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Application of Innovative and Emerging Technologies for the Remediation of POP-Contaminated Sites - A Comprehensive Review

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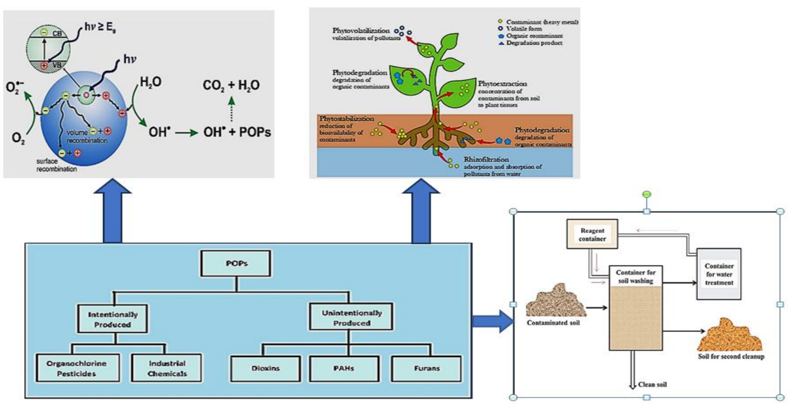
Persistent organic pollutants (POPs) are toxic chemical substances with a distinctive blend of physic-chemical properties that sustain their persistency for long periods when released into the environment. Many of these compounds were made initially for industrial application, crop production and the control of pests and diseases. Unfortunately, studies have revealed the extremely detrimental effects of the POPs to humans and the environment, due to the poor management of the chemicals. Some of these chemicals are hormone disruptors, linked to diseases like reproductive defects and cancer. A critical assessment of the most current developments in POP remediation technologies for soil is contained in this review. The effective and innovative types of POPs remediation technology were evaluated in this article. Furthermore, innovative and emerging techniques with high remediation performance such as the advanced oxidation processes, nanotechnology, and phytoremediation were thoroughly reviewed. In addition to analyzing the advantages and disadvantages of each technique, this comprehensive review emphasizes the importance of integration strategy in water treatment technologies. The information provided on the emerging, diverse clean-up techniques for remediating POPs contaminated sites would be of great benefit to researchers, policy makers, and environmental professionals facing the challenges of POPs removal from soil.

Graphical abstract



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1. Introduction

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Global industrialization and rapid urbanization have made living without chemicals highly improbable for the present advanced society. Chemicals are utilized in diverse sectors, such as pharmaceuticals, construction, leather, and pulp and paper making, which are fundamental to our quality of life [1]. After World War II ended, the advent of scientific breakthroughs and awareness, where researchers began to understand the non-biodegradability and persistence of some chemicals in the environment started [2]. These chemicals could persist for extended periods, propelling through water, soil, sediments and the atmosphere while increasing to levels that could destroy the ecosystems and impair the health condition of people [3]. The ability of these toxic chemicals to defy natural photolytic, chemical and biological decomposition could be attributed to their unique blend of physicochemical properties, which promotes their stability and longevity in the environment. These chemicals are generally referred to as persistent organic pollutants (POPs) [4–6]. Following their release into the environment, the POPs disperse through the air and accumulate on surface soils through wet and dry depositions, forming secondary sources of contamination in soil, which are thereafter, released as secondary emissions to the atmosphere. According to several studies, POPs are mostly produced *via* agricultural activities in rural regions, but in urban areas, they are produced during industrial emissions, hydrocarbon combustion and inadequate wastewater treatment, among other factors [7]. In summary, the following factors could have contributed to an increase in the rate of pollution: ongoing industrialization, irrational mineral resource extraction and smelting, prolonged sewage irrigation and sludge application to soil, anthropogenic atmospheric deposition and fertilizer and pesticide use in agriculture. Other factors include leachate from municipal and chemical landfills; abandoned dumpsites, accidental spills of chemical or waste materials; improper underground injection of liquid wastes and placement of septic tank systems in hydrological and geological unsuitable locations [8].

Soil pollution has steadily grown into a global environmental issue. It has worsened recently, resulting in a major negative impact on people's health. The persistence of toxic chemicals in soils is affected by some variables which include soil characteristics, weather conditions, the type of chemical applied, irrigation design and cropping technique [9,10]. POPs have been detected in humans, animals and plants. Several studies have associated the presence of residual chemicals (POPs) in the human body with diseases such as cancer [5,9,11]**.** Some of these chemicals have been recognized as hormone disrupters that can impair the normal operation of the endocrine and reproductive systems in people and wildlife [12]**.** Furthermore, their propensity to bio-accumulate and biomagnify in food chains poses a risk to human health [9]. Therefore, the minimization and eradication of POPs became of interest to the world, leading to a call for control measures to be taken.

Remediation technologies serve to immobilize contaminants, separate them from environmental media, or destroy them. Currently, soil remediation may be done through different ways [13–16]. These approaches can be categorized into three: chemical remediation, physical remediation, and bioremediation [8]. Although the common physical-chemical conventional remediation methods like incineration and solvent extraction are highly effective, they are also more expensive and can adversely alter the qualities of water and soil. Furthermore, secondary pollutants may be formed. All these make the remediation processes costly and sometimes ineffective, especially for ex-situ treatments, while some do not address or remove the contaminant. Due to these inadequacies, some countries have devoted resources to developing advanced, innovative/emerging remediation technologies and tools for evaluating the applicability and sustainability of the different technical options [17]. The current and emerging remediation technologies of interest discussed in this article include physical/thermal remediation methods (e.g supercritical fluid extraction, vitrification, pyrolysis, vapour extraction, electrokinetics, etc), chemical methods (e.g. soil washing *via* green solvents, advanced oxidation process), biological processes (e.g bioventing, biosparging, biostimulation) electrokinetics, phytoremediation techniques and nanoremediation techniques [15,18–20]

The selection of appropriate technologies, though often difficult, is an important step for the successful remediation of a contaminated site since most remediation technologies are site-specific [21]. POP remediation has been transformed by advanced oxidation technologies like the photocatalysis, ozonation and photo-Fenton techniques. The photo-Fenton process involves the breakdown of pollutants by hydroxyl radicals, which are formed when iron and hydrogen peroxide are exposed to UV or light. Ozonation introduces powerful ozone oxidizers into aqueous systems and several pesticides and industrial chemicals are degraded *via* these methods. Nanoremediation technology is another type of emerging remediation technique that is based on the use of nanoparticles. Over the past ten years, several polluted grounds have been treated and restored *via* nanoremediation, according to publications posted on the USEPA and environmental nanotechnology websites. Nanoremediation has led to a notable 80% reduction in operational cost and treatment period of polluted locations compared to conventional remediation methods, according to results from research conducted [22]. Likewise, bioremediation is a rapidly developing technology that involves the application of certain types of living microorganisms to soil and water to degrade, metabolize, or immobilize substances like pesticides, organic pollutants, and hydrocarbons and produce a better media quality. The methods applied for the bioremediation of chemical contaminants include: 1) the introduction of nutritive media (biostimulation) to modify contaminated media i.e to provide nutrition to soil microbiota by adjusting pH and adding nutrients which improve the carbon, nitrogen and phosphorous ratio (C: N: P) [23], 2) the introduction of an aeration system (bioventing), which is a process of aerating soil/water to stimulate in-situ biodegradation of organic contaminants [22], 3) the addition of microbial population (bacteria and fungus) together with any biocatalyst (gene and enzyme) to breakdown organic and inorganic pollutants under controlled conditions. Phytoremediation is an emerging technique that uses special plants, enzymes extracted from plants, unique planting procedures and other techniques to increase the degradation rate of contaminated soil, water and gaseous pollutants. Mechanisms involved in phytoremediation are phytodegradation, phytoextraction, phytofiltration, phytovolatilization and phytostabilization [24].

Currently, innovative methods that involve more efficient and economical approaches like combining remediation strategies to achieve a high success rate of POP elimination have been developed. As a result, merging several approaches has currently demonstrated greater efficacy, better economic benefits and a larger application scale. The integrated remediation strategies include physical-chemical, physical-chemical-biological and biological-microbial techniques.

Several investigations are now being conducted on this kind of remediation technique. However, a thorough scientific overview of the current integrated remediation approach and bio-microbial techniques for the treatment of POPs-contaminated media is still lacking. Furthermore, environmental protection policies which are specific by type, distribution and extent of contamination, are very crucial for the control of POPs and the preservation of the environment. A proper integrated environmental strategy comprising of efficient policies/regulations and appropriate decontamination technologies is one of the main concerns for the years to come.

The focus of this study is on soil, the intricate nature of POP contamination, and the necessity for adaptable, flexible solutions. Consequently, the study examines several emerging and advanced remediation techniques for cleaning soils polluted with organic materials Apart from assessing the advantages and disadvantages of each technique, the article also covers integrated remediation methods that are intended to clean up soils contaminated by organic compounds and the necessity of considering sociological, economic, and environmental factors to create effective POPs remediation plans. This review is a useful resource for scientists, policymakers, and environmentalists tackling the long-term threat posed by organic pollutants in our soil media.

