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# **Phytoremediation Mechanism for Emerging Pollutants : A Review**

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**ABSTRACT:** As a result of urbanization and industrialization, emerging pollutants have become a global concern due to contamination and their potential adverse effects on the ecosystem and human health. However, the characteristics and environmental fate of emerging pollutants remain unclear due to the limitations of current technologies. Emerging pollutants are predominantly released into the environment through anthropogenic activities and accumulate in water, soil, air, and dust. Despite their typically low concentrations in the environment, exposure to these pollutants can result in endocrine disruption and other health impacts on the human body, as well as oxidative stress in organisms. Phytoremediation is a green biotechnology that utilizes plants in association with microorganisms to mitigate pollutants in contaminated areas through various mechanisms. It represents a cost-effective and environmentally friendly approach, although its efficacy can be hindered by both the biological condition of plants and ecological factors. Moreover, phytoremediation generally requires a longer remediation timeframe compared to alternative technologies. The remediation of emerging pollutants aligns with the "green liver model" theory, which encompasses translocation, internal transformation and conjugation, and sequestration as classification categories. Presently, several challenges are being encountered in this field, including a lack of information regarding emerging pollutants and their metabolism in plants, the absence of a modeling framework and standardized monitoring practices, limitations in sampling and analysis technologies, as well as phytoremediation technologies. Therefore, further research is warranted to delve into the behavior of emerging pollutants and their interactions with plants, aiming to develop or enhance existing technologies. Additionally, the concept of phytomanagement should be considered, as it offers a sustainable approach to environmental remediation.

**KEYWORDS:** Emerging pollutants; environmental fate; phytoremediation; green liver model.

#### **1. Introduction**

emerging pollutants (EPs) encompass natural or synthetic compounds or microorganisms that are presently not subject to regulation under environmental laws and are not routinely monitored in the environment. Nevertheless, they have the potential to pose risks to the environment and human health [1–4]. Technical limitations may result in EPs being either newly identified substances or compounds that have existed in the environment for an extended period without recognition. These pollutants can be found throughout the environment, including soil, surface water, groundwater, and the atmosphere, occurring at extremely low concentrations ranging from picograms per liter (pg/l) to nanograms per liter (ng/l). A prominent feature of EPs is their continuous release into the environment as an outcome of ongoing manufacturing and consumption activities. Given their novelty to humans, their environmental fate and the adverse effects they may have on the ecosystem and human health remain largely unknown. The European aquatic environment has identified a minimum of 700 EPs and their metabolites. EPs can be classified based on their origin, nature, use, potential effects, and environmental fate. Common groups of EPs include pharmaceutical and personal care products (PPCPs), surfactants, industrial chemicals, pesticides, nanomaterials, and biological toxins. They can enter the environment through various point and diffuse sources, persist over time, and contaminate soil, water, and the atmosphere. Eventually, they can enter the food chain through bioaccumulation, thereby posing a threat to human health [5].

In order to address the issue of EPs, various remediation technologies have been implemented to mitigate the presence of these pollutants in contaminated areas. These technologies include advanced oxidation processes, adsorption, microbial degradation, and enzymatic catalysts. Table 1 provides an overview of the current remediation technologies available for EPs. While each of these technologies is effective and offers unique advantages, their overall cost is high, thereby limiting their application on a large scale. Phytoremediation, on the other hand, is a green biotechnology that utilizes plants to eliminate pollutants. This approach is cost-effective, as it harnesses solar-driven energy, and it is environmentally friendly compared to physical or chemical remediation technologies that can cause damage to the environment. Since plants are ubiquitous and they absorb both organic and inorganic substances from the environment, they possess the ability to trace pollutants and can be used to degrade or remove them through various mechanisms. Plants have demonstrated remarkable success in removing heavy metals, dyes, and polychlorinated biphenyls. Moreover, the efficiency of phytoremediation can be enhanced through the involvement of microbial communities [6]. Genetic engineering also plays a role in overcoming the limitations of phytoremediation, particularly in the context of hyperaccumulating plants [7].

This article provides a comprehensive overview of EPs, including their occurrence, sources, environmental fate, and their adverse impacts on the environment and human health. Furthermore, it covers the mechanisms of phytoremediation, its advantages and disadvantages, as well as its efficacy in addressing EPs. A case study focusing on flame retardants in a landfill in Brazil is also examined. Lastly, future challenges and prospects are discussed to further enhance phytoremediation technology in effectively tackling EPs.

