UDC 616.43:577.15:616-074-07
DOI 10.59598/ME-2305-6045-2023-109-4-25-34

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ENDOCRINE-DISRUPTING CHEMICALS (EDCS), THEIR SOURCES, HEALTH CONCERNS AND BIODEGRADATION OF EDCS USING LACCASE

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At present, the presence of endocrine disruptor chemicals in the environment are important factors that are affecting the functioning of environmental systems and the health of individuals. Endocrine-disrupting chemicals are present in a wide variety of consumer products and interfere with the functioning of hormones and causing growth and development-related problems in exposed individuals. Laccase is a copper-containing enzyme that has shown its potential to degrade Endocrine-disrupting chemicals. The microbial production of laccase requires a rich source of lignin along with cellulose, hemicelluloses, and other proteins. Thus, lignocelluloses rich wastes may be considered as good substrates for the production of laccase using microorganisms. In this article, we have discusses the fate of endocrine disruptors, and role of laccase in the biodegradation of endocrine disruptors.

Key words: endocrine disrupting chemicals, pesticides, xenibotics, biodegradation of endocrine disrupting chemicals, laccase.

INTRODUCTION

Industrialization and increase in agricultural production both have significantly enhanced the quality of human life. Industrialization produces a variety of chemicals (organic and inorganic), and consumer products including cosmetics, fertilizers, pesticides, solvents, house-hold items, etc. It is observed that the processing, usage, and disposal of these products cause environmental pollution directly or indirectly. These compounds are found to negatively influence the proper functioning of ecosystems and also adversely affect the health of humans and wildlife [2, 14]. These synthetic compounds exhibit the properties like persistence, toxicity, bioactivity, bioaccumulation [14, 24]. The wide usage nature of some synthetic chemicals (xenobiotics, and endocrine disruptors, etc.) is causing human exposure as unavoidable and exposure takes place during the entire life cycle including during pregnancy [12, 28]. Human exposure to some of these chemicals is associated with growth and development-related health disorders. Endocrine disruptor chemicals (EDCs) are the example of such synthetic chemicals which are used in the manufacture of the large number of daily use and housel hold products. Due to the wide usage of endocrine disruptor compounds in the synthesis of a variety of items, and the daily use of these items, the concentration of these compounds is increasing continuously in the environment due to disposal.

Generally agriculture is assumed to be environmentally friendly activitiy but many agricultural practices negatively effect the nature of the environment. Agricultural activities like cultivation, weed removal, and pest management are ivolved with usage of chemicals to increase the productivity. There is increasing usage of chemical fertilizers, herbicides, and pesticides to increase the agricultural productivity. The nonscientific use of these chemicals are causing imbalance of nutrients in the soil, and environment pollution. Even the use of new herbicides are not providing sustainable results [22]. Even, inappropriate use of pesticides and herbicides is contributing to the development of resistance in pests, and weeds against these agents. Including this, these chemicals enter into soil, and water sources, and also becoming potent source of environmental pollution. Moreover, some of them persist in environment, enters in the tisues of invertibfates, and vertebrates, bioaccumulate and entres in food chains. The humans are being exposed to pesticides through environmental and dietary exposure. Moreover, pesticides such as 2,4-D, acetochlor, aldrin, carbofuran, DDT etc are also recognoized as endocrine disruptors [25].

The technology always aims to provide the solution of any problem in a sustainable way and integrated strategy may be used to manage the harmful environmental pollutant by biodegradation using enzymes. These approaches using enzymes are considered as ecofriendly and cost effective. In

