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Bioremediation of endocrine disruptors

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Abstract

Bioremediation has become a novel technique for the detoxification and clean-up of endocrine disruptors, which is now a global concern. Endocrine disruptors, which are known to be chemicals or compounds that interfere with the production, transportation, excretion, and overall activities of the endocrine system, have also emerged as a universal challenge. This is because endocrine disruptors are unavoidable, and exposure to these compounds can occur in places like homes, schools, farms, and water, food, and air. These endocrine disruptors range from naturally occurring phytoestrogens to phthalates found in plastics, polychlorinated biphenyls, dioxins, bisphenol A, bisphenol S, phenol compounds, some pesticides, fungicides, pharmaceuticals, and heavy metals. Some physical and chemical methods were previously utilized for the detoxification of endocrine disruptors, but their demerits included high environmental toxicity, high cost, and inability to completely detoxify these toxic pollutants. There is a growing attention towards the removal of endocrine disruptors from the environment through the utilization of the catalytic activity of some oxidative enzymes like oxidoreductases (lignin peroxidases, manganese peroxidases, laccases, tyrosinases). These enzymes are extracted from the microorganisms and immobilized on a carrier support, or used in their free form, or the whole microorganisms are used for the bioremediation. These approaches have gained universal acceptance because they are specific, efficient, and environmentally friendly. Immobilization technique has become a novel approach to enhance stability, enzyme activity, and also preserve the 3-dimensional structure of the enzyme in severe reaction conditions.

Keywords: Bioremediation, endocrine disruptors, endocrine system, immobilization, oxidoreductases

1. Introduction

Bioremediation involves the utilization of live organisms, notably microorganisms, plants, or their products, to degrade pollutants or toxicants and convert them into non-toxic or less toxic forms [1]. Bioremediation has become an emerging suitable technology in tackling environmental (soil and water bodies) pollution because it is more effective and environmentally friendly when compared to the use of synthetic chemicals, which adversely affect the environment. Bioremediation has also become an important tool for the mop-up of some contaminated or polluted areas by harnessing the biological activities of these plants and microorganisms to detoxify the pollutants. Bacteria, fungi, algae, and yeast are microbes that have been mostly utilized for bioremediation purposes due to their physiological abilities to detoxify, degrade, or change pollutants into less toxic ones [2].

In some cases, these microorganisms can be indigenous microorganisms present onsite or isolated somewhere else and transferred to the site or material to be treated [3]. The success rate of bioremediation is determined mostly by the chemical nature of the pollutant, its concentration, and the applied environmental factors, which impact the microorganism growth, consequently determining the extent of degradation [4].

Bioremediation systems operate under oxygenated and non-oxygenated conditions. The oxygenated condition is mostly used in the biodegradation of most pollutants, while the non-oxygenated condition is applied during the degradation of some recalcitrant compounds with specific microorganisms.

The versatile nutritional requirements of these microorganisms have also been exploited for bioremediation. This is because of their ability to change, alter, and use toxic pollutants for energy and increased biomass manufacture [5].

Furthermore, microbes participate in bioremediation through their enzymes, which facilitate the degradation of target pollutants through biochemical responses. Bioremediators are bio-agents that are utilized in bioremediation.

Advantages of bioremediation

- Bioremediation needs minimal effort and is easily done onsite, with the avoidance of the disruption of crucial normal activities.
- Bioremediation is one of the most cost-effective techniques used for mop-up of areas polluted with hazardous chemicals when compared to the conventional methods, and it has been an effective method for the treatment of oil-polluted sites [6].
- Dangerous chemicals are not utilized; rather, nutrients in the form of fertilizers, which are normally included to facilitate microbial growth, are usually degraded to water and harmless gases at the end of bioremediation [7].
- Bioremediation helps in the complete degradation of most pollutants while transforming some hazardous compounds into less harmful ones, thereby eliminating the liability often occasioned by the treatment and disposal of contaminated materials.
- It is a natural process and a welcome waste treatment technology for polluted sites that involve the soil or materials that include water. Harmless products, including water, $CO_{2,}$ and cell biomass, are usually the residues after treatment procedures.
- It is environmentally friendly and sustainable.

Disadvantages of bioremediation

- This technique is mostly hinged around biodegradable compounds. Since some pollutants cannot be biodegraded, they cannot be applied to every polluted site.
- There are uncertainties that the products of bioremediation may persist in the environment or may be more harmful compared to the parent compound.
- There is a need for more research to develop bioremediation technologies that are specific to sites with pollutants that are not evenly distributed in the environment.
- Since biochemical reactions associated with the organisms used in bioremediation are specific, specific site factors are required for it to be successful.
- Bioremediation requires a much longer treatment time than other methods like incineration, excavation, and removal of soil.

Bioremediation techniques

Each environmental pollutant has a unique way of removal, which depends on its nature. There are a variety of criteria to give thought to when making a choice of bioremediation technique, some of which include the nature of the pollutant, complexity and extent of pollution, environment of pollution, site of application, cost of application, and policies guarding the environment [8, 9]. When considering the site of application, techniques for bioremediation can be classified into two: the *Ex-situ* and the *In-situ*.

Ex-situ bioremediation technique (EBT)

This involves the excavation of the agents of pollution from the polluted sites, after which they are transported to another site for adequate treatment. EBTs are usually considered with regard to the cost of treatment, complexity of pollution, type of pollutant, extent of pollution, location, and geography of the area polluted [10].