<b>Remediation</b>	<b>Mechanism</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>Reference</b>
<b>Technologies</b>				
Microbial Bioremediation	The use of microorganism to convert toxic chemicals/substances into low-level toxic substances and immobilize them.	- Easy to culture - High microbial population - Fast mutation - Cost-effective - Eco-friendly - No harmful by-product	Limited to environmental condition	[8]
Electrokinetic Remediation	Application of low potential on the electrode to induce the migration of pollutants to the electrode through the main transport processes of electromigration, electroosmosis and electrophoresis.	- In situ implementation - Minimal soil disruption - Well suited for fine- grained, heterogeneous media - The post-treatment volume of waste material is minimized - Cost-effective	- Acidification and alkalization of the soil - High energy consumption - Low mass transfer efficiency - Limitation in remediate organic compound with low solubility - unable to fully release organic pollutants attached to clay particles and organism	$[9-10]$
Advanced Oxidation	The production of free radicals that oxidize and decrease the toxicity of contaminants.	- Effective in treating recalcitrant organic pollutant - Transformation of organic compounds to simpler stable inorganic compounds - Little/no sludge production	- High energy requirement - Intensive chemical requirement - Produce intermediate pollutants due to incomplete mineralization - High cost - $H_2O_2$ used may be harmful to humans.	$[11-12]$
Membrane Filtration	Passage of wastewater through a thin membrane for the purpose of removing pollutants not removed by previous treatment processes.	- Simple to operate - Eco-friendly - Effective in removing microcontaminants - Limited space requirement - Low-rate sludge production	- Generation of huge volumes of concentrates - High energy consumption associated with high operation pressures - Replacement of membrane is required	[13]
Adsorption	The use of solid materials to remove some substances from liquid or gas through attachment.	- High effluent quality - Simple to operate - Cost-effective - Wide range of adsorbent can be used - Low energy demand	- Regeneration of spent adsorbent - Long treatment time	$[11]$

**Table 1.** Current remediation technologies for EPs

# **2. Overview of Emerging Pollutants**

Figure 1 shows the main routes and sources of EPs. There are some common EPs listed below and a brief discussion of their sources and environmental fate are provided. Table 2 displays the examples for each EPs.



**Figure 1.** Main route and source of EPs.

### *2.1. Pharmaceutical and personal care products (PPCPs)*.

According to the United States Environmental Protection Agency (USEPA), PPCPs are defined as health and cosmetic products used by individuals or products used to enhance the health of livestock in agribusiness. They represent a type of EPs, many of which have complex and combined chemical structures. In addition to manufacturing sites and hospitals, PPCPs can enter the environment through various pathways as they are products used in everyday human activities. For instance, the improper disposal of unused pharmaceuticals into toilets or drains. Research has revealed that urine is the primary source of PPCPs excretion in humans, contributing up to 90% of the input for the contamination of prescription and non-prescription drugs. The parent compounds of these residues, resulting from the incomplete metabolism of medications, are excreted through urine and feces into sewage treatment plants and subsequently enter the environment without proper degradation due to technical limitations and their persistent organic pollutant characteristics. Furthermore, PPCPs can also be introduced into the environment through manure leaching from farmland and the direct discharge of veterinary pharmaceuticals into the ecosystem [14‒15]. Although the concentration of PPCPs found in the environment is relatively low, ranging from nanograms per liter (ng/l) to micrograms per liter (μg/l), they can have more detrimental impacts on non-target organisms than on humans. Synthetic estrogens, for example, are toxic even at low concentrations [16]. Due to the unique characteristics such as polarity, optical activity, and semi-volatility possessed by PPCPs, they are considered pseudo-persistent, with constant inputs from sewage treatment plants, leading to a steady-state concentration in the aquatic environment [15, 17]. Through irrigation with treated effluents or reclaimed water, PPCP compounds can be introduced into agricultural soil, gradually accumulating and contaminating the soil and groundwater [18]. Moreover, research has also detected PPCPs (e.g., licit and illicit drugs, benzothiazoles, benzotriazoles, etc.) in the atmosphere. It has been demonstrated that PPCPs can be transported to remote surface waters through dry deposition and the removal of particles by snow and rain [19].

### *2.2. Surfactants.*

Surfactants, also referred to as surface-active agents, possess the capability to reduce the surface tension of water and other liquids. They are a key ingredient in household cleaning products, PPCPs, textiles, paints, polymers, and pesticides. In industrial applications, surfactants serve as lubricants, hydraulic fracturing fluids, and agents for cleaning oil spills [16,20]. Based on their ionic behavior, surfactants can be categorized into four groups: anionic (e.g., linear alkylbenzene sulfonic acid (LAS)), cationic (e.g., quaternary ammonium compounds (QACs)), nonionic (e.g., alkylphenol polyethoxylates (APEOs)), and amphoteric (e.g., amine oxides (AOs)) [21]. LAS and APEOs have been globally banned due to their highly toxic degradation products in the aquatic environment and their estrogenic properties. Surfactants can enter the aquatic environment through urban runoff and wastewater streams [16,20]. The United States Environmental Protection Agency (USEPA) highlights per- and polyfluoroalkyl surfactants (PFASs) as emerging surfactants that have raised global concerns due to their persistence and resistance to environmental degradation. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are two examples of PFASs that have been extensively used for their unique oil and water repellent properties. These substances are released into the environment during primary and secondary manufacturing processes. Other sources of PFOS and PFOA include wastewater treatment plants, landfills, and sewage sludge [22].

