

Mitigation and remediation technologies for organic contaminated soils

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Abstract Organic contaminated soils have become a widespread environmental problem, which may lead to a great threat to the quality of agricultural production and to human health. Physical, chemical, and biological technologies have been employed for the mitigation and remediation of organic contaminated soils. This paper reviews the progress of mitigation and remediation technologies for organic contaminated soils and suggests two different strategies for the mitigation of ‘slightly-contaminated’ agricultural soils and the remediation of ‘heavily-contaminated’ soils/sites, respectively. On this basis, directions for future research in this field are suggested.

Keywords organic contaminated soil, mitigation, remediation, bioavailability

1 Introduction

The contamination of soils by organic pollutants has become a widespread environmental problem. Soil organic contaminants, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine compounds (OCs), organophosphorous compounds (OPs), phenols, and so on, are of great environmental concern due to their widespread occurrence, persistence, complexity, and possible effects on health [1–4]. A large number of surveys over the world have provided a rich source of essential data about spatial distributions and concentration levels of soil organic contaminations [5–11]. Contamination levels in different regions around the world vary greatly. There are several factors influencing the spatial distributions of contamination, such as the contents of soil organic matter, long-range atmospheric transport, types of

land use, population density, and gross domestic product (GDP) [3,8–10,12]. Different actions should be conducted for organic contaminated soils: mitigation for the ‘slightly contaminated’ agricultural soils and remediation for the ‘heavily contaminated’ sites (Fig. 1).

Generally speaking, the contamination has spread from urban to rural areas, and the agricultural soils are widely but relatively lightly contaminated. In China, about 93,000 km² of soil were contaminated by pesticides. Tao and Wang [8] pointed out that the highest PAH concentrations in Tianjin were measured in urban soils, followed by rural village soils. The toxic organic contaminants, such as PAHs, would enter vegetables and crops cultivated on the contaminated soils and cause a great threat to the product quality and subsequently to human health [13–20]. However, in some developing countries, such as China, the slightly contaminated soils are still used for agricultural production to ensure food supply due to the shortage of cultivatable land [21–23]. There is an urgent need for in situ contamination mitigation techniques to reduce the uptake of contaminants from soil to plants, in order to obtain safe agricultural products from the slightly contaminated soils.

On the other hand, since the 1980s, a number of researches and policies have focused on the remediation of heavily contaminated soils/sites because of their greater environmental impact. The data from ISI Web of Knowledge reveals that to date, there are more than eight thousand papers concerned with soil remediation, and the amount of literature in the field has increased a hundred-fold in the past 20 years. In the United States, the approach to soil remediation is based on directives issued by the environmental protection agency (EPA) [24]. In Canada, the Council of Ministers of the Environment encourages each province to conduct remediation and reclamation efforts. At present, the European countries are also creating standards that will serve as the foundation for comprehensive remediation strategies. Recently, in China, more and

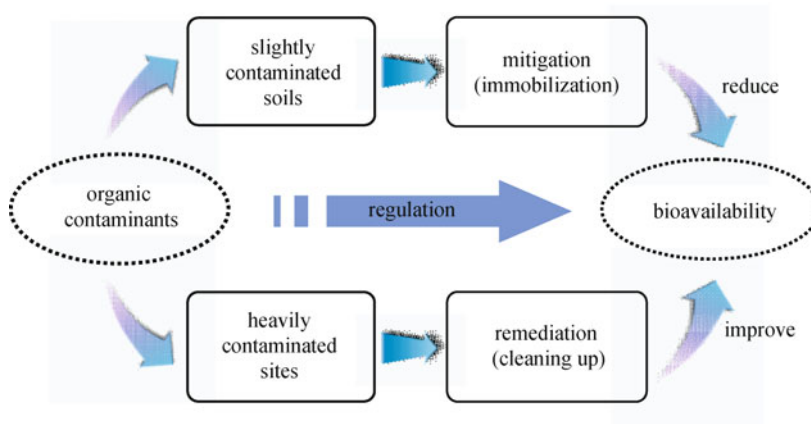


Fig. 1 Strategies of mitigation and remediation for slightly, and heavily contaminated soils/sites

more academic institutions and environmental enterprises are involved in the remediation of organic contaminated soils.

2 Mitigation technologies for organic contaminated soils

Although there are several mature technologies for soil remediation, the remediation process will inevitably result in change or suspension of the normal soil function. For the slightly contaminated agricultural soils, remediation is not the best choice because of the relative high-cost, especially for areas that are short of cultivated land. How to reduce the bioavailability of organic contaminants and restrain their transposition from soil to plant is an interesting problem.

Plants uptake organic contaminants via several pathways: root uptake from the soil, foliar absorption from the atmosphere, and particle-phase deposition onto the waxy cuticle of the leaves [25]. The low-volatility organics may enter plants generally via root uptake from soil solution [26,27], and the concentration of contaminants in the plant is mainly determined by its effective concentration in the soil solution [28]. Thus, the decrease of effective concentration of organic contaminants in the soil solution may be the key to reduce the bioavailability of organic compounds for plants.

