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Pesticide Soil Pollution: An Overview about Advantages and Disadvantages of Different Remediation Technologies

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Abstract
The use of pesticides presents a looming danger to the living elements of our ecological system, crops, and the well-being of our species. As an outcome, various organic contaminants pollute the soil. Different physical, chemical, and biological remediation techniques have been employed for the decontamination of pesticide-polluted soils. Remediation technology should always be affordable, on-site or in-situ, and capable of restoring the soil's natural functionality. The presence of multiple pesticides can pose challenges in effectively remediating them from the soil. The present work examines the scientific literature on the benefits and drawbacks of various existing and emerging soil remediation techniques. Customized technology choices and designs for specific site conditions enhance the effective cleanup of polluted areas. The present study, which evaluates and contrasts various technological approaches, shall serve as an invaluable tool for determining the optimal soil remediation method for a given contamination dilemma.

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Introduction
Pesticides are chemicals used to reduce, remove, prevent, or destroy any pest.Insecticides, fungicides, herbicides, molluscicides, nematicides, bactericides, piscicides, rodenticides, avicides, animal repellents, antimicrobials, and soil fumigants are examples of pesticides.[1] Pest infestation destroys approximately 45% of annual food production.[2] Pesticide use helps

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to keep pests away from crops and can improve crop yield and quality.[1] In modern times, there are more than 500 substances that are authorized and utilized globally as pesticides or their derivatives. Following the conclusion of the Second World War, the application of pesticides in the farming sector has experienced a steady escalation, resulting in heightened food production worldwide. Among the nations in South Asia, India is the most significant consumer of pesticides, accounting for 3% of global usage in the protection of crops. Organophosphates, organochlorins, and neonicotiniods are some of the most commonly employed pesticides in India.[3]

However, due to their unscientific and excessive application, 80 to 90% of pesticides applied reach organisms other than their target organism and are deposited on non-target soil and water, contributing to agro-ecosystem pollution[3,2] Pesticides possess the capability to disturb the functioning and composition of the ecosystem as they enter the food chain and have adverse effects on the biotic elements of the ecosystem, including soil organisms, plants, animals in the wild, aquatic creatures, and domesticated animals.The widespread presence and enduring impact of diverse pesticides and organic pollutants derived from agriculture have caused significant harm to humanity due to their ability to accumulate in living organisms and their high levels of toxicity. These pesticides have been observed to disrupt the proper functioning of the endocrine and reproductive systems in various organisms. Specific pesticides such as dichlorodiphenyltrichloroethane (DDT), chlordane, aldrin, dieldrin, endrin, mirex, heptachlor, and hexachlorobenzene have detrimental effects on both human health and the environment.[2] According to the Indian Council of Medical Research (ICMR), approximately 1 million lives are lost annually worldwide due to the persistent effects of pesticide poisoning, resulting in long-term illnesses.[3]

Numerous techniques for remedying the presence of pesticides in soil have been devised and put into practice, with the aim of eradicating, lessening, and segregating them.However, remediation through the separation and destruction of soil contaminants is time-consuming and costly.[4] Physical, chemical, and biological methods are the three main approaches used in the separation and destruction of contaminants, depending on the contaminants' characteristics, soil porosity, soil pH, and so on.[5] The selection of the remediation technique for a polluted site is based on factors such as the nature and concentration of pollutants, soil type, and properties, climate conditions, regulatory obligations, the presence of additional contaminants, as well as cost and time constraints.[6]

As a result, this study covers the procedure, benefits, and drawbacks of the physical, chemical, and biological techniques that are currently accessible for the restoration of pesticide-polluted soil.

Physicochemical Methods

Immobilization Technologies

The prevention of soil contaminant migration from waste is achieved through immobilization techniques. These techniques include containment methods, solidification/stabilization methods, and vitrification methods, which are the three primary approaches utilized.[7]

Containment-Immobilization

The primary goal of containment is to prevent or control the leakage or leaching of contaminated liquids or semi-liquids into non-contaminated areas. Pumping, draining, capping, and the installation of slurry walls are all basic containment techniques.[7] There are several kinds of containment technology. They are broadly classified as active andpassive methods. Slurry walls were built in the field using settlement plates, vane shear, and earth pressure cells. Within a few days, shear strength increases and permeability decreases, preventing contaminants from leaking from the containment zone.[8] A soil comprised of clay and the presence of octadecyltrimethyl ammonium bromide, a cationic surfactant, as well as reactive barriers modified with kaolinite, montmorillonite, kaolinite, and palygorskite clay minerals, were all subjected to leaching and permeability experiments.More than 85% of the added pesticide compound was washed away through the unaltered natural clay barrier in the soil.[9]

Containment immobilization is not a true remediation technique; it simply keeps contaminants from leaking into the surrounding environment. Additional chemical and biological techniques are applied to remediate containment contaminants. The technique of containment immobilization has found extensive application in addressing soils that are severely contaminated. Because applied containment technologies are not completely satisfactory, they require close supervision and continuous monitoring.[10]

Solidification

The process of solidification is used to remediate toxic waste or highly polluted soils. The foundation of this method is the solidification or decrease in the mobility of pollutants, the majority of which are heavy metals. Preventing polluted items from endangering the environment is the aim.[11] The processes of solidification and stabilization are distinct. Stabilization is a chemical process that converts hazardous waste materials into less harmfulsubstances,and solidification is the process of converting waste materials to solid or semi-solid formsto reduce the permeability or leaching of contaminants.[7]

During a heat stability experiment, a total of 33 pesticide combinations, comprising 32 insecticides and 4 additional pesticides, were subjected to examination. The study involved placing the samples on a thermostat at 54°C for 14 days. The findings indicate that the majority of the active ingredients in the pesticide mixtures displayed reduced stability compared to their individual formulations.[12] Contaminants containing low-volatile organics can be managed through stabilization. The effectiveness of solidification/Stabilization technologiesislimited for pesticide remediation.[6]

Vitrification

Vitrification is a thermal decontamination technique that converts polluted soil into a stable vitreous product.The process of vitrification involves turning toxic waste into items that resemble glass.As per the Environmental Protection Agency of the United States, it is the "best demonstrated available technology" for heavy metals and radioactive waste. Nevertheless, it stands as the costliest method for immobilization.[7]

Ex-situ and in-situ vitrification are both possible. Graphite electrodes are inserted into the soil during in-situ vitrification to generate a high electric current, while the high temperature (over 1,700°C) melts the soil into a molten block.[13]

According to various reports, immobilization technologies were used to remediate pesticide-contaminated soils such as Dichloro diphenyltrichloroe thane (DDT), Dichloro diphenyldichloroe thylene (DDE), Dieldrin, Terbuthylazine, Carbofuran, chlorpyrifos, Diuron, Atrazine, and others. A 16-foot-deep trench was created to treat about 305 m^3 of contaminated soil using in-situ vitrification. Pretreatment concentrations of 4,4-DDT and Dieldrin were 13000 and 4600 g/kg, respectively. Both pesticide concentrations were reduced to less than 16 g/kg after in-situ vitrification.[14]

Separation Technologies

Separation technologies are used when contaminants in soil are recalcitrant and persistent, making them less accessible to other destructive remediation methods.