### *2.3. Plasticizers.*

Plasticizers are organic compounds with a low molecular weight that are extensively used in the production of plastics. Their addition to materials enhances elasticity and plasticity, thereby improving the efficiency of the manufacturing and formulation processes. In addition to their use in plastic production, plasticizers are also utilized in the automobile industry, medical products, and various consumer goods. According to the United States Environmental Protection Agency (USEPA), a significant number of plasticizers fall under the category of priority organic pollutants. These substances exhibit endocrine-disrupting effects, which can have negative impacts on the hormone systems of animals and humans. Their lipophilic nature facilitates easy penetration through natural barriers, such as human tissues, due to their high mobility. Despite their low molecular weight, their dispersion in the environment can be influenced by factors such as temperature, plasticizer concentration, solubility, and diffusion coefficient [21]. Bisphenol A (BPA), the most commonly used plasticizer, along with its derivative Bisphenol A diglycidyl ether (BADGE) and Phthalates, are examples of emerging pollutants that are widely present in products used in our daily lives. These pollutants enter the environment through leaching from plastic containers, aging plastics, and the burning of plastic materials. The emission of BPA into the air is estimated to be 16,584 kg per year [23]. These substances act as endocrine disruptors and exhibit toxic and carcinogenic effects on both humans and animals [16]. Phthalates, in particular, have alternative routes of environmental release since they are not physically bound to the polymer matrix. Losses during the manufacturing process, weathering, and evaporation are some examples. Di(2-ethylhexyl) phthalate (DEHP) is a primary phthalate ester pollutant that has been identified as a priority hazardous substance by the European Commission. In Germany, DEHP has been found to be the main compound present in airborne PM\_10 particles in urban and industrial areas [19].

#### *2.4. Microplastics.*

Microplastics are emerging pollutants that form as a result of the weathering and degradation of plastic materials into small fragments and fibers, typically smaller than 5mm in size. They can be classified into two main groups: primary microplastics and secondary microplastics. Primary microplastics are intentionally manufactured for specific purposes, such as personal care products and cleaning agents, while secondary microplastics are generated through the physical, chemical, and biological breakdown of larger plastic waste under certain conditions. Microplastics can enter the environment through various sources. Anthropogenic sources include wastewater irrigation, agricultural plastic film, landfill leachate, wastewater treatment plants, shipping activities, and incineration. Natural sources include atmospheric deposition and flooding [24]. Once introduced into the environment, microplastics tend to accumulate in various environmental media, particularly in soils, as their mobility within soil is very limited, leading to an increase in their concentration over time [25]. Microplastics have now been detected in virtually every location, including the Arctic, with concentrations ranging from 38 to 234 particles per cubic meter of frozen ice. This widespread distribution is due to the ability of microplastics to be transported through the atmosphere via wind, reaching remote and sparsely inhabited areas. Furthermore, microplastics, which possess a hydrophobic surface, have the capacity to absorb or concentrate other hazardous environmental pollutants, such as heavy metals and organic compounds, present in the environment. As a result, they can act as carriers, facilitating the transfer of these pollutants into organisms and contributing to their accumulation [26].

#### *2.5. Flame Retardants.*

Flame retardants are additives used in products such as vehicles, electronic devices, and furniture to enhance their fire resistance and comply with fire safety regulations. Among them, brominated flame retardants (BFRs), particularly polybrominated diphenyl ethers (PBDEs), are classified as emerging pollutants (EPs) and persistent organic pollutants (POPs). However, due to their high stability and toxicity in the environment, they have now been restricted, raising health concerns. PBDEs, characterized by their lipophilic nature, have the ability to bioaccumulate in fatty tissues, leading to adverse health effects in both animals and humans [16]. Furthermore, PBDEs exhibit longer half-lives in soil compared to other environmental matrices. Consequently, novel brominated flame retardants (NBFRs) have been developed as alternatives to replace BFRs, with decabromodiphenylethane (DBDPE) being the most commonly used among NBFRs. Unfortunately, research has indicated that NBFRs can pose similar impacts to the banned BFRs, as they share similar physicochemical structures. NBFRs display persistence, long-range transport through the atmosphere, toxicity, and bioaccumulation. Industrial sites such as NBFR production sites, electronic waste recycling and disposal sites, and wastewater treatment plants are the main sources of NBFRs in aquatic systems. Through dry and wet deposition, NBFRs can enter soil, causing detrimental effects on agricultural soil and terrestrial ecosystems [27-28]. Since PBDEs and NBFRs are not chemically bound to materials, they can be easily released from products through processes such as volatilization, air partitioning, abrasion, leaching, and direct contact with dust [29].

### *2.6. Pesticides.*

According to the United States Environmental Protection Agency (USEPA), pesticides are defined as substances or mixtures that are capable of preventing, destroying, repelling, or mitigating pests. These pests can be targeted species, leading to the classification of pesticides into four categories: insecticides, herbicides, fungicides, and rodenticides. Pesticides can also be classified based on similarities in their chemical structure. Organochlorine pesticides (OCPs) are classified as persistent organic pollutants (POPs) due to their toxicity, stability, low polarity and aqueous solubility, high lipid solubility, and ability to bioaccumulate. OCPs are extensively used in agriculture and are a major contributor to soil contamination. They are released into the environment directly during agricultural activities and can be transported by wind and rain to surrounding areas. OCPs can reach groundwater through surface runoff or leachate from landfills. Additionally, they are used for aquatic plant control, leading to significant pollution of surface water. OCPs have been detected worldwide, including in remote regions such as Antarctica and the Arctic, indicating their capability for long-distance migration [21,30]. While most developed countries have banned the use of OCPs, illegal usage still occurs in developing countries. Specifically, dichlorodiphenyltrichloroethane (DDT), which is hazardous, persistent, and has a long half-life of up to 15 years, continues to be widely used in developing countries despite restrictions on its agricultural use [31].



