamination and its effects usually take longer time (months or even years) to manifest. Cleaning up soil by biological methods is also often cheaper than by other physical or chemical processes [19].

Physicochemical treatment involves the applications of physical (mechanical, thermal) and/or chemical processes in remediation. Compared to biological measures, physicochemical methods are less sensitive to toxicity of the contaminants, more flexible to operation conditions, but more aggressive to the soil and the environment.

Soil washing uses water, sometimes assisted with mechanical process such as scrubbing or chemical additives, adsorbent such as activated carbon to
move out the contaminants. Aeration and soil vapor extraction are mostly used for volatile organic contamination (such as petroleum). While in aeration, contaminated soil is spread thinly and tilled or turned to accelerate evaporation, in soil vapor extraction, volatile contaminants are pulled out of the ground through extraction wells installed vertically or horizontally. On the other hand, encapsulation or capping refers to physical isolation and containment of the contaminated soil with a clean layer or “cap”. While passive cap is no real treatment but just mainly containment and cannot be considered as a radical measure, reactive cap or barrier using reactive activated carbon, biochar [20] with zero-valent iron coated with palladium can be helpful with contaminant desorption and degradation [21].

Chemical extraction refers to the use of solvents or surfactants to enhance solubilization of hydrophobic organic contaminants. Concerning about the fate of the added chemicals, biosurfactants and ecosolvents (such as sunflower oil proven to be effective for PAHs removal from contaminated soils [22]) are more desirable though there are other practical factors which should be taken into account [23, 24]. Advanced oxidation processes such as ozonation [25], Fenton oxidation [26] can be used for remediation of POPs contaminated soils, sometimes combined with bioremediation [27]. While ozonation is better applied after bioremediation [28], Fenton rapid oxidation pretreatment before bioremediation can improve the effectiveness of solely bioremediation for highly contaminated soil [5]. Reductive dechlorination of chlorinated POPs such as HCB could be achieved by nano iron, bimetallic iron (noble metal such as Ag, Pd, Cu coaching to Fe° surface) or with photocatalytic and electrocatalytic processes [29].

Thermal treatment can be divided into three different mechanisms such as thermal desorption, thermal decomposition and solidification. Thermal
desorption uses heat to vaporize contaminants thus, separating them from the soil such as thermally enhanced soil vapor extraction, steam-stripping or supercritical fluid extraction. Thermal desorption does not destroy the contaminants as in thermal decomposition (pyrolysis). Thermal decomposition often involves very high temperatures of hundreds and up to more than a thousand °C in incineration. Some studies even indicated the high effectiveness of microwave energy in soil remediation from POPs, allowing quick contaminants decomposing at 1200-1300 °C in minutes [29, 30]. On the other hand, solidification is similar to encapsulation of the contaminated soil but using hot materials such as hot asphalt mixtures in asphalt batching or molten glass in vitrification (1600-2000°C). These processes immobilize inorganic pollutants and destroy organic pollutant through pyrolysis [10].

These soil remediation technologies can also be categorized in terms of treating onsite (in situ) or excavating the soil to treat elsewhere (ex situ). The main advantage of ex situ methods is that they generally require shorter time with more controllable conditions for more uniformity treatment, compared with in situ methods. However, because ex situ treatments involve soil excavation, they are also more costly. Moreover, ex situ treatments can imply the risks of habitat alteration as well as large-scale material handling and thus are not so favorable for long-term management. In situ treatments which allow soil to be treated without being relocated and transported, can be more attractive and can result in significant cost saving. Since conventional in situ technologies are usually very site specific and often work best on permeable soils but are difficult to apply on low permeable soils, there is a necessity to develop new alternatives for in situ soil remediation [1].
Electrokinetic remediation (EK) has emerged as a potential measure for in situ soil decontamination. Electrokinetics is based on the application of low-level direct current to solubilize and mobilize a wide range of metals and organic contaminants via electromigration, electroosmotic and electrophoresis phenomena. Electrokinetic remediation is especially unique because of its ability to work in low permeability soils which is very difficult to treat for most other techniques.

On the other hand, though still in development stage, ultrasound has been investigated and employed in many environmental applications. Ultrasonic irradiation applied into contaminated soils can increase desorption and mobilization of contaminants as well as porosity and permeability of soils through ultrasonic cavitation [31]. Ultrasonic waves can promote formation of free strong oxidative radicals leading to oxidation of contaminants [32], and the high local temperature and pressure formed during ultrasonic cavitation can destroy contaminants through pyrolysis processes [33]. Moreover, the use of ultrasound also brings several advantages such as no generation of dangerous breakdown products, compact, transportable equipment, allowing on-site treatment [34].

Considering many positive points of electrokinetic and ultrasonic processes, the combination of these two techniques is expected to provide effective decontamination of persistent organic pollutants from low permeability clayey soils.
2. LITERATURE REVIEW

2.1 Environmental Applications of Ultrasound

Ultrasound refers to inaudible sound waves with frequencies greater than the upper limit of human hearing (> 20 kHz). Ultrasound has been used for diverse purposes in different areas such as mining processing, industrial welding, surface cleaning, medical scanning, ultrasonic therapy, material science, nanosynthesis, non-destructive testing, defoaming, drying and supercritical fluid extraction in food technology [35, 36, 37, 38].

In terms of frequency (Fig. 2), ultrasound can be classified as (i) power ultrasound which is applied in chemistry (sonochemistry) and industrial processing, mostly with low frequency between 20 kHz – 100 kHz and sometimes up to 1000 kHz; (ii) therapeutic ultrasound with higher frequencies from 1 MHz – 3 MHz, used in medical treatment such as transdermal drug delivery or high intensity focused ultrasound in cancer therapy; and (iii) diagnostic ultrasound with low power and very high frequency in the range of 1 MHz – 18 MHz, often above 5 MHz for medical imaging (ultrasonography) and non-destructive testing [39, 40]

![Figure 2. Sound frequency classification](image-url)
Among various uses of ultrasound, this section focuses on the application of ultrasound in environmental science and technology, from water and sludge treatment, soil and sediment remediation, air purification to environmental analysis.

Although ultrasonic applications in environmental areas are still in developing stage, they are growing rapidly, attracting more and more interests [41], because of many advantages they offer: environmental friendliness (no toxic chemicals are used or produced) and low energy demands. It is also a compact and transportable method that can be used on-site [36, 42, 35, 37, 43].

2.1.1 Theoretical Background

Like any sound wave, ultrasound is transmitted via a series of compression and rarefaction cycles induced in the molecules of the medium through which it passes [44]. Compression cycles push molecules together, while expansion cycles pull them apart. At sufficiently high power, associated with high negative pressure, the rarefaction cycle may exceed the attractive forces of the molecules of the liquid and cavitation bubbles will form. When the cavity reaches a critical size, the cavity implodes, producing intense local heating (up to ~5000 K) and tremendous pressures (up to ~1000 atm) within very short lifetimes less than a microsecond, implying the existence of extremely high heating and cooling rates (>10^9 K/s) [45]. It has been speculated that transient supercritical water is obtained during the collapse of cavitation bubbles generated sonolytically [46]. Water sonolysis leads to the formation of reactive ·OH and ·H radicals which then undergo following reactions to produce H_2O_2 [33, 47]:

\[
H_2O_2 \rightarrow H_2O + \cdotOH
\]
The asymmetric collapse of cavitation bubbles close to or on a solid surface results in the formation of liquid microjets directed towards the surface at speeds of up to hundreds meters per second [40, 48]. The extreme conditions generated by ultrasonic cavitation provide a unique interaction of energy and matter, increasing reaction and mass transfer rates, and causing high energy chemical reactions to occur [49]. Moreover, ultrasound is able to produce microscopic flames in cold liquids by a process known as sonoluminescence. Since imploding cavities can cause molecules excited into high-energy-states, these molecules emit visible light when they return to their ground state [45].

Sonochemical reactions can be altered by both ultrasonic (frequency, power) and experimental (temperature, pH, types of the materials) conditions. While it was suggested in several studies that a higher frequency enhanced the liquid to vapor phase mass transfer and the formation of ·OH radicals [50], sonochemical reactions do not depend greatly on frequency. Because the major effect of frequency is to change the critical size of a cavity before implosion (the resonant radius of a bubble is inversely proportional to the ultrasonic frequency – a higher frequency results in a lower resonance radius and a shorter duration of implosion), this does not change the cavitation process significantly [45]. On the other hand, the dynamics of cavity growth and implosions are strongly dependent on local conditions such as states (liquid, extended solid surfaces in liquids or solid particles), characteristics (solvent vapor pressure, viscosity, surface tension, density, etc.) of the
materials and the ambient gas in surrounding liquid (heat capacity ratio, thermal conductivity and solubility). Cavitation is favored by the liquids of high vapor pressure, low density, low surface tension, and low viscosity. Better cavitation is also produced with the ambient gas of higher heat capacity ratio, lower thermal conductivity and higher solubility [50, 51]. It should be noted that, unlike most of chemical reactions, sonochemical reactions decrease with increasing ambient temperature. It is because the higher the ambient temperature, the more extra vapor there is inside the cavity, which cushions the implosion of the cavity and lowers the temperature of this collapse [45].

Generally, the hot-spot concept has been adopted to explain the sonochemical phenomena. In the hot-spot model, three regions are postulated (Fig.3): (i) a hot gaseous nucleus, (ii) an interfacial region, and (iii) bulk solution at ambient temperature [33, 52]. A local hot-spot is created when gases and vapors inside the cavity are compressed, generating intense heat that raises the temperature of the liquid immediately surrounding the cavity. Though local temperature of the hot-spot is extremely high, the local area itself is so small that the heat disperses rapidly, thus keeping the bulk liquid at ambient temperature [45]. Oxidative degradation by free radicals often involves hydrophilic species and can occur within the collapsing bubble, at the interface of the bubble, and in the surrounding liquid. On the other hand, hydrophobic and volatiles species are often degraded thermally at the gas phase or gas-liquid interface [53].
These chemical effects (sonochemistry) are used in most of ultrasonic applications in environmental remediation, especially in organic decontamination. On the other hand, the physical (mechanical) effects of ultrasound are also useful in environmental applications such as enhancing membrane cleaning, coagulation, regeneration of adsorbents [54, 55], air purification, sludge dewatering and metal leaching. An overview of some key points is summarized in Table 1 and more details on recent studies that applied ultrasound in environmental science and engineering are discussed in the following sections.
Table 1. Overview of Ultrasound in Recent Environmental Applications

<table>
<thead>
<tr>
<th>Water Treatment</th>
<th>Targets</th>
<th>Ranges of ultrasonic parameters</th>
<th>Remarks</th>
</tr>
</thead>
</table>
|                 | Toxics, pesticides, pharmaceuticals, dyes, industrial chemicals, surfactants, solvents, gasoline | US power: 0.1 – 8 W/mL US frequency: 20 – 1700 kHz US duration: 10 – 360 min | - Most extensive researched in environmental applications of ultrasound.  
- Popular ultrasonic parameters for organic oxidation in water treatment are in the ranges of 0.3 – 2 W/mL power density; 20 – 100 kHz frequency and 30 – 180 min duration time.  
- Main mechanisms based on the chemical effects of ultrasound in solutions (hydroxyl radicals, pyrolysis).  
- Advantages: environmental friendly, non-selective.  
- Limitations: ultrasonication alone often cannot achieve complete mineralization and has low degradation rate.  
- Development: combined ultrasound and other treatment methods such as Fenton, Fenton-like processes, ozonation, other oxidant addition, catalysis, photolysis, electrochemical remediation, often gave much better results due to the synergistic effects.  
- Key affecting factors: ultrasonic power intensity and density, dissolved gas, initial concentration, additives. |

Organic oxidation
<table>
<thead>
<tr>
<th>Assisting organic adsorption</th>
<th>Targets</th>
<th>Textile dyes</th>
</tr>
</thead>
</table>
| Ranges of ultrasonic parameters | US power: 0.03 – 3 W/mL  
US frequency: 20 – 850 kHz  
US duration: 10 – 480 min | |
| Remarks | - Mainly applied in textile wastewater decolorization.  
- Common ultrasonic parameters for assisting organic adsorption are 20 – 40 kHz and 120 min.  
- Main mechanisms based on the physical effects of ultrasound that increase the specific surface area of adsorbents (sepiolite, activated carbon, exfoliated graphite, waste newspapers)  
- Advantage: enhancing the adsorption capacity.  
- Key affecting factors: ultrasonic power, initial concentration, type of adsorbent. | |

<table>
<thead>
<tr>
<th>Assisting biological treatment</th>
<th>Targets</th>
<th>Textile dyes, distillery wastewater</th>
</tr>
</thead>
</table>
| Ranges of ultrasonic parameters | US power: 90 – 600 W  
US frequency: 20 – 850 kHz  
US duration: 30 – 300 min | |
| Remarks | - Ultrasonication used as the pretreatment step prior to biological treatment.  
- Common ultrasonic frequency for assisting biological treatment is 20 kHz.  
- Main mechanisms based on the physical effects of ultrasound that break the pollutant molecules.  
- Advantages: facilitating the followed biodegradation, enhancing the treatment efficiency.  
- Key affecting factors: ultrasonic power, initial concentration | |
<table>
<thead>
<tr>
<th>Assisting coagulation</th>
<th>Targets</th>
<th>Algae removal, surfactant removal</th>
</tr>
</thead>
</table>
| Ranges of ultrasonic parameters | US power: 15 – 60 W | - Short ultrasonication time used as the pretreatment step prior to coagulation and electrocoagulation.  
- Common ultrasonic frequency for assisting coagulation is 20 – 40 kHz, and 5 – 60 s duration time.  
- Main mechanisms based on the physical effects of ultrasound that reduce the particle sizes of both coagulant and suspended solids.  
- Advantages: increasing the sorption capacity of coagulants, saving energy and intensifying electroflotation in electrocoagulation.  
- Key affecting factors: ultrasonic power. |
| US frequency: 20 – 150 kHz | US duration: 5 s – 20 min |
| US duration: 5 s – 20 min | Remarks |

<table>
<thead>
<tr>
<th>Assisting membrane filtration</th>
<th>Targets</th>
<th>Enhancing ultrafiltration and membrane cleaning</th>
</tr>
</thead>
</table>
| Ranges of ultrasonic parameters | US power: 60 – 120 W | - Common ultrasonic frequency for assisting membrane filtration is 25 – 45 kHz.  
- Main mechanisms based on the physical effects of ultrasound in membrane cleaning such as liquid jets and the mechanical breaking down of the fouled layer at the membrane surface.  
- Advantages: less dependent on the feed properties, increasing the flux.  
- Key affecting factors: ultrasonic frequency, power, and treatment time. |
<p>| US frequency: 25 – 100 kHz | US duration: 2 – 60 min |
| US duration: 2 – 60 min | Remarks |</p>
<table>
<thead>
<tr>
<th>Assisting disinfection</th>
<th>Targets</th>
<th>Bacteria inactivation</th>
</tr>
</thead>
</table>
| Ranges of ultrasonic parameters | US power: 19 – 480 W/L  
US frequency: 20 – 2000 kHz  
US duration: 10 – 180 min |
| Remarks | - Beside the high frequency ultrasound (1.5 – 2 MHz) used in the Ashland’s patent, common ultrasonic frequency in water disinfection is in the range of 20 – 40 kHz.  
- Main mechanisms based on the physical effects of ultrasound that break up the bacterial cells.  
- Advantages: environmental friendly  
- Limitations: although ultrasonication alone can be effective in water disinfection, it is high energy consumption  
- Development: novel disinfection techniques combining ultrasonication prior to ultraviolet irradiation shown to be both effective and cost-efficient. Ultrasonication also enhances saline solution disinfection by electrolysis.  
- Key affecting factors: ultrasonic power, duration time. |

<table>
<thead>
<tr>
<th>Assisting radioactive wastewater treatment</th>
<th>Targets</th>
<th>Fuel pin cleaning, radioactive water treatment</th>
</tr>
</thead>
</table>
| Ranges of ultrasonic parameters | US power: 2000 W  
US frequency: 38 – 40 kHz  
US duration: 30 – 100 min |
| Remarks | - Main mechanisms based on the physical effects of ultrasound that gathering the suspension radioactive particles for later filtration.  
- Development: the techniques are at their very early stage, with lots of room for future research. |
### Sludge stabilization

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<thead>
<tr>
<th>Targets</th>
<th>Sludge disintegration, dewatering</th>
</tr>
</thead>
</table>
| Ranges of ultrasonic parameters | US power: 0.2 – 2.4 W/mL  
US frequency: 20 – 200 kHz  
US duration: 10 – 60 min |
| Remarks | - Ultrasound is employed as the pretreatment step before anaerobic/aerobic biodigestion.  
- The most common frequency used for sludge stabilization is 20 kHz.  
- Main mechanisms based on the physical effects of ultrasound for sludge disintegration.  
- Advantages: less retention time, thickened sludge, improved biodegradability, increased methane gas production.  
- Key affecting factor: ultrasonic power. |

### Soil remediation

<table>
<thead>
<tr>
<th>Targets</th>
<th>Cr, Cu, Fe, Ni, Pb, Zn</th>
</tr>
</thead>
</table>
| Ranges of ultrasonic parameters | US power: 40 – 500 W  
US frequency: 20 – 30 kHz  
US duration: 20 – 200 min |
| Remarks | - Main mechanisms based on the mechanical effects of ultrasound that increase porosity of soil, and facilitating leaching and removal of metals.  
- Advantages: accelerating the detachment of contaminants.  
- Development: Ultrasound has been coupled with other methods such as soil washing with shaken tray, vacuum pressure extraction in multi-step process and chemical leaching with acid, acid and Fenton’s reagent and thiourea.  
- Key affecting factors: soil/water ratio, application time, pH of the slurry |
<table>
<thead>
<tr>
<th>Organic decontamination</th>
<th>Targets</th>
<th>Petroleum hydrocarbons, pesticides, herbicides, polycyclic aromatic hydrocarbons</th>
</tr>
</thead>
</table>
| Ranges of ultrasonic parameters | US power: 100 – 600 W  
US frequency: 20 – 40 kHz  
US duration: 30 – 180 min |
| Remarks | - Main mechanisms based on both the physical and chemical effects of ultrasound that assist organic desorption, destruction and oxidation.  
- Development: ultrasound has been studied in coupling with other methods such as surfactants addition, air floating, mechanical mixing, Fenton oxidation, electrokinetics.  
- Advantages: environmental friendly  
- Limitation: not so practical at field application.  
- Key affecting factors: soil/water ratio, ultrasonic frequency and power, type of organic pollutants |

<table>
<thead>
<tr>
<th>Waste treatment and recycling</th>
<th>Targets</th>
<th>Deinking office waste, biodiesel synthesis from waste cooking oil, anaerobic digestion of solid organic waste</th>
</tr>
</thead>
</table>
US frequency: 20 kHz  
US duration: 10 – 40 min |
| Remarks | - Mostly the tasks employ high energy, low frequency ultrasound.  
- Main mechanisms based on the physical effects of ultrasound.  
- Development: green synthesis is a very new, interesting emerging approach to waste treatment and recycling with lots of room for research and innovation.  
- Advantages: environmental friendly |
<table>
<thead>
<tr>
<th>Air pollution control</th>
<th>Targets</th>
<th>Suspended airborne particles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ranges of ultrasonic parameters</strong></td>
<td>US power: 350 – 400 W US frequency: 20 – 21 kHz</td>
<td></td>
</tr>
<tr>
<td><strong>Remarks</strong></td>
<td>- Main mechanisms based on physical effects of ultrasound (acoustic vibration) that facilitate particles agglomeration and precipitation for easy removal. - Key affecting factors: ultrasonic frequency, humidity.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Environmental analysis</th>
<th>Targets</th>
<th>Assisting solvent extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ranges of ultrasonic parameters</strong></td>
<td>US power: 80 – 300 W US frequency: 35 – 40 kHz US duration: 2 – 5 min (with ultrasonic probe); 5 – 30 min (with ultrasonic bath)</td>
<td></td>
</tr>
<tr>
<td><strong>Remarks</strong></td>
<td>- Main mechanisms based on the physical effects of ultrasound that assist the solid sample pretreatment (pollutant extraction) for analysis. - Development: Because of many advantages of ultrasound in this field, research on this topic growing remarkably over the last 5 years. The combination of microwave digestion and ultrasound is also promising. - Advantages: significant reduction of preparation time for analysis, high recovery rate, simple setup, no cross-contamination (high purity), reduction of solvent consumption, environmental friendly.</td>
<td></td>
</tr>
</tbody>
</table>
2.1.2 Ultrasound in Water Treatment

Due to the formation of free radicals and high localized temperatures and pressures, ultrasonic irradiation (ultrasonication) appears to be an effective method for the destruction of hazardous compounds in water [46, 56]. Organic degradation by ultrasonic irradiation is more favorable with the gas flow of oxygen or argon rather than that of air or nitrogen [53, 57, 58, 59, 60].

The beneficial effect of ultrasonication on the removal of several target compounds from aqueous solutions has been demonstrated in many studies. These compounds include phenol [61, 62, 63, 64], bisphenol [65], chlorophenols [66], nitrophenols, aniline, nitrobenzene [67, 68, 69, 70], trichloroethylene [71, 72], ethylbenzene [73], xylene [74], chlorobenzene [75], chloronaphthalene [69], polychlorinated biphenyls, azobenzene [50], nitroaromatics [76], hydrazine [77], alternative gasoline oxygenates [78], organophosphorous pesticides such as parathion, dimethoate, chlorpyrifos, diazinon [79, 80, 81], carbamate pesticides such as carbofuran [57], polycyclic aromatic hydrocarbons [82, 83], pharmaceuticals such as diclofenac, ciprofloxacin, ibuprofen, antibiotics [84, 85, 58], endocrine disrupting compounds such as 4-cumylphenol, dimethyl phthalate, estradiol [86, 87, 88], detergents and surfactants [33, 89, 90, 91, 92, 93]. Particularly, ultrasound has been studied widely for the decolorization of textile dyes [50, 53, 56, 94, 95].

Regarding the effects of pH, since pH of solution can affect the charge of substances, particularly polar aromatic compounds (negatively charged under alkaline condition like 4-nitrophenol, or positively charged at acidic pH like aniline), the neutral substances are more easy to diffuse and accumulate at
the hydrophobic interface of liquid-gas bubbles in comparison with their corresponding ionic forms (thus, the rate of 4-nitrophenol degradation decreases with increasing pH while the rate of aniline destruction exhibits a maximum under alkaline conditions). The pH of solution also affects the formation of H$_2$O$_2$ by water sonolysis as the yield of H$_2$O$_2$ has a maximum at a pH of approximately 3 and decreases with increasing pH [96].

Regarding the effects of ultrasonic power, it was found that degradation rates increased with increasing power. However, there is an optimum acoustic power because a great number of cavitation bubbles are generated at high acoustic intensity which can become a barrier to the successful transfer of acoustic energy through the liquid [97, 98, 99].

