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Review

Mobilization of contaminants: Potential for soil remediation and unintended consequences

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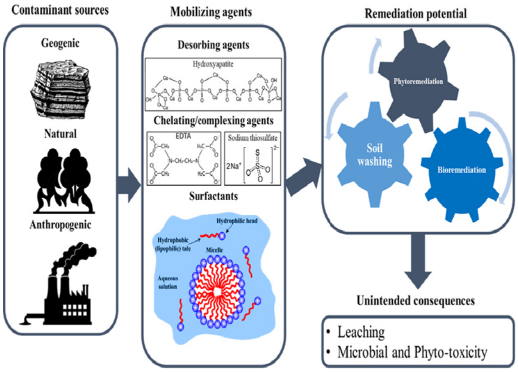
HIGHLIGHTS

- This review covered various approaches about mobilization of soil contaminants.
- Enhancing contaminants mobilization can promote the green remediation trials.
- Integrated mobilization approaches are suitable for contaminated soil remediation.
- The fate and toxicity of mobilization agents and contaminants need re-evaluation.
- The feasibility of soil remediation using mobilization agents has been evaluated.

GRAPHICAL ABSTRACT



Abbreviations: 2,4-D, 2,4-dichlorophenoxyacetic acid; AMD, Acid mine drainages; AOPs, Advanced oxidation processes; AOX, Absorbable organic halogens; CAPB, Cocamidopropyl betaine; CDTA, Cyclohexane diamine tera acetic acid; CEC, Cation exchange capacity; CMC, Critical micelle concentration; DDE, 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethylene; DEHP, Diethylhexylphthalate; DNAPL, Dense non-aqueous phase liquid; DOC, Dissolved organic carbon; DOM, Dissolved organic matter; DPC, Diphenylthiocarbazone; DTPA, Diethylenetriaminepentaacetic acid; EC, Electric conductivity; EDC, Endocrine disturbing chemicals; EDDHA, Ethylenediamine-*N*,*N*′-bis(2-hydroxyphenylacetic acid); EDDS, Ethylenediamine-N,N′-disuccinic acid; EDTA, Ethylenediamine tetraacetic acid; HIDS, Hydroxyiminodisuccinic acid; HPCD, Hydroxypropyl-b-cyclodextrin; EHPG, *N*,*N*′-ethylenebis-[2-(*o*-hydroxyphenyl)]-glycine; GHG, Greenhouse gas; HMs, Heavy metals; HOCs, Hydrophobic organic compounds; LAS, Linear alkylbenzenesulfonates; MBT, Monobutyltin; NPnEOs, Nonylphenolethoxylates; NPs, Nonylphenols; OC, Organic carbon; OM, Organic matter; PAHs, Polyaromatic hydrocarbons; PBDEs, Polybrominated diphenyl ethers; PCB, Polychlorinated biphenyl; PCDDs, Polychlorinated dibenzo-p-dioxins; PCDFs, Polychlorinated dibenzofurans; PFAS, Poly- and per-fluoroalkyl substances; PFBA, Perfluorobutane sulfonate; PFBS, Perfluorobutane sulfonic acid; PFDA, Perfluorodecanoic acid; PFPeA, Perfluoropentanoic acid; PFHpA, Perfluoroheptanoic acid; PFHxA, Perfluorohexanoic acid; PFHxS, Perfluorohexane sulfonate; PFNA, Perfluorononanoic acid; PFOA, Perfluorooctanoic acid; PFOS, Perfluorooctane sulfonate; PGOPE, Polyethylene glycol octylphenol ether; PHE, Phenanthrene; POPs, Persistent organic pollutants; PTEs, Potentially toxic elements; SDS, Sodium dodecyl sulfate; SOM, Soil organic matter; WWTPs, Wastewater treatment plants.

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ABSTRACT

Land treatment has become an essential waste management practice. Therefore, soil becomes a major source of contaminants including organic chemicals and potentially toxic elements (PTEs) which enter the food chain, primarily through leaching to potable water sources, plant uptake, and animal transfer. A range of soil amendments are used to manage the mobility of contaminants and subsequently their bioavailability. Various soil amendments, like desorbing agents, surfactants, and chelating agents, have been applied to increase contaminant mobility and bioavailability. These mobilizing agents are applied to increase the contaminant removal though phytoremediation, bioremediation, and soil washing. However, possible leaching of the mobilized pollutants during soil washing is a major limitation, particularly when there is no active plant uptake. This leads to groundwater contamination and toxicity to plants and soil biota. In this context, the present review provides an overview on various soil amendments used to enhance the bioavailability and mobility of organic and inorganic contaminants, thereby facilitating increased risk when soil is remediated in polluted areas. The unintended consequences of the mobilization methods, when used to remediate polluted sites, are discussed in relation to the leaching of mobilized contaminants when active plant growth is absent. The toxicity of targeted and non-targeted contaminants to microbial communities and higher plants is also discussed. Finally, this review work summarizes the existing research gaps in various contaminant mobilization approaches, and prospects for future research.

Contents

1. Introduction

In recent years, rapid population growth and urbanization has led to generation of tremendous amounts of hazardous waste, which are upsetting socio-economic activities and endangering environmental sustainability (Awasthi et al., 2022; Sridharan et al., 2022). Contaminants from wastes stream reach terrestrial and aquatic environments through waste disposal and industrial and mining activities (Bolan et al., 2022a; Kumar et al., 2021a). Environmental contaminants comprise inorganic nutrients (phosphates, nitrates) (Awasthi et al., 2022; Kumar et al., 2021b) and potentially toxic elements (PTEs) including chromium (Cr), arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg) (Ambika et al., 2022; Bolan et al., 2021a; Prasad et al., 2022) and organic compounds like persistent organic pollutants (POPs), perfluoroalkyl and polyfluoroalkyl substances (PFAS), polyaromatic hydrocarbons (PAHs), pesticides, and plastics and their additives (Anerao et al., 2022; Baskar et al., 2022; Sridharan et al., 2021a; Sridharan et al., 2021b). To remediate these range of pollutants from environmental matrices, several methods have been listed such as adsorption (Kumar et al., 2020b), photodegradation (Jasemizad and Padhye, 2022), advance oxidation process (AOP), (Kumar et al., 2020a), bioremediation (Bhujbal et al., 2022; Nie et al., 2020), electrokinetic remediation (Cameselle et al., 2021), electro-bioremediation (Li et al., 2020a), bioleaching (Xu et al., 2020a), phytoremediation (Rathour et al., 2022; Fuke et al., 2021). However, these remediation approaches are applied according to nature and level of pollutants, environmental conditions, and economics of the process (Baskar et al., 2022; Bolan et al., 2022a; Bolan et al., 2021c; Bai et al., 2019; Beolchini et al., 2013).

Land treatment is a specific process by which contaminants levels within the plant-soil-water matrix are controlled by various processes such as natural, physical, chemical, and biological. In the process of land treatment, soil being an important sink for environmental contaminants listed above, and they reach the food chain, mostly through drinking water, plants uptake, and animal transfer (Prasad et al., 2022; Sarkar et al., 2022; Zhou et al., 2022). Soil contaminants undergo various biological and chemical transformations, thereby impacting their mobility and bioavailability (Kumar et al., 2021c; Prabha et al., 2021; Sun et al., 2020b). Because mobility plays an important role in soil remediation, various soil amendments can be used to control the mobility and subsequent bioavailability of contaminants (Palansooriya et al., 2020). Immobilizing agents, such as liming materials, biochar, and phosphate compounds, are applied to decrease the mobility and bioavailability of pollutants (Guo et al., 2020; Bolan et al., 2022b; Shaheen et al., 2022; Sumalatha et al., 2022), while mobilizing amendments, like surfactants and desorbing and chelating agents, often used to boost the mobility and bioavailability of contaminants (Bolan et al., 2014; Kumar et al., 2021a).

Application of immobilizing agents is likely to reduce the uptake of contaminants by plants, thereby mitigating their potential to reach the food chain (Hemati Matin et al., 2020; Palansooriya et al., 2020). A prominent limitation of the immobilization method is that the solubilization and slow release of immobilized contaminants need to be monitored regularly (Palansooriya et al., 2020). However, the application of mobilizing agents enhances the removal of contaminants though phytoremediation, bioremediation, and soil washing (Fatin-Rouge, 2020; Medyńska-Juraszek et al., 2020; Rinklebe et al., 2020). In the process of mobilization-assisted phytoremediation, soil contaminants are solubilized by application of various amendments such as additives, organic acids, surfactants etc., which change the soil properties, increase the bioavailability of the contaminants, resulting improved phytoremediation (Barbafieri et al., 2017). Nevertheless, in the case of the mobilization technique, the mobilized contaminants are susceptible to leaching when there is no active plant uptake or during the process of soil washing, thereby leading to groundwater contamination and toxicity to plants and soil biota (Bolan et al., 2021c).

Numerous studies have discussed the mobilization and immobilization approaches to remediate contaminated soils (Bolan et al., 2014; Eckley et al., 2020; Tauqeer et al., 2021). These reviews summarized that the application of immobilization and mobilization approaches depends on the sources and nature of contaminants and the post-land use practice of contaminated sites. While there have been a number of reviews on the immobilization approach to the remediation of contaminated sites (Palansooriya et al., 2020; Bolan et al., 2022a; Khan et al., 2021; Kumar et al., 2021a), only limited number of reviews have considered the mobilization approach in relation to remediation of contaminated sites (Bolan et al., 2021c). The reviews covering the mobilization approach tend to focus on specific mobilization techniques such as the use of chelates (Bhandari and Prakash, 2022), surfactants (Liu et al., 2021), and desorbing agents (Bolan et al., 2014). Hence, the key objectives of this review are to critically explore the existing literature on various techniques applied in the mobilization approach to remediate contaminated sites along with their pros and cons. The unintended consequences of the mobilization approach for soil remediation are discussed in relation to the leachability of mobilized contaminants in the absence of active plant growth. Mobilization of targeted and non-targeted contaminants may cause toxicity to microbial communities and plants. Mostly applied mobilizing agents are not selective to specific heavy metal (HMs) and can mobilize other metals such as aluminium (Al) and Mn, resulting in toxicity to plants. Therefore, the toxicity of targeted and non-targeted contaminants to microbial communities and plants are also discussed. Finally, this review advocated the development of emerging integrated mobilization techniques to manage contaminant soils along with prospects for future research.

2. Methodology of the review

The current review work has been proposed to recapitulate the existing knowledge and scientific development about remediation of contaminated soil via different mobilization approaches. To make this review timely and up to date, recent literature data were collected from most imperative and accessible databases like Scopus, Web of Science, Google Scholar, ScienceDirect, and other reliable web sources as well as vetted knowledge from commercial sites using the following key words: mobilization of contaminants; soil washing; soil leaching; bioavailability of contaminants; soil remediation; phytoremediation; bioremediation (Fig. 1). We attempt to elucidate knowledge about the mobilization approach so that the bioavailability and mobility of contaminants can be manipulated, thereby achieving a risk-based remediation method of contaminated soil. This review gives an overview of existing data and highlights key areas for future research to address existing knowledge gaps, especially in relation to the unintended consequences of mobilization in relation to leaching and the toxicity of targeted and non-targeted contaminants to soil biota. Moreover, increased knowledge about mobilization techniques will benefit the risk-based in-situ remediation of contaminated sites.

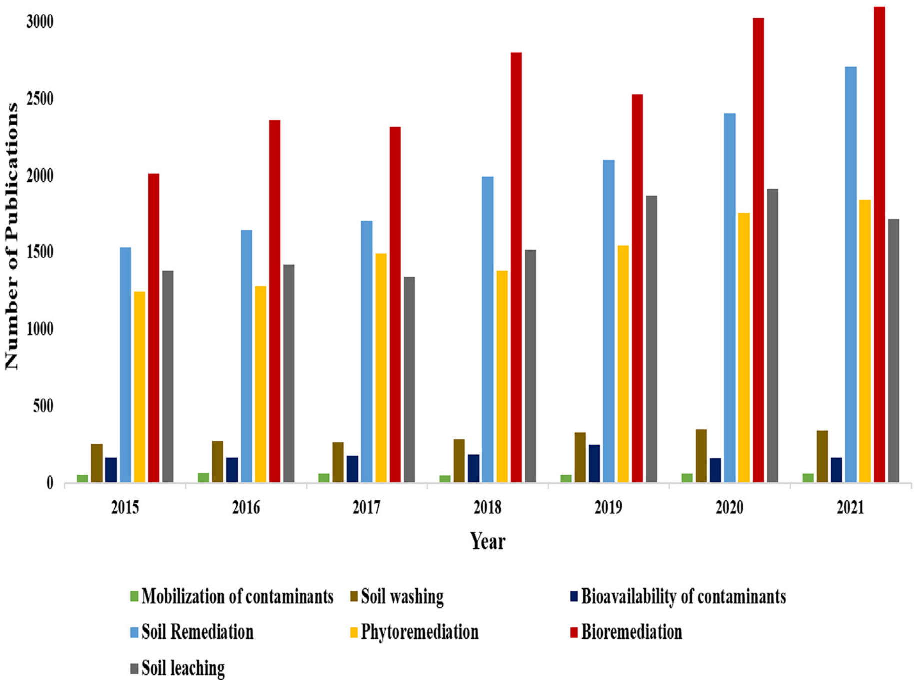

Fig. 1. Publications over the recent years related to mobilization approaches and remediation technologies applied for environmental pollutants.

3. Sources of contaminants

In terrestrial ecosystems, soil is the major sink for contaminants, just like sediments are in aquatic ecosystems. Contaminants enter the terrestrial and aquatic environments through waste disposal and industrial and mining activities (Hou et al., 2020). Soil contaminants can be organic compounds, such as PAHs, PFAS, polychlorinated biphenyl (PCB), pesticides, and plastics and their additives (Anerao et al., 2022; Baskar et al., 2022; Sridharan et al., 2022; Sooriyakumar et al., 2022), or inorganic chemicals, such as Hg, Cd, As, Pb, phosphates, and nitrates (Bolan et al., 2021a; Prasad et al., 2022). There are several recent reviews available which comprehensively discussed the source of inorganic and organic contaminants (Bolan et al., 2022b; Palansooriya et al., 2020; Hoang et al., 2021; Khan et al., 2021; Lenka et al., 2021), therefore, we are providing only a brief discussion on it.