2. Overview of the Persistent Organic Pollutants

2.1 The POPs

Persistent pollutants are carbon-based chemical substances with toxic properties that persist in the environment and bio-accumulate through the food chain [25]. Their presence in drinking water and groundwater poses a serious risk since they are easily transferred from one source to another and discharged into a different environment. POPs are known to be exceedingly hazardous even at low concentrations and can accumulate in the body due to their environmental persistence [25]. In addition, the presence of chemical compounds like polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and *polychlorinated bisphenyl (PCBs)* in soil sediments is known to affect/degrade soil fertility and quality. Therefore, the minimization and eradication of POPs became of interest to the world at large, which led to a call for control measures to be taken. The Stockholm Convention (SC) is a worldwide consensus, aimed at containing and eventually eradicating the release of POPs into the environment while protecting man and the ecosystems [26, 27]. Representatives from 92 nations signed an international treaty in Stockholm in the year 2001, to avert the release of the 12 original POP chemicals known as the "dirty dozen". Presently, there are a total of twenty-two POPs documented in the SC list.

The 12 persistent chemicals that were banned at the Stockholm convention (2001), are the nine pesticides (aldrin, endrin, chlordane, dichlorodiphenyl-trichloroethane (DDT), dieldrin, heptachlor, mirex, toxaphene and hexachlorobenzene), one industrial chemical (PCB) and two industrial by-products (PCDD and PCD. After an amendment in 2009 which came into effect a year later, nine groups of chemicals, namely chlordecone, lindane α-HCH, β-HCH, hexabromobiphenyl, tetra-BDE& penta-BDE, hexa-and hepta-BDE, PFOS and its salt PFOSF, and pentachlorobenzene, were added to the list. Endosulfan was added in 2011 as the 22nd banned POP. The twenty-two prohibited chemical compounds and their categories are listed in Table 1.

Table 1. Common chemical compounds (POPs) contained in the Stockholm Convention amendment [25].

Amendment 2001	Chemical compound	Category
1	Aldrin	Pesticide
2	Chlordane	Pesticide
3	Dieldrin	Pesticide
4	DDT	Pesticide
5	Eldrin	Pesticide
6	HC	Pesticide
7	Heptachlor	Pesticide
8	Mirex	Pesticide
9	PCBs	Industrial & by-product
10 & 11	PCDDs & PCDFs	By-product
12	Toxaphene	Pesticides
Amendment 2009 13	Chlordecone	Pesticide
14	α-HCH	Pesticide & by-product
15	ɓ-HCH	Pesticide & by-product
16	Hexabromo-bisphenyls	Industrial
17	Lindane	Pesticide
18	PFOFS, PFOS and its salt	Industrial
19	Pentachlorobenzene	Pesticide, industrial & by-product
20	Hexa-BDE &Hepta-BDE	Industrial
21	Tetra-BDE & Penta-BDE	Industrial
Amendment 2011 22	Endosulfan	Pesticide

In General, the POPs can be grouped into two main categories: I) intentionally manufactured chemicals and 2) unintentionally produced chemicals [2,26]. Intentionally produced POPs are chemical compounds deliberately produced to meet the demands of consumers. Intentionally produced POPs may be further categorized into two: 1) pesticides and 2) industrial chemical compounds [2]. Unintentionally produced POPs are chemical compounds generated as undesirable by-products during combustion or industrial activities. Polycyclic aromatic hydrocarbons (PAHs), and the furan and dioxin chemical compounds are the three main types of unintentionally produced by-products, although some intentionally produced industrial chemicals like Hexachlorobenzene, (HCB) and pentachlorobenzene (PeCB) are also specified by the Stockholm Convention as unintentionally produced POPs [6, 28]. A schematic representation of the f POPs group is shown in Figure 1.

2.2. Source, properties and fate of the POPs in environmental media

The POPs are mostly synthetic chemical products, intended for use in the agricultural (e.g., pesticides) and industrial sectors or emitted during industrial operations and incineration of refuse (e.g., dioxins and furans) [30]. Depending on their mode of introduction into the environment, the POPs could be from a natural or anthropogenic source [31]. Natural occurrences by which POPs could be emitted include volcanic emissions, vegetation fires (which release dioxins and dibenzofurans), petroleum seeps, decomposition of vegetative litter, hydrothermal processes and the erosion or disintegration of rocks containing petroleum hydrocarbons. The anthropogenic sources include the pesticide industries, chemical and petrochemical industries, Incineration plants, power plants, agricultural sprays, heating stations, electronic waste recycling facilities, uncontrolled degradation of home waste, city dumps and landfills [32,33]. The demolition of buildings, cement manufacturing, equipment repair, organochlorine pesticide storage, fly ash storage and fossil fuel burning are also anthropogenic sources of POPs [33, 34].

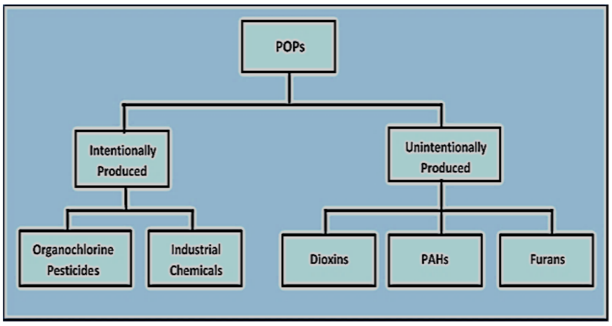

Fig. 1. Classification of POPs [29].

POPs are harmful chemicals that are extremely persistent and naturally non-biodegradable in the environment [3]. Their presence in drinking water and groundwater poses a serious risk since they are easily transferred from one source to another and discharged into a different environment. The POPs have severely impaired the aquatic food chain, spreading into many aquatic ecosystems through surface runoff, river inputs and atmospheric deposition [2]. POPs are typically lipophilic (fat-loving) and hydrophobic (water-repelling). They are repelled from aqueous systems and are preferably bonded firmly o organic material in both terrestrial and marine environments. They are also stored in fatty tissue and penetrate the lipids of organisms more readily than they do in the aqueous medium of cells. Due to their accumulation in the adipose tissues, these chemicals can remain in the biota for long periods where a low rate of metabolism exists. Therefore, POPs easily move up the food chain. Their build-up in the food chain is a function of the combined effect of metabolism and lipophilicity [2,35]. The biomagnification of POPs occurs when chemicals accumulate in large concentrations in the tissues of creatures ranked at the top of the food chain (e.g., fish, mammal species, birds, and humans) [9,11,33]. This happens when predators hunt animals that are hundreds of times their weight [36,37].

Most POPs are semi-volatile with a relative molecular mass ranging from 200 to 500 Da and vapour pressure lower than 1000 Pa [38]. These properties facilitate their long transboundary activities within the environment and thus, they can evaporate into the atmosphere at hot temperatures from sources such as water, soil and flora and migrate across international borders *via* water, air and migratory species [2,12]. The POPs are easily dispersed in the vapour phase at ambient temperatures and thus, have the potential to volatilize from soils, vegetation, and aquatic systems into the atmosphere and migrate over long distances before being re-deposited due to their resistance to airborne degradation processes [1]. Therefore, they have been detected in areas distant from where they were produced or emitted because the process of volatilization and condensation do reoccur regularly. These chemicals are dependent on both the surrounding temperature and their physico-chemical properties, and they can separate into particles and aerosols in the atmosphere [32,39].

POPs are distributed in low concentrations throughout the ecosystem by the flow of fresh air and marine waters and are persistent in the air, biota, soils, and sediments. Their half-life range from six months or several years in soil or sediment, to a few days in the atmosphere [2,40]. However, there are no rules or agreement among scholars on how long their half-life in a particular media should be for the term "persistent" to be appropriately used in their definition. Currently, there are thousands of identified POP compounds. A large number of the compounds belong to certain chemical families or series. [17,41,42]. The possible fate of pollutants in soil systems as depicted in Figure 2, include leaching into groundwater, biodegradation, volatilization to air, adsorption by plant, binding to soil-solid phases and transfer into organisms.

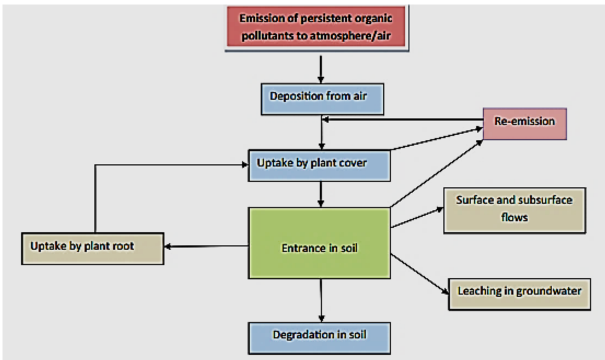

Fig. 2. Schematic illustration of fate of persistent organic pollutant in soil.