The effects of ultrasonic frequency are more complicated. Most of studies applied ultrasound of low to medium frequency and very rare studies applied ultrasound with frequency higher than 1000 kHz [100, 87, 101, 102, 103, 104]. It was stated that low frequency (20-100 kHz) ultrasonication is more suitable for the degradation of hydrophobic and volatile compounds, while medium frequency ultrasonication (300-600 kHz) is usually more effective in degrading hydrophilic and non-volatile organics such as dyes [53, 94]. But in fact, lots of studies applied low frequency ultrasound successfully for dye decomposition [50, 53, 95]. Higher frequency ultrasonication provided better degradation in some studies [99, 105, 101], and it was explained that because at higher frequencies, lifetime of cavitation bubbles is shorter, leading to quicker collapse and higher production of radicals [99]. However, the highest frequency does not necessarily provide the best performance and the optimum frequency varies in different cases [59, 106, 107].
Furthermore, the application of dual-frequency (20/40 kHz) ultrasonication to enhance the degradation of Methylene Blue solution in photocatalytic treatment (UV/TiO$_2$) provided much better degradation efficiency (98.4%) in a rapid time (18 minutes) than the single-frequency ones (53.9% and 62.2% for the 20 kHz and 40 kHz, respectively) [108]. Therefore, this innovative approach of applying dual-frequency or multiple-frequency ultrasonic irradiation is worth considering for future studies.

On the other hand, the use of power-modulated pulsed ultrasound showed more effective in terms of producing hydroxyl radicals and other oxidants in aqueous media as the organic degradation rate increased by a factor of three compared with continuous irradiation under equal acoustic input power [109]. The positive effect of the pulsed mode, especially over longer period of ultrasonication, was also confirmed in some studies [70, 92, 110].

As the use of ultrasound alone may not be an economical technique for wastewater treatment and is insufficient for complete mineralization [84, 90, 103, 111], hybrid techniques are suggested, which combined ultrasound with catalysts, additives or used it as an enhancement to some conventional methods [64, 112, 113].

**Ultrasonication and H$_2$O$_2$/Fenton/Fenton-like Catalysts**

Adding H$_2$O$_2$ could enhance the sonolysis reduction of organic matter [110, 114]. However, an optimum of H$_2$O$_2$ exists as further increased of H$_2$O$_2$ concentration could result in decrease of the removal efficiency. Moreover, overdose of H$_2$O$_2$ leads to the additional pollution and it is harmful for the microorganisms [112].
Since iron is an effective oxidation catalyst, capable of decomposing $\text{H}_2\text{O}_2$ (generated by water sonolysis) in a Fenton-like process to form hydroxyl radicals, the addition of $\text{Fe}^{2+}$ ions at low concentration increased the degradation rates of phenol and other phenolic pollutants (chlorophenol and dichlorophenol) by 20 kHz ultrasonication [67, 82]. On the other hand, compared to the Fenton process alone, the efficiency of the combined Fenton and ultrasound treatment was decreased. The explanation was speculated as iron ions and ultrasound could compete for $\text{H}_2\text{O}_2$ decomposition to water and oxygen rather than to reactive radicals [115]. However, more studies are needed to define the involved mechanisms.

Combined low frequency 20 kHz ultrasonication (US) and Fenton process provided the best decontaminations of dichlorvos pesticide as compared with either US+$\text{H}_2\text{O}_2$ or US+CCl$_4$ processes [116]. US+Fenton (25 kHz) also resulted in maximum removal of 2,4-dinitrophenol as compared with either US+$\text{Fe}^0$/H$_2$O$_2$ or US+CuO/H$_2$O$_2$ heterogeneous Fenton-like processes [117]. It was noted that maintaining a proper ratio of $\text{Fe}^{2+}$ and H$_2$O$_2$ in Fenton process is very important. In all the cases, the hybrid methods gave better results than sole ultrasonication. Especially, removal rate of 2,4-dinitrophenol was significantly increased in the US+Fenton system (98.7%) than in the US alone (5.8%) [117].

A new Fenton-like system using iron metal instead of ferrous salt and Ethylenediaminetetraacetic acid (EDTA) obviously improved the 20 kHz ultrasonic degradation of 2,4-dichlorophenol. It was explained that EDTA can break down the O-O bond of oxygen to eventually produce H$_2$O$_2$, activating Fenton-like reaction which leads to rapid degradation of organic pollutants in the Fe/EDTA system. Since H$_2$O$_2$ is costly and instable at ambient atmosphere, H$_2$O$_2$ generated in-situ is cost-saving and more
favorable. Additionally, the reactions can proceed under neutral pH, thus, pH adjustment is not necessary as in the traditional Fenton process (which shows very low efficiency at pH > 4) [118].

On the other hand, nanoparticles of iron species could be excellent catalysts for organic decontamination by ultrasonication. Nanoparticles of super-paramagnetic iron oxide were significantly more effective than micro-sized zero-valent iron or reactive divalent iron (Fenton’s reagent) [119]; and magnetic nanoparticles of zero-valent iron proved to be an effective low-cost alternative catalyst [101] in diclofenac removal by high frequency (861 kHz) ultrasound. The positive effects were attributed to the synergy of massive surface area of nanoparticles, enhanced mass transfer rate and enhanced cavitation events [101, 119].

Most of the studies on sono-Fenton for dye wastewater treatment were conducted with low frequency ultrasound (20 – 60 kHz), and high frequency ultrasound of 1700 kHz was used only in one study [120]. In all these studies, the combination of ultrasound and Fenton’s reagent (H₂O₂ and iron catalyst) performed much better than either Fenton oxidation or ultrasonication alone as ultrasound irradiation accelerating the production of hydroxyl radicals in the Fenton’s reaction [120, 121, 122, 123, 124, 125, 126]. It was found that the optimum pH for these systems is pH 3 and the increase of ultrasonic input power and Fenton’s reagent concentration favors the increase of decolorization rate. Decolorization rate was also higher when dissolved oxygen was present as compared with nitrogen and argon [126].

Sonocatalytic degradation of Acid Red B (ARB) dye using Fe doped zeolite Y catalysts with the assistance of low frequency (20 kHz) ultrasonication was found to be accelerated by the reaction between Fe (II) and Fe (III) ions
and H$_2$O$_2$ generated in situ by water sonolysis. While the dye degradation rates by ultrasonication alone and with the presence of undoped zeolite Y were less than 10% and up to 12% respectively, the degradation rates were remarkably increased up to 86% and 85% when the Fe (II) and Fe (III) doped zeolite Y catalysts presented, without any other additional oxidants, respectively. Thus, the presence of ultrasound eliminated the need for external H$_2$O$_2$ to enhance the Fenton-like process [127].

**Sonophotolysis and Sonophotocatalysis**

Since ·OH radicals are formed during TiO$_2$ photocatalysis, combination of the TiO$_2$ photocatalyst and ultrasound can take advantage of the sonoluminescence phenomenon to enhance the generation of these hydroxyl radicals. Using ultrasound (40 kHz and 39 kHz) as an irradiation source to induce TiO$_2$ performing catalytic activity for dyes degradation (azo dyes, Methylene Blue) confirmed that the degradation increased markedly in the presence of TiO$_2$ [128, 129, 130]. Sonocatalytic (42 kHz) degradation of various organic dyes by powder and nanotubes TiO$_2$ indicated that powder TiO$_2$ was more favorable for the treatment of anionic dyes while nanotubes TiO$_2$ was more effective for cationic dyes [131]. It might be attributed to the higher surface charge and higher surface area of the negatively charged TiO$_2$ nanotubes that made it easier for them to adsorb cationic organic dyes. On the other hand, the less charged TiO$_2$ powder was more easily to absorb the anionic organic dyes with high molecule weight and large hydrophobic middle section [131].

The combination of 283 kHz ultrasonication (sonolysis) and UV irradiation (photolysis) showed synergistic effect for diethyl phthalate mineralization [132]. The H$_2$O$_2$-assisted homogenous sonophotolysis of wastewater from
food industry significantly enhanced the mineralization (82%) as compared with each individual process (less than 41%) [133].

Recently, sonophotocatalysis, the combination of ultrasound, UV and catalysts, has appeared to be a promising alternative water treatment method. The synergistic effects of UV, TiO$_2$ catalyst and ultrasonication (25 kHz and 200 kHz) were observed in the degradation of phenol and aldehydes, respectively [134, 135]. The shock waves generated by ultrasound promote photocatalytic degradation of organic pollutants through many pathways such as increasing the specific surface area of TiO$_2$ by reducing its particle size, improving mass transfer to the TiO$_2$ surface, increasing dispersion of TiO$_2$ and interrupting recombination of excited electrons and holes on the catalyst. On the other hand, TiO$_2$ catalyzes the decomposition of H$_2$O$_2$ generated by ultrasonication, thus producing hydroxyl radicals, and TiO$_2$ particles act as nuclei of cavities, thus promoting the production of active species and pyrolysis [135].

Fenton and Fenton-like’s reagents were also efficiently employed for the sonophotocatalytic degradation of fenitrothion (insecticide) at 20 kHz, linuron (herbicide) at 200 kHz and p-nitrophenol at 25 kHz [136, 137, 138]. It was found that optimum loading of H$_2$O$_2$ exists, thus, beyond that the removal efficiency can be reduced. It was interesting to note that while normal Fenton reaction has optimum pH at 3, the simple handling and effective sonophotocatalysis with Ferrioxalate can be applied in a wide pH range [136].

Furthermore, some visible light responsive catalysts have been synthesized as an attempt to develop a photocatalytic system that can operate efficiently not only under UV irradiation but also under solar light irradiation. Shifting
the optical response to the visible range can expand the photocatalytic efficiency as UV light contributes only a small fraction (5%) of the solar spectrum. The sonophotocatalytic processes applied visible light responsive catalysts, Bi$_2$O$_3$/TiZrO$_4$ (at 20 kHz ultrasonication) and ZnFe$_2$O$_4$/TiO$_2$-Granular activated carbon (at 37 kHz ultrasonication) showed initial positive results in the degradation of 4-chlorophenol and phenol [139, 140].

Concerning the synergistic effect of sonophotocatalysis, comparative experiments among sonolytic (US alone), photocatalytic (UV+TiO$_2$ alone) and sonophotocatalytic processes (combining simultaneously US+UV+TiO$_2$) were conducted for Orange-G and Methyl Orange degradation. Though there were many other factors to consider, it is interesting to note that, while there was obvious synergistic effect of the sonophotocatalytic treatment at low (20 kHz) ultrasonic frequency (degradation rate of 90% compared with 8% of the US alone and 68% of the UV+TiO$_2$ alone processes) [141]. On the other hand, the sonophotocatalytic treatment of Orange G at high frequency (213 kHz) showed no synergistic enhancement but simply an additive effect of combining sonolysis and photocatalysis (degradation rate of 85% compared with 35% of the US alone and 59% of the UV+TiO$_2$ alone processes) [142].

Comparison among photocatalytic, sonocatalytic and sonophotocatalytic treatments of Rhodamine B dye using natural sunlight and 35 kHz ultrasound as irradiation source and pristine ZnO nanoparticles and ZnO/carbon nanotubes composites as catalysts confirmed the synergistic effect of the ZnO/carbon nanotubes sonophotocatalysis [143]. The synergistic effect was also achieved in the sonophotolytic advance oxidation (US+UV+Fe$^{3+}$) system for Reactive Black 5 dye treatment. However, the system could be affected differently in the presence of different organic ligands. While
oxalate, citrate, tartrate and succinate could enhance the dye degradation, NTA and EDTA exhibited strong inhibitions [144].

Very recently, the sonophoto-Fenton system, combining ultrasonication (850 kHz), UV irradiation and Fenton’s reagent for azo dye Orange II decolorization confirmed its synergistic effect, compared with either individual method. The decolorization rate was increased with the addition of Fenton’s reagent at the optimum molar ratio Fe\(^{2+}\):H\(_2\)O\(_2\) of 1:50. The decolorization rate obtained in the sono-Fenton system using heterogenous Fenton’s catalyst (Fe containing ZSM-5 zeolite/ H\(_2\)O\(_2\)) was lower than in the system using traditional homogenous Fenton’s reagent (FeSO\(_4\)/H\(_2\)O\(_2\)), due to more difficulty of the reaction between Fe\(^{2+}\) and H\(_2\)O\(_2\) [145].

**Sonoelectrochemical Remediation**

The integration of sonolysis and electrolysis, though still underdevelopment, has emerged as a potentially promising remediation method. Electrochemical process is promoted by the effects of ultrasonication such as shock waves, acoustic streaming and microjets, which activate electrode surface, enhancing electrolytic current mode and facilitating mass transfer of reaction solution. Both low frequency (22 and 24 kHz) and high frequency (850 kHz) ultrasounds successfully improved electrochemical decontamination of organic pollutants (nitrobenzene, trichloroacetic acid and phenol) [146, 147]. Significant reduction of energy consumption could be achieved through specifically designed sonoelectrochemical reactor [146] and innovative operating mode using dual-pulse system, which synchronized alternatively pulsed ultrasonic waves and electric waves [70].
The sonoelectrochemical system was found to be an effective and potential alternative for dye decolorization in recent researches [99, 148, 149]. Studying effects of different ultrasonic frequencies (40-60-80 kHz) showed that the highest degradation rate was achieved at 80 kHz, but by increasing frequency from 80 to 100 kHz, no significant effect was observed [99]. Studying effects of different supporting electrolytes showed that KCl and NaCl were much more effective than Na₂SO₄ and Na₂CO₃. Moreover, studying effects of various ultrasonic power showed that increase in ultrasonic power has decreased decolorization rate due to the degassing effect of the intermediate chlorine gas by ultrasound (chlorine gas generated from the electrode surface would escape rather than dissolved in the liquid to form hypochlorite, a strong oxidant for decolorization) [149]. Furthermore, the integrated sonoelectrochemical-Fenton processes using low frequency ultrasound (20 and 24 kHz) again confirmed their positive synergistic effect in dye removal [150, 151].

Furthermore, powerful synergistic effects were observed in the combination of 20 kHz and 120 kHz sonoelectrochemical processes and Fenton’s reagent (Fe²⁺/H₂O₂) for hydrophilic chloro-organic pollutants and nitrotoluenes removals. While external H₂O₂ addition was used in one study [152], H₂O₂ in situ electrogenerated by reduction of oxygen dissolved at the cathode (from oxidation of water at the anode) was used in another study [153]. H₂O₂ can be generated in situ which is one of the advantages of electro-Fenton oxidation compared with traditional Fenton oxidation. In addition, Fe²⁺ can be regenerated from the electro-reduction of ferric salts, thus it can be recycled in situ and coupled with H₂O₂ to continuously produce the Fenton’s reagent [153, 150]. It was noted that, despite of degassing phenomenon by ultrasonication (which caused less amount of oxygen dissolved in water at
the same temperature), the yield of electrogenerated \( \text{H}_2\text{O}_2 \) under sonoelectrolysis was higher than that of electrolysis due to the significantly enhanced mass transfer rate of oxygen toward the cathode also by ultrasonication [153].

Sono-electrochemical degradation of the chloro-organic compound 2,4-D by catalysts Pd and Pd/Fe resulted in complete mineralization of the substrate with the greatly shortened reaction time in comparison to traditional electrocatalytic processes. The bimetallic Pd/Fe catalyst performed even faster (in 5 minutes) than the pure Pd catalyst (in 10 minutes) and was more cost-efficient [154].

**Other Sono-catalytic/Sono-assisted Oxidation**

Of various heterogeneous catalysts tested (Pt, Pd, Ru, CuO.ZnO/Al\(\_2\)O\(\_3\)) on the removal of sodium dodecylbenzene sulfonate (SDBS) by low frequency (20 kHz) ultrasonication, CuO.ZnO/Al\(\_2\)O\(\_3\) was found to be the most effective in terms of both SDBS decomposition, total oxidation rates as well as \( \text{H}_2\text{O}_2 \) formation [82].

Cadmium selenide graphene and zero-valent aluminum were efficiently used as catalysts for dye degradation enhancement under 20 kHz ultrasonication [155, 156]. In both cases, the improvement was due to the sonocatalytic effects of accelerating the formation of hydroxyl radicals. In the case of zero-valent aluminium, it was found that the acidic environment was more favorable with the optimum pH 2.5 [156].

Investigating the catalytic effects of TiO\(\_2\) nanoparticles, SiO\(\_2\) nanoparticles and Al\(\_2\)O\(\_3\) microparticles on the ultrasonication of monolinuron herbicide at 20 kHz showed that TiO\(\_2\) gave a greater efficiency (about twice that with
ultrasound alone), SiO₂ was a little more efficient (about 1.5 times) but no real effect on the ultrasonication efficiency was found for Al₂O₃. It was explained that the nanoparticles provide nucleation sites for cavitation bubbles formation at their surfaces, leading to an increase in the number of bubbles when the liquid is irradiated by ultrasound, thus, enhancing sonochemical reaction yield. The additional positive effect of TiO₂ was suggested due to the long-lived active {TiOH⁻}⁺ species (formed by reaction of ·OH from the cavitation collapse at the surface of TiO₂) that can react with adsorbed monolinuron or can be decomposed into ·OH, which can either react with monolinuron in the solution or be recombined into H₂O₂. Furthermore, ultrasonifications of monolinuron with and without TiO₂ catalyst were again conducted at high frequency of 800 kHz. Interestingly, no improvement in the ultrasound efficiency at 800 kHz was found in the presence of TiO₂. It was supposed that these active species are not formed at 800 kHz, probably because at this frequency, particles are not used as nuclei for the generation of cavitation bubbles [157].

Comparing catalytic activities among three different composites CeO₂/TiO₂, SnO₂/TiO₂, ZrO₂/TiO₂ and pure TiO₂ under ultrasonic irradiation (40 kHz) of the organic dye ARB, it was found that the sonocatalytic degradation rates varied significantly in this decreasing order: CeO₂/TiO₂ > SnO₂/TiO₂ > TiO₂ > ZrO₂/TiO₂ > SnO₂ > CeO₂ > ZrO₂, with the corresponding removal ratios of ARB were 91.32%, 67.41%, 65.26%, 41.67%, 28.34%, 26.75% and 23.33%, respectively [158]. The CeO₂/TiO₂ composite demonstrated much higher sonocatalytic activity than pure TiO₂ powder. Furthermore, to improve the catalytic activity of TiO₂, composites of doping agents and TiO₂ such as Fe³⁺/TiO₂ [159, 160], Fe³⁺-C₆₀/TiO₂ [161], Ce³⁺/TiO₂ [160], La³⁺/TiO₂ [162], InVO₄/TiO₂ [163], CdS/TiO₂ [164], CdS-C₆₀/TiO₂ [165],
multi-walled-carbon-nanotubes-CdS/TiO$_2$ [166], Er$^{3+}$:YAlO$_2$/TiO$_2$ [167, 168] and Er$^{3+}$:Y$_3$Al$_5$O$_{12}$/TiO$_2$ [169] were synthesized and proved their effectiveness of enhancing sonophotocatalytic dyes degradation in many studies.

Results from studying the effects of some additives [Mn$_3$O$_4$, Cu$^{+2}$, Fe$^0$, KIO$_3$] and some radical scavengers [Na$_2$CO$_3$, perfluorohexane (C$_6$F$_{14}$) and t-butyl alcohol (C$_4$H$_{10}$O)] on the 35 kHz ultrasonication of olive mill wastewater showed that total phenol (88%), total aromatic amines (79%) and toxicity were removed efficiently and cost-effectively by ultrasonication alone at 60$^0$C within 150 min. Moreover, the addition of Fe$^0$, Fe$_3$O$_4$, KIO$_3$, Cu$^{+2}$ and perfluorohexane separately, enhanced the ultrasonication decontamination of the olive mill wastewater. It was suggested that total phenols are mainly eliminated by ·OH radicals outside the cavitation bubble during ultrasonication while total aromatic amines are mainly degraded by high temperature of pyrolysis in ultrasonic cavities [170].

Recently, sono-activated persulfate process has emerged as a highly promising advanced oxidation technique for wastewater treatment. Persulfate (S$_2$O$_8^{2-}$) is a strong oxidant and relatively stable during storage and handling. The combination of ultrasound and persulfate proved significant synergistic effects in the degradation of dinitrotoluenes, trichloroethane and ammonium perfluorooctanoate [171, 172, 173]. This was attributed to the ability of ultrasound in activating persulfate to generate sulfate radical (SO$_4^{\cdot-}$) which is considered even more efficient and powerful oxidant than ·OH. In another study, the combination of oxone (2KHSO$_5$.KHSO$_4$.K$_2$SO$_4$, a source of the strong oxidant that can generate sulfate radicals), cobalt catalyst and ultrasound (Oxone+Co$^{2+}$+US) for amoxicillin degradation displayed the best performance among other setups tested as shown in the order of removal
efficiency Oxone+Co$^{2+}$+US (85%) > Oxone+US (63%) > Oxone+Co$^{2+}$ (51%) > Oxone (22%) [174].

Ultrasound has been used to initiate catalytic reaction (sonocatalysis) for decolorization of dye solutions in several recent studies. While pH seems to not demonstrate significant effect in the process of ultrasonic irradiation alone [60], it can affect differently in the presence of different catalysts. Using immobilized cobalt ions (Co), persulfate (PS) and 35 kHz ultrasound (US) in different setups for the treatment of various dyes showed that for all the dye solutions, the decolorization efficiencies of these systems were in the order of PS+Co+US > PS+US > PS+Co > PS. This confirmed the feasibility of the combined cobalt activated persulfate and ultrasonication system, due to the enhanced formation of highly reactive sulfate radicals (SO$_4$•$^-$) and hydroxyl radicals through persulfate (S$_2$O$_8^{2-}$) activated by cobalt ions and ultrasound. Studying the effect of pH with the range from pH 2 to 11, it was found that pH has no practical influence in the system [175].

Ultrasonic (300 kHz) degradation of malachite green was intensified by the addition of bromide ions. The positive effect of bromide ions was explained due to the presence of dibromine radical anions (Br$_2$•$^-$) generated by reaction of bromide ions with hydroxyl radicals produced from water sonolysis. Though less reactive than hydroxyl radicals, dibromine radicals undergo radical recombination at a lesser extent, and thus would be more available than hydroxyl radicals for substrate degradation [176].

Ultrasound has also been successfully assisted ozone in organic decontamination of several studies, especially for dye wastewater treatment [177, 178, 179]. Although ozonation is known as an effective advanced
oxidation process for textile effluent treatment, the mass transfer of ozone from the gas-phase to the liquid-phase is often the limiting factor. Thus, ultrasound has been used in some studies for the enhancement of the ozone oxidation process. The degradation of reactive dyes using ultrasound (300 kHz, 520 kHz), ozone and combination of both methods showed that the effectiveness of ultrasound was lower than ozone for both bleaching (decolorization) and mineralization; however, the efficiency of ozone treatment is significantly enhanced by simultaneous irradiation of the treated solution with ultrasound. The synergistic effect was attributed to the mechanical effects of ultrasound to enhance mass transfer of ozone to accelerate its direct reactions with the dyes and the generation of excess radical species from the sonolysis of water, the normal chemical degradation of ozone and the thermal decomposition of ozone in the acoustic cavitation bubbles [177, 178]. Moreover, low frequency (20 kHz) ultrasound assisted ozone oxidation proved to be a rapid, efficient and low energy consumption process to decolorize the high concentration malachite green (triphenylmethane dye) wastewater [179].