Ex-situ bioremediation techniques include:

1. Biopile/Biopiling
2. Windrows
3. Bioreactor
4. Land farming

Biopile/Biopiling

The biopile bioremediation technique has to do with the piling of the already dug out polluted soil on the upper ground, followed by nutrient repair, which could, at some point, be followed by the introduction of air to enhance bioremediation by enhancing the activities of microbes. Biopiling involves: introduction of air (aeration), irrigation process, nutrient and leachate receiver systems, and a treatment base. Due to constructive features in biopiling, which include cost effectiveness, thus enabling effective biodegradation provided that the conditions of nutrient, temperature, and aeration are correctly controlled, the biopile *ex-situ* bioremediation technique is usually considered [11]. Following a 50-day study period [12] observed a 71% reduction in sum hydrocarbon concentration and an adjustment in the structure of bacteria in line with the pre-treatment of polluted soil samples before biopile forming and further biostimulation using fish meal. In order for the biopile to be more efficient, there is a need to sieve and aerate the contaminated soil prior to processing [13]. Enhancement of the biopile bioremediation process in a biopile set up (construct) can be achieved by the addition of materials that add bulk, which include: bark or wood chips, saw dust, straw, and other organic materials [14]. Biopile system is advantageous being that it conserves a lot of space when compared with other ex-situ bioremediation processes, but it has its downsides, which include maintenance and operational costs, insufficient or total lack of power supply, most importantly at work sites, which reduces effective distribution of air through the air pump to the polluted soil. Furthermore, because of the non-uniform distribution of air within the biopile setup (construct), overheating of the air could occur, leading to drying up soil in the bioremediation process, consequently inhibiting the activity of microbes and promoting evaporation/volatilization rather than biodegradation [15].

Windrows

The windrows bioremediation technique relies on occasional turning of contaminated piled up soil to facilitate the remediation process, thus accelerating the breakdown activities of indigenous bacteria and/or bacteria in transition state present in contaminated soil. Aeration, uniform distribution of pollutants, nutrients, and biodegradative activities are enhanced by the occasional turning of contaminated soil, alongside the input of water, thus sparking up the bioremediation rate, which could be achieved through incorporation, biomodification, and mineralization. Consequent to occasional turning practiced in windrows, its use in soils contaminated with toxic volatiles may not be ideal. Windrows treatment showed a heightened hydrocarbon removal rate compared to biopiling, though it was dependent on the soil type, which was more friable [16].

Bioreactors

In consonance with the name, a bioreactor is known as a container where raw materials are changed to particular product(s) after a series of bioreactions [10]. The flexibility of a bioreactor design allows for maximum degradation while minimizing abiotic losses [17]. Bioreactor vessel conditions mimic and maintain natural environments of cells, thus enhancing the natural cell processes and providing optimal growth surroundings. The different modes of operating the bioreactor comprise: Batch, fed-batch, sequencing batch, continuous, and multistage, and the decision on which to use depends mainly on capital expenditure and market economy. Feeding of the polluted samples into a bioreactor can be done in the form of dry matter or miry. When compared to the other ex-situ bioremediation techniques, the bioreactor has more advantage, which is mainly the first-rate control of the bioprocess parameters. The bioreactor-based bioremediation is said to be more efficient in that the limiting factors of bioremediation, which include controlled bioaugmentation, nutrient input, elevated pollutant bioavailability, and mass transfer (interaction between contaminant and microbe), can be effectively established. When tracking the modifications in microbial population dynamics, and seeking simple characterization of the bacterial community involved in the remediation process, a long or short-term operation of a bioreactor containing crude-oil contaminated miry is ideal [18, 19]. Treatment of soil or water contaminated by volatile substances can be achieved using bioreactors. These volatiles include benzene, toluene, ethylbenzene, and xylene. Genetically modified microorganisms can also be used for bioaugmentation, and after the bioreactor process, the organisms are destroyed. This is to make sure no foreign gene gets into environs after remediation. Though different operation parameters have made the bioreactor-based bioremediation prove efficient, using a one-factor-at-a-time approach to relate all parameters for optimal operating conditions could be time-consuming. In order to overcome this challenge, the design-of-experiment tone may be used. It provides information on the optimum range of parameters, making use of a set of independent variables (controllable and uncontrollable factors) across a specific region/level [20]. Bioreactor-bioremediation technique may not be a popular full-scale practice for some reasons which including the quantity of the contaminated soil to be remediated may be too much, and as such, more manpower is needed. It is capital-intensive and needs proper safety measures to transport the contaminant to the treatment site. These make this technique not cost-friendly [21]. On the other hand, if there is any parameter that is not controlled adequately or optimally maintained, it may become a limiting factor, thereby reducing microbial activities and, in turn, making the bioreactor-bioremediation treatment less effective. Hence, to get optimum performance in the bioremediation process, a proper understanding of microbial activity is of utmost need [22].

Land farming

This bioremediation process is one of the simplest remediation techniques given to the fact that it requires less cost and equipment for operation. Most of the time, the terminologies ex-situ and in-situ are used interchangeably while referring to land farming. This is mainly due to the site of treatment because, in land farming, it is common to excavate contaminated soils, while the site of treatment seemingly determines what type of bioremediation it is. If the contaminated soil is treated on site, it can be seen as in-situ; if not, it can be seen as ex-situ and have more common features with the rest of the ex-situ bioremediation techniques. When and if a contaminant lies <1m underneath the ground surface, bioremediation may proceed without excavating the ground, but for contaminants that lie >1.7m there is a need to transport them to the ground surface to enhance effective bioremediation [23].

In-situ bioremediation technique

In situ bioremediation techniques require treatment of contaminated substances at the site of contamination. This process is associated with little or no harm to the soil structure. The in-situ bioremediation processes can be grouped into enhanced and non-enhanced; the enhanced include bioventing, biosparging, bioslurping, and phytoremediation, while the non-enhanced include intrinsic bioremediation or natural attenuation. Success has been recorded in using *in situ* bioremediation techniques to treat chlorinated solvents, dyes, heavy metals, and hydrocarbon-contaminated sites. [24, 25, 26, 27]. The level of porosity of soil has a great influence on the use of *in-situ* bioremediation on any contaminated site. In order to achieve notable success, there is a need to take into consideration environmental conditions like nutrient availability, moisture content, status of electron acceptor, pH, and temperature [21].