3.1. Inorganic contaminants

PTEs are the prominent inorganic soil pollutants. Soil contamination due to PTEs such as As, chromium (Cr), Pb, Hg, antimony (Sb), Cd, nickel (Ni), copper (Cu), cobalt (Co) etc. has been reported globally and leads to various adverse impacts on health of the environments and living organisms, including humans (Palansooriya et al., 2020). For instance, PTE contamination via food chain is a grave problem which adversely impacts wildlife along with human health (Shaheen et al., 2020; Modabberi et al., 2018). Both anthropogenic and pedogenic processes can lead to environmental contamination by PTEs. The level of PTE in soil is equal to the sum of anthropogenic and geogenic sources minus losses because of soil leaching, soil erosion, volatilization and plant uptake (Palansooriya et al., 2020). PTEs mainly occur naturally (pedogenic) in a non-bioavailable form in the soil parent materials. However, man-made PTEs (anthropogenic) possess high bioavailability (Shaheen et al., 2020). The major anthropogenic sources of PTEs are industrial waste (processing, manufacturing) and domestic waste and phosphate fertilizers (Weissengruber et al., 2018). For example, phosphate fertilizers are the main source for PTEs in New Zealand and Australia, whereas, in U.S.A and Europe, biosolids are a prominent source of metal(loid) inputs into the environment (Bolan et al., 2014).

However, geological (pedogenic) processes can also contribute to metal(oid) contamination (Modabberi et al., 2018). For instance, for thousands of years, As from Himalayan sedimentary rocks have been transported by rivers in India and Bangladesh. Similar processes have occurred in Mexico and China (Bolan et al., 2014). Also, near to volcanic areas, volcanic ashes and plumes are the significant sources of PTE. However, PTE concentration in the soil depends on secondary mineral composition (Navarro et al., 2008). Individuals living nearby volcanic zones are likely to have higher exposure of PTE than those in reference areas. For instance, children living near Mt. Etna, Italy, found higher intakes of uranium (U), As, vanadium (V), and manganese (Mn) (Varrica et al., 2014). Therefore, snowballing threats to human health posed by elevated concentration of PTE in soils, recognizing and optimizing appropriate PTE polluted soil treatment technologies are important.

3.2. Organic contaminants

The major organic soil contaminants include PAHs, PFAS, endocrine disturbing chemicals (EDC), such as phthalates, and antibiotics (Anerao et al., 2022; Baskar et al., 2022; Kumar et al., 2021a). Among the EDC compounds, the most frequently reported in wastes used for soil application, such as biosolids and manures, comprise linear alkylbenzenesulfonates (LAS), nonylphenolethoxylates (NPnEOs), absorbable organic halogens (AOX), nonylphenols (NPs), PAH, PCB, di-ethylhexylphthalate (DEHP), polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzo-p-dioxins (PCDDs). Likewise, PAHs are a group of organic compounds, and due to their mutagenic, teratogenic, and oncogenic potency, 16 PAHs have been listed as priority contaminants by the Environmental Protection Agency of the United States (US EPA) (Kumar et al., 2021a). The sources of PAHs can be categorized as, petrogenic, pyrogenic, and natural/biological (Abdel-Shafy and Mansour, 2016). The petrogenic sources PAHs consist of stowage, vehicular emission, and uses of crude oil and its co-products (Guarino et al., 2019). Pyrogenic PHAs are generally emitted during the pyrolysis or/and burning of biomasses in depleted oxygen at high temperature (Balmer et al., 2019). Additionally, the conversion of fossil fuel such as coal into coal-tar/coke and refining of crude oil to generate lower chain length hydrocarbons, can result in the release of pyrogenic PAHs (Guarino et al., 2019; Abdel-Shafy and Mansour, 2016). Natural sources of PHAs emission in the environment include, forest fire, volcanic eruptions, and biological syntheses setting (Kumar et al., 2021a). PAHs present in solid matrices can easily bioaccumulate in soil organisms and plants through the food chain, ensuing direct and/or indirect human exposure (Bortey-Sam et al., 2014).

Similarly, PFAS are one of the prominent groups of organic contaminants found in biosolids from wastewater treatment plants (Baskar et al., 2022; Bolan et al., 2021b). PFAS have one or more C atoms with F atoms replacing the H substitutes, and, hence, they are called fluorinated organic chemicals (more than 3000 synthetic compounds) (Bolan et al., 2021c). The most prominent PFAS are perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and perfluorohexane sulfonate (PFHxS) (Shahsavari et al., 2021; Gao and Chorover, 2012). Due to their resistance to moisture and temperature PFAS are used in plastic and leather manufacture, non-stick cookware, fire-fighting foam, water-repellent fabrics, medical equipment, and fast-food wrappers (Ng et al., 2021). Composts, biowaste (biosolids), poultry and animal manure, and firefighting foam (aqueous film-forming foam) are important sources for input of PFAS into soil (Bolan et al., 2021b). Conventional wastewater treatment plants (WWTPs) are not able to treat PFAS (Lenka et al., 2021). Biosolids obtained from WWTP are thought to play a significant role in the widespread diffuse contamination of PFAS into the surrounding environment, because PFAS frequently occur in wastewater sludge, influents, and effluents (Lenka et al., 2021). Subsequently, PFAS are passed on in the food chain via plant uptake, eventually posing a threat to the ecosystem and health of the living organisms including human. Remediation of the soils contaminated with PFAS is highly challenging because of their complexity and thermal and chemical stability (Shahsavari et al., 2021). Hence, advanced integrated approaches are needed, which can efficiently remediate the soil polluted with POP such as PFAS, PAHs, EDC, etc.

4. Interaction mechanisms of contaminants in soil

Mobilization of contaminants is governed by several interactions between contaminants, soil particles and other adsorbents present in the soil, which vary significantly with the nature and properties of soil and target contaminants (Li et al., 2017a). Those interactions include ion exchange, ligand exchange, π-π interaction, hydrogen bonding, surface precipitation, electrostatic attraction, and diffusion into the interior structure of the sorbent (Sumaraj and Padhye, 2017). Due to heterogeneities of the soil matrix, contaminant-soil interactions often involve multiple mechanisms. Some of the mechanisms are briefly outlined below.

Ion exchange is a reversible reaction that occurs between ions present in soil solution and the soil-solid phase and it is driven by electrostatic interactions (Cheng et al., 2021). This mechanism is a stoichiometric process that replaces pre-sorbed ions on the soil surface by chemically equivalent ions, commonly contaminants ions. Ion exchange adsorbents including soil particles usually have counter ions of a higher concentration, higher valency, and ions with a smaller hydrated shell (Loganathan et al., 2014). Several studies reported the significant contribution of ion exchange as a potential mechanism for sorption of inorganic contaminants, such as HMs, phosphate, and ammonium (Reynier et al., 2015; Shaheen et al., 2013; Siroux et al., 2021). Ion exchange may rarely occur as a potential mechanism for the adsorption of organic compounds in soils because they are hardly converted into ionic forms (Cheng et al., 2021). However, some studies have shown ion exchange as one of the main mechanisms in the adsorption of antibiotics and other pharmaceuticals in aqueous solution (Feizi et al., 2020a; Liu et al., 2019).

Ligand exchange occurs when a contaminant and surface-bound metallic cation form a covalent bond, replacing the ligand previously bonded to the metallic cation (Loganathan et al., 2014). In this process, soil pH is a key factor governs the metal-soil interactions via ligand exchange, because the exchange process is governed by the ease of a charge transfer reaction (Awual et al., 2019). Diverse range of inorganic contaminates, including PTEs, radioactive metals, rare-earth elements and precious metals cab be removed via ligand exchange mechanism (Awual and Ismael, 2014; Awual et al., 2019).

Hydrogen bonding, a strong dipole-dipole attraction, can occur between the electropositive H atom in the soil particles and electronegative atoms, such as O, F, N, in contaminants. The adsorption energy of H bonding is weaker than that of ligand exchange (Loganathan et al., 2014). It is well investigated that H bonding plays a key role in adsorption of several organic compounds in aqueous environments (Li et al., 2017b; Liu et al., 2019; Guo et al., 2022).

Hydrophobic interaction is the mutual repulsion between molecules commonly possessing non-polar groups in their structure (Cheng et al., 2021). This interaction mainly occurs in the adsorption of organic contaminants in soils and water (Bai et al., 2019; Catherine et al., 2018; Feizi et al., 2020a). For instance, Cai et al. (2022) observed that increase in ionic strength and cations valency enhanced sorption of PFAS in soils through the hydrophobic interactions with soil surfaces. Therefore, enhancing the concentrations of cation soil solutions may mitigate the mobility and migration of PFAS via a soil profile.

π-π interaction is an electron transfer reaction that often occurs between an electron donor-acceptor pair of aromatic rings of organic contaminants and adsorbents including soil particles (Ahmed et al., 2014, 2015; Cheng et al., 2021; Jasemizad and Padhye, 2022; Wei et al., 2021). The π-π interactions have been reported as one of the main mechanisms in the adsorption of several organic compounds containing aromatic benzene rings, such as sulfamethoxazole, ciprofloxacin, propranolol, and clomipramine (Feizi et al., 2020a; Reguyal and Sarmah, 2018).

The PFOS as one of the most typical PFASs has been widely detected in soil and water (Gellrich et al., 2012). As a most preferable substitutes to PFOS, sodium p-perfluorous nonenoxybenzene sulfonate (OBS) is consistently being used in several fields and has been also detected in soils. In a recent study of Wei et al. (2021) found that the OBS can be adsorbed rapidly on the soil plausibly via electrostatic, hydrophobic, and π-π interactions. Some studies also reported that the soil organic matter content, ammonium nitrogen, soil pH, and clay content are important factors govern the adsorption of PFAS and OBS on soil (Li et al., 2018; Wei et al., 2021). For instance, Wei et al. (2021) observed that the OBS adsorption on the organic matter (OM) and nitrogen rich topsoil was higher than subsoil and reduced with increase in soil depth, because the contents of OM and ammonium nitrogen reduced with increase in soil depth. However, the hydrophobic interaction of PFAS and OBS and other organic contaminants with soil organic matter (SOM) depends more on its chemical composition than its content (Ahmed et al., 2014, 2015). In some studies (e.g., Ahmed et al., 2015; Li et al., 2019; Wei et al., 2021), they found that hydrophobic PFASs like OBS and PFOS effortlessly aid strong hydrophobic adsorption. Wei et al. (2021) concluded that apart from the conventional hydrophobic interaction participated in PFASs adsorption on soils, the electrostatic interactions, hydrogen bonding, and π-π interaction were possibly participated in the OBS adsorption on soils.

Electrostatic interactions comprise electrostatic attraction and repulsion between charged molecules. These interactions are the essence of a chemical ionic bond between anions and cations (Cheng et al., 2021; Vierke et al., 2014). Several studies have shown the dominant role of electrostatic interaction during the adsorption of inorganic and organic contaminants in soils (Higgins and Luthy, 2006; Du et al., 2014; Vierke et al., 2013; Li et al., 2018; Park et al., 2018). Electrostatic interaction is the important sorption mechanisms for PFASs in soils, because PFASs may exist in soils as anionic species owing to their low pKa values (Burns et al., 2008; Vierke et al., 2013). Therefore, an electrostatic attraction can form between the anionic functional head of PFASs and the cationic surfaces of the adsorbents such as oxides. Consequently, the Fe-oxides play an important role in providing cationic surfaces for electrostatic interaction and these sorption sites would become more important in variable charged soils. Also, the divalent cations may act as a bridge between anionic surfaces of soil sorbents and anionic charged functional head of PFASs (Higgins and Luthy, 2006; Du et al., 2014). The results of Wei et al. (2021) also demonstrated that multivalent exchangeable cations could play a key role in regulating sorption and transport of perfluoroalkyl carboxylic acids (PFCAs) in soils because the sorption can be enhanced via cation-bridging interaction.

Complexation mechanism typically occurs in much slower kinetic reactions than H-bonding and ion exchange (Awual et al., 2018). Inner-sphere complexation is chemical adsorption via direct bonding to the surface of minerals (Strawn, 2021). Complexation has been reported to be the main adsorption mechanism of toxic elements, nutrients, and organic pollutants in soils (Sako et al., 2009; Vithanage et al., 2013; Veselská et al., 2016; Xue et al., 2020; Fan et al., 2021) and water (Pintor et al., 2020; Wu et al., 2019; Yakkala et al., 2013). Chelating agents, such as ethylenediamine tetraacetic acid (EDTA), can desorb soil contaminants that are adsorbed through the complexation mechanism. Surface precipitation mechanism is also involved in the adsorption of toxic elements, nutrients, and organic contaminants in soils (Shaheen, 2009; Shaheen et al., 2013; Antoniadis et al., 2018). Therefore, exploring and evaluating the interacting mechanisms are imperative for effective soil remediation.

5. Interaction mechanisms of co-contaminates in soil

Several groups of co-occurring contaminants in the soil environment may interact with each other, thereby reciprocally impacting the distribution of their original forms as well as their transformation-migration in the environmental media. Interactions of contaminants during the chemical processes, such as organic partition, electrostatic interaction, catalytic redox, and complexation, drastically alter the original form of contaminants in soil (Ye et al., 2017). Additionally, these processes can also alter the physico-chemical characteristics, such as solubility (affect the leaching), binding ability (affect the adsorptive remediation), and bioavailability (affect the bioremediation) (Agnello et al., 2016).

Physico-chemical behaviour of the soil contaminants is significantly influenced by the formation of organic complexes, as the complexation alters the contaminant bioavailability and solubility. Complexation changes the existing forms of the soil contaminants, and hence alters their bioavailability and solubility. For instance, Monobutyltin (MBT) and 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethylene (DDE) enhance the sediment solubility and bioavailability of Cu to the soil biota (Almeida et al., 2009). Zhang et al. (2011) reported a reduction in the Cd (water-extractable) concentration in loam soil upon addition of PAHs, and the authors also interpreted PAHs to chelate PTEs in the soil. The effect of "salting in" refers to the increase in solubilization caused by cation-π bonds formed by the high affinity between organic soil pollutants (electron-rich) and metals (cations) (Ye et al., 2017). In sandy loam soil, 500 mg/kg of Cu and Al enhanced the bioavailability of phenanthrene extracted using hydroxypropyl-β-cyclodextrin (HPCD) and $CaCl_2$ (Obuekwe and Semple, 2013). Therefore, the efficiency of remediation depends mainly on the solubility of these chelated complexes. Lesser the solubility, lower the biotoxicity of the target contaminant; higher the solubility, higher the bio-accessibility and degradation efficacy.

Synchronous remediation is possible under certain conditions by redox reactions, when PTEs (As^{5+} and Cr^{6+}) of high oxidation potential react with the organic pollutants in soil (Dong et al., 2014). Lee et al. (2012) observed an enhanced reduction of co-dissolved As(V) and Fe(III) on the bacterial cell surface (*Geobacter metallireducens*) in a co-contaminated slightly acidic (pH 5.09) sandy loam soil with toluene (electron donor) and As (electron acceptor), where the electron transfer mechanism promoted a synchronous remediation. Naphthalene, when partitioned or dissolved in soil particles, can get oxidized by donating electrons to metal ions like Fe^{3+} (Yan and Lo, 2013). From the values of redox potential, the study suggested PTEs as a source of an 'in situ' metal coat. These metal coats promote dehalogenation of organic contaminants in the soil (Ye et al., 2017). Another study claimed that the presence of Cu^{2+} ions in soil enhanced the biodegradation of PCPs using Pd/Fe bimetallic particles (Shih et al., 2011). Moreover, the presence of Lewis acids (metal hydroxides and oxides) like Co^{2+}, Zn^{2+}, Cu^{2+} has been known to promote phosphorothioate and phosphate hydrolysis to catalyze the biodegradation of organic phosphorous pesticides (Seger and Maciel, 2006). Nevertheless a few highly soluble products of hydrolysis are potentially ecotoxic and difficult to degrade. Moreover, metal oxides could block the nucleophilic attack and inhibit the hydrolysis and remediation (Ye et al., 2017). Organic contaminants in soil can be accelerated by utilizing PTEs as potential catalysts. However, the possible interactions of incomplete or partial degradation products with the soil biota and their potential ecotoxicity are not explored in most of the remediation studies, and their impacts on the efficiency of soil remediation remain unclear.