Ozonation combined with ultrasonication in the degradation of p-Aminophenol (PAP) resulted in a synergistic increase of the overall rate. Although ozonation (72% and 90% PAP removal at 10 and 30 min, respectively) was more effective than ultrasonication (3% and 4% at 10 and 30 min), the efficiency of the combination of ozone and ultrasound (88% and 99% at 10 and 30 min) exceeded even the sum of those using ozone and ultrasound alone. It was explained that the synergy observed in combined treatment was mainly due to the effects of sonolysis in enhancing the decomposition of ozone in collapsing bubbles to yield additional free radicals [180].
**Ultrasound-assisted Adsorption**

As adsorption is a common and effective process for the removal of dyestuff from textile wastewater, the ultrasound-assisted adsorption was investigated, using high frequency (850 kHz) ultrasound and activated carbon as adsorbent for treatment of the reactive dye Yellow HE4R. While ultrasonication alone could only achieve decolorization (80.62%) and was ineffective in COD removal, in the presence of activated carbon, 99.9% decolorization as well as 85.22% COD removal were achieved. Thus, the combined process performed much better due to the physical and chemical effect of ultrasonication on the activated carbon [181].

Another type of adsorbent, the new porous carbon-based exfoliated graphite, together with low frequency (28 kHz) ultrasonication was applied for decolorization of azo dye scarlet 4BS and acid black 210. The combined processes also indicated enhancement in removal ratio and reduction of the treatment time compared with either individual method [182, 183]. The decolorization efficiency was better in the combined exfoliated graphite and ultrasound process (98%) than in the combined activated carbon and ultrasound (58%) [183].

Furthermore, the coupling of ultrasound-assisted exfoliated graphite adsorption with photocatalysis (TiO$_2$/Exfoliated Graphite-40 kHz US+UV) and ultrasound-assisted exfoliated graphite adsorption with H$_2$O$_2$ (Exfoliated Graphite-28 kHz US+H$_2$O$_2$) proved very positive synergistic effects in decolorization of some azo dyes [184, 185].

Ultrasonication was used as a pretreatment process to enhance the adsorption capacity of sepiolite, a natural clay adsorbent, for Methylene Blue removal.
The physical effect of ultrasonication (20 kHz, 5 hours) caused significant increase in the specific surface area of sepiolite, leading to improve its uptake capacity of Methylene Blue [186]. Very recently, an experimental method using gold nanoparticles loaded on activated carbon in the ultrasound-assisted (40 kHz) adsorption process for Methylene Blue removal was effectively developed [187].

**Ultrasound-assisted Biological Treatment**

Ultrasonication can be applied before biological treatment step to assist the process by stimulating enzyme activity [188] or breaking the pollutant molecules into simpler ones, thus facilitating the followed biodegradation by microorganisms [189]. Ultrasound can also be used as an auxiliary process for biochemical treatment of dyes. The decomposition of azodyes by laccase (enzyme), ultrasound (850 kHz) and combination of both treatments was investigated [190]. The laccase treatment showed high decolorization rates but could not degrade all the azodyes to the same extent and the enzyme could be deactivated in some unfavorable conditions. On the other hand, ultrasound treatment could decolorize all tested dyes after 3 h at a high energy input, and prolonged sonication leads to nontoxic ionic species. The combination of laccase and ultrasound performed the higher degradation rates among these operations. The findings indicated the possibility of saving time and energy by applying a simultaneous combination of laccase and low energy input ultrasound treatments for decolorization of azodyes [190].

In another study, continuous low frequency (20 kHz) ultrasonication of 5 hours was used as an initial step, followed by 8 hour microbial (*Rhodotorula mucilaginosa*) treatment for decolorization of Reactive Red 2, Reactive Blue 4 and Basic Yellow 2 dyes. This hybrid method proved fairly effective with
the removal rates up to 93%, 88% and 40% for Reactive Red 2, Reactive Blue 4 and Basic Yellow 2 dyes, respectively [191].

**Ultrasound-assisted Coagulation**

Ultrasound proved to significantly enhance the removal of toxic algae by coagulation through breaking down gas vesicles in algae cells [192, 193]. In both studies, ultrasonications were conducted within only short duration times of 5 – 15 s. It was observed that variation in ultrasonic frequency did not have remarkable effect while increasing ultrasonic power beyond certain value resulted in negative outcome as higher power makes it difficult for the aggregate algae to form larger clusters [192]. Therefore, proper power supply should be considered in order to obtain the most effective, energy-efficient and economical performance.

In another study, short-term pretreatment with ultrasound, followed by alum coagulation gave a marked increase in permeate flux of a biological microfiltration effluent. It was attributed to ultrasound in fouling mitigation as it can break up suspended solids. However, as the result, smaller particles can also accelerate the clogging of the membrane pores, thus prolonged ultrasonication feed pretreatment may counteract the reduction of irreversible fouling [194].

Furthermore, low frequency ultrasound (20 - 22 kHz) also effectively intensified electrocoagulation treatment of effluents containing surfactants, oil and heavy metals [89, 195]. Main benefits that ultrasound brings during electrocoagulation treatment are: (i) saving electrical energy due to the free radicals and outgassing effect in the cavitation raising the electrical conductivity, thus maintaining a constant current at lower voltages, (ii)
intensifying electroflotation due to the release of gas at the electrodes [89], and (iii) increasing the sorption capacity of the coagulant (magnetite) through increasing surface area by reducing their particle size [195].

**Ultrasound-assisted Membrane Filtration**

Employment of ultrasound to enhance ultrafiltration and membrane cleaning has emerged as an effective and promising approach in wastewater treatment. Ultrasound assisted filtration is less dependent on the feed properties [196]. The application of ultrasound in both mechanical and chemical cleaning for fouled membranes resulted in much higher flux recovery, particularly at low frequency and high power setups [197]. Lower frequency ultrasound seems to have higher cleaning efficiencies than higher frequency ultrasound [198, 199]. Ultrasonic membrane cleaning was based on the liquid jets generated by ultrasonic cavitation and the mechanical effects of ultrasound that break the fouled layer at the membrane surface and thus increased the flux [196]. Intermittent ultrasound irradiation was found more desirable than continuous irradiation mode, not only for its effective flux enhancement but also for lowering energy consumption and prolonging the lifetime of the membranes used [196, 197, 200].

**Ultrasound-assisted Disinfection**

High power, low frequency (20-40 kHz) ultrasound has proved to be effective in water disinfection, due to the shear forces generated by the collapse of acoustic cavitation bubbles, that are able to break up the cells and suspended particles [201, 202]. However disinfection by ultrasonication alone requires very high energy, therefore ultrasonication should not be
considered as a sole alternative to conventional disinfection for economic aspects, but rather be coupled together with other techniques [42, 203, 204].

Low frequency 20 kHz ultrasonication combined with chlorine (chlorination) or chlorine dioxide significantly improved the biocidal action [42, 205]. On the other hand, it is interesting to note that low power, high frequency (1.5 – 2 MHz) ultrasound employed in the Ashland’s patented Sonoxide Ultrasonic Water Treatment Technology eliminates the need for chemical addition in controlling of bacterial, algae and biofilms throughout an entire chemical-free industrial system [206].

While ultraviolet germicidal (UV-C) irradiation has been widely known and used, the UV disinfection is often hindered by suspended solids as they scatter UV light and provide shielding for bacteria. Novel disinfection techniques which combine low frequency pretreatment ultrasonication (20-40 kHz) and a subsequent ultraviolet irradiation have shown to be both effective and cost-efficient [203, 207, 208]. The synergistic disinfection effect of the system was attributed to the capability of ultrasound in reducing the mean size of suspended solids, thus leading to increasing germicidal effect of UV-C.

Results from the study of low frequency (40 kHz) ultrasound coupled with electrolysis to disinfect saline solution showed that ultrasonication amplified the effect of electrolysis through: (i) enhancing the mixing of bacterial suspensions in the vicinity of the electrode surface where the hypochlorite is being generated; (ii) the mechanical breaking effect of cavitation on the bacterial cell wall, making them more susceptible to attack by hypochlorite; (iii) the cleaning effect of ultrasound on the electrode surface, preventing fouling build up, thus maintaining more efficient electrolysis [209].
Recently, the first study to demonstrate 36 kHz sonoelectrocatalytic disinfection using TiO$_2$ fabric as an anode for effective inactivation of E. coli bacteria was conducted, showing excellent synergistic performance [210].

**Ultrasound-assisted Radioactive Wastewater Treatment**

Although ultrasonic surface cleaning is a well-established technology used in many industrial processes, there are only very few reports on ultrasound used in radioactive surface cleaning [211]. Kumar et al. (2014) are the pioneers to develop the ultrasonic cleaning for external surface of plutonium bearing components in the nuclear fuel fabrication. The radioactive particulates were contained inside the liquid medium (for later filtration), reducing the chance for any air-bone activity to release. The technique was conducted without any damage to the thin walled fuel tubes and was shown to be quite effective, achieving the cleaning efficiency of more than 99% with 38 kHz ultrasonication in 30 minutes [211]. High decontamination efficiency of more than 97% was also achieved in another radioactive wastewater treatment process (40 kHz, 100 minutes) with specific ultrasonic reactor designed that applied the ultrasonic standing wave effect for gathering the suspension radioactive oxide particles into the pressure node plane [212].

**2.1.3 Ultrasound in Sludge Stabilization**

Recently, ultrasound application has emerged as a promising technique for the pretreatment of waste activated sludge for subsequent sludge treatment, mostly in anaerobic digestion but also in aerobic digestion [213, 214]. Comparing with other pretreatment methods, ultrasonication exhibits a great potential of not being hazardous to environment and economically competitive [215]. The use of ultrasound to enhance sludge digestion could
be achieved at full scale and effectively result in less retention time, thickened sludge, improved biodegradability, improved solids destruction, substantial increases in methane gas production and better residual solids dewatering [215, 216, 217, 218, 219]. It was suggested that the positive effects of ultrasonication were attributed to mechanisms such as hydro-mechanical shear forces, oxidizing effects of free radicals, thermal decomposition of volatile hydrophobic substances in the sludge and increase of temperature during ultrasonication [220].

Low frequency ultrasound was more effective than high frequency for sludge treatment, indicating that the mechanical effects, instead of free radicals, were primarily responsible for the enhancement [218, 221]. The most popular frequency used for sludge stabilization is 20 kHz or in the range of 20-40 kHz. However, high frequency (200 kHz) ultrasound also showed positive results in sludge disintegration and moreover, in sludge decontamination (surfactant removal) [222].

High power density ultrasound could improve sludge disintegration, cell lysis, and inactivation [221]. The higher the sonication power employed, the higher rate of sludge disintegration, but increasing power beyond certain value showed no significant effect on excess sludge reduction [223, 224]. Ultrasonication could disintegrate sludge solids, and with longer duration time, bacteria cells could be destroyed [225, 226]. It was found that low density and long duration ultrasonication was more efficient than high density and short duration ultrasonication at the same energy input for sludge disintegration [223, 227].

Low power ultrasound treatment could improve sludge dewaterability, depending on the sludge disintegration level. When sludge disintegration
level was too low, sludge dewaterability did not change significantly. When sludge disintegration level was high, many fine particles were produced, leading to decrease in sludge dewaterability. With a proper sludge disintegration level, an improvement of sludge dewaterability could be achieved as after disintegration, the sludge fragments could be re-flocculated to tighter flocs with the help of conditioning agents [227]. Ultrasonic pretreatment followed by anaerobic digestion can improve both sludge digestion and dewatering [228]. The dewatered sludge had less viscosity and elasticity than untreated sludge [229, 230].

Synergistic effects were found in combined alkaline (NaOH) and ultrasonication pretreatment for enhancement of aerobic as well as anaerobic digestion of waste activated sludge [224, 231]. The efficiency of these combinations was in descending order: simultaneous treatment (NaOH and ultrasonication (US) at the same time) > NaOH treatment followed by US > US followed by NaOH treatment [231]. It was found that lower specific energy input in ultrasound pretreatment yielded higher synergistic effect [224].

Significant improvement of sludge disintegration was also observed in the combined sono-thermal pretreatment. In addition, methane production and total COD reduction were also enhanced by the combined ultrasonication and thermalization. However, because of their high energy consumption, this method was assessed as unfeasible for practical application [232].

Furthermore, the optimization experiments on ultrasonication pretreatment of activated sludge under pressures resulted in the optimum pressure of 2 bars regardless of temperature conditions. Since best energy efficiency would correspond to short ultrasonication at the optimum pressure under adiabatic
condition, the under pressure ultrasonication pretreatment promises a significant potential for energy saving in sludge treatment [233].

2.1.4 Ultrasound in Sediment and Soil Remediation

Not only ultrasound can degrade the chemicals itself, ultrasonic waves can also increase porosity and percolation rate of soil, accelerating desorption and facilitating removal of entrapped contaminants. Therefore, ultrasound has been investigated for sediment and soil remediation from variety types of contaminants from heavy metals to organic compounds [234].

*Ultrasound-assisted Heavy Metals Removal*

Ultrasound has been used to aid precious metals recovery by the cleaning action that removes an unwanted clay coating from raw ore, accelerates leaching of minerals from the ore as well as improves filtration rates [235]. The mechanism of metal removal is based on the mechanical effects of ultrasound which cause particle size reduction and detachment [236]. More than a decade ago, low frequency (20-22 kHz) ultrasound was investigated for enhancement of several soil washing processes such as passing water across the contaminated soil on an ultrasonically shaken tray [235], coupling ultrasonication with vacuum pressure extraction in an integrated multi-step technology [236], or ultrasonication of diluted soil [237]. In recent studies, low frequency power ultrasound was efficiently used to aid the chemical leaching of heavy metals by acid [238, 239], acid and Fenton’s reagent [240], thiourea [241] from electroplating, sewage sludge and kaolin, respectively. Ultrasound improved the soil remediation in all the studied cases.
Ultrasound-assisted Organic Desorption

Power ultrasound (low frequency) has been used in many soil (sludge)-washing studies for desorption of non-aqueous phase liquid such as vegetable oil [242] and petroleum hydrocarbons (diesel [243, 244, 245, 246, 247], crude oil, bitumen, etc. [248, 249, 250]). The flushing processes were sometimes combined with surfactants [243, 247], air floating [248] or mechanical mixing [245]. Ultrasound-induced desorption is based on the mechanisms of physical breakage of bonds by hot spots, particle surface impingement, the fragmentation of long-chain hydrocarbons by microjets, and microstreaming generated by acoustic vortices in the media pores [243, 249]. Experimental results indicated that ultrasonication can enhance oil removal considerably and the level of improvement depends on factors such as ultrasonic power, water washing flow rate and soil type. The finer the particle size, the higher the surface area and the capillary force, leading to reduction in the removal efficiency [246, 247, 250]. Removal increased slightly with power intensity, but only up to a certain level [242, 243, 246]. The solid concentration of the slurry also played an important role [244]. Removal efficiency could be improved with a multistage ultrasonic treatment process [243].

Furthermore, as carbon particles provide strong sorption sites for hydrophobic organic contaminants and thus reducing their freely dissolved concentrations, a powdered activated carbon amendment assisted with ultrasonication was developed and proved to be more effective than mechanical mixing in decreasing the bioavailability of phenanthrene and pyrene [251].
Ultrasound-assisted Organic Destruction

Power ultrasound of 20 kHz was found to be able to destroy major contaminants, herbicides, pesticides such as atrazine, simazine, DDT, lindane, 2,4,5-T, TBT, endosulfan, PCB, PAHs and petroleum hydrocarbons [252, 253, 34, 254] in soils and sediments. It was observed that radical formation was negligible but pyrolysis dominated in cavitation reactions in slurries [252]. Several advantages of high power ultrasonic technology compared with conventional methods were indicated including high destruction rates, no dangerous breakdown products and low energy demand leading to low-cost. Moreover, the technology can be made rather compact and transportable, allowing on-site treatment [34].

On the other hand, the application of low power high frequency (1.6 MHz) ultrasound was showed to be effective in degrading DDT dispersed in water and sand slurry. However, in practice, due to intensity limitations of low volume coverage, high attenuation of energy, currently available high frequency ultrasound equipment is not ideal for heavy duty application such as soil remediation [255].

Ultrasound-assisted Advanced Oxidation of Organic Pollutants

A combination of ultrasound (47 kHz) and Fenton advanced oxidation (sono-Fenton process) for soil remediation from volatile organic pollutants was initially developed with toluene and xylenes as model contaminants and with different Fenton-like catalysts (iron sulfate, iron chloride and copper sulfate) as well as different concentrations of H₂O₂. It was found that, when H₂O₂ were present, the addition of a Fenton catalyst increased the efficiency of the process, especially iron sulfate for toluene and copper sulfate for xylenes.
removals. It was also observed that increasing H₂O₂ concentration enhanced the removal of all the contaminants. The total efficiency of the process was noticeably improved when applying ultrasonication. [32].

Another sono-Fenton-like process using naturally occurring mineral iron as catalyst with different ultrasonic powers (100, 200, 400 W) was investigated for soil remediation from naphthalene. The results indicated that mineral iron was able to catalyze the degradation of naphthalene in the presence of ultrasound at various concentrations of H₂O₂. At the optimum condition, the maximum of 97% reduction in naphthalene concentration in soil after 2 h of treatment could be achieved. For practical use, it was suggested that in order to prolong the lifetime of the sonotrode, improvement in the reactor design is necessary [256].

2.1.5 Ultrasound in Waste Treatment and Recycling

Recently, interests on ultrasonic applications have been even extended into waste treatment and recycling. High intensity (1-2 kW), low frequency (20 kHz) ultrasound has been found effective in facilitating the deinking of recoverable office waste and Indigo prints within 10-20 minutes with the removal efficiency can reach up to 100% [257, 258]. On the other hand, sonochemical reactors have successfully synthesized biodiesel from waste cooking oil due to the enhanced emulsification effect and mass transfer rate by low frequency ultrasound (20 kHz, 200 W). After the same operation time of 40 minutes, the sonochemical reactors showed clearly better conversion efficiency (89.5%) than the conventional stirring method (57.5%) [259].

While there have been several studies on the employment of ultrasound as pretreatment prior to biological process in wastewater treatment and sludge
stabilization, the study by Cesaro and Belgiorno (2013) is the first attempt to use ultrasound as pretreatment to enhance further anaerobic digestion of solid organic waste. The efficiencies of sonolysis (20 kHz) and ozonation in improving anaerobic biodegradability of the organic fraction of municipal solid waste for enhancing biogas production and energy recovery were investigated. It was found that both pretreatments significantly improved the solubilization of the solid organic waste. However, ultrasonication appeared to be more competitive than ozonation as it was more effective, less costly and was without formation of undesired by-products [260].

2.1.6 Ultrasound in Air Pollution Control

The application of ultrasound in air pollution control is based on acoustic agglomeration, a process in which, ultrasonic waves induce relative motion and collisions among pollutants suspended in the air, causing them to adhere together to form larger assembled particles [35, 37]. This acoustic agglomeration facilitates the precipitation of small air pollutant particles for easy removal. It was noted that while low frequency ultrasonic agglomeration is more cost and energy efficient, high frequency ultrasonic agglomeration is more retention efficient, particularly for very small particles in submicron range [261]. The presence of humidity could enhance the acoustic agglomeration of submicron particles much smaller than 1 μm in diesel exhausts [262].

2.1.7 Ultrasound in Environmental Analysis

The application of ultrasound in solid (food, sediment, soil) sample pretreatment prior to analysis for determination of contaminants has attracted remarkable interests recently. The number of studies on the topic has grown
significantly; within just over last five years, more than a hundred publications have been published and reviewed in four recent articles [263, 264, 265, 266]. Compared with other conventional methods, main advantage of the ultrasound assisted extraction is the dramatic reduction of the preparation time. For example, it can take only 30 min instead of 24 hours required by conventional shaking method [267]. Moreover, the use of ultrasound as assistance in solvent extraction for environmental analysis also brings many other benefits such as high recovery rate (which can be up to near 100% [268]), significant reduction of solvent consumption [269], high purity of the extracts obtained, no-cross contamination, simple setup and ease of operation [263, 264, 265, 266].

On the other hand, in recent decades, microwave heating has been used in analytical and organic laboratory practices as a very effective and non-polluting method as compared with conventional digestion which often takes at least several hours of prolonged heating and stirring in strong acid solution. Then, the simultaneous microwave and ultrasound irradiation has been recognized as a new technique for atmospheric pressure digestion of solid and liquid samples in chemical analysis. The coupling microwave-ultrasound gave significant improvement such as reduction of digestion time, reduction of the quantity of reagents and reduction of contamination. In addition, the process could be totally automatic and more safety. The combination of these two types of irradiation in physical processes like digestion, dissolution and extraction appears very promising [270].
2.2 Electrokinetic Remediation of Organic Contamination

Electrokinetics (EK) is defined as the formation of fluid flow and transportation of charged particles in soil-water systems (porous media) under the influence of an electric field. A low-intensity direct current applied through the soil can cause the contaminants drive from the soil to one of the electrodes where it would be collected or treated. Electrokinetic remediation is also known as electroremediation, electro-reclamation or electrochemical soil remediation [271], a soil-flushing technique enhanced by electric field, particularly effective in fine-grained soil of low permeability [272].

2.2.1 Principles of Electrokinetics

The principle of electrokinetic remediation - the transportation and removal of contaminants in soil solution, are based on three mechanisms: electroosmosis, electromigration and electrophoresis. Electromigration is the transport of ions and ionic species to the electrode of opposite charge, electroosmosis is the movement of soil moisture or groundwater from the anode to the cathode, and electrophoresis is the transport of charged particles or colloids under the influence of an electric field; contaminants bound to mobile particulate matter can be transported in this way [273].

Electromigration is faster than electroosmosis. But electromigration of metals through the soil requires pH control at the cathodes. Specialized electrodes should also be utilized to prevent the corrosion by acid generation at the anode and that requires higher maintenance and operation costs. However, using electroosmosis for organics removal reduces the need for specialized electrodes since most organic remediation is not affected by pH. While electromigration has been used for the removal of metal contaminants,
electroosmosis has often been used for the removal of organic contaminants (non-ionic).

Since soil particles often have a negative surface charge, when immersed in an electrolyte, the particles attract cations, creating a positively charged boundary layer (referred to as the charged double-layer) next to the surface of the soil particles. Application of a voltage difference across a section of soil causes movement of cations and associated water within the double-layer toward cathode. Then, the remaining interparticle pore fluid also moves in the same direction as the double-layer fluid due to viscous drag interactions [274]. Electroosmosis provides uniform pore water movement in most types of soil [275]. Electroosmotic flow rate is primarily a function of applied voltage. The entire soil mass between the electrodes is basically treated equally and the whole bulk fluid moves at the same rate as the cation double layer, thus electroosmosis is so effective in clayey soils. Electroosmosis can be utilized to remediate contaminated soils in situ by flushing out the pore fluid and contaminants (or to deliver nutrients, surfactants, etc.). The transport of larger charged molecules and particles (cationic or anionic surfactant micelles, microorganisms) under the influence of an electric field is called electrophoresis [274]. Contaminants bound to mobile particulate matter can be transported in this manner.

