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REVIEW ARTICLE

Immobilized laccase: an effective biocatalyst for industrial dye degradation from wastewater

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Abstract

Environmental concerns due to the release of industrial wastewater contaminated with dyes are becoming more and more intense with the increasing industrialization. Decolorization of industrial effluents has become the top priority due to the continuous demand for color-free discharge into the receiving water bodies. Different dye removal techniques have been developed, among which biodegradation by laccase enzyme is competitive. Laccase, as a green catalyst, has a high catalytic activity, generates less toxic by-products, and has been extensively researched in the field of remediation of dyes. However, laccase's significant catalytic activity could only be achieved after an effective immobilization step. Immobilization helps strengthen and stabilize the protein structure of laccase, thus enhancing its functional properties. Additionally, the reusability of immobilized laccase makes it an attractive alternative to traditional dye degradation technologies and in the realistic applications of water treatment, compared with free laccase. This review has elucidated different methods and the carriers used to immobilize laccase. Furthermore, the role of immobilized laccase in dye remediation and the prospects have been discussed.

Keywords Immobilization · Remediation · Wastewater purification · Green catalyst · Biodegradation · Industrialization

Introduction

Dyes are an important class of natural and man-made colored substances that have a diverse range of applications in chemical industries (pharmaceutical, pesticide), paper and textile plants, coal refineries, beverages, and food industries due to their aesthetic and other functional properties (Selvaraj et al. 2021). It is estimated that about 800,000 tons of dyes are manufactured globally from different industrial sectors out of which 200,000 tons are contributed from the textile industries (Solayman et al. 2023). Dyes released in the water bodies are mostly resistant to decolorization and persist on the water surface for a longer duration. This hinders the penetration of sunlight into the water bodies affecting photosynthetic activity, preventing plant growth, providing bioaccumulation, and promoting toxicity (Birhanlı et al. 2022). Most of the dyes are toxic and recalcitrant in nature due to the presence of phenolic rings and functional groups which cause severe threats to the living ecosystem and detrimental damage to the natural resources (Sarkar et al. 2017).

Diverse physical and chemical methods such as membrane filtration, adsorption, advanced oxidation, the Fenton process, ozonation, irradiation, and coagulation have been used to degrade the dye contaminants in industrial wastewater (Khan et al. 2023). Membrane filtration can clean, concentrate, and remove the color from wastewater in practical applications and has many distinct features such as resistance to microbial attack, temperature, and chemical toxicity. The ion exchange process is efficient in the degradation of soluble dyes, and there is no loss of adsorbent during the regeneration process. The advanced oxidation process has gained importance as this technique completely degrades the dye into CO_2 and H_2O and requires a short reaction time (Valli Nachiyar et al. 2023). However, the high operating cost, clogging of the membranes, use of chemicals, the release of secondary pollutants, and a large amount

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of sludge formation have limited the utility of the above methods (Solayman et al. 2023). Therefore, it is crucial to use sustainable and environment-friendly solutions for the remediation of dye pollutants and their derivatives present in industrial effluents. In this context, the biodegradation of dyes by the use of biological methods, i.e., by the application of biocatalysts, seems to be a promising approach (Zdarta et al. 2018a). Biocatalysts, due to their high efficiency, eco-friendliness, excellent chemo, stereo, and regio-selectivity, are a great substitute for the traditional chemical catalyst. Enzymes can operate over a wide range of pH, temperature, and salinity range for high and low contaminant concentration and can catalyze targeted conversion reactions without the need for chemical solvents, high temperatures, and pressures. Various biocatalysts, such as azoreductases, phenol oxidases, and peroxidase, have been applied in the degradation of natural and synthetic dyes from water resources (Daronch et al. 2020). Azoreductase can only degrade azo dyes and require the presence of additional cofactors such as $NADH_2$ and $FADH_2$, whereas peroxidases can catalyze the reactions only in the presence of hydrogen peroxide and can only degrade synthetic dyes. Phenol oxidases are a group of enzymes that can degrade a large group of synthetic dyes without the additional need for a cofactor.

Laccase (EC: 1.10.3.2) is one of the most abundant polyphenol oxidases that can efficiently degrade a large number of recalcitrant compounds in the presence of atmospheric oxygen and release water as a single by-product (Daronch et al. 2020). The typical laccase structure generally consists of 500–550 amino acids with a molecular weight of about 50–130 kDa and having four copper ions in its catalytic center. The T1 (type I) copper gives an intense blue color to the enzyme and is electron paramagnetic resonance (EPR) detectable. The T2 (type II) copper is also EPR detectable but is colorless whereas the T3 (type III) copper gives no EPR signal. The T2 and T3 copper atoms form a trinuclear cluster where the binding and multielectron reduction of dioxygen takes place as depicted in Fig. 1 (Gu et al. 2021).

The excellent catalytic properties, selectivity, and diverse substrate range of laccases make it a promising biocatalyst in water treatment (Kapoor et al. 2021; Chen et al. 2022). However, different factors such as high enzymatic cost, ineffective recovery of product and enzymes, structural and functional instability under adverse conditions of temperature, pH, solvents, and sensitivity towards denaturing agents have limited the practical applications of free laccase (Daronch et al. 2020; Zhou et al. 2021). Immobilization of laccases on suitable support can overcome these challenges and enhance the potential applications of laccase in wastewater treatment processes. Immobilization offers multiple advantages, such as excellent catalytic activity, an increase in mechanical resistance, and enhanced stability towards a broad range of temperatures, pH, storage, and other operational conditions (Zhou et al. 2021; Sutaoney et al. 2022). Immobilization also causes the dispersion of enzyme molecules, leading to better accessibility towards the substrate molecule and extra stability of the enzyme towards denaturation by the organic medium. Additionally, immobilization smoothens the execution of the reaction due to the facile separation of the enzyme from the product. This not only helps in minimizing the protein contamination in the product but also helps in the efficient recovery and reusability of enzymes, thus increasing their economic viability and enabling their usage in batch, fed-batch, and continuous mode operations (Chen et al. 2022; Lou et al. 2023). This review aims to cover recent studies on methods of laccase immobilization, support materials used, and their comparative performances. It also gives insight into the mechanism of dye degradation

