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Review

Bacterial Laccases as Biocatalysts for the Remediation of Environmental Toxic Pollutants: A Green and Eco-Friendly Approach—A Review

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Abstract: Biological treatment methods for the biodegradation of anthropogenic toxic pollutants are eco-friendly in nature and are powered by a variety of microbial enzymes. Green chemistry and enzymes play a crucial role in catalyzing the biodegradation of organic and inorganic pollutants including azo dyes; polyaromatic hydrocarbons; lead; organic cyanides; aromatic amines; mono-, di-, and polyphenols; polymers; and mercury. Laccases form a prospective group of multifunctional oxidoreductase enzymes with great potential for oxidizing different categories of organic and inorganic pollutants and their diversified functions, such as pigment formation, lignin degradation, and detoxification of industrial wastes including xenobiotics mainly from the pharmaceutical, paper textile, and petrochemical industries. Therefore, it is very important to study laccases as green and environmentally friendly alternatives for the degradation of xenobiotics. This review article will cover comprehensive information about the functions and properties of bacterial laccases for a deep understanding of their scope and applications for effective bioremediation of recalcitrant xenobiotics.

Keywords: biodegradation; laccases; oxidoreductases; green biocatalysts; xenobiotics

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1. Introduction

Laccases are the potential enzymes for oxidoreductases (a broad group of enzymes that catalyze electron transfers from one molecule to another), which are widely distributed in nature in plants, bacteria, fungi, and insects [1–3]. They are suitable for green catalysis, organic synthesis, and the biodegradation of environmental xenobiotics due to their high efficiency and sustainable applications. A wide variety of organic compounds can be oxidized by laccase, and they can be widely applied in the biodegradation of pollutants for detoxification of environments, such as delignification and pulp-bleaching, treatment of textile dyes, wastewater treatment, and treatment of other environmental xenobiotics [4–10].

During the last few decades, laccases from different sources, such as plants, algae, fungi, and bacteria, have been identified. Among all of these, bacterial laccases have drawn great interest due to their good tolerance for organic compounds and high thermal stability. Bacterial laccases have industrial advantages over fungal laccases due to their high activity and high thermal stability, their reactivity over a wide range of pH values, and their resistance to denaturation by detergents as compared to fungal laccases. The enzymes isolated from bacterial cultures are laccase-like enzymes that have been found to resemble fungal laccases; however, their activities are different [11]. The biological functions of laccases can be attributed to the source of origin as well as physiological and pathological conditions [11,12]. The intrinsic characteristics of laccases, such as their efficiency and sustainable applications, make them acceptable as green catalysts for the treatment of xenobiotics and for organic synthesis. Laccases are known as prospective alternatives to conventional synthetic treatment techniques due to their biodegradation potential and minimal side effects [13,14]. These are oxidative biocatalysts containing copper in their active site, and they oxidize different substrates by using molecular oxygen as a co-substrate [15]. Laccase is a very suitable enzyme to oxidize phenolic compounds, dyes, pharmaceuticals, polyaromatic hydrocarbons, pesticides, and other pollutants [16]. During this reaction, four copper atoms are an integral part of the reaction, and the last receptor of the electron is oxygen. The general mechanism of the reaction is shown in Figure 1.

