

SUSTAINABLE MATERIALS | VOLUME 1  
BIOREMEDIATION FOR  
ENVIRONMENTAL POLLUTANTS



Editor:  
**Inamuddin**

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# **Sustainable Materials**

*(Volume 1)*

## ***Bioremediation for Environmental Pollutants***

Edited by

**Inamuddin**

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# **Sustainable Materials**

*(Volume 1)*

*Bioremediation for Environmental Pollutants*

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## Fungal Bioremediation of Pollutants

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**Abstract:** Advancement in industrialization and urbanization has caused an influx of contaminants into the environment polluting the soil, water, and air. These contaminants come in various forms and structures, including heavy metals, petroleum hydrocarbons, industrial dyes, pharmaceutically active compounds, pesticides, and many other toxic chemicals. The presence of these pollutants in the environment poses a serious threat to living things, including humans. Various conventional methods have been developed to tackle this menace, though effective, are however not safe for the ecosystem. Interestingly, bioremediation has offered a cheap, effective, and environmentally safe method for the removal of recalcitrant pollutants from the environment. White-rot fungi (WRF), belonging to the basidiomycetes, have shown class and proven to be an excellent tool in the bioremediation of the most difficult organic pollutants in the form of lignin. White-rot fungi possess extracellular lignin modified enzymes (LMEs) made up of laccases (Lac), manganese peroxidase (MnP), lignin peroxidase (LiP), and versatile peroxidase (VP) that are not specific to a particular substrate, causes opening of aromatic rings and cleavage of bonds through oxidation and reduction among many other pathways. The physiology of WRF, non-specificity of LMEs coupled with varying intracellular enzymes such as cytochrome P450 removes pollutants through biodegradation, biosorption, bioaccumulation, biomineralization, and biotransformation, among many other mechanisms. The application of WRF on a laboratory and pilot scale has provided positive outcomes; however, there are a couple of limitations encountered when applied in the field, which can be overcome through improvement in the genome of promising strains.

**Keywords:** Basidiomycetes, Bioaccumulation, Biodegradation, Biomineralization, Bioremediation, Biosorption, Biotransformation, Fungi, Heavy metals, Industrial dyes, Laccases, Mycoremediation, Peroxidase, Pesticides, Petroleum hydrocarbons, Pharmaceutical products, Pollutants, Oxidation, Synthetic pesticides, White-rot fungi.

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## INTRODUCTION

Man's effort to provide an easy and comfortable life for himself through industrialization and urbanization has become a threat to him and the ecosystem at large [1 - 4]. Infrastructural construction, mining, transformation of raw materials, electroplating, smelting, extraction of petroleum, and farming, among many other anthropogenic activities have caused and is still causing deleterious effects on the ecosystem [5]. Most of these anthropogenic activities, release harmful substances into the environment (air, soil and water), which if not properly cleaned or disposed of effect biotic activities in the ecosystem [6]. These harmful substances include polymers, cyanide compounds [7], papers and pulp [8], heavy metals [9 - 11], pesticides, industrial dyes, pharmaceutically active compounds (PhACs) [12], petroleum hydrocarbons [13, 14], chlorendic acids [15] among many others. Some of these pollutants such as heavy metals (*i.e.* mercury, cadmium, arsenic, chromium, copper, selenium, and lead), when present in the environment in large amounts impair the metabolism of living organisms including man [11, 16]. Some of these heavy metals cause cancer, skin inflammation, nausea, dizziness, and headache [17]. Other pollutants such as pesticides have caused chronic illnesses leading to the global loss of about 1 million lives annually [18]. This event of loss of lives and resources is no exception to petroleum pollutants, which arises as a result of oil spills during drilling of oil wells, leakage of underground tanks, vandalization of storage tanks among many more occurrences. This eventually affects the diversity of biological niches, deaths of aquatic organisms, affects the productivity of plants and causes starvation in man [14].