The term ‘stabilization’ or ‘immobilization’ traditionally referred to the use of some organic materials or phosphates to reduce the mobility and bioavailability of heavy metals, such as lead in soil [29]. However, a stabilization or immobilization method can also be applied in the field of mitigation of soil organic contamination. To improve the content of organic matter and subsequently enhance the soil retention of organic contaminants is the principle of immobilization technology. Natural organic matter, such as peat, coal, humic substance, and plant ash, are the

traditional materials for immobilization technology. Recently, biochars, organoclays, and surfactants have become the new materials for the mitigation of soil organic contamination.

2.1 Mitigation technologies with sorbent materials

Some sorbent materials, such as biochars and organoclays, have been proposed as effective environmental and agronomic supplements for reducing the mobility and biological effectiveness of organic contaminants [30–33].

Biochar is a fine-grained charcoal produced by thermal decomposition of organic material (wood, manure, crop residues, solid waste, etc.) under a limited supply of oxygen (O_2) and at relatively low temperatures ($< 700^\circ C$). It is produced to improve soil productivity, carbon storage, or filtration of percolating soil water. Recent attention has been given to biochar as a kind of sorbent material due to its high binding affinity to organic contaminants. Yu and Kookana [33] investigated the effectiveness of two types of biochars in reducing the bioavailability of two insecticides in the soil. With the biochars, the plant residues for chlorpyrifos and carbofuran decreased to 10% and 25%, respectively, in that control treatment.

Organoclay is an organically modified phyllosilicate, derived from naturally occurring clay minerals. An organophilic surface is generated by exchanging the original interlayer cations for organocations, such as cationic surfactant. As a result, the organoclays are usually manufactured as powerful sorbents for nonionic organic contaminants. For example, the organobentonites are used to remove organic contaminants from wastewater [34]. Recently, the organobentonites were used as sorbent materials for the mitigation of soil organic contamination. Liu and Zhang [30] reported that the concentrations of hexachlorocyclohexanes (HCHs) in roots and shoots of ryegrass were reduced by 53.9%–87.6% and 37.4%–56.6% through the addition of 8% organoclays.

2.2 Mitigation technology with cationic surfactant

Cationic surfactants can significantly enhance the sorption of hydrophobic organic compounds (HOCs) onto soils and have been proposed to create contaminant barriers in order to reduce the possibility of their reaching other environmental loci, such as the subsoil, groundwater, and plants [35–37]. Basic studies have found that the cationic surfactant can significantly enhance the sorption of HOCs onto soils and subsequently reduce their concentrations as well as their mobility in the soil solution [38,39]. The schematic diagram of organic contaminant immobilization by organic matter derived from cationic surfactants adsorbed by soils is shown in Fig. 2. The sorption of cationic surfactant onto the soil through cationic exchange forms a new sorbent for the organic contaminant, resulting in a significant increase of the apparent partition capability of the organic contaminant.

In the soil-water system with a cationic surfactant, the organic contaminants should be sorbed onto both the natural organic matters and the mineral-adsorbed surfactants. The apparent solute distribution coefficient (K_d^*) in solid-water mixtures with a coexisting surfactant may be expressed in the form of

$$K_d^* = \frac{K_{oc}f_{oc} + K_{ss}f_{soc}}{1 + K_{mn}X_{mn} + K_{mc}X_{mc}}, \quad (1)$$

where f_{oc} and f_{soc} are the natural organic-carbon fraction and the surfactant organic-carbon fraction in the solid, respectively. K_{oc} and K_{ss} are the carbon-normalized solute distribution coefficients with the natural organic matter and the sorbed surfactant in solids, respectively. If we defined K_d as the solute distribution coefficient in solid-water mixture without surfactant, the total extent of sorption enhancement can be expressed as K_d^*/K_d . Some experiments conducted with cationic surfactants revealed that the K_d^*/K_d ratios were greater than 1 and negatively correlated with f_{oc} and K_{ow} of contaminant (Table 1).

The cationic surfactant may be a promising reagent for the mitigation of soil organic contamination. Gelineer [35]

Table 1 K_d^*/K_d values of organic contaminants with the presence of myristylpyridinium bromide (MPB) [40]

contaminants	paddy soil	fluvio-aquic soil
p-nitrophenol	4.89–150.0	3.13–42.9
phenol	5.45–50.27	4.28–44.91
naphthalene	3.32–20.49	3.00–16.86

created a soil sorption zone by in situ injection of cationic surfactant. Sánchez et al. [36] used a cationic surfactant to enhance the soil retention of organophosphorous insecticides. Recently, cetyltrimethylammonium bromide (CTMAB) and dodecylpyridinium bromide (DDPB) were separately introduced to a soil-plant system. Results indicated that the cationic surfactants significantly reduced the plant uptake of PAHs (Fig. 3). The maximum reductions of phenanthrene and pyrene were 66% and 51% for chrysanthemum (*Chrysanthemum coronarium* L.), 62% and 71% for cabbage (*Brassica campestris* L.), and 34% and 53% for lettuce (*Lactuca sativa* L.), respectively [37]. Besides, CTMAB with the concentration of 0–400 mg·kg⁻¹, which showed no negative impact on plant growth as well as soil microbial biomass and activity.