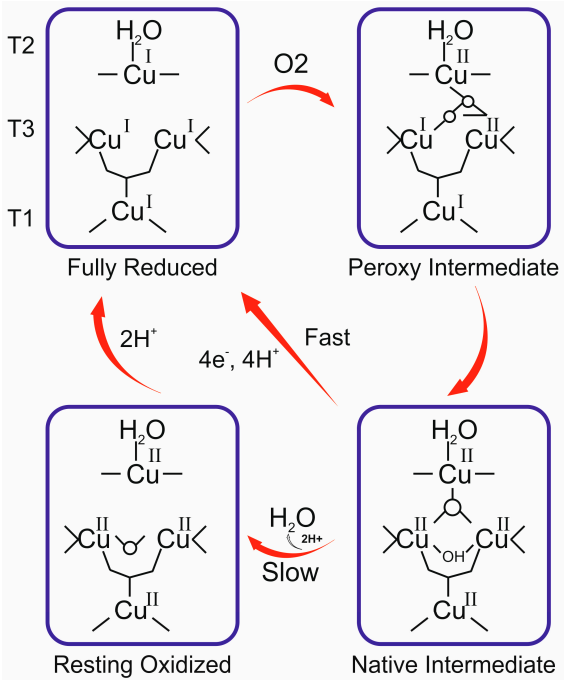

Figure 1. General mechanism of the reaction of bacterial laccases (adopted from [17]).

Laccases have huge applications as green biocatalysts in diversified areas of biotechnology, such as the synthesis of fine chemicals, environmental remediation; biosensor designing; pharmaceutical, cosmetic, and personal care products; decolorization of synthetic dye; and detoxification of the environment by removing recalcitrant xenobiotics [17–19]. Microorganisms are able to produce laccases in their natural habitat in the process of the biodegradation of substrates, protection, virulence, sporulation, and synthesis of pigments [20].

Many studies have been focused on fungal laccases (white rot fungus) due to their high thermal stability, high redox potential, and biotechnological utility [21]; however, the production and utility of fungal laccases are obstructed due to their small tolerance for difficult conditions, low desired pH ranges, lengthy fermentation periods, slower growth rates, and difficulties with heterologous hosts [22,23]. On the contrary, bacterial

laccases have a diverse range of bioremediation potential because the optimal nutrient and environmental conditions are provided by bacteria through biostimulation processes, the ability to tolerate a wide range of temperatures and pH levels, easy genetic manipulations, and exceptional stability in the presence of inhibitors [24]. Nevertheless, the literature survey reveals that not much information is available on bacterial laccases, their detailed properties, and their applications. Furthermore, the mechanism of stability of bacterial laccases at temperature and pH extremes and their enzymatic enantioselectivity have been reported in a few studies only. Therefore, there is a need to understand the role of bacterial laccase in biodegradation along with its molecular properties and mechanism of action. The main aim of this review article is to evaluate the potential for bacterial laccases as biocatalysts in the bioremediation of environmental xenobiotics as green and viable alternatives.

2. Bacterial Laccases

2.1. Sources and Evolution

The bacterial laccase was first reported in *Azospirillum lipoferum*, which was isolated from the rhizosphere (plant root) [25]. Since then, most of the identified laccases have belonged to the Bacillus and Streptomyces genera, such as *Bacillus subtilis*, *Bordetella campestris*, *Caulobacter crescentus*, *E. coli*, *Mycobacterium tuberculosum*, *Yersinia pestis*, etc. [26,27]. Streptomyces laccases work on pigmentation, antibiotics, and morphogenesis, and they are helpful in lignin degradation [28]. Many species have also been reported for the detoxication of post-methanated distillery effluents and pulp–paper waste, which contains chlorolignin [29,30]. According to a recent study, *Bacillus atrophaeus* laccases' genes were coded, which corresponds to a protein with 278 amino acids [31]. Many species of laccase-producing bacteria were reported in the last decade, including *Bacillus* [32], *Pseudomonas* species [33], the *Geobacillus* species [34], *Marinomonas mediterrânea*, and *Pseudomonas putida* [35]. The latest research isolated different strains of laccase-producing bacteria in waste released from the soap industry [36]. The researchers emphasized that the bacterial species may be of significant importance commercially in producing laccase during the scaling-up process at the bioreactor level.

2.2. Production Conditions, Properties, Substrates, and Mediators

Some species of bacteria, such as the *Streptomyces* sp., are known to produce extracellular laccases that are useful in micropollutant degradations [37]. One of the cheaper and more easily available substrates for laccase production is agricultural waste, such as rice bran, banana peel, and sawdust. The production of laccase is significantly affected by the optimum growth time, the intensity of light, the optimum pH and shaking conditions, and the amount of dissolved oxygen and organic salts, though different microorganisms require different amounts of time for an optimum yield of laccase [38] (Figure 2).