Besides these transport processes, many other reactions may occur in a DC field such as desiccation due to heat generation, gas generation due to electrolysis of water, decomposition or precipitation of salts and minerals, ion exchange, development of pH gradients, sorption processes and electrochemical transformations [276]. The electricity applied to the soil directly results in heating of the soil. The soil warming not only increases the mobilization of volatile organics but also increases the electroosmotic
permeability by lowering the viscosity of the pore water. Application of
direct electric current in water induces electrolysis. This electrolysis of water
is the dominant electron transfer reaction at electrodes during the
electrokinetic process [273].

\[
\begin{align*}
\text{Oxidation at anode:} & \quad 2\text{H}_2\text{O} - 4e^- \rightarrow 4\text{H}^+ + \text{O}_2 \uparrow \\
\text{Reduction at cathode:} & \quad 4\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- + 2\text{H}_2 \uparrow
\end{align*}
\]

Oxidation of water at the anode generates an acid front, accumulated with H\(^+\) ions, while reduction at the cathode produces a base front with excess OH\(^-\) ions. As a result, a pH gradient is always generated between anodes (usually with pH as low as 2) and cathodes (usually with pH up to 12), in the electrokinetic process.

Electrokinetic technology has been shown to be efficient in the removal of partially polar organic species, such as phenol and nonpolar ones such as polycyclic aromatic hydrocarbons (PAHs), atrazine, chlorinated solvent perchloroethylene, BTEX compounds (benzene, toluene, ethylene and xylene) [275, 277, 278, 279, 280, 281]. With nonpolar organic species, the applicability of electrokinetic remediation was effective by the assistance of different solubilizing agents.

**Factors affecting Electrokinetics**

*Soil types:* Bench-scale and pilot-scale tests indicated that the technology can be successful in clayey to fine sandy soils. However, contaminant transport rates and the efficiency of the process depend heavily on soil type and mineral composition [282].
Soil pH: Changes in soil pH can change the chemical states of contaminants as well as the magnitude and direction of electroosmotic flow, affecting the transport of contaminants in soil pore fluid. When the soil pH is lower than the point of zero charge (pzc, a zero zeta potential of soil particle surface), the direction of electroosmotic flow is reversed, from the cathode towards the anode [283, 284].

Degree of saturation: Depending on the target transport mechanism, the degree of saturation affects both electroosmosis and ionic migration. Soils of high water content and low ionic strength provide the most favorable conditions for transport of contaminants by electroosmotic and ionic migration [282].

Voltage and current levels: Electric current intensities used in most reported studies are in the order of a few A/m². High current levels generate more acid and increase the total ionic concentration that will decrease the overall electroosmotic flow. Selection of the most appropriate current density and voltage gradients depends on the soil electrochemical properties, especially electric conductivity. Soils with higher electric conductivities require more charge and higher currents than lower conductivity soils. A voltage gradient in the order of 1 V/cm can be used as an initial estimate. Increasing the current densities (or voltage gradients) will increase transport rates under ionic migration but will also increase energy expenditure and cost of the process. An optimum current density or voltage could be appropriately selected based on the soil properties, electrode spacing, and time requirements of the process [282].

Electrode materials and arrangement: Decontamination by electrokinetics is also influenced by the chosen electrode materials and arrangement [285].
Suitable electrode materials were often selected based on their performances in terms of current density, chemical stability and corrosion resistance. Moreover, the study on effects of electrode arrangement showed that electrodes in direct contact with the soil presented less electrical resistance and more decontamination than the electrodes separated from the soil by physical barriers [285].

**Electrokinetics impacts on soil health**

Application of electrokinetics alters both the physico-chemical characteristics of the soil and the exposed microbial community. While soil pH change by electrokinetics may reduce microbial number and diversity, the low direct electric current can increase biodegradation of hydrocarbons and stimulating soil enzyme activities, making electrokinetics and bioremediation combination possible [286, 287, 288]. However, sometimes, electrokinetics may increase negative effects of toxic contaminants or electrolytes on microbial community under specific pH change [288, 289]. Therefore, soil parameters, electric current, electrode, electrolyte and their interactions should be carefully considered for a healthy soil environment or a successful combination of electrokinetics and bioremediation.

**Main advantages and limitations of electrokinetic soil remediation** [1, 273, 278]

**Advantages:**

- Useful for site remediation under conditions which normally limit in situ approaches such as fine-grained sediments or low permeability soils.
• Versatile, can be used to enhance other treatment methods like bioremediation, chemical oxidation or soil vapor extraction.
• Less impact on existing landscaping, buildings or structures than ex situ technologies or soil washing.
• Not require heavy equipment, excavation, or installation of large plants, thus, reducing cost.
• Cost efficient compared with costs for other in situ and ex situ methods.

Limitations:

• Limited by solubility of contaminants in aqueous phase and desorption of contaminants from the soil matrix. The process is also not efficient when the target ion concentration is low and non-target ion concentration is high (not selective).
• Acidic conditions and electrolytic decay can corrode some anode materials. Inert electrodes, such as carbon, graphite, or platinum, must be used so that no residue will be introduced into the treated soil mass.
• When higher voltage is applied to the soil, the efficiency of the process decreases because of the increased temperature.
• Removal efficiency is significantly reduced if soil contains large rocks or gravel.

Electrokinetic technology has been applied successfully in the remediation of inorganic contaminant and has been shown to be highly efficient in the removal of partially polar organic species, such as acetic acid and phenol. However, because of their low solubilities and slow desorption rates, hydrophobic organic compounds are difficult to remove from subsurface
environments with traditional electrokinetic technology. Therefore, the remediation process of these compounds using the electrokinetic method has been combined with other treatment processes. Besides combination with other processes, electrokinetics also have been developed in different designs (such as vertical design, circulation of electrolytes) or with various operation modes (rotation of electrode matrix, non-uniform, periodic modes) to enhance its performance. Fig. 4 summarizes enhanced electrokinetic processes for organic contaminated soil remediation which will be briefly described in the following sections.
Figure 4. Enhanced electrokinetic processes for organic decontamination
2.2.2 Electro-Bio Remediation

Bioremediation has potential to restore contaminated soil but it is time consuming. The method can be accelerated by using electrokinetics. Electrokinetic bioremediation technology is developed to activate the growth of microorganisms that are capable of transforming organic contaminants in soil by promoting the transport of nutrients [278]. Electrokinetics can produce uniform transport and mixing of additives for bioremediation [290]. Injecting nitrate and ammonium to organic, tropical, clayey soil was feasible; however, the injection of phosphorous did not prove to be successful [291].

Disseminating bacteria by electroosmosis in three different soil types (garden soil, fine sand, and clay) was compared to those controls without electricity, showing clearly that electroosmosis stimulates bacterial spreading even in low-permeability soil such as clay, although the migration velocity was lower than in other soils tested [292]. The high clay content of the soil limited oxygen and nutrient supply to the microbial community because of slow diffusion and low hydraulic conductivity [293]. Thus, electrokinetic remediation is especially indicated for clayey soils, to increase the diffusion rate of nutrients and microorganisms. It was observed that the creosote degradation proceed ten folds faster in soil treated with an electric field than in the control cells without current or microbial activity [293].

Electrokinetics can enhance bioremediation in overcoming the limitation of cold climate areas, where biodegradation is often a slow process, because electricity increased the soil temperature to a level suitable for active microbial degradation [294]. It was found that high initial contaminant concentrations showed significantly higher relative degradation than low initial concentrations [294].
Electro-reclamation in the form of an Electrokinetic Fence can be applied as an in situ method to fence off and remediate polluted sites or groundwater plumes [295]. ElectroBioFence is a long and narrow zone that intensifies biodegradation due to increased temperature and availability of nutrients. Nutrients are often electrically charged compounds and thus can be dispersed through the soil electrokinetically. The organic pollutants are degraded by enhanced microbiological activity, either within or downstream of the zone. Electrokinetic biofences can be independent of the subsurface soil composition and applicable to relatively great depths (>10m) and under buildings without disturbance of the groundwater flow regime. Because it is an in situ treatment, there is no need to pump huge amount of groundwater. Godschalk and his company, Holland Milieutechniek (2005), have performed successfully an electrokinetic biofence remediation project for the site of a chemical laundry, polluted with volatile chlorinated hydrocarbons, at Wildervank, Netherlands. After running the ElectroBiofence for nearly 2 years, the contaminants were being dechlorinated and the chloride index was decreasing [296]. One interesting thing was that the power supplied for the biofence was from solar energy panels.

Electrokinetic bioremediation of soil mixed contaminated by both organic and heavy metal pollutants is often challenging because the toxicity of heavy metals can be harmful for microbial community. A new electrokinetic bioremediation was developed for mixed Pb and oil decontamination from polluted soil, with the addition of EDTA to enhance heavy metal removal and the addition of Tween 80 to enhance oil removal. This enhanced electrokinetic bioremediation resulted in greatly reduced Pb toxicity, leading to improved microbial degradation of oil. It was found that regular electrolyte refreshment was favorable for maintaining high electric current...
and under optimum operation condition, more than 80% removal of both Pb and total petroleum hydrocarbons was achieved [297].

2.2.3 Electrokinetics with Flushing Agent Enhancement

The contaminant transport during electrokinetic treatment of soil contaminated with nonpolar contaminants occurs primarily by electroosmosis. Therefore, the process is not effective unless the contaminants are soluble in pore fluid or are converted to soluble form. Hydrophobic compounds adsorb strongly to the soil and hence the electrokinetic treatment of soil contaminated with such compounds will be feasible only if the contaminants are desorbed from the soil and made soluble in the pore fluid. Thus, surfactants, cosolvents, chelants and complexing agents are often employed to increase desorption and solubilization. Since they may react differently with different contaminants, compatibility of flushing solutions and contaminants should be considered. In general, non-ionic surfactants are often chosen because of their higher solubilization capacity, lower cost and higher biodegradability as compared with cationic and anionic ones [298].

Many studies have investigated the applications of surfactants and cosolvents in electrokinetic remediation to enhance the mobility of low polarity or non-polar contaminants through low permeability soil [277, 299, 300, 301, 302, 303, 304, 305, 306]. Since electroosmosis is the main electrokinetic movement of low polarity or non-polar contaminants, optimization of this phenomenon is necessary for effective decontamination. It was noted that controlling pH at 7 in the anode chamber and increase electric charge could accelerate electroosmotic flow through soil, leading to increased
mobilization and removal of low polarity contaminants like PAHs [305, 306].

On the other hand, contrary to observation at the laboratory scale, the recent pilot scale research for surfactant (sodium dodecyl sulfate) enhanced electroremediation of natural soil contaminated with phenanthrene showed that gravity and evaporation fluxes were more relevant than electrokinetic fluxes, and the desorption of phenanthrene promoted by electric heating seemed to be a significant removal mechanism. Although the treatment time was as long as four months, the average removal rate achieved was only 25%. The pilot scale experiment indicated that decontamination of the soil was feasible but could require long operation time and high energy consumption [307].

Because of their non-toxicity, biodegradability and low affinity of sorption to a solid phase at a wide range of pH values, cyclodextrins are considered advantageous over regular surfactants. The hydrophobic cavity of the cyclodextrin serves as the binding site for the low polarity contaminant, and the hydrophilic shell with its charged group facilitates movement through the soil toward the electrode well under electrokinetic conditions, enabling this method for removal capability of both polar and low polarity contaminants [300]. Cyclodextrin-electrokinetic process was proven to be a cost effective and environmental friendly method for remediation of soil contaminated by low polarity organics, naphthalene and 2,4-dinitrotoluene, and petroleum hydrocarbons [300, 308]. Hydroxypropyl cyclodextrin (HPCD) was also used as a flushing solution during the electro-Fenton process for the removal of pentachlorophenol (PCP) from soil [309]. It was reported that HPCD increased the efficiency of pollutant degradation and this beneficial effect of HPCD on PCP degradation rate was explained by the formation of a ternary
pollutant-cyclodextrin-iron complex capable of directing the hydroxyl radicals towards reaction with the pollutant [309].

Four flushing agents, including two surfactants (5% Igepal CA-720 & 3% Tween 80), a cosolvent (20% n-Butylamine) and a cyclodextrin (10% HPCD), were used in a feasibility study to enhance electrokinetic remediation of manufactured gas plant soils contaminated by both PAHs and heavy metals [303]. It was found that all four flushing agents were capable to enhance PAHs removal, with Igepal CA-720 surfactant yielded the highest removal efficiency due to partial solubilization of PAHs. While maximum electroosmotic flow was observed in the cosolvent enhanced system, followed by the HPCD enhanced system and comparatively low flow observed in the surfactant-enhanced system; PAHs solubilization was more effective in the surfactant and HPCD enhanced systems than in the cosolvent system. Because of high soil pH due to high soil buffering capacity, heavy metals remained strongly adsorbed, precipitated and were not removed in all the tested systems [303].

Later on, similar attempts to use flushing agent enhanced electrokinetics for both PAHs and heavy metals mixed contamination remediation had been conducted in several studies [272, 310, 311, 312, 313, 314]. It was confirmed that solubilization, electroosmotic flow, and concentration of the flushing agents were the critical factors that contribute to the removal of PAHs [311]. Catholyte conditioning maintained the soil pH as acidic, leading to enhanced desorption of metals but making the soil positively charged, resulting in decreased and reverse electroosmotic flow which in turn inhibited metals removal through electromigration and PAHs removal through electroosmotic flow [272]. Surfactants and complexing agents were commonly used to increase desorption and solubility of organic (PAHs) and metal pollutants,
respectively [313], but the ecotoxicity of chelating agent such as EDTA should be considered [312]. The selection of processing fluid and pH control are the key variables for effective removal, hence, there must be a pre-evaluation of flushing agents and their compatibilities to the soil types and the pollutants [313]. Both the simultaneous addition of complexing agents and surfactants [313] and the sequential application of a chelating agent (such as citric acid), followed by a surfactant-enhanced electrokinetics [314] were shown to be effective in the mixed contamination remediations.

The surfactant aided electrokinetics coupled with carbon nanotube barriers was studied for the removal of 1,2-dichlorobenzene from spiked soil [315]. Because of its high specific surface area, high reaction ability and high electron transfer capacity, carbon nanotube barrier is expected to highly remove the soluble contaminants by adsorption. Although both methods helped in the soil remediation, results showed that the removal of 1,2 dichlorobenzene in the coupling system was mainly contributed by surface sorption on carbon nanotube barriers rather than by electrokinetic process [315].

Moreover, an innovative 2-stage process combining soil electrokinetic remediation and liquid electrochemical oxidation was developed for benzo(a)pyrene removal from spiked kaolin. In the first step, ethanol and Brij 35 were tested as flushing solutions. While no presence of the contaminant in either chamber was observed in the case of ethanol as flushing solution; 17% of initial benzo(a)pyrene was detected in the cathode chamber without pH control, and up to 76% of initial benzo(a)pyrene was detected in the cathode chamber when pH was set at 7.0 in the anode, in the case of Brij 35 as flushing solution. In the second step, mobilized benzo(a)pyrene in the liquid collected from the electrokinetic process was
further oxidized by electrochemical treatment, reaching 73% contaminant degradation after 16 h treatment [298].

2.2.4 Electro-Fenton (EK-Fenton) and other Oxidation-enhanced Electrokinetics

Fenton and other oxidation processes were successfully integrated with electrokinetics to treat low permeability soil contaminated with organics [316, 317, 318, 319]. Among various advanced oxidation processes, the Fenton process has received much interest in the destruction of biorefractory organic pollutants in various media because of its strong oxidizing capability [320, 321]. The EK-Fenton phenomenon is characterized by a complex process, which includes the effects of electroosmosis, electromigration, electrolysis reactions and the mineral catalyzed Fenton-like reaction. Fenton’s reagent can either be generated in the system or applied externally [322, 323, 324].

The EK and Fenton processes were successfully combined for in situ treatment of various organic compounds (e.g. TCE, phenol, 4-chlorophenol, and diesel fuel) in different soil types, catalyst types and electrode materials. Biodegradation was even further incorporated in the EK-Fenton process for treating pentachlorophenol (PCP) contaminated soils. It was found that 100% PCP destruction could be obtained within a reasonable treatment time by combining these three technologies. Results of cost analysis have shown that the EK-Fenton process is very low in operating cost [316].

The study on the applicability of the EK-Fenton process for the remediation of low permeability soil contaminated with phenanthrene reported that the phenanthrene degradation yield was proportional to the transfer rate of the
acid front and \( \text{H}_2\text{O}_2 \) stability. Therefore, to effectively treat sorbed contaminant on soils during the EK-Fenton process, an injection of acid is necessary in such an extent that it does not decrease the electroosmotic flow rate [325].

The relationship between the chlorine content of contaminant molecule and degradation rate was studied using various chlorophenols including PCP, 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and the degradation sequence was obtained as 2,4-DCP>2,4,6-TCP>PCP>4-CP [326].

Results from the study of EK-Fenton processes for the removal of hexachlorobenzene (HCB) from kaolin under different conditions indicated that EK-Fenton was effective in HCB remediation from kaolin; about 64% HCB removal achieved in the test using beta cyclodextrin as flushing agent [327, 328], and 76% HCB removal achieved in the test using high concentration of hydrogen peroxide (30% \( \text{H}_2\text{O}_2 \)) with inherent iron in the kaolin and without cyclodextrin [329]. It was observed that in the absence of cyclodextrin, the oxidation was faster but there was an accumulation of contaminants in the anode part of the system [329]. Moreover, it was also noted that the positions of electrodes and the way Fenton’s reagent was added into the system had a significant influence on the remediation efficiency [328, 330].

EK-Fenton remediation of dredge marine sediment contaminated with petroleum hydrocarbons (TPH, total petroleum hydrocarbons) and metals were carried out, testing EDTA and Tween 80 as flushing solutions. After 30 days of treatment, the EK-Fenton-EDTA showed the better performance with the highest removal of TPH and metals [331].
A new oxidation-enhanced EK was developed, applying different oxidants (H₂O₂, NaClO, KMnO₄ and Na₂S₂O₈) and catholyte pH control (3.5 and 10) for the remediation of soil contaminated by both heavy metal copper and organic compound pyrene. The results showed that low pH favoured the migration of copper and KMnO₄ was the best among the tested oxidants for pyrene degradation; but unfortunately, KMnO₄ prevented the migration of copper by forming copper oxide. It was found that the use of Na₂S₂O₈ and catholyte pH at 3.5 were the optimum operation conditions for remediation of the mixed contaminated soil by copper and pyrene, with removal rates achieved of 50% and 94%, respectively [332].

Recently, combination of the surfactant Igepal CA-720 and the oxidant persulfate in electrokinetic remediation of polychlorinated biphenyl (PCBs) contaminated soil was proven to be effective [333]. It was observed that PCBs was partially solubilized and transported towards anode by Igepal CA-720 while persulfate moved from cathode to anode by electromigration; and the optimum dosage of Igepal CA-720 and persulfate were 2% and 20%, respectively for PCBs extraction and oxidation from the contaminated soil. It was noted that the addition of zero-valent iron as activator for persulfate turned out to be not a good choice as the zero-valent iron consumed most of the persulfate and limited its transport into the cell [333].

2.2.5 Electrokinetics and Permeable Reactive Barriers

In order to inhibit the extension of contaminants in the groundwater, “sorptive barriers” or “permeable reactive barriers” (PRB) may be installed across the flow path, capturing the contaminated plume and destroying the contaminants without soil or water excavation [334]. This innovative technology has been tested to treat both inorganic and organic pollutants.
**Zero-valent Metal PRB**

Zero-valent metals can be used in reactive barriers as reducing agents for dechlorination of many chlorinated hydrocarbons. Combination of electrokinetics (EK) and zero-valent metal (ZVM) for the remediation of perchloroethylene (PCE) contaminated soils showed that the best PCE removal efficiency can reach 99% after 10-day treatment, and the zero-valent zinc processes gave better PCE degradation than zero-valent iron. The EK-ZVM technique can maintain the neutral pH status with the appropriate operational parameters of sodium carbonate 0.01 M as anolyte, 1.0 V/cm voltage gradient and ZVM installation close to the anode [335].

To investigate the potential use of atomizing slag as an inexpensive PRB material coupled with the EK processes in order to remediate contaminated ground of low permeability soils, the lab-scale EK and EK with PRB experiments were conducted. The results showed that the trichloroethylene (TCE) concentrations of effluent solution through the PRB material were much lower than those of EK remediation without atomizing slag, due to the reaction between TCE and the reactive material that caused dechlorination of TCE. The removal efficiencies for TCE and Cd both achieved approximately 90%. Thus the coupled technology of EK with a PRB system could be an effective, in situ remediation, and applying atomizing slag as the PRB reactive material seems very promising for the dechlorination of TCE [336].

As pentachlorophenol (PCP) transports back-and-forth and accumulates between anode and cathode, it is difficult to remove PCP by EK alone. Therefore, a permeable reactive barrier filled with reactive Pd/Fe was installed between anode and cathode to improve the efficiency of EK remediation for PCP. The mechanism of PCP removal was proposed,
involving the transport of PCP by EK into the PRB compartment, the dechlorination of PCP to phenol by Pd/Fe in the PRB and the subsequent moving out of phenol by electroosmosis. When positioning PRB right at the middle of the reactor and controlling PRB pH, the EK-PRB system was proven to be effective for PCP decontamination from soil [337].

The combination of Triton X-100 surfactant-enhanced electrokinetics and microscale Pd/Fe PRB proved to be efficient and promising for the remediation of hexachlorobenzene (HCB) contaminated soil. The results suggested that Triton X-100 was an effective enhancement agent for HCB removal, both in the electroosmotic movement and in the Pd/Fe degradation. The combined EK-PRB greatly enhanced the removal of HCB compared with the EK alone (60% versus 13%), indicating that in general, the degradation by the reactive Pd/Fe particles in the PRB rather than the movement by electroosmosis, played a predominant role in HCB removal [338].

**Lasagna™ Process**

Lasagna™ is a novel integrated electrokinetic technology that creates permeable zones in close proximity sectioned through the contaminated soil region and turn them into “treatment zones” by introducing appropriate materials (sorbents, catalytic agents, microbes, oxidants, buffers, etc.). Electroosmosis is utilized to transport contaminants from the soil into “treatment zones”, where contaminants are removed from the pore water by sorption, immobilization or degradation [339]. Thus Lasagna™ technology reduces distance the mobilized contaminant would have to travel before being removed/degraded and at the same time reduces the time required to remediate a site [274].
Lasagna™ remediates soils and soil pore water contaminated with soluble organic compounds and is especially suited to sites with low permeability soils where electroosmosis can move water faster and more uniformly than hydraulic methods, with very low power consumption. However, Lasagna™ does not work well in sandy soils where there is not enough hydraulic resistance to create significant electroosmotic gradients. Highly electrically conductive soils such as coastal or saline soils are also not practical because of the high current draw and excessive soil heating. Both vertical and horizontal configurations have been conceptualized, but fieldwork to date is more advanced for the vertical configuration [340]. Trichloroethylene (TCE) contaminated soil was treated effectively using the Lasagna™ process. The levels of contamination before treatment were as high as 1500 mg/kg and post treatment levels were around 1 mg/kg [340]. The removal of the model organic compound p-nitrophenol from the soil was also very efficient, 98% in the pilot unit [339].

While activated carbon is the most common adsorbent used in Lasagna™ processes, a low-cost, easily available bamboo charcoal was employed, aiming to enhance the in situ electroremediation of 2,4-dichlorophenol (DCP) and Cd from sandy loam at different polarity reversal intervals of 12 h and 24 h. It was found that higher removal efficiency and lower energy consumption was achieved with the polarity reversal interval of 24 h, though in both operation modes, the periodic polarity reversal helped keep soil moisture at a suitable level (favorable for electroremediation of contaminated soil with high permeability like sandy loam) and keep soil pH stable (around 7.2-7.4, close to the initial pH). On the other hand, bamboo charcoal was proven to be an excellent adsorbent for both 2,4-DCP and Cd, making it a potential substitute for activated carbon. Moreover, its high water holding
capacity and high cation exchange capacity may also help to maintain soil moisture content and pH [341].