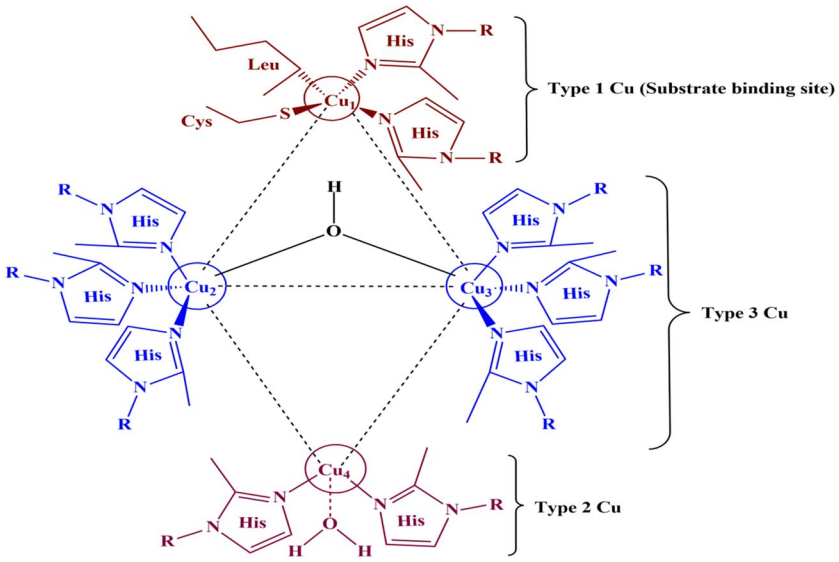


Fig. 1 Structure of laccase active site (Malhotra and Suman 2021)

through immobilized laccases and the role of mediators. Additionally, the review summarizes the degradation efficiency of different industrial dyes by immobilized laccase obtained from different sources.

Laccase immobilization methods

Immobilization of enzymes occurs through reversible and irreversible coupling methods that can be physical or chemical, depending upon the force of attraction. Figure 2 presents different methods of immobilization of laccases. These immobilization methods exhibit different properties, advantages, and drawbacks, as elaborated in the following section.

Adsorption

Adsorption is a simple and inexpensive immobilization method in which laccase accumulates on the surface of the solid support via physical adsorption (hydrophobic, hydrogen bonding, and van der Waals interactions) or ionic adsorption (by ionic interactions). Efficient physical adsorption occurs only when the adsorbent's pore size is 1.2–1.7 times larger than the adsorbate molecule (Chen et al. 2022). In several studies, laccase immobilization through adsorption has been performed by simply mixing the enzyme with a specific adsorbent. The free and loosely bound enzymes are removed after a wash, and the derived immobilized enzyme is used in its native form (Sharma et al. 2021; Gu et al. 2021). Immobilization via adsorption is a fast, worthwhile technique that requires mild operating conditions and no alteration in the conformation of laccase. The immobilization efficiency depends on different parameters such as pH, the ionic strength of the medium, and the hydrophobicity of support. However, the weak binding force results in the leaching of laccase, causing reduced catalytic activity (Gu et al. 2021). Carriers used in this method to be eligible for adsorption should have a high mechanical and chemical resistance and a large surface area. Agarose, ion exchange resins, bentonite, cellulose, porous glass, graphene, fullerene, and many other supports have been used in physical and ionic adsorption (Zhou et al. 2021). Silica-based support materials have been frequently utilized as a carrier for laccase immobilization via adsorption due to their ordered porous structure, tuneable pore size, high surface area, and improved thermal resistivity (Zdarta et al. 2018a). Organic supports are also suitable for the adsorption of laccase enzymes due to adequate porosity and surface properties. Hence, biochar from various sources is getting wide attention for the adsorption of laccase enzymes (Pandey et al. 2022).

Entrapment

Entrapment is another physical method of immobilization in which laccase is physically confined in a polymeric matrix (organic polymer or silica sol–gel) where the substrate and product can be transferred outside the matrix, but the enzyme cannot (Zhou et al. 2021). In this method, laccase

