Environmental Perspectives of Microwave Applications as Remedial Alternatives: Review

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Abstract: Microwave energy has been widely used in several domestic, industrial, and medical applications such as food sterilization, organic/inorganic syntheses, polymerization, dehydration, analyses and extraction, and biological destruction. This paper summarizes the potential applications of microwave energy as remedial alternatives for various types of wastes and diverse contamination of soils, sludge, or wastewaters. The major subjects covered in the paper are focused on sludge processing, medical waste treatment, contaminated soil remediation, wastewater remediation, activated carbon regeneration, and integrated remedial methodology. The extent of microwave treatment and microwave-assisted application promoting a specific technology has been highlighted relative to the conventional methods. Also, a few novel microwave involved processes, and the integrated experimental design of remedial schemes were presented. The application of microwave energy was proven to be superior to the use of conventional heating on accelerating reaction rates, improving yields, and selectively activating or suppressing reaction pathways. Besides the thermal effect, the nonthermal effect caused by microwave irradiation and its influence on the specific remediation cases have also been discussed. When applying the integrated remedial methodology, the effects of microwave irradiation improving the photocatalytic capacity of TiO2 have been detailed. Conclusively, microwave technology is a potentially viable and powerful alternative to the decontamination of soil, sludge, wastewater, as well as the treatment of certain types of waste.

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Introduction

Microwaves lie in the segment of the electromagnetic spectrum from 300 MHz to 300 GHz, while most microwave applications fall within 3 and 30 GHz (Appleton et al. 2005). In order to avoid interference with radar and telecommunication frequencies, domestic and industrial microwave ovens generally operate at 2.45 GHz corresponding to a wavelength of 12.2 cm and energy of 1.02 × 10^{-5} eV (Jacob et al. 1995). Another frequency of microwave irradiation used in industrial applications is around 900 MHz with a longer wavelength of 37.2 cm, which can provide up to 100 kW in larger process heating applications (Eskicioglu et al. 2007). Microwaves are a form of electromagnetic energy that can be transferred to the subject material by the interaction of the electric-field component of the wave with charged particles in the material. Microwave energy absorbed by the subject material will be converted into heat; however, not all materials can be heated by microwaves. The materials, which absorb the microwave radiations, are termed dielectrics and characterized by possessing very few free charge carriers and exhibiting a dipole movement (Oespchuck 1984). When the microwaves are applied to dielectric materials with an oscillating electric field, the dipoles within the material attempt to realign themselves and flip around the applied field. Under microwave irradiation at 2.45 GHz, the dipoles realign themselves approximately 2.5 billion times per second due to the alternating electromagnetic field (Vorster et al. 2001). The dipole movement generates friction inside dielectric materials and the internal energy is dissipated as heat. The dielectric constant is a measure of the material’s capability to retard microwave energy as it passes through, while the loss factor is a measure of the material’s capability to dissipate the energy (Haque 1999). The dielectric properties of a material are related to temperature, moisture content, density, and material geometry (Metaxas and Meredith 1993). The materials with high loss factor are easily heated through microwave irradiation; moreover, ionic conduction and dipolar rotation are two important mechanisms of energy dissipation in the material (Kingston and Jassie 1985).

According to their microwave absorption characteristics, materials may be classified as conductor, insulator, and absorber (Church 1993).

- Conductors possess a property to reflect the incident waves off the material surface. Metals such as copper, brass, silver, and aluminum are good conductors, and waveguides in a microwave oven are often made of brass or aluminum.
- Insulators such as Teflon and polypropylene (PP) are substantially transparent to the microwaves and possess a property to partially reflect and transmit the incident waves traveling through the material, but not store microwave energy in the form of heat. Insulators are often used in microwave ovens to support the material to be heated.
- Absorbers possess a property to absorb microwave radiation, direct energy transfer, and thus effectively heated at room temperature. Their ability to absorb microwave energy is related to...
the loss tangent of the materials, which depends on the functional groups and the volume of the molecules (Gabriel et al. 1998).

Since the Raytheon Company of North America first produced the microwave oven in 1951 (Oeschpuch 1984), microwaves have demonstrated the potential to provide rapid, energy-efficient heating of materials. Heating is one of the most common processes employed by the process and manufacturing industries, and microwave heating has been widely applied in food processing, wood drying, plastic and rubber treating, and curing and preheating of ceramics (Jones et al. 2002). Compared with conventional heating, microwave heating has the advantages of shorter heating time, selective heating, better process control, and no direct contact of heated materials. However, one drawback of microwave heating is the hotspot phenomenon, which is a type of thermal instability resulting from the nonlinear dependence of the electromagnetic and thermal properties of the material on temperature (Reimbert et al. 1996). Because of this nonlinear dependence, the formation of standing waves within the microwave cavity may result in higher-energy exposure and an increased heating rate in some regions. Thus, cavity design is an important factor in the control or the utilization of this hotspot phenomenon (Jones et al. 2002; Appleton et al. 2005).

Microwaves have been applied in many scientific and technological fields to heat dielectric materials (Kingman and Rowson 1998; Zlotozynski 1995). In the field of analytical chemistry, microwave is commonly applied as a very useful form of auxiliary energy to extract a wide range of organic compounds, including polycyclic aromatic hydrocarbons (PAHs), phenols, total petroleum hydrocarbons, pesticides, polychlorinated biphenyls (PCBs), triazines and fats from soils, sediments, or biological tissues (Kornilova and Rosell-Mele 2003). Microwave extraction method was also introduced to the determination of metals in geological samples (Lu et al. 2003), and it was proven effective for metal fractionation in sewage sludge (Perez-Cid et al. 2001). Desulphurization of coal was the first reported case of applying microwave energy to the treatment of minerals in 1978 (Zavitsanos 1978), and subsequently, many technological applications on microwave treatment of minerals have been developed, including heating, drying, carbothermic reduction of oxide minerals, leaching, roasting, pretreatment of refractory gold ore and concentrate, spent carbon regeneration, and waste management (Haque 1999). Also, there is significant potential of applying microwave energy as an alternative heating source in the treatment of waste streams and environmental remediation (Appleton et al. 2005). A number of microwave heating applications in environmental engineering have been evaluated, including contaminated soil remediation, waste processing, minerals processing, and activated carbon regeneration (Jones et al. 2002). From the point of view of environmental engineers, the major subjects of microwave treatment or microwave-assisted applications reviewed in this paper are focused on sludge processing, medical waste treatment, contaminated soil remediation, wastewater remediation, activated carbon regeneration, and integrated remedial methodology.

### Microwave Application on Sludge Treatment

The expenses of sludge treatment and disposal usually share a major fraction of the capital and operational cost in a sewage treatment plant. Sewage sludge is a multiphase medium, containing water, mineral, organics, and cells of microorganisms (Wojciechowska 2005). The sludge consists of a polymeric network formed by microbial cells and extracellular polymeric substances (EPS), and the hydrolysis of EPS and microbial biomass limits the rate and extent of direct anaerobic degradation (Higgins and Novak 1997). Sewage sludge may absorb microwave energy due to its high water content, and thus microwave irradiation is applicable for sludge treatment. The most common treatment methods of sewage sludge include sludge landfill, cropland application, incineration, and ocean dumping; however, none are exempt from drawbacks (Werther and Ogada 1999). In contrast, many advantages of applying microwave energy on sludge treatment have been reported on reducing volume (Menendez et al. 2002), improving dewaterability (Wojciechowska 2005), enhancing digestibility (Eskicioglu et al. 2007), pathogen destruction (Hong et al. 2006), and stabilizing heavy metal (Hsieh et al. 2007) of sludge. Table 1 summarizes various types of microwave applications on sludge treatment.

#### Microwave-Induced Pyrolysis

Pyrolysis, typically, occurs in the absence of oxygen, under pressure, and at operating temperatures above 450°C, and uses indirect heat to convert solid organic materials into gases and liquids. Compared with incineration, pyrolysis seems to be less of a pol-
lutan because it concentrates the heavy metals in a solid carbonaceous residue (Caballeró et al. 1997). In general, poor receptors of microwave energy such as soils, sediments, and sludge cannot be heated directly up to the required temperature for pyrolysis. As the wet sludge is subjected to microwave irradiation, only drying of the sludge takes place. By means of microwave energy, it takes less than 90 s to reach a maximum heating temperature around 200°C. Microwave heating of the sewage sludge not only removes moisture content but also sweeps away some of the volatile matter (Menéndez et al. 2002).