**Electrochemical Redox Barriers**

One potential application of electrokinetic processes is the development of reactive electrochemical barriers for cleanup of mobile contamination plumes in groundwater [290]. Unlike the previous case of permeable reactive barriers, the system does not require any reactive materials. The mechanism of this process is based on electrochemical redox reactions originated by water electrolysis under DC currents. The water electrolysis causes reduced environment and generation of hydrogen at the cathode and oxidized environment and generation of oxygen at the anode. The system has enhanced the reductive dehalogenation of chlorinated solvents. Significant advantages of electrochemical redox barriers over other types of barriers are: continuous source of electrons, controllable rate of redox reactions, providing both reducing and oxidizing (or sequential) conditions, no need for additional reactive chemicals, electrode material is not consumed and may be reused and flexibility in reversing the polarity of the electrodes [290].

**2.2.6 Induced Polarization Electro-Chemical-Geo-Oxidation**

Electro-Petroleum, Inc. in Wayne, PA, USA and Electrochemical Processes, llc. in Stuttgart, Germany have developed the ElectroChemical Remediation Technologies (ECRTs) as an innovative, cost-effective, and rapid method for treating organic contamination in soil [342, 343]. ECRTs can destroy organics in situ in the vadose zone and ground water aquifers by using the ElectroChemicalGeoOxidation (ECGO) process, which is considered the next generation in electrokinetics.
ECGO is a geophysical process based on the phenomena of Induced Polarization (IP). ECGO utilizes a low voltage, low amperage AC/DC current passed between one or more electrodes pairs driven into the ground (soil, sediment, sludge, or groundwater) to rapidly address a wide range of both organic and inorganic compounds. When a direct electric current (DC) is imposed in the earth with a superimposed alternating current (AC) via in situ electrodes, the soil particles become polarized and develop electrical properties similar to a capacitor, discharging electricity. The energy given off induces redox reactions, which decompose organic contaminants. Empirical evidence indicates that reaction rates are reversibly proportional to grain size [275]. The soil particle surface area and the soil to water ratio are key parameters in determining the effectiveness of the technology.

ECGO is also a patented in situ technology available from ManTech International Corporation that remediates soil and water contaminated with organic and inorganic compounds [278]. The process utilizes induced electric currents to create oxidation-reduction reactions which lead to the mineralization of organic constituents (or the immobilization of inorganic constituents) present in a volume of soil and groundwater between the electrode locations. ECGO relies on the induced polarization of naturally occurring conducting surfaces in soil and rock particles. These conducting surfaces are composed of elements such as iron, magnesium, titanium and elemental carbon. Heavy metal impurities that are also naturally-occurring further contribute to the process by acting as catalysts for the redox reactions. Depending on the site conditions, accessibility, and targeted constituents, the ECGO process may take 60 to 120 days [278].
2.2.7 Circulation-enhanced Electrokinetics (CEEK)

One major disadvantage of EK is the soil acidification during EK operation, which may dramatically destroy the soil constituents, affecting the soil zeta-potential that causes decreasing electroosmotic flow. Therefore, the EK process with circulation system was designed to neutralize the pH of working solution and soil for avoiding the above problems [344, 345, 346]. The electrodes installed in the reservoir without attachment on soils can decrease the pH deviation of the soil matrix [346]. A siphon pipe and a pump were used to automatically neutralize the acid produced at the anode with the base produced at the cathode during EK operation. A hexane extractor was used to trap the organic compounds released from the contaminated soils [344]. Experimental results showed that this CEEK produced roughly stable pH (around 6) and conductivity of working solution, current density, and electroosmotic flow rate. All selected chlorinated organic compounds were effectively removed from the soil with removal efficiency ranging from 85 to 98% after 2 weeks [344].

2.2.8 Upward Electrokinetic Soil Remediation (UESR)

An upward electrokinetic soil remediation (UESR) process is designed with vertical non-uniform electric field generated between an anode embedded in soil and a cathode placed on the soil surface. Unlike conventional electrokinetic treatment that uses boreholes or trenches for horizontal migration of contaminants, the UESR process uses vertical non-uniform electric field causing upward transportation of contaminants to the top surface of the treated soil. The main advantages of the UESR technology are minimization of site disturbance as well as reduction of treatment costs because a clean-up of contaminated site takes place on the soil surface [347].
Experiments demonstrated the feasibility of simultaneous removal of heavy metals (Cu, Pb) and organics (p-xylene, phenanthrene) from kaolin with this UESR process with removal efficiencies of phenanthrene, p-xylene, Cu and Pb were 67%, 93%, 62% and 35%, respectively after 6 days of treatment [347].

2.2.9 Periodic Electric Potential Application

It was postulated that applying the electric potential in a periodic mode, or disconnecting the voltage periodically, would increase micellar solubilization and enhance electrokinetic remedial efficiency. Then, experiments were conducted to assess the effects of employing a periodic voltage application during an electrokinetically enhanced in situ flushing process for PAHs contaminated clay soils. Four different bench-scale tests were conducted, using the non-ionic surfactant Igepal CA 720 as flushing solution, with the voltage gradient applied continuously or periodically (5 day on and 2 day off), under relatively low voltage (1.0 V/cm) and high anode buffering (0.1 M NaOH) as well as high voltage (2.0 V/cm) and low anode buffering (0.01 M NaOH) conditions [348]. The results of these experiments confirmed the positive effect of the periodic voltage application with considerable high contaminant removal which was attributed to a pulsed electroosmotic flow, a pulsed surfactant molecular movement produced that generated a flushing action increasing solubilization and physically mobilizing the PAHs contaminants. Moreover, compared to continuous mode, the periodic mode tests sustained a relatively high average current value for a longer duration [348].
2.2.10 Non-uniform Electrokinetics and Rotational Mode

Non-uniform electrokinetics system with an electrode matrix, which operated with periodic polarity-reversal or rotational operation mode to accelerate bioremediation by mixing organic pollutants and bacteria in soil, was studied with a phenol-contaminated sandy loam. Compared with the unidirectional and bidirectional operation, the results showed that the rotational operation could effectively stimulate the biodegradation of phenol in the soil if adopting appropriate time intervals of polarity-reversal and electrode matrixes. With a reversal interval of 3 h and a square-shaped electrode matrix, a maximum phenol removal of 58% was achieved in 10 days and the bioremediation rate was increased about five times as compared to that with no electric field applied [349].

In another study, the electrokinetic remediation with sandy loam as the model soil and 2,4-dichlorophenol (2,4-DCP) as the model organic pollutant was investigated at two non-uniform operation modes (bidirectional and rotational) in a hexagonal matrix. Periodically, the electric field reverses its direction at bidirectional mode and revolves a given angle at rotational mode. The results showed that the non-uniform electric field could effectively stimulate the desorption and movement of 2,4-DCP towards anode. At the bidirectional mode, an average 2,4-DCP removal of 73.4% was achieved in 15 days, and the in situ biodegradation of 2,4-DCP was increased by about three times as compared with that uncoupled electric field, whereas 34.8% of 2,4-DCP was removed on average in the same period at the rotational mode. While the bidirectional mode was more effective and cost efficient, the rotational mode provided better remediation’s uniformity in soil [350].
2.2.11 Ultrasound-assisted Electrokinetic Remediation

While electrokinetic remediation was applied to remove mainly heavy metals and ultrasound was applied to decontaminate mainly organic substances, these two techniques was combined for the removal of heavy metal Pb and phenanthrene in natural clay, confirming the synergistic effects on the pollutants migration as well as decontamination [31]. The decontamination efficiency in the combined electrokinetic and 30 kHz, 200 W ultrasonic system (91% for Pb and 90% for phenanthrene) was higher than in the simple electrokinetic remediation alone (88% for Pb and 85% for phenanthrene). It was observed that ultrasound caused decreasing fluid viscosity, increasing flow rate, porosity, and permeability as well as mobilizing sorbed contaminants [31].

Based on the literature review, it was found that very few studies (probably only one [31], as far as we know) that combined both electrokinetics and ultrasound in the remediation of POPs contaminated clayey soils. Since the integration of electrokinetics and ultrasound may bring positive synergistic effects, more exploration is needed in this research field.
3. OBJECTIVES

Aim of the study was to investigate the effectiveness of ultrasonic treatment, individually and as an enhancement for electrokinetic treatment in the remediation of persistent organic contamination from low permeability clayey soils. The specific objectives of this study were:

- To investigate the effects of ultrasonic treatment with various experimental conditions on the decontamination of POPs from different types of clayey matrices (paper I, II).
- To investigate the coupling effects of electrokinetic and ultrasonic remediation on the decontamination of POPs from kaolin, in different experimental set-ups (paper III, IV, V).
- To investigate the comparative enhancements of electrokinetic remediation using 2-hydroxylpropyl-β-cyclodextrin surfactant and ultrasound for the decontamination of POPs from kaolin (paper VI).
4. MATERIALS AND METHODS

4.1 Materials

4.1.1 Model POPs and Clay

The representative persistent organic pollutants chosen in the study were hexachlorobenzene (HCB), a typical polychlorinated hydrocarbon and three polycyclic aromatic hydrocarbons (PAHs), phenanthrene (PHE), fluoranthene (FLU) and chrysene (CHR). HCB is considered as one of the twelve worst offenders (known as the “dirty dozen”) in the Stockholm Convention on POPs, and the three PAHs are listed in the US EPA’s 16 priority pollutant PAHs [2, 351, 352]. Hexachlorobenzene and fluoranthene were purchased from Sigma-Aldrich, phenanthrene and hexane solvent from Merck and chrysene from Acros Organics. All chemicals were of analytical grade and used without further purification.

Table 2. Properties of the model POPs [353, 354, 352, 355]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Hexachlorobenzene (HCB)</th>
<th>Phenanthrene (PHE)</th>
<th>Fluoranthene (FLU)</th>
<th>Chrysene (CHR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₆Cl₆</td>
<td>C₁₄H₁₀</td>
<td>C₁₆H₁₀</td>
<td>C₁₆H₁₂</td>
</tr>
<tr>
<td>Chemical structure</td>
<td><img src="image" alt="Hexachlorobenzene" /></td>
<td><img src="image" alt="Phenanthrene" /></td>
<td><img src="image" alt="Fluoranthene" /></td>
<td><img src="image" alt="Chrysene" /></td>
</tr>
<tr>
<td>Molecular mass (g/mol)</td>
<td>284.78</td>
<td>178.23</td>
<td>202.26</td>
<td>228.28</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.04</td>
<td>1.18</td>
<td>1.25</td>
<td>1.27</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>231</td>
<td>101</td>
<td>110.8</td>
<td>254</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>322</td>
<td>332</td>
<td>375</td>
<td>448</td>
</tr>
<tr>
<td>Water solubility at 25°C (mg/L)</td>
<td>(insoluble)</td>
<td>(insoluble)</td>
<td>(insoluble)</td>
<td>(insoluble)</td>
</tr>
</tbody>
</table>
Model low permeability clayey soil used in the experiments was white kaolin purchased from VWR International. Kaolin was often used as the model clay due to its high content of clay and negligible content of organic matter [356]. Main characteristics of the kaolin were measured and summarized in Table 3. For pH and electric conductivity measurement, 10 g kaolin was mixed with 20 ml distilled water, using the pH meter (pH 730 inoLab, WTW series) and the portable EC meter (water proof EC Testr low, Eutech Instruments Pte, Ltd.), respectively. The dry bulk density of kaolin was measured by weighing the given volume (100 cm³) of kaolin. Cation exchange capacity was estimated by determination of exchangeable cations (K⁺, Ca²⁺, Mg²⁺). Organic content was measured by Loss-on-Ignition method. Particle size distribution was measured by hydrometer method.

<table>
<thead>
<tr>
<th>Table 3. Main characteristics of kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Dry bulk density (g cm⁻³)</td>
</tr>
<tr>
<td>Moisture (%)</td>
</tr>
<tr>
<td>Electrical conductivity (μS cm⁻¹)</td>
</tr>
<tr>
<td>Cation exchange capacity (cmol kg⁻¹)</td>
</tr>
<tr>
<td>Organic content (%)</td>
</tr>
<tr>
<td>Particle size distribution:</td>
</tr>
<tr>
<td>% sand (&gt; 0.05 mm)</td>
</tr>
<tr>
<td>% silt (0.05-0.002 mm)</td>
</tr>
<tr>
<td>% clay (&lt; 0.002 mm)</td>
</tr>
</tbody>
</table>

4.1.2 Equipment

The ultrasonic processors used in these experiments were the UP100H and UP200H from Hielscher – Ultrasound Technology, with operating frequency
of 30 kHz and 24 kHz, maximum power of 100 W and 200 W, respectively.
The power of these ultrasonic processors could be controlled in the amplitude range of 20-100%.

The designed plexiglass cylinders used in the study consisted of a central chamber (ϕ 10 cm x 20 cm) and two electrolyte chambers (ϕ 10 cm x 4 cm) for anode and cathode parts (Fig 5a). In the middle of the central chamber, there was a rectangular hole of approximately 14 cm x 7 cm for the acoustic horn position and for putting the kaolin inside. The electrolyte chamber had two small holes for electrode position, gas ventilation and pH checking by pipette. Kaolin in central chamber was separated from electrolyte chambers by polypropylene filtercloths (Sigma-Aldrich).

![Diagram of ultrasonic processor and electrolyte chambers](image)

**Figure 5.** (a) Plexiglass cylinder and (b) plastic pan [V]

The rectangular plastic pans used in the study were of 20 cm x 14 cm x 8 cm dimensions (Fig. 5b). Titianium (III, IV, VI), graphite and iron electrodes (V) of 1 cm diameter and 10 cm long were connected to the direct current power supply.
4.2 Methodology

4.2.1 Kaolin preparation

Kaolin was artificially contaminated with the POPs of target concentrations. Because of the low solubility of POPs in water, hexane was used as solvent to dissolve completely the POPs required to yield the target concentrations [357]. Kaolin was soaked with these solutions at the ratio of approximately 500 ml solution per 1 kg kaolin. Then, the mixtures were stirred well to make the sample homogenous. The mixtures were kept in fumehood nearly a week for solvents to evaporate entirely. Samples were taken to determine the actual initial concentrations of POPs in kaolin, because some portion of contaminants may be lost along the process. Then, kaolin and water were mixed at appropriate ratios by glass rod to get homogenous slurries.

4.2.2 Experiments

The slurries were then treated by ultrasonication alone (US), electrokinetics alone (EK) or combined electrokinetics and ultrasound (EK+US). The experimental conditions are summarized in Table 4. More details on different experimental conditions in different tests were described in the Appendix. The experimental concept of the study was resumed in Fig. 6.
Experiments

US Tests
- Different experimental conditions in different types of clays [I,II]

EK+US Tests
- Electrodes separated in different compartments in plexiglass cylinders [III, V]
- Electrodes put directly into the slurries in plastic pans [IV, V]

Comparative tests EK+SF vs. EK+US [VI]

Figure 6. Experimental concept diagram
<table>
<thead>
<tr>
<th>Test</th>
<th>Initial POPs concentration (mg/kg)</th>
<th>kg kaolin per test</th>
<th>Water: Kaolin ratio</th>
<th>US Frequency (kHz)</th>
<th>US Power (W)</th>
<th>US Mode</th>
<th>EK Voltage (V)</th>
<th>EK Analyte</th>
<th>EK Anode</th>
<th>EK Apparatus</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>US [I]</td>
<td>HCB, PHE, FLU 100 (HCB, PHE)</td>
<td>0.1</td>
<td>1:4:1</td>
<td>24, 30</td>
<td>20-200</td>
<td>Pulse mode 1, continuous</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1-6 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>1:2:1</td>
<td>24</td>
<td>40, 100</td>
<td>Pulse mode 0.5 and 1, intermittent</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15-46 h</td>
</tr>
<tr>
<td>US [II]</td>
<td>HCB, PHE</td>
<td>0.1</td>
<td>1:3:1</td>
<td>30</td>
<td>20-140</td>
<td>Pulse mode 1, continuous</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1-6 h</td>
</tr>
<tr>
<td>EK [III]</td>
<td>HCB, PHE, FLU 100 (HCB, PHE)</td>
<td>0.65</td>
<td>1 1.5:3:1</td>
<td>1.1</td>
<td>-</td>
<td>-</td>
<td>30 NaOH 0.01 M, Na₂CO₃ 0.01 M</td>
<td>Titanium</td>
<td>Plexiglass cylinders</td>
<td>10 15 days</td>
<td></td>
</tr>
<tr>
<td>EK-US [III]</td>
<td>HCB, PHE, FLU 100 (HCB, PHE)</td>
<td>0.65</td>
<td>1 1.5:3:1</td>
<td>1.1</td>
<td>24 30</td>
<td>100 Pulse mode 0.8 and 1, continuous</td>
<td>30 NaOH 0.01 M, Na₂CO₃ 0.01 M</td>
<td>Titanium</td>
<td>Plexiglass cylinders</td>
<td>10 15 days</td>
<td></td>
</tr>
<tr>
<td>US [IV]</td>
<td>HCB, PHE, FLU</td>
<td>0.5</td>
<td>1:2:1</td>
<td>24</td>
<td>100</td>
<td>1 h per day Pulse mode 1, continuous</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15 days</td>
</tr>
<tr>
<td>EK [IV]</td>
<td>HCB, PHE, FLU</td>
<td>0.5</td>
<td>1:2:1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30 Water</td>
<td>Titanium</td>
<td>Plastic pan</td>
<td>-</td>
<td>15 days</td>
</tr>
<tr>
<td>EK-US [IV]</td>
<td>HCB, PHE, FLU</td>
<td>0.5</td>
<td>1:2:1</td>
<td>24</td>
<td>100</td>
<td>1 h per day Pulse mode 1, continuous</td>
<td>30 Water</td>
<td>Titanium</td>
<td>Plastic pan</td>
<td>-</td>
<td>15 days</td>
</tr>
<tr>
<td>US [V]</td>
<td>C, S, 75, 100 (CHR)</td>
<td>0.5</td>
<td>2:1</td>
<td>30</td>
<td>100</td>
<td>Pulse mode 1, continuous</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>24 h</td>
</tr>
<tr>
<td>EK [V]</td>
<td>CHR</td>
<td>0.5</td>
<td>2:1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30 Water</td>
<td>Graphite, Iron</td>
<td>Plexiglass cylinders, plastic pan</td>
<td>-</td>
<td>10 days</td>
</tr>
<tr>
<td>EK-US [V]</td>
<td>CHR</td>
<td>0.5</td>
<td>2:1</td>
<td>30</td>
<td>100</td>
<td>5 h on the first days and 1 h per day for the rest days, Pulse mode 1, continuous</td>
<td>30 Water</td>
<td>Graphite, Iron</td>
<td>Plexiglass cylinders, plastic pan</td>
<td>-</td>
<td>10 days</td>
</tr>
<tr>
<td>EK+SF [VI]</td>
<td>HCB, PHE</td>
<td>0.5</td>
<td>1:1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30 0.5% HPCD</td>
<td>Titanium</td>
<td>Plastic pan</td>
<td>-</td>
<td>14 days</td>
</tr>
<tr>
<td>EK-US [VII]</td>
<td>HCB, PHE</td>
<td>0.5</td>
<td>1:1</td>
<td>30</td>
<td>100</td>
<td>2 h on the first day and 1 h per day for the rest days</td>
<td>30 Water</td>
<td>Titanium</td>
<td>Plastic pan</td>
<td>-</td>
<td>14 days</td>
</tr>
</tbody>
</table>
In the first part of the study, the potential of ultrasound in POPs contaminated soil remediation was investigated solely [I, II]. The experiments were carried out in three different types of clayey soils (synthetic clay, natural farm clay and kaolin) with various experimental conditions (water ratio, duration time, power input).

Figure 7. Sketch of the experimental set-up: US, EK and EK+US tests [IV]

In the second part of the study, comparative experiments were conducted with US alone, EK alone and EK+US tests, to examine the coupling effects of combined ultrasound and electrokinetic remediation (Fig. 7). The experiments were carried out in the designed plexiglass cylinders [III, V] or in the plastic open pan [IV, V]. Iron anodes were also used to test the possible similar effects of Fenton’s reagent [V]. The comparable uses of HPCD surfactant (SF) and ultrasound as assistances for the electrokinetic remediation were also examined [VI].
4.2.3 Extraction and Analysis

After experiments, samples were measured for pH and were dried in oven at 80 °C overnight. The dried samples were then pulverized for analysis. Samples were analyzed in duplicates for quality assurance. One gram of sample was mixed with 5 ml hexane in glass tube and was put into ultrasonication bath for 30 minutes to get the organic compounds extracted into hexane solvent. The glass tubes were centrifuged at 5000 rpm for 10 minutes [356]. The supernatants were then taken into 2 ml glass vials for GC-MS (Agilent 5975) analysis to determine the residual concentrations [I-VI].

5. RESULTS AND DISCUSSION

5.1 Ultrasonic treatment [I, II]

Sonolysis of organic compounds in slurries occurs through complex mechanisms involving thermal decomposition and hydroxyl radical oxidation. In ultrasonic treatment tests, various experimental conditions and aspects were examined and observed. Relationships among key relevant factors affecting the ultrasonication experiments for POPs contaminated soils remediation were summarized in Fig.8 and were explained more in the following sections.
Figure 8. Summary of the relationships among factors affecting ultrasonic remediation of POPs contaminated soils

5.1.1 Effect of Water Content

Sonolysis 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 [33]. Therefore, amount of water is an important factor, especially with clayey soils, which have high water absorption capacity, and thus need a certain high water amount to become slurry for desorption and oxidation.

In general, the results showed that the higher the water ratio, the higher the remediation efficiency, particularly in the cases of natural farm clay and synthetic clay, which gave the best performance at the highest water:soil ratio tested (3:1). Although theoretically, it is beneficial to have high water ratio (more hydroxyl radicals can be produced), the excessive water content can impair practical application of the process in the field-scale. Moreover, in the case of kaolin, there was no significant difference in the
decontamination efficiencies with the water:soil ratios of 2-4:1. Therefore, the water:soil ratios chosen for later experiments were in the range of 1-2:1.

5.1.2 Effect of Ultrasonic Power

The effects of various power inputs applied during ultrasonication on the reduction of POPs concentration were observed. The higher power applied did not always result in the higher removal rate. In the case of kaolin and synthetic clay, the differences among the results of various power tests were not as significant as in the case of natural farm clay. The optimal power level may depend on the types of soils, the amount of soils and other factors such as ultrasonic frequency. Generally in this study, the remediation efficiency reached the highest at 100 W and then decreased at 140 W. This could be attributed to the effect of ultrasonic cavitation, which took the power away and thus caused reduction in the effective sonication power on the soils [242, 358].

5.1.3 Duration Time and the Heating Effect

Since ultrasonication induces high concentration of energy, one of its physical effects is heating, i.e. the increasing temperature of the bulk solution [49]. The variation of soil media’s temperature during ultrasonication showed that temperatures of the bulk slurries increased up to a certain value in the first hour and then remained around that value (about 60°C) for the rests of the duration time. The increase in temperature also depended on the types of clayey soils, due to different compositions. When duration time was long enough, water started to evaporate; slurries got dried and turned to solid phase. Therefore, ultrasonic treatment should not be carried out continuously.
over a very long time. Moreover, considering energy cost, it is important to choose an optimal operation time.