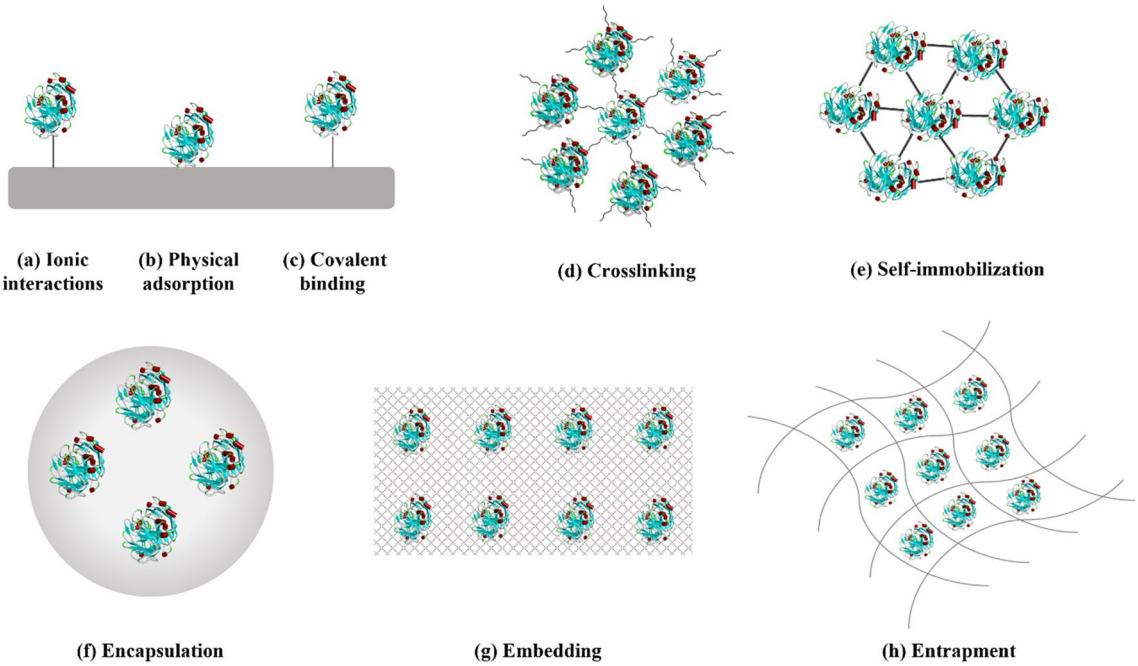


Fig. 2 Different methods of immobilizing laccase

is first added to the monomer solution, which leads to its entrapment by the subsequent polymerization process, thus preventing direct contact of the enzyme with the environment. This process is simple, economical, cost-effective, and requires mild immobilization conditions. Additionally, there is no structural change due to the absence of a covalent bond between the enzyme and substrates (Daronch et al. 2020). Laccase immobilization through entrapment is an environment-friendly, cost-effective, and easy immobilization technique. Entrapment is commonly used in combination with cross-linking methods, which enhances the polymerization of laccase with free amino groups due to the introduction of electrostatic interactions and cross-linking agents, thus resulting in stronger covalent bonds (Chen et al. 2022). However, this technique has a high diffusion barrier and mass transfer limitation between the enzyme's active sites and substrate. This allows the movement of only small molecules and may inhibit macromolecular structures from crossing the network. Therefore, the selection of the pore size of the carrier plays a critical role in entrapment. Polymers of natural origin (bio-polymer) such as agar–agar, polyacrylamide, collagen, and gelatin have been applied for the entrapment of fungal laccases (Asgher et al. 2017).

Covalent immobilization

Covalent immobilization is a chemical method where the reactive groups present on the carrier (support) surface interacts with the protein's amino acid side chain residues (Chen et al. 2022). The protein functional groups mainly contain nucleophilic amino acids (lysine, histidine, and arginine) and thiol (cysteine) that form covalent bonding. The side chain of the lysine residues, called epsilon (ε) amine, is mainly used for covalent attachment to the support material (Wang et al. 2023). Strong covalent bonds are formed at the enzyme's surface between the non-essential amino acids and support material, due to which the amount of enzyme leakage decreases significantly. Due to the presence of a positive charge at physiologic conditions, the primary amines are outward-facing and often located on the protein surface, and they are usually accessible for conjugation and provide good bond stability without denaturing the protein structure (Rodrigues et al. 2021). Proper immobilization requires a condition where the enzyme's reactive group should react with a functional group of support, but usually, the functional group available on the support materials is not active enough to react with the enzyme's active group. Therefore, modification or activation of the solid support is required to generate the activated group. Functional group activation may be done in the enzyme, but due to limitations in alteration, activation of support materials is preferred. However, it is also necessary to prevent the involvement of active site amino acid binding with support as it could lead to the complete loss of immobilized enzyme activity (Habimana et al. 2021; Rodrigues et al. 2021; Wang et al. 2023). Enzymes often become more stable after being covalently immobilized, making them more resistant to a broader range of temperatures and pH levels than free enzymes. Because of these properties, laccase enzymes have been immobilized several times on various support materials such as SiO_2 graphene oxide (GO), nanocarriers, and, glutaraldehyde as a linker for the enhancement of catalytic activity, stability, and reusability in dye degradation studies (Kashefi et al. 2019). Epoxy-activated supports such as Eupergit have been used frequently due to their ability to react with all nucleophile groups present on the protein surface such as lysine, histidine, cysteine, and tyrosine. A crude laccase from *Trametes versicolor* has been immobilized on polyacrylamide alginate cryogel for the degradation of dyes and wastewater treatment. Inorganic ceramic supports have also been used for the covalent immobilization of laccase (Yavaşer and Karagözler 2021). Nanotubules, due to their unique features such as high mechanical strength, excellent biocompatibility, high enzyme loading, and quick mass transfer, have been used as a support material in the covalent immobilization of laccase (Habimana et al. 2021).

Cross-linking

In this method, the intermolecular cross-linkage is achieved between the enzyme molecules and bi- or multifunctional reagents, in which the enzyme acts as its carrier. Cross-linking is an attractive immobilization method due to its scalability and robustness; however, the choice of concentration and time of cross-linking has a considerable role in laccase immobilization. Glutaraldehyde is the commonly used reagent for cross-linking due to its low cost, robustness, and ease of availability (Sharma et al. 2021; Chen et al. 2022). Increasing interest has been developed for cross-linked enzyme crystals (CLECs) and cross-linked enzyme aggregates (CLEAs), which are carrier-free immobilization methods. Altus Biologics used CLEC as an industrial biocatalyst for the first time in the 1990s. It has been proved earlier that CLECs are significantly more stable to denaturation by heat and solvent than soluble and lyophilized (freeze-dried) powder (Wang et al. 2023). The operational stability and reusability of CLECs are ideally suited for industrial applications. On the other hand, disadvantages associated with CLECs include the high cost caused due to the laborious procedure and the high purity of enzyme required for crystal formation (Chen et al. 2022). Cross-linked laccase crystals (CLLC) showed 113%, 173%, 114%, and 139% higher degradation efficiency than the free laccase from the wastewater contaminated with dye from the Chenab Textile Industry, M-tax, Sitara, and National Silk and Rayon Mills, respectively (Perveen et al. 2022).

CLEAs are produced by simple precipitation of the enzyme from an aqueous solution by adding precipitating agents such as ammonium sulfate, acetone, and ethanol, followed by a cross-linker (Wang et al. 2023). In the CLEA methodology, the enzyme from the crude fermentation broth can be directly used for immobilization. Purification and immobilization of enzymes take place simultaneously as a single unit operation, and therefore, the purity of the enzyme is not a concern. This methodology has also been applied to cofactor-dependent enzymes (Zhou et al. 2021; George et al. 2023). The single-step process of CLEA has many benefits, such as ease of preparation and handling, cost-effectiveness, rapid recovery, reusability, and extra stability towards heat denaturation, autoprotein hydrolysis, and organic solvents (Bilal et al. 2021; Chen et al. 2022). Because of the various advantages of this carrier-free immobilization technique, it has been utilized for the immobilization of laccases from bacterial and fungal sources. CLEAs are typically extracted from the reaction mixture using filtration or centrifugation. However, these separation procedures would result in internal mass transfer restrictions if CLEAs are clumped together. To solve this issue, magnetic nanoparticles (MNPs), that are easily recycled using an external magnetic field, are added to create magnetic CLEAs (M-CLEAs). The preparation of several M-CLEAs of fungal laccases to remove environmental contaminants has been proven to be successful (Wang et al. 2021). However, CLEA due to its harsh operating conditions, leads to a considerable loss of enzyme activity, making it difficult to control particle size and processing (Chen et al. 2022).