Black carbons and organoclays sometimes showed better immobilization effect than cationic surfactants [30,37]. However, the solid reagents may be more difficult to interfuse into the soil compared with liquid reagents, such as surfactant solutions.

3 Remediation technologies for organic contaminated soils

For most heavily contaminated sites, mitigation technology may not be suitable. Several effective methods are being currently employed in soil remediation. In situ and ex-situ are two distinct classes of remediation technology. Washing, venting, and biodegradation are commonly used in in situ remediation due to their lower cost and greater convenience. Ex-situ remediation, which means excavating a contaminated area and transporting it to a remote site

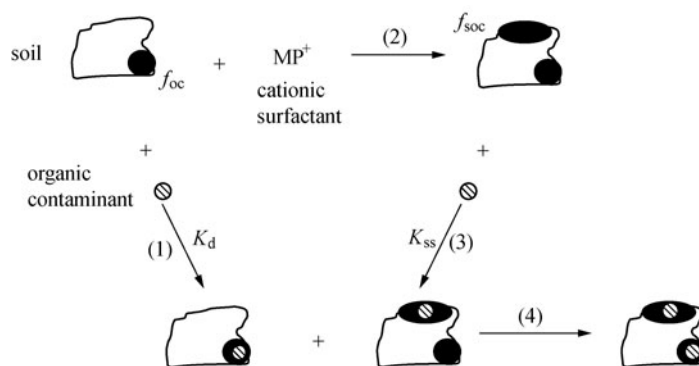


Fig. 2 Sorption enhancement of organic contaminant by cationic surfactant [40]

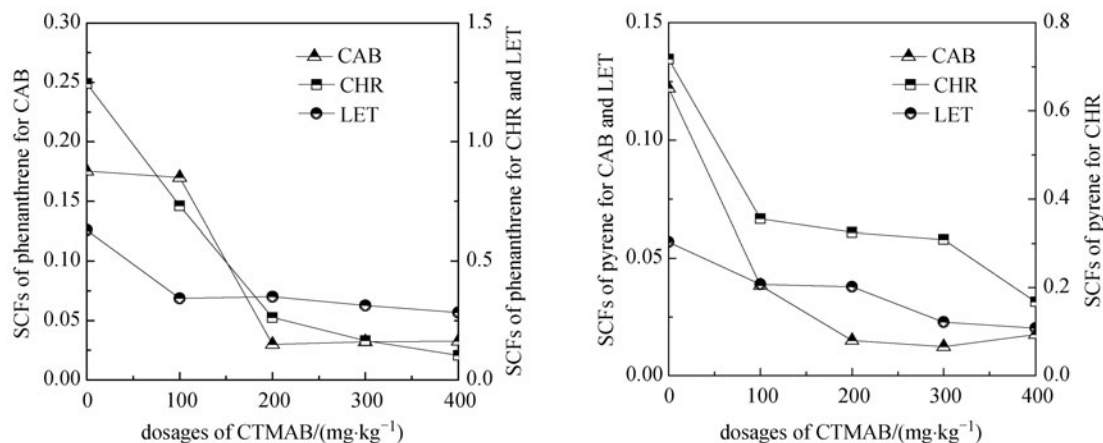


Fig. 3 Shoot concentration factors (SCFs) of phenanthrene and pyrene as a function of CTMAB dosages. CAB, CHR and LET were presented for cabbage, chrysanthemum, and lettuce, respectively

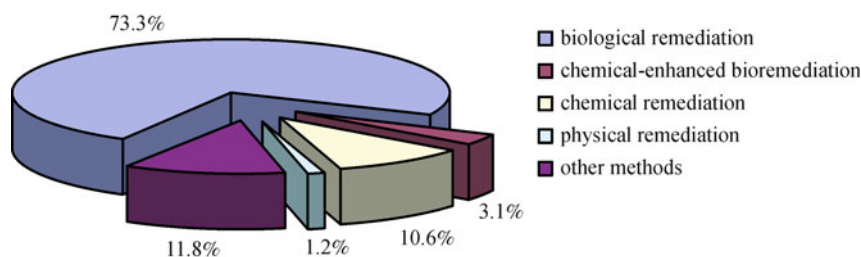


Fig. 4 Percentage of literature studies conducted for different categories of soil remediation technologies (Statistics of the data from ISI Web of Knowledge)

before cleaning it, usually has the advantage of more complete control over the cleaning processes. Both in situ and ex-situ remediation can be classified into four categories: physical, chemical, biological technique, and their combinations. Figure 4 showed the percentage of each remediation technology in the research body and in applications. The cost comparison of the remediation methods is listed in Table 2. The selection of an effective strategy depends on the properties and functions of the contaminated soils and also the economic cost.