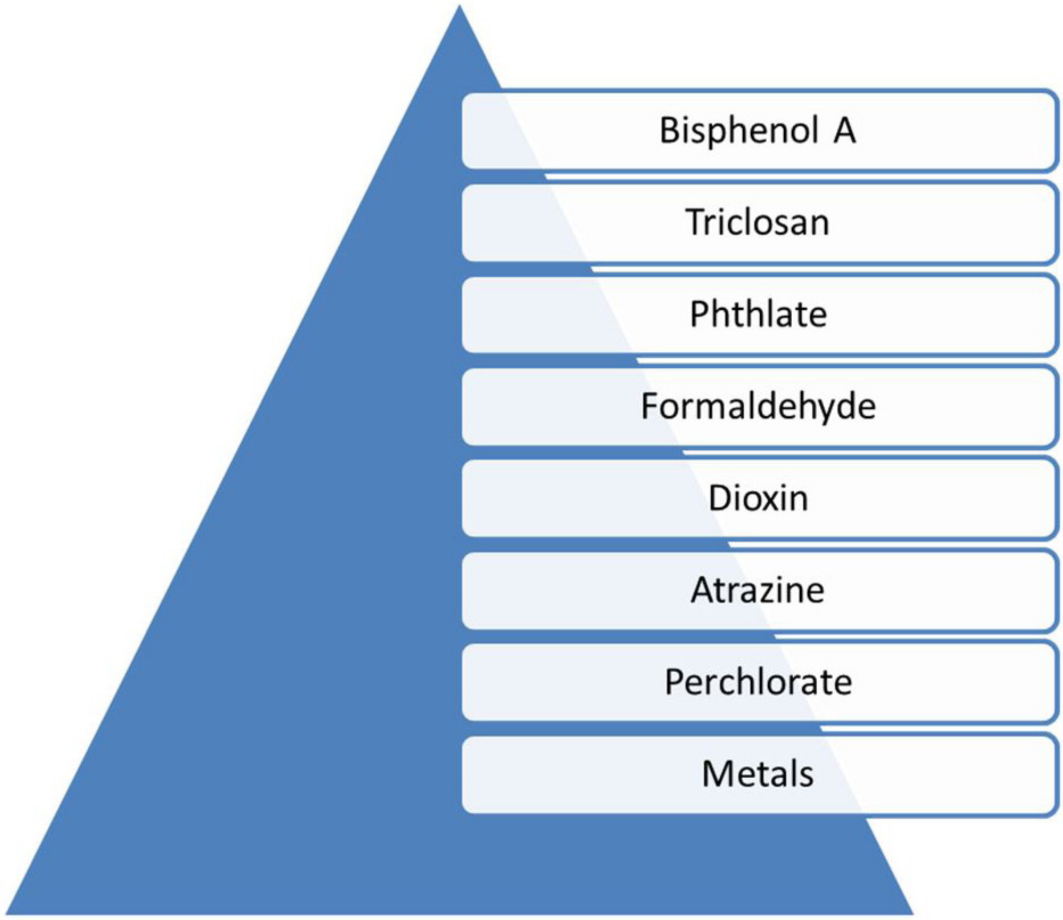

Figure 1 – EDCs are present in a wide variety of daily used items such as water bottles, cosmetics, pharmaceuticals, pesticides, and toothpaste etc

this article, the authors have discussed the properties of EDCs, their health impact, and the role of laccase to degrade the EDCs.

Endocrine-disrupting chemicals. Endocrine-disrupting chemicals or endocrine disruptors (EDCs) are substances found in the environment that interfere with the synthesis of the hormones, secretion, transport, and metabolism, or mimic the structure of hormone that causes an alteration in hormone-associated homeostasis that affects the growth and development of individuals [11].

Both types of compounds i.e. manmade and natural compounds have been identified as endocrine disruptors. Any compound is characterized as an endocrine disruptor on the basis of certain properties such as compound should possess endocrine property, and it should demonstrate hormone receptor association to exhibit endocrine action in the individuals [26, 31].

EDCs are found in many household products including cosmetic, human, and animal food items, consumer goods, and pharmaceuticals. EDCs can be categorized on the basis of origin into different groups such as industrial (alkylphenols, polychlorinated biphenyls (PCBs), and dioxins), agricultural (fungicides, herbicides, insecticide, pesticides, and phytoestrogens, etc), residential (bisphenol A, polybrominated biphenyls, and phthalates, etc.), and pharmaceutical (parabens) (Fig. 1). Including this, many types of heavy metals like mercury, lead, cadmium, and arsenic are also categorized as EDCs (Lauretta et al. 2019). A large number of EDCs have been identified their systematic role (table 1).