Encapsulation and embedding

Encapsulation involves trapping the substance to be immobilized within a separate, distinct compartment or capsule made of a different material than the matrix or support material. The substance is enclosed within the capsule, forming a discrete entity within the matrix or support material. The capsule acts as a protective barrier that separates the immobilized substance from the surrounding matrix or support material, providing a physical barrier and preventing direct contact between the substance and the matrix or support material (Majewski et al. 2017). Encapsulation allows the co-immobilization of coupled enzyme systems to carry out multi-enzyme reactions but limits the mass transfer. The sol–gel silica matrix, layer-by-layer (LBL) techniques, alginate beads, emulsion spinning, and metal–organic framework (MOF) have been used for laccase encapsulation (Cao et al. 2021). Patel and co-authors observed improved laccase encapsulation yield (90.1%), by zinc and laccase-based inorganic-protein hybrids, thus demonstrating a favorable effect of metal ions on laccase encapsulation (Patel et al. 2022). Metal–Organic Framework, due to their remarkable functionality, surface area, and pore size, is an outstanding support material and has been widely used for laccase encapsulation (Birhanlı et al. 2022). In the application of wastewater treatment study, laccase was encapsulated in copper alginate beads with a magnetic core shell. It was observed that out of the total laccase loaded, 85.5% was immobilized on the bead, and no structural change was observed in the actual wastewater condition. Laccase activity was enhanced due to the release of copper ions from the gel matrix of the copper alginate system which in turn interacted with the active center of laccase thus increasing the reaction rates (Le et al. 2016). Enzyme stabilization against microbial degradation in actual bioremediation processes is a challenge. The encapsulation method has been used with nanoparticles to overcome the degradation possibility of laccase, and notably, considerable improvement in the stability of nano-encapsulated laccase against microbial degradation in wastewater has been reported (Koyani and Vazquez-Duhalt 2016).

Embedding refers to the process of incorporating the substance to be immobilized directly into the matrix or support material during its formation. The substance is homogeneously distributed within the matrix and becomes an integral part of the matrix with no clear demarcation between the substance and the matrix. Embedding uses natural gels such as agarose gels, gelatin, alginate, and synthetic gels like poly-acrylamide and polyvinyl alcohol for embedding the enzyme. Alginate, due to its non-toxicity and moderate gelling properties, is the most commonly used biopolymer for embedding (Wang et al. 2023). Laccase immobilized via embedding on Ca-alginate beads retained 87% of its initial activity after 20 days of storage in comparison to the free laccase (22%). The immobilized laccase also had a 20% higher pH (7.0–9.0) stability than the free laccase and retained 91.2% of its activity after 1.5 h of incubation at 55 °C (Daâssi et al. 2014). The embedding method due to its ease of operation and minimal enzymatic loss is the most commonly used method for enzyme immobilization for industrial applications. However, embedding has certain limitations on pore diffusion, leakage of the enzyme, and microbial contamination (Wang et al. 2023).

Two-step immobilization

To increase the efficiency of immobilization, different immobilization methods can be combined so that the obtained method has an overall better performance. The physical method of immobilization is favorable in stabilizing the immobilized enzyme's catalytic activity, whereas the chemical method helps in maintaining stability. Combining these methods could be considered an efficient technology to produce immobilized enzymes possessing both the features of physical and chemical methods (Zhou et al. 2021). Ji and co-authors immobilized laccases via physical adsorption and

chemical bonding on a PVDF membrane coated with carbon nanotubules. The prepared biocatalytic membrane had excellent stability, reusability, and regeneration ability (Ji et al. 2016). In another study, immobilization of laccase was performed over a magnetic amino-functionalized metal–organic framework. Due to the benefits of two-step immobilization, covalent binding, and adsorption, the immobilized laccase demonstrated exceptional resilience to extreme temperatures and pH levels, as well as enhanced immobilization efficiency and substantial activity recovery (Amari et al. 2021). Laccase immobilized on alkali-modified biochar with combined adsorption, and crosslinking method had a significant immobilization yield (67.40%) and enzyme loading (180.81 mg/g) efficiency (Wang et al. 2022a). A combination of different methods used in laccase immobilization is depicted in Fig. 3.

Laccase immobilized carriers and their advantages

To have a high-quality immobilized laccase enzyme for bioremediation, not only optimization of the immobilization techniques is required, but also the selection of carrier used as supporting material is crucial. The suitable carrier material should be non-toxic, inexpensive, eco-friendly, have high loading capacities, prevent undesired adsorption and denaturation, and be conductive to boost the stability of immobilized laccase by safeguarding the laccase structure from harsh environmental conditions (Daronch et al. 2020; Somu et al. 2022).

The laccases have been immobilized on various support materials using the above-discussed methods of immobilization and different yield and kinetic parameters were reported. The information on support materials used for immobilization is presented in Table 1.

The carrier materials can be broadly classified into organic materials, inorganic materials, and composite/hybrid materials. Different support materials have various advantages and disadvantages as depicted in Fig. 4.

Inorganic materials

Inorganic materials such as silica-based and other oxide-based materials are widely used as carrier materials for laccase immobilization due to their efficient mechanical, thermal, and microbial resistance along with porosity and rigidity properties (Daronch et al. 2020). The presence of functional groups such as carboxyl and hydroxyl on the surface of inorganic materials makes it convenient for the adsorption of the enzyme. Silica (SiO_2) and its derivatives are frequently used as inorganic carrier material. The hydrophilicity of the silica surface and the presence of hydroxyl