**Table 2.** Examples of each EPs.



#### **3. Major Challenges**

Up to now, the information regarding EPs still remains largely unknown and there might have new EPs that have not been recognized yet. The usage or disposal of the existing chemical can become the new origin of EPs. The huge amounts of EPs and their transformation over time due to the alteration in production makes it difficult to detect, identify and quantify EPs and their transformation products. The current technologies can only be applicable for certain classes of EPs but not the full range of EPs that possess concern. Besides, the detection limits of current techniques are not inadequate as some of the EPs can only be detected in extremely low concentrations. Most of the sampling and analysis methods for recent concern EPs such as nanomaterials, microplastics, and ionic liquids are still at the infant stage or even not exist. In addition, a harmonized EPs monitoring is not fully implemented yet in most of the countries in the world. Similarly, the development of modelling framework of transport and environmental fate for EPs are still poor except for pesticides [3].

In the case of phytoremediation, the technologies still facing several limitations that might affect the efficiency of the process. The metabolism of the EPs and their possible interference with primary and secondary plant metabolism is still mysterious. The challenge of dealing with high and heterogeneity concentration over a large scale of the contaminated area and variable climate conditions still haven't been solved. Although research points out that phytoremediation can clean up the co-contaminants, it is still at laboratory scale instead of applying in real fieldwork and thus further studies need to be developed to gain more

knowledge on possible adverse or synergistic influences of co-contaminants on their mutual accumulation and detoxification [40].

A case study was conducted in a landfill from Araraquara City, in the Sao Paulo state in Brazil in 2015 [29]. The aim of this case study is to find out the most abundant FRs and their partition and fate in the landfill through collecting and analyzing soil, dust, leachate and well water samples. The landfill site has shut down after it reached its maximum capacity in 2009 and it is now turned to operate as a solid waste reception point of the city and the store of electronic waste as well as bulky waste. The company responsible for the electronic waste collect the waste periodically and sent to the final destination. Unlike electronic waste, bulky waste is disposed directly on the soil in the open air as there is no company responsible for the collection. There is also a recycling cooperative in the landfill area [29]. The samples were collected at different points of the landfill, including electronic waste and bulk waste storage area, leachate pond, offices, recycling cooperative, concierge room and wells. According to the investigation, fifteen FRs were quantified in the soil samples and the results showed that there was a huge difference for the concentration of several compounds at different sampling sites, indicating that FRs levels were influenced by different FRs sources in each sample place. The compounds are tris(2-chloroisopropyl) phosphate (TCIPP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-ethylhexyl) phosphate (TEHP), tris(phenyl) phosphate (TPHP), decabromodiphenyl ether (BDE-209) and DBDPE. Organophosphorus flame retardants (OPFRs), particularly TPHP, TBOEP, TCIPP and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) which contribute the most, were discovered in all the soil samples and have a concentration ranging from 0.39 to 192 ng/g. BDE-209 was the most plentiful congener among PBDEs with the detected concentration of 2500 ng/g. In the case of NBFRs, both 1,2-bis(2,4,6 tribromophenoxy) ethane (BTBPE) and DBDPE were found in the soil sample, having a concentration of 27.8 and 116 ng/g respectively. The highest concentration of FRs was contributed by the electronic waste and flexible polyurethane foam products disposed on the soil in the open air. This can be proved by high levels of BDE-209, DBDPE, BTBPE, TPHP and TCIPP detected in the sample, which is in accordance with the usage of these substances in the electronic components and polyurethane foam [29].

The FR concentration and distribution in the dust were impacted by various FR sources at different sampling sites. PBDEs and NBFRs were mostly detected at the store of electronic waste and recycle cooperative while OPFRs were mainly being discovered indoors such as offices and concierge rooms. At the electronic waste storeroom, the top three BFRs' compounds that had contributed to the highest concentration were BDE-209 (28800 ng/g), BTBPE (6840 ng/g) and DBDPE (5910 ng/g). These three compounds were all used in the production of electronic equipment. Besides, PBDE congeners also presented in a concentration ranging from 9.30 to 1280 ng/g in the same storeroom. The second-highest concentration of BFRs was detected at the recycling cooperative. Both DBDPE and BDE-209 were in the same magnitude order with the concentration of 4990 ng/g and 4140 ng/g respectively. It was deduced that DBDPE usage was increasing in manufactured products in Brazil as most of the plastic materials found in the recycling cooperative were comparatively new. Within the indoor areas, the presence of TBOEP was due to PVC floor covering and floor polisher formulations containing TBOEP. The other OPFRs found in the indoor areas were TPHP (2173 ng/g), TCIPP (2126 ng/g) and 2-Ethylhexyl diphenyl phosphate (EHDPHP) (up to 1758 ng/g). The concentration of OPFRs in indoor areas was higher than in outdoor areas because of the usage of products containing OPFRs and the lower dilution effect by outdoor particles [29].