Microwave-induced pyrolysis of poor microwave absorbers is possible if the subjected material is mixed with a dielectric material for effective improvement of microwave absorption such as carbon (Ben-Chanaa et al. 2000) or certain metal oxides (Monsef-Mirzai et al. 1995). Menéndez et al. (2002) have tested the use of the carbonaceous residue (char) produced in the pyrolysis of the sewage sludge as a microwave receptor, and the result showed that a maximum temperature of 900°C can be reached after 2 min of microwave heating. Compared with the pyrolysis by an electric furnace, microwave pyrolysis performed slightly more completely due to the higher ash content of the pyrolyzed samples. Both microwave drying and microwave pyrolysis of the sewage sludge demonstrated a significant volume reduction of more than 84%. On the other hand, pyrolyzed samples showing a basic nature are quite different from the slightly acidic dried samples. The basic nature and the porous property of the char obtained by the pyrolysis of sewage sludge would make itself suitable for application as economical adsorbents of acidic pollutants such as H₂S, CH₃SH, phenols, etc. Besides, the fuel gases and liquid produced from the processes are other financial rewards for microwave-induced pyrolysis.

**Sludge Conditioning**

Conditioning is an essential process to improve sludge dewatering characteristics in sewage sludge processing, since dewatering may reduce the sludge volume, thus resulting in less expense for the transport and disposal of sludge. In general, the dewaterability of sludge is poor due to the adherence of water molecules onto the organics in the sewage sludge. A variety of conditioning methods have been employed to affect the bonding of water molecules with organic matter, including treatment with polyelectrolytes, ultrasonic treatment, and microwave irradiation. Microwave irradiation causes the oscillating movement of water dipoles, dissipates the friction heat, and accordingly, boils water molecules bound in sewage sludge. As a consequence, the release of the bound water also is accompanied by the burning of microorganism cells during sludge conditioning by microwave irradiation. Wojciechowska (2005) pointed out that application of microwave irradiation for sludge conditioning can also offer additional advantages of sludge sanitation.

Wojciechowska (2005) has studied the microwave treatment on the dewaterability of sewage sludge, and the results showed that the effect of the microwave conditioning depends on sludge type and contact time. The optimal contact time of microwave conditioning was found to be 180 s for primary and mixed sludge and 120 s for digested sludge, while the values of specific resistance to filtration rapidly increased when extending the exposure time of microwave radiation. Excessively increasing the contact time not only throws energy away but also impairs the conditioning effects. Microwave conditioning of sewage sludge causes a significant increase of organic matter in the sludge liquor, and this fact is coherent with the destruction of microorganism cells. The pollutant burden can be reduced if microwave treatment is followed by polyelectrolyte dosing, plus this combined conditioning produces better results compared with microwave conditioning alone.

**Sludge Pretreatment for Improving Digestibility**

The main fraction of waste-activated sludge commonly consists of EPS and microbial cells that are resistant to direct anaerobic degradation. Rather than microbial cells, EPS and divalent cations may be the most important parameters governing sludge hydrolysis and determining floc structure, integrity, and strength (Novak et al. 2003). Several pretreatment alternatives such as mechanical, thermal, ultrasound, chemical, enzymatic, and thermochemical methods can be utilized to disrupt the polymeric network formed by EPS and divalent cations before the process of anaerobic digestion, and thus biodegradability of waste-activated sludge is enhanced as well as dewaterability (Eskicioglu et al. 2006, 2007). Microwave irradiation is a novel pretreatment alternative in that the heating effect can cause the breakage of the EPS and divalent cation network, and also an athermal effect caused by polarized parts of macromolecules aligning with the poles of the electromagnetic field may bring about the possible breakage of hydrogen bonds (Loupy 2002).

Microwave application on the pretreatment of anaerobic digestion accounts for its potential of decomposing complex chemical compounds and transforming them into simple compounds. Eskicioglu et al. (2006) utilized soluble organic matter of waste-activated sludge and cumulative biogas production of anaerobic digestion to characterize the effect of the microwave pretreatment. The enhancement of both soluble chemical oxygen demand (SCOD) of the microwave-irradiated sludge (361%) and biogas production after 23 days of anaerobic digestion (475%) provides evidence of successful microwave pretreatment for improving sludge digestibility. A recent study confirms the existence of the microwave athermal effect on the basis of higher biogas production from microwave pretreated sludge samples than conventional heating samples, although there is no discernible microwave athermal effect on SCOD of sludge (Eskicioglu et al. 2007). Also, a linear relationship between microwave temperature and the level of sludge hydrolysis was found in a tested range of 50–96°C.

**Sludge Sanitation**

Based on the consideration of future land application, pathogenic organisms accumulated in biosolids including bacteria, viruses, protozoa, and helminthes have to be removed before the final disposal. Because sludge has a high dielectric loss factor, microwave energy can be utilized to prepare pathogen-free sludge that may be recycled through land application as a soil conditioner or fertilizer (Hong et al. 2006). The ability of microwave irradiation to interact with cells of microorganisms has been already proven. Woo et al. (2000) reported inactivation of *E. coli* and *Bacillus subtilis* colonies exposed to microwave irradiation. Harris et al. (1989) found that few bacteria survived after 60 s of microwave exposure and none survived after 90 s. Hong et al. (2004) pointed out that fecal coliform, an indicator organism in biosolids, can be destructed by microwave irradiation at lower temperatures than external heating. The destruction of the coliform bacteria performed through the mechanism of cell wall damages and denaturation of DNA isolated from fecal coliform when using microwave energy. Also, microwave irradiation caused stronger inhibition in
bacterial activity than external heating, and it was found that bacterial activity almost ceased at temperatures above 68°C. Microwave irradiation of sludge provides a viable and economical option of pathogen destruction due to the necessity of lower temperature and shorter processing time.

**Microwave-Enhanced Stabilization of Heavy Metal**

Industrial sludge containing heavy metals and toxic compounds is liable to release them through landfill leachate if waste landfill is the final destination of industrial sludge. Hence, industrial sludge must be immobilized and stabilized before landdilling to cut down the potential release of heavy metals, and several scientific works attempted to explore microwave application on this subject (Gan 2000; Chen et al. 2005; Hsieh et al. 2007). The heavy metal sludge from printed circuit board manufacturing wash water was a typical studied case where metal hydroxide sediment sludge was detoxified through microwave heating, drying, and metal ion immobilization within the sediment solids. The wash effluent from printed circuit board manufacturing contains a high level of heavy metal ions, including Cu²⁺, Zn²⁺, Ni²⁺, Cr³⁺, and Pb²⁺, and special polymers used as chelating agent, and accordingly the produced sludge is abundant with metal hydroxide through a polyelectrolyte flocculation and precipitation process. Gan (2000) reported that microwave radiation showed a remarkable effect on immobilization of heavy metals within a sediment solid structure; for example, microwave treatment may result in a reduction of leachable Cu²⁺ and Pb²⁺ by 27- and 11-fold from the hydroxide sediments over a period of 12 weeks. Microwave drying of hydroxide sediments can reach around 230°C, and subsequently, conduct strong interaction and binding of free metal ions with dipolar polymeric molecules in sediment solids, so-called ion immobilization. Microwave-treated sediment solids have a net positive surface charge, and thus show a high affinity of adsorbing the anionic molecules.

Three remedial options of industrial sludge treatment are vitrification, cement solidification, and extraction by acids or solvent. Due to high cost and disposal trouble caused by vitrification and cement solidification, the extraction alternative gives an environmental and economical solution of detoxifying industrial sludge and recovering valuable metals (Kuo et al. 2005). Most of the copper ions in sludge can be recovered by extraction using sulfuric acid; however, the concentration of copper ions in the residue of the acid-extraction process is high (Chen et al. 2005). Kuo et al. (2005) demonstrated a case of microwave acid extraction to remove copper from industrial sludge, and the result showed that microwave irradiation greatly enhanced the removal efficiency of copper relative to traditional acid extraction. The significance of factors affecting the efficiencies of microwave acid extraction followed in descending order as the addition of a microwave absorber, the microwave power input, and the solid/liquid ratio. During acid extraction, the extracted sludge showed that the most copper partition shifted from Fe–Mn oxides bound to organic matter bound.