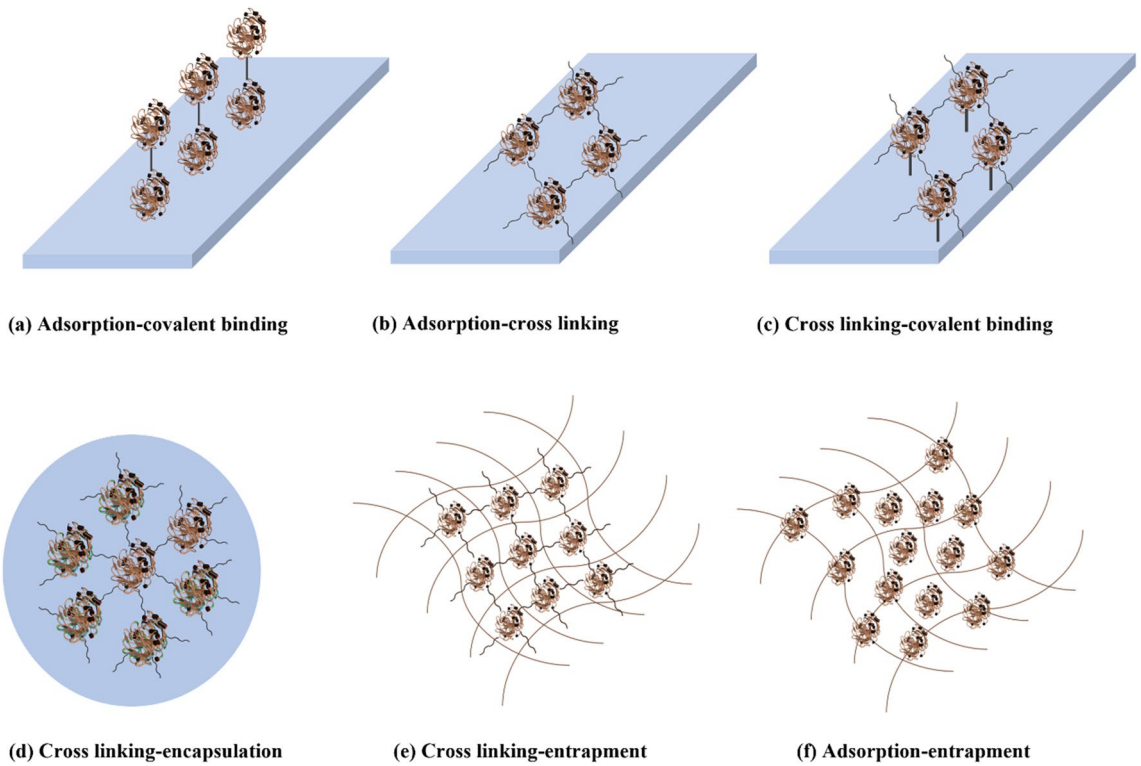


Fig. 3 Two-step immobilization techniques

Table 1 Support material used in laccase immobilization by different methods and kinetic parameters

Type of support material	Immobilization method	Material used	Immobilization yield/efficiency	Kinetic parameters	Features of support	Ref.
Biochar	Adsorption	Corn cob	75%	N. A	Hydrophobicity-16.5 $\mu g g^{-1}$ Porous diameter-18.3 A° Surface area-0.84 $m^2 g^{-1}$	(dos Santos et al. 2022)
	Adsorption	Rice straw	66%	K_1-4.6×10^{-3} s^{-1} K_2-3.6×10^{-3} gU^{-1} min^{-1}	Bulk density-0.17 gcc^{-1} Surface area-29.68 $m^2 g^{-1}$	(Imam et al. 2021)
	Adsorption	Rice straw	Adsorption amount-757.58 mgg^{-1}	K_1-7.3×10^{-3} s^{-1}	Surface area-55.38 $m^2 g^{-1}$ Pore diameter-5.2 nm	(Wang et al. 2022b)
	Covalent	Almond shell	Laccase binding-25.3 ± 2.8 U g^{-1}	N. A	Surface area-12.6 $m^2 g^{-1}$	(Lonappan et al. 2018)
	Adsorption	Maple	64.2%	K_m-2.68 mM	Surface area-613.6 $m^2 g^{-1}$ Pore volume-0.695 $cm^3 g^{-1}$	(Li et al. 2018)
	Adsorption	Coconut fibers	38% at pH 7	K_m-0.05 mM V_{max}-0.13 $mMmin^{-1}$	N. A	(Cristóvão et al. 2011)
Metal–organic framework	Adsorption	Mesoporo-us Zr	Adsorption capacity-221.8 mgg^{-1}	K_m-0.217 mM V_{max}-0.072 $mMmin^{-1}$	Surface area-453.8 $m^2 g^{-1}$ Pore volume-0.25 $cm^3 g^{-1}$	(Pang et al. 2016)
Carbon nanotubules	Covalent	Fe_3O_4-MWCNTs@SiO_2	N. A	K_m-0.502 mM V_{max}-20.7 $mMmin^{-1}$	Pore size-11.47 nm Surface area-428.1 $m^2 g^{-1}$	(Habimana et al. 2021)
Nanoparticles	Covalent	Silica	92%	K_m-0.5 mM V_{max}-3.58×10^2 $mMmin^{-1}$	Mean size-615 nm	(Gahlout et al. 2017)
	Covalent	Tannic acid/polyethylenimine Fe_3O_4	Laccase loading-39.9 mgg^{-1}	K_m-1.296 mM V_{max}-0.02 $mMmin^{-1}$	Diffraction peak-2θ = 30.07° at 220 crystal plane	(Li et al. 2022)
Nanosheet	Covalent	Graphene oxide	64.6%	K_m-1.16 mM V_{max}-0.0458 $mMmin^{-1}$	Diffraction peak-2θ = 6.62°	(Kashefi et al. 2019)
Nanofibers	Covalent	Cellulose	88%	K_m-0.343 mM, V_{max}-2.76 Umg^{-1}	Pore size-170 nm	(Sathishkumar et al. 2014)
CLEA	Cross-linking and entrapment	Chitosan	79%	K_m- 0.120 mM V_{max}- 597 UmL^{-1}	N. A	(Aslam et al. 2021)
Biomimetic titania	Adsorption and encapsulation	Protamine-titanium dihydroxide	97.6%	K_m -12.47 mM V_{max}-21.5 $mMmin^{-1}$	Particle size-30–50 nm	(Zhang et al. 2018)
Electrospun nanofibers	Adsorption and encapsulation	Poly (l-lactic acid)-*co*-poly (ε-caprolactone) (PLCL)	340 mg g^{-1}	K_m-0.315 mM V_{max}-1.44 $mMmin^{-1}$	Avg diameter-469 nm	(Zdarta et al. 2019)
Zeolite	Adsorption	Lac@ZSM-5	42%	K_m-1.81 mM V_{max}-0.00032 $mMmin^{-1}$	Specific surface area-461.5 $m^2 g^{-1}$ Average pore diameter- 2.0 nm	(Ameri et al. 2021)