Table 2 Cost comparison of remediation methods for organic contaminated soils [41]

type of treatment for organics	range of costs/(\$·ton soil ⁻¹)
physical remediation	120–1500
chemical remediation	80–440
in situ bioremediation	50–150
phytoremediation	10–35

3.1 Physical remediation

Physical remediation refers to separating the contaminants from soil through thermal, electrokinetic, or other physical techniques.

Thermal remediation is suitable for volatile/semivolatile or thermal unstable contaminants. The principle behind this technique is the application of heat to either volatilize or destroy the organic contaminants in soils. For instance, incineration of soil at high temperatures ranging from 870°C to 1200°C effectively destroys organic contaminants, such as PAHs [42]. Microwave technology, for its advantages of rapid, selective, and simultaneous heating, becomes a feasible thermal method in soil remediation [43].

Air stripping accompanied with vapor extraction is another in situ remediation technology. Air stripping injects air into the saturated zone to strip away volatile organic compounds in the soil. The volatile contaminants transfer in a vapor phase to the unsaturated zone where soil vapor extraction (SVE) can then capture and remove them. Thermally enhanced vapor extraction induces a hot airflow to increase the volatilization of organic contaminants from the soil. After raising the temperature from 23°C to 100°C, the flux of trichloroethylene (TCE) increased by a factor of 19 [44].

Electrokinetic remediation aims to drive the ionic contaminants to the oppositely charged electrode by a low-level direct current electric potential. This technology has been utilized for more than a decade to treat the soils

contaminated with heavy metals [45], and now, it is also applied to the removal of organic substances. The removal of organic contaminants generally results from the combined effects of the electroosmotic flow of water and the electromigration of dissolved ions toward the appropriate electrode. However, the target contaminants often have high hydrophobicities, strong sorption capabilities, and low aqueous solubilities. As a result, electrokinetic remediation may be quite time consuming, and the whole process may even take several years [46]. Surfactants and cyclodextrins are commonly used as solubilizing agents of electrokinetic technology. Ko [47] reported that the electrokinetic experiments using hydroxypropyl- β -cyclodextrin (HPCD) solutions showed greater phenanthrene removal from a model clay soil, and the removal efficiency depended on the HPCD concentration used. The removal efficiency was increased from less than 30% without an HPCD and to more than 70% with 6.85 mM HPCD and Na_2CO_3 buffer.

The physical remediation technologies take advantage of being fast and effective. However, thermal treatment, especially incineration, creates a great disturbance on the contaminated soil. Air stripping or vapor extraction may become ineffective when the contamination levels become decreased. When soil water content is less than 10%, electrokinetic treatment also becomes less effective. Moreover, toxic by-products, such as chlorine (Cl_2), may be produced in the electric field. Besides, the cost of physical remediation may be the highest.

3.2 Chemical remediation

Chemical remediation techniques mainly include chemical oxidation as well as solvent washing/extraction. Chemical oxidation applied with oxidants, such as H_2O_2 , modified Fenton's reagent, activated sodium persulfate or permanganate, is a traditional technique in wastewater treatment and remediation [48,49]. With similar principles, chemical oxidation has been applied to remediation of both organic contaminated soil and sediment. Some of the literature has reviewed exhaustive studies on this technique [50]. Here, the chemical remediation refers in particular to the solvent washing and extraction processes.

In the mid-1980s, the Superfund Amendments Reauthorization Act (SARA) first provided specific statutory justification for soil washing [24]. Several kinds of solvents have been chosen in the application of soil washing and extraction techniques, including water, organic solvents, such as ethanol and methanol, different kinds of surfactants, vegetable oils, cyclodextrins, and certain supercritical fluids [50]. In fact, there is no universal soil-washing process. Large-scale chemical washing is always accompanied with certain powerplant and followed by certain recovery steps. For example, EPA has suggested some soil-washing systems using drum

washers, trammels, stirred tanks, and sometimes soil warming sections [24].

3.2.1 Surfactant-enhanced remediation

Surfactant-enhanced remediation (SER) has been suggested as a promising remediation technology [51–55]. Desorption enhancement of hydrophobic organics from soil by surfactants is the key principle of the surfactant-washing process. A surfactant, containing both hydrophobic and hydrophilic portions, can form a micelle with both hydrophobic core and hydrophilic surface, especially when above the critical micelle concentration (CMC). The surfactant can effectively enhance the water solubility of hydrophobic organics by partitioning them into the hydrophobic core. The literature has reported the mechanism and kinetics of the solubilization process of surfactants [56–59].