Song et al. (2008) reported saponin (a biosurfactant) to remediate phenanthrene and Cd simultaneously from the soil. Cd and Zn amplified this solubilization effect of surfactants (saponin) on the target contaminant (phenanthrene) by reducing the electrostatic repulsion of phenanthrene (head group) with the surfactant molecules (Zhou et al., 2011). The solubilization increased with decreasing pH. Pounds et al. (2004) reported the generation of hazardous PTE-organic compounds including trimethyltin and methylmercury via organic reactions of organic pollutants and PTEs (Sn, Hg). Moreover, chemical reactions of co-occurring contaminants are vulnerable to soil characteristics, such as DOM, pH, Eh, temperature, which also affect the remediation efficiency (Ma et al., 2020). Overall, these soil properties, interacting mechanisms, occurrence of co-contaminates are key for any soil remediation technologies to be implemented, since they greatly influence the remediation efficiency of any technologies.

6. Soil amendments to mobilize contaminants in soils

Mobilization of pollutants in soil can be accomplished via organic amendments (Hoang et al., 2021), solubilization (Kour et al., 2021), desorption (Rodríguez-Garrido et al., 2020), chelation (Sun et al., 2020a), and complexation processes (Zhang and Zhou, 2019). It leads to relocation of pollutants from the soil-to-soil solution, thus increasing their mobility and subsequent bioavailability (Fatin-Rouge, 2020; Palansooriya et al., 2020) (Table 1). Several investigations have applied diverse range of amendments to mobilize pollutants from the solid phase and improve their mobility and bioavailability, as discussed below in detail.

6.1. Composts

The impact of organic supplementations, like composts, on the bioavailability, mobility, and leachability of the soil contaminants is governed by the specific pollutant type, properties of the organic amendment, and soil type and characteristics such as electric conductivity (EC), cation exchange capacity (CEC), pH, and dissolved organic carbon (DOC) (Hoang et al., 2021; Farid et al., 2022). Opposite to the immobilization effect, the supplementation of organic amendments, like compost, improves availability of organic and inorganic soil pollutants, and this improvement might be owing to the dissolved organic matter (DOM) from the amendments. The DOM fraction disrupts the association between the mineral and organic pollutants, resulting in the release of the accompanying pollutants into the soil solution (improved bioavailability and accessibility) (Chen et al., 2019; Hoang et al., 2021). Moreover, DOM improves the solubility as well as mass transfer of organic pollutants into the liquid phase, so that microorganisms have direct accessibility of DOM-bound organic contaminants (Cai et al., 2017; Hoang et al., 2021). Yang et al. (2014) showed that DOM derived from pine-needle litter decreased sorption of fluoranthene and phenanthrene by soil constituents. Likewise, mobilization of soil polyaromatic hydrocarbons (PAHs) was enabled by DOM present in compost. The DOM can tightly amalgamate with PAHs sorbed by the soil constituents (Hoang et al., 2021). Furthermore, amending residues of harvested crops, left on the soil, can improve the DOC fraction of the soil (Zhao et al., 2018), which can hinder sorption and facilitate mobilization of the soil organic contaminants (Wang et al., 2019). DOC was reported to be effective in mobilizing contaminants strongly adsorbed by adsorbents (Bao et al., 2020; Hoang et al., 2021; Hussain et al., 2018).

Furthermore, several researches (Shaheen et al., 2017a; Shaheen et al., 2017b; Farid et al., 2022) have confirmed the effect of compost on mobilization of inorganic contaminants. For example, amending polluted soils with compost containing 641.95 mg/L DOC and 13.06% total carbon, may enhance the mobilization and leachability of PTEs, specifically As (Hartley et al., 2010). Higher leachability of As from soil amended by compost was detected, because DOC competed with PTEs for sorption, leading to enhanced mobilization of As and, consequently, its uptake by plants. Moreno-Jiménez et al. (2013) detected improvement in mobility of Cu, As, and Se from flooded soils amended with compost derived from olive-mill waste. It happens due to improved pore water DOC quantity. Clemente et al. (2010) revealed the influence of compost mulch on the mobility of PTEs, such as As and Sb, after 24 months. Compost mulch improved the iron (Fe) concentration and organic carbon (OC) content in the soil pore water, resulting in improved Sb and As mobility along with enhanced uptake of PTEs in sunflower and lettuce (Bolan et al., 2014). Wu et al. (2012) stated that common carbon-based amendments, such as clover and rice straw, will be more effectual than synthetic chelating substances, like ethylenediamine-N,N′-disuccinic acid (EDDS), in increasing the phytoremediation capacity in Cd-polluted soils. These organic supplements can also supply soluble organic matter, hence improving mobilization of PTEs, which contaminate groundwater (Palansooriya et al., 2020; Yan et al., 2020).

6.2. Chelating agents

A key aspect in the elimination of pollutants from polluted soils arises from the availability of the pollutants. Ageing of pollutants, which results in leaching of pollutants from easily available to non-available sites, decreases their ability to be removed from contaminated sites (Kumar et al., 2021a). Hence, the most challenging factor in remediation of contaminated sites is the decreased availability of pollutants, which are impounded in the matrix of aged soils. In that context, chelating agents are able to increase the desorption and mobility of the pollutants (Checa-Fernandez et al., 2021) and, hence, improve the availability of the pollutants. Chelating substances that have strong affinity for PTEs can be applied to improve the solubility of PTEs in soil by forming soluble PTE chelates (Nurchi et al., 2020). Diverse groups of chelating agents, like EDTA, EDDS, *N*,*N*′-ethylenebis-[2-(*o*-hydroxyphenyl)]-glycine (EHPG), ethylenediamine-*N*,*N*′-bis(2-hydroxyphenylacetic acid) (EDDHA), and diethylenetriaminepentaacetic acid (DTPA), are applied to improve the remediation of organic and inorganic contaminants (Sun et al., 2020a; Zhang and Zhou, 2019).

The importance of chelators in improving the bioavailability of toxic metals like zinc (Zn), Fe, and copper (Cu) is well understood (Bolan et al., 2014). Removal of PTEs from polluted soils via mobilization of them using chelating compounds has been investigated (Ifon et al., 2019; Nurchi et al., 2020). Chelating compounds have been successfully applied to mobilize PTEs, such as Pb and Cu, thus influencing their consequent plant uptake (Shaheen and Rinklebe, 2015). The efficiency of any chelating agent in mobilization of soil PTEs is governed by various parameters, such as the ionic state of the PTEs, ratio of PTE: chelate, stability constants, occurrence of contending ions, soil pH, stability of the PTE-chelate complex, ageing of the polluting PTE, and extent that the PTEs hold on to the soil (Bolan et al., 2014; Checa-Fernandez et al., 2021; Nurchi et al., 2020). Kirkham (2000) recommended application of EDTA in improving the phytoremediation metal(loid)s capacity of plants, when plants are grown with supplementation of sludge biosolids. The results of the studies showed that uptake of metal(loid)s by sunflower (*Helianthus annuus* L.) was increased when EDTA was applied as a mobilizing agent. Likewise,

Table 1

Selected studies on the potential application of soil amendments in the mobilization of contaminants in soils.

Contaminants	Soil amendments	Highlight of the study	Reference
Zinc (Zn), lead (Pb) and chromium (Cr)	Municipal green-waste compost	Increase the HMs uptake potency of plants; Increase the risk of vegetable contamination with Zn, Pb and Cr.	(Medyńska-Juraszek et al., 2020)
Anionic toxic elements (CrO_2^{4-}, AsO_3^-, Sb(OH) 6$^-$).	Biochar	Biochar amendment enhanced the mobility of anionic toxic elements.	(Guo et al., 2020)
Silver (Ag), antimony (Sb), tin (Sn), and titanium (Ti)	Biochar	Biochar mitigated Ag leaching, but encouraged Sb, Sn, and Ti mobilization, owing to the wider range of E_H (−12 to +333) and pH (4.9–8.1) in the biochar amended soil than the un-amended soil (E_H = −30 to +218; pH = 5.9–8.6)	(Rinklebe et al., 2020)
Hydrocarbons (heptadecane, pristane, and decylcyclohexane)	Organic amendment	A positive correlation existed between the contaminant bioavailability and the contaminant level in the amended soil.	(Chen et al., 2019)
Cr, Zn, copper (Cu), cadmium (Cd)	Chicken and cow manure	Increased the mobility (water-extractable fraction) of HMs in rhizospheric soil.	(Zhang et al., 2015)
Heavy metals (HMs)	Digestate from anaerobic digestion of biowaste, fly ash, ammonium sulfate	Improved Mg, K, Fe, Mn, Cu, Zn, and P mobilization, reduced Hg mobilization.	(Paz González et al., 2014)
Soluble metals and As	Biochar and organic compost	Independently, both amendments encouraged significant solubilization of As to pore water (>2500 μg l^{-1}).	(Beesley et al., 2014)
Cu and Zn	Pine bark compost and sheep-horse manure and	Increasing dose of sheep–horse manure and pine bark compost improved soluble Cu; pine bark also improved Zn solubility, while sheep–horse manure decreased.	(Pérez-Esteban et al., 2014)
Pesticides	Mature and immature municipal waste composts	DOM extracted from fresh-immature compost had greater potency to mobilize the sorbed pesticides than the DOM from the mature compost. The pesticide desorption takes place because of cationic and competitive interactions between DOM, pesticide, and soil surfaces.	(Barriuso et al., 2011)
Cd	Humic acid-based amendments	The aged amendments remarkably improved the levels of Cd in rice shoots, except humic-potassium. The humic acid-based amendments could decrease exchangeable fraction of Cd in soil but the effect was not insistent. The unaged amendments would lead to lower Cd accumulation in rice seedlings than the aged amendments.	(Yu et al., 2017)
Cd, Cu, Pb, and Zn	EDTA	The EDTA was more efficient in mobilizing and removing Pb and Cu than Cd and Zn. This might be due to the strong complexation ability of EDTA with Pb and Cu and geochemical distribution of the target PTEs	(Sun et al., 2020a)
Cd, cobalt (Co), Cu, Zn, Cr and Pb	EDTA and citric acid	EDTA generates anionic complexes. Citric acid generate neutral metal complexes in the soil pH conditions (pH = 2–4). Citric acid was much more efficient in the dissolution and transportation out of the soil specimen of complexed metals.	(Cameselle et al., 2021)
Cu, Pb, and Zn	EDDS, HIDS, EDTA, and DTPA	The PTEs were extracted/mobilized at a relatively higher rate under acidic to neutral conditions (pH 5 and 7), while the highest extraction being detected at pH 5.	(Hasegawa et al., 2019)
Cd	Humic substance	Cd elimination was boosted by a higher concentration of humic substance, longer washing duration, close to neutral pH, and higher solution/soil ratio	(Meng et al., 2017)
Cd, Co, Cr, Cu, Pb, and Zn	EDTA, Citric acid and Acetic acid	The remediation of Cd, Co, Cu and Zn was over 70%, whereas Cr and Pb exhibited very limited remediation (below 12%) due to their strong immobilization in the soil.	(Cameselle and Pena, 2016)
Co^{+2}, Zn^{+2}, Cd^{+2}, Cu^{+2}, Cr (VI), Pb^{+2} and Hg^{+2}	Citric acid and EDTA	The collective impact of the soil pH and the complexing agents leads to mobilization of HMs.	(Figueroa et al., 2016)
Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}	Lignin based poly(acrylic acid) (LBPAA)	The LBPAA-assisted elution process decreased the quantity of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions in polluted soil to 22.57%, 52.60%, 13.63% and 17.95%, correspondingly.	(Zhao et al., 2019)
Iron (Fe), aluminium (Al), SOM, PAH	Complexing agents	The complexing agents mobilized polyvalent metal ions, particularly Fe and Al from the soil. They also mobilize SOM and accompanying PAH molecules.	(Yang et al., 2001)
Cd, Ni, Cu, As, Zn and Pb	11 types of surfactants	Texapon N-40 exhibited higher remediation of Zn (86.6%), Cu (83.2%) and Ni (82.8%). Tween 80 eliminate a high amount of Cd (85.9%), Zn (85.4%) and Cu (81.5%) and Polafix CAPB potentially eliminate the Zn (83.2%), Ni (79%) and As (49.7%)	(Torres et al., 2012)
Cd, Ni, As, Cr, Zn and organic pollutants	EDDS with surfactant	EDDS with surfactant can mobilize Cd, Ni, As, Cr and Zn as well as organic pollutants through soil washing process.	(Wen and Marshall, 2011)
Phenanthrene (PHE)	Citric and malic acid	Enhance desorption	(Vázquez-Cuevas et al., 2020)
PFASs	Methanol with ammonium acetate	Amendments improved the desorption and recoveries of most cationic and zwitterionic PFASs	(Munoz et al., 2018)
PFOA, PFBS, PFOS	$CaCl_2$ and NaN_3	Desorption percentage of PFOA, PFBS and PFOS were 15–19%, 18–27% and <4%, correspondingly	(Milinovic et al., 2016)
PFOS	Oxalate and root exudates	Oxalate improved PFOS desorption by 1.43–17.14-fold, effects of root exudates were comparable to those of oxalate.	(Tang et al., 2017)

chelating substances like citric acid, and EDTA improve mobilization of PTEs in soil and enhance phytoextraction efficiency (Shaheen and Rinklebe, 2015; Ojuederie and Babalola, 2017).

6.3. Complexing agents

Application of complexing substances, like thiosulfate, to mobilize PTEs in soils is gaining attention (Grifoni et al., 2017). For instance, Moreno et al. (2005b) reported that the supplementation to soil of sulfur (*S*)-comprising ligand substances, like sodium (Na) or ammonium thiosulfate ($(NH_4)_2S_2O_3$), obtained from mine tailings polluted with Hg, can result in the leaching of Hg and further improve its uptake and accretion in roots along with the aerial parts of plants. They observed that the Hg level in *Brassica juncea* increased to 85 mg/kg when it was grown in a soil having 3.4 mg/kg Hg concentration. The transfer factor was as high as 25. Moreno et al. (2005a) conducted a field trial to study phytoremediation of Hg at a HM-contaminated site in the Coromandel district of New Zealand. They found that Hg uptake by plants could be improved after amendment of soils with sulfur-containing ligands and humic acid, even though the outcomes were generally inconsistent. Grifoni et al. (2017) saw that thiosulfate amendment increased uptake of both Hg and As by plants, with an efficiency equivalent to phosphate amendments generally used to mobilize As. Repeated supplementation of mobilizing agents improves metal accessibility in soil, increases HM uptake by plants, and, subsequently, improves remediation. Repeated thiosulfate treatments increased Hg and As concentrations in the shoots of *B. juncea*, although toxic impacts of Hg decreased plant biomass and total bioaccumulation of both Hg and As (Moreno et al., 2005b).