To overcome the limitations of continuous ultrasonication for long treatment process, intermittent ultrasonication was suggested. In contrast to continuous operation, intermittent operation takes some hours off and on alternatively during ultrasonication operation, for example, 1-4 hours of ultrasonication per day for several days. Intermittent operation can either be in full pulse mode (pulse mode of 1 or continuously) or in other pulse mode (e.g. pulse mode of 0.8 means 0.8 s on and 0.2 s off).

pH of all the soils tested remained stable during the experiments. This confirmed the fact that there was no formation of ions H⁺ or OH⁻ during ultrasonication. It can be concluded that the soil’s pH is not affected by ultrasonication.

5.1.4 POPs Removal

It was found that the POPs degradation rates depended very much on the types of the contaminants. In all of the tests, HCB was the most difficult to treat with the highest residual concentrations remained. This can be explained by the fact that HCB has a very stable chemical structure. Among the POPs, PHE had the highest removal efficiencies maybe because PHE is more water soluble than HCB and FLU.

In general, the concentrations of the model pollutants reduced gradually with time. However, with high initial POPs concentration (500 mg/kg), there were no significant differences between the residual concentrations after 1 hour and 6 hours. It was observed that at constant water content, ultrasonic
frequency and power, the remediation decreased with increased initial POPs concentrations.

On the other hand, in the case of low initial POPs concentration (100 mg/kg), with intermittent operation, better remediation rates could be achieved in longer time of ultrasonication. In the case of low initial PHE concentration and with favorable experimental condition, complete removal of PHE was obtained after 15 hours of intermittent ultrasonication.

**5.2 Electrokinetic and ultrasonic treatment [III, IV, V, VI]**

Various comparative experimental set-ups of ultrasonic test alone, electrokinetic test alone, surfactant-assisted electrokinetic test and ultrasound-assisted electrokinetic test were examined for the remediation of kaolin contaminated with representative POPs. Table 5 provides an overview of the key comparative findings from all the tests and more explanation were described in the following sections.

<table>
<thead>
<tr>
<th>Aspects</th>
<th>Key comparative findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current progress</td>
<td>EK+US &gt; EK</td>
</tr>
<tr>
<td>Electroosmotic flow</td>
<td>EK+US &gt; EK (in tests with plexiglass cylinders)</td>
</tr>
<tr>
<td>pH value</td>
<td>US does not affect pH of soils</td>
</tr>
<tr>
<td></td>
<td>pH patterns along kaolin profile quite similar</td>
</tr>
<tr>
<td></td>
<td>among EK and EK+US</td>
</tr>
<tr>
<td>POPs removal</td>
<td>EK+US &gt; EK &gt; US</td>
</tr>
<tr>
<td></td>
<td>For average PHE removal: EK+US &gt; EK+SF</td>
</tr>
<tr>
<td></td>
<td>For average HCB removal: EK+SF &gt; EK+US</td>
</tr>
</tbody>
</table>

Table 5. Summary of the key comparative findings
5.2.1 Current Progress and Electroosmotic Flow

It was observed that in most of the time, the initial currents in the EK+US tests were higher than in the EK tests. The currents of both EK and EK+US tests fluctuated in quite similar pattern (mostly in a narrow range of 0.02-0.03 A), which had higher initial current (0.04-0.06 A) and tended to decrease along the time and then became constant (0.01-0.03 A). Since current mainly results from the electromigration of ions through pore fluid, the higher currents observed in EK+US tests may be attributed to the ultrasonic effects, which made the slurries more porous and permeable. The decrease of current values over time may be explained through the fact that as mobile ions constantly electromigrated towards the electrodes, they were neutralized by reacting with the soil, with other species in the slurries or with the opposite charged electrode [348]. Because of evaporation (and electroosmosis towards cathode), the slurry’s moisture tended to decrease along the time (particularly in the anode parts), and this could also affect the currents.

In the tests with plexiglass cylinders, the anolyte level decreased over time due to the electroosmotic flow from anode to cathode. Therefore, anolyte was added daily to maintain its level. The cumulative amount of this anolyte addition was recorded for calculating the electroosmotic flow. It was observed that the electroosmotic flows of EK+US tests were higher than of EK tests. This implied that ultrasound increased the liquid outflow due to sonication effects that increased the matrix porosity and permeability [31].
5.2.2 Distribution of pH

There was no significant difference of pH distribution along the kaolin profiles between EK and EK+US tests. This again confirmed the previous finding that ultrasonication did not affect the pH of the kaolin slurry and thus pH distribution pattern was affected solely by the electrokinetic process. In both EK and EK+US tests, the section near anode had the lowest pH and the section near cathode had the highest pH because the electrolysis of water created acid front at anode and base front at cathode. Due to electromigration and electroosmosis, the low pH solution (high H⁺ concentration) generated at anode moved towards cathode [348]. Since the electromigration of H⁺ was concurrent with the electroosmotic flow and the mobility of ion H⁺ is about 1.76 times higher than that of OH⁻ [282], the low pH solution migrated faster and dominated the kaolin profiles. Moreover, as the initial pH of kaolin was around 4.7, most of the kaolin profiles had the pH values in the range of 4-6.

5.2.3 POPs Removal

Certain amounts of POPs were removed from kaolin in all the treatment tests through complex mechanisms of electrokinetic and ultrasonic processes. Ultrasound increased kaolin porosity and permeability as well as desorption of the low soluble POPs, thus enhanced electroosmotic mobilization of these contaminants. Moreover, ultrasonication could induce high fluid-solid sheer stresses [235], thermal decomposition, and hydroxyl radical oxidation [33] that contributed to the sonolysis of these POPs in the slurries.

Residues of POPs tended to remain the highest at the central part of the kaolin profile and decreased at the two electrode ends and this could be seen clearer in EK tests than in EK-US tests because of the physical water-kaolin
mixing effect of ultrasound. Oxygen produced at anode could be attributed to organic oxidation in these parts. During experiments, kaolin accumulated in anode side due to electrophoresis (as kaolin particle’s surface charge is negative) while water accumulated in cathode side (due to electroosmotic flow). Therefore, slurries in the cathode parts were more dilute and the contaminants there might be more easily desorbed and removed from kaolin. On the other hand, in both EK and EK+US tests, the two PAHs, PHE and FLU, tended to be removed more in the anode side while HCB tended to be removed more in the cathode side. It could be explained that the two PAHs were more easily destroyed by oxidation than HCB, and HCB can be desorbed, mobilized and removed from the dilute slurries.

Among all of the POPs tested, HCB was the most difficult to treat because of its very stable chemical structure and low water solubility. The initial POPs concentration was an important input parameter as low initial contaminant concentration tests gave better remediation efficiencies than higher initial contaminant concentration tests.

In all of the experimental set-ups, the EK+US tests gave the highest POPs removal efficiencies and the US alone tests gave the lowest POPs removal efficiencies. In general, with the same conditions, the removal efficiencies from EK+US tests were 2-17% higher than the EK alone tests, depending on various set-ups and on the contaminants. In the case of series tests for CHR remediation, the EK+US test in pan with iron anode provided the highest average CHR removal. In all of the cases, ultrasound assistance provided better uniformity of the remediation because of its mixing effect.

Comparative tests between surfactant-assisted electrokinetic remediation (EK+SF) and ultrasound-assisted electrokinetic remediation (EK+US)
showed that EK+US test demonstrated better PHE removal, while EK+SF test performed slightly better HCB removal. This again implied that the remediation mechanism of PHE involved with oxidation degradation while HCB removal was more attributed to the enhanced desorption and solubilization.
6. CONCLUSIONS

This study investigated the effectiveness of ultrasonic treatment, individually and as an enhancement for electrokinetic treatment in the remediation of persistent organic contamination from low permeability clayey soils. HCB, PHE, FLU and CHR were chosen as the representative POPs and kaolin as the model low permeability clayey soil. From the experimental observation, key findings are summarized in the following points:

- Ultrasonication could reduce the POPs contamination in low permeability soils but the remediation efficiency was low, particularly in short duration time. For complete removal, ultrasonication should not be considered as a single treatment process but rather be integrated with other appropriate techniques.

- The efficient treatment of soil by ultrasonication required a certain amount of water. Practically, the reasonable water:soil ratio of the soil slurry could be in the range of 1-2:1.

- Because of the heating effect observed during ultrasonication, soil slurry could be dried out, and thus ultrasonic treatment should not be operated over very long time. The intermittent ultrasonication could overcome this heating effect for longer term treatment.

- Ultrasonication did not affect pH of the slurries.

- The combined electrokinetic and ultrasonic treatment proved positive synergistic effect in POPs removal than each single process alone, though the level of enhancement was not high, only from 2-17%.
• Ultrasonication sustained higher current, higher electroosmotic flow and more uniform remediation in the combined EK+US tests, as compared with the EK alone tests.

• Initial contaminant concentration is an important input parameter that can seriously affect the remediation effectiveness. Removal efficiency decreased with increasing initial contaminant concentration.

• Among the POPs, HCB was the most difficult to treat because of its high chemical stability and low water solubility.

Although the lab-scale study showed some potential of ultrasonic and electrokinetic treatment in POPs decontamination from low permeability medium, the technique is far from large-scale practical application. Therefore, for practical scale-up systems, further studies are needed, considering technical design, economic factor and limitations of physical impacts such as heating effect and noise during ultrasonication. On the other hand, as the EK+US tests used the model kaolin, more research on real contaminated clay soils should be conducted to examine their interaction and effectiveness on real life situation. In addition, besides HCB, PHE, FLU and CHR, further studies on many other POPs contamination remediation are also needed.
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Publication I

Ultrasound-assisted treatment of kaolin artificially contaminated with phenanthrene, fluoranthene and hexachlorobenzene

Thuy Duong Pham, Reena Amatya Shrestha, Mika Sillanpää, Jurate Vinkutyte


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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 (HO2·) 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):

\[
\begin{align*}
H_2O &\rightarrow OH^- + H^+, \\
OH^- + H &\rightarrow H_2O, \\
2OH^- &\rightarrow H_2O + \frac{1}{2} O_2, \\
2OH^- &\rightarrow H_2O_2.
\end{align*}
\]

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).
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).

Ultrasonic 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). Ultrasonics may also be used as an enhancement method for electrokinetic treatment of heavy metals and polycyclic aromatic hydrocarbons in contaminated soils (Chung and Kamon 2005; Flores et al. 2007).

Soil contamination is a critical issue because of its significance to 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 (Petigirard 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 µS, 18 MΩ, $T = 22 \pm 1^\circ C$; pH 7.1).

Laboratory scale experiments were performed in triplicates in a closed Pyrex glass reactor (0.004 m³) 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 Hagerson 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 Saranley (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>
<thead>
<tr>
<th>Table 1. Main characteristics of kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Dry bulk density (g cm⁻³)</td>
</tr>
<tr>
<td>Moisture (%)</td>
</tr>
<tr>
<td>Electrical conductivity (µS cm⁻¹)</td>
</tr>
<tr>
<td>Cation exchange capacity (cmol kg⁻¹)</td>
</tr>
<tr>
<td>Organic content (%)</td>
</tr>
<tr>
<td>Particle size distribution:</td>
</tr>
<tr>
<td>% sand ( &gt; 0.05 mm)</td>
</tr>
<tr>
<td>% silt (0.05–0.002 mm)</td>
</tr>
<tr>
<td>% clay ( &lt; 0.002 mm)</td>
</tr>
</tbody>
</table>

POPs removal efficiency from artificially contaminated kaolin was calculated:

$$Removal\ efficiency = \left(1 - \frac{c_f}{c_i}\right) \times 100$$

where $c_i$ was the initial and $c_f$ was the final POPs concentration (mg kg⁻¹).

Kaolin was artificially contaminated with HCB, PHE and FLU at target concentrations of 500 mg kg⁻¹ (Phase 1 – high initial concentration, continuous ultrasonication) and 100 mg kg⁻¹ (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

<table>
<thead>
<tr>
<th>PHASE 1</th>
<th>Water content</th>
<th>Test</th>
<th>V-water (ml)</th>
<th>Frequency (kHz)</th>
<th>Power (W)</th>
<th>Duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHASE 1</td>
<td>High initial POPs concentration</td>
<td>Short time, continuous ultrasonication</td>
<td>100 g kaolin/test</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Test</td>
<td>V-water (ml)</td>
<td>Frequency (kHz)</td>
<td>Power (W)</td>
<td>Duration (h)</td>
<td></td>
</tr>
<tr>
<td>PHASE 1</td>
<td>W1</td>
<td>100</td>
<td>30</td>
<td>100</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>PHASE 1</td>
<td>W2</td>
<td>200</td>
<td>30</td>
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Table 2. Summary of experimental conditions for ultrasound-assisted tests during Phase 1 and Phase 2

<table>
<thead>
<tr>
<th>PHASE 2</th>
<th>Power</th>
<th>Low initial POPs concentration</th>
<th>500 g kaolin/test</th>
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<td>Power</td>
<td>Long time, intermittent ultrasonication</td>
<td>500 g kaolin/test</td>
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<td></td>
<td>Pulse mode</td>
<td>V-water (ml)</td>
<td>Frequency (kHz)</td>
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<tr>
<td>PHASE 2</td>
<td>1. Minimum conditions</td>
<td>0.5</td>
<td>500</td>
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<tr>
<td>PHASE 2</td>
<td>2. Optimum conditions</td>
<td>1</td>
<td>1000</td>
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</table>

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 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.

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$^{-1}$ 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 analy-
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 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 µm × 0.25 µm nominal). Carrier gas was helium argon (99.999% at 1.0 mL min$^{-1}$) with the flow of 1.2 ml min$^{-1}$.

The following chromatographic conditions were adopted: the temperature was from 80 °C (1 min) to 150 °C at 15 °C min$^{-1}$, then from 150 °C to 200 °C at 5 °C min$^{-1}$, and finally from 200 °C to 300 °C at 10 °C min$^{-1}$. The injector temperature was set at 250 °C and 1 µL 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.

![Figure 2](image)

**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 wavelengths, 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 Keek 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 (Keek et al. 2002). Thus, due to very severe localized energy and temperature changes, the adsorbed POPs will be subjected 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 300 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 µM min⁻¹, 4 µM min⁻¹, and 0.1 µM min⁻¹ 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.

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⁻¹) 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%.
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).

Two 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 (PAH) residues from a clay soil using sonication and a Soxhlet procedure: a comparative study, Journal of Environmental Monitoring 1: 63–67.


Kim, Y. U. 2000. Effect of sonication on removal of petroleum hydrocarbon from contaminated soils by soil flushing me-
ОЧИСТКА УЛЬТРАЗВУКОМ КАОЛИНА, ИСКУССТВЕННО ЗАГРЯЗНЕННОГО ФЕНАНТРЕНОМ, ФЛУОРАНТЕНОМ И ГЕКСАХЛОРОБЕНЗЕНОМ

П. Т. Дуонг, Р. А. Шреста, М. Силланпää, Ю. Виркуйте

Резюме

Применение ультразвуковой радиации для очистки почв является новой, быстро развивающейся технологией. Основной целью работы было оценить воздействие ультразвука на деградацию устойчивых органических загрязнителей, таких, как гексахлорбензен, 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 гексахлорбензена 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 Вт и больше, 67%-ная влажность) было меньше, чем при минимальных условиях реакции (1.84 кВтч).

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

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Publication II

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

Reena Amatya Shrestha, Thuy Duong Pham, Mika Sillanpää


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

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A R T I C L E   I N F O

Article info

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

Keywords: Ultrasonication Soil remediation POPs

A B S T R A C T

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 at 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.

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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 phenomena: 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]. Ultrasonic irradiation could also enhance membrane filtration of wastewater [6] and sludge stabilization [7,8]. Ultrasonication exhibits a great potential of being environmentally 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].

Ultrasonication 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 another 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...
by persistent organic compounds at high concentrations. Because of their low permeability, clayey soils are often 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, temperature affecting ultrasonic 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 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 (VVR), 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 in porcelain mortar with pestle. They were then sieved in a 2-mm-

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 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 were 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.

Table 1

<table>
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<th>Kaolin</th>
<th>Synthetic clay</th>
<th>Natural soil</th>
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<td>pH</td>
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Table 2

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<td>2</td>
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<td>1</td>
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<tr>
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<td>~30</td>
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<td>~30</td>
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</tbody>
</table>

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 were 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.

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.

3.2.3. Extraction and analysis

After ultrasonic irradiation, the temperatures and pH of slurries were measured. 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 were 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.

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

3.1. Water ratios

From contaminated kaolin. Thus, the removal efficiency was almost double. There is not much difference in 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 silt 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 silt 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 20kHz [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 1h, then slowly increased to 63°C. Then, it remained constant. The temperature increased from 20°C to 52°C in first 1h 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 1h and 6h. 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.
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 ultrasound 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.

References


Publication III

Combined ultrasonication and electrokinetic remediation for persistent organic removal from contaminated kaolin

Thuy Duong Pham, Reena Amatya Shrestha, Jurate Virkutyte, Mika Sillanpää


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Combined ultrasonication and electrokinetic remediation for persistent organic removal from contaminated kaolin

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A R T I C L E   I N F O

Article history:
Received 7 May 2008
Received in revised form 1 August 2008
Accepted 1 September 2008
Available online 18 September 2008

Keywords:
Soil remediation
Electrokinetics
Ultrasonound
Persistent organic pollutants

A B S T R A C T

Electrokinetics alone (EK) and ultrasonically enhanced electrokinetics (EK-US) tests were studied to compare and examine the combining effects of these two methods on the removal of the three persistent organic pollutants (POPs): hexachlorobenzene (HCB), phenanthrene (PHE) and fluoranthene (FLU) from kaolin. Two pair tests were conducted into two experiments with different initial low (100 mg/kg) and high (500 mg/kg) contaminant concentrations. Results from the experiments show that, generally, EK-US tests have higher electroosmotic flow, higher current and better performance than EK alone tests. However, ultrasonic enhancement can increase the removal rate only up to about 10% most. Among the three POPs, HCB is the most difficult to treat because of its very stable structure while the other two PAHs are easier to remove.

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1. Introduction

Soil contamination is a critical issue as a threat to public health, food system and groundwater. Contaminants like persistent organic pollutants (POPs) are of particular concern due to their long lifetime and toxicity. Being hydrophobic, these POPs adsorb strongly the soil texture, thus they are often very difficult to treat, especially in low permeable clayey soil. Among many soil decontamination technologies, electrokinetics has emerged as a potential in situ alternative, specifically able to work in low permeable soil. Electrokinetic remediation technique is based on the application of low-level direct current, which is used to mobilize contaminants via electromigration, electroosmosis and electrophoresis phenomena. Unlike metals or charged ions which are removed electrokinetically from soil mainly by electromigration, non-polar contaminants such as most organic compounds are transported primarily by electroosmosis, and the process might not be effective unless the contaminants are soluble in pure fluid. Therefore, desorption and solubility of POPs should be enhanced to improve the mobility of these hydrophobic compounds. Several techniques can be used with electrokinetics to improve the performance such as surfactant addition [2–5], design and operation enhancement like using LasagnaTM model, rotational operation mode, or upward peristaltic pump [6–8]. Electrokinetics can also be successfully integrated with advanced oxidation processes such as Fenton’s process to treat low permeability soil contaminated with biorefractory organic pollutants [9–14], or combined with permeable reactive barriers to remediate both inorganic (As, Cd, …) and organic contaminants [15,16].

On the other hand, ultrasonication has been growingly applied in environmental remediation [17]. Ultrasound has been used as an advanced oxidation process for destruction of organic pollutants [18], pre-treatment process to improve wastewater [19] and saline solution disinfection [20], enhancement for membrane filtration [21] and sludge stabilization [22,23]. Compared to conventional methods, ultrasonication can bring several benefits as it is environment friendly (no toxic chemical is used or produced) and low cost [24]. Ultrasonic energy irradiated into contaminated soils can increase desorption and mobilization of contaminants and porosity and permeability of soil through developing of cavitation [25]. Moreover, organic contaminants can be destroyed through pyrolysis or oxidation by strongly oxidative free radicals that generated during ultrasonication [17].

In this study, electrokinetics alone (EK) and electrokinetic combined with ultrasound (EK-US) tests were investigated to examine the coupling effects of these two methods on persistent organic removal from clayey medium. Kaolin was used as model clayey medium, along with three model compounds: hexachlorobenzene (HCB) and the two PAHs, phenanthrene (PHE) and fluoranthene.
The representative persistent organic compounds chosen in these experiments were HCB (99%), a typical polychlorinated hydrocarbon and two PAHs, PHE (97%) and FLU (98%). The hexachlorobenzene and fluoranthene were purchased from Sigma–Aldrich Co., Germany. Phenanthrene and hexane were purchased from Merck (Germany). All chemicals were of analytical grade. Model clayey soil used in the experiments was white kaolin (Sigma–Aldrich Co., Germany). Kaolin was often used as the model clay due to its high content of clay (hydrophobic organic components tend to adsorb in the clay/silt-size fraction because smaller particles have large surface areas and clay minerals have electrical charges associated with them [4,26]), negligible content of organic matter, low cation exchange capacity and inertia [5]. Some main characteristics of kaolin are summarized in Table 1. 10 g kaolin was mixed with 20 ml distilled water for pH measurement (using pH meter: pH 730 inolab, WTW series) and electric conductivity measurement (using the portable EC meter: Water proof EC Testr low, Eutech Instruments Pte, Ltd.). The dry bulk density of kaolin was measured by weighing the given volume (100 cm$^3$) of kaolin. Cation exchange capacity was estimated by determination of exchangeable cations ($K^+$, $Ca^{2+}$, $Mg^{2+}$). Organic content was measured by Loss-on-Ignition method. Particle size distribution was measured by hydrometer method.

The ultrasonic processors used in these experiments were UP100H and UP200H from Hielscher – Ultrasound Technology (Germany), with operating frequency of 30 kHz and 24 kHz, maximum power of 100 W and 200 W, respectively. The power of these ultrasonic processors can be controlled in the amplitude range of 20–100%. Titanium electrodes of 10 cm long and 1 cm diameter were connected to the direct current dual power supply. Two plexiglass cylinders were used for electrokinetics (EK) and combined electrokinetic–ultrasonic (EK-US) tests. Two plexiglass cylinders were connected to the direct current dual power supply. Two plexiglass cylinders were used for electrokinetics (EK) and combined electrokinetic–ultrasonic (EK-US) tests.

Two plexiglass cylinders used for electrokinetics (EK) and combined electrokinetic–ultrasonic (EK-US) tests: (1) cathode parts, (2) central parts, (3) anode parts, (4) ultrasonic processor.