For well water and leachate, only OPFRs were investigated due to the characteristic of high solubility and low biodegradability. In the case of well water, TCIPP, TDCIPP and tris(2chloroethyl) phosphate (TCEP) were observed in the downstream of bulky waste area, each had the concentration of  $159 \pm 3$  ng/L,  $13.46 \pm 0.04$  ng/L and  $7.96 \pm 0.40$  ng/L respectively. The presence of the three compounds was due to the polyurethane foam products which also had influences on soil samples mentioned earlier. At the same location, the ratio of TCIPP concentration with TDCIPP was a lot larger than the one observed in the soil sample, and TCEP was detected in the well sample but absent in the soil sample. This phenomenon can be explained as TDCIPP has a higher affinity for the organic matter in soil compared to TCIPP and TCEP. The absence of TCEP in the soil downstream of the bulky waste area may be due to the low usage of polyurethane foam and low affinity to the soil, leading to high lixiviation. To summarize, improper disposal of polyurethane foam and other products which add in chlorinated OPFRs may result in groundwater contamination. Regarding leachate, it was observed that TCIPP had the highest concentration in the sample because of its high usage and low biodegradability. In contrast, there was no detection of aryl phosphates as their behaviour of faster biodegradation and lower solubility. Although the landfill site had ended its operation in 2009, TCIPP, TBOEP, TDCIPP, TCEP, tris(butyl) phosphate (TNBP) and tris(isobutyl) phosphate (TIBP) were still found in leachate, meaning that the release of OPFRs has not stopped yet. In conclusion, this study illustrates that FRs in landfill may be the possible source that causes soil and groundwater contamination if not handled properly [29].

### **4. Negative Impact of Flame Retardants**

Excessive usage of FRs can contaminate the environment through various media, such as water, dust, air and soil. Most of the FRs are grouped as POPs due to their lipophilicity and stable structure, making them persist in the environment and in the wildlife globally. Nowadays, these FRs are also being observed in the biological samples, including human serum, breast milk, plasma and urine, indicating that they have the potential in bioaccumulation and biomagnification through entering the food chain and endanger human health. It is proved that FRs have the endocrine disrupting effect, meaning that they can disturb natural hormones in the body that function as the balancing of homeostasis, reproduction, development or behaviour [41].

Taking OPFRs as an example, the main routes of OPFRs to the aquatic and terrestrial system are through wastewater discharge, surface runoff and rainfall. Aquatic animals can uptake OPFRs through gill absorption. Another entrance of OPFRs is through ingestion and it is found that TCEP and tris (1-chloro-2-propyl) phosphate (TCPP) could spread among the animals as a consequence of the relationship between predators and preys. Also, inhalation is the most important adsorption pathway of OPFRs for the organism in the environment, especially in indoor environments. Exposure to OPFRs regardless chronic or acute may result in adverse development, neurotoxic, carcinogenic and oxidative stress. Besides, OPFRs can disrupt the sex hormone balance through alterations of steroidogenesis or estrogen metabolism. Research also discovers that several OPFRs cause inhibition of cell viability, increase reactive oxygen species (ROS) production, induce DNA lesions, and increase leakage of cellular respiration enzymes [42]. Another study evaluates the effects of Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) on human corneal epithelial cells (HCECs). TCDPP is a type of OPFRs that commonly be detected in indoor dust. According to the study, exposure to a certain concentration of TDCPP may lead to a reduction of cell viability, alteration of cell morphology and stimulation of HCEC cytotoxicity to induce cell apoptosis. Besides HCECs, a high concentration of TDCPP can change thyroid and prolactin hormone levels as well as degrade the quality of sperm [26]. Nowadays, the co-contamination of OPFRs and other pollutants in the environment is not unusual. For instance, the presence of OPFRs and cadmium (Cd) stimulates the antioxidant system of the clam, named *Corbicula fluminea*, and the oxidative stress levels are affected by the OPFRs. By increasing the concentration of OCPRs, the oxidative stress levels and lipid peroxidation of the clam increase as well. This is because the uptake of OPFRs in the digestive tract and the storage of Cd in the digestive cell lysosomes exacerbates oxidative stress and stimulate the release of contaminants [42].

Concerning the terrestrial ecosystem, the effect of BDE-209 on the antioxidant system of earthworm *Eisenia fetida* has been investigated. BDE-209 is normally being observed in soil and sediments due to its low water solubility and vapour pressure. Thus, it causes soil contamination from the excessive e-waste source. The earthworm is significant to maintain the health and fertility of the soil ecosystem. It has an effective antioxidant system to fight against the elevated amount of ROS stimulated by various environmental contaminants in order to prevent oxidative stress. However, earthworm exposes to BDE-209 fail to remove and detoxify ROS as the activity of antioxidant enzymes is changed and inhibited, resulting in severe lipid peroxidation and oxidative stress [43].