3. Health and Environmental Effect of POPs Contamination

3.1 Health impact of POPs

The human population's exposure to POPs could adversely affect their health profile during their lifetime. Pesticides (including herbicides) are long-lasting in the environment and can accumulate in the fatty tissues of humans and animals [43]. All the POPs known as "dirty dozen" are endocrine disruptors that interfere with hormonal processes [12]. Furthermore, a disturbance in the ratio of 'energy storage–energy balance' of the endocrine system can cause obesity, which results in metabolic illnesses like reduced bone mineral density or a high rate of bone fractures [5,44]. High concentrations of POPs in low-density lipoproteins of the body have been associated with numerous types of cancers like the breast cancer. Women continuously exposed to PFOS and PFOA are at risk of breast cancer [45,46]. Thyroid cancer has been linked to 2,3,7,8-tetrachlorodibenzo-p-dioxin pesticide [47,48]. Furthermore, thyroid hormones, which are important in cell development and differentiation, can be affected by dioxin exposure [49].

The PCBs and PBDEs, even in small concentrations, can adversely affect young children's brain development, which could result in prolonged behavioural issues. Lower scores in IQ and concentration ability of kids have been associated with higher levels of polybrominated-diphenyl ethers (PBDE) in maternal blood [5]. Exposure to PCDD/F and PCBs has been linked to reproductive disorders such as pregnancy loss, decreased fertility, high endometriosis levels, low testosterone levels and low sperm counts [9,50]. Likewise, PAH exposure from any source has been known to have short-term effects like skin irritation, eye irritation, nausea, diarrhoea, vomiting and disorientation in humans. Long-term PAH exposure effects include DNA mutations, developmental abnormalities, leukaemia, impaired immunological function, cataracts and cancers (e.g., skin, lung, bone, brain and scrotal cancer) [51,52]. Exposure to PCBs and chlorinated pesticides induces the development of insulin resistance. Children develop diabetes as a result of exposure to polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans [5,53].

3.2 Ecological impact of POPs

An important component of agricultural ecosystems is the soil microflora, which is important for both fundamental soil function, fertility and overall crop yield. The genotoxicity of organophosphates, carbamates and organochlorines has been reported elsewhere [54]. They are believed to prevent mitosis in plant meristematic cells [55]. Pesticides affect plant physiology by lowering the net photosynthetic rate, growth, and biomass production, which eventually reduces the overall yield and productivity. In addition, the plant's metabolic breakdown of carbon and nitrogen is affected by pesticides [56,57]. Fungicide application to plants reduces ribulose-1.5-bisphosphate formation, inhibits RuBisCO carboxylation and lowers RuBisCO levels. This adverse impact which produces stomatal and nonstomatal effects contribute to the reduction of CO_2 assimilation in plants

Likewise, long-term research has proven that synthetic pesticides impacts the physical, chemical, and biological characteristics of soil by disturbing the structural and functional aspects of living organisms that are present in soil [57]. POPs adsorbed into the soil will alter the microbial populations in the soil, which will destroy plants and disrupt the symbiotic relationship between the microorganisms and the plants [58]. Toxic pesticides lower the pH of topsoil, which can adversely affect microbial activity and reduce nodulation of legume plants, leading to nitrogen deficiency [59]. Moreover, the continuous use of toxic pesticides results in irreversible changes to the microbial diversity of the soil, which indirectly affects other organisms that depend on the soil. Pesticides are removed from soils by soil bacteria *via* hydrolysis, conjugation, oxidation, and reduction [60], hence, any decline in the microbial population would ultimately cause a large decline in soil fertility. The agricultural yield will be reduced since the soil fertility has been affected. Bacterial dehydrogenase and soil cellulase have been observed to decline after the application of endosulfan and chlorpyrifos [60,61]. In sandy loam and loamy soil, metabolites of quinalphos like quinoxaline-2-thiol and 2-hydroxyquinoxaline, and metabolites of chlorpyrifos such as 3,5,6-trichloro-2-methoxypyridine and 3,5,6-trichloro-2-pyridinol, have been linked to the inhibition of the process of bacterial ammonification. Earthworms are important soil organisms that aerate the soil by properly mixing soil nutrients, making the soil fertile. Pesticide application has the potential to seriously impede this function. Pesticides substantially impair the capacity of the earthworms to reproduce and develop, increase their mortality rate, alter their enzymatic function and even change their feeding pattern [62]. Furthermore, organisms such as the useful arthropods (spiders and beetles) are poisoned by pesticides while the soil flora and fauna that are present in the impacted areas are affected both directly and indirectly by pesticides, after the destruction of the beneficial soil microorganism [63]. The remediation of contaminants will also be affected when the function of microbial biosynthetic pathways is disrupted, leading to poor degradation.

4. Emerging Remediation Technologies for the Treatment of POP-Contaminated Soil

4.1 Physical remediation technologies

Physical remediation refers to the process of decontaminating soils *via* physical methods [15]. The current physical remediation techniques discussed in this section include the thermal and emerging physical techniques. Currently, physical methods commonly used for removing pollutants from soil are vitrification (which immobilizes pollutants), thermal desorption (which separates pollutants from soils), supercritical fluid extraction and electrokinetics.

4.1.1 Thermal Desorption

This is an *ex-situ* procedure for removing volatile and less volatile chemicals that adhere to waste surfaces by heating to temperatures high enough to volatilize the contaminants. The contaminated soil could be heated using steam and microwaves of infrared radiation to volatilize the pollutant (e.g., Hg, As) [64]. Thermal desorption systems employ bed temperatures (from 170 to 550 °C) to volatilize certain pollutants from water, but the system does not generally oxidize or decompose organic molecules. The process removes the vaporized chemicals from the polluted medium *via* direct/indirect heat exchange or air/inert gas. Thus, a two-step technique is used in most thermal treatment systems. Step 1 involves applying heat to polluted soil or silt to evaporate the pollutants and change their form into a gas stream. In Step 2, the gas stream from Step 1 is collected, condensed, or destroyed [8,65]. As a result, it is not a stand-alone technology; but requires further treatment of the emitted gases. Direct- or indirect-contact thermal desorption machines are often used to handle the less volatile organic compounds (LVOCs), insecticides and other chemicals having boiling points up to about 300 °C. Higher-temperature systems are required for the removal of contaminants such as PCBs, dioxins and furans that have boiling temperatures exceeding 300 °C [66]. Unfortunately, when used to treat hazardous waste, thermal desorption, followed by direct combustion (e.g., using an afterburner) can be likened to an incineration system and may cause acceptance issues with people living in the surrounding area. In addition, the treated soil may be unable to sustain the microbiological activities necessary for degrading the pollutants. This may cause problems if the treated soil is used to replace a previously polluted site [66,67]. An illustration of the thermal desorption process is depicted in Figure 3.

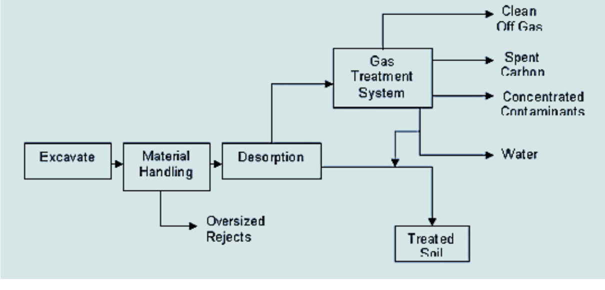

Fig. 3. High-temperature thermal desorption of polluted soil [19].

4.1.2 Vitrification

Vitrification, or molten glass formation, is a method of solidification and stabilization that uses a powerful source of energy to "melt" soil or other solid materials at extremely high temperatures (1600–2000 ºC), thereby immobilizing most inorganic pollutants after solidification [64]. This method of contaminants destruction combines pyrolysis/incineration and oxidation processes in an oxygen-deficient environment and an oxygen-rich environment respectively [68]. It may be performed *in situ* (directly on the polluted soils) or after separating the pollutants from the soil. *In situ* vitrification involves placing electrodes of graphite into a polluted enclosed area and with the generation of electric current, the soil's surface melts (> 1,700 ºC). The heat gets transferred into the deep parts of the soil and cause the melting and entrapment of contaminants within the matrix when cooled. A molten block is thus formed, which decreases the leaching properties of the pollutants [69]. Various systems containing organic compounds (including pesticides and PCBs), inorganics and radionuclides can be treated with this method. Organic impurities are usually eliminated, whereas the inorganic contaminants are bound within the vitrified matrix [68]. The capacity of this strategy to atomically bind a wide range of hazardous compounds into a glass matrix, often with a large reduction in waste volume, is one of its' alluring features [64, 69]. This technology provides an affordable solution for complex environmental media with diverse recalcitrant pollutants or strict clean-up requirements. The resulting melt's size is nonetheless constrained. Although the method is frequently used *in-situ*, it might not be suitable for locations where the contaminated soil is close to houses or other structures [64].