Mercury (Hg) is generally targeted as the PTE that can be removed from soil via volatilization (Chang et al., 2019). Previously, Moreno et al. (2005a) detected that thiosulfate application decreased the quantity of soil with Hg volatilization by *B. juncea*. It also encouraged Hg accumulation in plants. A trial performed in closed volatilization compartments showed that the diurnal quantity of Hg volatilization from *B. juncea* planted in mine-tailing soil irrigated with water was 23 times higher than the quantity emitted from the control (non-planted) mine-tailing soil. However, after thiosulfate irrigation, the diurnal quantity of Hg volatilization from planted mine-tailing soil was just 6 times higher than the control. Previously, Yang et al. (2001) applied acids and sodium salt as complexing agents to mobilize PAHs, polyvalent metal ions, and dissolved natural organic carbon (DNOC) from contaminated soil. The application of complexing agents effectively mobilized polyvalent metal ions, predominantly Al and Fe from soil. Metal ion complexes are able to disturb humic–(metal ion)–mineral linkages, leads to increase in mobilization of associated PAH compounds and SOM into the aqueous phase and/or decrease the degree of cross-linking in the SOM phase, which could hasten the diffusion of PAH compounds (Yang et al., 2001). Overall, these findings revealed that complexing substances could be used as soil amendments to influence mobilization of contaminants in soil.

6.4. Surfactants

Environmentally friendly surfactant-based strategies have gained consideration for the elimination of contaminants from diverse media due to their eco-sustainability, better contaminant-removal potency, flexibility, and the fact that they are built on “green chemistry” concepts (Rasheed et al., 2020). Surfactants can enhance water solubility of the pollutants and concurrently improve their availability in soils (Aioub et al., 2019). Surfactants can be synthetic or natural, and they are categorized based on their ionic charge as anionic, cationic, non-ionic, or zwitterionic (Moldes et al., 2021). Once the concentration of a surfactant in aquatic media exceeds its particular critical micelle concentration (CMC), generation of micelles takes place (Majeed et al., 2020). These micelles can act as a hydrocarbon-like segment and encourage the mobilization of pollutants from the media (Fatin-Rouge, 2020). However, the application of surfactants at polluted sites is a double-edged sword. They encourage the solubility of the pollutants, but, concurrently, they lessen the availability of the pollutants and they also are noxious to endogenic microbial communities (Kumar et al., 2021a). Dell'Anno et al. (2018) delivered a comprehensive discussion on application of biosurfactants in mobilization of PAHs from polluted soils.

The efficiency of the surfactant treatment procedure is ruled by several factors, such as concentration of the surfactants, their hydrophilic-lipophilic equilibrium, the pollutants' octanol-water partition coefficient (K_{ow}), soil pH, soil salinity, DOM, temperature, and co-solutes (Lamichhane et al., 2017). Surfactants containing both hydrophilic and hydrophobic functional groups are generally applied to ease the desorption process of POPs and ensuing soil flushing. Nevertheless, several PFAS such as, PFOS and PFOA, are themselves act as surfactants, which produced ambiguity in predicting the behaviours of PFAS mobility. For instance, Pan et al. (2009) reported that cetyltrimethylammonium bromide (CTAB) (cationic surfactant) substantially increase the sorption of PFOS to solid matrices owing to the initial sorption of CTAB by solid matrices, which leads to adsorption of PFOS by exposed CTAB's hydrophobic tails. However, sodium dodecyl-benzene sulfonate (SDBS), which is an anionic surfactant exhibited a concentration-dependent behaviour. When SDBS concentration was lower than 4.34 mg/L, an increased in PFOS sorption, while SDBS concentration greater than 21.7 mg/L, an increased in PFOS desorption was observed (Pan et al., 2009). Guelfo and Higgins (2013) observed that sodium dodecyl sulfate (SDS), which is an anionic surfactant, lessened the sorption of PFOS, perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA) at low concentration, while enhanced the sorption of long chain PFAS, such as perfluorobutane sulfonic acid (PFBS), perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), and perfluorobutane sulfonate (PFBA). Generally, anionic surfactants could be able to increase the water solubility of PFAS, resulting reduced PFAS sorption to soils and enable the mobilization of PFAS. Nevertheless, application of surfactants in the field, their physicochemical and biological interactivity, and production cost needs to be considered before application of a surfactant (Bezza and Nkhalambayausi Chirwa, 2016).

Torres et al. (2012) studied the application of 11 types of surfactants as soil washing agents in the mobilization of PTEs, such as Cd, nickel (Ni), Cu, As, Zn, and Pb from industrial wastes. Texapon N-40, which is an anionic surfactant, displayed good removals of Zn, Cd, and Ni, which were 86.6%, 83.2% and 82.8%, respectively. Tween 80 released a significant quantity of Cu (81.5%), Cd (85.9%), Zn (85.4%), As (49.7%), Ni (79%), and Zn (83.2%) and cocamidopropyl betaine (CAPB), which is a mixture of organic compounds derived from coconut oil and dimethylaminopropylamine, from soil. Mobilization of PTEs also can be achieved by changing the pH of the media through application of additives, like complexing substances, along with surfactants. Wen and Marshall (2011) observed that the application of EDDS along with a surfactant mobilized As, Cr, Ni, Cd, and Zn, in addition to organic contaminants, during soil washing, while Cu, Fe, Mn, and Ca were detected in the left-out fraction. Once EDDS was applied at a high pH, elimination of Pb and Zn was decreased owing to the generation of an anionic hydroxide complex, whereas As and Cu concentrations were higher due to their interaction with oxides of iron. Various surfactants, such as SDS (anionic), CTAB (cationic), and Triton X-100 along with diphenylthiocarbazone (DPC) have been used, because of their potency in eliminating PTEs with increasing pH levels (Doong et al., 1998).

Microbes secrete surface-active agents called as biosurfactants, which improve bioavailability of pollutants (Kaczorek et al., 2018). These biosurfactants reduce the interfacial tensions of the pollutant and increase their mobility and water solubility. This is evident by micellar solubilization of POPs or through alteration of the pollutant matrix. For example, the soil-water interfacial tension is decreased (Ren et al., 2018). Furthermore, hydrophobicity of the microbial cell surfaces and their interlinked relation with hydrophobic pollutants are decreased by biosurfactants. However, few field experiments have been executed by applying biosurfactants to mobilize organic and inorganic pollutants, because of their high production cost. Hence, research needs to be done to make production of biosurfactants cost-effective so that they can be applied in reclamation of polluted sites.

6.5. Desorbing agents

Supplementation of phosphate fertilizers to Pb–As(V) polluted soils has led to improved solubilization and, consequently, leaching of oxyanions like As(V), Cr(VI), and selenite from soils (Alam et al., 2007). Seaman et al. (2001) showed that hydroxyapatite added to PTE-polluted sediments caused increased concentrations of As(V) and Cr(VI) in the sediment solutions. This was ascribed to enhanced sorption competition by $H_2PO_4^-$ with its counterpart oxyanions (Karczewska et al., 2009). Nevertheless, the impact of $H_2PO_4^-$ on desorption of HMs is governed by soil properties, their sorption efficiency, and degree of saturation with a specific HM ion (Smith et al., 2002). Also, phosphate can exhibit strong competition with the molybdate anion (MoO_4^{2-}) for adsorption sites, leads to increased mobilization of MoO_4^{2-} (Goldberg, 2010; Smith et al., 2002). Neunhäuserer et al. (2001) observed that phosphate supplementation enhanced the phytoremediation of soils polluted with Mo, because the soluble phosphate fertilizers increased the solubility of the soil Mo, enabling its remediation via phytoremediation.

Table 2
Selected studies on the removal of organic and inorganic contaminants from soil using soil washing/flushing.

Contaminant(s)	Type of soil	Extraction reagent	Remediation method	Findings	Reference
Organic contaminants					
2,4-Dichlorophenoxyacetic acid (2,4-D)	Synthetic contaminated soil	SDS and Brij 30	Surfactant-enhanced soil washing	SDS showed the best result with 50% pesticide removal by applying single soil-washing step and up to 80% by applying two successive soil-washing steps.	(Bandala et al., 2010)
Petroleum hydrocarbons	Genuinely diesel-contaminated soil	Tween-80	Combination of surfactant improved soil washing and electro-Fenton method	>99.5% mineralization of the hydrocarbons was achieved within 32 h	(Huguenot et al., 2015)
Crude oil	Artificially oil-contaminated Sand, Ottawa	Phenolate, carboxylate and benzoate salts	Switchable anionic surfactants by soil washing	All switchable surfactants could remove the crude oil from sand at 50 °C and afford successive oil separation from the water after CO_2 treatment.	(Ceschia et al., 2014)
Diesel	Synthetic contaminated soil with diesel	Tween-80	Combination of soil washing and electrochemical AOPs	An increase in Tween-80 concentration improved the extraction efficiency of diesel. Higher removal efficiency of diesel in soil washing effluent was achieved using electro-Fenton process than electro-oxidation process.	(Liu et al., 2020)
Lindane	Soil from a quarry located in Toledo, Spain	SDS	Surfactant-assisted soil washing and electrochemical oxidation	An efficient method with the key role of surfactant/soil ratio in the improved efficiency of the washing operation and subsequent electrolysis.	(Muñoz-Morales et al., 2017)
PHE	Artificial contaminated soil	Tween-80	Surfactant-improved soil washing and sulfate radical based AOPs	90% removal of PHE was achieved with positive effects of extraction time, the concentration of surfactant and liquid to soil ratio, and negative effects of temperature. UV/$S_2O_8^{2-}$ process showed almost complete degradation of PHE and 80% recovery of Tween 80.	(Bai et al., 2019)
PHE	Artificial contaminated soil	Nonionic surfactants Triton X-100 (TX-100) and polyethylene glycol dodecyl ether (Brij35)	Soil washing and subsequent ozone oxidation	PHE removal efficiency by TX-100 and Brij-35 was 80.2% and 73.8%, respectively. Degradation efficiencies of PHE, TX-100 and Brij-35 were 99%, 99% and 45%, respectively, at 20 mg/L ozone for 2 h.	(Liu, 2018b)
PHE	Artificial contaminated soil	SDS and Tween-80	Soil washing followed by UVC and UVC/peroxydisulfate	98.2% of PHE removal was achieved at pH 8.6 within 30 min irradiation with 6 W UVC, while the addition of 2 mM peroxydisulfate to the system showed 98.7% removal within 8 min. Soil washing recycling tests confirmed that the recovered SDS could be reused directly without the addition of surfactant and the soil washing performance changed slightly during three cycles.	(Wang et al., 2020)
Diesel	Farmland purple soil at Yanting Agro-Ecological Experimental Station, China	Linear alkylbenzene sulfonates (LAS)	Surfactant-enhanced soil flushing	Complete removal of n-alkanes at lower concentrations in the subsoil was observed. 14%–96% removal range of n-alkanes (indicating the diesel) in the topsoil was observed.	(Guan et al., 2018)
Chlorinated organic compounds (COCs)	Soil contaminated with a real DNAPL	E-Mulse 3	Soil flushing followed by Fenton process	Applying 15 g/L of the surfactant solution in the soil flushing step could extract most of DNAPL from the soil. COCs degradation considerably increased by increasing the dosage of hydrogen peroxide (H_2O_2). After Fenton process, the surfactant solution was reusable.	(Dominguez et al., 2019)
PAHs	Artificial contaminated soil	SDS	Combination of soil washing followed by iron-activated persulfate oxidation	Iron-activated persulfate oxidation is an efficient method of soil remediation, washing effluents containing PAHs and SDS.	(Qiu et al., 2019)
Petroleum	Abandoned oilfield site located in Liao oil field in Northeast China.	Nonionic surfactants: Tween20 and Triton X-100 Cation surfactant: CTAB; Anionic surfactants: Dodec-MNS, NPS-10	Soil washing	Higher petroleum removal efficiency was achieved using montmorillonite and illite with an excellent petroleum washing rate than that using chlorite and kaolinite. Higher petroleum desorption efficiency was achieved with anionic surfactant Dodec-MNS in montmorillonite, chlorite,	(Li et al., 2016)

(continued on next page)

Table 2 (*continued*)