Chen et al. (2005) investigated the effect of stabilizing Cu²⁺ in acid-extracted sludge by microwave irradiation with the addition of some reagents such as Fe, Na₂CO₃, and Na₂SiO₃. Without any additive reagents, the effect of microwave treatment on sludge stabilization depends highly on the property of the original sludge. The additive reagents Na₂CO₃, and Na₂SiO₃ did not provide regular and effective assistance in sludge stabilization by microwave irradiation. A remarkable effect of using microwave energy on the reduction of the Cu²⁺ leaching from 179.4 to 6.5 mg/L with the addition of iron powder was noticed, and the stabilization time was shortened from 9 to 3 min, as well in the Fe additive system. This result implied that a dosage of 2% dry sludge weight of Fe was recommended for promoting the stabilization of Cu²⁺ in sludge.

A recent study by Hsieh et al. (2007) found that the addition of aluminum metal powder made the thermal copper stabilization much more efficient and effective with microwave irradiation as compared to α- and γ-aluminum oxides, and accordingly, the stabilization of the heavy metal sludge is governed by the valence instead of the lattice arrangement of Al species. The reaction between copper ions and aluminum metal is regarded as a solid-phase reaction, and the stabilization of the heavy metal sludge likely results from the formation of thermodynamically stable metal–alumina–oxide species. The addition of aluminum, as well as the reaction temperature, were recognized as major factors in stabilizing copper in heavy metal sludge. The treated sludge using the microwave stabilization process can be denominated as the stabilized sludge, and further reuse of the stabilized sludge as an adsorbent for removing aqueous metal ions was examined by Hsieh et al. (2006). The negative surface charge of the stabilized sludge shows the high capacity and affinity of adsorbing metal ions onto the stabilized sludge, and the measured zero-point-charge of the stabilized sludge was between pH 9.2 and 9.5. The adsorption capacity of copper ions onto stabilized sludge (around 23 mg/g) was greater than many other solid wastes.

**Medical Waste Treatment**

Medical waste can be classified to as general waste or special waste, and it is sometimes identified as nonregulated medical waste for general waste and regulated medical waste for special waste (Lee et al. 2004). In most economically developing counties, inappropriate treatment and final disposal of medical wastes have raised serious concerns due to their potential of causing adverse impacts on public health and the environment. Inappropriately managed pathological and hazardous medical wastes may be the source of intrahospital infections and pose serious occupational health risks to healthcare workers. In general, pathogen destruction can be attained through proper thermal, chemical, and irradiative treatment (Diaz et al. 2005). Incineration has been historically employed for the treatment of regulated medical waste because of its advantages on pathogen destruction, waste volume reduction, and waste heat recovery. As medical wastes were incinerated with status lacking proper controls and emission reduction devices, chlorine-containing components such as polyvinyl chloride and disinfectants may transform into dioxins and furans (Alvim-Ferraz et al. 2000). Besides, another problem regarding on-site incineration of medical wastes is the emission of heavy metals in the form of fumes or vapors, particles, and ashes (Fritsky et al. 2001).

With respect to the risk of potential exposure associated with hazardous emissions from the incineration of medical wastes, there is an essential plea to develop innovative technologies for the better practice of managing medical waste. Several alternative treatment methods have been proposed to replace incineration, including microwaving, autoclaving, radioimaging, and electro-technologies. Among these alternatives, microwaving and autoclaving are considered as positive alternative treatment methods to incineration (Lee et al. 2004). Microwave disinfection of medical waste is an accepted technology in the United States, and many of units have been successfully operated. Microwave disinf...
Microwave Remediation of Contaminated Soil

Microwave-assisted soil remediation has been applied to the cleanup of sites contaminated with volatile and semivolatile compounds, and microwave remediation is especially effective for the decontamination of polar compounds. Most soil constituents are transparent to microwaves, and thus the applied microwave energy is concentrated on contaminants and pore water. Several removal or immobilization mechanisms of soil contaminants such as thermal desorption, destruction, and vitrification are involved in the process of microwave heating depending on the types of contaminants, soil properties, and the addition of microwave absorbers. Similar to the method of soil vapor extraction, thermal desorption may cause vaporization of volatile and semivolatile organic compounds at temperatures below the ignition point of the contaminants, and it is also applicable to some volatile metal species such as mercury, arsenic, and lead. Destruction of contaminants was conducted by breaking the bonding within their molecular structure at a higher temperature than thermal desorption, and it is usually required to add a certain amount of microwave absorbers and conductors to contaminated soils for reaching the destruction temperature. Vitrification, an encapsulation method, oxidizes or thermally decomposes contaminants and immobilizes residual contaminants in a vitreous formation. Laboratory-scale trials of using microwave energy to remediate contaminated soils were mainly focused on the contamination with pentachlorophenol (PCP) (Abramovitch et al. 1998), PCBs (Abramovitch et al. 1999a), PAHs (Abramovitch et al. 1999b), hexachlorobenzene (HCB) (Abramovitch et al. 1998; Yuan et al. 2006), chromium (Tai and Jou 1999a), and heavy metals (Abramovitch et al. 2003).

Decontamination of Organic Compounds by Microwaves

It is well known that incineration of soils contaminated with chlorinated compounds may induce the formation of dioxins; for this reason catalytic reduction of chlorinated compounds is a better alternative for soil decontamination. Abramovitch et al. (1998, 1999a,b), have developed a series of studies investigating the decomposition of HCB, PCP, PCBs, and PAHs by using microwave energy, and the efficiencies of removing these compounds through microwave treatment are compared in Table 2. A modified machinable aluminum bomb, which allows the circulation of air around a quartz insert, was designed for solving the hot-spot problem during microwave irradiation (Abramovitch et al. 1998). The tested samples were prepared from clean soil by spiking a targeted compound, and a reagent containing Cu2O or Al powder and 10 N NaOH was blended into the tested samples. A 750 W domestic microwave oven at 2.45 GHz was employed, and heating of HCB-spiked samples was programmed as 1 min at 80% power and 2 min at 100% power in sequence. In the presence of Cu2O or Al powder and 10 N NaOH, the decomposition of HCB in soil was very effective (>80%) in all conditions and almost completely (>96%) under the optimum control. The decomposition of PCP in soil was found to be 94% at most under a similar control of reagent addition and microwave irradiation followed by acidification. Another 1,000 W microwave oven at 2.45 GHz was employed for high-pressure work, and heating of the PCBs-spiked samples was regularly maintained 25 min at full power or longer. The selection of 2,2',5,5'-tetrachlorobiphenyl (TCBP) and 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP) as the targeted compounds were used to prepare the soils contaminated with PCBs. The decomposition of TCBP in soil was remarkable with 97.9% using the reagent Cu2O/10 N NaOH and 87.7% using the reagent Al/10 N NaOH. Comparatively, the use of Cu2O/10 N NaOH and Al/10 N NaOH can only bring about 46 and 71% decomposition of HCBP in soil, and this result implicated that HCBP was more resistant to decomposition than TCBP. A trial of replacing 10 N NaOH with aqueous HCl showed that the decomposition of TCBP in soil was still effective for using Cu2O (93.4%), Al (91.8%), and Zn (98.7%).

Abramovitch et al. (1999a) continued their earlier work to investigate the possibility of in situ remediation of PCB-contaminated soils by microwave energy, and their first trial was to use graphite and metal rods instead of the Cu2O and Al powder used in the previous study. PCB-spiked samples were placed in the quartz insert of the modified ceramic aluminum bomb and microwave irradiated in a microwave oven allowing air circulation to keep the ceramic alumina relatively cool. The use of graphite powder led to much less decomposition of HCBP (47.2%) in soil; however, complete decomposition was achieved for most of the other PCBs. The decomposition of Aroclor 1254 and Aroclor 1268 was also successful in the presence of graphite fibers and 10 N NaOH within the sealed bomb. In order to simulate the condition of in situ remediation, testing of the spiked samples was conducted in an open-vessel system, which was a modified microwave oven equipped with an inverted funnel, a condenser tube, and a water vacuum pump for collecting off-gas materials. In an open-vessel system using graphite fibers and
The occurrence of soil vitrification in all cases catalytically hydrogenated and quantitatively dechlorinated by iron wire and pencil lead were equally effective and copper wire was rather inefficient, and the desorbed Aroclor 1254 was surrounded by the rod could be achieved. Testing results showed that iron wire and pencil lead were equally effective and copper wire was rather inefficient, and the desorbed Aroclor 1254 was modified from a 750 W domestic microwave oven at 2.45 GHz, heating as it was used in the previous study Abramovitch et al., 1999a, and bacterial colonies for the restoration of their original fertility.