A wide range of molecules can be oxidized by laccases, and more than a hundred compounds have been identified as substrates for laccases; however, it is difficult to oxidize all types of substrates directly by laccases due to their large sizes, which obstruct their penetration into the active site of the enzyme, and their high redox potentials. To remove this difficulty, many chemical mediators that are suitably oxidized by laccase are used, and, eventually, the oxidized forms are able to interact with the substrate with high redox potential. Bacterial laccases comprise enzymes with low redox potential, from 0.4 to 0.5 V, which can withstand more difficult conditions than fungal laccases [30]. Table 1 shows an overview of a few bacterial organisms and substrates along with some optimum conditions for action.

Table 1. Production conditions and characteristics.

Name of the Organism	Substrate Used	Optimum Temperature for Activity (°C)	Optimum pH of Activity	Mol. Wt. of Protein	References
Aquisalibacillus elongatus	2,4-dimethoxy phenol	40	8.0	69	[38]
Azospirillum lipoferum	Syringaldazine	70	6.0	81.5	[39]
Bacillus Subtilis MTCC1039	Guaiacol	30	5.0	NR	[40–42]
Bacillus Subtilis MTCC 2414	Guaiacol	30–40	7.0	NR	[41–43]
Bacillus cereus TSS1	Guaiacol	37	7.0	NR	[42–44]
Bacillus tequilensis SN4 MTCC 11828	2,4-dimethoxy phenol	85	8.0	75% pH	[43–45]
Bacillus safenis DSKK5	NR	37	6.2	NR	[31,44,45]
Bacillus subtilis WPI	2,2′-azino-bis(3-ethylbenzothiaziline-6-sulphonic acid	25	NR	NR	[31,45,46]
Bacillus licheniformis LS04	2,2′-azino-bis(3-ethylbenzothiaziline-6-sulphonic acid 2,4-dimethoxy phenol Syringaldazine	60	4.4	NR	[31,45,46]
Pseudomonas aeruginosa	2,2′-azino-bis(3-ethylbenzothiaziline-6-sulphonic acid	35	6.0	NR	[46–48]
Pseudomonas putida F6Q	Syringaldazine	30	7.0	59	[47–49]
Stenotrophomonas maltophilia	Syringaldazine	60	6.8	NR	[48–50]
Streptomycetes species	2,2′-azino-bis(3-ethylbenzothiaziline-6-sulphonic acid	35	6.0	NR	[46–48]
Streptomycetes cyaneus	2,2′-azino-bis(3-ethylbenzothiaziline-6-sulphonic acid	60	4.5	NR	[49–51]
Streptomyces bikiniensis	Syringaldazine	6–7	50–60	69	[50–52]
Geobacillusthermocatenulatus	2,2′-azino-bis(3-ethylbenzothiaziline-6-sulphonic acid	37	6.2	NR	[51–53]
Bacillus HR03	Syringaldazine, 2,4-dimethoxy phenol	55	5.5	20	[31,52,53]
Pseudomonas desmolyticum	Hydroquinone	60	4.0	43	[31,53,54]