# **5. Mechanism of Phytoremediation**

Phytoremediation is defined as the process that uses plants associated with microbes for removal, stabilization, transference, and destruction of toxic pollutants from the environment [44–45]. In the process, the plants grow in the contaminated area and they uptake the contaminants to the root system along with the water and nutrients. The roots are harvested once they are saturated with the contaminants [46]. The plants used for phytoremediation are suggested to be fast-growing species with extensive roots systems and high transpiration rates [47]. Phytoremediation can be more efficient with the help of plant growth-promoting bacteria because they have the ability to emit phytohormones and biosurfactants, inhibit phytopathogens in host plants, tolerate abiotic stress and reduce toxicity to the plants via biosorption or bioaccumulation. This can be attributed to the high ratio of surface area to volume of bacteria cells, and they can emit various hormones, organic acids and antibiotics to boost plant growth [4, 48]. Depending on the types of contaminants and the contaminated matrix, there are several mechanisms involved in phytoremediation including phytostabilization, phytodegradation, phytoextraction, phytovolatilization, phytostimulation and rhizofiltration. Figure 2 illustrates the mechanism of phytoremediation while Table 3 shows the examples of plants and pollutants that can be remediate for each mechanism.

# *5.1. Phytostabilization.*

The mechanism of phytostabilization is to immobilize the contaminants from soil or groundwater via adsorption or accumulation onto roots or precipitation within the rhizosphere. It aims to reduce the mobility of the contaminants and prevent migration and reentrance into the environment [51]. The covered plants in the contaminated area also avoid soil erosion and surface runoff due to the wind and rain [47]. The root exudates normally consist of amino acids, carbohydrates, enzymes, lipids, organic acids, and phenolic compounds [52]. Plants release root exudates which can act as nutrient sources and chemo-attractant of high diversity of microbes in the rhizosphere. Besides, root exudates can also regulate pH and detoxify the contaminants in the soil [51].

Mechanism	<b>Levels</b>	<b>Plant Species</b>	<b>Pollutants</b>	Reference
Phytodegradation	Whole plant	Chromolaena odorata, Eichhornia crassipes, Scirpus grossus, Myriophyllum aquaticum, Phragmites australis, Algae, poplars, stonewort	Sodium dodecyl sulfate, malathion, ethion, petroleum hydrocarbon, trinitrotoluene, ibuprofen	[32, 47, 49]
Phytostimulation	Root	Sesbania cannabina, Medicago sativa, Sorghum x drummondii	Petroleum hydrocarbons, hydrocarbons from oily sludge, polycyclic aromatic hydrocarbons, Sulfamethazine, DDT, chlorinated solvent	$[47, 49 - 50]$
Phytovolatilization	Shoot	Typha latifolia, Brassica juncea, Populus deltoides and Populus nigra, Eucalyptus sideroxylon, Poplars, alfalfa	Heavy metals (Se, As, Hg), perchloroethylene, trichloroethylene, lower chlorinated benzenes, chlorinated ethenes, BTEX compounds	[47, 49]
Phytoextraction	Whole plant	Calendula officinalis, Centella asiatica, Eichhornia crassipes, Arabidopsis thaliana, Helianthus annuus, Brassica juncea	Polycyclic aromatic hydrocarbons, heavy metals (Cd, Cr, Cu, Pb, Ni, Cs), Triclosan, Sulfamethoxazole, DDT, pyrethroids	[32, 47, 49]
Phytostabilization	Root	Senna multijuga and peat, Festuca rubra, Osmanthus fragrans, Ligustrum vicaryi, Cinnamomum camphora, Loropetalum chinense, Euonymus japonicus, Erica australis Grasses, Brassica juncea, poplars	Heavy metals (Cu, Cd, Cr, Pb), sulphur, DDT	$[47, 49 - 50]$
Rhizofiltration	Root	Pistia stratiotes, Arundo donax, Phragmites australis, Phleum pratense, Agropyron smithii, Bouteloua gracilis, Lemna minor	Heavy metals (Fe, Cr, Pb, Cu) Uranium, 137 cesium, dimethomorph	[8, 49]

**Table 3.** Plant species and remediated pollutants for each phytoremediation mechanism.

### *5.2. Phytodegradation.*

Phytodegradation, also known as phytotransformation, degrade or break down contaminants using plants through the metabolic process. The plants absorb the contaminants through their root system perform internal and external metabolic processes, in which plant enzymatic activity and photosynthesis oxidation are involved [51]. Both the hydrolases and oxidases are used to hydrolyze the contaminants into smaller units and alter the contaminant functional

group respectively [52]. There are some enzymes being discovered in the plants such as dehalogenase, nitroreductase, peroxidase, laccase, and nitrilase to accelerate the degradation process [47]. However, phytodegradation is only applicable for a certain range of contaminants' solubility and hydrophobicity. It is shown to have effective removal of personal care products, pesticides and herbicides [52].