Because of the low solubility of POPs in water, hexane was used as solvent to dissolve completely the POPs required to yield the target concentrations [27]. Kaolin was homogeneously soaked and stirred with these solutions at the ratio of approximately 500 ml solution per 1 kg kaolin. Then it was kept in fumehood nearly a week for solvent to evaporate entirely. Initial concentrations of POPs in kaolin were measured by taking random samples from contaminated kaolin. Kaolin was mixed with certain amount of distilled water to make slurry. There were two different experiments, each was conducted in the same two tests: electrokinetic alone (EK) and combined electrokinetic–ultrasonic (EK-US) tests. Different initial conditions in these two experiments are summarized in Table 2. The slurry in EK-US tests was subjected to ultrasonic waves at the same condition of 5 h on the first day and 1 h per day for the rest of experimental period. In both EK and EK-US tests, catholyte solution was distilled water. During experimental period, the voltages were kept constant at 30 V (the voltage gradient was 1.5 V/cm), and evolution of the electric current was recorded daily.

At the end of experiments, the dual power supply was switched off. Six samples along the kaolin profile, numbered 1–6 from anode to cathode, were taken and were dried in ovens at 80 °C overnight. The dried kaolin was then pulverized for pH measurement and POPs analysis. Samples were analyzed in duplicates for quality assurance. 1 g of sample were mixed with 5 ml hexane in glass tube and was put into ultrasoundation bath for 30 min to get the organic compounds extracted from kaolin intohexane solvent. The glass tubes were centrifuged at 5000 rpm for 10 min [5]. The supernatants were then taken into 2 ml glass vials for GC–MS (Agilent 5975) analysis.

### Table 1

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
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<tr>
<td>pH</td>
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<tr>
<td>Dry bulk density (g cm$^{-3}$)</td>
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<tr>
<td>Moisture (%)</td>
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<tr>
<td>Electric conductivity (µS cm$^{-1}$)</td>
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<tr>
<td>Cation exchange capacity (cmmol kg$^{-1}$)</td>
<td>3.1</td>
</tr>
</tbody>
</table>

### 3. Results and discussion

#### 3.1. Current progress

Fig. 2 shows the changes in electrical current during experiments. As seen in this figure, current of EK and EK-US tests fluctuated in quite similarly patterns that tended to decrease along the time. Because of ultrasonic wave effect, most of the time, current in EK-US tests was higher than in EK tests. At the beginning, current in EK-US tests was particularly high (0.05 A in experiment I and 0.06 A in experiment II), while current in EK tests was 0.04 A in both experiments. Since the current primarily results from electrophoresis of ions through the pore fluid, the high current seen at the start of the voltage application is most likely due to the high con-
Table 2
Summary of experimental conditions.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial POPs concentration (mg/kg)</th>
<th>Amount of kaolin (g)</th>
<th>Amount of water (ml)</th>
<th>Voltage (V)</th>
<th>Ultrasound frequency (kHz)</th>
<th>Ultrasound power (W)</th>
<th>Ultrasonication pulse mode</th>
<th>Anolyte solution</th>
<th>Duration (days)</th>
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<td>100</td>
<td>650</td>
<td>1000</td>
<td>30</td>
<td>24</td>
<td>100</td>
<td>0.8</td>
<td>NaOH 0.01 M</td>
<td>10</td>
</tr>
<tr>
<td>II</td>
<td>500</td>
<td>1000</td>
<td>1000</td>
<td>30</td>
<td>30</td>
<td>100</td>
<td>1</td>
<td>Na_2 CO_3 0.01 M</td>
<td>15</td>
</tr>
</tbody>
</table>

Note: Ultrasonication pulse mode = 0.8 means 0.8 s on and 0.2 s off, pulse mode = 1 means continuously on during ultrasonication time.

ductivity of the initial pore solution [28]. Current decreased into 0.01–0.02 A after 4–6 days then remained constant (experiment I) or with only little change (experiment II) to the end of experiments. The current values decreased over time because the mobile ions are constantly electromigrating towards the electrodes, and, as they migrate, these excess ions are neutralized by reacting with the soil, with other species in solution, or with the oppositely charged electrode [29].

3.2. Electroosmotic flow

Because of electroosmotic flow from anode to cathode, the anolyte level in anode part decreased after 3–4 days. From that time, more anolyte addition was needed daily to maintain its level. Cumulative anolyte quantity used over experimental time was recorded (Fig. 3) and represented for electroosmotic flow. Fig. 3 shows that the cumulative anolyte quantity (or electroosmotic flow) from EK-US tests was higher than from EK tests in both experiments. It means that the ultrasonic process has a role to increase the liquid outflow due to sonication effects that increase the soil porosity and permeability [25]. Especially in experiment I, the amount of daily additional anolyte in EK-US test (100 ml), much higher than in EK test alone (around 30 ml), thus the gap between them got wider and wider and by the end, cumulative anolyte quantity of EK-US test was nearly double that of EK test. However, in experiment II, from the 5th day to 13th day, both EK-US and EK tests had the same amount of 50 ml anolyte addition per day. Therefore, the cumulative anolyte patterns of EK-US and EK tests in experiment II are basically the same. The difference in electroosmotic performance of experiments I and II can be explained by their difference in initial water content.

3.3. pH of electrolytes and kaolin sections

During experimental period, pH of anolyte and catholyte from the tests were measured and recorded daily. Despite different initial pH of anolyte solutions (NaOH 0.01 M, pH 1.77 in experiment I, and Na_2 CO_3 0.01 M, pH 10.15 in experiment II), these experiments have followed quite the same pH pattern. Both EK and EK-US tests from experiments I and II were coming to reach the same pH value in anolyte (slightly fluctuated around 2) and catholyte (slightly fluctuated around 12) after 1–2 days of operation. These patterns are not anything new but already known fact that can be observed in most electrokinetic studies. It is explained by electrolysis of water that created oxygen gas and hydrogen ion (acid front) in anode and hydrogen gas and hydroxide ion (base front) in cathode. Moreover, it should be noted that ultrasonication in central part of the reactors did not have any effect on pH of electrolytes.

Once the experiments were completed, samples from six sections, numbered 1–6 (anode to cathode), were measured for pH in each test. Fig. 4 shows the pH profile along the kaolinite sample. In both EK and EK-US tests of the two experiments, Section 1 (near anode) has the lowest pH and Section 6 (near cathode) has the highest pH because of the acid front generated at anode and base front generated at cathode. As a result of electroosmosis and electromigration, low pH (high H^+ concentration) solution generated at anode was transported in the soil and moved towards cathode [29].
The low pH solution migrated faster because the electromigration of H\(^+\) is concurrent with the electroosmotic flow and the mobility of H\(^+\) is about 1.76 times higher than that of OH\(^-\) [30]. Moreover, since the initial kaolin itself has pH of 4.72, most of kaolin profile has pH in the range of 4.5–6.5, while only section 6 (near cathode) has exceptional high pH of 8–10. There is no big difference of pH between EK and EK-US tests. Our previous studies on ultrasonication of kaolin slurry demonstrated that ultrasound did not affect pH of kaolin slurry. In general, pH in experiment I is lower than pH in experiment II, although anolyte solution in experiment I, NaOH 0.01 M, has higher pH 11.77 than Na\(_2\)CO\(_3\) 0.01 M, pH 10.15 in experiment II. It could be explained by the fact that Na\(_2\)CO\(_3\) solution has higher buffering capacity (can neutralize more H\(^+\)) than NaOH solution.

3.4. Residual POPs distribution

POPs analysis of electrolytes gave negligible results. Contaminant concentration along the kaolin profile after experiment is described in Fig. 5 as residual percentage. As seen in Fig. 5, certain amounts of POPs had been removed in all treatment tests through complex mechanisms of electrokinetic and ultrasonic processes. Ultrasonication increased kaolin porosity and permeability as well as increased desorption of these low-soluble POPs. Therefore, electroosmotic migration of these contaminants was enhanced. Moreover, ultrasonication can induce high fluid–solid shear stresses [31], thermal decomposition, and hydroxyl radical oxidation [17] that involve sonolysis of organic compounds in the slurries.

According to our own experience, there is negligible effect on residual concentration between experimental conditions of 24 kHz or 30 kHz frequencies at 100 W, and NaOH or Na\(_2\)CO\(_3\) 0.01 M electrolytes. Therefore, Fig. 5 shows that initial concentration is an essential input parameter that does affect treatment’s outcome, as the residual percentages in experiment I (low initial concentration of 100 mg/kg) are obviously lower than that of experiment II (high initial concentration of 500 mg/kg), despite the shorter treatment duration time in experiment I. However, it should be noted that experiment I has the advantage of high initial water content with smaller amount of contaminated kaolin per test, moreover, the pulse mode 0.8 also can induce stronger ultrasonic performance than the continuous mode.

Along the kaolin profile, residual concentrations tend to be lower near electrode parts and accumulate higher in the central part. This
the three POPs, concentration of HCB remains the highest even in all tests of experiments. The difference between residual concentration of HCB and the other two PAHs is shown particularly in experiment I, where the initial contaminant concentration is lower and even clearer in kaolin sections near electrodes. HCB is more difficult to remove than PHE and FLU because of its very stable chemical structure and low water-solubility property. And for the rest two PAHs, FLU is easier to remove than PHE, maybe because of the unstable five-membered ring in the middle of its chemical structure.

The contaminant removal efficiency is calculated by inverting residual percentage. In experiment I, removal rates of EK alone test are in the range of 53–71% with an average of 63% for HCB, 75–98% with an average of 84% for PHE, and 84–95% with an average of 90% for FLU, while that of EK-US test are in the range of 70–88% with an average of 74% for HCB, 82–96% with an average of 88% for PHE, and 82–97% with an average of 90% for FLU. On the other hand, in experiment II, removal rates of EK test are in the range of 27–42% with an average of 34% for HCB, 40–55% with an average of 47% for PHE, and 47–59% with an average of 52% for FLU, while that of EK-US test are in the range of 29–56% with an average of 34% for HCB, 40–55% with an average of 47% for PHE, and 47–59% with an average of 52% for FLU.

4. Conclusions

It could be concluded from the two experiments that removal efficiency of POPs in EK-US tests are higher than that of EK alone tests, however ultrasonic enhancement can increase the removal rate only up to about 10%. More electroosmotic flow in EK-US test than in EK test. Initial contaminant concentration is an essential input parameter that can determine the removal effectiveness despite different treatment processes. Removal efficiency decreases with increasing initial concentration. Among the three POPs, HCB is the most difficult to treat because of its high stability while the other two PAHs are easier to remove, in which the removal rate of FLU achieves the highest. Enhancement of electrokinetic by ultrasonication can be taken as one of the feasible methods to remove PAHs from contaminated soil.

Acknowledgement

Authors would like to thank the Maj and Tor Nessling Foundation, Helsinki, Finland, for their financial support in this research.

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Publication IV

Electrokinetic and Ultrasonic treatment of kaoline contaminated by POPs

Thuy Duong Pham, Reena Amatya Shrestha, Mika Sillanpää


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Electrokinetic and Ultrasonic Treatment of Kaolin Contaminated by POPs

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Abstract: Three tests were conducted using ultrasound alone, ultrasound as an enhancement for electrokinetic test and electrokinetic test alone to compare the removal performance of the three persistent organic pollutants, hexachlorobenzene, phenanthrene, and fluoranthene from low permeability kaolin. Results show that the removal efficiency in ultrasonically enhanced electrokinetic test was the highest among experiments, though the removal rates improved were small only. The assistance of ultrasound in electrokinetic remediation can help reduce these hydrophobic organic compounds by increasing their mobility, desorption for electroosmotic migration, and also by degrading them through free radical oxidation forming during cavitation process.

Keywords: Clayey soil remediation, electrokinetic process, persistent organic compounds, ultrasonication

INTRODUCTION

As a key component of environmental chemical cycles, soil contamination often contributes to water and air pollution (1). Any hazardous substance
present in a soil matrix represents a threat to public health and ground
water. Among these pollutants, persistent organic compounds are of par-
ticular concern because of their long life span and toxicity. Therefore,
decontamination of soils through the removal of these organic contami-
nants becomes a more and more urgent problem in the present world. Site
conditions, contaminant types, contaminant source, and the potential
impact of the possible remedial measure determine the choice of a reme-
diation strategy and technology. No single technology is appropriate for
all contaminant types and various site-specific conditions (2).

For organic contamination particularly, a variety of site remediation
technologies are available, which can be categorized as ex-situ and in-situ
treatments. Since ex-situ treatments involve soil excavation, they can be
costly. On the other hand, in-situ treatments are attractive because of
potential low cost and avoiding or lessening hazardous waste spreading,
since it allows the soil to be treated without being excavated and trans-
ported (3). However, the conventional in-situ treatments such as bioreme-
diati, soil washing etc., are usually very site-specific and often work best
on homogenous, permeable soils but are difficult to apply on low perme-
able soils (4). Fortunately, electrokinetics has emerged as an innovative
in-situ technology that can deal with this problem. The electrokinetic pro-
cess can extract heavy metals, radionuclides, and organic contaminants
from saturated or unsaturated soils, sludges, and sediments (5–7). Because
of the applicability to a broad range of organic and inorganic contami-
nants, and especially the ability to work in low permeable soils, there has
been considerable interest in electrokinetic processes in recent years (8).

The electrokinetic remediation technique is based on the application
of low-level direct current, which is used to mobilize and separate
contaminants via electromigration, electroosmotic, and electrophoretic
phenomena. Unlike metal or charged ions which are removed electroki-
etically from soil mainly by electromigration, non-polar contaminants
like most organic compounds are transported primarily by electroosmo-
sis, and the process would not be effective unless the contaminants are
soluble in pore fluid. Therefore, enhancement is needed to improve mobi-
lity of hydrophobic compounds, which tend to adsorb strongly to the
soil, particularly the low permeability one.

On the other hand, ultrasonic irradiation applied into contaminated
soils can increase desorption, mobilization of contaminants, as well as
porosity and permeability of soil through developing of cavitation (9).
Moreover, ultrasonic waves can promote the formation of free strong
oxidative radicals that involve the oxidation of contaminants (10,11),
and the high local temperature and pressure forming during ultrasonic
cavitation can destroy the contaminants through pyrolysis processes
(12). The use of ultrasound offers several advantages such as lack of
dangerous breakdown products, and the low energy demand and technology can be made quite compact, transportable, allowing on-site treatment (13).

In this study, ultrasound was used as a treatment method alone and as an enhancement for the electrokinetic test to improve the removal performance of the three persistent organic pollutants (POPs), hexachlorobenzene (HCB), phenanthrene (PHE), and fluoranthene (FLU) from low permeability kaolin.

EXPERIMENTAL

The representative persistent organic compounds chosen in these experiments were HCB (99%), a typical polychlorinated hydrocarbon and two PAHs, PHE (97%), and FLU (98%). Hexachlorobenzene and fluoranthene were purchased from Sigma-Aldrich (Germany). Phenanthrene and hexane were purchased from Merck (Germany). All chemicals were of analytical grade. Model clayey soil used in the experiments was white kaolin purchased from VWR International (Finland). Kaolin was often used as the model clay due to its high content of clay, negligible content of organic matter, low cation exchange capacity and inertia (14). Some of the main characteristics of kaolin are summarized in Table 1.

The ultrasonic processor used in the experiments was UP200H from Hielscher – Ultrasound Technology (Germany), with an operating frequency of 24 kHz and a maximum power of 100 W. The power of this ultrasonic processor can be controlled in the amplitude range of 20–100%.

Kaolin was artificially contaminated with these three POPs at target concentrations of 100 mg kg\(^{-1}\). The amount of kaolin used for each test was about 500 g. Because of the low solubility of these organics in water, their concentration was increased to 1000 mg kg\(^{-1}\) in a 10:1 kaolin-water mixture before applying the ultrasound treatment.

<table>
<thead>
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<tr>
<td>pH</td>
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<tr>
<td>Dry bulk density (g cm(^{-3}))</td>
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<tr>
<td>% silt (0.05-0.002 mm)</td>
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<tr>
<td>clay (&lt;0.002 mm)</td>
<td>75.9</td>
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Figure 1. Sketch for experiment set-up: Ultrasonic (US) test, Electrokinetics (EK) test, Ultrasonically enhanced Electrokinetics (EK + US) test.
hexane was used as a solvent to dissolve them completely for the target concentration (15). Kaolin was soaked with this solution at the ratio of approximately 500 ml per 1 kg kaolin. It was stirred well to make kaolin spiked homogeneously. Then, it was kept in fumehood nearly a week for the solvent to evaporate entirely and the kaolin could be ready for experiments. Samples were taken to check the actual initial concentrations of POPs in kaolin, because some portion of contaminants may be lost along the process.

The scheme of these experimental setups was described in Fig. 1. Experiments were conducted in three tests for 15 days. In each test, 500 g kaolin was mixed with 600 ml distilled water to make slurry. The ultrasonic (US) test was carried out in a plastic beaker. The electrokinetic (EK) test and ultrasonically enhanced electrokinetic (EK + US) test were conducted in two rectangular plastic pans with 20 × 14 × 8 cm dimensions. Titanium electrodes of 10 cm long and 1 cm diameter were connected to the direct current dual power supply. The constant voltage applied in both EK and EK + US tests was 30 V, with the initial direct current of 0.03 A. The kaolin slurry in US alone and EK + US tests were subjected to 100 W ultrasonic waves at 24 kHz for 1 hour per day, during 15 days. Water was added manually on the anode side of EK and EK + US tests, about 50 ml per day, to compensate the lost amount due to evaporation over a long time of experiment and maintain certain moisture for treatment.

At the end of the experiments, the dual power supply was switched off. Samples were dried in an oven at 80 °C overnight. The dried kaolin was then pulverized for pH measurement and POPs analysis. Samples were analyzed in duplicates for quality assurance. One gram of sample were mixed with 5 ml hexane in a glass tube and was put into ultrasonication bath for 30 minutes to get the organic compounds extracted from the soil into hexane solvent. The glass tubes were centrifuged at 5000 rpm for 10 minutes (14). The supernatants were then taken into 2 ml glass vials for GC-MS (Agilent 5975) analysis to determine the residual POPs concentration.

RESULTS AND DISCUSSION

Current Progress

Figure 2 shows the changes in electrical current of EK and EK + US tests during experimental period, when the voltage was kept constant at 30 V. As seen in this figure, most of the time, the current in the EK test fluctuated around 0.03 A. On the other hand, the current in EK + US test had been rising up to 0.05 A within first 3–4 days, then declined and remained...
around 0.03 A till the end of the experiment. It could be considered that the higher current in EK + US test at the beginning of the experiment is attributed to ultrasonication effects, which made the slurry more porous and permeable. It was observed that the slurry's moisture tended to decrease along the time (especially in anode parts) because of electroosmosis towards the cathode as well as because of evaporation, and this can affect the current of the tests since the current primarily results from electromigration of ions through the pore fluid (16). Therefore, after 5 days of operation, when the current started to fall, water was added regularly into the test pans, to maintain certain moisture and current.

pH Distribution

At the end of the experiments, samples were taken from nine positions, numbered as distributed in pan matrix (Fig. 3). Figure 3 shows that the pH distribution among pan matrix follows quite the same pattern in both tests as there is no big difference of pH between EK and EK + US tests. Our previous studies on ultrasonication of kaolin slurry also demonstrated that ultrasound did not affect pH of kaolin slurry. Sample 2 (near anode) had the lowest pH of 1.97 (EK test) and 2.11 (EK + US test) while sample 8 (near cathode) had the highest pH of 10.28 (EK test) and 9.91 (EK + US test). It is explained by the acid front generated at the anode and the base front generated at the cathode. As a result of electroosmosis and electromigration, low pH (high H⁺ concentration) solution generated at the anode was transported in the soil and moved towards the cathode (17). The low pH solution migrated faster because the electromigration of H⁺ is concurrent with the electroosmotic flow and the mobility of H⁺ is
about 1.76 times higher than that of OH⁻ (6). Moreover, the initial pH of kaolin is 4.68. Therefore, pH of most of samples were lower than 7, except those samples near the cathode. Samples at the center of the pans (numbered 4, 5, 6) had a pH of around 5–6.

**POPs Removal**

The study investigated the effectiveness of combining ultrasound and electrokinetic treatment in POPs removal from a contaminated clayey medium. As described previously, electrokinetic remediation is particularly helpful for clayey soil treatment while this type of low permeable soil is often a problem for other techniques. However, electrokinetic remediation is more effective with metal or charged ion removal through electromigration than non-polar contaminants or organics removal through electroosmosis. In contrast, ultrasonic irradiation, is specifically used for organics removal through enhancing the desorption and mobilization of these contaminants, as well as their destruction by oxidation and pyrolysis. Thus, ultrasonication can help as a complement or enhancement for electrokinetic remediation. The combination of these two methods was expected to have coupling effects that take advantage of
the strong points from both techniques. The remediation mechanisms involve complex ultrasonic and electrokinetic processes. Ultrasound increases kaolin porosity and permeability as well as increases desorption of the low-soluble POPs (9), therefore, electroosmotic migration of these contaminants was enhanced. The electroosmotic flow was not checked but the electroosmotic phenomenon was observed obviously through the accumulation of water into the cathode side. Moreover, ultrasonication can induce high fluid–solid shear stresses (18), thermal decomposition, and hydroxyl radical oxidation (12) that involves sonolysis of organic compounds in the slurries. The POPs concentrations in kaolin samples of EK and EK + US tests after experiments are described in Fig. 4 as average residual percentages of samples from anode, central and cathode parts. Figure 4 shows that in both EK and EK + US tests, all three POPs concentrations had been reduced to certain levels, in which, residual percentages of the two PAHs, PHE (16–26%) and FLU (20–34%), are considerably lower than that of HCB (47–67%). This could be explained by the very stable chemical structure of HCB that makes it difficult to treat. Residues of POPs tended to concentrate mostly highest at the central part and decrease at the two electrode ends. Oxygen produced at the anode can be attributed to organic oxidation in this part. During experiments, kaolin accumulated in the anode side due to electrophoresis (since kaolin particle’s surface charge is negative) while water accumulated in the cathode side of the pan. Thus, the slurry in the cathode part was more dilute and contaminants there were more easily desorbed and removed from the kaolin. On the other hand, in both tests, the two PAHs had been removed more in anode side while HCB had been removed more in the cathode side. It could be explained that the two PAHs are more easily destroyed by oxidation than HCB, while HCB

![Figure 4](image-url)
can be desorbed, mobilized and removed from the dilute slurry. In general, residual concentrations of POPs from EK + US test are lower than that of EK alone test. In addition, the POPs residues distributed along the soil profile in EK + US test were also more homogeneous, compared to EK test alone, because of the physical mixing effect of ultrasound.

The contaminant removal efficiency is calculated by inversing average residual percentage. Figure 5 shows the POPs removal efficiency from different treatment methods. Generally, more than 40% HCB and significant amounts of PAHs (up to 80%) were removed by all methods. Removal efficiencies of POPs in EK + US test were the highest and that in US test alone were the lowest among the three tests (Fig. 5). There is no big difference among the three treatments for HCB removal. However, PAHs removal can be improved by electrokinetic remediation and ultrasonically enhanced electrokinetic remediation.

CONCLUSIONS

Results from experiments show that combined electrokinetic and ultrasonic treatment did prove positive coupling effect in PAHs removal than each single process alone, though the level of enhancement is not much. However, among the three POPs, HCB is the most difficult to treat because of its high stability and the removal of HCB from all three tests did not perform big difference. The assistance of ultrasound in electrokinetic remediation can help reduce POPs from clayey soil by
improving the mobility of hydrophobic organic compounds and degrading these contaminants through pyrolysis and oxidation.