Soil Washing

This technique involves the dissolution or suspension of contaminated soils in a solution of water. This method eliminates contaminants from the soil by transferring them from bigger soil particles to the liquid phase(Figure 1). The optimal conditions for soil washing include wash or rinse temperature, surfactant concentration, and pH.[15] Soils must contain at least 50% sand and gravel to be suitable for soil washing.[10]

Solvent Extraction

Ex-situ solvent extraction separates contaminants from soil by applying high-shear energy and dissolving them in organic solvent solutions. The supercritical fluid extraction (SFE) method separates various contaminants such as pesticides, phenols, and hydrocarbons. Methanol is frequently used as the primary solvent in this method, along with carbon dioxide (CO_2). By channeling CO_2 through the soil, contaminants are solubilized in methanol and collected for disposal.[17] Subcritical water extraction (SCWE) was used to extract parathion, diazinon,and phenthoate from polluted soil. The extraction efficiency was 99.9%, and the final pesticide concentration was less than 0.5 mg/kg at 150°C and 2 MPa. The water flow rate was 0.5 mL/min, and the total extraction time was 20 minutes.[18] Solvent extraction remediation studies were conducted on soil contaminated with p,p'-DDD, p,p'-DDE, p,p'-DDT, and toxaphene. Methanol was utilized as the solvent, maintaining a ratio of 1.6 parts methanol to soil.This solvent extraction technique reduces pesticide concentrations in soil by more than 99% while also reducing the amount of material required for further extraction by 25%.[19]

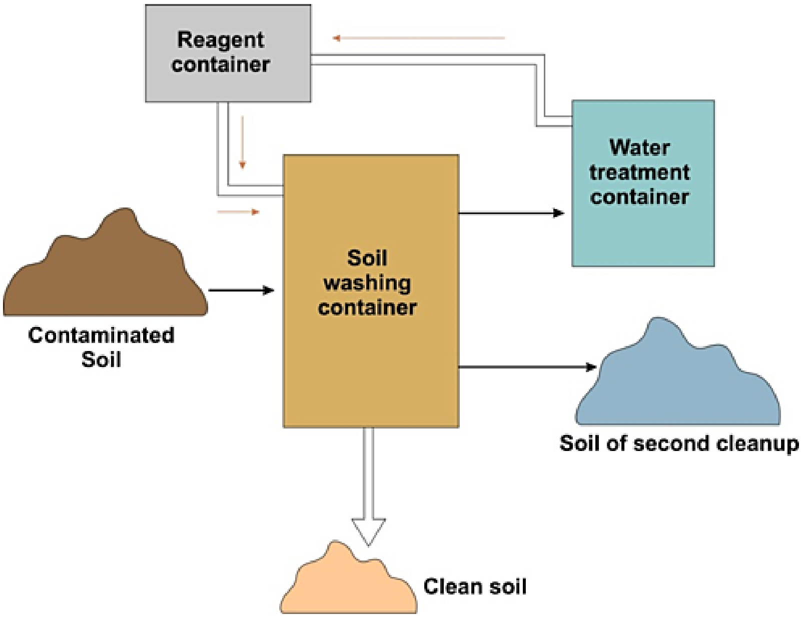

Fig. 1: Soil washing process for treatment of polluted soils.[16]

Solvent extraction is currently commercially available for pesticide-contaminated soils. The prime drawback of utilizing this methodology is the exorbitant expense associated with ex-situ implementation.In addition, a certain level of pressure is maintained to keep the solvent liquid and prevent vaporization as the temperature rises. Low permeability soils necessitate high-pressure solvent extraction over a longer time period.[15]

Surfactants

Surfactants that reduce aqueous solution surface tension are used to solubilize soil contaminants.[4] The formation of a micelle with a hydrophobic core and a hydrophilic surface is possible with a surfactant that contains both hydrophobic and hydrophilic components. By segregating hydrophobic organics into a hydrophobic core, the surfactant elevates its water solubility.Surfactants showed variable degrees of solubilization of hydrophobic organic compounds depending on their electrical characteristics, polarities, HLB numbers, and CMC values.[20] Industrially synthesized synthetic surfactants include sulphonates, Brij 35, ethoxylated alcohols, Triton, and sodium dodecylbenzene sulphonate (SDBS). Surfactant and absorbent were used to treat the soils of two sites contaminated with chlordane, DDT, and Mirex. As a surfactant, Triton X-100 was used, and activated carbon was used as an absorbent. According to the findings, triton X-100 improves soil washing and contaminant adsorption by activated carbon.[21] In another study, surfactant concentration, pH, and ionic strength were studied as potential factors in pesticide removal. For the removal of 2,4-dichlorophenoxyacetic acid (2,4-D) from contaminated soils, two surfactants, sodium dodecyl sulfate (SDS) and ethoxylated lauryl ether (Brij 30) were used. Up to 50% and 80% of 2,4-D were removed in a single wash and two continuousitems of washings with SDS, respectively, whereas Brij 30 removes only 13% of 2,4-D in optimal conditions. The optimal SDS and Brij 30 concentration was 5g/L. The extraction efficiency is greatest when the pH is close to neutral. Even a small pH change to 8 resulted in a significant reduction in pesticide extraction. Brij 30's percentage of extraction was shown to increase when sodium chloride was used to change the ionic strength of the extraction mixture. The addition of 1% NaCl increased extraction from about 12% when no NaCl was added to 30%, whereas no such effect was observed in the case of SDS.[22]

Biosurfactants, such as rhamnolipids, are more environmentally acceptable for pesticide-contaminated soil remediation because they are compatible with and beneficial to the soil environment. The drawback of synthetic surfactants is that they are hazardous to the soil microbial population and challenging to remove from the soil due to the development of high-viscosity emulsions and limited water solubility.[10]

Cyclodextrins

Cyclodextrins are used to remove pesticides from contaminated soil as non-toxic alternatives to surfactants and organic solvents. Cyclodextrins entrap many organic compounds in their structural ring due to a low polarity cavity with a small and stable molecular structure. Cyclodextrin can thus solubilize a wide range of organic contaminants.[23] Many studies have found that cyclodextrins' nanoporouscarbon structure is effective at removing pesticides such as DDT, Dichlorodiphenyldichloroethane (DDD), and DDE.[5] An ex-situ soil wash study was conducted to extract soil pollutants using carboxylmethyl—cyclodextrin. The removal efficiency for organochlorine pesticides was 94.7% with two continuous soil items ofwashings at 60oC temperature and 40 kHz ultrasonication in 50 mL L-1 maize oil for 20 minutes, 87.2% for mirex, 98.5% for endosulfans, and 92.3% for chlordane.[24] In a study, 25 g/L of methylcyclodextrin as well as 100 ml / L of sunflower oil at 50 ° C and 35 kHz for 30 minutes removed approximately 99% of organochlorine pesticides (OCP), DDT, endosulfans, heptachlor, and chlordane from solution.[25]

Although all cyclodextrin research has been conducted on a laboratory scale, pesticides that form strong inclusion complexes can be removed by using a low cyclodextrin concentration. Higher amounts of cyclodextrins should be used in soil with high pesticide contamination. The findings suggest that cyclodextrins could be effective in cleaning up pesticide-contaminated soils.[10]