Bioventing

The bioventing technique involves airflow stimulation control by supplying oxygen to the unsaturated zone. This increases bioremediation by increasing inbred microbial activity. The technique can be utilized to bioremediate soils polluted with vaporous and semi-vaporous organic compounds and also for the recovery of free products such as light non-aqueous phase liquids, thus remediating capillary, unsaturated, and saturated zones. The effectiveness of bioventing was reported by [28], who recorded and reported a 93% contaminant removal in the treatment of phenanthrene-contaminated soil after 7 months. In the repair of sites contaminated with light spilled petroleum products, bioventing has gained popularity among other in-situ bioremediation techniques [29]. The number of injection points is a key factor in the success of bioventing-based bioremediation, as this helps to achieve uniform distribution of air. For hydrocarbon removal from a contaminated site, a single well bioventing is ineffective, and this is in line with [30], who observed that in a sub-antarctic hydrocarbon contaminated site and attributed it to a shallow water table and thin soil cover, which led to the development of a channel. Consequently, when the microbioventing process, making use of nine small injection rods (0.5m) apart, was done on the same site under similar conditions, there was a sizable amount of hydrocarbon removed, and this was because of a steadier dispersal of oxygen, thus increasing biodegradation. A relatively high oxygen concentration may be obtained by injecting pure oxygen into a soil with low permeability rather than injecting air. Furthermore, in trying to accelerate the degradation of obstinate compounds, ozonation may be a useful tool to enhance partial oxidation [21]. Bioventing bioremediation or field treatment time may be prolonged, which is a result of the environmental factors as well as different characteristics of the unsaturated zone to which air is introduced, and this makes it difficult to achieve similar results as in the laboratory study not achievable.

Bioslurping

Bioslurping uses a "slurp" extending into the free product layer, drawing up liquids from this layer in an identical form to how a straw draws liquid up from a vessel. The upward movement of Light Non-Aqueous Phase Liquid (LNAPL) to the surface, where it is then isolated from water and air, is initiated by a pumping mechanism. Following complete free product removal, the bioslurping system can be made to run as a conventional bioventing system to conclude the remediation process [26]. There is a combination of vacuum-enhanced pumping, soil vapour removal, and bioventing to achieve soil and groundwater remediation by indirect supply of oxygen and acceleration of pollutant degradation [31].

Biosparging

Biosparging is another in-situ bioremediation process in which air is injected into the soil subsurface to stimulate microbial activities, hence promoting pollutant removal from polluted soil. In this process, air is injected at the saturated zone, which causes upward movement of volatile organic compounds to the unsaturated zone, promoting biodegradation. Pollutant degradability and soil permeability are the major factors that determine the effectiveness of biosparging [21]. Treatment of water tables polluted with petroleum products, particularly diesel and kerosene, is usually carried out using biosparging. Biosparging of benzene, toluene, ethylbenzene, and xylene (B-TEX) contaminated water table plume gave rise to a shift from non-oxygenated to oxygenated conditions as shown by high dissolved oxygen redox potentials, nitrate, sulphate, and total culturable heterotrophs with a correlating decrease in melted ferrous iron, sulphide, methane and total anaerobes and methanogens [32]. However, predicting the direction of airflow is the major limitation of biosparging.

Phytoremediation

Phytoremediation, as a technique in bioremediation, harnesses the use of plant interactions to degrade pollutants in polluted sites. These interactions include physical, biochemical, biological, chemical, and microbiological. There are many mechanisms that are utilized in phytoremediation, which depend on the nature of the pollutant. These pollutants may be inorganic elements or organic compounds, and the mechanisms may include accumulation/extraction, degradation, filtration, stabilization, and volatilization. Inorganic contaminants (toxic heavy metals and radionuclides) are easily removed by taking them out, transforming them, and secluding them. Also, organic pollutants (hydrocarbons and chlorinated compounds) are mostly removed by degradation, rhizoremediation, stabilization, volatilization, and when some plants like willow and alfalfa are involved, mineralization can be applied. [33, 34]. Extent of toxicity of pollutant to plant, plant survival rate and adaptation to environmental situations, the plant root system (fibrous of tap root system and the use of either of them is dependent on how deep the pollutant has gone and above ground biomass which should not be available for plant feeding), monitoring of the site and time desired to achieve cleanliness needed are some of the factors that are to be considered when selecting a particular plant as a phytoremediator. Moreover, the plant should have a very high resistance to plant diseases and pests [35]. The process of biodegradation using plants (phytoremediation) requires uptake (which is mostly by an inactive process), change of location from roots to shoots (this is carried out by xylem flow), and build up in shoots [36]. The nature of the pollutant and the type of plant are some factors that make the phytoremediation process vary. It is believable that most plants that grow on a contaminated site are good phytoremediators. It can therefore be said that the success of any phytoremediation approach is dependent mainly on improving the remediation capacities of the domestic plants growing in contaminated areas by bioaugmentation. This could be with endogenous or exogenous plant rhizobacteria, or by biostimulation. One of the main benefits of using the phytoremediation technique in a contaminated site is the bioaccumulation of some precious metals in some parts of the plant, which are recovered after remediation. This process is called phytomining. Selenium-enriched material recovered from phytoremediation sites and their possible applications as food, in making feedstuff, and the biofortification of farm products was reported by [37]. Low cost of maintenance and setup, prevention of erosion and conserving of soil structure, prevention of leaching of metal, and environment-friendly are other benefits of phytoremediation. [38, 39]. Furthermore, with the phytoremediation technique, the fertility of the soil may be improved due to the addition of organic matter [40]. However, some factors like lengthy remediation time, contaminant concentration, harmfulness, and bioavailability to plants, slow growth rate of plants, and plant roots depth impede the utilization of phytoremediation in the clean-up of polluted sites [34, 39, 41].