Abramovitch et al. (1999b) also extended their trial to in situ decomposition of PAHs in soil, and the bench-scale model of an open-vessel system was employed to simulate in situ microwave heating as it was used in the previous study (Abramovitch et al. 1999a). Pencil lead and iron wire were used as the conductor of microwave energy, and PAH-contaminated soils were prepared from clean soil by spiking benzo(a)pyrene, benzo(b)fluoranthene, dibenz(a,h)anthracene, benzo(a)anthracene, 1-nitropyrene, and benzo(f)fluoranthene, individually. The open-vessel system was modified from a 750 W domestic microwave oven at 2.45 GHz, and heating of the PAH-spiked samples was regularly programmed as 10 min at 5%, 10 min at 10%, 10 min at 30%, and then 10 min at 100% power. The analysis showed that no decomposition products could be extracted from the soil following remediation. Microwave irradiation of the 14C-labeled TCBP resulted in 22% desorbed TCBP and 1–2.5% evolved 14CO2, and the dechlorinated fragments were very tightly bound and possibly encapsulated by the partially vitrified soil. Based on the determination of the decomposed products, the possible mechanisms of TCBP decomposition seemed to be self-condensation, dechlorination, oxidation, reduction, hydration, and fragmentation using microwave energy. This proposed method of in situ remediation is limited to the length of the conductor rods and the depth of the water layer, which may absorb and dissipate microwave energy. The remediate soils should reintroduce humus and bacterial colonies for the restoration of their original fertility.

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Table 2. Examples of Soil Decontaminations of Organic Compounds by Microwave Irradiation

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Addition</th>
<th>Microwaving</th>
<th>Decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCB&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Cu₂O (1% wt)/10N NaOH</td>
<td>1 min/600 W, 2 min/750 W</td>
<td>80.4–87.4%</td>
</tr>
<tr>
<td></td>
<td>Al (1% wt)/10N NaOH</td>
<td>1 min/600 W, 2 min/750 W</td>
<td>97%</td>
</tr>
<tr>
<td>HCB&lt;sup&gt;b&lt;/sup&gt;</td>
<td>MnO₂ (10 wt%)/50% H₂SO₄</td>
<td>10 min/750 W</td>
<td>100% (removal)</td>
</tr>
<tr>
<td></td>
<td>Fe (10 wt%)/5M Na₂SO₄</td>
<td>10 min/750 W</td>
<td>93.9% (removal)</td>
</tr>
<tr>
<td></td>
<td>10N NaOH</td>
<td>10 min/750 W</td>
<td>98.4% (removal)</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>10 min/750 W</td>
<td>71.3% (removal)</td>
</tr>
<tr>
<td>PCB&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Cu₂O (1.5% wt)/10N NaOH</td>
<td>1 min/600 W, 2 min/750 W</td>
<td>94.4%</td>
</tr>
<tr>
<td>PCB&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5% GAC</td>
<td>15 min/700 W</td>
<td>&gt;90%</td>
</tr>
<tr>
<td></td>
<td>5% GAC</td>
<td>15 min/300 W</td>
<td>70%</td>
</tr>
<tr>
<td>TCBP&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Cu₂O (4% wt)/10NNaOH</td>
<td>25 min/1000 W</td>
<td>97.9%</td>
</tr>
<tr>
<td></td>
<td>Al (4% wt)/10N NaOH</td>
<td>25 min/1000 W</td>
<td>87.7%</td>
</tr>
<tr>
<td></td>
<td>Cu₂O (4% wt)/10% HCl</td>
<td>90 min/400 W</td>
<td>93.4%</td>
</tr>
<tr>
<td></td>
<td>Al (3% wt)/15% HCl</td>
<td>40 min/400 W, 40 min/400 W</td>
<td>91.8%</td>
</tr>
<tr>
<td></td>
<td>Zn (10% wt)/36% HCL</td>
<td>25 min/1000 W</td>
<td>98.7%</td>
</tr>
<tr>
<td></td>
<td>Graphite (0.5%)/10N NaOH&lt;sup&gt;d&lt;/sup&gt;</td>
<td>10 min/600 W</td>
<td>100%</td>
</tr>
<tr>
<td>HCBP&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Cu₂O (3% wt)/10N NaOH</td>
<td>20 min/1000 W</td>
<td>46.1%</td>
</tr>
<tr>
<td></td>
<td>Al (3% wt)/10N NaOH</td>
<td>20 min/1000 W</td>
<td>71.1%</td>
</tr>
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<td></td>
<td>Graphite (0.5%)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1 min/600 W, 2 min/750 W</td>
<td>47.2%</td>
</tr>
<tr>
<td>DCBP&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Graphite (0.5%)/10N NaOH</td>
<td>10 min/600 W</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>Graphite (0.5%)/10N NaOH&lt;sup&gt;f&lt;/sup&gt;</td>
<td>10 min/750 W</td>
<td>98.6% (1.4% desorbed)</td>
</tr>
<tr>
<td>Aroclor&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Graphite (0.5%)/10N NaOH</td>
<td>1 min/600 W, 2 min/1000 W</td>
<td>100%</td>
</tr>
<tr>
<td>Benzo(a)-pyrene&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Pencil lead</td>
<td>10 min/38 W, 10 min/75 W, 10 min/225 W, 10 min/75 W</td>
<td>98.3% (1.7% desorbed)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Abramovitch et al. (1998).
<sup>b</sup>Yuan et al. (2006).
<sup>c</sup>Liu and Yu (2006).
<sup>d</sup>Abramovitch et al. (1999a).
<sup>e</sup>Reaction carried out in an open vessel; others in a closed reactor.
<sup>f</sup>Abramovitch et al. (1999b).
contaminated soil. The proposed microwave in situ decomposition process has been proven to be a more competitive alternative for the remedied of PCB- and/or PAH-contaminated soils as compared with some industrially developed bench-scale technologies and is shown in Table 3.

The use of MnO2 as a microwave absorber to remediate HCB-spiked contaminated soil was first investigated by Yuan et al. (2006). HCB-spiked samples were prepared from diatomite, mixed with MnO2 or Fe powder, added to H2SO4, NaOH, H2O, or Na2SO4 aqueous solution, and then sealed in a vial for carrying out the decomposition of HCB in a 750 W domestic microwave oven at 2.45 GHz. The result showed that MnO2 works efficiently to decompose HCB in strong acidic media and restricts the decomposition in basic and neutral media. The complete removal of HCB can be attained in the presence of MnO2 (50%) with 10 min microwave irradiation. Even though the decomposition of HCB was much faster in acidic media than in basic media using Fe powder instead of MnO2, the difference of HCB removal was not significant whether using solutions of H2SO4, NaOH, H2O, or Na2SO4. Without addition of any microwave absorbers, more than 95% removal of HCB was observed with 10 min microwave irradiation when adding aqueous solutions alone. Microwave treatment of practical HCB-contaminated soil could induce a promising decomposition in basic media, and the contaminant level was reduced from 55.8 to 0.91 mg kg−1. Also, removal of HCB in soil was 71.3% when using water as a microwave absorber.