Contaminant(s)	Type of soil	Extraction reagent	Remediation method	Findings	Reference
				and kaolinite.	
Nitrobenzene (NB)	Artificial contaminated soil	Sodium dodecyl benzene sulfonate (SDBS)	Surfactant enhanced soil washing followed by effluent oxidation with persulfate	76.8% of NB (47.3 mg/kg) removal was observed by 24 mM of SDBS at a mass ratio of solution to soil (20:1) 97.9% NB removal and 51.6% SDBS removal was achieved by the addition of 40 mM persulfate and 40 mM Fe^{2+} after 15 min reaction.	(Yan et al., 2015)
PAHs	Artificial contaminated soil	TX-100	Soil washing effluents treated by wheat straw biochars produced at different temperatures	71.8–98.6% of PAHs removal and 87% of TX100 recovery was achieved by the biochars. For a specific dose of biochar, PAHs removal and TX100 loss enhanced by increasing pyrolytic temperature.	(Li et al., 2014)
Atrazine	Artificial contaminated soil	Surfactant fluids	Soil washing followed by electrolysis with boron doped diamond (BDD) anode	The combined method is effective for atrazine removal with surfactant/soil ratio as an important parameter	(dos Santos et al., 2015)
Mineral oil D80	Artificial contaminated soil	11-dimethylaminoundecyl sulfate sodium salt (DUSNa), as a CO_2-switchable anionic surfactant	Surfactant-enhanced soil washing	Under CO_2 treatment, 92.1% of the oil was retrieved, and 90.8% of the DUSNa was recycled over 3 cycles of DUSNa-enhanced soil washing	(Xu et al., 2018)
Diesel and motor oil	Real industrial hydrocarbon contaminated soil, Bacau, Romania	Citric acid	Electrokinetic oxidant soil flushing	The treatment showed >65% removal of hydrocarbons with various oxidants ($KMnO_4$, $Na_2S_2O_8$ and NaOCl).	(Sandu et al., 2017)
PerFluoroOctane Sulfonate (PFOS)	Soil samples from a PFOS polluted site, Australia	Ethanol	Soil flushing	After flushing with 5 bed volumes of 50% ethanol, >98% removal of PFOS was obtained.	(Senevirathna et al., 2021)
O-dichlorobenzene and p-dichlorobenzene (o, p-DCB)	Artificial contaminated soil	Biosurfactants (saponin, alkyl polyglycoside) Chemically synthetic surfactant (Tween-80)	Surfactant-enhanced soil flushing	Remediation efficiency of o, p-DCB was highest for saponin and lowest for Tween-80. Saponin solution (4 g/L) showed maximum remediation of o-DCB and p-DCB to be 76.34% and 80.43%, correspondingly.	(Pei et al., 2017)
Sulfolane	Artificial contaminated soil	Milli-Q water	Soil washing followed by UVC/O_3, UVC/H_2O_2, alkaline ozonation and neutral Fenton reagent/soil flushing with subsequent UVC/H_2O_2/O_3	An efficient removal of sulfolane from the soil was obtained using water as an extraction solvent. The subsequent AOPs could effectively degrade sulfolane in the soil washing/flushing solution.	(Yu et al., 2018)
Aliphatic and aromatic fractions of gasoline constituents	Raw soil samples spiked with gasoline	SDS	Soil washing	The remediation efficiency of aliphatic and aromatic fractions of gasoline enhanced by an increase in temperature and pH of the washing solutions.	(Gitipour et al., 2015)
PAHs	Soil from petrochemical complex, Asalooyeh, Iran	Triton X-100 and Brij 35	Soil washing	Maximum removal efficiency of PAHs was detected using 5 g/L of Brij 35 at 80 °C within 60 min. An increase in temperature, surfactant concentration, and washing time resulted in higher removal efficiency.	(Madadian et al., 2014)
Total petroleum hydrocarbon (TPH)	Soil from diesel-contaminated coastal site, South Korea	Tween-80	Soil flushing	A decrease in the number of diesel-degrading microorganisms was observed after the injection of the surfactant. Although the soil flushing with Tween-80 increased the extraction of diesel, it negatively influenced in-situ diesel biodegradation.	(Kwon et al., 2018)
Diesel	Artificial contaminated soil	SDBS, SDS, Brij 35, TX 100, saponin, polysorbate 80 (Tw 80) and tannin	Surfactant-enhanced soil flushing	Combination of surfactant mixture and microbubbles improved the removal efficiency (88.7%–97.1%).	(Huang et al., 2020a,b)
TPHs	Soil from a major oil refiner	Biopolymer and polystyrene foam beads	Soil washing	Combination of biopolymer and polystyrene foam beads yielded 94% TPHs reduction.	(Wilton et al., 2018)
Inorganic contaminants					
Mercury (Hg), Pb, Zn, Cd, Cu and As	Paddy field derived from the Quaternary red clay and modern floodplain sediments near a smelter	$FeCl_3$	Combination of soil washing and in situ immobilization	Combining soil washing and immobilization with lime could effectively amend metal polluted soil, while the addition of biochar or carbon black after washing showed low influences on stabilizing the metals.	(Zhai et al., 2018)
Cd and Pb	Real-site contaminated soils located in a smelter of Jiaozuo, China.	Ethylene diamine tetraacetic acid (EDTA)	Combination of soil washing and freeze-thaw	The combined method could efficiently remove the residual fractions of Cd and Pb in the clay soils.	(Rui et al., 2019)
Cu, Pb, and Zn	Contaminated soil collected from Busan, South Korea	HCl (0.1 M)	Soil washing wastewater using spent coffee grounds	Maximum removal efficiencies for Cu (68.73%), Pb (57.23%) and Zn (84.55%) were achieved at 2.5 g of spent coffee grounds within 300 min and 328 K.	(Futalan et al., 2019)

Table 2 (*continued*)

Contaminant(s)	Type of soil	Extraction reagent	Remediation method	Findings	Reference
Cu and Zn	Soil collected from former agricultural land within a highly populated area in Campania Region, Southern Italy	Ethylenediamine disuccinic acid (EDDS) a chelating agent	Soil washing process	The soil washing method using EDDS as a chelating agent was effective for Cu and Zn removal from real contaminated soils. Only the exchangeable and reducible fractions of Cu (100%) and Zn (80.9%) could be efficiently extracted using the soil washing process.	(Race et al., 2016)
Cu, Zn	Soil from a former agricultural site polluted by illegal dumping of industrial wastes, Land of Fires, Italy	EDDS/*Lactuca sativa*	Soil washing and subsequent phytoremediation	44–77% Cu removal and 18–47% Zn removal through soil washing The adsorbed HMs and EDDS into the soil had a negative effect on the plant's growth, while the highly efficient washing method showed no adverse effect on the plants. Up to 88% Cu removal and 95% Zn removal was observed via phytoremediation, mainly due to leaf uptake.	(Komínková et al., 2018)
Organic and inorganic contaminants					
PAHs and HMs	Contaminated soil collected from a former manufactured gas plant site, Jiangsu, China.	Methyl-β-cyclodextrin (MCD) and EDDS	Combination of ultrasound-assisted soil washing and bioaugmentation	84.5% of PAHs removal and 81.3% of HMs removal was achieved after two successive washing cycles. The residual PAHs removal reached up to 86.8% by inoculation of PAHs-degrading bacterial strains with the addition of nutrients in 16 weeks.	(Chen et al., 2016a)
Hydrophobic organic contaminants (HOCs) (PBDEs, PCBs, and PAHs), HMs (Pb, Cu, and Ni)	Abandoned electronic waste recycling plant, Xuzhou, Jiangsu, China	Methyl-β-cyclodextrin (MCD) and tea saponin (TS)	Ultrasound-assisted soil washing	The method simultaneously mobilized most of HOCs polybrominated diphenyl ethers (PBDEs), and HMs. 93.5 of HOCs removal and 91.2% of HMs removal was achieved with 15 g/L MCD and 10 g/L TS after 2 cycles of one-hour ultrasound-assisted washing cycles. A remarkable reduction in operating time was detected in ultrasound-assisted soil washing compared to soil washing without ultrasound.	(Chen et al., 2016b)
HMs (Pb, Cu, Zn) and low-level petroleum hydrocarbon	The polluted site located at the Yongsan railroad depot in Seoul, Republic of Korea.	Hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), tartaric acid and EDTA	Soil washing	HCl was found as the best washing agent for HM removal. Tartaric acid revealed the highest removal for total petroleum hydrocarbons. For the removal of both petroleum hydrocarbon and HMs, tartaric acid could be a possible washing agent.	(Moon et al., 2016)
Organochlorine pesticides (OCPs) and HMs (Cd and Pb)	Soil collected from an abandoned pesticide factory, Shiyan, Hubei, China	Maize oil, carboxymethyl-b-cyclodextrin, and vetiver grass	Enhanced soil washing and phytoremediation	The combination of ultrasonication and elevated temperature with maize oil and carboxylmethyl-β-cyclodextrin was efficient for contaminants extraction from soil. The remediation efficiency of OCPs, Cd, Pb, mirex, endosulfans, and chlordanes were >87% after 2 successive washing cycles. After three months of vetiver grass cultivation and nutrient addition, 34.7% of the residual total OCPs was degraded, and the soil's microbiological functions were partly restored.	(Ye et al., 2014)

The uptake of As by plants can be stimulated by P via two routes. Firstly, As(V) can play a role as a P analog. Therefore, it is easily taken up by plants through a P-transporter route (Bolan et al., 2014), whereas a P deficit may increase uptake of As by plants. A high level of P in the solution may impede As uptake by plants (Lei et al., 2012). Secondly, in comparison to As(V), P is preferably adsorbed by the soil and, hence, competes for adsorption sites. In that way, P facilitates As desorption from the soil solution and consequent uptake by plants (Ravenscroft et al., 2001). Bolan et al. (2015) described the impact of P availability on the mobility of As(V) and subsequently its change in bioavailability with allophanic and non-allophanic soils as well as its change when adsorbed onto the soil compared to when it is in solution. The P-effect on uptake of As by plants in a soil system and solution culture can be ascribed to competitiveness of P for both As absorption by plant root system and adsorption by soil constitutes. In the soil system, supplementation of P enables As mobility as well as its bioavailability. In solution culture, supplementation with P results in competition with As for absorption via the plant root system, thus reducing uptake of As. Nevertheless, the net impact of phosphate on As phyto-availability in a soil system is governed by *P. Phosphorus* and As compete with each other to control root uptake (rhizofiltration) of As.

7. Mobilization as a sustainable and green remediation method

Application of mobilizing agents enhances the elimination of pollutants from soil by applying techniques such as soil washing (Liu et al., 2018), soil flushing (Wang et al., 2020), phytoremediation (Antoniadis et al., 2021), and bioremediation (Ite and Ibok, 2019). Many studies have investigated the mobilization of organic and inorganic contaminants in soil using one or a combination of these techniques (Tables 2 and 3). They are described in detail below.

7.1. Soil washing and soil flushing

Soil washing, an efficient physicochemical extraction process, is practised by transferring different organic and inorganic pollutants from the soil into an aqueous stream using extractants (Befkadu and Quanyuan, 2018) (Fig. 2). This technique is conventionally performed ex situ, where extractants, such as chelating agents, oxidizing agents, acids, bases, and surfactants, are applied to the soil to move contaminants from the soil into an aqueous solution (Trellu et al., 2016). The polluted soil is excavated and treated at the surface (Befkadu and Quanyuan, 2018).

Soil flushing is in situ soil washing, in which the contaminants are removed by passing an extraction fluid via the polluted soil (Fig. 3). Thereafter, the extraction fluid can be treated, recovered, and reused (Liu et al., 2018). The advantages of this method are less damage to the soil ecosystem and lower excavation and transportation costs, because no excavation is required. However, an extended treatment time can make the site unusable during soil flushing (Befkadu and Quanyuan, 2018). Commonly, soil washing is preferred over soil flushing due to reduced contact time between extracting agents and soil contaminants. Soil washing also allows users to better monitor the treatment efficiency (Trellu et al., 2016).

7.1.1. Extractants

Extractants are used to improve the solubility and biodegradability of the desorbed soil contaminants (Trellu et al., 2016). Surfactants are one of the most commonly used extractants. Surfactant-enhanced soil washing, which was initially developed for the petroleum recovery industry, is used to restore soils containing high levels of various organic contaminants, such as hydrophobic organic compounds (HOCs) and pesticides (Bandala et al., 2010; Paria, 2008). Surfactants are especially appealing for such applications due to their lower toxicity and higher biodegradability than most organic solvent-based systems (Befkadu and Quanyuan, 2018; Cheng et al., 2017). Due to being a fast, efficient, and cost-effective method, surfactant-enhanced soil washing is the prevalent soil washing technique (Bandala et al., 2010; Paria, 2008).

Surfactants have both hydrophilic (head group: water soluble) and hydrophobic (tail group: water-insoluble) groups and, hence, are called amphiphilic molecules. Surfactants can be zwitterionic, cationic, anionic, or non-ionic based on their surfactant head group (Deshpande et al., 1999). A variety of non-ionic, anionic, cationic, and mixed surfactants is used for remediation of polluted soil (Befkadu and Quanyuan, 2018). It was described that non-ionic surfactants, with higher solubilization capacities, are generally more attractive for soil remediation than cationic and anionic surfactants, due to absence of an electrical charge, which minimize its possible toxicity as well as its comparatively lower CMC (Cecotti et al., 2018; Cheng et al., 2017). For example, Tween-80, a non-ionic surfactant, was shown to effectively extract diesel from synthetically polluted soil (Liu et al., 2020). Another study claimed that the recovered Tween-80 was effective in flushing phenanthrene (PHE) from polluted soil (Bai et al., 2019). Other non-anionic surfactants, such as polyethylene glycol dodecyl ether (PGDE) (Brij-35) and polyethylene glycol octylphenol ether (PGOPE) (TX-100), were also found to be effective for removal of PHE through soil washing (Liu, 2018b). Similarly, E-Mulse 3, a non-ionic surfactant, was observed to be efficient in remediation of polluted soil with a dense, non-aqueous phase liquid (DNAPL) from lindane wastes through soil flushing (Dominguez et al., 2019).

Anionic surfactants can be more effective for specific contaminants. For example, SDS, an anionic surfactant, showed higher removal efficiency for 2,4-dichlorophenoxyacetic acid (2,4-D) than a non-ionic surfactant, ethoxylated lauryl ether (Brij 30) (Bandala et al., 2010). Similarly, SDS was used as a soil washing fluid for the effective removal of lindane, and its removal efficiency increased under high surfactant/soil ratios (Muñoz-Morales et al., 2017). The application of cationic surfactants is limited due to the possibility of their sorption to negatively charged soil particles. Table 2 summarizes the selected studies on different soil washing or flushing approaches for the elimination of organic and inorganic pollutants from soils.

The presence of toxic metals can inhibit the biodegradation of organic contaminants (Chen et al., 2016a). Metals, unlike organic contaminants, do not degrade microbially or chemically and may persist in soil for a longer duration. Hence, it is important to manipulate their bioavailability by applying soil amendments in HM-contaminated soils. Mobilizing agents, such as desorbing and chelating agents, are used in soil washing to improve removal of HMs by enhancing their mobility and bioavailability (Bolan et al., 2014). In some soils, HMs and HOCs, requiring different remediation techniques, coexist, making the situation challenging for the restoration of contaminated soil. Several studies have investigated the amelioration of co-contaminated soils, and such soils require a mixture of extractants for effective decontamination of soils (Chen et al., 2016a; Chen et al., 2016b; Moon et al., 2016) (Table 2).

7.1.2. Treatment with soil washing or flushing effluents

Soil washing or flushing with extractants results in effluents containing the contaminants and extractants, resulting in secondary pollution. Therefore, it is required to remove the contaminants from the effluent and recover or reuse the extractants (Wang et al., 2020). The most common post-treatments for the removal or degradation of contaminants in the effluents formed after soil washing or flushing are ultrasound-assisted soil washing (Chen et al., 2016a; Chen et al., 2016b), advanced oxidation processes (AOPs) (Liu et al., 2020; Qiu et al., 2019; Yan et al., 2015; Yu et al., 2018), ozonation (Liu, 2018a, 2018b; Yu et al., 2018), the Fenton process (Dominguez et al., 2019; Huguenot et al., 2015; Yu et al., 2018), electrochemical processes (dos Santos et al., 2015; Liu et al., 2020; Muñoz-Morales et al., 2017), adsorption (Futalan et al., 2019; Li et al., 2014), and biological treatment methods (Chen et al., 2016a). These remediation techniques may decrease the levels of contaminants through their removal or enhance the bioavailability of recalcitrant organic pollutants from the washing solution (Befkadu and Quanyuan, 2018). The removal mechanisms of organic contaminants from soil washing effluent using these techniques have been reviewed by Trellu et al. (2016).

7.2. Bioremediation

Application of living organisms to remove environmental pollutants through metabolism refers to bioremediation (Chen et al., 2021; Jeyasundar et al., 2021). This process is divided into two categories: (1) bioremediation by plants or phytoremediation and (2) bioremediation by microorganisms or microbial remediation (Dotaniya et al., 2018; Ali et al., 2022; Bhanse et al., 2022). The combined application of bacteria and plants is also highly effective to treat the organic and inorganic compounds from contaminated soils, as compared to phytoremediation or microbial remediation applied alone (Agnello et al., 2016; Chen et al., 2017; Langella et al., 2014; Xu et al., 2020b; Jeyasundar et al., 2021) (Fig. 4). Bioremediation has been extensively applied as a preferred technique to degrade organic and inorganic soil contaminants (Table 3).