Treatment approaches in bioremediation

There are different treatment approaches employed in bioremediation. They include biostimulation, bioaugmentation, and intrinsic bioremediation.

Biostimulation

This is the process of injecting specific nutrients at the pollution site to enhance or stimulate the activities of microorganisms present at the site. These indigenous microorganisms (bacteria, fungi, yeast) are first supplemented with special nutrient substances (fertilizer), the limiting nutrient, growth supplement, and trace minerals or electron acceptors to enhance their growth, which will result in efficient removal or detoxification of the pollutants [42]. Also, biostimulation involves the modification of the environmental conditions, like pH, temperature, oxygen, or moisture, to speed up the enzymatic reactions in the existing microbes for the degradation of the pollutants. The major benefit of biostimulation is that the bioremediation will be handled by the natural microbes present in the environment, and are most time, evenly distributed on the pollution site.

Bioaugmentation

Bioaugmentation is a bioremediation approach that involves the addition of a pollutant-degrading microorganism (either natural, foreign, or genetically modified) to an environment to supplement the degradation capacity of the native microorganisms on the polluted site. The basis of this approach is that the native microbial population may not have the capacity to degrade the wide range of pollutants available in a complex mixture, or that the population may be too small to handle the level of pollution [43]. Also, bioaugmentation can be most appropriate when there is a need for urgent degradation of the pollutants or when the addition of the microorganisms will reduce the lag period before the commencement of the bioremediation process [44]. In this approach, either a novel microorganism with a history or study of being able to degrade the pollutant is introduced into the pollutant site, or the native microorganisms are isolated from the contaminated site, cultured, genetically modified to support the remediation of the particular pollutant, and returned to the site. Where novel or foreign microorganisms are used, they must be able to survive the foreign and hostile environment, adapt to the various abiotic factors, and compete favourably with the native microbes and predators.

Intrinsic bioremediation

This is the degradation of environmental pollutants into harmless forms through the activities of the indigenous microbial population at the pollution site. Intrinsic bioremediation is a natural approach that utilizes the native microorganisms and the nutrients present on the pollution site. No additional nutrient or microorganisms is needed. For intrinsic bioremediation to be successful, the inherent capacity of the native microorganisms to degrade the pollutants should be tested and proven at both laboratory and field levels before its application.

Recent advances in bioremediation

The utilization of some genetically engineered microorganisms to enhance the bioremediation of specific contaminants like endocrine disruptors, pesticides, and hydrocarbons by influencing their ability to utilize such contaminants is gaining ground. This ability to genetically improve the degradation capacity of these microorganisms is due to the diverse nature of the genetic makeup and metabolic activities of these microbes, which can be explored to insert the gene needed for the production of a particular metabolic enzyme that can degrade the particular pollutant [45].

Endocrine system

It is a normal body function which consists of a network of glands without ducts in the animal body that produce chemical messengers, identified as hormones, which are circulated through blood to target locations, which are the different body organs and tissues/cells. Based on their mode of production of hormones, these glands are named endocrine, meaning “secreting within”. The normal daily activities, including feeding, sleeping, and to drink, and other long-term effects like reproducing, growing, aging, immunity, and so on, are maintained by hormones. The endocrine system works in concert with the nervous and immune systems, which also share their functionaries [46]. The endocrine system is composed of three sections, which include: the brain section-a nucleus of the hypothalamus, the pituitary gland section, and the target endocrine gland section. The target destinations of the hormones bear the specific receptors, which, upon binding, induce signaling pathways involved in specific biological functions. There are eight such major glands along with many minor glands which are grossly conserved in the animal kingdom (including humans) and share similar morphology among mammals, which include:

Pituitary, Pineal, Thyroid, Thymus, Adrenal, Pancreas, Gonad (Testes in Male and Ovary in Female)

Categorizing endocrine glands

Endocrine glands are categorized into central, peripheral, primary, and secondary. Those glands present in the cranium, which are part of the brain Central endocrine glands are those which are present within the cranium and are part of the brain (hypothalamus, pituitary and pineal glands) are known as the central endocrine glands. All the other glands that exist on the outside of the cranium are known as peripheral. The functions of the primary endocrine organs are solely to produce hormones, whereas the secondary endocrine organs are primarily to perform some other biofunctions and, in addition, produce hormones to support and sustain their primary functions. Hormonal production in secondary endocrine organs is dedicated solely to a specific cell group or tissue components. A major example of a secondary endocrine gland is the pancreas. From the definitions of primary and secondary endocrine glands, it merits being a primary endocrine organ, but it is partly primarily endocrine, being that it possesses solely a specific cell group called the “islets of langerhans” spread along its entire length (tail part majorly) which is endocrine, while the remaining part of the pancreas is exocrine and produces enzymes for digestive functions which move out through ducts. In the same vein, the hypothalamus, though taken as a primary endocrine organ, has solely neurons in specific nuclear groups that are endocrine [47].

The pituitary gland

This gland is known as the prime regulator of all outlying endocrine glands and is situated in the hypophyseal fossa, which is alternatively known as the pituitary fossa and is located at the center of the mid-sagittal fossa of the bottom of the skull. Majorly, hormones of the pituitary are produced through the adenohypophysis section, excluding oxytocin and vasopressin/antidiuretic hormone, which are produced through the neurohypophysis section [46].

Functions

The synthesis of tropic hormones from the anterior pituitary through the hypophyseal portal system is regulated by the hypothalamic releasing or inhibitory hormones. The posterior pituitary hormones oxytocin and vasopressin control the hemodynamic state of the human body, and oxytocin is also required in inducing the delivery and expulsion of breast milk in females [46].

Pineal gland

The small pine cone-like gland situated behind the diencephalon is heavily packed with sensory nerve endings. The cell components of the gland are pinealocytes and neuroglia cells, and it is densely filled with afferent nerve terminals. The gland is mostly vascular and abundant in sympathetic innervation.