4.1.3 Supercritical fluid (SCF) technique

Supercritical fluid extraction (SFE). is a comparatively environmentally friendly extraction technique that eliminates the need for an organic solvent. It applies high diffusion coefficients, reduced viscosities like gases, and densities that are extremely comparable to those of liquids. Extraction is usually from a solid matrix, but it can also be from liquids [70]. The SCF selected to remove contaminants must have a stronger affinity for impurities than for the solid matrix's bulk material. Supercritical carbon dioxide (SCCD) with temperature and critical pressure of 31ºC and 74 bar respectively, is commonly used in SCE procedures. Carbon dioxide is employed because of its low chemical reactivity, non-toxicity, non-flammability, affordability and high diffusivity [70]. It is used either alone or in combination with co-solvents (carriers, modifiers), like methanol,(critical temperature 239 ºC; critical pressure 81 bar) [71, 72]. The SCF extraction is the first phase in a two or multi-step remedial procedure whereby an extraction vessel is filled with the sample and carbon dioxide is applied to extract analytes under pressure. After being moved to a fraction collector and depressurized, the carbon dioxide loses its solvation ability [73]. The next stage is the destruction of the contaminants. Neither the pollutants nor the soil/sediment is destroyed by SCE technique, rather, the extracted contaminants are concentrated and thereafter, eradicated effectively *via* a less expensive method [67, 71]. A primary benefit of this method is its ability to separate and dry the product with a basic process while the gas may be collected, recycled/ used again without the need for further purification. The extracts are quite clean and may require little or no cleaning. SCFs are frequently referred to as "green solvents for the future" since they have the potential to replace traditional organic solvents. Moreover, the SCF also provides low energy consumption when used in industrial processes [74]. A Schematic diagram for operating the supercritical fluid extraction equipment is presented in Figure 4. Although SCF produces high extraction efficiency (up to 99.9%), it is capital and machine-intensive as it requires additional extraction treatment methods [67, 71, 75]. Furthermore, only a few grams of the material may be stored in the extractor's tiny capacity, which is a disadvantage when a larger sample mass is needed to obtain a greater limit of detection (LOD) during instrumental analysis [73].

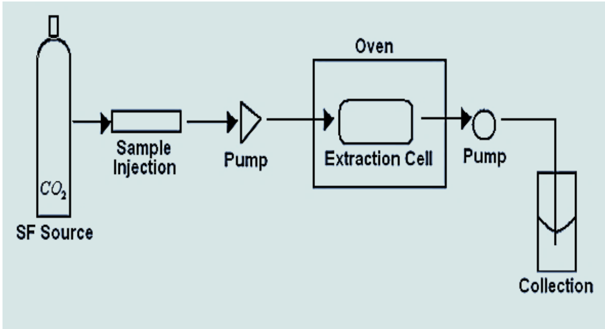

Fig. 4. Schematic representation for operating supercritical fluid extraction equipment [70].

4.1.4 Electrokinetic technique

Electrokinetic technique is an innovative method that employs direct electric current for the removal of organic pollutants and other contaminants (inorganic and heavy metal) from soil and water [76, 77]. In this method, low-voltage direct current electric potential is applied through electrodes (anode and cathode). The low-voltage electric current causes the mobilization of contaminants and their transportation toward electrodes placed inside the contaminated soil matrix. Contaminants formed on these electrodes are pumped out for further treatment. Electro-osmosis, electromigration, diffusion, and electrophoresis, are different transport mechanisms induced by electric current [78, 79]. The soil's pH is usually altered *via* direct electrokinetic remediation. To maintain the pH level, certain buffer solutions must be added to the cathode and anode. Both saturated and unsaturated soils can be effectively treated using this method. In addition to the contaminants, the presence of hematites, carbonates, and gravel reduces the cleanup efficiency of this approach. Electric remediation techniques are more advantageous than conventional remediation since they require less labor, have higher economic returns, and are more ecologically friendly [15]. Nonetheless, there are still some limitations to the usage of electric remediation technology for soil remediation, such as the inability to completely eliminate petroleum pollutants that are bonded to clay particles and organisms in sediments and soil, even though the effectiveness of electric remediation largely depends on the molecular structure of the soil contaminants, pollutant concentration, ionic migration, and other factors [15, 80].

4.2 Chemical remediation technologies

Chemical remediation is a technique that utilizes chemical reactions and solvents to eliminate or degrade pollutants in contaminated soil, into non-toxic small molecules [81]. However, choosing the right chemicals and using them in the right proportion is crucial to the chemical remediation procedure, in order to avoid regeneration of secondary pollutants (re-contamination) in the environmental media.

4.2.2 *Chemical dehalogenation*

Direct chemical stripping of halogen atoms from organics in soils, sediments and sludge is applied in the chemical dehalogenation process. Chemical dehalogenation refers to procedures in which a chemical solution is added to the affected media to initiate a substitution reaction [82]. This reaction causes the displacement of the contaminant's halogen atoms by other atoms or functional groups. Similarly, chemical dehalogenation could also be dominated by an elimination process, whereby the halogenated atoms and other elements (e.g. hydrogen), are eliminated from an aliphatic compound at the same time, with a double or triple bond left in the remaining organic molecule [67]. The purpose of the dehalogenation process is to detoxify the contaminants to levels that allow the waste stream to fall within the acceptable limits for disposal or re-use regulatory standards [83]. Halogenated aromatic compounds, such as PCDDs, PCDFs, PCBs, chlorobenzenes, chlorinated phenols, organochlorine insecticides, halogenated herbicides and aliphatic compounds, can be de-halogenated using an alkaline glycolate or base-catalyzed reagent like ethylene dibromide or dichloromethane [19]. Metals, such as Zero valent iron (ZVI), can also be utilized for the dehalogenation process [84]. Reactive metallic species have been proven to have the ability to effectively treat waste streams containing halogenated compounds like PCBs [83]. A schematic representation of the dehalogenation technique is presented in Figure 5.

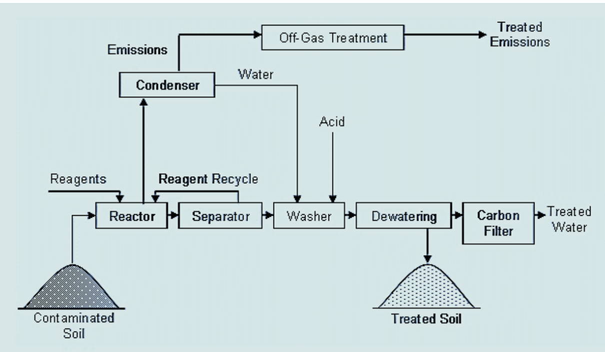

Fig. 5. Chemical (glycolate) dehalogenation of contaminated soil [19].

4.2.3 *Soil washing*

Soil washing is an *ex-situ* approach utilizing physical and/or chemical procedures. This is a novel approach to soil remediation that concentrates harmful pollutants into a smaller volume and removes them from the soil by using liquids and a mechanical process, as illustrated in Figure 6 [85,86]. A variety of chemicals like acids, complexing agents and surfactants, are used as washing liquids. The soils are separated from the contaminant *via* these methods: 1) by dissolving/transferring them in a wash solution, which is then treated using standard wastewater treatment techniques, 2) or by using attrition scrubbing, gravity separation, and particle size separation (which are methods akin to those in sand and gravel operations) to reduce the mixture into a smaller soil volume [87]. Usually, surfactants with both hydrophilic and hydrophobic qualities are incorporated appropriately. The amphoteric characteristic of the surfactants enhances the dissolution of both hydrophobic and hydrophilic organic pollutants [88]. In addition, varieties of surfactant types, including cationic, anionic, non-ionic, and zwitter-ionic surfactants, have been effectively applied for the remediation of contaminated soils [89]. The extraction surfactants ought to be stable, have a low absorption onto soil or soil organic matter (SOM), and have strong solubilization capability. Anionic surfactants have comparatively greater critical micelle concentrations (CMC) than cationic surfactants. On the other hand, cationic surfactants are far more likely to adsorb onto the soil [90]. These flaws restricted their field use for soil restoration [88]. Therefore, for soil restoration, neutral or anionic surfactants are preferred over cationic surfactants [88–90].

Attrition results in scouring, abrasion, scrubbing, and particle disintegration by generating frictions and collisions amongst the particles themselves. Thus, the performance of gravity separation techniques can be enhanced when attrition washing is applied as a pre-treatment [91]. The impact of attrition could (1) lead to the breakdown of agglomerated particles and the loss of coatings and films enclosing soil particles, producing fine particles known as attrition sludge (2) enhance the liberation of pollutants by fracturing and separating large clumps of soil particles into decontaminated and contaminated soil particles. (3) change a particle's form [86,92]. Soils contaminated with hydrocarbons, inorganics, and semi volatile organic compounds (SVOCs) can be restored using this method [19, 86].