Although ultrasound has shown up as quite effective in many studies on organic removals from water, the combination of ultrasound and electrokinetics for soil remediation is still just a recent idea realized in laboratory scale. More future works should be conducted in considering some technical limitations in scale-up, transducer design, physical effects such as noise, medium heating etc., and many other practical aspects.

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Publication V

Electro ultrasonic remediation of polycyclic aromatic hydrocarbons from contaminated soil

Reena Amatya Shrestha, Thuy Duong Pham, Mika Sillanpää


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Electro ultrasonic remediation of polycyclic aromatic hydrocarbons from contaminated soil

Reena Amatya Shrestha • Thuy Duong Pham • Mika Sillanpää

Received: 13 May 2009 / Accepted: 27 March 2010 / Published online: 16 April 2010
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Abstract The polycyclic aromatic hydrocarbons (PAHs) with high molecular mass are renowned for their high persistence in the soil, hydrophobic and toxicity. Remediation of these pollutants is still an unsolved task and needs more researches to be performed. The coupling of electrokinetics (EK) with ultrasonic energy (US) has advantages on desorbing and migrating PAHs from contaminated soil. US and EK work together to destroy PAHs. The objective of this study was to treat PAHs contaminated soil by using EK and ultrasonication. The contaminated oil contained about 100 mg kg⁻¹ chrysene. Experiments with US, EK and combined EK and ultrasound were conducted in reactors and pans with and without iron anodes. Results indicated that the removal was more effective with lower concentrations of chrysene. The average removal was better in experiment with combined EK and ultrasound using iron anode. This might be due to increase in electroconductivity by iron ions.

Keywords Chrysene Electrokinetics Electroosmosis Soil remediation Ultrasonic energy

1 Introduction

Pollution by chemicals creates serious problems to environment. Among the main soil pollutants, polycyclic aromatic hydrocarbons (PAHs) are of particularly hazardous. PAHs persist in the environment, and bioaccumulated through the food web, causing adverse effects to human health and the environment [1]. Chrysene was taken as the model pollutant, a representative of PAHs and large hydrophobic compounds with four fused aromatic rings. In case of PAHs, the hydrophobic nature increases with increase in weight [2]. It is not produced for commercial purposes but it is released into the environment as a by-product of many industrial processes such as distillation of coal, distillation or pyrolysis of fats and oils [3]. If it is in the air, it adsorbs to soil and dust particles and is dispersed over large areas, contaminating both soil and watersheds [4, 5]. Once entered in the soil they accumulate in horizons rich in organic matter where they are likely to be retained for many years due to their persistence and hydrophobicity [6].

Its half life depends on the matrixes. For example, 1.25 h in air, 4.4 h in water, years in soil. There are limited studies on microbial degradation of chrysene due to its negligible solubility and high soil–water distribution ratios, which stand against its ready microbial utilization and promote its accumulation in the solid phases of terrestrial environment [7]. Approximately 60% of the chrysene can be removed in the slurry reactor with nutrients and microorganism [8]. A white rot fungus can have the capability to degrade 30 mg PAHs kg⁻¹ soil, but operation time was 30 days. It is difficult to distinguish analytically between chrysene disappearance due to microbial degradation and that from adsorption to soil [9]. There is still lack of knowledge in biodegradations and absorption by soil. The rhizospheric microflora is found to be stimulated to degrade chrysene [10]. Masten and Davies [11] used ozone to overcome the limitations imposed by the low aqueous solubility of PAHs on their rate of biodegradation and/or dissolution for in situ chemical oxidation processes. It was found that the degradation decreased with increase
in molecular mass in PAHs. It was also concluded that after 4 h of exposure to ozone, the chrysene concentration in a contaminated soil was reduced 100–50 mg kg$^{-1}$). 7.8% of chrysene was removed in 30 min at a KMnO$_4$ concentration of 160 mM from about 65 mg kg$^{-1}$ [12].

There is a great need of fast, low cost, environmental friendly and in situ remediation technologies. Among in situ remediation technologies, electro-osmosis remediation method (EOR) has become a promising, inexpensive, publicly accepted and innovative technique for removing organic contaminants from contaminated soil. This technique is best suited for a low-permeable soil. Most of organic pollutants will not precipitate or bind to soil differently at higher or lower pH values. With electroosmosis (EO), a higher pH actually increases pore water movement. Organic pollutants move along with pore water towards the electrode. Upon their migration to the electrode, the pollutants accumulate by the electrode or are transported into the water, which need secondary treatment such as electroplating, precipitation/co-precipitation, pumping near the electrode or complexion with exchange resins [13, 14].

It is often very difficult to treat chrysene contaminated clayey soil especially with low permeability only by electrokinetic method as the hydrophobic and non-polar nature help chrysene to adsorb strongly in the soil texture. Therefore, the enhancement is necessary to improve the mobility of it. Several techniques can be used with electrokinetics (EK) to improve the performance such as surfactant [15–18], design and operation enhancement [19–21]. Compared to conventional methods, ultrasonication can bring several benefits like environmental friendly (no production of toxic chemicals) and low cost [22]. Ultrasonic energy (US) applied into contaminated soils can increase desorption and mobilization of contaminants and porosity and permeability of soil through developing of cavitation [23]. Moreover, organic contaminants can be destroyed through pyrolysis or oxidation by strongly oxidative free radicals that generated during ultrasonication [24].

The research-work was focused on the development of in situ electro ultrasound remediation process that has a potential for removal of chrysene, a hydrophobic PAH from contaminated soil without using any surfactants and any other chemicals.

2 Materials and methods

Chrysene was purchased from Acros organics and hexane from Merck. All chemicals were of analytical grade. The ultrasonic processor used in these experiments was UP100H with operating frequency of 30 kHz, power of 100 W and 10 mm horn diameter from Hielscher—Ultrasound Technology Company. The power of these ultrasonic processors could be controlled in the amplitude range of 20-100%. Graphite electrodes of 10 cm long and 10 mm diameter were connected to the direct current dual power supply. Two plexiglass cylinders were used for EK and combined electrokinetic-ultrasonic (EKUS) tests. Each plexiglass cylinder consists of a central chamber (Φ 10 cm × 20 cm) and two electrolyte chambers (Φ 10 cm × 4 cm) for anode and cathode parts (Fig. 1). In the middle of the central chamber, there is a rectangular hole of approximately 14 cm × 7 cm for acoustic horn position and easily handling with the soil input. The electrolyte chamber has two small holes for electrode position, gas ventilation and pH checking by pipette. Soil in central chamber is separated with electrolyte chambers by polypropylene filter cloths (Sigma-Aldrich Co., Germany). Kaolin (VWR) was used as a model low permeability clayey soil. The physical and chemical properties of kaolin were determined based on the methods prescribed by Soil Science: Methods and Applications [25] and are shown in Table 1.

![Image](image_url)
2.1 Ultrasonic treatment

Kaolin was artificially contaminated with chrysene at initial concentrations of 25, 50, 75 and 100 mg kg\(^{-1}\). Because of the low solubility of POPs in water, hexane was used as solvent to dissolve completely the POPs required to yield the target concentrations [26]. To contaminate the kaolin, chrysene–hexane solution was slowly added to dry kaolin. The mixture were stirred with stainless steel spoons within glass beakers and then placed in fume hood for nearly a week until the hexane completely evaporated. Samples were taken to determine the actual initial concentrations of POPs in kaolin, because some portion of contaminants may be lost along the process. The dry kaolin was then mixed with deionised water to simulate field moisture conditions for ultrasound process.

A series of laboratory batch ultrasound experiments was conducted on chrysene-contaminated kaolin with different concentration of chrysene (0, 25, 50, 75 and 100 mg kg\(^{-1}\)) to know maximum removal efficiency of ultrasound at 100 W for 24 h. Samples were taken every 2 h.

2.2 EK treatment

The cell designed, shown in Fig. 1 consists of a polyethylene body which has negligible capacity of adsorption of chrysene. The amount of dry kaolin packed in the cell was approximately 500 g. There were two compartments for electrodes filled with tap water. The graphite electrode was always taken as cathode. The separation distance between the two compartments was 20 cm. The filter cloth membrane was placed between cell and compartment in each site to allow the exchange of electrolytes into and out of the compartment. Two types of experiments were conducted in simple electrokinetic treatment with graphic anode and iron anode (iron might show similar effects as Fenton). The duration of experimental period was 10 days.

2.3 EKUS treatment

The kaolin–water mixed slurry in EKUS tests was subjected to ultrasonic waves at the same condition of 5 h on the first day and 1 h per day for the rest of experimental period (10 days). In both EK and EKUS tests, catholyte solution was tap water. During experimental period, the voltages were kept constant at 30 V (the voltage gradient was 1.5 V cm\(^{-1}\)), and the change of currents was recorded daily. Similar experiments for EK and EKUS were carried out in an open pan without separation chambers for electrodes. The dimensions of pan were 20 cm × 14 cm × 8 cm and pan was made of HDPE (Fig. 1). Approximately 500 g of contaminated kaolin was put into it. Electrodes were inserted into soil at end of the pan. These experiments were designed in considering of implementation of the process in the field.

In all experiments, the ratio of water and soil was maintained about 2:1. The sonochemistry based on the fact that a liquid is exposed to sufficiently large acoustic field [27]. The convenient of hydraulic transport of soil in slurries is typically by 40% by weight [28].

2.4 Extraction and chemical analysis

At the end of experiments, the dual power supply was switched off. The final soil mass was divided into five sections in case of reactor and nine sections in case of open pan experiments, from anode to cathode. These samples were dried in an oven at 80 °C over 24 h. The dried kaolin was then pulverized for analysis. Samples were analyzed in duplicates for quality assurance. One gram of 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 4000 rpm for 20 min [18]. The supernatants were then put into 2 mL glass tubes. TA Finnigan Trace 2000 GC equipped with a Finnigan Polaris Q mass spectrometer was used for determining the remained concentrations of chrysene in the extracts. pH values of the soil samples were also measured in time series and all sections of final soil mass at the end of the experiments.

3 Results and discussion

3.1 Ultrasonic treatment

Figure 2 gives the idea about the efficiency of removal of chrysene from the soil. It shows that the efficiency of
removal depends on the concentration of pollutants in soil. After 24 h ultrasonication, the removal percentages were about 70, 62, 59 and 50 from 25, 50, 75 and 100 mg kg\(^{-1}\). It was found that the oxidation of organic compounds by sonocation highly depends on the concentration \([29, 30]\). That means the expose with ultrasound covers more in low concentration. At constant moisture content, frequency and power of the ultrasound processor, the remediation decreased with increase in concentration of pollutants. The average removal percentage in case of 100 mg kg\(^{-1}\) was about 45.

3.2 Treatment in the reactors

The electrolytes in both cathode and anode compartments consisted of negligible amount of chrysene. The removal percentage of chrysene was observed in EK and EKUS with and without iron anode (Fig. 3). Chrysene removal was higher in anode side in both EK with and without iron anode. In case of EK with iron anode, the removal percentage slightly increased by 1%. It may be due to function of dissolved iron that helped to increase the electroconductivity in the kaolin. It is clearly shown that removal increased 5% more in the anode side in which iron anode was used. In case of ultrasonication, the removal was uniform through out the soil but the removal percentage was increased by 1% in EK. This is different than the lower molecular PAHs. It was found that the removal percentage of PAHs having lower molecular mass and less numbers of aromatic rings than chrysene was 10% more than that of EK \([31]\). This shows that the rate of remediation depends upon molecular mass and numbers of aromatic rings in PAHs. The removal was high at the anode side in the experiment with EK only. It might be due to migration of chrysene with water (EO) towards cathode and also by oxidation reaction of chrysene by oxygen formed there.

In case of experiment with EKUS, remediation was high at cathode because water content was relatively higher there. Amount of water content helped in production of OH-radicals \([23]\).

Figure 4 shows the change in current during experiments and pH after experiments. The pH values in the anolyte and catholyte were about 2.0 and 11 during EK and EKUS without iron anode experiments whereas with iron anode, pH of anolyte was about 6.0 and that of catholytes, 11.0. After completing of experiments, the soil samples were divided into five sections in 4 cm difference from

![Fig. 2 Chrysene removal from kaolin on treatment of ultrasound alone](image)

![Fig. 3 Removal of chrysene in the reactor](image)

![Fig. 4 pH and current change in the reactor](image)
anode and then pH of them were measured. 0–4 cm section nearby anode had lowest pH values around 4.8 and highest pH values around ~10.2 are nearby cathode for experiments without iron anode and pH values around ~6.4 for experiments with iron anode. It happened because of acid front generated at anode and base front at cathode. Due to EO and electromigration, H+ ions moves towards the cathode and OH− ions moves towards anode. As the small H+ ions, they can move twice times faster than OH− ions [32, 33]. In case of experiments with iron anode, pH values were almost same through the sample soil. It may be because iron ions migrated from the anode maintained the pH. There was no significant difference in pH of EK and EKUS. It was already proved in our previous studies on ultrasonication of contaminated kaolin slurry. Figure 5 shows the change in electrical current during the experiments. It has been seen that the current of EK and EKUS tests fluctuated in quite similar pattern that tended to decrease along time and then became constant.

3.3 Treatment in the pans

The percentage of chrysene removal was measured from each of nine sections after 10 days long of each experiment in the pans. The sections were divided as shown in Fig. 5. The results of measurement are shown in Fig. 6. The removal percentage was somewhat better than that in reactor treatment. The average removal in EKUS was nearly 2% more than in EK without iron anode whereas it was 3% more in EKUSF than in EKF with iron anode in pan. The removal in both EK is higher at anode side. It was always observed in the pan that the kaolin moved to the middle due to migration of water towards the cathode from anode.

Figure 7 shows the pH profile of soil after completing the experiments and the change in current during the experiments. The trend of current was similar as in reactor, but the pH in experiments with and without iron anode had similar result as in pan. The iron ions could not move fast in this case. The pH values were lower at anode side and higher at cathode side. It might be due to same reasons as in reactors.

4 Conclusion

It could be concluded that

- It is possible to treat higher ringed aromatic hydrocarbons contaminated soil by ultrasonication within a few hours.
- Removal efficiency of chrysene in EKUS is higher than in EK alone.
• Removal efficiency decreases with increase in initial concentrations.
• Soil pH can be maintained by using iron anode in the reactor.
• Efficiency increased in EK-pan experiments but removal was not in uniform across the soil.
• Nearly uniform removal had taken place in the experiments in which both ultrasonication and EK processes were used.
• The highest average removal is in the experiment with EKUS in pan with iron anode (shown in Fig. 8).

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.

References
Publication VI

Technical note: Removal of hexachlorobenzene and phenanthrene from clayey soil by surfactant- and ultrasound-assisted electrokinetics

Thuy Duong Pham, Reena Amatya Shrestha, Mika Sillanpää


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TECHNICAL NOTES

Removal of Hexachlorobenzene and Phenanthrene from Clayey Soil by Surfactant- and Ultrasound-Assisted Electrokinetics
Thuy Duong Pham1; Reena Amatya Shrestha, Ph.D.2; and Mika Sillanpää3

Abstract: Removal of nonpolar contaminants such as most organic compounds are transported primarily by electroosmosis in electrokinetic remediation, thus the process is effective only if the contaminants are soluble in pore fluid. Hydrophobic organic compounds such as hexachlorobenzene (HCB) and phenanthrene (PHE) can adsorb strongly to clayey soil. Therefore, in this study, enhancements were done by adding 2-hydroxylpropyl-β-cyclodextrin surfactant and ultrasonication comparably to assist the electrokinetic treatment in improving the mobility of these hydrophobic compounds. The results show that HCB and PHE were mobilized and removed in both cases. But HCB is more difficult to remove than PHE, because of its highly stable nature and low water-solubility property. Ultrasound-assisted test performed better PHE reduction than surfactant-assisted test, because ultrasound can degrade the contaminant through oxidation by free radicals.

DOI: 10.1061/(ASCE)EE.1943-7870.0000203
CE Database subject headings: Soil treatment; Electrokinetics; Ultrasonic methods.
Author keywords: Soil remediation; Electrokinetics; Surfactant; Ultrasound.

Introduction
Electrokinetic treatment has emerged as a potential technique for in situ soil remediation (Pamukcu and Huang 2001) and especially unique because of the ability to work in low permeability soil. Electrokinetic remediation technique is based on the application of low-level direct current, which is used to mobilize contaminants via electrokinetic processes. Unlike metal or charged ions which are removed electrokinetically from soil mainly by electromigration, nonpolar contaminants such as most organic compounds are transported primarily by electroosmosis, and the process will not be effective unless the contaminants are soluble in pore fluid. Therefore, enhancement is needed to improve mobility of hydrophobic compounds, which tend to adsorb strongly to the soil, particularly low permeability soil such as clay. Many researchers successfully used different surfactants in electrokinetics to enhance the mobility of low polarity or nonpolar contaminants through low permeability soil (Kommalapati et al. 1997; Reddy and Saichek 2002; Jiradecha et al. 2006; Maturi and Reddy 2006; Saichek and Reddy 2005; Yuan et al. 2006, 2007; Zhou and Zhu 2007; Park et al. 2007). On the other hand, ultrasonic energy applied into contaminated soils can increase the desorption and mobilization of contaminants and porosity and permeability of soil through the development of cavitation (Chung and Kamon 2005). In this study, using 2-hydroxylpropyl-β-cyclodextrin surfactant and ultrasound as assistance for the electrokinetic remediation process of hexachlorobenzene (HCB) and phenanthrene (PHE) was examined comparably. Results from the preliminary tests that applied these two methods will be discussed in the paper.

Materials and Methods
The persistent organic compounds chosen in the experiment were HCB (99%), a typical polychlorinated hydrocarbon, and PHE (97%), a representative polycyclic aromatic hydrocarbon. Cyclodextrins were considered advantageous over regular surfactants because of its nontoxicity, biodegradability, and low affinity of sorption to the solid phase (Maturi and Reddy 2006), then hydroxypropyl cyclodextrin (HPCD) was chosen to use as flushing solution in the surfactant-assisted electrokinetic (SFEK) test. HCB and the surfactant 2-hydroxylpropyl-β-cyclodextrin (HPCD) were purchased from Sigma-Aldrich, while PHE, hexane solvent from Merck. All chemicals were of analytical grade. Model clayey soil used in the experiment was white kaolin purchased from VWR International. Kaolin was often used as the model clay due to its high content of clay, negligible content of organic matter, low cation exchange capacity, and inertia (Yuan...
Table 1. Main Characteristics of Kaolin

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Particle size distribution:
- % sand (>0.05 mm) 3.9
- % silt (0.05–0.002 mm) 20.2
- % clay (<0.002 mm) 75.9

Ultrasound waves at 30 kHz were applied for 2 hours on the first day and 1 hour per day for the rest of the experimental period.

Results and Discussion

During the experimental period, the voltage was kept constant at 30 V in both SF-EK and USE-K tests. Fig. 3 shows that current in both tests fluctuated quite similarly, within a narrow range of 0.02–0.03 A, despite different flushing solutions (HPCD surfactant in SF-EK test and water in USE-K test). It was observed that current tended to decrease along the time because of decreasing moisture (evaporation). Therefore, surfactant solution and distilled water were added regularly into SF-EK and USE-K pans, respectively, to maintain certain moisture and current.

After experiment, samples were taken from nine positions as labeled in Fig. 2. Samples were measured for pH and were dried in oven at 80°C overnight. The dried kaolin was then pulverized for analysis. Samples were analyzed in duplicates for quality assurance. One gram of sample were mixed with 5 mL hexane in the glass tube and was put into ultrasonication bath for 30 min to get the organic compounds extracted from the soil into hexane solvent. The glass tubes were centrifuged at 5000 rpm for 10 min (Yuan et al. 2006). The supernatants were then taken into 2 mL glass vials for GC-MS (Agilent 5975) analysis to determine the residual concentration.

Samples from USE-K test have slightly lower pH than samples from SF-EK test. Our previous studies on ultrasonication of kaolin slurry demonstrate that ultrasound did not affect pH of kaolin.

ml distilled water and then the kaolin slurry was subjected to 100 W ultrasonic waves at 30 kHz for 2 h on the first day and 1 h per day during the rest of experimental period.

After 14 days of experiment, the dual power supply was switched off. Samples were labeled according to the matrix distribution of them in the pan (Fig. 2). Samples were measured for pH and was dried in oven at 80°C overnight. The dried kaolin was then pulverized for analysis. Samples were analyzed in duplicates for quality assurance. One gram of sample were mixed with 5 mL hexane in the glass tube and was put into ultrasonication bath for 30 min to get the organic compounds extracted from the soil into hexane solvent. The glass tubes were centrifuged at 5000 rpm for 10 min (Yuan et al. 2006). The supernatants were then taken into 2 mL glass vials for GC-MS (Agilent 5975) analysis to determine the residual concentration.
slurry, thus this slightly decrease pH in USEK test could be explained by the migration of acid front due to the increasing water flow induced by applied ultrasonic energy (Chung and Kamon 2005).

The contaminant concentrations in kaolin samples after the 14 day experiment are described as residual percentage in Fig. 5. Overall view from both tests shows that HCB and PHE were desorbed, migrated and removed by SFEK and USEK processes. Residual concentrations of PHE (less than 20%) were much lower than HCB, though all HCB remained were already less than 62%.

In SFEK test, residual concentration of PHE decreased from anode to cathode, while residues of HCB concentrated mostly highest at the central part and decreased from the center to the two electrode ends. The results show that, although both contaminants are hydrophobic organics, with surfactant-assisted electroosmosis, PHE is more easily to mobilize than HCB. On the other hand, in USEK test, the residual concentrations from different sample positions did not vary much. To examine these performances, it should be noted that, during experiment, kaolin accumulated in anode side (electrophoresis phenomenon, since surface charges of kaolin particles are negative) while water accumulated in cathode side (electroosmosis phenomenon) of the close pan (no outflow-water was taken out). Then, slurry in cathode part was more diluted and contaminants there were more easily desorbed and removed from kaolin. These electrokinetic effects performed less clearly in USEK test than SFEK test because of the physical water-kaolin mixing effect of ultrasound. Thus, the residual concentrations were more homogeneously distributed in USEK test than in SFEK test.

The contaminant removal efficiency is calculated by inverting the residual percentage. Generally, more than 40% HCB and significant amounts of PHE (more than 80%) were removed by both methods. In SFEK test, removal efficiency of HCB achieved 44 to 67%, with an average of 57%; and removal efficiency of PHE achieved 79 to 98%, with an average of 91%. In USEK test, removal efficiency of HCB achieved 38 to 61%, with an average of 48%; and removal efficiency of PHE achieved 80 to 99%, with an average of 97%. In general, HCB is more difficult to remove than PHE, because of its very stable chemical structure and low water-solubility property. USEK test demonstrated better PHE removal, while SFEK test performed slightly better HCB removal.

Conclusions
The assistance of surfactant or ultrasound in electrokinetic remediation can help reduce HCB and PHE from clayey soil by improving the mobility of these hydrophobic organic compounds. Moreover, ultrasound can degrade these contaminants through oxidation by free radicals forming during cavitation process. Ultrasoundication is rather effective with PAHs such as PHE than HCB, mostly because the chemical structure of PHE is not very stable such as HCB. However, more studies should be investigated with different surfactants, different ultrasonic power and frequencies to have a better view of the issue.

Acknowledgments
The writers would like to thank the Maj and Tor Nessling Foundation, Helsinki, Finland, for their financial support in this research.

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