K_1 first-order rate constant, K_2 second-order rate constant, Km Michaelis constant, V_{max} maximum velocity

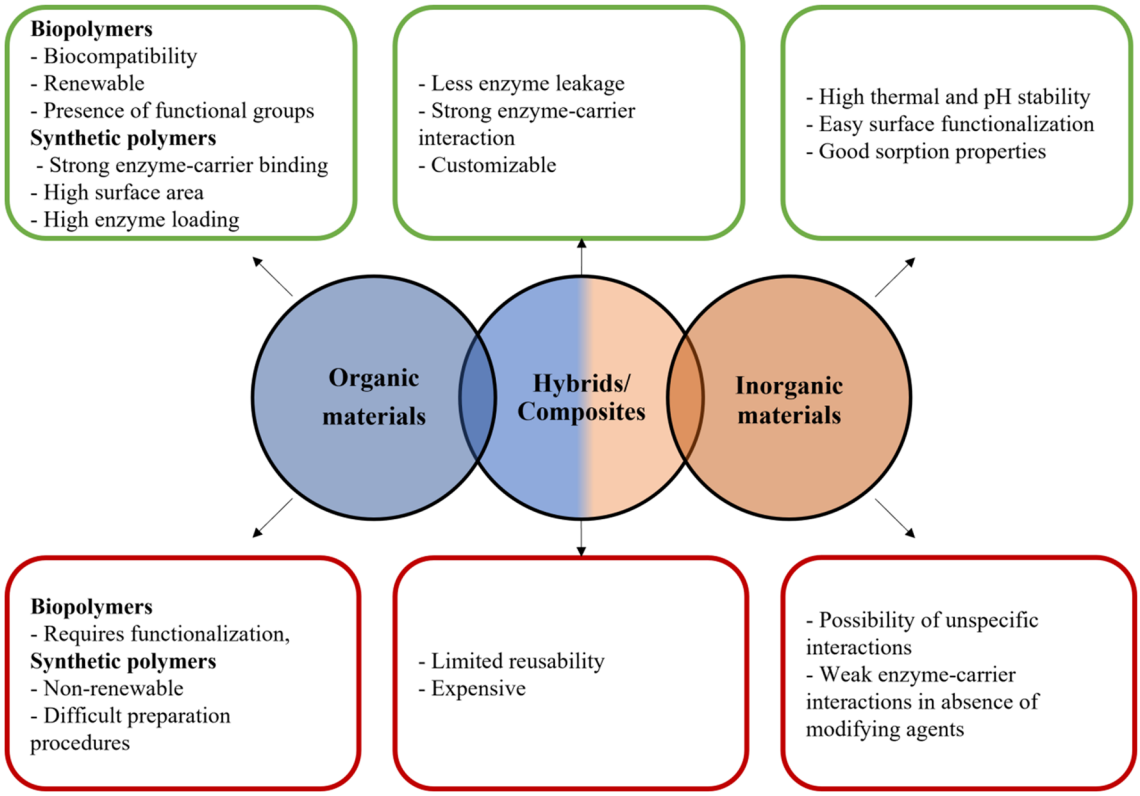


Fig. 4 Advantages (green) and disadvantages (red) of different support materials for laccase immobilization

groups provide better immobilization of enzymes via adsorption, covalent bonds, and even encapsulation (Zdarta et al. 2018a). Salami and co-authors reported the use of epoxy-functionalized silica in the presence of cyclohexyl isocyanide (crosslinker agent) for laccase sequestration and observed a significant increase in the immobilization yield from 20 mg/g (in the absence of isocyanide) to 50 mg/g (in presence of isocyanide) (Salami et al. 2018). Another silica-based support is the nano-porous zeolite-X (ZX). Wehaydi and group used this matrix to immobilize laccase from *Polyporus durus* ATCC 26726 and reported an immobilization yield of 83%, a reduction in the activation energy of the catalytic reaction with subsequent improvement in thermal stability. The immobilized laccase retained 93.5% of initial enzyme activity compared to the free laccase which retained only 5% at a temperature of 60 °C. The sequestered laccase when investigated against dyes, Remazol Brilliant Blue R (RB 19) and Acid Blue 225 (AB 225), 100% decolorization was obtained for both dyes after 15 min and 45 min incubation for RB 19 and AB 225 respectively (Wehaidy et al. 2019). Inorganic sources such as mineral clays (halloysite, kaolin) are also used as immobilization carriers due to their abundance in nature, low cost, reusability with low mass transfer resistance, and low microbial corrosion (Fomina and Skorochod 2020). A study on the laccase adsorption on the kaolinite was made by Wen and co-workers and investigated the degradation of malachite green effluent along with heavy metal, Cd (II). The Kaolin-Laccase retained 50% of the initial activity with nearly 80% decolorization for malachite green after 5 cycles. Over 98% decolorization of malachite green and 25% removal for Cd (II) was reported by Kaolin-Laccase in the presence of 3, 5-dimethoxy-4-hydroxybenzaldehyde (SA) (mediator) (Wen et al. 2019). In summary, inorganic materials are cheap and have an easy immobilization process. However, there is a possibility of enzyme leakage and reduced catalytic performance with such materials as they are susceptible to adsorption immobilization. Interest has been driven towards multipoint enzyme immobilization technique that facilitates stable binding and reduces enzyme leakage by maintaining the three-dimensional structure of laccase, thus improving its functionality and even the purity of the enzyme against harsh operational and storage conditions (Antecka et al. 2018).