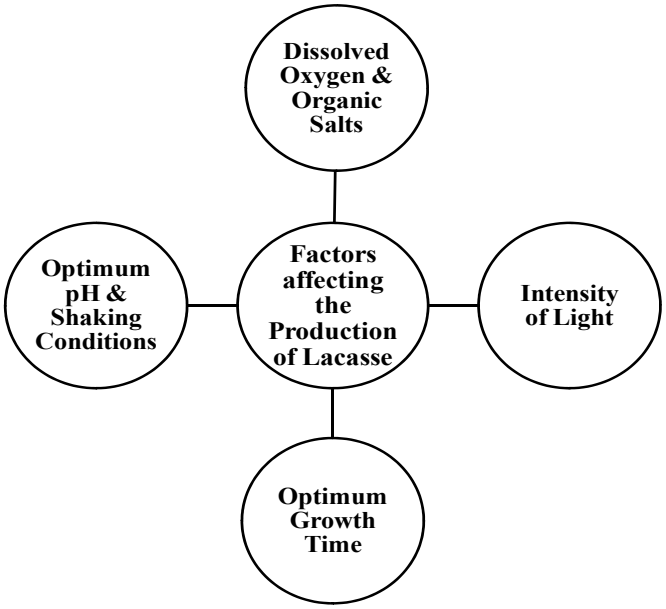

Figure 2. Factors affecting the production of Laccase.

Laccase is a type of enzyme that is substrate-specific, which oxidizes a wide range of substrates, acts as a biocatalyst in the synthesis of organic compounds, and stops reactions of many aromatic organic contaminants. The degradation of highly toxic contaminants leads to a green and eco-friendly environment, and the organic synthesis via the production of nonhazardous by-products leads to bioremediation [38,39]. Substrates such as 2,2′-azino-bis (3-ethylbenzothiazoline6-sulfonic acid), 2,6-dimethylphenol, syringaldazine, guaiacol, etc. are extensively used and are the most commonly used substrates for enzyme assays. The binding of the substrate with protein by using syringaldazine is shown in Figure 3.

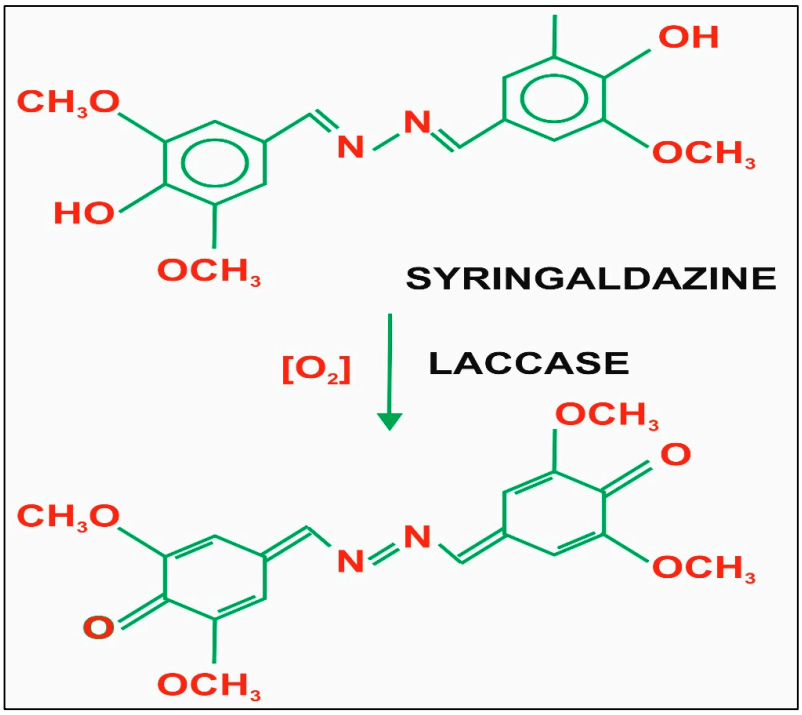

Figure 3. Structure of the substrate syringaldazine [55].

Substrates with a large redox potential, such as azo dyes, anthraquinolic dyes, etc., are not degraded or oxidized by laccase, directly. These kinds of substrates require an electron shuttle mediator between the laccase and themselves [40]. Basically, the mediators are those low molecular weight laccase substrates whose enzymatic oxidation produces stable intermediates with high oxidation potential. The first kind of such a synthetic mediator was 2,2′-azino-bis (3-ethylbenzothiazoline6-sulfonic acid), which is used to function as a laccase substrate mediator with enhanced enzyme action [41].