7.2.1. Phytoremediation

Phytoremediation uses plants to reduce contaminant load in soil, and it is classified as a green technique because it has no negative impact on soil quality (Kumpiene et al., 2017; Antoniadis et al., 2021). Mature plants are applied to eliminate the organic and inorganic pollutants from the soil. The plants can then be harvested, treated, and disposed (Kumpiene et al., 2017; Mohammed et al., 2020). Phytoremediation includes different strategies such as phytoextraction, phytostabilization, phytovolatilization, and phytodegradation, and the plants use a combination of these strategies to remove contaminants from soil (Antoniadis et al., 2017; Dotaniya et al., 2018; Shaheen et al., 2019; Mohammed et al., 2020). In phytoextraction, contaminants are accumulated directly into aboveground parts of plants, which can be removed. In phytostabilization, contaminants accumulate in

Table 3
Selected references on the removal of organic and inorganic contaminants from soil using bioremediation.

Contaminant(s)	Type of soil	Plant species	Organism species	Bioremediation method	Findings	Reference
Organic contaminants						
Oil hydrocarbons	Soil from a former industrial area devoted to oil refining	*Geraniums, poinsettias* and *Buxus*	–	Chemical oxidation and phytoremediation combined with direct current technology (DCT)	Significantly higher efficiency was observed in the two combined techniques (electrooxidation with H_2O_2 and phyto-electroremediation with poinsettias).	(Rada et al., 2019)
Dichlorodiphenyltrichloroethane (DDT)	Soil from a long-term cotton field, Henan province, China	Tall Fescue (TF) and Perennial Ryegrass (PR)	*Pseudomonas* sp. SB	Phytoremediation assisted by microbes	The soil bacterial community was remarkably influenced by the plant species. The removal efficiency of 59.4% for fertilizer + TF, 65.6% for fertilizer + TF + *Pseudomonas*, 69% for fertilizer + PR, 65.9% for fertilizer + PR + *Pseudomonas* was observed.	(Wang et al., 2017)
Crude oil	Soil from an oil well, Yan'an, China	–	Indigenous bacteria	Chemical oxidation followed by bioremediation	Low H_2O_2 level led to a high population of remaining indigenous bacteria and improved nutrient mobilization and bioremediation.	(Xu et al., 2016)
Petroleum	Artificial contaminated soil	Sunflower (*Helianthus annuus* L.)	–	Electrokinetic remediation combined with phytoremediation	Electro-phytoremediation by supplying reversal polarity showed high removal efficiency for total petroleum hydrocarbon (TPH). The main operational parameters were microbial degradation in the rhizosphere and transportation of organic compounds through the soil associated with the reversal polarity.	(Rocha et al., 2019)
Di(2-ethylhexyl)phthalate (DEHP)	Artificial contaminated soil	–	Earthworms (*Eisenia foetida*)	Chemical oxidation followed by bioremediation	Up to 94% toxicity reduction was observed with 2.5% H_2O_2. The bioremediation was efficient after five months of treatment, showing similar results as uncontaminated soil.	(Ordoñez-Frías et al., 2020)
Oil	Artificial contaminated soil	Ornamental flowering plants	–	Phytoremediation	Gazania showed a strong tolerance in soils contaminated by oil. 45–49% decrease of TPH level in soil was observed by the 180th day with Mimosa, Zinnia, Gazania, and cypress vine.	(Ikeura et al., 2016)
Pyrene	Artificial contaminated soil	*Sorghum bicolor*	*Pseudomonas aeruginosa*	Phytoremediation assisted by Indole Acetic Acid (IAA) and microbes	Pyrene removal was significantly higher in planted treatments than unplanted ones. IAA and *Pseudomonas* sp. considerably enhanced pyrene removal and plant biomass.	(Rostami et al., 2016)
Crude-oil	Soil in the vicinity of an oil exploration and production company, Pakistan	*Leptochloa fusca* and *Brachiaria mutica*	Endophytes	Augmentation-assisted phytoremediation	Crude-oil degradation, plant growth, and soil health were improved by endophytes augmentation. Use of *B. mutica* showed 80% oil degradation.	(Fatima et al., 2018)
PHE	Soil from oil refinery, Shandong Province, China	–	Fungus *T. longibrachiatum* FLQ-4, *Sphingomonas*, *Sphingobacterium*, *Acidovorax*, *Massilia*, *Flavobacterium*, *Cupriavidus*,	Fungal bioremediation	An increase in PHE removal was observed. The variety and number of indigenous bacteria in the bioaugmented soil with fungi enhanced dramatically. The PAH biodegradation was	(Li et al., 2021a, 2021b)

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Table 3 (*continued*)

Contaminant(s)	Type of soil	Plant species	Organism species	Bioremediation method	Findings	Reference
			Aeromicrobium, and unclassified *Chitinophagaceae*		attributed to cooperative metabolism by fungi and indigenous bacteria as fungal bioaugmentation supported indigenous functional Proteobacteria.	
TPH	Soil from an abandoned plant at Yangtze River Delta, China,	–	Indigenous bacterial consortium	Bioremediation assisted by bacterial consortium and biosurfactant (sophorolipid)	The method was effective in bioremediation of TPH-contaminated soil. Sophorolipid improved the bioavailability of TPH in polluted soils and enhanced TPH biodegradation via co-metabolism.	(Feng et al., 2021)
Weathered TPHs	Soil from an automobile service and disposal yard, South Australia	–	*Pseudomonas* spp.	Natural attenuation, biostimulation, bioaugmentation.	Bioremediation of the TPHs was inhibited when biostimulation and bioaugmentation were combined. - *P. putida* and *P. aeruginosa* showed great potential in remediating weathered TPHs.	(Ramadass et al., 2018)
TPHs	Soil from Shengli oil field, China	–	Petroleum-degrading bacteria	Bioremediation using bacteria immobilized on biochar	The method was effective in biodegradation of TPHs after 60 days of remediation with a significant role of immobilized microbes on spent mushroom substrate as biochar.	(Zhang et al., 2019)
PAHs	Soil from a refinery, Isfahan, Iran	–	*Bacillus Licheniformis* ATHE9, *Bacillus Mojavensis* ATHE13	Bioremediation	Naphthalene could be removed by *B. mojavensis* in 72 h while acenaphtylene, acenaphthene, dibenzo(*ah*) anthracene, benzo(*ghi*) perylene and indeno pyrene in 96 h. - Several indigenous bacteria showed the potential for PAHs remediation from soil.	(Eskandari et al., 2017)
PAHs	Soil from an abandoned coking plant site, Shenyang, China	–	*Pseudomonas*, *Bacillus*, *Mycobacterium*, *Rhodococcus*, *Sphingomonas*	Electro-bioremediation	The method effectively removed PAHs from the soil. Electro-bioremediation could enhance the removal of total PAHs (~69%) and high ring (4–6 ring) (~66%), which are about 29% and 44% higher than those under bioremediation alone, respectively.	(Li et al., 2020a)
TPHs	Soil from rice cultivation fields near an oil storage unit at Sibsagar District, Assam, India	–	*Pseudomonas aeruginosa* SR17	Biosurfactant enhanced bioremediation	The efficiency of rhamnolipid biosurfactant produced from *P. aeruginosa* was found to be better than synthetic SDS. >80% degradation of total TPH was observed by application of rhamnolipid biosurfactant (1.5 g/L) in soil samples.	(Patowary et al., 2018)
TPH	Soil from an abandoned factory at Yangtze River Delta, China	–	*Sphingomonas changbaiensis* and *Pseudomonas stutzeri*	Biosurfactant enhanced bioremediation	Bioremediation of TPH from soil with bioaugmentation was improved by biosurfactant alkyl polyglycosides. *S. changbaiensis* and *P. stutzeri* preferred to degrade the heavy fraction (C_{24}-C_{30}) and the light fraction (C_{10}-C_{16}), respectively.	(Li et al., 2020b)
TPH	Soil from an oil well, Yan'an, China	–	Indigenous bacteria	Fenton pre-oxidation followed by bioremediation	Bioremediation of TPH was improved by highly matching between the population of residual indigenous bacteria and nutrient.	(Xu et al., 2017)
TPH, alkanes and PAHs	Soil from the Totonaca region, near	*Panicum maximum*	Earthworm (*Pontoscolex corethrurus*),	Combination of bioaugmentation, phytoremediation, and	Combination of the grass with earthworms and the bacterial improved PAHs removal after	(Rodriguez-Campos et al., 2019)

Table 3 (*continued*)

Contaminant(s)	Type of soil	Plant species	Organism species	Bioremediation method	Findings	Reference
	Papantla, Veracruz, Mexico		encapsulated bacterial consortium	vermiremediation	112 days.	
Petroleum	Artificial contaminated soil	*Suaeda heteroptera Kitag*	*Nereis succinea*, *Pseudomonas putida*	Bioremediation	Planting Suaeda heteroptera Kitag could considerably enhance the removal of petroleum. The addition of *Pseudomonas putida* as oil-degrading bacteria could considerably increase the removal efficiency. *N. succinea* could promote the growth of *S. heteroptera*	(He et al., 2019)
Chlorimuron-ethyl	Artificial contaminated soil	–	*Rhodococcus* sp. D310-1; *Enterobacter* sp. D310-5	Bioremediation	Chlorimuron-ethyl could be effectively removed (~87% under optimal condition) by the bacterial consortium.	(Li et al., 2017a)
PCBs	Soil from Lhenice dumpsite, South Bohemia, Czech Republic	–	*Pleurotus ostreatus* and *Irpex lacteus*	Bioremediation	*P. ostreatus* could effectively degraded PCBs with up to 50% degradation in rhizosphere soil.	(Stella et al., 2017)
Petroleum	Artificial contaminated soil	–	*Streptomyces* sp. Hlh1	Bioremediation	*Streptomyces* sp. Hlh1 could grow and degrade TPH, n-alkanes, and PAHs in soil.	(Baoune et al., 2019)
Phorate	Artificial contaminated soil	–	*Brevibacterium frigoritolerans*, *Bacillus aerophilus* and *Pseudomonas fulva*	Bioremediation	The mixed cultures of three microorganisms could degrade phorate with about 98% removal in inoculated soils.	(Jariyal et al., 2018)
Hexachlorocyclohexane (HCH)	Soil from a Landscape Reserve	–	*Rhodococcus wratislaviensis* Strain Ch628	Bioremediation	The efficiency of *R. wratislaviensis* in the degradation of HCH was higher than that of indigenous microflora.	(Egorova et al., 2017)
Spent engine oil	Artificial contaminated soil	–	Earthworm (*Alma millsoni*) and bacterium (*Bacillus* sp.)	Bioremediation	Bioremediation of soils contaminated by spent engine oil was synergistically improved in the presence of *A. millsoni* and *Bacillus* sp.	(Adeyi et al., 2018)
PHE	Artificial contaminated soil	–	*Bacillus kochii* strain AHV-KH14	Bioremediation	Up to 98% biodegradation efficiency of *B. kochii* was achieved for contaminated soil with 50 mg/kg PHE and 1.5% salinity.	(Feizi et al., 2020b)
Inorganic contaminants						
Cd, Zn and Pb	Soil from a zone influenced by zinc smelter in Poland's Silesia Region	Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies* L.) and oak (*Quercus robur* L.)	–	- Phytoremediation supported by sewage sludge	Due to their outstanding adaptability, Scots pine and Norway spruce can be applied in soil remediation. There is the possibility for the risk of recontamination using Oak in phytoremediation owing to the accumulation of high level of HMs in its leaves.	(Placek et al., 2016)
As and Pb	Soils from an industrial site, Tuscany, Italy	*Lupinus albus*, *Helianthus annuus*, *Brassica juncea*, and *Pteris vittata*	–	Assisted phytoremediation	The application of various mobilizing agents such as EDTA and EDDS improved the plants' extraction efficiency for As and Pb.	(Barbafieri et al., 2017)
As	Soil from farmland in Chenzhou, Hunan Province, China	*Pteris vittata* L.	–	Combination of phytoremediation and soil flushing of phosphate	About 54% As removal was achieved by the combination method and 47% As removal in only the flushing method.	(Yan et al., 2017)
Cd	Soil from loam layer of Guangzhou suburb, China	*Solanum nigrum* L.	*Enterobacter cloacae* (Y16)	Microbe-assisted phytoremediation	About 95% Cd recovery was achieved. Plant growth was aided by *E. cloacae* colonization, allowing a higher accumulation of	(Xu et al., 2020)

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Table 3 (*continued*)

Contaminant(s)	Type of soil	Plant species	Organism species	Bioremediation method	Findings	Reference
					mobilizable Cd.	
Multi-metal	Soil from former mining sites located at Ronneburg, Germany, and Kopparberg, Sweden	*Agrostis capillaris, Deschampsia flexuosa*, *Festuca rubra*, and *Helianthus annuus*	Isolated bacteria from rhizosphere soil of endemic plants	Microbe-assisted phytoremediation	On German soil, *H. annuus* demonstrated high extraction potential for some metals without inoculation. When *F. rubra* and *A. capillaris* were mixed with the bacterial consortium, there was a substantial improvement in extraction. After mixing in bark compost, *A. capillaris* was the best option when combined with the microbial consortium on the site in Sweden.	(Langella et al., 2014)
Cd and Fe	Unpolluted soil from the South China and polluted soil from mine tailings in Dabao Mountain, Guangdong, China	*Hibiscus cannabinus*	*Enterobacter* sp. strain EG16	Bacterial-enhanced phytoremediation	Plant growth was improved by inoculation with EG16 which reduced the accumulation of metals in *H. cannabinus*.	(Chen et al., 2017)
Pb and Cd	Artificial contaminated soil	Sunflower (*Helianthus annuus* L.)	–	Phytoextraction	Dry and fresh weights of the growing plants steadily reduced by raising level of HMS in soil. The use of 200 mg Pb and Cd/kg soil decreased the fresh weights and length of shoot and root. Cd removal was more favorable than Pb removal by *H. annuus*.	(Alaboudi et al., 2018)
Cu, Zn, and Cd		*Phyllostachys praecox* and *Sedum plumbizincicola*	–	Phytoremediation	The simultaneous application of plants resulted in considerable improvement of soil phytoremediation.	(Bian et al., 2018)
Cr	Artificial contaminated soil	–	*Azotobacter S8, Bacillus subtilis* and *Pseudomonas putida*	Bioremediation	*Azotobacter* S8 could remove up to 22.82% and 11.08% Cr for 19 mg/kg and 38 mg/kg Cr-contaminated soil.	(Purwanti et al., 2017)
Cd and Zn	Artificial contaminated soil	Wheat	*Rhodobacter sphaeroides*	Bioremediation	Bioremediation with *R. sphaeroides* increased the ratio of Zn/Cd in wheat. The exchangeable phases of Zn and Cd in soil after bioremediation were decreased by 100% and 30.7%, respectively.	(Peng et al., 2018)
Cd	Soil from Gümüsköy mining area, Turkey	Turkey native plants (*Alyssum saxatile*, *Cynoglossum officinale*, *Anchusa arvensis*, *Onosma* sp., *Glaucium flavum*, *Phlomis* sp., *Carduus nutans*, *Silene compacta*, *Verbascum thapsus*, *Isatis*, and *Centaurea cyanus*)	–	Phytoremediation	Mean Cd levels in the soil, shoot, and root of native plants were 82.8, 43.5, and 55.4 mg/kg, respectively. *Carduus nutans* and *Phlomis* showed the ability to be bioaccumulator for phytoremediation of Cd-contaminated soils.	(Palutoglu et al., 2018)
Hg	Forest soil	–	*Aspergillus flavus* strain KRP1	Bioremediation	The KRP1 strain could remove 98.7% and 97.5% mercury from static and shaken systems, respectively. The KRP1 strain showed potential in bioremediation via a biosorption mechanism.	(Kurniati et al., 2014)
Ni	Artificial contaminated soil	*Helianthus annuus*	*Pseudomonas libanensis* TR1 and *Claroideoglomus claroideum* BEG210	Microbial assisted phytoremediation	Inoculation of *P. libanensis* alone or in combination with *C. claroideum* considerably improved plant growth. Inoculation enhanced exclusion of sodium (Na^+), phytostabilization of Ni, and detoxification of Ni and Na^+.	(Ma et al., 2019a,b)