Surfactants with different electrical properties, polarities, hydrophile-lipophile balance (HLB) numbers, and CMC values showed a different solubilization efficiency of hydrophobic organic compounds. Nonionic surfactants, such as Triton X-100, have been widely used because of the high efficiency of solubilization [60,61]. However, a low concentration of nonionic surfactant tends to increase rather than decrease of the sorption of HOCs to the soil [62,63] due to the soil-adsorbed nonionic surfactant [64], which may disfavor the use of nonionic surfactant for the SER. Therefore, there is a critical washing concentration (C_w) [65], which can be defined as

$$C_w = C_{\text{aq}} + C_{\text{soil}} = \frac{K_{\text{ss}}f_{\text{soc}}}{K_{\text{oc}}f_{\text{oc}}K_{\text{mc}}} + \text{CMC} + C_{\text{soil}}, \quad (2)$$

where C_{aq} is the concentration of surfactant in the solution; C_{soil} is the concentration loss of surfactant as sorption onto soils; K_{oc} and K_{ss} are the carbon-normalized solute distribution coefficients with the natural organic matter and the sorbed surfactant in solid, respectively; f_{oc} and f_{soc} are the natural organic-carbon fraction and the surfactant organic-carbon fraction in the solid; K_{mc} is the micelle-water partition coefficient of HOCs in surfactant solution; and CMC is the critical micelle concentration of a surfactant. For the remediation objective, the surfactant initial concentration must be greater than the C_w . The washing efficiency of organic compounds from the contaminated soil by surfactants and the corresponding C_w values depend on the surfactant structure, contaminant properties, and, in particular, the soil composition. Generally speaking, the surfactant with higher solubilization capacity for HOCs would be selected, and it would be more effective for the organic contaminant with higher hydrophobicity. The surfactants are more effective in enhancing HOC desorption from the contaminated soils with lower clay content and higher organic contents [66].

Mixed surfactants have been proposed for SER because of its synergistic advantages, and it may be more suitable for a wide range of soil conditions [51,67]. The mixed surfactants showed higher cloud points but lower Krafft points as well as CMC values compared to the single ones. Due to the formation of mixed micelles and the corresponding decrease of the CMC, the presence of anionic surfactant not only reduced the sorption loss of nonionic surfactant onto the soils but also enhanced the solubilization of nonionic surfactant for HOCs [68]. For example, Tween80 mixed with 10% of SDBS showed greater efficiency of soil washing for phenanthrene [67].

3.2.2 Soil washing/extraction by other solvents

Washing contaminated soil by mixtures of several organic solvents is more common in laboratory studies. Organic solvents, such as ethanol, methanol, cyclohexane, and dichloromethane, have also been used in effectively washing or extracting PAHs from contaminated soil [69]. The advantage of organic solvents lies in their great capability for dissolving the target contaminants. However the organic solvents always have unacceptable impacts on human health and soil quality. A regeneration technique is necessary to improve washing systems for organic solvents.

Chemical remediation technologies are effective for soils with a wide range of contaminant concentrations. The time taken to complete cleanup by chemical washing/extraction is relatively short. However, the residual solvent in the soils may require secondary treatment; otherwise, it may have a significant impact on the environment.

3.3 Biologic remediation

Biologic remediation as a generalized conception contains both bioremediation and phytoremediation.

3.3.1 Bioremediation

Bioremediation is a promising approach that has been used to remediate the organic contaminated sites. It can be

defined as ‘the process, whereby organic wastes are biologically degraded under controlled conditions to an innocuous state’ [70]. The goals of these techniques are to remove organic contaminants from the contaminated environment and/or to transform them to a less harmful product using the indigenous microbiological community [71]. Microorganisms including bacteria and fungi, which are capable of these transformations, have been isolated and identified from the contaminated sites (Table 3).

The degradation pathways of some major organic contaminants have been clearly understood. The detailed degradation pathways for PAHs [70,92], DDT [93], and atrazine [94] are available in other review articles. Due to the complexity and variety of possibilities, the degradation pathways of PAHs, especially the high-weight-molecular PAHs, have been studied for decades. The aerobic metabolism of PAHs requires first the ring cleavage by a series of specific enzymes and then further metabolism to carbon dioxide and water (Fig. 5). However, the specific steps and intermediate products of ring cleavage are different for various microbial systems. On the other hand, the mechanisms of PAHs degradation in an anaerobic environment are still not fully tested. Recently, a possible mechanism had been proposed for the anaerobic degradation of naphthalene [95], which began with the carboxylation and hydrolysis of the aromatic ring. Detailed information is available in reference [71].

The efficacy of bioremediation has been investigated under ideal conditions. While due to complex environmental factors (such as nutrient conditions, soil pH, and available oxygen) inhibiting the growth of degraders and/or decreasing the bioavailability of contaminants, field applications of bioremediation are still very limited.