# *5.3. Phytoextraction.*

Phytoextraction, also called phytoaccumulation, phytosequestration, phytoadsorption or phytomining, is the process that makes use of hyperaccumulating plants to uptake and translocates the contaminants from the environment by roots and transport it to above-ground biomass like leaves and shoots [46]. Sometimes, the contaminants can also be degraded metabolically by special carrier proteins, transporters and enzymes [52]. Hyperaccumulating plants refer to the plants that have the ability to accumulate metals or contaminants at the rate of 100 times higher than that of non-hyperaccumulating plants [46]. The selected plants should be able to have heavy biomass, large storage for absorbed contaminants, high tolerance to the concentration and toxicity of the contaminants, rapid growth rate and abundant root system [47]. In the case of organic compounds, they can be sequestered and stored into the vacuoles of root cells [46].

# *5.4. Phytovolatilization.*

Phytovolatilization refers to the mechanism that removes contaminants from soil and water by converting them into volatile form and release them into the atmosphere through transpiration. During the process, the contaminants are detoxified and converted into water-soluble form before the transpiration occurs in the leaves [51-52]. The diffusion of the volatilize contaminants to the atmosphere is through the open stomata and sometimes, they can diffuse through the stems before they travel to the leaves. Unlike other plants, hyperaccumulating plants can avoid the accumulation of contaminants in the epidermis and mesophyll of the leaves as the plants have a high evaporation rate. Thus, the negative effects for the hyperaccumulating plants can be minimized [51]. This process is effective for the removal of organic contaminants [52].

## *5.5. Phytostimulation.*

Phytostimulation, also known as rhizodegradation, makes use of the mutual relationship between plants and microbes to break down the contaminants present in the rhizosphere metabolically [53]. Plant roots boost the microbial activity in the rhizosphere by enhancing aerobic transformation, loosing soil for more surface area, transporting water, increasing the bioavailability of organic carbon and being the nutrients and energy sources of microorganisms in the form of exudates. Meantime, microbes also promote the biological activities of the plant roots. This mechanism is effective in treating organic contaminants, including pesticides, aromatics and poly-aromatic hydrocarbon [46].

## *5.6. Rhizofiltration.*

Rhizofiltration or phytofiltration is the process that absorbs, concentrates and precipitates the contaminants from polluted water through the root system. It is similar to phytoextraction, but it is applicable in water rather than soil. Through the root system, the water is being filtered and consequently, the toxic contaminants are being removed. Similarly, the chosen plants should have the characteristics of high root biomass, high accumulation capacity, high adsorption surface and high tolerance to pollutants [45-46].



**Figure 2.** Phytoremediation mechanism.

#### **6. The Benefits and Drawbacks of Phytoremediation**

Phytoremediation is an emerging remediation technology that successful gain interested worldwide and is being implemented to remediate contaminants. It can be applied either insitu or ex-situ depending on the condition. It is said to be the most cost-effective treatment among other technologies with require high capital costs and labour fees. Besides, the plants absorb the sunlight as their energy source and thus there is minimal operation cost needed. In addition, phytoremediation is an eco-friendly method because it neither alters the soil properties nor damages the soil microflora at the sites. In contrast, it helps minimize the diverse impact of the environment by reducing surface runoff, protecting the area from contaminated winds and dust, restoring land and maintaining a healthy ecosystem. Also, the precious contaminant like heavy metals can be regenerated after harvesting the plants and bioenergy can be produced by burning the plant biomass. Due to the advantages owned by phytoremediation, it is popular and has a high social acceptance among the public [46].

However, phytoremediation also has disadvantages and limitations. The efficiency of phytoremediation can be limited by several factors, such as plant type, soil type and condition temperature, pH, and altitude [54]. Besides, it requires a long period for remediation as the process depends on plant catabolism capacities and root depths. Normally, it is only applicable for shallow depths less than 5 m [46]. As a consequence of autotrophic metabolism, most of the plants cannot fully mineralize the organic pollutants particularly the most recalcitrant due to the absence of biochemical machinery. Thus, the pollutants that are absorbed by plants make reintroduced to the soil or volatilize into the air again [55]. Also, the introduction of exotic plants species may affect biodiversity as it forms a competitive relationship with the indigenous species. Furthermore, it is not easy to find a suitable plant that have the properties to be a hyperaccumulation species for phytoremediation. Hence, more research is needed in order to better understand the technology and overcome the limitations before implementing it on a commercial scale [56]. In 1994, Sandermann introduced the "green liver model" theory illustrated in Figure 3 suggesting that the response of plants to the xenobiotic molecule is quite similar to the function in mammalian liver except for the excretion that only occurs in mammals [55,57]. Through the observation, it is found that the remediation of most EPs complies with the theory and the overall detoxification process can be sequenced into three phases which are translocation, internal transformation and conjugation, and sequestration. In phase 1, EPs translocate to the plant tissue through active transport that makes use of soil water and transpiration stream or through passive diffusion. For EPs that are semi-volatilized and have low molecular weight, they can be absorbed or compartmentalized from the atmosphere. Volatile organic compounds can be either partitioned into waxy cuticles and delivered to the stomata or translocated through the phloem.



Figure 3. Green Liver Model Theory.