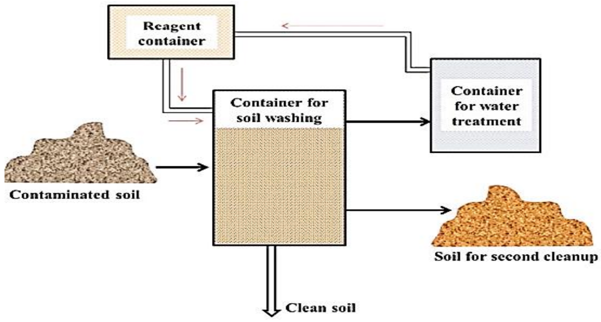

Fig. 6. Washing of contaminated soil [87].

4.2.5 *Chemical oxidation/reduction*

Petroleum pollutants in soils can break down into non-toxic or comparatively less toxic compounds through an oxidation-reduction reaction. Redox agents commonly utilized include peroxymonosulfate [93], sodium bisulfite, persulfate, sodium percarbonate, hydrogen peroxide, zero-valent iron, and Fenton reagent [78,93–95]. Kan et al. [96] conducted chemical oxidation studies using crystallographic **manganese oxides** to remove polycyclic aromatic hydrocarbons from contaminated soils. The experimental results showed that the remediation efficiency was significantly improved with crystallographic manganese oxides. Likewise, Liao et al. [97] studied the use of activated persulfate in chemical oxidation remediation methods for soil contaminated by polycyclic aromatic hydrocarbons. The light and heavy fraction remediation efficiencies were 39% and 90%, respectively, indicating a relationship between soil composition and structure, and oxidation remediation effectiveness.

The chemical oxidation-reduction method does not require specific criteria for the type or concentration of chemicals, and it has a short treatment duration. This method, in particular, can degrade certain petroleum pollutants that are poorly soluble in water and are non-volatile. However, the amount of chemical agents used throughout the treatment process affects the performance of the soil remediation process. Inadequate application of chemicals may result in inadequate soil restoration, while excessive application of chemicals would cause secondary contamination. Thus, the direction of future research will be the precise modulation of the amount of additional chemical agents [15]. Although POPs can be chemically treated to alter their properties into less harmful chemicals through the oxidation/reduction process, the method is not always suitable for all POPs and can result in the generation of toxic by-products [98].

4.2.6 Advanced Oxidation Process (AOP)

Advanced oxidation method doesn't produce large volumes of harmful sludge or move pollutants from one phase to another like chemical precipitation and adsorption remediation technologies [99–101]. AOPs effectiveness is largely dependent on their ability to produce reactive hydroxyl (OH) radicals with a 2.8 V redox potential [102]. OH is the second most reactive species after fluorine atoms, with a rate constant of about 10^6 –10^9 M^{-1} s^{-1} and a speed that is 106 – 1,012 times faster than ozone [103, 104]. AOPs are often categorized as homogeneous or heterogeneous processes based on whether the process requires a single phase or heterogeneous catalysts [1, 6, 105]. Electrical, microwave, ultraviolet rays and sonolytic energy are all forms of light used in homogeneous AOPs. Others include the UV/H_2O_2 technique, UV/Photolysis, UV/Ozone, and Photo-Fenton technique. Contrarily, heterogeneous AOPs use a catalyst in the solid phase while the pollutants are in the aqueous phase. Photocatalysis falls within this category [31, 105]. Fenton, Ozonation, and Photocatalysis are the three most popular advanced oxidation technologies [106].

4.2.6.1 Fenton oxidation systems

The most often used AOP technique for the restoration of pesticide-contaminated site is the Fenton method. During the Fenton process, H_2O_2 is decomposed in the presence of iron, into hydroxyl radicals according to the following reactions with a kinetic constant value of 70 $M^{-1}s^{-1}$ at pH = 3 [18,19] [102,104]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^{\cdot}OH \quad \text{pH 3, } K_1 = 70\ M^{-1}\ s^{-1} \qquad (1)$$

$$RH + {}^{\cdot}OH \rightarrow H_2O + R^{\cdot} \rightarrow \text{Further oxidation} \qquad (2)$$

$$R + {}^{\cdot}OH \rightarrow {}^{\cdot}ROH \rightarrow \text{Further oxidation} \qquad (3)$$

The decomposition of H_2O_2 produces highly reactive OH (Eq.(1)) that can oxidize organic compounds (RH or R) by hydrogen abstraction (R) or hydroxyl addition (ROH) [16]. The highly reactive molecules (R and ROH) can be further oxidized (Eqs. (2) and (3)) [6,107]. Furthermore, the Fenton-like reaction produces hydroperoxyl radicals (HO_2) that are less reactive than OH but can also oxidize organic contaminants [102,104]. The application of the Fenton process for the removal of POPs from contaminated soil has been investigated in recent times. Fenton reaction treatment of pendimethalin-contaminated soil was evaluated by Miller et al. [108]. According to his report, Fenton oxidation eliminated almost all of the pendimethalin that was initially found in the soil. Likewise, the degradation of twenty-four PAHs by Fenton oxidations was assessed in a recent laboratory study. According to the report from this study, the elimination of PAHs containing two and three rings was found to be 89 % and 59 %, respectively, whereas the corresponding percentage removal for PAHs with four, five, and six rings ranged from 0 % to 38 %.

On the other hand, studies have shown that applying the Fenton process directly to the soil can be extremely aggressive and detrimental to the bacteria therein [109]. This constraint was addressed through the use of the combined remediation process, which involves washing the soil and then oxidizing it with Fenton technique. Significant advancements have been achieved using this method. The main benefits of the Fenton process are its high performance and non-toxicity, which may be achieved at ambient temperature and normal atmospheric pressure [110]. Nonetheless, there are some drawbacks to the traditional Fenton method, foremost among them being a severe pH dependency. The ideal pH range is between 2.5 and 4.0; below this range, the process can solvate protons and yield oxonium ions (H_3O^{2+}), thereby increasing H_2O_2's stability and decreasing its reactivity with ferrous ions. Beyond this range, colloidal ferric species are formed due to the reduction of the dissolved fraction of iron species [110, 111].

4.2.6.2 Photocatalysis

Photocatalysis refers to the process of activating a reaction with a photocatalyst, using ultraviolet, visible, or infrared energy [89]. Many semiconductors, such as ZnO, TiO_2, CdS, GaP, and NiO, have been studied as photocatalysts in recent years. Because of its special qualities, which include low cost, high photoactivity, non-toxicity, degrading efficiency, and photocatalytic stability, TiO_2 in the anatase form was selected as the most appropriate [21]. TiO_2 has a band gap of 3 to 3.2 eV with a maximum absorption wavelength (εmax) of 400 nm [112]. When exposed to this wavelength of light, the surface of TiO_2 warms up as photocatalytic degradation occur, potentially reaching temperatures of 3,000 ^{o}C. In essence, electrons (e-) and holes (h+) could be generated on the surface of the TiO_2 upon light irradiation [113, 114]. Then, the (h^+) and (e-) may further react with water (H_2O) and oxygen (O_2) respectively, to create different types of reactive radicals like the hydroxyl radicals (OH*) and reactive oxygen species (O_2*) as shown in Figure 7. The reaction that takes place is often an oxidation reaction which uses the radicals to decompose the contaminant. TiO_2 is capable of degrading a wide range of POPs in soil [6, 115].

Direct photocatalytic treatment has been used for the elimination of 80 % of organic pollutants from soils contaminated with low concentrations of these pollutants after a 24-h radiation, without any pretreatment or modifications [110]. Nevertheless, when dealing with soils heavily contaminated with high levels of POPs, the initial separation of the pollutant from the contaminated soil before photocatalytic degradation becomes necessary in the photodegradation process. Therefore, *ex-situ* methods like solvent washing and extraction are typically employed to initially isolate the pollutants from soils. Soils polluted with chemical compounds like pesticides (DDT, profenofos, quinalphos and antrazine), and PFOA have been successfully treated using this method [6, 115].

4.3 Nanoremediation Technique

Nanoremediation is an innovative remediation technique that relies on the use of nanomaterials. It addresses the formidable challenges of 21st century such as the pollution crisis, contaminated land management and restoration of environmental imbalance and presents innovative solutions for the quick and efficient removal of pollutants from the polluted environment [12, 116, 117]. The technologies employing nanostructures have the potential not only to reduce the overall costs of cleaning up of large-scale contaminated sites, but also to reduce clean-up time, eliminate the need for disposal of treated contaminated materials, and to reduce contaminant concentration to near zero-all *in-situ* [22,118]. Nanoremediation technologies entail the applications of reactive nanomaterials such as metal oxides, nanodots, bimetallic nanoparticles, carbon nanotubes, nanoclusters and nanocomposites for the degradation and mineralization of contaminants [22, 119].