Liu and Yu (2006) explored the role of granular-activated carbon (GAC) on microwave remediation of PCB-contaminated soil that GAC acts not only as microwave absorber but also as reductant for dechlorination. A novel reactor, a modified 850 W domestic microwave oven at 2.45 GHz equipped with a quartz column reactor, a thermocouple, and a condensing system, was designed to create a pseudovacuum environment without the use of nitrogen sweep gas or the installation of vacuum pump. A model compound of 2,4,5-trichlorobiphenyl (PCB29) was spiked to prepare the testing samples, and three different levels of GAC were added to the samples before being subjected to microwave irradiation. The results showed that rates of the PCB29 removal were determined by microwave power, soil moisture content, and the addition of GAC. The addition of GAC effectively enhanced the heating temperature to 200–500°C depending on the introduced amount after 15 min microwave irradiation. A successful case at 700 W microwave power demonstrated that more than 90% degradation of PCB29 was achieved with 5% added GAC and 0.54% water content after 15 min microwave irradiation. For a higher water content (>15%) case, it was observed that the removal of PCB29 from the soil was through thermal desorption instead of decomposition or a fixation mechanism.

In the presence of soil moisture, the removal of polar and nonpolar compounds in soil is possible through steam distillation, by which microwave-generated steam may cause trapped contaminants thermally desorbed and vaporized. Kawala and Atamanzuk (1998) reported the remediation of trichloroethylene (TCE)-contaminated sand in a pilot-scale microwave heating system, mainly consisting of a microwave generator, a power supply, and a stub antenna. Sand weighing 1,000 kg was loaded in a cylindrical container 1 m in diameter and 0.9 m in height, and a contaminant discharge was simulated by decanting 40 L of TCE onto the soil. A perforated PTFE tube was installed in the vertical axis of the container, connecting to a vacuum pump to act as a vapor extraction well. In the pilot-scale system, microwave energy was supplied intermittently every 12 min work time with a 3 min pause, and vapor generated in the heated soil was drawn by a convective air stream to the condenser. The decrease of TCE was found to be only 0.01–2.2% in the heated zone after 24 h remediation, and a maximum local temperature reached 70°C at the middle depth of the soil container. During 75 h of remediation, the energy supply summed up 36 kW h or 130,000 kJ resulting in 19 kg of TCE and 11.6 kg of water removed.

A similar laboratory study by Di and Chang (2001) investigated the possible removal of PCBs from contaminated soil by microwave-generated steam. The experimental apparatus consisted of a microwave generator, a waveguide, a water circulator, a microwave applicator, a quartz column, a condenser, a vacuum pump, and several power meters or thermocouples. A column for the containment of samples was placed in a waveguide connected to a laboratory microwave generator, and the subjected microwave power was unidirectional, resulting in partial absorption of microwave energy by the sample. The PCB-contaminated soil was amended with water between steaming cycles, and then irradiated about 2 min to boil the water at 600 W in the system. This procedure was repeated 10–15 times until the PCBs were removed from the soils. The results showed that a faster water evaporation process concurred with a higher microwave power application, and 98% removal of PCBs in soil can be achieved at a steam-to-soil mass ratio of 3:1 using microwave-generated steam. Evaporation was identified as the dominant mechanism for the removal of PCBs from the soil, moreover, increased solubility of PCBs into the heated aqueous phase contributed to their removal from the bound phase.

Decontamination of Toxic Metals by Microwaves

The microwave in situ decomposition process developed by Abramovitch et al. (1999a, 1999b) was successfully applied to remediate soils contaminated with PCBs and PAHs as mentioned earlier, and the trial of using the same technology to remediate soils contaminated with toxic metals such as Cd2+, Mn2+, Th4+, Cr3+, and Cr6+ has been reported (Abramovitch et al. 2003). The bench-scale model of an open-vessel system mainly consisted of a 564 W domestic microwave oven, a rudimentary vapor trap, and a reactor vial. The rudimentary vapor trap was built with an inserted funnel connected to a cold trap outside the oven for the
collection of any volatile organic or inorganic materials. Pencil lead was vertically inserted in the center of the soil samples, and a plug of glass wool was loosely overlaid above the soil. Testing samples were prepared by spiking the targeted metals, and several heating programs up to 12 min at full power were used for microwave irradiations. For Mn\(^{2+}\), Cd\(^{2+}\), Th\(^{4+}\), or Cr\(^{3+}\)-spiked samples, the extractable concentration after remediation exceeded the level of that normally present in the clean soil was observed. The result corresponded to a complete immobilization of these metals, and the remediation of Cr\(^{6+}\)-spiked samples was found to be more than 99% for a high level and up to 93% for a low level of spiking. The soil was partially vitrified in this process, which makes in situ remediation of toxic metals in soil by means of microwave energy viable.

Microwave energy can be applied to the vitrification of contaminated soils, coinciding with immobilizing heavy metal ions in soil. Tai and Jou (1999a) reported a laboratory practice of immobilizing Cr-contaminated soil with the addition of GAC and iron wire through microwave irradiation. The initial level of Cr\(^{6+}\) in testing samples was 260 mg/L by spiking K\(_2\)CrO\(_4\), the addition of two microwave absorbers was used upon selection—GAC overlaid uniformly on soil and iron wire inserted into the soil. Samples were irradiated 50 min at 800 W in a domestic microwave oven, and vitrified glass/ceramic and nonvitrified soil formations were noticed after microwave treatment. The U.S. Environmental Protection Agency (USEPA) allowable leaching concentration of 5.0 mg/L for chromium served as the threshold of determining the success of this microwave immobilization process. The results showed that the immobilization rate was affected by the reactor’s surface area exposed to microwave irradiation, along with the immobilization of chromium in soil reaching above 90% in most cases. Vitrification phenomenon can be regarded as an indicator of the effective immobilization, but it is not a prerequisite for immobilizing chromium in soil. A vitrified glass/ceramic formation was developed within the 15 min treatment with the concurrence of a great enhancement on immobilization, while the nonvitrified soil formation achieved only partial immobilization that could not guarantee success of the treatment. Immobilization of chromium in soil was successfully demonstrated by microwave energy with the addition of GAC or iron wire, and the efficiency of this technique was affected by the initial contaminant level, irradiation time, reactor surface area, and the additive.

**Microwave Remediation of Wastewater**

The heating effect of microwave energy may overcome the activation energy barrier and accelerate the reaction rate of many chemical reactions, and one practical case of microwave heating was applied to enhance the reduction of perchlorate in water by elemental iron (Oh et al. 2006). Perchlorate salt serves as an oxidizer in solid propellants for rockets and missiles, and the removal of perchlorate is ineffective by carbon adsorption and ultrafiltration due to its high water solubility. Zero-valent iron can transform perchlorate to chloride; however, the occurrence of these reduction reactions is very slow under ambient condition. A 500 W microwave digester was evolved as a heating source, in which the batch reactor could be maintained at a desired temperature between 125 and 200°C. The results showed that the rate and extent of perchlorate reduced by elemental iron increased with the rise of the heating temperature. Rate constants of perchlorate reduction at elevated temperature were approximately raised by three orders of magnitude compared to that at room temperature. Perchlorate removal by elemental iron reached 79, 91, and 100% within 2 h at 150, 175, and 200°C, respectively. Thus, the microwave-assisted iron reduction process may be an alternative for complete removal of perchlorate from industrial discharge.

Abramovich and Caprocotta (2003) proposed a simple method of filtering contaminated water through a plug of soil followed by microwave irradiation of the soil to decompose the contaminants. PCP is selected as one example of using such a filter-adsorbent method, by which water contaminated with other organic pollutants such as lindane, dieldrin, and aldrin can be remediated. The laboratory-scale model was operated in such a way that the prepared PCP solution was filtered slowly under vacuum through a plug of clean soil, and the contaminated soil was subsequently subjected to microwave irradiation in the open-vessel system as used in the microwave in situ decomposition process (Abramovich et al. 1999a, b). The results showed that the filtrate was contaminant free and no PCP could be extracted from the soil. While using the acidified soil as a filter adsorbent, the filtrate was still contaminant free, but 28.7% of PCP could be extracted from the soil. This finding revealed that PCP possibly formed an unextractable complex, such as metal phenoxides, with the soil at a higher pH environment. By the proposed scheme, the adsorbed PCP in soil can be destructed completely or decomposed fragments bound irreversibly to the soil under microwaving.