Depend on the adsorption capacity of the plants and their enzymatic system, EPs can be further translocated or just simply adsorbed on waxy cuticles. EPs that are highly hydrophobic can be mobilized by the exudates through competing for binding sites in the soil. Meanwhile, the bacteria in the rhizosphere can further remove the toxicity of EPs maintained in the soil. In phase 2, a metabolic process which is the transformation of EPs occurs before conjugation to increase the hydrophilicity of EPs so that they can diffuse into the cytoplasm via the apoplast pathway. The transformation process includes oxidation, reduction, methylation, dehalogenation, hydroxylation and photolysis. Conjugation then takes place to detoxify EPs and give protection to fight against the oxidative stress caused by xenobiotics. During the process, enzymes such as glycosyltransferase, glutathione S-transferases, peroxidases, and hydrolases integrate the transformed metabolites with natural molecules like sugar, amino acid and malonate to increase their solubility. In phase 3, most of the metabolites and conjugates are sequestered in cell vacuole, in the apoplast, or bonded with the cell walls covalently. Only a few compounds can volatilize to the atmosphere through the stomata. The released conjugates and plants exudates can be further reabsorbed to promote the bioavailability of EPs that are retained in the environment [57].

### **7. Future Challenge and Prospect**

In order to better settle the problem of EPs in the future, huge research and studies need to be done to have a well understanding of their characteristic, behaviour and ecotoxicological effects in the environment. The deficiency of analytical and sampling methods suggesting that there is a need to develop a new mechanism for routine monitoring to better identify EPs in full scale. Besides, the monitoring practices should be standardized universalized to get a more accurate result for analyzing and interpreting the data. A parameterized model for EPs should be developed as well to access the transport and accumulation of EPs under different meteorological conditions, land use, EP release scenarios and EP forcing on a catchment scale [1]. In regards to phytoremediation, the metabolic pathway of most EPs should be approached to prevent the toxic metabolites from releasing and to enhance the efficiency of phytoremediation. Scientists should always validate the laboratory result to the field condition because the performance and efficiency of the plants in the lab are under a controlled situation whereas the real environment condition is more complex. Co-cropping or co-planting can be implemented to boost the phytoremediation efficiency, but it should be well experimented before application to avoid any antagonism [40]. Moreover, research regarding the enzymatic system of the plants in detoxifying and degrading EPs should be carried out as well in order to design more suitable engineered plants that provide higher efficiency [6]. The good news is that research demonstrates that engineering endophytic bacteria not only can be used as site monitoring tools through its gene expression, but also more effective than the bacteria added to the soil due to the bioaugmentation, and thus boost the plant growth, the tolerance to toxicity and eventually the efficiency of phytoremediation. Therefore, this concept should be addressed, and further observation is required to ensure it is not harmful to the environment [40,58]. In addition, the idea of phytomanagement has arisen recently and it is defined as the involvement of plants in minimizing and controlling the risks resulted from soil pollution and at the same time make use of this resource profitably and sustainably through producing salable biomass. Under this idea, the contaminated soil is a valuable resource for the production of bioenergy and thus it is a sustainable and economical approach [59, 60].

### **8. Conclusion**

EPs are a global concern, but their environmental fate and impact are still unknown. EPs include PPCPs, surfactants, industrial chemicals, pesticides, and microplastic. Industry, daily use, wastewater treatment, and agriculture cause most EPs. Anthropogenic activities release EPs into the environment, where they pollute water, soil, dust, and air and destroy ecosystems. After inhalation or ingestion through food and water, EPs can harm human health even at low concentrations of pg/L to ng/L. EPs are carcinogenic, mutagenic, and endocrine disruptors. Oxidative stress can also kill organisms. EPs can co-contaminate with other environmental pollutants, complicating the situation. EPs can pollute the environment if not properly disposed of, as shown by the Brazil landfill flame retardant case study. Therefore, phytoremediation is implemented to clean up the contaminated area by degrading or removing the toxic pollutants using plants assisted with microorganisms. It has six different mechanisms involved in the process which are phytostabilization, phytodegradation, phytovolatilization, phytostimulation, phytoextraction, and rhizofiltration. These mechanisms match different pollutants and plants to maximize efficiency. Phytoremediation is low-cost, solar-driven, eco-friendly, and produces biomass that can be used for bioenergy regeneration. However, time constraints and plant species and ecological conditions may affect its efficiency. Moreover, it is only applicable for the shallow region. The remediation of EPs is found to follow the "green liver model" theory which consists of three stages: translocation, internal transformation and conjugation, and sequestration. The major challenges facing today are the lack and limitation of techniques to detect EPs and the associated modelling framework is also deficient. Systematic monitoring of EPs is not achieved in most countries. Concerning phytoremediation, the metabolism of EPs in plants are still questionable. High and heterogeneous concentrations over a large contaminated area and variable climate conditions remain a challenge. Most processes have yet to be tested in the field. The interactions between EPs and plants should be investigated to improve present technology. The analytical, sampling, and modeling framework has to be expanded to include more EPs. Data can be interpreted globally when monitoring procedures are standardized across the board. Following the experiment, co-cropping or co-planting can be used to improve phytoremediation effectiveness. Endophytic bacterium engineering enhances phytoremediation and site monitoring. Phytomanagement is both ecologically and economically sustainable, and it should be expanded. Because wastewater treatment facilities are the primary source of EPs, phytoremediation in built wetlands should be used prior to discharge.

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