Table 3 (*continued*)

Contaminant(s)	Type of soil	Plant species	Organism species	Bioremediation method	Findings	Reference
Cd, Zn and Pb	Soil from zinc smelter in Silesia Region of Poland	Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies* L.) and oak (*Quercus robur* L.)	–	Phytoremediation assisted by sewage sludge	Densely covered plants were generated by a single application of sewage sludge. Plants were able to completely use the slow release of macronutrients from sewage sludge to promote their growth and production. In comparison to untreated plants, the levels of Cd, Zn and Pb in plant biomass were significantly lower.	(Grobelak et al., 2017)
Cr	Artificial contaminated soil	–	Microbacterium sp. Y2	Electrokinetics combined with bioremediation	After 8 days of remediation by this method, the removal efficiency of Cr could reach about 90.7%.	(He et al., 2018)
Pb	Soil from mine tailings in Anshan Iron and Steel Company	*Solanum nigrum* L.	*Mucor circinelloides*	Phyto and bioremediation	40.2%, 47.2%, and 58.6% bioremediation was observed in Phytoremediation, microbial remediation, and microbial/phytoremediation, respectively. Inoculation of *M. circinelloides* could enhance *S. nigrum* L. growth and Pb removal.	(Sun et al., 2017)
Hg	Artificial contaminated soil	–	*Lecythophora* sp. fungus, DC-F1	Bioremediation by combining a fungus and biochar	Both DC-F1 and biochar efficiently decreased Hg in soil.	(Chang et al., 2019)
As	Soil from paddy fields of Phulia Village in Nadia District, West Bengal, India	–	*Micrococcus* sp. KUMAs15	Bioremediation	Under the culture conditions, KUMAs15 tolerated elevated amounts of As and oxidized arsenite. KUMAs15 showed high As accumulation ability.	(Paul et al., 2018)
Organic and inorganic contaminants						
HMs and petroleum hydrocarbons	Soil from an urban site near a fuel station	Alfalfa (*Medicago sativa* L.)	*Pseudomonas aeruginosa*	Bioaugmentation-assisted phytoremediation	Alfalfa could tolerate and thrive in mildly co-polluted soil. *P. aeruginosa* stimulated plant growth and reduced plant stress. The removal of petroleum hydrocarbon improved by a collaboration of Alfalfa and *Pseudomonas aeruginosa*.	(Agnello et al., 2016)
HMs and petroleum hydrocarbons	Soil from a petrochemical facility in Sao Paulo State, Brazil.	Sunflower (*Helianthus annuus* L.)	–	Biosurfactant (rhamnolipid)-assisted phytoremediation	Cultivation of sunflowers in soils with 4 mg/kg of the rhamnolipid showed 58% removal of TPH, 48% removal of PAHs, and 20–41% removal of HMs.	(Liduino et al., 2018)
HMs (Cd and Pb) and engine oil	Artificial contaminated soil	Indian mustard plants	–	Chelate-enhanced phytoremediation	Compared with EDDS, EDTA was more effective to increase both the levels of HMs in the plants and rhizodegradation of organic contaminant.	(Ramamurthy and Memarian, 2014)
PAH and HMs (Cr, Pb and Cd)	Soil from an agricultural field in the surroundings of Vigo, NW Spain	*Brassica rapa*	–	Electro-phytoremediation	Using 1 ACV/cm potential gradient around *B. rapa* could effectively remove anthracene and phenanthrene but minorly metals. Alternating current for large-scale applications may be the most appropriate electric field.	(Cameselle and Gouveia, 2019)
Naphthalene, PHE, Pb, Cd, and Cr	Artificial contaminated soil	Sunflower (*Helianthus annuus*) and oat plant (*Avena sativa*).	–	Biomass and chemical-enhanced phytoremediation	Growth characteristics and biomass of the plants Improved by the addition of compost amendments and biochar. Use of biochar and compost amendments enhanced the remediation of Cd and Pb, but the use of amendments had little effect	(Chirakkara and Reddy, 2015)

(continued on next page)

Table 3 (*continued*)

Contaminant(s)	Type of soil	Plant species	Organism species	Bioremediation method	Findings	Reference
					on Cr removal. The studied amendments enhanced PAH degradation.	
PBDEs, Cu, Pb, Zn and Ni	Soil from e-waste recycling plant in Taizhou city, Zhejiang Province, China	–	Soil bacterial community	Combination of metal stabilization, persulfate oxidation and bioremediation	Persulfate oxidation decreased the organic matter in soil, resulting in a remarkable reduction of bacterial density. About 95% degradation and 60% mineralization were achieved by the hybrid treatment.	(Ma et al., 2020)
Acetochlor and Pb	Artificial contaminated soil	*Eragrostis pilosa* seeds	*Serratia* sp. QSxin4	Bioremediation	QSxin4 could significantly decrease the toxic effects of acetochlor on the germination of seeds. QSxin4 could bioremediate acetochlor-contaminated soil with high Pb levels.	(Xin et al., 2021)
TPH and Pb	Artificial contaminated soil	–	Soil microbiota	Natural attenuation and biostimulation	Biostimulation was more effective than natural attenuation. Bacterial diversity was affected by the presence of contaminants and nutrients.	(Khudur et al., 2019)
Endosulfan and Cd	Artificial contaminated soil	–	Mushrooms (*Pleurotus eryngii* and *Coprinus comatus*)	Combined bioremediation	Co-cultivation of *P. eryngii* or *C. comatus* showed higher biomass of mushroom than their individual cultivation. >87% endosulfan removal was obtained for all treatments.	(Wang et al., 2018)

roots and become immobilized. In phytovolatilization, water-soluble pollutants are absorbed by the plants and then emitted or evaporated into the air. In phytodegradation, different types of root exudates are secreted from plants, which degrade or break down the pollutants in soil (Chen et al., 2017; Dotaniya et al., 2018; Favas et al., 2014; Mohammed et al., 2020). Furthermore, a plant's roots could act as a nutrient source for soil microbes, resulting in an increase in the degradation rate of the contaminants (Ikeura et al., 2016).

Other remediation techniques can be coupled with phytoremediation to improve the removal of pollutants from soils. For instance, chemical

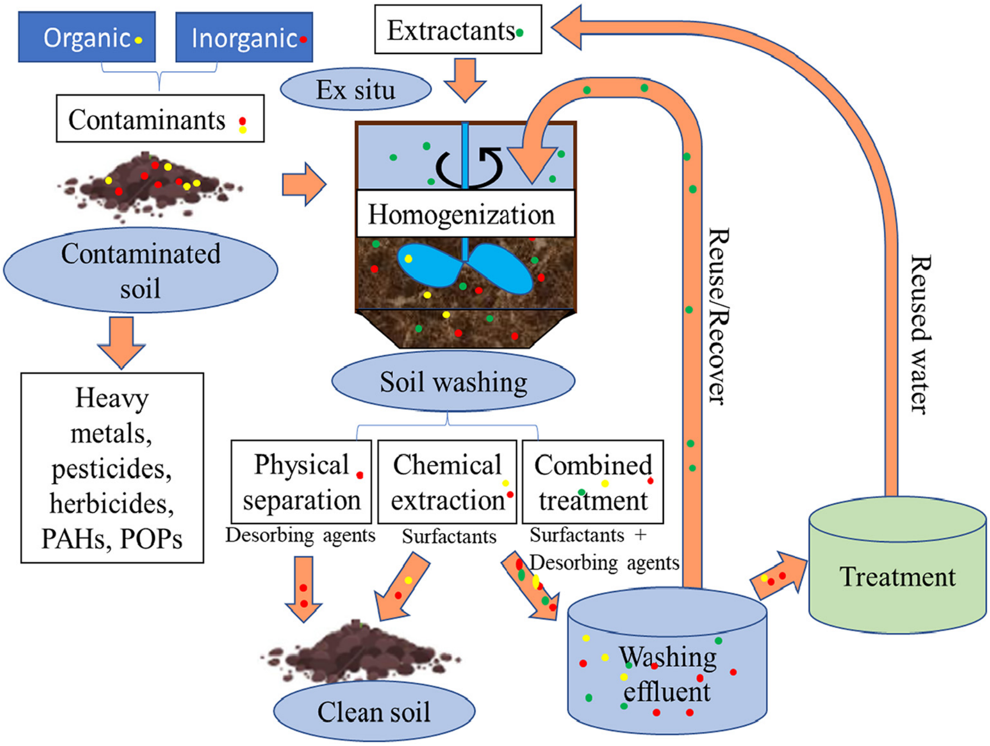

Fig. 2. Schematic representation of soil washing method for mobilization of contaminants.

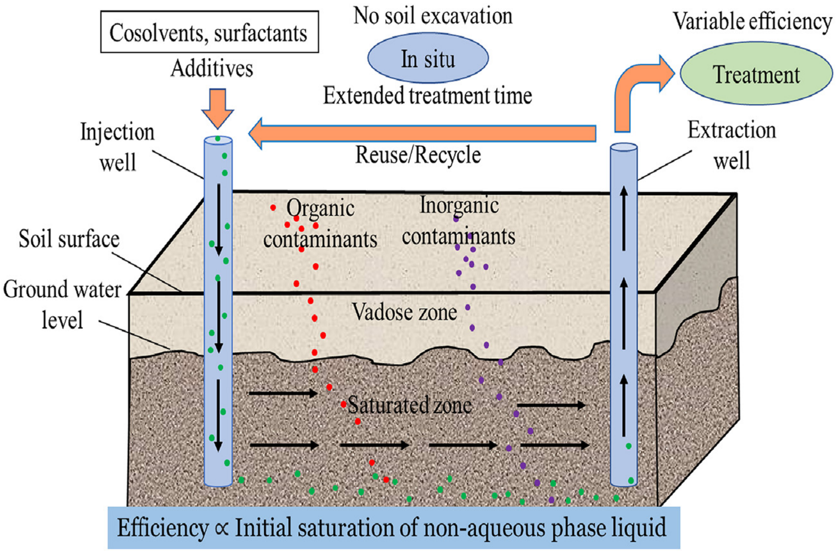

Fig. 3. Diagrammatic representation of soil flushing method for mobilization of contaminants.

additives can be used in combination with plants to alter the soil properties and increase the bioavailability of contaminants (Barbafieri et al., 2017). Chelating agents, like surfactants and EDTA, and weak acids, such as citric acid, are commonly used additives that can improve plants' uptakes of contaminants (Barbafieri et al., 2017; Ramamurthy and Memarian, 2014; Rostami et al., 2016). The combination of microbial remediation and phytoremediation has been extensively studied and can assist in the removal and degradation of various contaminants from soils (Langella et al., 2014; Wang et al., 2017).

7.2.2. Microbial remediation

Owing to being cost-effective and environmentally friendly, bioremediation by microorganisms, such as bacteria and fungi, has been widely applied for the remediation of different inorganic and organic contaminants (Cheng et al., 2018; Ite and Ibok, 2019). In this technique, microorganisms use the contaminants as nitrogen, carbon, and energy sources and convert them into non-toxic or less toxic forms (Dotaniya et al., 2018; Jeyasundar et al., 2021). However, microbial remediation has the limitations of low predictability, prolonged treatment time, dependence on environmental factors, and being inefficient for soils with high contaminant levels (Cecchin et al., 2017; Koshlaf and Ball, 2017).

A bioremediation process must take into account numerous factors, including the existence of appropriate microbial species that can degrade the target pollutant, the bioavailability of the target pollutant to the soil faunas, the presence of nutrients for stimulation of microbial activity, and the occurrence of optimal soil environmental conditions (pH, temperature, and moisture) (Morillo et al., 2020; Ali et al., 2022). Bioremediation of the contaminants can be accomplished via three strategies: natural

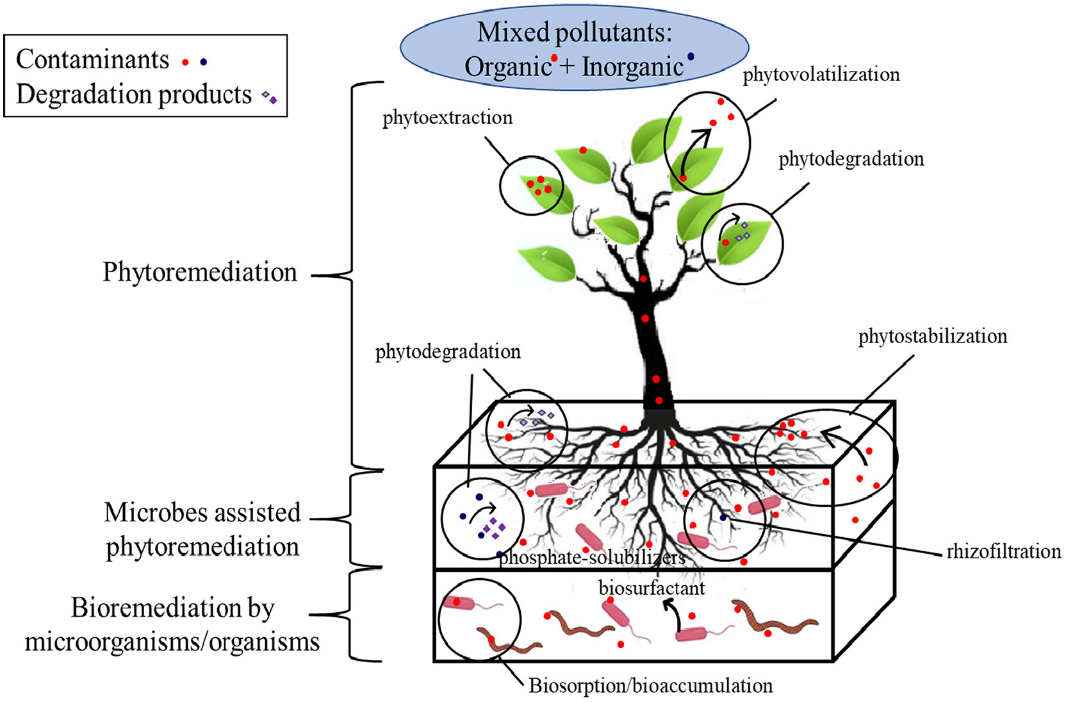

Fig. 4. Schematic representation of microbial assisted phytoremediation of environmental pollutants.

attenuation, bio-stimulation, and bio-augmentation. In the process of natural attenuation, the growth and degradation activity of microbes depends on natural processes. In bio-stimulation, the growth of microorganisms can be enhanced by the modification of environmental conditions. In bio-augmentation, the microorganisms that are evolved to degrade the target contaminants can be inoculated into the contaminated soil (Chen et al., 2017; Garbisu et al., 2017; Ma et al., 2019a,b).