The widespread usage of EDCs, universal consumption, improper disposal of compounds having EDCs, and accidental discharge are causing the release of EDCs into the environment. A large number of EDCs have been identified in soil and water sources (surface water, groundwater, and sewage water) and are also associated with adverse effects on marine life, make prone to exposure to EDCs. It is found that EDCs can exhibit their role even at very low concentrations (fig. 2) [32, 35]. Thus removal of EDCs from the environment is necessary for human health and urgent

Table 1 – Source and effect of different endocrine disrupter chemicals on human health

Endocrine Disrupter compounds	Sources	Effect on Humans
Bisphenol-A	All plastic containing bags, Food cans, plastic bottles, ATM slips, Shopping bills/slips, Water pipes, Polycarbonate tableware, most of Food containers, Water storage bottles and Baby milking bottles.	Neurological disfunctioning, thyroid disfunction, Breast cancer, Reproductive failure and disturbed sexual behaviour, Heart disease
Arsenic	Pesticides, Wood preservatives, Glass manufacturing, Herbicides, Microwave, Light-emitting, diodes Lasers, Photoelectric cells, and semiconductor devices, Tobacco	Skin cancer, Cancers of the bladder and lungs, Vomiting, Abdominal pain and diarrhoea, increase chances miscarriage, stillbirths, low birth weight, and infant mortality, Skin lesions, decreased performance in tests of intelligence and long-term memory loss, Headaches, Increased risk of diabetes
Mercury	Thermometers, Switches, and Some light bulbs, CFL light bulbs, thermal power plants, Boilers, Steel production plants, Cement plants, Incinerators	Impairment of speech, Skin rashes, Mental disorders like swings of mood and loss of memory, loss or reduction of hearing and peripheral vision, destruction movement coordination like writing or walking, body & hands feels like ‘pins & needles’ feeling every time, Muscle weakness
Dioxin	Meat, Fish, Milk, Eggs and Butter	Diabetes, Heart problems, Reduced fertility, reduced sperm activity and low counts, interfered Embryo development and miscarriage, many type of Cancers
Atrazine	Corn crops, Drinking water	Breast cancer, belated puberty and prostate inflammation in animals, Prostate tumours
Phthalate	Plastics, drinking water bottles, Pesticides, Ventilator tubes, Blood collecting bags and infusion tubing, nutrition feeding bags, soft toys, plastic, food packing	Hormone misbalancing, Lower sperm count and reduced mobility, defects in the male reproductive system by birth, Diabetes, Obesity and thyroid irregularities, uneasy lactation, irregular ovulatory cycles, undescended testicles in men, birth defect in babies, and low numbers of sperm, and testicular tumours and cancers
Triclosan	Toothpaste, Drinking water, Face wash, Detergent, Soap, Antibacterial floor cleaners, Shampoos and conditioners, Shaving gel, Deodorants and antiperspirants	Breast and Liver cancer, risk of food allergy, imbalance hormones i.e male testosterone and female estrogen, and may also influence the thyroid systems, which regulate our body, weight, growth and metabolism.
Perfluorooctanoic acid	Carpet-care liquids, Treated apparel, Treated textiles, Treated non-woven medical use apparel, Industrial flooring wax and removers, tiles, Stone, Food wrapping papers, Dental floss, many cookware	Alteration of thyroid hormone levels. Blood serum levels, decreased semen quality
Organophosphates pesticides	Spray to kill crop pests	Male infertility, bad impact on brain development in kids, and thyroid function
Glycol ethers	Cosmetics, paints, house cleaning products, Brake fluid and oils	Cause problems to Painters, blood abnormalities and lowers sperm counts, reduced fertility, unborn child
Formaldehyde	Woodstoves, Incinerators, Refineries, Forest fires, and fumes, Hair smoothing spa, hair straightening products, skin cleaning agents, Glues	Sino nasal and nasopharyngeal cancer, Skin redness or irritation.
Lead	Paint, Ceramics, Pipes, Gasoline, Batteries, Cosmetics, Food products, Candy, Folk Medicine, Sindoor, Jewellery	High blood pressure, reduced fertility, Nervous breakdown, Muscle and joint pain, Cataracts, Memory or concentration disorders
Perchlorate	Milk, Drinking water, Fertilizers	Body growth and brain development in infants and young children

problem. EDCs are also considered difficult to eliminate from the environment.