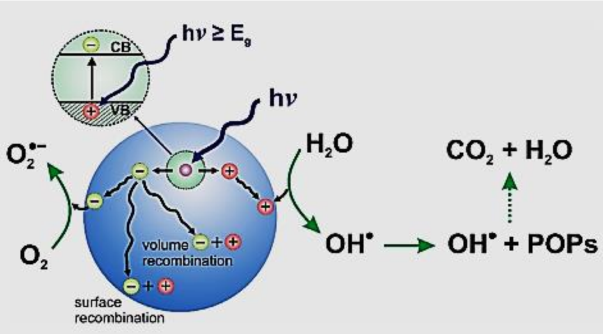

Fig. 7. The mechanism for radical generation and photocatalytic degradation of persistent organic pollutants [6].

These nanomaterials, can be made in the form of catalysts, chemical oxidants, nanosensors, and adsorbents, which enable the prompt adsorption and concurrent removal of pollutants like volatile organic compounds, pesticides, medicines, aromatic heterocycles, heavy metals, and chlorinated biphenyls from water, air, and contaminated land sites [120, 121]. Certain characteristics of these nanoparticles make them highly effective in eliminating pollutants. Their broad surface area, high reactivity, and tailored surface functionalities enable them to effectively adsorb, detoxify and degrade the dangerous and recalcitrant pollutants in environmental media [122–124]. Multiple POP removal by nanoparticle-based technology may arise, based on the specific nanomaterials employed. Nanoscale zero-valent iron (nZVI), for example, has been used to chemically decrease and immobilize POPs like the chlorinated solvents. Similarly, Polycyclic aromatic hydrocarbons (PAHs)-contaminated soils have been effectively restored by using nanoparticles such as activated carbon, which absorb and store the pollutants, thereby minimizing their potential impact [30,98].

A schematic representation of the application of nanomaterials for soil remediation is presented in Figure 8.

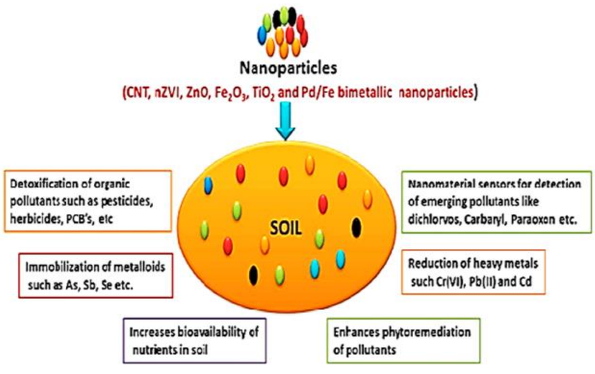

Fig. 8. Illustration of pollutant remediation in soil using nanomaterials.

4.4 Soil Remediation using Microbes

Bioremediation is an effective technique that employs microorganisms to transform complex organic contaminants into simpler ones [64]. Organic compound's biodegradation often occurs in multiple-step in the presence of some microorganisms working in synergy. Bioremediation is a cost-effective and environmentally safe procedure that uses microorganisms to remove organic contaminants from soil and water in contrast to other conventional technologies (incineration, solvent extraction, gas phase chemical reduction, alkali metal reduction, landfilling). The rate of biodegradation is influenced by certain factors in the different environmental media. The pace and length of time for complete biodegradation in soil is influenced by temperature, moisture, the constituent and performance of bacterial flora, the contaminants characteristics and "age", soil components and activity and the presence of nutrients [125].

Different species, such as bacteria, fungi and algae participate in microbial biodegradation [126]. Aerobic bacteria that require oxygen to operate include pseudomonas and escherichia, while syntrophus, syntrophobacter, desulphovibrio and syntrophus are anaerobic bacteria that do not require oxygen [126]. *In-situ* bioremediation involves adding nutrients, oxygen, moisture, or other amendments to polluted wastes like contaminated groundwater, soil or sediments, without disturbing or moving the affected media. Conversely, waste and harmful chemicals are collected and transported to a chosen location for the bioremediation process in *ex situ* bioremediation [126,127]. Mineralization (complete breakdown to inorganic components) of biodegradable pollutants occurs during bioremediation, while partial degradation that produces organic intermediates may also occur [126,128]. The following strategies are considered when bioremediation technology is employed to eliminate persistent organic pollutants.

4.4.1 Bio-augmentation.

It entails introducing microbes (either native or exogenous) or any biocatalysts (genes and enzymes) with a particular catabolic function (under controlled conditions) into a contaminated site to supplement the native microbial population and accelerate or induce pollutant degradation [1,16]. This bioremediation method is employed when the naturally occurring degrading micro-organisms are few in number or unavailable**.** Environmental conditions such as pH, moisture content, quantity of nutrients, and the type of contaminants all affect bio-augmentation performance. Bio-augmentation is mostly suitable for treating PAHs [129].

4.4.2 Bioventing

This is a popular *in situ* remediation method that involves injecting air or oxygen through wells into contaminated soil or water (in the unsaturated zone) to promote the growth of existing microorganisms while preventing or reducing the off-gassing of volatized organic contaminants into the atmosphere [16,78]. Bioventing can eliminate less volatile organic contaminants due to its reduced air requirement and ability to treat less permeable soils. It is cost effective, simple to set up and operate, and requires less time to treat contaminated media. Bioventing works well in the vadose or unsaturated zone. Petroleum hydrocarbon-contaminated soils have been effectively remedied using this method However, pollutant concentrations that are too high may hinder the efficiency of the procedure [16,78].

4.4.3 Biostimulation

Biostimulation is the process of modifying contaminated media to provide nutrition to soil microbiota, elevate the C: N: P ratio and enhance the function of contaminant-degrading microorganism *via* changing pH, nutrients addition (nitrogen, phosphorous, carbon, organic biostimulants) and oxygen addition (electron acceptor) [1]. Since these nutrients are essential for life, they enable microbes to produce the enzymes required for the breakdown of pollutants. It is one of the major methods for boosting the effectiveness of soil bioremediation for crude oil and PAHs removal [78]. Abed et al. [130] investigated the use of NH_4Cl and NaH_2PO_4 as nitrogen and phosphorus sources for the biostimulation of oil-contaminated desert soil. They observed that after the addition of nutrients, the oil removal efficiency increased by 20%. Similarly, organic biostimulants such as ammonium sulphate, phycocyanin (a proteic emulsifier extracted from the Spirulina platensis biomass) and residual biomass of S. platensis, are effective in bioremediation application. For instance, soil contaminated with 4% of diesel and biodiesel was biostimulated for 60 days with these organic biostimulants. The biomass of S. platensis was found to be the most effective biostimulant for diesel removal as after 60 days of biostimulation, 63.89 % of the diesel was degraded, while the extracted phycocyanin of Spirulina platensis was found to be the most effective biostimulant for biodiesel removal because after 60 days of biostimulation, a biodegradation value of 88.75% for biodiesel was obtained [131].

4.4.4 Biosparging

Biosperging is based on the idea that nutrients and air can be introduced into the layers of soil below the water table, where they aid naturally occurring organisms degrade toxins. Microorganisms native to the area are typically used in this *in-situ* method [132]. It can be used for the treatment of various types of petroleum products that have either dissolved in groundwater, or have become adsorbed to the soil just below the water table as well as within the capacity of capillary fringe [133]. It is frequently employed in conjunction to SVE, particularly when volatile compounds are present [16].

4.4.6 Phyto-remediation

Phytoremediation is an emerging technology that uses plants to localize, immobilize, decompose and extract specific chemical compounds from soil and wastewater [134]. The word "phytoremediation" is derived from the Greek word "phyto" (plant) and the Latin word "remedium" (clean, restore). The types/mechanisms involved in phytoremediation are phytodegradation, phytoextraction, phytofiltration, phytovolatilization and phytostabilization [24]. Phytodegradation (rhizodegradation or phytostimulation) is a process where the degradation of contaminants is achieved through the use of plant's rhizosphere [83,125]. The layer of soil at the top of the plant roots' zone contains the rhizosphere, which is made up of different type of microorganisms including certain fungi, nitrogen-fixing bacteria and protists with root secretions. Microorganisms are stimulated by the degradation process through the secretion of carbon-based nutrients from the plant's roots. The plants use hydrolytic enzymes and metabolites to degrade the contaminants. The pollutant's molecule is either attached to the hydroxyl functional group or oxidized during hydrolysis. After that, the harmful substances are removed by detoxifying enzymes [24,135]. Thus, the degradation of pollutants subsequently occurs by this symbiotic activity between plants and microorganisms [24,136].