Because microbes perform a key role in maintaining soil ecosystems, the diversity of the microbial community and its structure are crucial for maintaining and indicating the health and function of soil ecosystems (Chang et al., 2019). Some bacterial strains, such as *Pseudomonas aeruginosa*, are able to improve the bioavailability of contaminants by producing biosurfactants, through which the solubility of poorly water-soluble organic compounds and the mobility of toxic metals can be enhanced (Agnello et al., 2016; Feng et al., 2021; Patowary et al., 2018). Moreover, some microorganisms can mobilize the contaminants as well as enhance the plants growth, resulting in improved rates of phytoremediation (Agnello et al., 2016; Rostami et al., 2016; Xu et al., 2020b) (Table 3).

The bioleaching is also a promising bioremediation technology applied to remediate PTE polluted soils owing to its operation simplicity, and low cost (Xu et al., 2020a). The bioleaching is a process in which microbes and their metabolites directly or indirectly mobilize the insoluble contaminants such as, PTEs from solid media via oxidation, reduction, complexation, adsorption, or dissolution (Gao et al., 2021). The microbes applied in the process of bioleaching predominantly belong to eosinophilic, inorganic autotrophic bacteria such as, *Leptospirillum ferrooxidans*, *Acidithiobacillus thiooxidans*, and *Acidithiobacillus ferrooxidans*. Microbes can mobilize PTEs from solid matrices via chelation by microbial metabolites and siderophores, autotrophic and heterotrophic leaching, and methylation-induced volatilization. In this process, dissolution of insoluble metal complexes and minerals, including sulfides, oxides, phosphates, and more complex mineral ores takes place. Finally this process leads to desorption and exchange of metal ions with organic matter (OM) or clay minerals in the soil (Gadd, 2004).

Microbial strains selection is one of the most important and crucial step in the process of bioleaching (Gao et al., 2021). The autotrophic acidophilic microbes having Fe/S oxidizing metabolic pathway can mobilize available and total PTEs from different environmental matrices via the bioleaching (Camargo et al., 2018; Beolchini et al., 2013). Particularly, the microbial strains isolated from acid mine drainages (AMD) have been considered as potential candidate for the process of bioleaching (Ma et al., 2019a,b; Hao et al., 2019). However, less consideration has been paid to investigate the bioleaching efficiency of autotrophic acidophiles isolated from AMD on PTE polluted soil. In comparison to autotrophic microbes, heterotrophic microbes have been gain much more attention in the bioleaching owing to their ability to utilize organic acids (Gao et al., 2021). Typically, organic acids (acetic acid, propionic acid and hexanoic acid) can interrupt the sulfur and ferrous oxidation capability of the autotrophic acidophiles (Xu et al., 2020a). Additionally, few investigators revealed that the mixotrophic acidophile consortia comprising autotrophs as well as heterotrophs can be able to immobilize PTEs efficiently than single pure microbe due to their improved environmental adaptability (Yuan et al., 2022; Emenike et al., 2017). A recent pot experiment demonstrated the bioleaching and microbial-assisted phyroextraction of Cd from contaminated paddy soil using the mixotrophic acidophiles (Hao et al., 2019). This study revealed that, application of the mixotrophic acidophiles improved Cd concentration in plant tissues by 78% compared to deionized water treatment, which showed the importance of the mixotrophic acidophiles in the process of microbial-assisted phytoextraction.

In addition to soil microbes, soil macrofauna such as earthworms (*Eisenia fetida*) is well known for its potency to assimilate several soil contaminants via soil ingestion and/or direct dermal contact, hence play an key role in remediation of polluted soil (Xiao et al., 2022; Boughattas et al., 2019). Meanwhile, *E. fetida* is well known as ecosystem engineers, and it can modify soil properties via burrowing, casting, and redistribution of OM in the soil (Gan et al., 2021). Furthermore, application of *E. fetida* in soil can also affect the soil microbial diversity (Ma et al., 2017) and the bioavailability of HMs (Gan et al., 2021). Huang et al. (2020a,b) previously demonstrated the successful application of *E. fetida*, which significantly improved the extraction of HM from soil by *Phaseolus vulgaris* L, revealing a positive relationship between *E. fetida* and plants in terms of HM removal. Štolfa et al. (2017) also reported increase in bioavailability of selenium (Se) for wheat crop when *E. fetida* inoculated in HM contaminated soil.

8. Unintended consequences of mobilization of contaminants

The unintended consequences of the conventional mobilization approaches have been discussed in relation to contaminant leaching. Mobilization of targeted and non-targeted contaminants may cause toxicity to microbial communities and plants (Naidu et al., 2021; Vocciante et al., 2019). For example, most chelating agents are not selective to specific HMs and can mobilize other metals, such as aluminium (Al) and Mn, thereby resulting in toxicity to plants (Bolan et al., 2014).

8.1. Contaminant leaching

Application of mobilizing agents at contaminated sites has its own limitations. For instance, soil amendments can solubilize toxic soil contaminants or pollutants other than the target, making them bioavailable to the biota (zootoxicity, phytotoxicity) (Bolan et al., 2015; Chen et al., 2019). This can increase the risk of groundwater contamination. For example, a study showed that amendment of synthetic chelates under field conditions increased the PTE concentrations (Evangelou et al., 2007). Various factors influence the leachability of PTEs during chelate-enhanced phytoextraction: soil characteristics (OM), nutrients, carbonates, soil type, chelate concentration, pH, operating mode (split, full dose), time of application (during germination or harvesting), water level, plant species, root zone conditions, and uptake of solubilized metal(loid)s (Bolan et al., 2021a; Kaur et al., 2020; Shaheen et al., 2019). For example, the risk of groundwater contamination increases when EDTA is applied during (immediately before or after) germination due to the absence of root mass to absorb the target PTEs (Bolan et al., 2014).

For As mobilization and phytoremediation, desorbing agents like phosphate amendments are widely employed to displace and solubilize the adsorbed As from soil (Grifoni et al., 2017). For instance, at As-contaminated sites, phosphate fertilizers enhanced the bioavailability of As to apple trees (grown for phytoremediation) (Davenport and Peryea, 1991) via competitive anion exchange. Applying potassium phosphate increased the As leaching and mobilization from plum and apple orchard soils (Codling and Dao, 2007). Amendment of 18% phosphorus pentoxide (0.4% (w/w), 7.2% P soluble in H_2O) increased the soil As leachability by a 13-fold increase.

Liphadzi et al. (2003) examined the impacts of chelate on the soil mobility of PTEs in a sludge farm (very fine sandy loam soil). Without EDTA, the PTE concentrations in the leachate were very low. In the absence of plants, Zn, Cd, Fe, Cu, and Pb leached with EDTA in the columns. The concentrations of those HMs surpassed the drinking-water standards, while poplar plants reduced the Zn, Fe, and Cu concentrations in the leachate (within the standards). The authors concluded that EDTA-treated sludge (irrespective of the presence of plants) contaminated the ground water with PTEs from the soil.

In experimental trial with and without barley (*H. vulgare* L.) grown in columns, Madrid et al. (2003) observed that, at early stages, the plant roots are able to immobilize Zn, Mn, Cd, Pb, Fe, and Ni in EDTA-treated soil, but concentrations of Pb, Cd, Mn, Fe, and Mn in the drainage water was found many folds higher than the drinking water standards, indicating the leaching of these metals. Similarly, many studies have reported the possible environmental risks of nitrilotriacetic acid (NTA) and N-(2-hydroxyethyl)iminodiacetic acid (HEIDA) (Chiu et al., 2005), cyclohexane diamine tera acetic acid (CDTA) and diethylenetriaminepentaacetic acid (DTPA) (Cooper et al., 1999), EDDS (Meers et al., 2005), ethyldiglycol acrylate (EDGA) (Römkens et al., 2002), and EDTA (Jiang et al., 2003) on metal mobility.

Strategies to control leaching of pollutants, such as splitting the dosage and drainage control, have been proposed and have been applied. However, the dosage splitting of the mobilizing agents also retards the effectiveness. For example, EDTA applied in different dosages poorly enhanced the uptake of HMs by plants compared to a single dose (Grčman et al., 2001). Another study suggested collection and recycling of metal-enriched drainage water for further phytoremediation to enhance the metal uptake (Madrid et al., 2003). However, these techniques have their limitations. They are expensive and present the risk of HM leaching during heavy rainfall. Robinson et al. (2003) highlighted potential groundwater pollution by metal mobilization, with little enhancement in phytoremediation, caused by chelate-assisted phytoextraction, and they questioned its feasibility to address the current environmental legislations and norms.

8.2. Microbial- and phyto-toxicity

Mobilization of contaminants increases their bioavailability, thereby causing toxicity to soil microorganism and higher plants (Fuke et al., 2021). On the one hand, some PTEs (Zn, Cu) play an important role in physiological processes (metalloenzyme components) of all living organisms including soil microorganisms (Alloway, 2013). On the other hand, excessive concentrations of most PTEs inhibit microbial growth, reproduction (protein denaturation), metabolism (functional disturbance), and morphology (reduced cell membrane integrity) in soil (Adriano, 2001). Furthermore, PTEs can denature soil microbial enzymes and interact with the active sites and the substrates for soil microbial enzymes (Duan et al., 2022). PTEs also alter the microbial communities in soil, which indirectly impacts soil enzymatic activities (Zhang et al., 2022).

Long-term PTE contamination of soils is hazardous to soil microbial respiration, activity, and functions (Zamulina et al., 2021). At higher concentrations, the toxic impacts of PTEs can result in decreased microbial diversity and alteration in the rate of important biological activities, including nutrient cycling, which underlie ecosystem functions (Fuke et al., 2021). The microorganisms of PTE- contaminated soils generally have been known to change their functional activities, such as decreased biomass synthesis (per unit organic substrate consumed) and increased metabolic quotients (qCO_2) (Palansooriya et al., 2020). This indicates an impaired metabolic conversion efficiency of carbon substrates to biomass. Furthermore, PTE-contaminated soils have higher energy requirements for biomass synthesis than uncontaminated soils (Peco et al., 2021).

Microbial functional diversity is a complex indicator of anthropogenic impacts on soil ecology, including PTE contamination (Zamulina et al., 2021). There are two strategies involved in the ability of microbes to function effectively in PTE-contaminated environments. Firstly, transmembrane systems for PTE pumps (*sil* and *mer* operons aid resistance against silver (Ag) and Hg toxicity) have evolved in many microbes including bacteria (Silver and Phung, 1996). These pumps help in scavenging and removing PTEs from the cell (i.e., accumulating in vacuoles), thus protecting the internal cell structures from PTE toxicity. The second mechanism includes evolution of microbes to produce PTE-resistant enzymes, which provides resistance toward PTE toxicity (Mondal et al., 2019).

9. Conclusions and perspectives for future research

Bioavailability is a key factor to be considered in risk-based remediation of contaminated sites, and a range of soil amendments need to be used to manipulate the mobility and subsequent bioavailability of contaminants. Mobilizing amendments are applied for efficient removal of contaminants though phytoremediation, bioremediation, and soil washing. While chelating and desorbing amendments have been effective in the mobilization of inorganic contaminants, such as PTEs, natural and synthetic surfactants have been found to be successful in the mobilization of POPs. Metals, unlike organic pollutants, do not degrade microbially or chemically and may persist in soil for a longer duration. Hence, mobilizing agents are used in soil washing to improve removal of PTEs by enhancing their mobility and bioavailability. Although mobilization techniques and mobilizing agents help to reduce the total contents of contaminants in soil, however, application of mobilizing agents at contaminated sites has its own limitations. Application of mobilizing agents solubilizes toxic soil contaminants or pollutants other than the target, making them bioavailable to the biota. Mobilization of targeted and non-targeted contaminants may cause toxicity to microbial communities and plants. Furthermore, their application can also increase the risk of groundwater contamination due to leaching of contaminants. Therefore; it is important to adopt mobilization approaches that apply soil amendments when plants are actively growing at the contaminated sites and those that undertake soil washing operations soon after the application of soil amendments.

Given the current knowledge of the mobilization approach for soil remediation, the following research areas can be explored in the future:

- Field studies demonstrating the value of various mobilizing amendments for the successful application of soil remediation need to be investigated.
- Sometime application of organic amendments can antagonistically immobilize the contaminants in soil by forming organo-metallic complexes. Therefore, future research must consider this aspect before applying organic amendments as mobilizing agents.
- The fate and toxicity of mobilized contaminants to soil microbes and higher plants need to be examined.
- The effect of mobilizing agents on activity, abundance, and diversity of soil microorganisms, which play a imperative role in the mobilization and removal of contaminants, needs to examined under field conditions.
- The combination of microbial remediation and phytoremediation has been extensively studied and can assist in the removal and degradation of various contaminants from soils. However, application of this technology supplemented with mobilizing agents needs to be prioritized in future research.
- Because some mobilizing amendments, such as composts, can act as a source of soil contaminants like PTEs, advanced treatment techniques should be developed to remove these contaminants in the mobilizing amendments.
- Mobilizing agents are used in soil washing to improve removal of PTEs by enhancing their mobility and bioavailability. However, in some cases, co-existence of PTEs and organic contaminants make the mobilization challenging and ineffective. Therefore, future research must explore some new innovative technics to restore and rejuvenate those cases.
- Research on different physicochemical processes for modifying the soil amendments, including advanced functionalisation, is needed to efficiently mobilize contaminants.
- Site-specific and contaminant-specific integrated approaches to remediate contaminated sites involving a range of mobilizing amendments need to be developed.
- Finally, techno-economic and life cycle assessment studies need to be conducted in future research, to access the economic feasibility and environmental impact of soil remediation by mobilization approaches.

CRediT authorship contribution statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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