There are in situ and ex-situ methods for field bioremediation of contaminated soils. Land farming, as an in situ treatment providing nutrient, water, and oxygen, stimulates the indigenous microorganisms to enhance the bioremediation. For example, a land-farming treatment of diesel-contaminated soils was achieved by aeration and addition of fertilizer [96]. Land farming is one of the preferred methods due to its low cost. However, this treatment can only promote the growth of degraders but

Table 3 Common organic contaminant degraders in soil

genera	organic contaminants	Ref.
<i>Pseudomonas</i>	naphthalene, phenanthrene, fluoranthene, 1,1-diphenylethylene, 1,1-diphenylethane, DDT	[72–76]
<i>Mycobacterium</i>	fluorene, phenanthrene, fluoranthene, pyrene, n-alkanes, chlorfenvinphos, diazinon, pirimiphos-methyl, temephos	[77,78]
<i>Burkholderia</i>	fluorene, phenanthrene, fluoranthene, pyrene, benz[a]anthracene, dibenz[a, h]anthracene	[78,79]
<i>Sphingomonas</i>	12 PAHs, γ -HCH	[80–82]
<i>Rhodococcus</i>	atrazine	[83]
<i>Cunninghamella</i>	pyrenen, benz[a]anthracene, benzo[a]pyrene	[84–87]
<i>Phanerochaete</i>	fluorene, anthracene, phenanthrene	[88–90]
<i>Aspergillus</i>	naphthalene	[91]

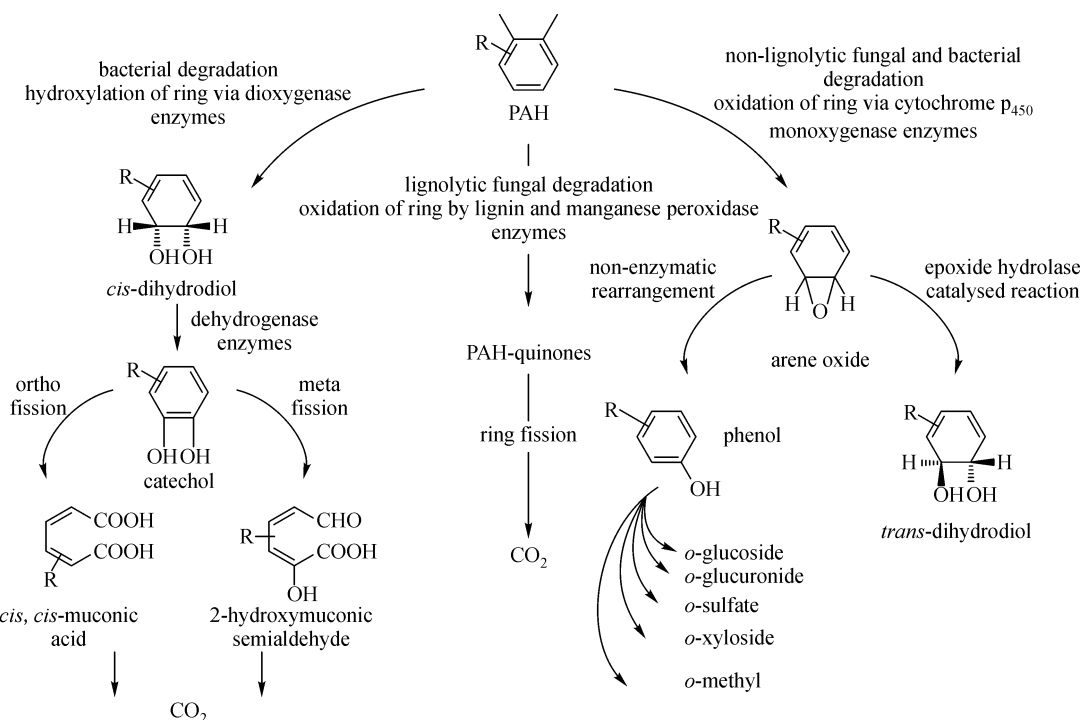


Fig. 5 Main aerobic degradation pathways for PAHs [92]

cannot affect the bioavailability of contaminants, which plays a more important role in the bioremediation.

Biopilling and composting of soil are typical ex-situ treatments for organic contaminated soil. These methods are more effective than land farming but with higher cost. For example, using a biopile system to remediate petroleum hydrocarbon contaminated soils [97], the decay rate and removal ratio can be enhanced to 0.0196 d^{-1} and 87% from 0.0069 d^{-1} and 45%.

3.3.2 Phytoremediation

Phytoremediation is a biological remediation technique for environmental cleanup using plants and their associated microbes [98,99]. During the last two decades, it has attracted much attention as a refined innovative, cost-effective, and noninvasive method [99]. There are various types of phytoremediation techniques, such as rhizofiltration, phytoextraction, phytostabilization, phytovolatilization, phytostimulation, and phytodegradation.

Rhizofiltration, *phytoextraction*, and *phytostabilization* are usually used to treat metals in water or soil. However, trees can be used as a hydraulic barrier, one of the rhizofiltration techniques, to prevent organic contaminants from leaching downward or from migrating horizontally [100]. *Phytovolatilization* is the plant evapotranspiration of metals, such as selenium, mercury [101], and volatile hydrocarbons, such as MTBE [102], after uptake in plant issues.