Carbon adsorption, a widely used process of water purification, has been found to be capable of removing various synthetic organic compounds, chlorinated solvents, and petroleum hydrocarbons from effluents. A trial of using microwave energy associated with GAC adsorption for removing contaminants from water was reported (Jou and Tai 1998; Tai and Jou 1999b), and the proposed process used a GAC packed bed to adsorb contaminants such as benzene, toluene, xylene (BTX), and phenol from effluents; then employed a microwave radiation field to decompose the sorbed contaminants within GAC, likely the so-called GAC regeneration. Treatment of the waters contaminated with 20 mg/L benzene, 30 mg/L toluene, 24.6 mg/L xylene, or 13.4 mg/L BTX was very effective, and the sorbed contaminants were all completely decomposed to H\(_2\)O and CO\(_2\) within 90 s in a 1,000 W microwave oven (Jou and Tai 1998). The maximum adsorption of phenol was found to be 220 mg/g when treating an initial effluent of 400 mg/L by the GAC packed bed, and the adsorption effect of a two-stage GAC packed bed was superior to a single-stage system. Both single- and two-stage GAC packed beds demonstrated successful removal from phenol-contaminated effluent, and the following microwave treatment performed the complete destruction of phenol sorbed in GAC through the mechanisms of thermal desorption, steam distillation, thermal destruction, and arcing destruction (Tai and Jou 1999b). During microwave heating of GAC, arcing phenomena were observed in 30–60 s, enhanced in 90 s, and then turned into a glowing flame. The temperature of the microwave-irradiated GAC was believed to reach 1,200–1,800°C during the occurrence of arcing, and the local temperature was suspected to shoot up to 5,000–10,000°C at the arcing spot.

**Microwave-Assisted Regeneration of Activated Carbon**

There are two types of regeneration techniques of activated carbon beds commonly used in the industrial application—the ther-
mal regeneration method using steam, carbon dioxide, or inert atmosphere and the chemical regeneration method using pH-swing or solvent extraction (Ania et al. 2007). A significant deterioration of the adsorbent’s pore structure was inevitable after regeneration, and thus the specific surface area available for adsorption was reduced (Abdul and Campbell 1996). Microwave irradiation can induce homogeneous and quick thermal reactions due to its characteristics of molecular-level heating, so it is considered a potentially viable alternative for regeneration of exhausted GAC. The laboratory-scale trials of using microwave energy to facilitate both thermal regeneration (Ania et al. 2007; Quan et al. 2004) and chemical regeneration of activated carbon (Dabek 2003) have been reported.

Ania et al. (2007) investigated regeneration of activated carbon used in the purification of pharmaceutical wastewater by microwave irradiations, and salicylic acid served as the targeted bon used in the purification of pharmaceutical wastewater by exhausted GAC. The laboratory-scale trials of using microwave energy to facilitate both thermal regeneration (Ania et al. 2007; Quan et al. 2004) and chemical regeneration of activated carbon (Dabek 2003) have been reported.

Another thermal regeneration study investigated the microwave regeneration of different GACs exhausted with Acid Orange 7 (AO7), a colorant in textile and paper industries (Quan et al. 2004). The GACs used in the experiments were originally made from coconut shells, almond nucleus, and coal. The GACs were saturated with AO7 in a continuous-flow adsorption column, then dried at 120°C for 6 h, and regenerated for 5 min in a modified 850 W domestic microwave oven. A quartz reactor installed into the oven was connected to a condensing system, by which the distillate as well as the vapor were collected in a 0.1 N NaOH solution. The adsorption-microwave regeneration cycles were repeated four or eight times, and the regeneration yields were very high in most cycles. The adsorption capacities of the three virgin GACs followed in ascending order as coconut shell-, coal-, and almond nucleus-based GACs. The original neutral-pH character of all three GACs tended to shift to a basic character after microwave irradiation, thus resulting in the reduction of forming deposits inside the carbon matrix in successive cycles.

As mentioned in the section of microwave remediation of wastewater, microwave irradiation was employed alone for its thermal effect or incorporated with GAC for the decomposition of sorbed pollutants onto the GAC. Several research works proposed different microwave-incorporated remedial techniques for treating various toxins in aqueous solutions, such as microwave irradiation in association with GAC (Bo et al. 2006), H2O2 (Klan and Vavrik 2006; Zhang et al. 2006), UV/H2O2 (Han et al. 2004; Klan and Vavrik 2006), TiO2 nanotube (Zhanqi et al. 2007), TiO2-mounted activated carbon (Liu et al. 2007), and UV/TiO2 (Horikoshi et al. 2002, 2004b) techniques. Comparisons with treatment efficiencies of various microwave-incorporated remedial processes are summarized in Table 4.

A microwave-assisted oxidation process using a GAC fixed bed was proposed for the removal of p-nitrophenol (PNP) form its aqueous phase (Bo et al. 2006). A quartz cylindrical reactor containing GAC was established in a modified domestic microwave oven (500 W), and the PNP solution as well as an air steam were drawn through the reactor in a continuous-flow mode. In this process, GAC acts as a microwave absorber as well as the catalyst for PNP degradation, and air supplies as the oxygen source for the oxidation of PNP. Under microwave irradiation, the effluent in the reactor was heated to a boil and the GAC fixed bed reached 220–300°C on the top, which was in favor of decomposing PNP on the GAC surface. The result showed that 90% PNP removal was achieved from an initial contaminated level of 1,330 mg/L after 3 h treatment. A higher removal of PNP occurred at a condition of high microwave power, high GAC dose, or long reten-
As the microwave-assisted oxidation process, a GAC fixed bed improved the biodegradability of wastewater apparently, and PNP could experience sequential oxidative reactions and ultimately mineralized through the proposed process.

### Microwave-Enhanced Advanced Oxidation Techniques

The microwave (MW) effect of various microwave-enhanced advanced oxidation techniques including MW/UV, MW/UV/H₂O₂, MW/UV/TiO₂, and MW/UV/TiO₂/H₂O₂ was examined on the degradation of 4-chlorophenol (4-CP) with or without microwave irradiation (Zhihui et al. 2005). A modified domestic microwave oven (750 W) and an electrodeless discharge mercury lamp (110 W) were employed to allow the reaction mixture to interact with UV irradiation in a microwave field. The comparison showed a sensational result that the degradation rates with microwave irradiation were nearly double those without microwave irradiation. 4-CP could not be degraded either by H₂O₂ alone or by microwave alone, but it was oxidized to a considerable extent when incorporating H₂O₂ with microwave irradiation. This finding can be explained since microwave irradiation causes localized superheating to induce the generation of OH radical from H₂O₂, thus promoting the oxidation of 4-CP. In the UV process, microwave irradiation can generate more electronically excited states of 4-CP, resulting in a higher efficiency of 4-CP removal. The role of microwave irradiation in the integrated TiO₂ process is to cause the polarization effect of the highly defected TiO₂, and thus improve the photocatalytic efficiency of TiO₂ for 4-CP removal. Another study on the degradation of 4-CP also pointed out that microwave irradiation played an important role in enhancing the generation of reactive OH radicals in the MW/UV/TiO₂ system (Ai et al. 2005). The employment of the MW/UV/TiO₂ process can perform nearly complete degradation as well as complete dechlorination of 4-CP, which is superior to the UV/TiO₂ process.

Klan and Vavrik (2006) examined the effect of microwave irradiation on the photolytic noncatalytic oxidative degradation under UV irradiation. A modified 900 W microwave oven offered the source of microwave radiation, and a conventional high-pressure Hg discharge lamp (400 W) served as the UV irradiation source. The MW/UV/H₂O₂ process proved to be very successful in the degradation of phenol, chlorobenzene, nitrobenzene, 4-CP, and PCP in addition to the degradation rates of five tested aromatic compounds by the MW/UV/H₂O₂ process was superior to the MW/H₂O₂ process and the UV/H₂O₂ process. Han et al. (2004) also reported that microwave irradiation caused considerable improvement in phenol degradation in a UV/H₂O₂ system. A reactor was subjected to UV irradiation from an 8 W low-pressure Hg lamp and microwave irradiation from a 1,000 W microwave generator at 2.45 GHz. The degradation rate of phenol was found to be 60% higher with microwave irradiation, and microwave irradiation gave an even larger extent of improvement on the TOC removal than the disappearance of phenol. It revealed that the MW/UV/H₂O₂ process could effectively decompose most degradation intermediates of phenol and eventually mineralize them into CO₂ and H₂O. The kinetic study illustrated that the governing reaction of phenol was attacked by OH radical without microwave irradiation in the UV/H₂O₂ system; meanwhile, a direct reaction of phenol with H₂O₂ might be dominant with microwave irradiation in the system. Zhang et al. (2006) investigated the degradation of acid orange (AO7) in a MW/H₂O₂ system, and a microwave electrodeless lamp filled with Hg and Ar was utilized as the light source in a 700 W domestic microwave oven. The light emission of the microwave electrodeless lamp was mainly in the range of the visible region; however, the microwave electrodeless lamp was more effective than the traditional electrode lamp in AO7 degradation. The use of a microwave electrodeless lamp with H₂O₂ was found to be more effective than its single use in AO7 degradation, and the microwave electrodeless lamp provided simultaneous irradiation of waste streams by both microwave and UV-VIS light.