Organic materials

Organic materials include natural and synthetic polymeric materials. Natural organic materials such as alginate, chitosan/chitin, gelatin, cellulose, and many more are inexpensive, non-hazardous, and can be derived from

microorganisms, plants, and animals which bind enzymes in reversible and irreversible ways showing higher thermal stability and mechanical resistance (Datta et al. 2013; Latif et al. 2022). Mostly chitosan and chitin are used for laccase immobilization due to properties such as biocompatibility, easy availability, low cost, non-toxicity and mechanical strength (Yanat and Schroën 2021). Chitosan was used by Jaiswal and co-authors to immobilize the laccase from *Carica papaya* using the entrapment technique by adsorption and covalent bonds for dye discoloration (Jaiswal et al. 2016). They obtained an immobilization yield of 98% without any cross-linking agent. The laccase immobilized in the chitosan beads removed 100% of Indigo Carmine dye within 8 h of incubation and reported with increase in the optimum pH range from 8 to above 9, increase in thermostability and catalytic efficiency by threefold and tenfold respectively compared to the free enzyme (Jaiswal et al. 2016). In a similar study of laccase immobilization by entrapment method alginate-gelatin mixed gel was used as carrier material, with an immobilization yield of 86.6%. The removal percentage of Congo Red dye by the immobilized laccase was about 80% compared to 60% by the free laccase (Reda et al. 2018). However, the general durability of natural organic materials is poor and is easily destroyed, and degraded by environmental microbes, shortening their use cycle. On the other side, the synthesized polymeric materials have greater resistance and catalytic activity with improved lifetime and strength of the carrier material. Polystyrene, polyamides, polyvinyl alcohol, polypropylene, polyethylene glycol, and polyacrylonitrile are some of the common synthetic organic polymers (Zdarta et al. 2018a). In a study by Jiang and co-workers, uniform polyurea microspheres were prepared using monomer isophorone diisocyanate in a water-acetonitrile solvent mixture through precipitation polymerization. The laccase was immobilized onto the microspheres via glutaraldehyde coupling and investigated for the degradation of Remazol Brilliant Blue R (RBBR) dye. 20.63 mg of laccase was immobilized for per gram of microspheres which removed 64.1% of RBBR after 5-h treatment. The immobilized laccase retained 65% of its initial RBBR decolorization activity after seven reaction cycles (Jiang et al. 2017). Synthetic organic material types lack hydrophilicity, making it easy to separate at the end of the process, and high-standard activities have been shown on the application.

Hybrids and composites

Recently novel hybrid materials made by combining the characteristics of inorganic and organic materials have gained much attention in recent years due to their exceptional thermal and chemical stability and very good mechanical properties (Zdarta et al. 2018b). Since these materials are of both organic and inorganic origin, three types of hybrids do exist: inorganic-inorganic, organic-organic, and inorganic-organic (Zdarta et al. 2018b). Magnetic nanomaterials and metal-organic frameworks (MOFs) are among the few materials that make good enzyme carriers for immobilization. Different metal ion and ligand combinations provide more structural choices for MOF materials. As a result, it can better meet design specifications (Deska and Kończak 2019). Peng and co-workers synthesized a MOF composite, a MOF/polyvinyl alcohol (PVA) cryogel. The hybrid material termed as MPF/PVA was used to construct a MOF/PVA immobilized laccase, i.e., MOF/PVA/Lac. The immobilized laccase exhibited enhanced pH stability, thermal stability, and operational stability and removed 95.86% of alizarin green within 12 h, retaining more than 60% of initial activity after six cycles (Peng et al. 2021). Although MOFs are effective supports for laccase immobilization, metals involved in organic and inorganic materials pose a safety risk of causing cytotoxicity in practical applications (Gao et al. 2022a).

Role of immobilized laccase in remediation of dyes

Immobilized laccases have been extensively used for the remediation of different categories of dyes because of their broad substrate specificity and can function in both intra and extracellular pathways of dye degradations, thus enhancing the remediation efficiency for a particular kind of dye (Singh et al. 2015; Birhanlı et al. 2022). Due to its high redox potential, fungal laccase has been widely preferred compared to bacterial laccase in dye degradation. So far, most of the fungal laccase research has been performed on white rot fungus. For commercial applications, laccase isolated from filamentous fungi comprising of the phylum Ascomycetes and Basidiomycetes, such as *Trametes versicolor*, *Irpex lacteus*, *Phanerochaete chrysosporium*, and *Pleurotus ostreatus* has been given attention (Deska and Kończak 2019).

Dyes and their chemistry

Dyes are a group of complex unsaturated organic compounds having chromophores and auxochromes as their basic components. Chromophores are responsible for color production whereas auxochromes help in intensifying the dye color. Different types of dyes are used in the textile industry and can be basically classified into two types. Based on industrial applications, dyes can be classified into reactive, vat, disperse, basic, acidic, direct, and solvent dyes as described in Table 2. Whereas based on chemical structure, dyes are classified into two major categories: anthraquinone and azo dyes (Ismail and Sakai 2022).

Anthraquinone dyes consist of the basic anthracene structure (three fused benzene rings) with two carbonyl

groups on the central ring. Anthraquinone dyes differ from azo dyes in the sense that the C = O group in the former acts as an electron acceptor, thus requiring an electron-donating group to react and degrade their structure. This feature, in combination with resonating effect in the anthracene structure, leads to higher stability and difficult degradability of the anthraquinone dyes compared to the azo dyes (Routoula and Patwardhan 2020). Azo dyes are the largest class of commercial dyes (comprising more than 50% of all the synthetic dyes). It is estimated that about 80% of the azo dyes are used in the textile industry due to their ease of synthesis, long shelf life, cost-effectiveness, and availability in a wide range of colors (Khan et al. 2023). Additionally, the biological activities of azo dyes make them important antibacterial, antiseptic, antiprotozoal, and wound healing agents (Sarkar et al. 2017; Kapoor et al. 2021). Azo dyes have one or more azo (N = N) groups along with the sulphonic (SO_3^-) or other electron withdrawing group linked to its aromatic molecular structure generating electron deficiency in their structure which makes them difficult to degrade (Kapoor et al. 2021). Consequently, after production, processing, and utilization, the rest of the dye is mainly released into the water bodies. The occurrence of these dyes in the aquatic ecosystem is the cause of serious ecological and health concerns. Literature studies have revealed the presence of hepatotoxicity in albino rats, nuclear anomalies in experimental animals, blindness, edema, allergic reaction, splenic sarcoma, and chromosomal aberrations in mammalian cells due to the ingestion of water contaminated with azo dyes such as metanil yellow, acid yellow 23, direct blue 71, and reactive blue 5 (Sarkar et al. 2017; Selvaraj et al. 2021; Jankowska et al. 2022).