Phytostimulation, also called *rhizodegradation*, is the most important mechanism of phytoremediation [103]. The plant-derived exudates, which can act as surfactant and/or nutrients, not only increase the bioavailability of contaminants but also promote the growth of indigenous microorganisms, thus facilitating the biodegradation of organic contaminants in the rhizosphere.

Phytodegradation, also called *phytotransformation*, refers to the uptake process, involving a compound specific active process and a passive process, and the degradation of organic compounds directly via their own enzymatic activities. Chiou et al. [28] proposed a partition-limited model for the plant uptake of contaminants and considered the process as essentially a series of partition uptakes. In this respect, the equation of the concentration of a contaminant (C_{pt}) in a whole plant or a specific part can be expressed as

$$C_{\text{pt}} = \alpha_{\text{pt}} + C_{\text{w}}(f_{\text{pom}}K_{\text{pom}} + f_{\text{pw}}), \quad (3)$$

where C_{w} is the contaminant concentration in external water, K_{pom} is the partition coefficient of the contaminant between plant organic matter and water, f_{pom} is the total weight fraction of the plant organic matter, and f_{pw} is the water weight fraction. α_{pt} is a quasi-equilibrium factor. The partition-limited model [28,104] and the modified model [105] were often used to predict the root and shoot concentrations of organic chemicals.

The efficiency of phytoremediation is affected by the plant species, soil properties, and bioavailability of

contaminants. The ability for plant uptake of contaminants is not only species-specific but also subspecies-specific. White et al. [106] reported significant differences in the uptake of p, p'-DDE by several subspecies. The efficiency of the plant uptake also depends on root depth. The root depth of herbaceous species is typically 50 cm, while it is 3 m for trees. A longer plant root may have more possibility to reach contaminants. The plant uptake of organic compounds also depends on the lipid contents of the plant. Zhu and Gao [104] reported that the root concentrations of PAHs were positively correlated with root lipid contents ($p < 0.05$). As autotrophic organisms, plants cannot efficiently metabolize organic contaminants due to the lack of corresponding enzymatic machinery, often resulting in slow remediation [107]. With the introduction of bacterial or mammalian genes encoding degradation enzymes, the transgenic plants remediation are likely to enhance phytoremediation efficiency and clean-up contaminated soils. The transgenic plants have been used to remediate soils contaminated with herbicides [108], explosives [109], and chlorinated solvents [110] and showed significant enhancement of plant tolerance, uptake, and detoxification performances.

The capacity for plants to uptake a target organic compound depends on their lipophilicity. The lipophilicity is one of the most important factors affecting interfacial processes, including the solubility in the water phase, sorption onto plant roots, movement across plant membranes, and distribution in plants. Researchers reported that there was a significant linearity relationship between BCF (Bioconcentration Factor) and the octanol-water partition coefficients (K_{ow}) of organic chemicals. Contaminants with $\log K_{ow}$ ranging from 0.5 to 3.0 are most likely to be taken up and distributed in plants [111–114].

Soil conditions, including pH, pK_a , organic and water content, carbon: nitrogen ratio, and texture, could influence the growth and uptake process for plants and microorganisms and the interactions between the soil-rhizosphere-microbial-plant system. White et al. [115] reported that the addition of soil amendments with different C:N ratios resulted in different plant growth and, thus, different TPHs residues.

The quantitative and semiquantitative results were often obtained by green house studies. The application of phytoremediation at a field scale is more difficult and complex, but the results are encouraging. Banks et al. [116] reported that both lower TPH concentrations and reduced toxicity were achieved in the phytoremediation trial. Vervaeke et al. [117] found that 57% of mineral oil was removed after 1.5 years in the willow-planted treatment, while only 15% was removed in the control treatment. To provide a useful guide and more practical information, it is necessary to carry out further studies on phytoremediation at the field scale.

The biological remediation technologies are always

more economical than traditional physical and chemical methods. In addition, the advantages of in situ biotechnologies lie in the lower risk of exposure to cleanup personnel and less environmental impact. However, there are also some disadvantages associated with biological remediation technologies. First, the efficiency of common bioremediation and phytoremediation are not very satisfactory especially for nonpolar contaminants due to their high hydrophobicity and strong sorption on soils. Additional technologies are needed to improve the bioavailability of the nonpolar contaminants. Second, bioremediation or phytoremediation often take a longer time period than other options. Besides, how to control the growth of plant or microorganism in different soil conditions may be another challenge of biological remediation.

3.4 Combined remediation

To treat the practical contaminated soil with greater efficiency but less risk and cost, some integrated technologies have been developed. From an engineering point of view, most of the remediation technologies, especially for the ex-situ ways, are conducted using physical technologies. Much work has been devoted to developing other new remediation programs combined with physical technologies. For example, chemical or biological treatment is commonly used as a second step after excavating the soil from contaminated sites. The soil washing processes are usually reinforced by thermal or electrokinetics technologies. Sometimes, the oxidative degradation of organic contaminants is promoted by microwaves or power ultrasound [118]. However, in recent years, integrated chemical-biological technologies have attracted most attention.