Phytofiltration is a type of phytoremediation that uses plant roots (rhizofiltration), shoots (caulofiltration), or seedlings (blastofiltration) to remove pollutants from contaminated surface water or wastewater [137]. The used plants are thereafter collected and discarded [138]. Phytostabilization is another method of immobilising or stabilising pollutants (such heavy metals or POPs) by using plants resistant to metallic contaminants. This lowers the availability of the pollutants and prevents them from migrating into the environment through the food chain. Another method of phytoremediation is called phyto-extraction, which entails removing contaminants from soil or water using a plant's rhizosphere and root systems, then moving and accumulating those pollutants in the plant's stem, leaves, and shoots [135,139,140]. Likewise, phytovolatilization technique functions by employing plants to draw toxins from the soil through their roots and then converting those toxins into less dangerous volatile forms. The different types of plants that have been applied for pollutants remediation include sorghum, cottonwood, fescue, willow and legumes (clover, cowpeas) [135].

Phytoremediation technique has several advantages. Like solar-powered systems, it employs natural plant processes, which is environmentally beneficial and reduces labour, equipment usage and operational expenses. By stabilising heavy metals, it reduces the possibility of contaminants spreading by metal-leaching and erosion. An additional advantage of this approach is that it preserves the soil's fertility during the phytoremediation process [137]. However, the full-scale deployment of this technology is still limited because of factors which include unfavourable climatic circumstances, the length of roots that plants must have, the possibility of ingesting contaminated plants, the length of time needed for plant development and the remediation efforts. The process of phytoremediation has been used to remove a wide range of contaminants like metals (such as Zn, Cu, As, and Cd), pesticides, PCBs, PAHs, crude oil, and chlorinated solvents [126,136,141]. An illustration of the various phytoremediation processes involved in the removal of POPs is presented in Figure 9.

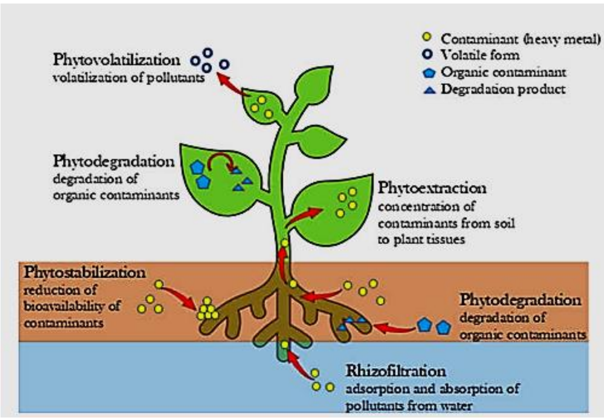

Fig. 9. Schematic diagram of phytoremediation processes [142].

5. Integrated Remediation Strategy

5.1 Combined remediation techniques

Hybrid and integrated remediation are an innovative approach that can be applied to address the complexity and enduring nature of POP contamination. This strategy offers viable solutions for more wholesome and pure ecosystems and water sources while considering all the numerous aspects of POP elimination. It is an all-inclusive approach that considers the economic, social, and environmental elements of remediation activities [118]. Combining several approaches for synergy is the process of judiciously integrating several restorative approaches to create a complete and effective remedy. This strategy strives for an improved outcome by utilizing the complementary strengths of each methodology [98]. The integrated remediation technique include physical-chemical combined remediation, physical-chemical-biological combined remediation and microbial-phytoremediation technology, among other types of combined remediation methods [15].

Table 2. Advantages and disadvantages of several emerging and innovative technologies used for POP removal.

Technology	Types	Advantages	Disadvantages
Physical treatment	Solvent extraction/soil washing	Volume reduction or minimization of contaminants, implement easily and quick	Contaminant transfer to another phase, large amount of solvent required, high cost
Thermal treatment	Thermal desorption	Volatile contaminants treated over a broad range of moisture contents, high removal efficiency, no excavation required for in situ treatment	Costly for large volumes of contaminated soils, volatization and release of contaminants from the soil into the air at high temperature. Reduced efficiency at low temperature
	Vitrification	Easily applied for remediation of highly contaminated soils, destroys contaminants quickly	High cost, transforms treated soil into glassy composition
	Supercritical fluid	Low energy consumption when used in industrial processes. the gas may be collected, recycled and used again without the need for further purification.	Capital and machine-intensive. Requires additional extraction treatment methods
	Electrokinetics	Minimal requirement of equipment, safe, suitable for clays with low permeability and heterogeneous soil Used for in situ or *ex-situ* treatment, cost-effective, low electrical energy	Time-consuming, microbial activity may be affected as a result of soil nutrient mobilization Not efficient in low contaminant concentration
Chemical treatment	Photocatalytic remediation Chemical oxidation/ reduction	Environmental-friendly nature Relatively inexpensive and highly efficient method Free reducing radicals formed from sulfite Good stability of photocatalyst in the aqueous phase, for example TiO_2, ZnO, *etc* High activity and non-toxicity Efficient recovery & reasonable recyclability of photocatalyst Low cost, easy to operate, and fully destroy the organic pollutant chemical structure Required abundant resources such as sunlight, oxygen and photocatalyst. Short treatment duration. Suitable for certain petroleum pollutants that are poorly soluble in water or non-volatile.	Low energy utilization rate Low absorption of light High investment costs related to the equipment and compound Fast photogenerated electron-hole recombination. Limited visible light response Poor treatment for high concentrated organic pollutants The degraded by-product lack of study in terms of the chemical structure and its toxicity. Inadequate application of chemicals may result in inadequate soil restoration Possibility of secondary contamination due to excessive application of chemicals
Bioremediation and Phytoremediation	Bioventing Biosparging Bio-augmetation Bio-stimulation Phytovolatization Phytostabilization	Environmental-friendly nature Cost- efficiency depends on materials- Reduces risk of secondary pollutant generation Lower labor and equipment. Plants tolerate higher concentrations of pollutants compared to several microorganisms.	Slow process, phytoremediation may take longer to reach pollutant concentrations Phytotoxicity, toxicity of the contaminated water may affect the development of the plants Produces stress conditions to plants
Nanotechnology	Nanomaterials	Highly versatile -Surface-active High specific surface area Nano size Good me vchanical stability	Requires more studies about toxicity Low aggregation affinity Problematic recovery

5.1.1 Physical-chemical combined remediation technique

The properties of pollutants are taken into consideration when applying the physical and chemical remediation techniques to enhance the removal of the contaminants from the soil through a separation process, fixation, and/or modification of their existing forms. Researchers have recently discovered that combining physical and chemical remediation methods considerably enhanced the efficacy of remediation while lowering costs [143]. For instance, Chen et al. [144] investigated the effects of ultrasonic and thermal activation of sodium persulfate on the decomposition of soil polluted with organochlorine pesticides. The elimination efficiency of the combined remediation techniques was shown to be higher by 11.6% in comparison to the oxidation by sodium persulfate alone. Furthermore, the treatment efficacy was superior to that of the ultrasonic and thermal activation of persulfate when used separately. Likewise, dehalogenation *via* chemical reagent can be employed in conjunction with other methods, such as low-temperature thermal desorption and solvent extraction or biodegradation techniques, if additional volatile organics, semi-volatile organics, or metal pollutants are present in soil [83]. Electrokinetic treatment combined with different surfactants and complexing agents, has been used to increase the desorption and solubility of contaminants. This combined method has already been used to remediate soils polluted by alkanes, halogenated hydrocarbons [79,145], polychlorinated biphenyl [20,145], and polycyclic aromatic hydrocarbons [20,146]. Furthermore, the degradation of POPs can be effectively performed by electrokinetics combined with the Fenton technique which yields a better result than each technique used alone. During the combined remediation process, heavy metals and POPs in the soil solution are migrated with electro-osmotic flows and electro-migration, and degraded by hydroxyl free radicals produced at the anode (under acidic conditions) *via* Fenton reactions [76,147]. Physical and chemical remediation methods have the benefits of a shorter remediation period, simple operation, and wide application range. However, combined remediation techniques also have some drawbacks due to their high cost, the propensity to cause secondary pollution and the destruction of soil properties [81].

5.1.2 Physical/chemical-microbial combined remediation technology

Bioremediation is a relatively effective and affordable technique that minimizes interference with soil texture, porosity and biodiversity during soil restoration. However, its use is limited due to the lengthy remediation process. Furthermore, the environment and the soil's characteristics are crucial to the efficiency of this technique [81,143]. Physicochemical techniques can be used to considerably enhance the environmental conditions for this technique since the natural soil environment may not be suitable for bioremediation. As a result, the combined bioremediation technique can produce a greater remediation impact [81]. For instance, to treat soil polluted with polybrominated diphenyl ether, Ma et al. [148] utilized low concentrations of persulfate (20 mmol/kg soil) for initial pretreatment. Despite a decrease in the amount of organic matter in the soil due to the persulfate oxidation, a degradation rate of 94.6% was observed while the amount and activity of microorganisms were recovered 90 days following the bioremediation method, In a similar study, Mora et al. [149] investigated the use of permanganate oxidant for the simultaneous bioavailability of microbes and biodegradation of petroleum hydrocarbons. Following two months of bioremediation, 100% of the polycyclic aromatic hydrocarbons and 92% of the aliphatic hydrocarbons were removed from the soil.