The debilitating effects of pollutants in the environment cause a man to respond rapidly through conventional methods in a bid to alleviate the damages it causes [19, 20]. Some of these conventional methods developed include; soil flushing, land filling, burning, vitrification, electroreclamation/electrokinetics, solidification and stabilization, removal and containment among many others, though rapid but do not eradicate the pollutants, rather they change their location and state from one form to another [4, 19, 21]. The disadvantage of conventional methods is that they are not environmentally friendly, they are expensive, require more labor and expose more surfaces to pollutants. The use of conventional chemicals to treat a polluted environment also has adverse effects in the long run [2]. Some of the methods applied in the treatment of soils affect the soil structure and quality, and the efficiency of some of the methods is limited to certain depths [2, 9, 19]. As a result of all these setbacks, man has searched for a means to alleviate the environmental problems posed by pollutants, out of which biological methods have proven to be environmentally friendly, with little or no adverse effects on the environment [2, 20]. A process where biological materials are used in the cleanup of pollutants from the environment is known as bioremediation [2, 4].

### Fungal Bioremediation

Bioremediation involves the transformation or degradation of hazardous pollutants from a toxic form to a less toxic absorbable form [2]. Among the natural bioremediation processes, microbial bioremediation has stood to be the most effective in the removal of pollutants from the environment [4]. Microorganisms remove pollutants either by biodegradation, bioaccumulation, biosorption, biotransformation or biomineralization [10]. Bioremediation strategy could either be *in-situ* (i.e. treatment of pollutants in the site of contamination) or *ex-situ* (i.e. taking the pollutants away from the contamination sites for treatment) [2, 4, 20, 22]. However, the former is safe and cheap unlike the latter, which is expensive and a potential threat to the health of laborers involved and exposes the pollutants to more surfaces [2, 4]. Among the bioremediation technologies, the use of fungi, particularly those belonging to the basidiomycetes has distinguished themselves as an effective tool in the remediation of an environment polluted by recalcitrant xenobiotics, a technology known as mycoremediation [2, 23, 24]). Their metabolites and body structures coupled with the fact that they can withstand toxic compounds and still perform in an environment depleted of nutrients have made them cheap and effective for a safe and sustainable strategy in alleviating polluted environment [23, 25].

### Pollutants and Their Classification

There are different types of pollutants that are generated by various industries. These pollutants could come in the form of solid, liquid, or gases. Their nature, chemical composition and structure could vary from simple monomers to a complex polymer of aromatic rings. They include petroleum hydrocarbons, chemical compounds (i.e. industrial dyes and pesticides), and heavy metals [26].

### Petroleum Hydrocarbons

The use of petroleum based products is almost inevitable in the world we live today. Aside from being used as a form of energy to power machines, vehicles, trains, aeroplanes, generators, heating mantles, and cookers; some components of petroleum are also used in the production of various forms of plastics, chairs, rubbers, fibers for reinforcement of concretes, fittings in electric appliances, cutlery, among many other uses [13, 27]. Right from the exploration of petroleum to its conversion (refining), down to its transportation and storage, the environment one way or the other gets polluted by harmful substances present in petroleum [13, 28, 29]. Petroleum is composed of a various complex mixture of hydrocarbons [28], which is distinguished mainly into aromatic hydrocarbon, saturated hydrocarbon and non-hydrocarbon compounds [30, 31]. Aromatic hydrocarbons are complex with high melting and boiling point due to the presence of benzene ring(s), which makes them difficult to degrade away from the

environment [32]. These features are however absent in saturated hydrocarbon, which their molecular structure is made up of carbon-hydrogen bond and carbon-carbon bond. These bonds could either be straight, branched, or in circle, they lack complex molecular structures (*i.e.* benzene ring) with lower melting and boiling point. Saturated hydrocarbons are easily degraded as such do not persist in the environment [31].