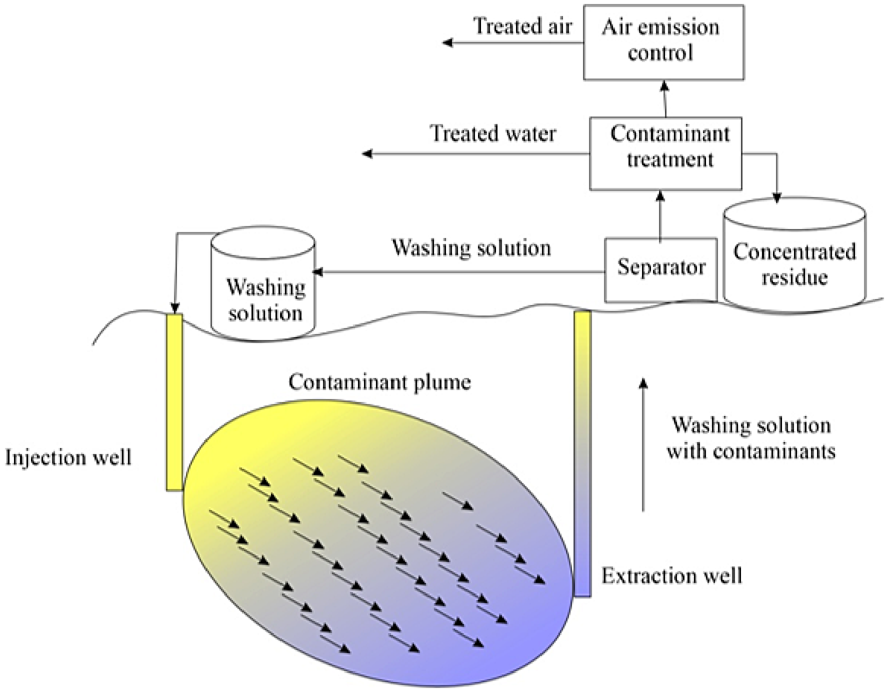

Fig. 2: In situ soil flushing process.[6]

Soil Flushing

Soil-flushing is a method of treatment in which a flushing solvent is introduced into or applied to the contaminated site's surface(Figure 2). Despite the paucity of studies in this area, chemically enhanced flushing can effectively remove a variety of contaminants.[26] This method can be used to remove radioactive materials, inorganic chemicals, metals, organic compounds, and inorganic compounds. To improve the efficiency of this technique, appropriate additives are used. This process's sludge can be reused by mixing it with soil or by further treatment with solvent extraction, solidification, or vitrification and then mixing it with soil. Another remediation technology must be used to treat the contaminated soil to reduce the amount of material, this technique is often used as a pre-treatment.[13]

A medium organic content soil was artificially contaminated with phosalone, and an ethanol aqueous solution was used to flush the soil. 99% phosalone extraction was achieved by using a flushing solution containing 10% ethanol by volume.[27] Sixteen different solvents were used to flush contaminated soil with hexachlorocyclohexane (HCHs), DDTs, chlordane, and mirex. Ethyl acetate is the most effective at removing HCHs (87.6%) and DDTs (86.9%). And the organic solvents' chlordane removal efficiency was 70% with petroleum ether and 63.5% with mirex and propanol.[28]

Other techniques, such as electrokinetic methods, activated carbon, and biodegradation, can be combined with soil flushing. Because soil flushing is performed on-site, there is no need to excavate, handle, or transport polluted soil to the treatment area.As a result, the study's cost is reduced. However, soil flushing necessitates the use of additional technology to completely remove contaminants from soils.[6]

Oxidative Process

Advanced oxidative processes, among other methods, have great potential for soil remediation and can be applied as a pre- or post-treatment in several other investigations. The pollutantsare degraded using this technique by mineralizing into inorganic compounds, water, carbon dioxide, or even inert components.[17] Pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and total petroleum hydrocarbons (TPHs) are remedied from contaminated soil using advanced oxidative processes (AOPs).[29] Five types of advanced oxidative processes including Fenton oxidative processes, plasma oxidation, ozonation, TiO_2 photocatalysis, and persulfate oxidation are discussed here.

Fenton Advanced Oxidation Processes

The advanced oxidation process in Fenton is the oxidation of iron ions (Fe^{2+}) to hydrogen-containing mediums (H_2O_2), generating a reactive hydroxide atom (•OH), and acts by oxidizing organic contaminants toward less harmful by products[17] (Figure 3).This technique can benefit from the use of light, electrical current, and ultrasound. The electrical current generates in situ hydrogen peroxide by reducing O_2 in the presence of Fe^{2+}, which avoids the continuous addition of hydrogen peroxide. Hydroxyl radicals are produced in the photo-Fenton process by activation of iron (III) alone or with hydrogen peroxide.[5]

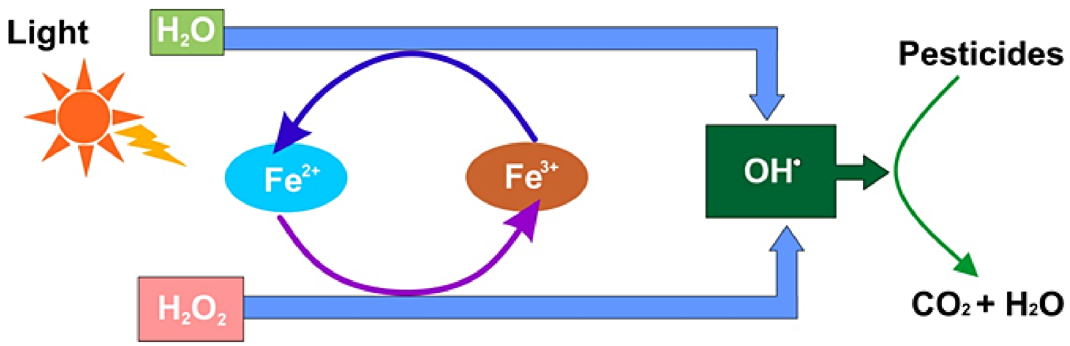

Fig. 3: Photo–Fenton degradation of pesticides.[30]

Although the Fenton oxidation process is effective in eliminating pollutants from the environment, soil remediation with this technology is not widely explored worldwide.[17] Soil contaminated with organochlorine pesticides was cleaned using the Fenton oxidation method, which involves Fe^0, EDTA, and air. DDT degraded and was removed from contaminated soils efficiently at room temperature, neutral pH, and atmospheric pressure.[31] DDT and DDE were removed from contaminated soils using soil washing and the photo-Fenton oxidation process. Washing with TritonX-100 solution removes 66% DDT and 80% DDE from soils. After 6 hours of solar Fenton oxidation, 99% of DDT and 95% of DDE were removed from wastewater.[32]

The total transformation of organic contaminants into CO_2 and H_2O with zero-waste sludge is one of the benefits of this oxidation technique. Another benefit of this technique is its capacity to degrade a wide variety of pollutants in a single process without being selective.[5] Acid pH dependency is the key barrier, with an ideal range in an aqueous medium of 2.8 to 3.0. This makes it hostile to soil-based microorganisms and may even change its features, and can hamper agriculture of a large number of important crops.[17]