5.1.3 Enhancing phytoremediation with endophytes (Microbial-phytoremediation technology)

The use of growth-enhancing bacteria and naturally occurring bacteria that can degrade pollutants in phytoremediation techniques, could improve the effectiveness of the process [150]. Endophytes refer to bacteria, fungi, or other microbes that exist within plant tissues but do not cause disease [151]. Therefore, microbial-phytoremediation is the process of employing the mutualistic symbiosis between plants and microbes to enrich, fix and degrade pollutants in the soil [152,153]. Most plants form a symbiotic association with different microorganisms that are found around their roots or in their intercellular spaces. Natural endophytes can aid in the phytoremediation of groundwater and polluted soil along with providing the plants with further unique benefits like stress tolerance, nitrogen fixation, and phosphate solubilization [150]. In addition, the physical and chemical qualities of the soil, as well as its structure, may all be improved by the plant's root system, thus creating an environment more conducive to microbial function and development. Plant roots can secrete substances that contribute to microbial metabolism and hasten microbial degradation of organic pollutants. Kwasna et al. [154] extracted P. putida VM1450 strain from poplar trees and successfully used it to accelerate plant biomass growth and improve the phytoremediation of organochlorine pesticides. Likewise, a novel endophyte was separated from a hybrid poplar by Kang et al. [155]. According to their report, the endophyte decreased 80% of trichloroethylene (TCE) in the medium without the use of toxic inducers like phenol or toluene. Despite being in its very early stages, this method has the potential to be widely used to remove organic compounds from polluted environmental sites [150].

5.2 Regulatory framework and monitoring of POPs

The effective remediation and management of Persistent Organic Pollutants in soil and water require regulations and monitoring strategies. This section explains how laws and monitoring strategies can lower POP pollution and protect public health and the environment. International, national, and regional environmental regulations are important. The primary objective of the Stockholm Convention on Persistent Organic Pollutants, is to eliminate or reduce POPs that pose a threat to both human health and the environment [37,156]. A summary of some important regulatory agencies, their functions and challenges are presented in Table 3. The SC agreement permits countries to design policies and programs to control and eradicate dangerous substances [157]**.** This global collaboration advances our understanding of POPs, the state of the environment, and remediation alternatives. The global response against POP pollution is shown *via* international treaties and legislation. These laws encourage novel approaches to remediation and provide the cooperative and legal framework needed to protect public health and ecosystems. Maintaining these agreements is essential to creating a cleaner, healthier environment. Although the Stockholm Convention provides a global framework, national and regional laws are also essential to the implementation and enforcement of POP control measures. To address their unique POP contamination issues and sources, countries modify their laws, standards and policies in accordance with the Convention's guidelines. International agreements must be observed and reported by member countries. International accords facilitate technological transfer, research collaboration, and information sharing among countries [158]. Evaluating regulatory initiatives, identifying POP issues, and making informed decisions all depend on the data obtained. In addition to international efforts, national and regional laws guarantee observance and implementation in certain jurisdictions, thereby enhancing global research.

The monitoring and assessment of POP pollution are crucial aspects of regulatory frameworks. Monitoring is the methodical gathering of data about POP levels in the environment as well as animals, and people. Assessment involves evaluating the causes and risks of POP. Data are used to evaluate remediation activities, identify polluted sources, and guide policy decisions [159]. Data gathering involves the collection of air, soil, water, sediment and biota samples in order to assess the level of pollution in such areas. Finding contaminated locations, pollution sources and potential dangers to ecosystems and human populations is made easier with the help of careful monitoring. Moreover, in addition to environmental monitoring, biological modeling assesses the accumulation of POPs in live organisms. This method, frequently applied to humans and animals, provides insight into the bioavailability and biomagnification of POPs in food chains

Table 3. Regulatory framework and monitoring of persistent organic pollutants (POPs) in soil and water. Adapted from [98].

Regulatory Agency	Related Regulations	Monitoring Techniques	Challenges/Limitations	Key findings
World, Health Organization (WHO)	International Health Regulations (IHR), Guidelines for Drinking- Water Quality	Biomonitoring, air and water quality assessments	Limited global enforcement power, lack of standardized methods	Global cooperation essential for effective control
Stocholm Convention	Global treaty on POPs	Global monitoring, information sharing network, reporting requirements	Challenges in enforcing compliance, monitoring in developing regions	Reduction in production and use of prohibited POPs
United Nations Environment Programme (UNEP	Basel Convention on the Control of Transboundary Movements of Hazardous Wastes	Tracking prohibiting transboundary transportation of POPs, enforcing waste management regulations	drawbacks in the regulation of certain POPs, poor enforcement in some regions	International collaboration needed for waste control
United State Environmental Protection Agency (USEPA)	Clean Air Act, Clean Water Act, Toxic Substances Control Act	Air and Water Quality monitoring, soil sampling	Limited information on emerging POPs, capital-intensive	Identification of priority pollutants is crucial
National Environmental Agencies	Country-specific regulations and standards	Local monitoring pograms, on-site assessments	Lack of uniformity in regulations, limited resources for monitoring	Importance of context-specific regulatory measures
European union (EU)	Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH), Water Framework Directive	Assessment of Air and Water quality, sediment analysis	Varied implementation among member states, data comparability	harmonized monitoring strategies required
China	Measures for the Environmental Management of New Chemical Substances (MEP Order 7)	Environmental Impact Assessment, National monitoring networks, soil analysis, Air and water monitoring,	Rapid industrial growth poses challenges in monitoring compliance,, liimitations in enforcing regulation	Increasing efforts in regulating and monitoring POPs Stricter regulations and monitoring for selected POPs, adoption of preventive measures is critical Effective in reducing production and use of targeted POPs

6. Conclusion and Future Research Perspective

Persistent organic chemicals are of great concern to man and the ecosystem due to their toxicity and bioaccumulation tendencies. Anthropogenic activities, especially from the industrial and agricultural sectors, are considered the primary sources of these pollutants. Diseases such as cardiovascular disorder, reproductive dysfunction, cancer and tumour growth are associated with the POPs. Researchers have also revealed their negative impact on wildlife. The exponential impact of these compounds is due to their high stability, bioaccumulation properties and trans-boundary activities. This review article offers a methodical overview of technologies for treating POP-contaminated sites and remediating soil. Different current and emerging technologies for soil treatment, generally grouped into physical, chemical and biological technologies, were extensively discussed. Each remediation technology's advantages, disadvantages, operations and strategy were extensively reviewed. These methods have demonstrated positive outcomes for the remediation of POP-contaminated matrices. Unfortunately, a single remediation method cannot effectively remediate all sorts of contaminated sites due to the complexity of the actual soil constituent, the diversity in the form of pollutants, the uneven distribution of pollutants and the variation in the degree of soil contamination. From the various literature assessed in this review, it can be inferred that integrating physical, chemical and biological remediation can facilitate the remediation process and modify the damaged site in a way that encourages restoration. Furthermore, the combined remediation approach is more economical, effective and eco-friendly. With regard to the assessment of remediation technologies for polluted soil to achieve remarkable results, several researchers have conducted extensive and rigorous scientific studies on the environmental issues brought about by POPs in recent years. Future research should be expanded in the following areas to address several challenges related to the cleanup of POP-contaminated soil:

1) In nanotechnology, nanomaterials are being investigated to improve POP removal while mitigating environmental consequences, leading to a surge of interest in nanotechnology. However, further investigation is necessary to completely understand the benefits, limitations and long-term effects of nanomaterials used in POP clean-up on the environment and human health.

2) The biological remediation method has a wide range of application and tremendous remedial potential. It is therefore, important to identify and cultivate plants that are effective in degrading organic contaminants in order to develop the corresponding pollutant's microbial remediation process. Thus, to improve the performance of phytoremediation techniques for soil restoration, further bioengineering research is required.

3) When implementing integrated treatment approach, cost reduction should be a major priority.

4) Future research direction should be on strengthening the soil restoration procedures; synthesizing new green-chemical reagents for remediation and investigating novel types of remediation machinery to increase the economic benefits of the current techniques.

5) In order to prevent both their explicit and unforeseen disastrous effects in the coming years, more investigation into the environmental chemistry, ecotoxicology, human toxicity and epidemiology of novel and unregulated chemical compounds is essential. These studies will eventually help the government set environmental standards or regulations to guarantee that both man and his environment are adequately protected from the impact of these chemicals. Likewise, government institutions and non-governmental agencies should enlighten/educate the public about the risks and impact of POPs on humans and the ecosystem.

Author Contributions

Anna E. Ivbanikaro: Writing original draft, Writing, Review & Editing; Raissa Okwuosa: Supervision, Review, & Editing; Charity Maepa: Project administration.

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