Impact of EDCs on Health. Studies on human, animal models, cell lines and epidemiological analysis have revealed that EDCs pose a major worry to public health (table 1). It is found that EDCs follow different mechanisms of action to exhibit their effects. Initially, it was assumed that EDCs performed impairment in the hormonal activity by interacting with nuclear hormone receptors but scientific studies have revealed that EDCs interact with many receptors including nuclear receptors, non-steroid receptors, membrane-bound receptors, orphan receptors, and many pathways such as steroid hormone synthesis or metabolism-related enzymatic pathways, and other mechanisms affecting endocrine and reproductive systems (fig. 2). It is suggested that common disorders caused by EDCs are; problems associated with the female and male reproductive system, cancer, thyroid, metabolic disorders, diabetes, obesity, and cardiovascular diseases [11].

EDCs as the target for degradation are classified based on the functional groups, chemical structures, and pharmacological properties into five different groups such as organic pollutants (dioxins, phenols, and polycyclic aromatic hydrocarbons), hormones having hydroxyl and phenolic carbonyl groups, pesticides containing heterocyclic rings and aromatic rings, plasticizers (phthalates and bisphenols), and additives of personal care (phenones and parabens) [37].

Degradation of EDCs. Different techniques ranging from physical, chemical, and biological have been explored for the treatment of EDCs into complete degradation or conversion into less harmful products form but the wide applicability of EDCs, continuous population rise, and limited waste management approaches have made the removal of EDCs as a challenge. A variety of molecules originating from home and industry are released into water bodies without regulation; including emerging pollutants suspected to have effects on the environment and health [12].

The common methods to remove EDCs from water sources are adsorption, membrane treatment, flocculation, precipitation, and conventional wastewater treatment processes but these con-

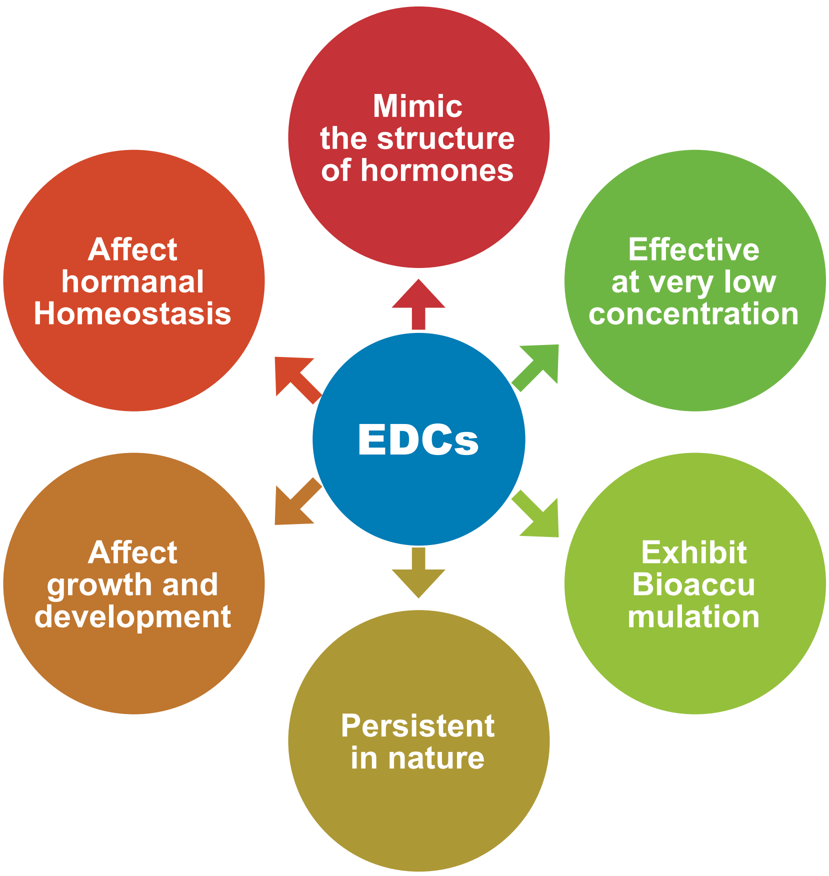

Figure 2 – Different properties of endocrine-disrupting chemicals reflect their health risks

ventional approaches are not efficient and have associated technical limitations [7, 19]. It is found that flocculation and precipitation are not effective in the removal of nonylphenol and Bisphenol A. The removal efficiency for bisphenol A was found less than 10 % [15]. Similarly, the membrane treatment method was not good and failed to remove hormones especially Bisphenol F [15]. Photocatalytic degradation is the process that uses solar radiation to degrade EDCs. Though photocatalytic degradation of EDCs seems to be a considerable approach however the efficiency of the processes is dependent on photocatalyst [26, 37].