Persulfate-Based Advanced Oxidation

AOP becomes a more viable method for degrading developing organic contaminants. The sulfate radical has recently been investigated for its marked superiority and potential for use in the degradation of emerging contaminants due to its elevated oxidation potential (E^0 = 2.5-3.1 V), which is similar to •OH (E^0 = 2.8 V), as well as it's non-selective to the contaminants. Furthermore, because of their high solubility, these solid persulfate oxidants are easy to transport and apply.[33] The activation methods for persulfate - including homogeneous catalysis (such as heat, UV, ultrasonic, and alkaline) and heterogeneous catalysis with metal or carbon catalysts - are of utmost importance. Homogeneous catalysis is more typically utilized for soil remediation.[34] The thermoactivated persulfate oxidation process was used to study chlorpyrifos degradation. Around 30% of chlorpyrifos was degraded at 70 °C, with a decay rate of (1.8 ± 0.5) × 10^{-3} min^{-1}. Increasing the temperature could hasten the degradation of persulfate, as a result, the elevation of oxidizingcomponents, especially SO_4^- would increase, facilitating the oxidation of the target compounds.[35] Using activated persulfate with ferrous and copper ions, propachlor was broken down. Early on, persulfate activation by Fe^{2+} ions lead toa fast breakdown, but this was soon followed by a sharp decline in efficiency because the sulfate radicals quickly depleted Fe^{2+}. At higher Cu^{2+} concentrations, however, Cu^{2+} activated persulfate has a longer decomposition effect and correspondingly higher decomposition enhancement.[36] According to one study, heat-activated persulfate degrades atrazine effectively. After 2 hours of treatment at 60 °C in the presence of 1 mM persulfate, 50 M atrazine completely disappeared. Increased initial concentrations or temperatures of persulfates significantly improved the efficiency of decomposition.[37]

When compared to traditional oxidation methods such as H_2O_2, permanganate (MnO_4), O_3, and persulfate relatively stronger oxidant persistence and increased redox potential (E^0 = 2.01 V) allow it to reach the polluted zone area across long-distances in the subsurface.Moreover, the utilization of persulfate for soil remediation requires lesser soil oxidant demands compared to H2O2 and permanganate, thereby rendering it a more economical approach. In real-world soil remediation with a low soil-to-water ratio, achieving ideal mixing between activator-oxidant and/or oxidant-soil is challenging. As SO_4^- and •OH have a short life span and strong oxidation, they may decrease before reaching deeper soil layers. Consequently, the efficiency of degradation can decline with increasing soil thickness.[34]

TiO_2 Photocatalysis

Photocatalysis, a method of environmental remediation in which semiconducting metal oxides act as a catalyst, has piqued the interest of researchers in recent decades. Titanium dioxide (TiO_2), gallium phosphide (GaP), nickel oxide (NiO), tungsten trioxide (WO_3),zinc oxide (ZnO), and cadmium sulfide are semiconductors used as catalysts in photocatalysis studies (CdS). TiO_2 stands out as the most effective photocatalyst due to its non-toxic nature, exceptional photoactivity, resistance to chemical reactions, ease of accessibility, and affordability.[29] According to research, aniline is completely degraded in photocatalysis using only TiO_2 or ozone. Photocatalysis techniques have many advantages in aniline degradation, and the photocatalyst can be reused through regeneration, lowering the cost of chemicals used in the studies.[38]

TiO_2 photocatalysis was employed to degrade diuron in contaminated soil using an ex-situ approach.For up to 120 hours, the experimental setup was exposed to solar light. The top 4 cm of the contaminated soils demonstrates effective diuron destruction by TiO_2 photocatalyst.[39] The maximum degradation of pyridaben was achieved by performing a photocatalysis study with TiO2 and UV light irradiation at 300 nm and 360 nm UV wavelength. The complete removal of pyridabed achieved within 60 min and 140 min for 300 nm and 360 nm respectively.[40]

Plasma Oxidation and Ozonation

The technique creates high-voltage electrons, which activate reactive molecules such as ozone (O_3), hydroxyl (OH), oxygen (O), and hydrogen peroxide (H_2O_2) to form free radicals.[17] One of the most significant active species in plasma discharge processes that contributes to the breakdown of organic pollutants is H_2O_2.[29] The benefits of plasma oxidation include (i) high efficiency in producing a variety of oxidizing agents and radicals, (ii) the ability to treat various contaminants with varying concentrations, and (iii) the contaminated soils requiringlittle pretreatment. The plasma oxidation reaction, on the other hand, is relatively uncontrollable. The large volume of plasma generation and sustainment is a significant challenge for the widespread application of this technique.[41]

Ozonation is another oxidation process that is used to degrade contaminants in soil. The application of ozone and ultraviolet radiation generates hydrogen radicals, and these hydrogen radicals oxidize pesticide contaminants in the media. Ozonation has proven to be an effective oxidation method for eliminating pesticide pollutants from both soil and wastewater during the treatment process. By increasing the concentration of ozone, the rate of oxidation can be accelerated. By increasing the ozonation time and pretreatment humidification, the reaction kinetics of ozonation can be improved.[30]

Electro-Kinetic Remediation

In this method, two electrodes are inserted into the soil to generate low voltage currents of mA/cm2, causing the movement of pollutants into the soil. This method effectivelyremovespolar biomolecules and heavy metals from soil, sludge, and sediments.[13] This technology has been used for decades to remediate heavy metals contaminated with heavy metals., and is now being used to remove organic substances. The extraction of organic pollutants typically entails the interplay of electroosmotic water flow and electromigration of ions to the appropriate electrode.[20] The elimination of pollutants from the electrode's surface can be achieved by precipitation, ion complexation, or pumping. A significant drawback associated with the use of this procedure has been the potential for the precipitation of elements such as heavy metals near the cathode.[13] Electro-kinetic (EK) and electro-kinetic Fenton coupled (EKF) technologies were used to remove HCSs and DDT. The elimination efficiency of HCHs (30.5%) and DDT (25.9%) is lower in individual EK. Even though the EKF has a higher degradation rate of 60.9% for HCHs and 40% for DDT42.The removal of 2,4-dichloro phenoxy acetic acid (2,4-D) from contaminated soil was accomplished using electrokinetic soil flushing techniques. For 40 days, a fully automated ex-situ bench-scale setup was run. The results show that 50% of the 2,4-D was removed, 25% remained in the soil, and the remaining 25% was volatilized.[43]

Electrokinetic remediation technology is rapidly being utilized to remove organic, inorganic, explosives, radionuclides, and other contaminants in contaminated soils and wastewater.