In liquid media, the growth of bacteria is usually faster than that of fungi, which favors scaling-up processes for the production of laccase [56]. In different bacteria, different inorganic metals and detergents affect the yield of laccase distinctly. In many cases, inorganic metals (Mg^{+2}, $Hg^{+2,}$ and Zn^{+2}) highly inhibit the activity by changing the protein conformation, indicating that the enzymatic yield of laccase was not dependent on positively charged metals [57]. According to one hypothesis, Hg^{+2} decreases the yield of laccase, which shows the important role of a thiol-possessing amino acid in laccase activity [58,59].

3. Catalytic Activity and Substrate Specificity

As compared to fungal laccases, bacterial laccases find few industrial applications due to their low expression levels and catalytic feature. Recently, attention has been paid to the engineering of bacterial laccases, such as directed evolution approaches, heterologous functional expression, etc., which have been used by many researchers to reduce these hurdles. The relationship between the laccase's structure and function has been determined recently with the resolution of the crystal structure of many laccases [60]. The 2,2′-azino-bis(3-ethyl benzothiazoline-6-sulphonic acid bound structure shows that 23 amino acids surround the substrate, among which His419, His497, and Cys492 are coordinated with T_1Cu, and a disulfide bond is formed between Cys229 and Cys322. The five residues remain unaltered [61]. The catalytic efficiency is influenced by the mechanism of mutation, which is the change in the interaction between the enzyme and the substrate, as well as the variety of redox potential in the T_1Cu site. The quantity and length of the hydrogen bonds may also be changed between the laccase's pocket residues and the substrate. Figure 4 shows the catalytic action of the laccase.

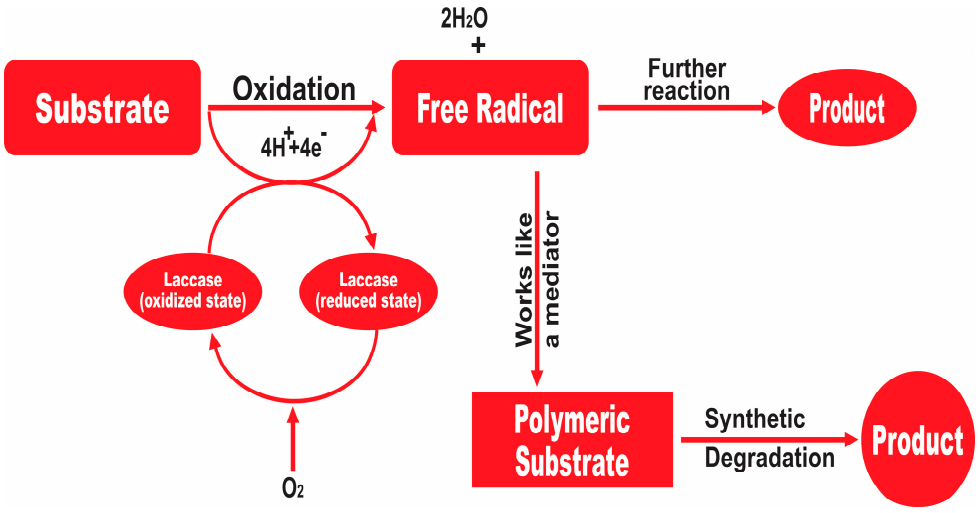

Figure 4. Catalytic action of laccase.

Laccases have low specificity to the substrate and are adaptable to a high variety of chemical compounds released from several industries that continuously expand their diversification according to the evolution of human impact on the environment, but there are challenges, such as the optimization of the process of biosynthesis and the action of these enzymes to the level of industrial applications. Since the biosynthesis of enzymes through microbes is an expensive process, the use of cheap culture media, mutant strains

with good productive potentials, and the cultivation of fungi under solid-state fermentation with the synthesis of laccases can reduce the cost of the biosynthesis process. Another way to cut costs is the treatment of xenobiotics at the source itself, where the enzymes are present in minimal amounts. In order to ensure environmental sustainability, regular monitoring of the technological processes and technologies is a must. As a result of technological advancements, only laccases are now studied extensively.