Bioremediation or biodegradation is considered an environment-friendly technique to eliminate EDCs. Generally, three types of bioremediation processes are being used for the elimination of EDCs and these are bio-stimulation, bio-augmentation, bio-stimulation, and natural attenuation. There are varieties of microorganisms (Bacillus subtilis, Enterobacter sp., Klebsiella pneumonia, Paenibacillus sp., Phanerochaete chrysosporium, Pseudomonas putida, Serratia marcescens, and Trametes versicolor, etc.) that have been identified for the biodegradation of EDCs [5, 6, 13].

Since aerobic biodegradation of EDCs is very slow and many EDCs may remain present for up to more than 40 years [24]. Thus, there is a requirement for an alternative method that is efficient and fast. Enzyme-based biodegradation of EDCS is an attractive and promising approach for the degradation of EDCs [33]. Among these, oxidative enzymes are the choice of molecules for degradation of EDCs due to their versatility, the possibility of large-scale production, and properties modification [21]. Many types of enzymes used in the biodegradation of EDCs are laccases, lipases, and Peroxidases. Out of these enzymes, laccase is considered one of the promising candidates for the sustainable removal of EDCs. It has been observed that laccase caused enhanced biotransformation of EDCs, such as nonylphenol, bisphenol A, and triclosan. A biodegradation efficiency of 89-100 % has been observed of EDCs removal [16].

Degradation of EDCs using laccase. Laccases are explored in many industrial applications such as textile, food, pharmaceutical, and, pulp

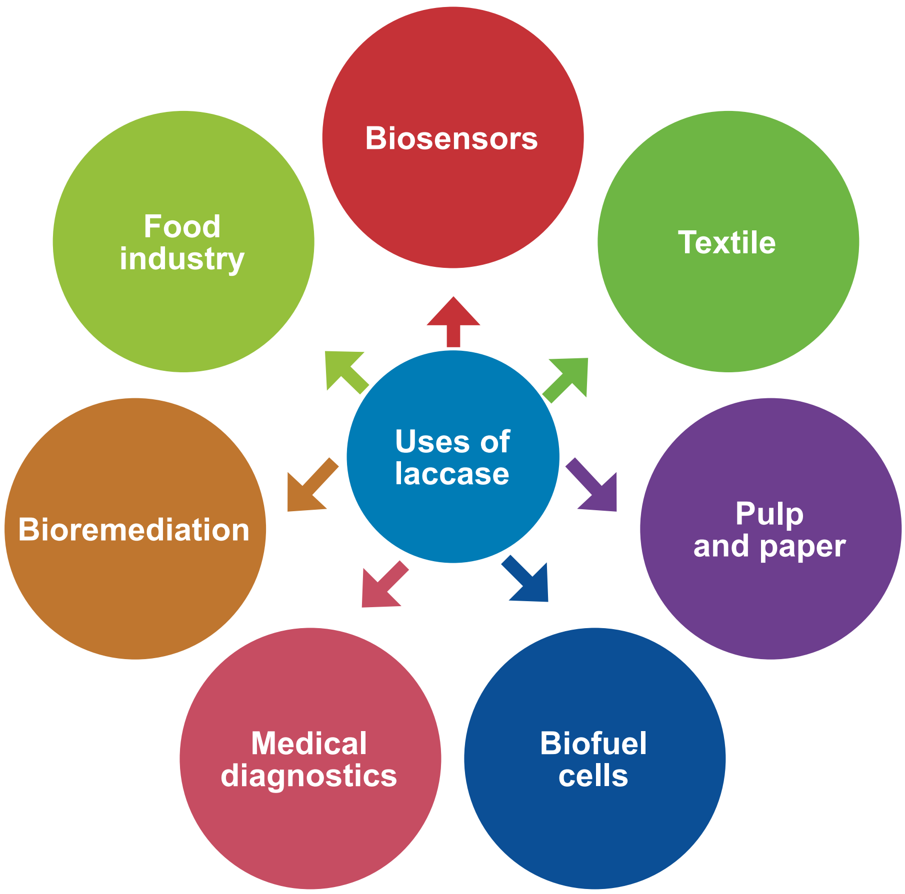

Figure 3 – Applications of laccase in various industrial activities

and paper industry, etc (fig. 3). These enzymes may also be used in the designing of biofuel cells, biosensors, and bioremediation agents. Laccases have attained attention due to their potential to perform oxidation of both nonphenolic and phenolic lignin-related compounds as well as recalcitrant environmental contaminants [9, 27, 29].