Persistent organic pollutants (POPs) in the environment exist among the polycyclic aromatic hydrocarbons (PAHs), which are made up of complex benzene structures [33, 34]. The European Community (EC) and the United States Environmental Protection Agency (USEPA) have prioritized the control of 16 PAHs. These are: acenaphthene, anthracene, pyrene, fluorene, naphthalene, fluoranthene, phenanthrene, benzo(b)fluoranthene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene, benzene(ghi)perylene, indene, diphenyl(a,h)anthracene, acenaphthylene and (1,2,3-cd) pyrene [30, 34 - 36]. PAHs get into the environment through the burning of fossil fuel (*i.e.* premium motor spirit (PMS), diesel, kerosene), incineration of petroleum products (*i.e.* synthetic plastics, tyres), oil spills, untreated effluents from chemical and petroleum industries, among many others release these harmful and toxic substances into the environment affecting the vitality of living things in the ecosystem [13, 28, 31, 33, 37, 38]. Sulphur compounds such as thiols, sulphides, disulphides, naphthobenzothiophene cyclic sulphides, benzothiophene, dibenzothiophene; oxygen compounds such as alcohols, ethers, esters, carboxylic acids, furans and ketones; and nitrogen compounds such as pyridine, indoline, carbazole, benzo(a)carbazole, benzo(f)quinolone, indole, and nitriles are all part of non-hydrocarbon compounds present in petroleum as well as some metals, which most times are contained in the nonvolatile part of petroleum hydrocarbon [26, 33, 35]. When compared to the three groups of petroleum hydrocarbon, maximum carbon numbers are seen among the non-hydrocarbon compounds (*i.e.* porphyrin). In water, non-hydrocarbon compounds are insoluble with high boiling and fusion point. Thus, they persist in the environment alongside PAHs and are difficult to remove causing deleterious effects to live things such as mutagenicity [28, 30].

### Heavy Metals

Metals and metalloids that exhibit metallic features such as malleability, conductivity, ductility, ligand specificity, malleability and cation stability with a relatively high atomic weight, density and an atomic number  $\geq 20$  excluding alkaline earth lanthanides, alkaline metals, and actinides are regarded as heavy metal (HM) [11, 34, 39, 40]. Seiyaboh and Izah [41] simply define HM to be metals with a specific gravity greater than 5 cm<sup>3</sup>. Some HM (*i.e.* copper,

manganese, iron and zinc) are essential micronutrients required for metabolism in a biological system in minute quantity and become dangerous when their concentration increases above the safe level [11, 34]. The environment is constantly exposed to an influx of HM pollutants from various anthropogenic activities such as mining, metal forging, electroplating, burning of fossil fuel, smelting, sewage sludge, dyeing, agricultural activities, forest burning, biosolids, ore mining, electronic waste, batteries waste, coal combustion, wood preservatives, personal care products (PCPs) such as cosmetics, biosolids waste treatment plant, tannery and other untreated industrial effluents among geological activities such as weathering of rocks and volcanic eruptions all release varied concentration of HM to the environment (Table 1) [9, 10, 16, 39 - 43]. Biological degradation of HM is not feasible as such, they remain persistent in the environment taking one form or the other [9, 40, 42].

Table 1. Some heavy metals and their various sources [16, 17].

Heavy Metals	Sources
Zn	Mining, refining, biosolids smelting, electroplating industry.
Pb	Combustion of leaded gasoline, municipal sewage, mining and smelting of metalliferous ores, glass manufacturing, paints, and industrial waste supplemented with Pb, lead batteries, X-ray shields, ammunition.
Cd	Sewage sludge, application of phosphate fertilizers, geogenic sources, metal refining and smelting, anthropogenic activities, burning of fossil fuel, production of batteries, welding, alloy pigment.
Hg	Wood and peat burning, volcano eruptions, forest fire, emissions from industries producing caustic soda, coal, mining, electrical industries, batteries, dentistry.
Ni	Automobile batteries, forest fire, kitchen appliances, land fill, industrial effluents, surgical instruments, steel alloys, volcanic eruptions, gas exchange in ocean and bubble bursting, weathering of geological materials and soils.
As	Mining and smelting, volcanoes, petroleum refining, wood preservatives, herbicides, animal feed additives, semiconductors, coal power plants.
Cr	Metal processing, chrome plating, solid waste, tanneries, sludge, metallurgy, leather tannings, electroplating industry, anti-corrosives, dyeing, cooking systems and boilers.
Cu	Smelting and refining, biosolids, electroplating industry, mining.