This technique is effective for removing polar pesticides such as organochlorine. In a bench-scale treatment test (140 minutes), 85% of the chlorophenol was removed.[44] The prime benefit of electrokinetic technique is its low cost and ability to be used both insitu and ex-situ.[11]

Physical Methods

Thermal Incineration

Thermal incineration is another commonly used remediation technology for organically contaminated soils. Organic contaminants are destroyed at high temperatures with high oxygen content, converting the contaminants to inorganic carbon dioxide and water. Thermal incineration effectively removes pesticides, halogenated and non-halogenated compounds, dioxins, and PCBs from contaminated soil.[13] This technique can remove contaminants at a rate of 99.99% or higher. High-temperature incinerators have been shown in studies to remove up to 99.9999% of PCBs and dioxins.[11]

In one study, PCBs contaminated sites were remedied using Infrared High-Temperature Incineration (IHTI) and Base Catalyzed Decomposition (BCD). Both methods resulted in a total amount of environmental damage. The IHTI produced carcinogens, respiratory inorganics, and organics during primary and secondary combustion, which cause terrestrial acidification, eutrophication, and global warming.[45]

Thermal Desorption

Thermal desorption can be utilized to treat contaminated soils containing volatile and semi-volatile toxicants such as PAHs, PCBs, total petroleum hydrocarbon (TPH), and DDT. The primary benefit of this technique over other technologies are that soil and contaminants can be recycled, there is no secondary pollution, it is highly efficient (99%), the treatment period is short, it is safe, and It can handle a variety of contaminants. The contaminants of interest are separated and removed from the soil, either directly or indirectly, by heating in a vacuum or a carrier gas.[46] Soils contaminated with DDT, DDD, DDE, Toxaphene, and hexachlorohexane were collected from a contaminated site, and thermal desorption was used to remove these contaminants. After 30 minutes at 350^{o}C, the thermal desorption technique removed more than 98% of each pollutant from the collected soils except DDE[47]

Thermal desorption is a highly successful technique for eliminating pesticides from contaminated soil. The temperature should be higher than the boiling point of the least volatile contaminants for the removal of a pesticide mixture.[47]

One of the main disadvantages of thermal desorption is the ex-situ method, which necessitates the excavation and transfer of polluted soil to the treatment location and is costly.

Various toxic gases were formed during thermal desorption, resulting in air pollution.[6]

Adsorption

Adsorption has been used to remove pesticides from soil and water. The most commonly used adsorbent in this technique is activated carbon. Activated carbon is used to clean up pesticides from pesticide manufacturing plants30. Surfactants can be used to increase the rate of adsorption of inorganic contaminants. These surfactants reduce surface tension, improve solvency, increase micellar solubilization, and aid in pesticide contamination extraction.[16] Adsorption-activated carbon was used to assess the adsorption and removal potential of diazinon. The adsorption result showed that NH4Cl-induced activated carbon removed 97.5% of 20 mg/L diazinon (NAC)[48] Granular activated carbon and pitch-based activated carbon fibers (ACF) were used in an atrazine adsorption study (GAC). The activated carbon fibers absorbed seven times more than the commercially available granular activated carbon. The main reason for this result is the AFC surface area. ACF has a surface area of approximately 1700m^2/g and GAC has a surface area of approximately 1100m^2/g.[49]

Various studies have found that organic acids, in the order citrate > oxalate > acetate, improve the adsorption of activated carbon electrodes for contaminant extraction or remediation performance.[50] OCPs-contaminated soils can be selectively remedied using surfactant-enhanced washing in conjunction with activated carbon.[21]

Ultrasonic Technology

Ultrasound waves are not detectable by the human ear. Ultrasound works primarily by forming cavitation bubbles in the matrix. The chemical reaction in the matrix is accelerated by the implosion of cavitation bubbles, microturbulence, high-speed collisions between matrix particles, and the formation of matrix microporous particles. Due to the continuous formation and collapse of cavitation bubbles, which causesthesonolysis of water to produce free radicals, the local temperature and pressure within the matrix rise dramatically.[5] The chemical reaction within the matrix is propelled by the intense forces of high-frequency sound waves, reaching up to 18 kHz, as well as high-pressure levels of up to 50 MPa, and scorching temperatures of up to 4726 °C, which degrades the contaminants. Ultrasound was used to remove diazinon in various concentrations. The results showed that increasing diazinon concentration (800, 1200, and 1800 ppm) increased degradation efficiency, but increasing solution volume decreased degradation efficiency.[51] Chlorpyrifos and Azinphos-methyl pesticides were degraded using an ultrasound method. The results showed that both contaminants degraded quickly using the ultrasound method. Within 20 minutes of being exposed to 130 kHz ultrasound, 98.96% chlorpyrifos and 78.50% azinphos-methyl were degraded.[52]

This technology can effectively remove different types of toxicants from the soil, including heavy metals, pesticides, hydrocarbons, chlorinated solvents, and petroleum hydrocarbons. The benefits of this ultrasonic technique include low installation and maintenance costs, as well as requiring less energy and space.[16] The power of the ultrasound, frequency, temperature, intensity, duration of the application, and soil particle size are all factors that influence ultrasonic technique performance.[53]

Nanotechnology

Nanotechnology can effectively reduce pesticide pollution. Nanoparticles have been used in a variety of biological disciplines, ranging from environmental studies to molecular biology, due to their diverse morphology and size. Iron-based nanoparticles like Fe_2O_3, Fe_3O_4, and nano zero-valent iron (nZVI) are commonly utilized in nanocomposites for the efficient removal and detoxification of organic pollutants from soil. These iron nanoparticles oxidize more easily and form pesticide aggregates. Other suitable technologies can easily degrade these pesticide aggregates.[10]

Using zero-valent iron(Fe^0), triazine dechlorination from soil was accomplished. Several studies have shown the mineralization of metolachlor and atrazine can improve remediation.[5] Iron nanoparticles have shown satisfactory results in removing contaminants in long-term treatment and different soils.[54] Using Fe nanoparticles, all types of organochlorine pesticides and their metabolites can be removed via photocatalysis and adsorption55. In the presence of light, nanoparticles can act as catalysts, reacting with pesticides to produce harmless molecules such as H_2O, N_2, and CO_2.[56]

Biological Methods

Bioremediation by Microorganisms

Biodegradation occurs naturally when soil-dwelling organisms degrade and metabolize various xenobiotic compounds and pesticides for nutrient supply. Soil microbes naturally mineralize various organic and inorganic compounds. These microbes' degradation capability can be increased in a short period with some modifications.

Four factors influence the speed of bioremediation in soil, including the availability of pesticides or their by-products to microorganisms, the physiological condition of those microbes, the survivorship of pesticide-degrading microbes at polluted sites, and the maintenance of a stable population of this microorganisms.[57] A diverse group of bacteria can degrade different pesticides in soil (Table 1).

Fungi are another biological agent that is commonly used for pesticide biodegradation and bioremediation (Table 2). Depending on the functional groups in the pesticides, different fungal strains can perform different biodegradation processes such as dechlorination, demethylation, esterification, deoxygenation, oxidation, and dehydrochlorination.[73]

Table 1: Pesticide degradation by various bacterial strains.