Functions

The pineal gland produces melatonin, a hormone that assists in the control of the circadian rhythm of the body (sleeping and waking of the body). It is a serotonin-derived hormone functioning together with the biological clock located in the suprachiasmatic nuclei (SCN).

Thyroid gland

This gland, sited in the neck, extending from C5 to T1 vertebrae, has some similarity to laryngeal cartilages and upper tracheal rings. It has a butterfly-like structural conformation with two lobes and a linking isthmus that lies forward of the 2-4th tracheal rings. The lobes of the gland lie on either side of the larynx and trachea, and while the gland itself is enclosed by pretracheal fascia [47].

Functions

The hormones T_3 and $T_{4,}$ which correspond to triiodothyronine and tetraiodothyronine/Thyroxine $T_{4,}$ are produced by the thyroid gland and are required in the control of the fundamental metabolic rate of the body.

Parathyroid gland: These small glands are found, two on each side, at the back (posterior) part of the lobes of the thyroid gland.

Functions: The parathyroid gland produces parathyroid hormones, which control calcium and phosphate stability in the human body.

Adrenal gland

The adrenal gland is a mini gland situated above each of the kidneys, capped in a renal fascia. It comprises two major parts: the cortex and medulla. The cortex secretes steroid hormones while the medulla secretes amine hormones. The gland is further grouped into parts: glomerulosa, fasciculata, and reticularis.

Functions

Distinct hormones are secreted from the cortex and medulla, which are required for the maintenance of key normal human body functions. The hormones from the cortex include sex steroids or gonadotrophins, mineralocorticoids, and glucocorticoids, while the medulla hormones include epinephrine or adrenaline and norepinephrine or noradrenaline, and dopamine in small amounts.

Pancreas

The endocrine part of the pancreas, which is the islet cells, is dispersed among the exocrine acini of the pancreas as clusters. The islet cell clusters are in large quantities towards the back part of the organ with highest density in the tail.

Functions

The islets are subdivided into three cells (α-cells, β-cells, and δ-cells). These secrete three different hormones. The alpha cells secrete glucagon, beta cells secrete insulin, while the delta cells secrete somatostatin, which are vital for the smooth metabolic performance of the body. Glycogenesis and glycogenolysis, which are the opposite aspects of glucose metabolism in the body, are regulated by insulin and glucagon, respectively, and consequently control the concentration of glucose in blood.

Ovary

The ovary is the female gonad, and it is positioned in the pelvis, one on each side, at the tail end of the tubes in the uterus. The endocrine unit of the ovary is a single follicle, and each of the follicles contains a germ cell/oocyte at the core, which is surrounded by an inner and outer layer that is made up of granulosa cells and theca cells, respectively.

Functions

The ovary secretes hormones estrogen and progesterone, which are vital in keeping up the health and functions of the female reproductive organs. The initiation and maintenance of pregnancy a functions of estrogen and progesterone, respectively. Through aromatization, androstenedione and testosterone, which are hormones secreted by the ovary in slight amounts, can be converted to estrogen.

Testes

The testis is the male gonad which is present in the pelvic region, bilaterally surrounded by the scrotum.

Functions

The testes secrete the hormone testosterone, responsible for gametogenesis, the development of male sexual behaviour, and the maintenance of the male reproductive system. An additional source of testosterone could be obtained from the male sex hormones produced in the adrenal gland by converting them.

Endocrine disruptors

Endocrine disruptors, which are most times referred to as hormonally active agents, endocrine-disrupting chemicals or compounds, are chemicals that interfere with the function of the hormonal or endocrine system. These chemicals interfere with the production, transportation, binding, action, and excretion of natural hormones in the body [48]. Endocrine disruptors are not avoidable and are also a global challenge as exposure can occur in a variety of places, which span across the office, farm, school, home, food, water, and the air we breathe. Numerous classes of chemicals, including plasticizers, flame-retardants, fungicides, pesticides, pharmaceuticals, heavy metals, and even naturally occurring compounds such as phytoestrogens, are endocrine-disrupting compounds [49]. Previous studies with cells and experimental animals have shown that endocrine disruptors can cause adverse effects in animals, and low-dose exposures to humans may give similar effects [50].

Types of endocrine disruptors

We are exposed to different types of endocrine disruptors in our daily activities because they are found in low doses in thousands of products available for household, medical, and industrial uses. The most commonly detected endocrine disruptors are as follows:

Phenol compounds: This class of endocrine disruptors includes:

- **Alkylphenols:** Alkylphenols are xenoestrogens because they mimic the action of human estrogen, and they are found in a variety of consumer goods [51]. The utilization of nonylphenols, which are alkylphenols, has been restricted in European countries due to their toxicity, persistence in the environment, and the tendency to bioaccumulate [52]. The long-chain alkylphenols are mostly used in the production of detergents, as additives for fuel and lubricants, polymers, as well as phenolic resins. They also serve as building block chemicals for the production of fragrances, some pesticide formulations, adhesives, antioxidants, thermoplastic elastomers, and fire retardant materials. Animal studies suggest that alkylphenol may reduce the production of sperm in males and may negatively affect the female reproductive system [53, 54]. Nonoxynol-9, which is an alkylphenol, is used as a spermicidal lubricant in some condoms.

- **Bisphenol A (BPA):** 2,2-bis(4-hydroxyphenyl) propane, also known as BPA, is a chemical used in the production of epoxy resins and polycarbonate plastics. It is mostly found in plastic food containers, food and drink packages, baby bottles, dental materials, and the inner lining of metal food and infant formula cans. Also, BPA is found in receipt papers used in grocery stores and restaurants because the paper is coated with BPA-containing clay for printing purposes [55]. BPA is a proven endocrine disruptor, and many research studies with laboratory animals showed that animals exposed to low doses of BPA had an increased rate of diabetes, breast and prostate cancers, reduced sperm count, reproductive dysfunction, early puberty, and neurological problems [56, 57, 58, 59].