4. Factors Affecting Degradation of Pollutants by Microbial Enzymes

The biodegradation of industrial pollutants is greatly influenced by chemical factors (such as chemical structure, especially the functional group of the pollutant, concentration, etc.), physiochemical and environmental factors (such as pH, temperature, aeration, BOD, salinity, etc.), and the type of microbial consortia used for the degradation of pollutants. For instance, textile dyes with low molecular weight and simple structure exhibit higher color removal rates than azo dyes with structural complexity. Singh et al. reported in their study that the enzymatic degradation of azo phenol is enhanced by electron-donating substituents, such as methoxy and methyl groups, while electron-withdrawing groups inhibit oxidation [62]. Among the environmental factors, the temperature is a very important factor that affects the functioning of both intracellular and extracellular microbial enzymes. At low temperatures, the enzymatic activity is reduced, thereby reducing the rate of microbial degradation of a pollutant [63]. However, the efficiency of enzymatic degradation potentially depends upon the availability, activity, and adaptation of the chosen microorganism. For instance, petroleum hydrocarbon degradation is mainly affected by the availability of a microorganism that can catabolize pollutants [64].

5. Applications of Laccases

Laccases as biocatalysts are gaining popularity in different fields from the application point of view. Laccases are potential green, biological tools that work efficiently in the air and release water as the only by-product. Hence, laccases, especially bacterial and fungal laccases, have wide applications when applied in different areas (Figure 5).

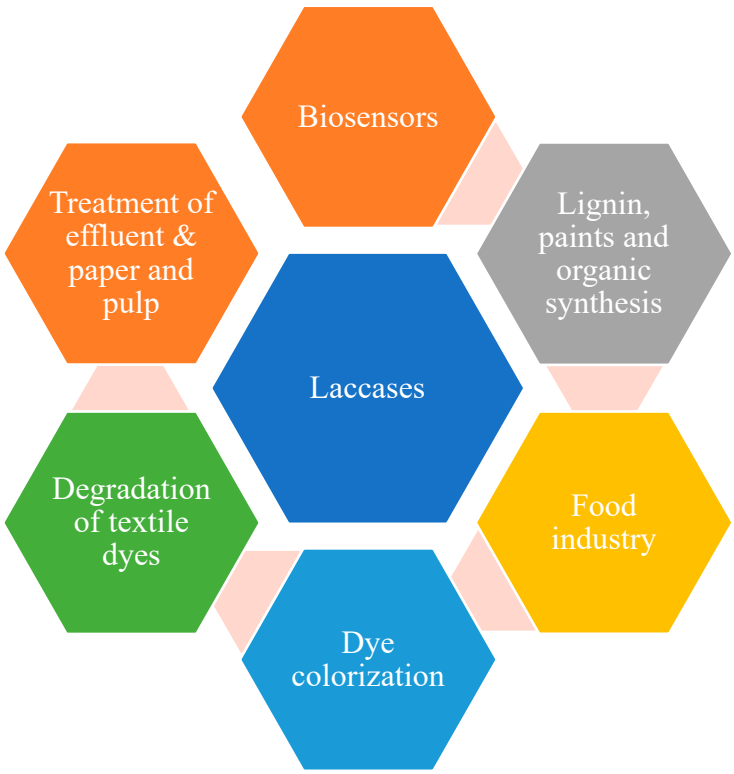

Figure 5. Applications of laccases.

5.1. Detoxification and Bioremediation of Industrial Effluents

Bacterial laccases have the capability of oxidizing all kinds of substrates, whether toxic or non-toxic. Various effluents from industries such as the pulp–paper, textile, pharmaceutical, distillery, and food industries are also treated by bacterial laccases. In the pulp–paper industry, laccase has become known for the removal of black liquor and the wastewater produced from pulp–paper mills [65]. Laccases work on phenolic lignin fragments in which the substrate reacts with the lignin polymer, resulting in the degradation of the lignin. Though decolorization by chemical bleaching is very effective, these methods have serious drawbacks due to the release of toxic byproducts. Delignification by laccase systems is a better method for reducing toxicity, and it has been adapted to current pulp production lines as a green and sustainable alternative.