Sl. No	Pesticide	Bacterial strain	Degradation efficiency
Organochlorine pesticides			
1.	DDT	*Bacillus sp.* *Staphylococcus* sp. *Stenotrophomonas* sp.	The degradation rate ranges from 28.48 to 58.08% when isolates were tested individually, but the rate increased to 82.63% when the mixed culture was used and the incubation period was 31 days.[58]
2.	Chlordane	*Streptomyces sp.*	Following 28 days of incubation 56% of chlordane was removed from soil sample.[59]

3.	Lindane	*Streptomyces sp*.	After 96 h of incubation 46 to 68%, lindane was removed60.
4.	γ-HCH	*Pseudomonas sp*.	After 10 days of incubation, 47.3ppb γ-HCHremained in the medium.[61]
Organophosphate pesticide			
5.	Diazinon	*Pseudomonas peli* *Burkholderiacaryophylli*	The degradation rate increases from 3.35 4.26 mg/l/d to 4.55, and 5.36 mg/l/d respectively when supplemented with 0.5% glucose.[62]
6.	Malathion	*Acinetobacter johnsonii*	The maximum degradation rate was 3.5837 mg/(L·h).[63]
7.	Chlorpyrifos	*Bacillus cereus*	After 7 days of incubation, 73.9% chlorpyrifos was removed from the medium.[64]
Carbamate pesticide			
8.	Carbofuran	*Flavobacterium sp., Pseudomonas sp*., *Sphingomonas sp.*	Approximately 98% carbofuran in 96 h of incubation.[65]
9.	Carbaryl	*Bacillus sp.* *Morganella sp.*	The degradation rates for both isolates were 94.6% and 87.3% respectively,[66]
Pyrethroid pesticide			
10.	Cypermethrin	*Bacillus thuringiensis*	Approximately 80% of the initial cypermethrin degraded within 15 days of incubation.[67]
11.	Cyfluthrin	*Photobacterium ganghwense*	After 120 h of incubation, 92.13% cyfluthrin was degraded.[68]
12.	Deltamethrin	*Microbacteriumchocolatum*	The deltamethrin degradation rate was 76% in agricultural soils.[69]
Neonicotinoids pesticide			
13.	Imidacloprid	*Ochrobactrum sp*. *Rhizobium* sp.	After 48 h of incubation approximately 67.67% was degraded.[70]
14.	Clothianidin	*Pseudomonas stutzeri*	Clothianidin degradation was approximately 62% within two weeks.[71]
15.	Acetamiprid	*Micrococcus luteus*	Maximum degradation rate was 69.84% in 24 h.[72]

Table 2:Pesticide degradation by various fungal strains.

Sl. No	Pesticide	Fungal strain	Country &References
1.	Chlorpyrifos	*Acremonium sp.*	The degradation rate was highest at 83.9% in a full nutrient medium.[74]
2.	β-cypermethrin	*Eurotiumcristatum*	The half-lives of β-cypermethrinrange from 3.382 to 11.517 days.[75]
3.	3-phenoxybenzoic acid	*Eurotiumcristatum*	The half-lives of β-cypermethrinrange from 1.749 to 3.194 days.[75]

4.	DDT	*Phlebiaacanthocystis*, *Phlebiabrevispora*	After 21 days of incubation, both isolates degrade 70 and 30% of DDT respectively.[76]
5.	Tribufos, azinphos-methyl, terbufos, and phosmet	Phanerochaete chrysosporium, Pleurotusostreatu,s Bjerkanderaadusta	After four days of incubation, these three isolates degrade 50 to 96% of the selected organophosphorus pesticides.[77]
7.	Endosulfan	*Aspergillus niger*	Complete mineralization of 400 mg/ml endosulfan was achieved in 12 days of incubation.[78]
8.	Lindane	*Aspergillus fumigates*	Approximately 94% of lindane was degraded in 72 h of incubation.[79]
9.	Lindane or hexachlorocy clohexane	*Fusariumpoae* and *Fusariumsolani*	The degradation of lindane by *F. poae* was 56.7 and 59.4% by F. solani.[80]
10.	Monocrotophos	*Aspergillus oryzae*	In 50 h of incubation, 70% of monocrotophos was degraded and at 168 h the pesticide became undetectable.[81]

There are some disadvantages to using fungi as a biodegradative agent, such as the fact that fungal biodegradation is much slower than bacterial biodegradation and that fungal degradation cannot completely remove pesticides.[73]

Bio-Airsparging

The technique of bio-airsparging can be employed to decrease the adsorption of volatile chemicals in the soil, dissolution in underground water, or the saturated zone whenever required. It is a biological technique that involves regularly injecting nutrients and oxygen into the saturated zone to boost the activity of microbes (Figure 4). This indigenous in-situ technology generally employs microorganisms and is less effective in the presence of non-biodegradable contaminants and non-stoppable pollutants.[13]

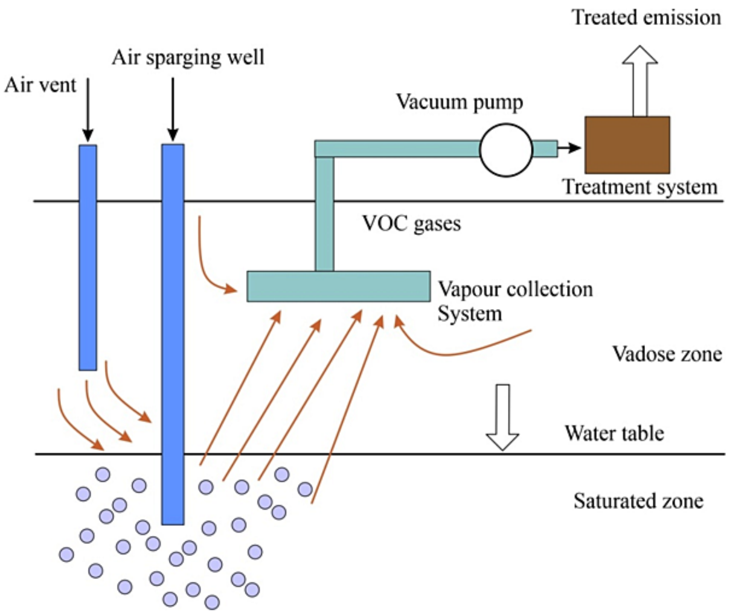

Fig. 4: Air sparging with soil vapor extraction process.[6]

Biosparging has been studied for the removal of toluene, ethylbenzene, benzene, and xylenes (BTEX) from petroleum-hydrocarbon spill sites. Within a 10-month remediation period, more than 70% of BTEX was removed using the biosparging system.[82] The primary drawback of this method is its slow rate of degradation, which can be time-consuming.

Bioventing

The venting process is critical because air injection occurs in contaminated media, minimizing the off-gassing of volatilized contaminants while maximizing in-situ biodegradation to the atmosphere at a predetermined rate. Bioventing only pumps air into the unsaturated zone, as opposed to bio-sparging, which pumps nutrients and air into the saturated zone.[6] The method of utilizing an anaerobic gas mixture containing a reducing agent for bio-venting was studied to eliminate DNT and DDT. The results showed that DDT was halved in 8.5 months with the presence of 1,1-dichloro-2, 2-bis(p-chlorophenyl) ethane as an intermediate substance. On the other hand, DNT was eliminated within six months without the need for an intermediate compound.[83] It was possible to access bio-venting studies at two different temperatures. Soils contaminated with toluene and decane were treated at 10^{o}C and 20^{o}C. The results showed that at 20^{o}C, 99.8% and 98.7% reductions in toluene and decane were achieved, respectively. At 10^{o}C, it required 1.6 times the duration and 1.4 times the volume of air to accomplish an equivalent outcome.[84]

Despite its high level of diversity, the primary principle of this technology is to ensure adequate airflow rates to supply enough oxygen to the contaminated area. This, in turn, facilitates the degradation of organic compounds through soil microorganisms.[11]