- **Bisphenol S (BPS):** This is an analogue of BPA. It is mostly found in thermal receipts, plastics, and in some personal care products [60]. It is mostly used now in some industrial processes due to the restrictions on the use of BPA. Although BPS has been used to replace BPA in "BPA-free items", research has shown that BPS is also an endocrine disruptor and can be as harmful as BPA [61].

Pesticides: These include the organophosphates, organochlorines, carbamates, and synthetic pyrethroids. Pesticides are often used for many purposes, like in homes, for commercial and agricultural pest control, thereby increasing the chances of human exposure. One most studied pesticides that can act as an endocrine disruptor is

Dichlorodiphenyltrichloroethane (DDT): DDT is an organochlorine insecticide. DDT was previously used as a pesticide against beetles on crops in early 1936, and the increased occurrence of dysentery, malaria, and typhoid fever gave rise to its use against mosquitoes and houseflies, which are the vectors of these diseases [62]. DDT was later found to negatively affect the reproduction of wildlife, especially birds and carnivores [63]. A human study revealed that pregnant mothers who are exposed to organochlorine pesticides may have an increased risk of having spontaneous abortion, stillbirth, and early delivery [64]. Further research on laboratory animals revealed that DDT can impair the development of male and female sex organs, persists in the environment, and can be biomagnified through the food chain, which led to its ban in the United States [65, 66]. However, DDT is still extensively used in some African and Asian countries as an anti-malarial insecticide.

Industrial chemicals: Some industrial chemicals that are regarded as endocrine disruptors include, but are not limited to, polychlorinated biphenyls and dioxins.

- **Polychlorinated biphenyls (PCBs):** PCBs are a class of chlorinated compounds that were widely used in the past as industrial lubricants, coolants, coatings, and insulation material for electrical equipment like transformers and capacitors. PCBs are equally found in consumer items like hydraulic fluid, fluorescent lights, televisions, and other electronic gadgets. Studies showed that exposure to PCBs increased the risk of skin and brain cancers [67, 68]. Some human studies suggest that women who are exposed to PCBs experience irregular menstrual cycles, increased risk of spontaneous abortion, and give birth to children with abnormal growth [69, 70]. However, the detrimental health effects of PCBs to both humans and wildlife and their ability to persist in the environment led to the ban on their use.

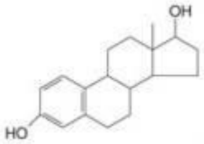
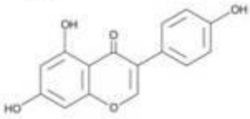
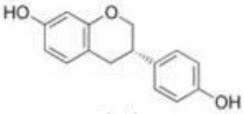
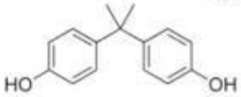
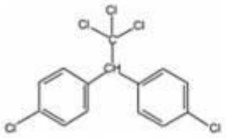
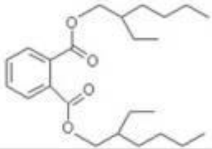
- **Dioxins:** Polychlorinated dibenzodioxins, which are commonly known as dioxins, are chemical compounds that are produced unintentionally during some industrial processes, like the manufacture of some industrial chemicals, pesticides, and PVC plastics. Also, burning of some medical or city waste leads to the production/release of dioxins into the environment. Although not all members of this class are toxic, studies have shown that the most toxic member of this class of compounds, considered to be an endocrine disruptor, 2,3,7,8-tetrachlorodibenzodioxin (TCDD) or dioxin which has been proven to induce mitochondrial dysfunction and premature senescence in both human and rodent neuronal cells [71, 72].

Polybrominated diphenyl ethers (PBDEs): PBDEs are a group of compounds that are found in flame retardants. These flame retardants are added during the manufacturing of plastics and textile products to reduce their flammability. PBDEs are used in plastic cases of televisions, computers, electronics, and other textile products. PBDEs are similar in structure to PCBs and have been shown to exhibit similar neurotoxic effects as PCBs [73]. PBDEs can also disrupt thyroid hormone balance, leading to some developmental and neurological deficiencies [74].

Phthalates: Phthalates are chemicals that are used as plastic softeners or plasticizers. They are used to reduce the rigidity of plastics, making them easier to bend. Phthalates are found in a variety of consumer goods like plastic food and beverage containers, PVC pipes, medical supplies, vinyl toys, inner lining of metal cans, etc. Phthalates have been shown to disrupt the endocrine system of animals, leading to increased reproductive dysfunction in male animals [75]. A particular phthalate, di(2-ethylhexyl) phthalate or DEHP, which is found in medical supplies like catheters, blood, and IV bags, has been shown to adversely affect the development of male reproductive organs and the production of normal sperm in laboratory animals [76]. Although no data is available on human studies, it is advisable not to expose young male babies to DEHP.

Phytoestrogens: These are plant hormones that are known to be endocrine disruptors. They resemble the natural human estrogen either in structure/or function. There are many classes of phytoestrogens, but the most hormonally active ones are the phenolic compounds like the isoflavones and coumestans, which are mostly found in soybeans and other legumes, nuts, wine, certain grains, wheat, and soya-fortified foods [77]. Phytoestrogens, especially genistein and diadzein from soya, have been shown to block the synthesis of thyroxine by inhibiting the activity of thyroid peroxidase, which catalyzes the iodination of tyrosine, thereby increasing the risk of goiter [78]. Table 1 shows the structures of some endocrine disruptors. Other endocrine disruptors include some herbicides (atrazine), fungicides (vinclozolin), parabens, perfluorooctanoic acid (PFOA), polycyclic aromatic hydrocarbons (PAHs), and some heavy metals like cadmium, lead, mercury, and arsenic.