A novel process employed microwave-assisted photolysis on TiO₂ nanotubes to degrade atrazine, and better efficiency of atrazine degradation was expected based on the larger surface area of TiO₂ nanotubes for improving its photocatalytic activity (Zhanqi et al. 2004a). Employment of TiO₂ nanotubes drew an exciting result that atrazine was completely degraded in 5 min and achieved 98.5% mineralization in 20 min. Since the energy of microwave radiation was insufficient to disrupt covalent bonds of organic molecules, the complete degradation of atrazine was attributed to both photolysis and photocatalysis. Microwave-

| Table 4. Comparisons with Treatment Efficiencies of Various Microwave-Incorporated Processes |
|-----------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|
| Process                                             | 4-CP (%)                                           | Phenol (%)                                         | Atrazine (%)                                        | Rhb (%)                                             | 2,4-D (%)                                           | BPA (%)                                             | Benzoic acid (%)                                   |
| MW                                                  | 2                                                 | 4                                                  | —                                                   | <1                                                  | <1                                                  | <1                                                  | —                                                   |
| UV                                                   | 22                                                | —                                                  | —                                                   | —                                                   | —                                                   | —                                                   | —                                                   |
| MW/UV                                               | 53                                                | 40                                                 | 69                                                  | —                                                   | —                                                   | —                                                   | —                                                   |
| UV/TiO₂                                             | 39                                                | —                                                  | —                                                   | 68                                                  | 33                                                  | 67                                                  | 14                                                  |
| MW/UV/TiO₂                                          | 83                                                | 87                                                 | 100                                                 | 97                                                  | 50                                                  | 95                                                  | 37                                                  |
| UV/H₂O₂                                             | 40                                                | —                                                  | —                                                   | —                                                   | —                                                   | —                                                   | —                                                   |
| MW/UV/H₂O₂                                          | 73                                                | —                                                  | —                                                   | —                                                   | —                                                   | —                                                   | —                                                   |
| UV/TiO₂/H₂O₂                                        | 50                                                | —                                                  | —                                                   | —                                                   | —                                                   | —                                                   | —                                                   |
| MW/UV/TiO₂/H₂O₂                                     | 92                                                | —                                                  | —                                                   | —                                                   | —                                                   | —                                                   | —                                                   |

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Zhihui et al. (2005).
Liu et al. (2007).
Zhanqi et al. (2007).
Horikoshi et al. (2002).
Horikoshi et al. (2003b).
Horikoshi et al. (2004a).
Horikoshi et al. (2004c).
assisted photodegradation of atrazine showing more efficiency than traditional photocatalytic degradation may be ascribed to the microwave-excited state of TiO₂, the microwave-induced hydrophobic nature of TiO₂, the microwave-generated defect sites on TiO₂, as well as the larger surface area of TiO₂ nanotubes. Another new trial of using microwave-assisted photocatalysis on TiO₂-mounted activated carbon to degrade phenol was proposed by Liu et al. (2007). Synthesized TiO₂-mounted activated carbon possesses a BET surface area of 800 m²/g and a strong optical absorption capacity with a bandgap around 360 nm. Microwave-assisted photocatalytic degradation using synthesized TiO₂-mounted activated carbon performed 87% removal of phenol, which was much better than that of microwave-assisted photodegradation (PD) (43%) and microwave irradiation (7%). Compared to commercial Degussa P-25 TiO₂, the degradation rate of phenol by synthesized TiO₂-mounted activated carbon was found to be twofold faster.

**Integrated Microwave/UV Illumination Technique**

Horikoshi et al. (2002) developed a series of studies to investigate the performance of an integrated microwave/UV-illumination method, which employed a 2.45 GHz, 1.5 kW microwave generator and a 75 W Hg lamp with 0.3 mW/cm² irradiance in the wavelength range of 310–400 nm. Microwave radiation and UV sources were established on the side of the reactor, orthogonal to each other. The Degussa P-25 TiO₂ was loaded in a sealed cylindrical reactor with the continuous microwave radiation and UV light under magnetic agitation. The integrated microwave/photocatalytic method in the presence of TiO₂ particulates was applied to the degradation of many pollutants in wastewater, including Rhodamine-B (RhB) (Horikoshi et al. 2002, 2003a), bisphenol-A (BPA) (Horikoshi et al. 2004a), 2,4-dichlorophenoxacycetic acid (2,4-D) (Horikoshi et al. 2003b, 2004b), 4-CP (Horikoshi et al. 2006), carboxylic acids, aldehydes, alkoxycarbonyl, and phenolic substrates (Horikoshi et al. 2004c).

The study of the degradation of RhB using the integrated microwave/UV-illumination method (PD/MW) process pointed out that aqueous RhB/TiO₂ dispersion absorbed 98.8% of microwave radiation, while TiO₂ particles alone absorbed 4.8% after 3 min of irradiation under aerobic conditions (Horikoshi et al. 2002). About 97% of the RhB solution was discolored after 180 min by the PD/MW process, which was superior to 68% discoloration by the TiO₂ photocatalytic method alone. Also, discoloration by the PD/MW method was found to be threefold faster than the UV/TiO₂ method alone and 10-fold faster than the thermally assisted UV/TiO₂ method. The PD/MW process prefered converting the two nitrogen atoms rather than breaking the rings or mineralizing the carbon atoms in the RhB structure. The yields of the two nitrogen atoms after 3 h of irradiation were 77% for the PD/MW process, 12.8% for the UV/TiO₂ method, and 8% for the microwave method. Microwave irradiation seemed to enhance the degradation of RhB, but it showed effectiveness in decomposing RhB rather than degrading the intermediates formed in the process. Another study of the degradation of RhB reported that the PD/MW process under UV/Vis irradiation induced deethylation and degradation of the intermediate in a relatively short time, and the nitrogen atoms in RhB were predominantly converted to NH⁺ ions after 120 min of irradiation (Horikoshi et al. 2003a). The microwave effect was obvious as coupling to the TiO₂ photocatalytic degradation with UV radiation, and the increase in the hydrophobic character of the TiO₂ surface through microwave irradiation facilitated adsorption of RhB with a consequent impact on the photodegradative process. Besides modifying the hydrophilic/hydrophobic balance in TiO₂ particles, microwaves also induced additional localized defects on the TiO₂ surface, and thus significantly affected the degradation kinetics. Therefore, the major difference between the thermally assisted UV/TiO₂ method and the PD/MW process revealed that microwave nonthermal effects impacted both the extent and efficiency of the photodegradation of RhB.