Landfarming

Land farming is the simplest bioremediation technique, requiring little expertise and capital. The introduction of contaminated soils, sediments, or sludges into the top layer of soil followed by periodic aeration enhances the microbial breakdown of the mixture.[85] Ex-situ and in-situ land farming can be practiced depending on the depth of different polluted zones in the soil. In the practice of remediation, the process of excavating and treating contaminated soil in its original location is referred to as in situ treatment. Excavation for bioremediation is not required if the pollutants are less than 1m beneath the soil surface, however, if the pollutants are more than 1.7m beneath the soil surface, the contaminated soil is excavated to the surface for effective remediation by autochthonous microorganisms.[16]

Transporting contaminated soil to the land farming site, mixed into the soil surface almost 10 centimeters thick in the case of ex-situ processing. It is a simple technique that requires little infrastructure and is less expensive. Landfarming was used in soil bioremediation where the soil was highly polluted with hexachlorocyclohexane (HCH) isomers (>5 g/kg). The researchers made a notable discovery regarding the four isomers under study. They observed that the α and γ isomers exhibited a remarkable removal rate of 89% and 82%, respectively. However, the β and δ isomers displayed a barely noticeable decrease in behavior.[10] Soils heavily contaminated with hexachlorocyclohexane (HCH) were used for land farming. After 11 months of treatment, 89% α-HCH and 82% γ-HCH were removed. The metabolites were identified as Pentachlorocyclohexene and tetrachlorocyclohexene.[86]

Biopiles

Biopiles add a piping system to a pile of contaminated soil, causing the pollutants to decompose aerobically by providing oxygen. To encourage microbial activity, nutrients are administered on the surface of the soil pile (Figure 5). The piles should be 3-4 meters tall and have a volume of tens to hundreds of cubic meters.[10]

The pile configuration boasts a primary benefit, wherein a considerable amount of polluted soil can be remediated within a limited expanse. However, installing and maintaining a pile system is costly. Another disadvantage of this method is that the hot air generated by the pile dries out the soil, reducing soil microbial activity.[16]

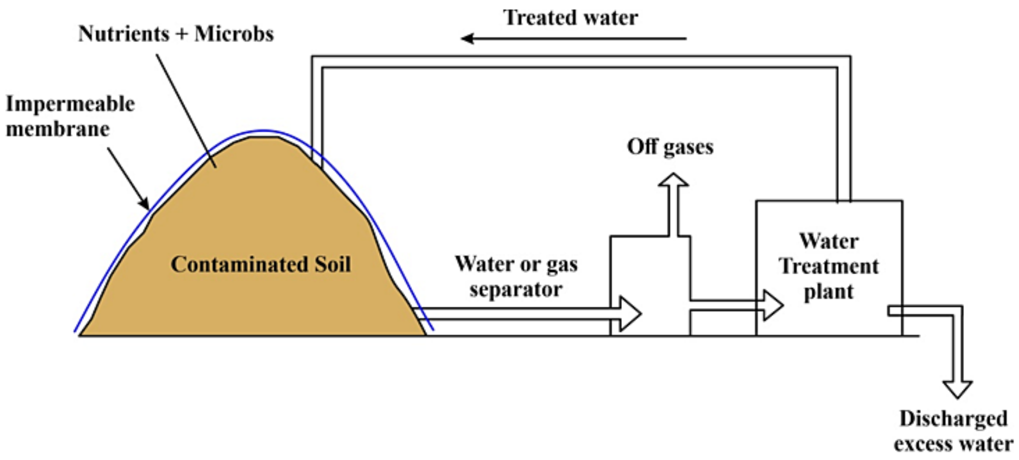

Fig. 5: Biopileprocess for treatment of polluted soil.[16]

Biopiles were used in a study to remove TPH from contaminated soil. After 66 days of incubation, 85% of TPH wasremoved from the contaminated soil.[87]

Composting

Another ex-situ solid-phase biological remediation technology is composting. The degradation of organic materials by increased biological activity requires a temperature range of 55 to 65°C for this technique. The blending of polluted earth with natural substances like plant waste and timber chips is undertaken to enhance its texture and oxygenation. To achieve a more effective composting process, one can manipulate environmental elements such as soil acidity, dampness, warmth, nourishment, and carbon-to-nitrogen ratio.[11]

The composting technique is primarily determined by the bioavailability and bioaccessibility of pollutants to soil microbes, as well as the pesticide composition in the soil.[10] The composting study was performed in a rotary drum composter for the removal of aldrin, endosulfan α, endosulfanβ,and lindane. In optimal temperature, pH,and moisture the degradation efficiency was 85.67% for aldrin, 84.95% for endosulfan α, 83.20% for endosulfan β, and 81.36% for lindane respectively within 7-8 hours.[88]

Bioslurry

Slurry bioreactors is an ex-situ technique where under controlled environmental conditions recalcitrant pollutants in soil are treated.[16] To improve contact between soil microorganisms and pollutants, water is mixed with contaminated soil to form a slurry. The slurry is then placed in the bioreactor to control environmental variables. Inoculation can be done regularly to improve degradationbecause all environmental variables in the slurry bioreactor are controlled and optimized, and the degradation rate is much speedier than in other biological technologies. The processed material is appropriate for immediate land application, much like soils that have undergone composting. The maximum time for complete contamination removal using this method is twelve months.[11] Bio slurry remediation studies for PAH-contaminated soil were conducted. The remediation process could yield a positive outcome due to specific operational conditions, including maintaining a temperature range of 20°C-25°C, doubling the amount of water in relation to the soil, and applying an aeration flux of 60 L/h. After 34 days, Pyrene exhibited a degradation of 90%, whereas benz[a]anthracene experienced a degradation of 33.3%.[89]

Control over critical environmental parameters, as well as their optimization and monitoring for the bioremediation process, are advantages of this technique over other technologies. One of the main drawbacks of this method is the high cost of installing and managing bioreactors.[10]

Phytoremediation

Phytoremediation is another innovative technology that is economically and ecologically advantageous.[4] The primary goal of phytoremediation is to detoxify or extract pollutants from the soil through the use of plants. Through the implementation of three plant-based mechanisms, we can address the issue of environmental pollutants. Firstly, phytoextraction is the absorption and buildup of harmful compounds in the leaves and stems of plants. Secondly, phytodegradation is the enzymatic transformation of these contaminants. Finally, rhizoremediation involves the release of organic acids, sugars, amino acids, and microbial growth factors in the plant root zone to promote the growth of beneficial soil microbes[85] (Table 3).

Table 3: Plants associated with phytoremediation of pesticides.