Table 1: Structures of some well-known anthropogenic and naturally occurring endocrine-disrupting compounds. BPA, bisphenol A; DDT, dichlorodiphenyltrichloroethane; DEPH, di(2-ethylhexyl) phthalate [102].

Compound	Structure	Classification
Estradiol		Endogenous Estrogen
Genistein		Soy Isoflavone
Equol		Metabolite of Daidzein
BPA		Plastics Component
DDT		Pesticide
DEHP		Phthalate

Routes of exposure to endocrine disruptors

Endocrine disruptors are found in a variety of products, including drugs, pesticides, chemicals used in plastic industries, and in some consumer products, industrial by-products, and pollutants. There are some endocrine disruptors that are also found in naturally produced botanical products. The following are the major routes through which humans are exposed to endocrine disruptors:

Food: Food accounts for the major route through which people are exposed to endocrine disruptors. Most people may be exposed to phthalates by consuming food that is cooked or stored in plastic containers or drinking beverages from plastic containers. A study showed that common food products like fish and other animal products from some grocery stores are contaminated with PBDE [79]. This is because these compounds are lipophilic and tend to be stored in the adipose tissues of animals that are exposed to them, which are equally transferred to humans through animal products. Infants may be exposed to BPA when they consume infant formula stored in BPA-coated metal cans. Some agricultural produce that is treated with pesticides like DDT and atrazine still retains some trace amount of these endocrine disruptors, ready for consumption.

Skin: Consumer goods like household cleaning agents (bar soaps, detergents, tub and tile cleaners) and personal care products (shampoo, conditioner, facial cleaner, lotions, toothpaste, etc) are potential sources of endocrine disruptors. A study showed that when these products are used in combination, one is potentially exposed to about 19 toxic compounds, with some being endocrine disruptors [80]. Absorption through the skin may happen, and it leads to the accumulation of these compounds within the body. Also, the spermicide nonoxynol-9, which is an endocrine disruptor, may be absorbed through the skin or mucous membranes when such condoms are used.

Water: Drinking water may contain low doses of phthalates, and the risk is increased when the water is stored in a plastic container for a long time. Also, well water located near hazardous waste sites may be contaminated with phthalates and alkylphenols. Drinking water from rivers without proper treatment may lead to exposure to these endocrine disruptors because some of these chemicals may leach into the environment during manufacturing processes and find their way into the groundwater, rivers, and oceans [81].

Air: Another source of endocrine disruptors is through fumes from some industries, agricultural, and commercial activities. Also, household dust can contain some endocrine disruptors like Lead and PCBs from weathering construction materials or furniture. Inhaling fumes from pesticide spray could expose one to endocrine disruptors.

Direct injections: Some medical practices can put some endocrine disruptors, especially phthalates, directly into the bloodstream. This may be through certain medical products that are stored and delivered in plastics, such as intravenous (IV) tubing, IV bags, and indwelling catheters.

How bioremediation of endocrine disruptors occurs

Due to the harmful effects of endocrine disruptors to the environment, wildlife, and humans, there has been an increasing awareness in the public community and a growing need on how to remove them from both terrestrial and aquatic ecosystems. Some physico-chemical methods that are being employed to achieve the degradation of these endocrine disruptors include: photodegradation, oxidation, absorption on active carbon, ultrafiltration, and nanofiltration. In this context, we'll focus on the use of bioremediation or biotechnological methods for the removal of endocrine disruptors.

The use of enzymes: Enzyme bioremediation has been environmentally friendly and most efficient in the degradation of endocrine disruptors because it is highly specific, selectively reducing the concentration of the endocrine disruptors while the other compounds remain unchanged [82]. In this process, the particular enzyme is either in its free form, which makes it insoluble in the reaction media, or immobilized on a solid carrier. Immobilization of enzymes has been a promising approach because it improves the catalytic activity and stabilization of the enzymes, as well as preserving the three-dimensional structure of the enzyme in the hostile conditions of the reaction environment [83]. It also enhances the repeated utilization and storage stability of the enzyme in continuous processes. In the enzymatic bioremediation of endocrine disruptors, oxidoreductases like peroxidases (lignin peroxidases, Manganese-dependent peroxidases), aromatic dioxygenases, some oxygenases, laccases, and tyrosinases have attracted some research attention.

Oxidoreductases have been demonstrated to catalyze the oxidation-reduction reactions involved in the biodegradation of endocrine disruptors like phenol compounds, some pesticides, herbicides, and fungicides [84, 85, 86].

Oxidoreductases are very efficient when immobilized on a carrier support, and a suitable carrier support not only preserves the oxidoreductases from denaturation but also maintains their catalytic activity for adequate degradation of endocrine disruptors and other toxic compounds [87, 86]. Also, immobilized oxidoreductases exhibit effective activity in diverse environmental conditions like pH, temperature, and enhance their heat stability [88].

Application of immobilized enzymes (Oxidoreductases) in the bioremediation of endocrine disruptors

Lignin Peroxidase: Lignin peroxidase (1,2-bis(3,4-dimethoxyphenyl) propane-1,3-diol:-hydrogen peroxide oxidoreductase; EC 1.11.1.14) catalyzes the oxidative cleavage or depolymerization of lignin in the presence of hydrogen peroxide (H_2O_2). Lignin peroxidase was initially extracted from the culture broth of a ligninolytic fungus called *Phanerochaete chrysosporium*, but recently, it has been found in many microorganisms, particularly the white-rot basidiomycetes [89]. According to [90], immobilized and free forms of lignin peroxidase have exhibited distinct abilities to oxidize a variety of aromatic phenolic and non-phenolic endocrine disruptors, including some other organic compounds like xenobiotics. A carrier support 3-aminopropyltriethoxysilane-modified spherical mesoporous silicas (SMS) was successfully fabricated by [91] and used for the immobilization of lignin peroxidase by covalent binding. The study also revealed that the protein loading and immobilized lignin peroxidase activity were 12.15mg/g and 812U/L, respectively, and that the SMS-immobilized lignin peroxidase showed better tolerance to a wider range of pH and better ability to be reused. It, however, showed lower temperature resistance than the free form of the enzyme. A study by [92] on the ability of immobilized and free ligninolytic enzymes including lignin peroxidase and manganese peroxidase to degrade the endocrine disruptor bisphenol A (BPA) revealed that immobilized oxidoreductases catalyzed the degradation of 90% of BPA after 8 hours of treatment while the free form of the enzyme caused 26% reduction in the degradation of the BPA, showing the protecting effects of immobilization on the enzymes.