Uncontrolled release of HM into the environment has gained global attention with different reports of their presence in the food we eat causing varying degrees of health disorders in humans (Table 2) [11]. HM can be accumulated by a biological systems such as plants and animals, they can be transferred from one trophic level to another since they can't be degraded [40]. Even at low concentrations, most HM (lead, selenium, mercury, silver, cadmium, arsenic

among many others) cause neurotoxic and cytotoxic effects, which could be mutagenic and carcinogenic to the biological system [10, 34, 40, 41]. Several reports of HM pollution have been made in the past. An incidence of HM poisoning was recorded in Minamata Bay, Japan in 1963 where lots of lives were lost as a result of consuming shellfish that have accumulated a high concentration of mercury in their system [11]. HM pollutants pose a serious threat to all forms of life directly or indirectly with no method so far suitable for total elimination [16].

Table 2. Some heavy metals and their toxic effects on human health [10, 17, 44].

Heavy Metal	EPA Regulatory Limit (ppm)	Toxic Effects
Ba	2.0	Elevated blood pressure, respiratory failure, cardiac arrhythmias, gastrointestinal dysfunction, and muscle twitching.
Cr	0.1	Diarrhoea, liver diseases, reproductive toxicity, renal failure, lung cancer, hair loss, chronic bronchitis, bronchopneumonia, irritation of the skin and the respiratory tract, liver diseases, nausea, headache.
Ag	0.10	Exposure may cause dermal tissues to turn grey or blue-grey, irritation of the respiratory tract and the lungs, breathing problems, stomach pain.
Cu	1.3	Kidney, liver and brain damage, metabolic disorders, headache, chronic anaemia, vomiting, abdominal pain, nausea.
Ni	0.2	Dry cough, chest pain, itching of the skin, headache, cancer of the sinuses, nose, lungs; dermatitis, kidney diseases, neurotoxic, immunotoxic, genotoxic.
Hg	2.0	Brain damage, impaired vision, insomnia, sclerosis, memory loss, autoimmune diseases, gingivitis, depression, dysphasia, ataxia, drowsiness, deafness, kidney and lungs failure.
Cd	5.0	Headache, coughing, vomiting, lymphocytosis, hypochromic anaemia, endocrine disruptor, testicular atrophy, itai itai, kidney diseases, emphysema, prostate and lung cancer.
Zn	0.5	Fatigue, impotence, dizziness, lethargy, depression, macular degeneration, icterus, hematuria, vomiting, liver and kidney failure, seizures, gastrointestinal irritation, ataxia, prostate cancer, macular degeneration.
Pb	15	Anorexia, hyperactivity, insomnia, reduced fertility, renal damage, reduced fertility, chronic nephropathy, elevated blood pressure, impaired neurons, learning deficits, shortened attention.
As	0.01	Brain damage, conjunctivitis, skin cancer, dermatitis, respiratory and cardiovascular impairment.
Se	50	Hepatotoxicity, dysfunction of natural killer cells, gastrointestinal disturbance.

Advancement in biotechnology and genetics has provided the platform for understanding the genes responsible for the secretion of various LMEs. Expanding knowledge in fields of ecology, engineering, enzymology, biochemistry, molecular biology, genetics and fungal physiology will give environmentalists the opportunity to explore other options such as up-regulation of enzymes responsible for catalytic potentials of WRF. Genes responsible for growth can also be enhanced so as to overcome the slow growth rate and still maintain its catalytic features. Modifications to the genome of promising WRF should be done to meet the physiochemical and climatic conditions, which have been a constraint to the full working capacity of WRF under field conditions. If this is achieved, environmental pollution currently observed will no longer be a problem to the ecosystem owing to the catalytic prowess of WRF.

### CONSENT FOR PUBLICATION

Not applicable.

### CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Declared none.

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