The PD/MW process was also applied to the degradation of 2,4-D using a similar apparatus (Horikoshi et al. 2003b). The degradation of 2,4-D by the PD/MW process was found to be more effective than the thermally assisted UV/TiO₂ method and the UV/TiO₂ photocatalytic method based on the assay by loss of UV absorptions, TOC decay, and the dechlorination. However, microwave irradiation alone of aqueous dispersion had no effect on either the break-up of the aromatic ring, the loss of TOC, or the dechlorination of 2,4-D. As mentioned earlier, microwave radiation may modify the nature of the TiO₂ surface such that the photodegradation of pollutants will become more efficient under the PD/MW process relative to the UV/TiO₂ method alone. The formation of OH radicals by the PD/MW process was found to be more efficient than that by the UV/TiO₂ photocatalytic method. Clearly, microwave radiation seems to act predominantly on the oxidative route to degrade pollutants, and have relatively minor impact on the reductive reactions occurring at the TiO₂ surface. A trial of conducting the PD/MW process in a modified microwave oven also reported its effectiveness on degradation of 2,4-D (Horikoshi et al. 2004b). A Teflon batch-type reactor with a double glass cylindrical plasma lamp (DGCPL) was incorporated into a domestic microwave oven used in the photocatalytic degradation of 2,4-D in which microwave irradiation was coupled to the UV–Vis irradiation emitted by the DGCPL source. The results echoed that the PD/MW process was about 10 times more efficient than the UV/TiO₂ photocatalytic method. The greater efficiency of the PD/MW process was ascribed to the nonthermal effect of microwave radiation on the opening of the aromatic ring of 2,4-D, but not apparently on the dechlorination process due to a negligible influence of microwave radiation.

Thermal and nonthermal effects of microwave irradiation originating from the PD/MW process were examined on the degradation of benzoic acid, diethyl phthalate (DEP), and dimethyl phthalate (DMP) (Horikoshi et al. 2004c). By using the experimental setup of the PD/MW process, a similar result was expected that the degradation of benzoic acid through the PD/MW process (37% TOC loss) was superior to the UV/TiO₂ method (14%) and the thermally assisted UV/TiO₂ method (10%). However, microwave irradiation alone had no consequence in the degradation of benzoic acid. Microwave thermal effects have a bearing on the cleavage of the aromatic ring of benzoic acid, and also its nonthermal effects might affect the generation and decomposition of intermediates and cause photoinduced desorption of benzoic acid from the TiO₂ surface. The degradation pathway of benzoic acid induced by the PD/MW process was quite different from that by the UV/TiO₂ method alone. It was observed in different microwave effects on ethoxycarbonyl and methoxycarbonyl compounds that microwave radiation alone had no consequence on DMP but resulted in significant degradation and partial mineralization of DEP. Microwave effects were significantly magnified in the course of the oxidative process when coupled with the TiO₂ dispersion, and the degradation of DEP by the PD/MW process was found to be sevenfold more efficient than the UV/TiO₂ method. Microwave irradiation caused the hydrophobic character of the TiO₂ surface, and it explained that the extent of
soils in a pilot-scale microwave heating system; along with an-

ization. The technique of using microwave-generated steam is

trapped contaminants through thermal desorption and evapor-
distillation can generate steam when microwaving water-logged

of microwave absorbers or conductors. One process called steam

temperature than thermal desorption usually requires the addition

heating, while destruction of contaminants occurring at a higher

pounds as well as volatile metal species through direct microwave

cause vaporization of volatile and semivolatile organic com-
taminants through various mechanisms such as thermal de-
sorption, destruction, and vitrification. Thermal desorption may

cause vaporization of volatile and semivolatile organic com-

ities, and the addition of microwave absorbers, the applied micro-

water content as well as the containing of microbial biomass.

Microwave treatment of sewage sludge can improve its de-

contaminated with PCP, PCBs, PAHs, HCB, and heavy metals.

waste management.

a combination of incineration and microwaving in the practice of

While taking the disposal expense of medical wastes into account,

of medical wastes by microwaving may result in nearly a 10-fold

bility. With the addition of char, the pyrolysis of sewage

sludge up to 900°C becomes real, which brings about a signifi-

volume reduction and the formation of the basic char either

for the successive addition or as economical absorbents.

Microwave disinfection of medical waste is another successful

application of microwave technology, which utilizes a steam-

based process to bring about pathogen destruction. The treatment

of medical wastes by microwaving may result in nearly a 10-fold

reduction of operational cost as compared to on-site incineration.

While taking the disposal expense of medical wastes into account,

the most economical treatment and disposal option turns out to be

a combination of incineration and microwaving in the practice of

hospital waste management.

Several laboratory-scale studies have successfully demon-

strated the application of microwave energy to remediate soils

contaminated with PCP, PCBs, PAHs, HCB, and heavy metals. Most

soil constituents are transparent to microwave, and thus the

applied microwave energy is concentrated on contaminants and

pore water. Depending on the types of contaminants, soil proper-
ties, and the addition of microwave absorbers, the applied micro-

wave energy may cause the removal or immobilization of soil

contaminants through various mechanisms such as thermal de-
sorption, destruction, and vitrification. Thermal desorption may

cause vaporization of volatile and semivolatile organic com-

pounds as well as volatile metal species through direct microwave

heating, while destruction of contaminants occurring at a higher

temperature than thermal desorption usually requires the addition

of microwave absorbers or conductors. One process called steam

distillation can generate steam when microwaving waterlogged

soils, and the microwave-generated steam can cause the release of

the trapped contaminants through thermal desorption and evap-

oration. The technique of using microwave-generated steam is

applied to the possible removal of TCE from the contaminated

soils in a pilot-scale microwave heating system; along with an-

other laboratory-scale trial which has confirmed the success of

nearly complete removal of PCBs from the contaminated soils by

microwave-generated steam. With the addition of microwave ab-
sorbers or conductors, the remediation of toxic metals in soil can

be accomplished through vitrification during microwave irradia-
tion. Vitrification of contaminated soils coincides with immobiliz-
ing heavy metal ions in a vitreous formation, and several

laboratory-scale trials have successfully demonstrated a complete

immobilization of heavy metals in soils by microwave application

with the addition of microwave absorbers or conductors.

Microwave energy is also successfully applied to the cleanup

of wastewater. The thermal effect of microwaving can promote

the iron reduction process to attain a complete removal of per-

chlorate from industrial discharge. Microwave irradiation inte-
grated with a GAC packed bed has been proven very effective for

the removal of the aqueous BTEX, phenol, and PNP. The aqueous

contaminants can be removed by GAC adsorption, and subse-

quently, desorbed or destructed under microwaving. Besides, mi-
crowave energy can be effectively utilized to facilitate the thermal

regeneration as well as the chemical regeneration of activated

carbons. GAC regeneration is favorable under a high temperature

and oxidizing environment, and the narrow micropores can be

enlarged after microwave treatment.

Several novel microwave-incorporated techniques have been

developed for the treatment of various toxins in aqueous solutions

recently, such as microwave irradiation in association with H2O2,

UV/H2O2 UV/TiO2, TiO2 nanotube, and TiO2-mounted activated

carbon. Microwave irradiation can cause localized superheating

to induce the generation of OH radical from H2O2 for an efficient

oxidation of aqueous pollutants. The MW/UV/H2O2 process

proved to be very successful on the degradation of phenol, chlo-

robenzene, nitrobenzene, 4-CP and PCP, by which the degrada-
tion rates of these aromatic compounds are superior to those by

the MW/H2O2 process and those by the UV/H2O2 process.

The employment of a TiO2 nanotube in the microwave-assisted pho-
todegradation of atrazine brings about almost a total mineraliza-
tion in 20 min, and this promising result may be ascribed to the

microwave-excited state of TiO2, the microwave-induced hydro-

phobic nature of TiO2, the microwave-generated defect sites on

TiO2, as well as the larger surface area of TiO2 nanotubes.

Compared with the commercial Degussa P-25 TiO2, the degrada-
tion rate of phenol by the synthesized TiO2-mounted activated carbon

was found to be twofold faster. The microwave effect is obvious

as coupling to the TiO2 photocatalytic degradation with UV ra-
diation, and the integrated microwave/UV illumination process

has effectively improved the degradation of RhB, 2,4-D, benzoic

acid, and DEP. Microwave radiation seems to act predominantly

on the oxidative route to degrade pollutants, and the nonthermal

effect of microwaving causing a hydrophobic nature on the TiO2

surface may affect the generation and decomposition of the de-
graded intermediates.

This paper has shown the potential of microwave applications

as remedial alternatives for the treatment of contaminated soil,

sludge, medical waste, spent activated carbon, and wastewater.

Microwave application and microwave-assisted technology ap-
pear to be very successful in many situations as a remedial tool,

while most of the successful cases are demonstrated on the labo-

ratory scale. Even though a number of benefits are apparently

applying microwave irradiation to promote the accomplishment

of remediation, full-scale application of the microwave-assisted

processes is still underway.
References


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