Manganese peroxidase: Manganese peroxidase (Mn (II): hydrogen-peroxide oxidoreductase; EC 1.11.1.13) is a glycosylated heme-containing enzyme that belongs to the class of oxidoreductases. The enzyme was first found in the culture extract of *P. chrysosporium*, but recently, it has also been identified in some white-rot fungi (WRF) and other bacteria [93]. Manganese peroxidase is one of the earliest enzymes utilized in the degradation of environmental pollutants, and it can catalyze the oxidation of many phenolic compounds, mono and dimeric phenols, and other endocrine disruptors in the presence of hydrogen peroxide [94]. According to a study by [95], manganese peroxidase, extracted and purified from *Anthracophyllum discolor* and immobilized on a nanoclay as a carrier support, was evaluated for its ability to degrade polyaromatic hydrocarbons (PAHs), which an endocrine disruptors. The result revealed that the immobilized manganese peroxidase showed about 80% and 65% efficiency in the degradation of pyrene and anthracene (which are PAHs). Also, the immobilized manganese peroxidase showed efficient biotransformation of anthracene in soil than the free form of the enzyme. However, reduced degradation efficiency was observed for fluoranthene and phenanthrene hydrocarbons.

Laccases: Laccases (*p*-diphenol: dioxygen oxidoreductases; EC 1.10.3.2) are extracellular oxidoreductases that are found in some bacteria and plants. Laccases are also found in some fungi like *Trametes versicolor*, *T. vilosa*, and *Cerrena unicolor*. Laccases from these fungi have been mostly applied in the bioremediation of endocrine disruptors due to their high catalytic activity, availability, and low cost [96]. These enzymes can catalyze many oxidation reactions, especially the single-electron oxidation of phenolic compounds and aromatic amines. A study by [97] evaluated the biodegradation capability of laccase enzyme, extracted from *Coriollopsis gallica* and immobilized on mesoporous nanostructures, on dichloropen (an organochlorine pesticide). The result revealed that both the cytotoxic and genotoxic effects of dichloropen were significantly reduced after oxidation by the enzyme laccase. Also, the same group extracted laccase enzyme from *Trametes versicolor*, immobilized it on *Hippospongia communis* sponging-based scaffold, and evaluated its efficiency in the biodegradation of BPA, BPS, and bisphenol F (BPF). The result showed almost 100% degradation of BPA and BPF, and over 40% degradation of BPS under optimal conditions. Other studies on the use of laccase enzymes, extracted from different sources, for the biodegradation of endocrine disruptors are highlighted in Table 2.

Tyrosinases

Tyrosinases (*o*-diphenol: oxygen oxidoreductases; EC 1.14.18.1) are enzymes that contain copper and are mainly found in bacteria, fungi, insects, plants, and mammals [98]. These enzymes are known to catalyze the synthesis of melanin and other pigments from the oxidation of the amino acid tyrosine. Tyrosinases are similar to laccases because they have broad substrate specificity and can catalyze the biodegradation of phenols, monophenol, and other substituted derivatives like BPA, chloro, and nitrophenols [99]. However, tyrosinases differ from laccases because the by-product of the oxidation of phenolic compounds or their derivatives is quinones rather than free radicals and water molecules generated by laccases [100]. Tyrosinase enzyme from *Agaricus bisporus* was immobilized on alginate matrix microspheres and used to evaluate the potency of tyrosinase in the biodegradation of BPA [101]. The result showed that 100% of BPA was degraded between 11days and 20days with stirring conditions.

Table 2: Bioremediation studies on the use of immobilized laccase for the bioremediation of some endocrine disruptors.

Source of laccase	Method of immobilization	Targeted endocrine disruptor	Rate of degradation (%)	References
T. versicolor	Covalent attachment	Bisphenol S (BPS)	Over 40% of BPS at optimum condition	[103]
T. versicolor	Covalent attachment	Bisphenol A	67.5% degradation in a packed bed reactor	[104]
Pycnoporus sanguineus(CS43)	Cross-linking approach	Bisphenol A	100% in less than 24 h	[105]
T. versicolor	Cross-linking approach	Bisphenol A	100% in less than 24 h	[105]
Pleurotus ostreatus	Ionic adsorption	Bisphenol A	Degraded 100 mg·L^{-1}Bisphenol A in 1 h	[106]
T. pubescensMB89	Entrapment	Bisphenol A	More than 99% in 2 h	[107]
T. versicolor	Covalent attachment	Bisphenol A	100% of BPA (pH 5, 30 °C)	[103]

Conclusion

Bioremediation has emerged as a promising tool for the degradation of most endocrine disruptors since most other techniques are either unfriendly to the environment or inefficient in the removal of these compounds. Oxidative enzymes like the oxidoreductases, which are categorized as the green biocatalysts, can efficiently catalyze the oxidation or degradation of many endocrine disruptors in both aquatic and terrestrial environments with no need for additional cofactors except the readily available molecular oxygen or hydrogen peroxide. The immobilization of these enzymes has significantly improved their catalytic activity and also enhanced their continuous application for the clean-up of polluted or contaminated environments.

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Authors' information

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