Laccase-mediated degradation of emerging contaminants and xenobiotic chemicals is one of the recent and important advantages to treat waste material and drinking water. These are involved in the catalysis of the oxidation of a wide category of xenobiotics compounds with the reduction of molecular oxygen to water. It is suggested that this property (oxidative degradation) has enabled the use of laccase to treat endocrine disruptors attractively than other enzymes because these enzymes do not require additional co-substrate or cofactor for activity. Though, researchers have demonstrated the role of mediators (acetosyringone) to enhance the efficacy of the reaction. Including this, the use of immobilized enzyme techniques is gaining attention as it is considered cost-effective and may be used at the industrial level. It has increased reusability, easier product separation, catalytic stability, and reduction of product inhibition [3, 8].

Natural sources of laccase. Laccases are broadly present in nature and present in a variety of organisms. These enzymes may be isolated from bacteria, fungi, lichen, plants, and insects, etc. Including this, laccases isolated from different sources demonstrate specific sequences and catalytic characteristics. In each category, different organisms produce laccases [9].

Bacteria. Laccases have been isolated from many types of bacteria such as Azospirillum lipoferum, Bacillus, Haloferax volcanii, Klebsiella, Marinomonas, Nitrosomonas, Proteobacterium, Pseudomonas, Streptomyces, and Yersinia [29]. Bacterial laccases have many properties such as stability in the range of pH, temperature, salt concentrations, and organic solvents [18, 29]. It is also found that bacterial laccases show activity in neutral to alkaline pH and these are more stable enzymes as compared to laccases isolated from fungal sources. Bacterial laccases are used in many processes such as metal oxidation, pigmentation, sporulation, UV protection, and xenobiotic degradation, etc. These enzymes are also a very good choice for wastewater treatment at a high salt concentration [34]. Due to the versatility of source microorganisms, bacterial laccases possess optimum alkaline pH, greater thermostability, salt tolerance, and low redox potentials, bacterial laccases are considered valuable functional complements as compared to fungal laccases in various biotechnological and industrial applications [1].

Fungi. Laccase enzymes are produced by Ascomycetes, Basidiomycetes, and Deuteromycetes, and out of these common sources of the fungal laccases are basidiomycetes (white-rot fungi such as Phlebia radiata, Pleurotus ostreatus, and Trametes versicolor). Further, many species of Trichoderma (such as; T. atroviride, T. longibrachiatum, and T. harzianum, etc.) have been studied as a source of laccases [17, 30]. Other fungal sources of laccases are Agaricus bisporus, Coprinus cinereus, Pleurotus ostreatus, Pycnoporus sanguineus and Phanerochaete chrysosporium [4, 36]. Fungal laccases have been found optimally active at acidic pH and they are not active at high temperature. Fungal laccases are generally glycosylated and the sugar portion provides conformational stability to the enzyme and also provides protection against inactivation from radicals and proteolysis [23]. Including this, the recombinant fungal laccases also have been used for the bioremediation process. It is found that most of the naturally occurring species are poor producers of laccases.

Plants. The laccases isolated from plants share their structure and reaction mechanisms with the fungal laccases but plant-based laccases are not extensively used in bioremediation and other industrial applications. Laccases have been isolated from many plants such as; Toxicodendron vernicifluum, Gossypium hirsutum, A. thaliana, Oryza sativa, Nicotiana tabacum, and Asparagus densiflorus, etc [1].