Since the biological remediation technologies have exhibited many environmentally friendly advantages, the bioavailability of organic contaminants in the soil has become a critical issue. Organic contaminants especially nonpolar contaminants are always less bioavailable due to their high hydrophobicity and strong sorption on soils. Chemical solubilization is one of the most efficient ways to improve the bioavailability of organic contaminants in the soil.

3.4.1 Surfactant-enhanced phytoremediation

If the phytoremediation was inducted alone, the regulatory cleanup standards are not satisfied sometimes [119]. The application of certain suitable concentrations of nonionic surfactant, biosurfactant, or anionic-nonionic mixed surfactants in the soil-plant system resulted in significant enhancements in the plant root uptake of organic contaminants [120–123]. The increase of root permeability and sorption capability of organic contaminants by the surfactant may be the reason for plant uptake enhancement

[123]. However, the contribution of plant uptake for contaminants removal was insignificant, and the removal of contaminants was mostly attributed to the activation of indigenous rhizosphere microorganisms by surfactants. The surfactants at a suitable concentration may first enhance the solubilization of organic contaminants and then simultaneously enhance the biodegradation of organic contaminants by indigenous microorganisms and the uptake by the roots (Fig. 6).

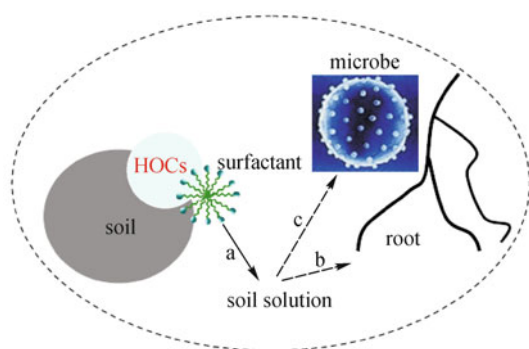


Fig. 6 Schematic diagram of surfactant-enhanced phytoremediation

3.4.2 Surfactant-enhanced bioremediation

Surfactant-enhanced bioremediation (SEBR) techniques have been accepted as a new potential technology for soil remediation. A large number of researchers have reported the enhancement of contaminant biodegradation by surfactants [124–128]. Tiehm [127] reported that the degradation rate of PAHs in soil treated with a low concentration of Sapogenat T-300 was more than two times higher than that of non-surfactant control.

Researchers pointed out that the most significant effect of surfactants on biodegradation lies on the desorption-enhancement of organic contaminant. The contaminants dissolved in soil solution could be utilized preferentially by microorganisms [124,127]. There are some other possible mechanisms, such as the increase of cell membrane permeability [129] and the express acceleration of the degrading enzymes [130] due to the existence of surfactants. However, a different point of view has been proposed by some other researchers, who found the negative effects of surfactant on contaminants biodegradation. The toxicity of the surfactants may inhibit the bacterial growth and enzyme activity [126,131]. The preferential utilization of surfactants by degraders may also be responsible for the inhibiting effect [132]. However, the mechanism has not been clearly proved.

From the different opinions on the effect of surfactants, selecting a suitable surfactant and suitable range of dosages is very important in its application. A surfactant with low-toxic and a positive effect on biodegradation will

meet the needs of SEBR. Biosurfactants, such as rhamnolipid, which are biologically produced by yeast or bacteria on various substrates, including sugars, oils, alkanes, and wastes, have attracted increasing attention in soil remediation due to their low environmental risk [133,134].

4 Future research directions

Understanding the sources and sinks of organic contaminants is the basic premise of preventing and controlling soil organic contamination. Under the guidance of the basic research on the transformation and ecological effects of organic contaminants, the national evaluation standard of soil environment as well as the technical standards of remediation for contaminated soil should be established. This may need the combined efforts of the government and a large number of scientists.

Soil remediation calls for new types of green reagents with higher cost-efficiency but lower environmental risk for the immobilization of soil organic contamination, in order to effectively produce safe agricultural products from the slightly contaminated soils. Furthermore, the mechanism and prediction model for chemical reagents to restrain the uptake of organic contaminants from soils to plant needs to be further investigated.

To construct genetically engineered microorganisms with low ecological risks and high degradation ability on specific contaminants appears to be a promising way to enhance the efficiency of bioremediation. Selecting suitable chemical reagents combined with a suitable dosage and predicting its efficiency in promoting the bioavailability of organic contaminants are of great significance.

On the other hand, adding certain anionic or nonionic surfactants into the soil after harvesting the edible part of plants, may enhance the following microbial-, and phytoremediation processes. Therefore, a new hyphenated technology for safe agricultural production followed by surfactant-enhanced microbial- and phytoremediation may be conducted.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant Nos. 20890111, 20737002, and 40973067).

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