5.2. Textile Dye Degradation and Decolorization

Chemicals of diverse compositions, ranging from organic to polymer products, are used in the textile industry. The chemical structure of dyes makes them fade-resistant on exposure to chemicals, heat, light, and water, and synthetic dyes hardly decolorize due to their synthetic nature. Many dyes are prepared from aromatic organic compounds, such as benzidine, which are highly carcinogenic [65]. Consequently, the textile industry's effluents, when disposed of in water, reduce light penetration into the water and strongly affect the photosynthetic process of green aquatic plants [66].

The contaminated water may be carcinogenic and pose threats to the environment and marine life due to the presence of degraded dye products, metals, halogens, etc. [67–69]. The laccases are considered promising solutions for chemically diversified dyes, including synthetic dyes [70,71]. The released reactive dyestuff can be bleached quickly by laccase as a part of the washing solution, which results in less processing time, cost, energy, and volume of water required for the desired quality of textile [72]. Laccases have been widely studied for the degradation of azo dyes [73,74]. The decolorization of some synthetic dyes, such as methyl orange, Congo red, methylene, and toluidine blue, etc., and the industrial effluents were achieved by the bacterial species *S. maltophilia* AAP56 [75].

5.3. Bioremediation of Food Industry Wastewater Effluents

The wastewater effluents released from the food industry contain a remarkable number of aromatic compounds, especially phenols, which have toxic effects on health [76]. According to a study, approximately 40–90% of phenolic compounds are removed in a co-immobilized form by 95% of the laccase units in a bioreactor [77]. Organic gel-trapped laccase removes organic aromatic compounds from aqueous suspensions, and the enzyme is reused without any efficiency loss [78]. Dark brown wastewater released from beer factories has a high concentration of polyphenols in bioremediation via *C. gallica* [79]. Sugarcane factories release vinasse as a by-product in the production of ethanol, which contains toxic organic matter and is also treated by the laccase from *T. versicolor* [74,80].

5.4. Other Applications

Many reports have shown that xenobiotics can also be degraded by laccases. According to a recent report, the bacterial laccase CueO's mutations of chemical plant sludge displayed that the mutants G276R, G276N, G276Y, and G276K can oxidize the carcinogen benzo[α]pyrene very efficiently [81]. The degradation of Tyramine (a toxic compound in food) by laccases can resolve the problems generated in food. In addition to the applications discussed above, laccases are also used in the production of polymers [82], indo-dye synthesis [83], biosensors, and bioremediation [84,85]. Laccases are green catalytic enzymes with great potential for the biodegradation of environmental xenobiotics. They have great potential for biotechnological applications, such as biosensors, biopulping, biobleaching, organic synthesis, biofuels, antimicrobial applications, etc. Laccases are currently being represented as the latest topic of research for the biodegradation of xenobiotic compounds, pharmaceutical products, and different dyes in an eco-friendly manner [86–92].

6. Conclusions and Future Prospects

This review article encompasses the latest available reports about the role of laccases as a green solution to the biodegradation of environmental contaminants and as biocatalysts. Laccases have huge potential in the bioremediation of waste generated by several industries, such as the pharmaceutical, pulp–paper, textile, and food industries, among others. Laccases are very useful novel biocatalysts in many industrial applications due to the versatile nature of the substrates. Efforts have to be made to design biodegradable dyes to enhance decolorization by laccase by using a modified substituent. Further research should put more focus on the natural mediators produced by laccase in a bio-environment during the degradation of lignin and the development of immobilized laccases that use an eco-friendly nanomaterial that can be recycled and hence reused. A greater understanding of the functioning of laccase will enhance the development of more economical and efficient applications of laccases.

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