CONCLUSION

Endocrine disruptor chemicals are used in the manufacture of the large number of daily use items and these compounds are released into environment during usage and disposal. These chemicals are found to interfere with the normal activity of hormones. Including this, human exposure to these chemicals may cause growth and development-related health disorders. Thus presence of EDCs in the environment is major health concern and their removal from the environment is required. Different methods are being used for the degradation of ECCs from the environment such as chemical, physical and biological. Out of these biological methods are considered environment frieldly approaches for EDCs removal. Laccase enzyme has many industrial applications including degradation of endocrine disruptors. Laccase enzymes are reported to catalyze the oxidation of various phenolic and non-phenolic compounds. Thus, these enzymes have a wide range of biotechnological and industrial applications and biodegradation of EDCs is considered one of the important usages. These enzymes are produced by microorganisms (bacteria, fungi) and plants. Researchers have used various types of substances as raw material (nutrients) for the growth of microorganisms to produce laccase and nowadays the use of agricultural waste is identified as a cost-effective strategy.

Conflict of interest. No conflict of interest has been declared.

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Reseived 21.06.2023

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ХИМИЧЕСКИЕ ВЕЩЕСТВА, РАЗРУШАЮЩИЕ ЭНДОКРИННУЮ СИСТЕМУ, ИХ ИСТОЧНИКИ, ПРОБЛЕМЫ СО ЗДОРОВЬЕМ И БИОДЕГРАДАЦИЯ С ИСПОЛЬЗОВАНИЕМ ЛАККАЗЫ

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В настоящее время присутствие в окружающей среде химических веществ, разрушающих эндокринную систему, является важным фактором, влияющим на функционирование экологических систем и здоровье отдельных людей. Химические вещества, разрушающие эндокринную систему, присутствуют в широком спектре потребительских товаров и нарушают функционирование гормонов, вызывая проблемы, связанные с ростом и развитием, у людей, подвергшихся воздействию. Лакказа – это медьсодержащий фермент, который продемонстрировал свой потенциал в процессе разложения химических веществ, разрушающих эндокринную систему. Микробиологическое производство лакказы требует богатого источника лигнина наряду с целлюлозой, гемицеллюлозой и другими белками. Таким образом, отходы, богатые лигноцеллюлозой, могут рассматриваться как субстраты для производства лакказы с использованием микроорганизмов. В статье представлен обзор химических веществ, разрушающие эндокринную систему, изучена роль лакказы в биодеградации химических веществ, разрушающих эндокринную систему.

Ключевые слова: химические вещества, разрушающие эндокринную систему, пестициды, ксениботики, биодеградация химических веществ, разрушающих эндокринную систему, лакказа.

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ЭНДОКРИНДІК ЖҮЙЕНІ БҰЗАТЫН ХИМИЯЛЫҚ ЗАТТАР, ОЛАРДЫҢ КӨЗДЕРІ, ДЕНСАУЛЫҚ ПРОБЛЕМАЛАРЫ ЖӘНЕ ЛАККАЗАНЫ ҚОЛДАНУ АРҚЫЛЫ БИОДЕГРАДАЦИЯ

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Қазіргі уақытта қоршаған ортада эндокриндік жүйені бұзатын химиялық заттардың болуы экологиялық жүйелердің жұмысына және жеке адамдардың денсаулығына әсер ететін маңызды фактор болып табылады. Эндокриндік жүйені бұзатын химиялық заттар тұтыну өнімдерінің кең ауқымында болады және гормондардың жұмысын бұзады, бұл әсер еткен адамдарда өсу мен дамуға байланысты проблемаларды тудырады. Лакказа-құрамында мыс бар фермент, ол эндокриндік жүйені бұзатын химиялық заттардың ыдырау процесінде өзінің әлеуетін көрсетті. Лакказаның микробиологиялық өндірісі целлюлоза, гемицеллюлоза және басқа ақуыздармен бірге лигниннің бай көзін қажет етеді. Осылайша, лигноцеллюлозаға бай қалдықтарды микроорганизмдерді қолдана отырып, лакказа өндіруге арналған субстрат ретінде қарастыруға болады. Мақалада эндокриндік жүйені бұзатын химиялық заттарға шолу жасалады, эндокриндік жүйені бұзатын химиялық заттардың биодеградациясындағы лакказаның рөлі зерттеледі.

Кілт сөздер: эндокриндік жүйені бұзатын химиялық заттар, пестицидтер, ксениботиктер, эндокриндік жүйені бұзатын химиялық заттардың биодеградациясы, лакказа.