Pesticide	Plant species	Remediation
Dimethoate and malathion	*Amaranthus caudate, Lactuca sativa, Nasturtium officinale, Phaseolus vulgaris*	Four plant species were used to detoxify the dimethoate and malathion-contaminated soil in the Kingdom of Saudi Arabia. For 50% removal of malathion & dimethoate, *Nasturtium officinale* takes 25 days, *Lactuca sativa* takes 23 and 30 days, *Amaranthus caudate* takes 24 and 28 days, and *Phaseolus vulgaris* takes 25 and 30 days respectively.[90]
Malathion, demeton-S-methyl	*Myriophyllum aquaticum, Spirodelaoligorrhiza L.*, *Elodea canadensis,*	*Elodea canadensis Spirodelaoligorrhiza* L., and *Myriophyllum aquaticum* transform demeton-smethyl and malathion in a similar manner, and after eight days of incubation, the transformation ranges from 83-95 and 29-48% for all three plants.[91]
Cypermethrin	*Pennisetum pedicellatum*	Rhizoremediation of cypermethrin was done by *Pennisetum pedicellatum*. 65-100% removed from the soil in 60 days. Aerobic, gram-negative bacteria *Stenotrophomonas maltophilia* is the main degradative agent.[10]
Ethion	*Eichhornia crassipes*	Phytodegradation and plant absorption may be the main mechanisms for ethion elimination by the plant, according to research on the ability of water hyacinth to do so. Ethion accumulated in shoots and roots was reduced by 55-91% and 74-81% respectively.[92]

Phytoremediation has many advantages, including a lower cost than other remediation technologies currently available. It also improves soil properties, reduces soil erosion, increases soil microbial diversity, and so on. Aside from these benefits, this technology has some drawbacks, including climatic conditions, plant tolerance to contaminants, a longer remediation duration for the restoration of contaminated land, and the concentration and bioavailability of the pollutants. This technique is only appropriate for sites with low contaminant concentrations that are dispersed over a large area.[10]

Discussion

Regarding immobilization, there are techniques such as pumping, draining, capping, clay slurry wall, solidification, and vitrification that prevent the movement of contaminants. Regarding organics and pesticides, solidification has poor efficacy and in the case of vitrification soil depth, long-term monitoring, and non-movable organics are the main limiting factor. However, an additional technique is necessary for the complete removal of the pollutants. Separation technology involves washing and soil flushing to remove contaminants, but this method requires an additional technique to remediate the contaminants completely, which is more expensive and can pose risks to the environment due to the use of synthetic surfactants. The problem with solvent extract is the production of toxic contaminants that needs further advanced treatment. Cyclodextrin can be more effective than other separation techniques because requires less time to mitigate bulk material at a low price. Oxidation processes involve the use of iron ions, light, ultrasonic waves, semiconducting metal oxides, plasma, ozone, ultraviolet radiation, and persulfate to oxidize organic pollutants in the soil. This method works well for totally mineralizing pollutants.The oxidation rate is also affected by the presence of dissolved oxygen, dissolved solids,competitive substrates, and so on.Although chemical treatments are capable of effectively treating contaminants present in high concentrations and have faster results, they can be more costly and harmful to the soil due to the use of intense heat, potent acids, and alkaline substances.

In the electro-kinetic process, a low voltage current is used to move heavy metals and organic-inorganic pollutants towards the electrode. Thermal incineration is an efficient technique for converting pollutants into CO_2 and water, but it produces carcinogens and respiratory inorganics and causes acidification, eutrophication, and global warming. It is also an ex-situ process, making it more expensive.Thermal desorption involves high temperatures and soil excavation and the efficiency of desorption can be more than 99%, which produces harmful gases. Pollution transfer from one medium (soil) to another is one of the main drawbacks of thermal treatments (gas). If the gases generated from thermal desorption are taken care of, then this is a fairly environmentally friendly technology. Adsorption with activated carbon and surfactants is useful for removing pesticides, but it has limitations in field applications. Sono-lysis requires high frequency, pressure, and temperature, making it an ex-situ process that depends on soil type and pesticide properties. The use of iron-based nanoparticles can effectively reduce pesticides from soil and can be enhanced by photocatalysis. Physical treatment necessitates some equipment installation as well as ex-situ treatments by excavating the contaminated soil to the treatment site. As a result, physical treatments are impractical and cost more than other available technologies

Remediation with micro-organisms is a natural process in which soil microbes break down pollutants into less harmful substances. The rate of degradation can be improved by injecting nutrients and oxygen into the soil to increase microbial growth and activity. Bio-air sparging or soil vapor extraction is an environment-friendly technique that can treat a large amount of soil at a low cost. Effectiveness in reducing volatile organic compounds and low time constrain it became more suitable for in-situ bioremediation technique. Landfarming has some limitations requiring a large amount of land and the contaminants can be transferred to an undisturbed site or atmosphere. Biopiles can be effective for soil with a low concentration of contaminants, the high heavy metal concentration may limit the growth of microbes. Composting and slurry bioreactorsrequire excavation of the contaminated soil to the treatment siteand also require organic additives and can be expensive. Phytoremediation involves using plants to extract or remove contaminants from the soil, which becomes more efficient when combined with soil microbes, especially in rhizoremediation. The main reason for selecting phytoremediation as a bioremediation technique is the minimal environmental disturbance, used on a large range of contaminants, minimal secondary byproducts, and its cost-effectiveness. When addressing organic pollutants, it is essential to prioritize the utilization of plants that facilitate phytodegradation instead of phytoextraction and accumulation. This distinction holds particular significance due to concerns regarding the potential transfer of pollution during crop disposal, as well as the risks associated with pollutant accumulation in the food chain. While biological technologies offer notable advantages, such as their ability to break down pollutants, they do have a few drawbacks. These include longer processing times and the potential for certain pesticides to break down into more harmful by-products during the bioremediation process. Moreover, the use of enriched microbes in contaminated soil can present challenges due to environmental fluctuations in factors such as pH, temperature, nutrient levels, moisture content, and competition from other microbes.

Conclusion

The scientific community is actively addressing the environmental concern posed by pesticides in soils, reflecting their significant attention to this matter. This article offers a comprehensive survey of diverse technologies used to remediate pesticide-contaminated soils. It covers the underlying principles, advantages, disadvantages, advancements, and limitations associated with these technologies. Additionally, the article presents research perspectives for each technology and examines their applicability restrictions.

Chemical treatments for pesticide-contaminated soils are quicker when compared to biological treatments. However,a drawback is that the residues generated from the separation techniques used in chemical treatments require extra treatment or disposal, leading to an escalation in project expenses. Probably the most efficient separationtechnique is the use of cyclodextrins as a pretreatment of the contaminated soil. Chemical treatments can be detrimental to soil microbes and other soil properties, thus limiting the potential future use of these soils. Physical methods are applied to specific areas where contamination of soil with banned pesticides or concentration is high. Adsorption with activated charcoal or thermal desorption is the best technique to mitigate this type of soil contamination problem. A widely used technique in biological remediation is the utilization of fungi and bacteria strains that possess the ability to break down pesticides. Despite its cost-effectiveness and efficiency, the success of this process relies on various factors, including soil nutrient availability, moisture content, oxygen, temperature, and pHlevel.Despite their limitations, composting and landfarming are the most feasible biological methods due to their low implementation costs and immediate readiness for use. Bio-air sparging and phytoremediation can be more applicable for an environment-friendly approach to the remediation of contaminants.

It is crucial to note that there is a dearth of research on the remediation of agricultural soils contaminated by pesticides on a field scale. Thus, further evaluation of the proposed remediation methods' effectiveness and associated costs in real-world field scenarios is necessary.To conclude, it is crucial to consider all the factors involved, such as pH, matrix type, temperature, the quantity of water and soil, investment cost, pesticide solubility, and more, when selecting the most appropriate method and material for pesticide removal. Hopefully, the literature review and discussion section can aid analysts in conducting an initial screening of the best technique based on their requirements.

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Conflict of 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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