Table 2 Different dye categories, properties, and their common chromophores

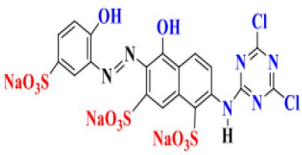
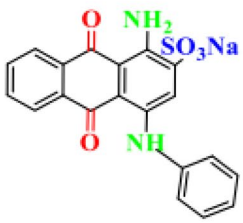
Dye	Features	Common chromophores	Examples	Ref.
Reactive dye	Water soluble and anionic in nature. Have good washing and light fastness properties. Available in powder, paste, and liquid form. Presence of reactive group in their structure.	Azo, halo-triazine, acryl, halo-pyrimidine, halo-quinoxaline, vinyl sulfone group	Reactive red 3  Reactive red 6 	(Ismail and Sakai 2022; Khan et al. 2023)
Acidic dye	They are salts of carboxylic (-COOH) and sulphuric acid (SO_3H). Highly water-soluble and anionic in nature. Electrolytes and acidic (2-6) conditions are required for the dyeing process.	Sulfonated azo, xanthene, anthraquinone, nitrodiphenylamine, and triphenylmethane group	Acid Blue 25  Acid Yellow 36	(Ismail and Sakai 2022; Khan et al. 2023)

Table 2 (continued)

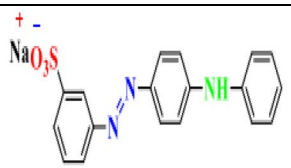
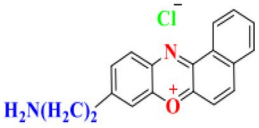
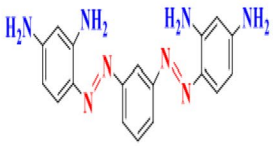
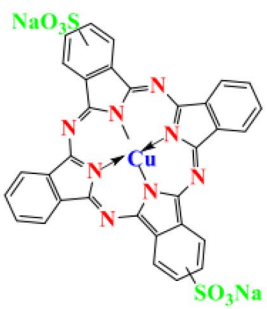
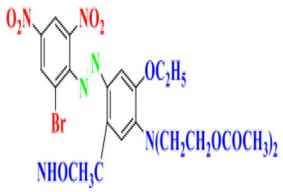
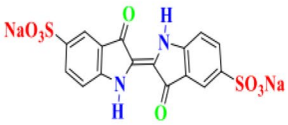
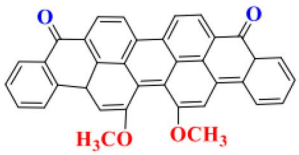
	Primarily form ionic bonding but can also participate in H bonding and Van der Waals interaction. Available in powder, paste, and liquid form. Have an affinity for protein and polyamide fibers.		 Acid orange 7 	
Basic dyes	These dyes are cationic in nature and are originally colorless. They exhibit color only in their salt form. Have cationic groups such as $-NR^{3+}$ and $-NR^{2+}$. Have low solubility in water and are highly soluble in alcohol. Have low light fastness properties.	Azo dyes, acridine, di and triphenylmethane, thiazine, oxazine, azine, and xanthene group	Basic Blue 6  Basic brown I 	(Ismail and Sakai 2022; Khan et al. 2023)
Direct dyes	These dyes are adsorbed on the fibers via H bonding, van der Waal forces, and dipole-dipole interaction. Also known as substantive dyes. Anionic in nature.	Azo, phthalocyanine, stilbene, thiazole, and oxazine group	Direct Blue 86 	(Ismail and Sakai 2022)
Dispersive dyes	Have low water solubility. Form H bonds and van der Waals force.	Nitrodiphenylamine, anthraquinone, azo, and methine	Disperse blue 79	(Ismail and Sakai 2022)

Table 2 (continued)

	Non-ionic in nature.	group		
Vat dyes	These dyes are soluble in hot water. Few exceptional dyes are soluble in the presence of a trace of Na_2CO_3. Urea can be used to enhance solubility at temperatures ranging from 50°C to 60°C. They are non-ionic in nature.	Anthraquinone, indigoid group	Vat acid blue 74  Vat green I 	(Valli Nachiyar et al. 2023)
Sulfur dyes	Non-ionic and insoluble in water.	Phenothiazonethian throne, thianthrene, thiazone, and thiazole group	Sulfur brilliant green 	(Valli Nachiyar et al. 2023)

Mechanism of dye degradation

Laccase, in the presence of atmospheric oxygen and by the release of water molecules, catalyzes a broad range of phenolic and non-phenolic compounds, mainly by three different types of reactions. The first mechanism is the direct oxidation of phenolic substrates, and the second type of reaction is the indirect oxidation of non-phenolic compounds in the presence of natural or synthetic mediators. The third type of reaction follows the coupling mechanism with the reactive intermediates formed in the direct oxidation step (Morsy et al. 2020).

Laccase degrades the anthraquinone dyes by delocalizing the conjugated π electron system of the core and its substituents and generally follows reductive, hydroxylation, deamination, and oxidative pathways. The lower metabolites obtained after the degradation of chromophores have lower toxicity. Anthraquinone dyes can also act as a redox mediator in the degradation of azo dyes (Legerská et al. 2016).

Laccase, through a highly non-specific free radical mechanism, can degrade a large group of azo dyes into intermediate phenolic compounds and prevents the formation of toxic aromatic amines. This is achieved by the formation of electron-devoid carbocation, which leads to the formation of highly reactive intermediates that are attacked by the nucleophiles (-OH, $-SO_3$), causing an asymmetric cleavage of the azo (N=N) bond (Ardila-Leal et al. 2021). This is followed by oxidative reactions, desulfonation, deamination, demethylation, and dihydroxylation, depending on the type of dye used for the degradation (Rawat et al. 2022). Laccase oxidizes the phenolic ring of azo dye into a phenoxy radical which is further oxidized to produce carbonium ion. Nucleophilic attack of water on carbonium ion in the presence of molecular oxygen leads to the formation of an unstable 4-sulfophenyldiazene, and benzoquinone. 4-sulfophenydiazene under aerobic conditions gets oxidized to phenyldiazene radical. The latter further loses molecular nitrogen to finally produce a sulfophenyl radical, which is scavenged by O_2 to produce 4-sulfophenyl hydroperoxide (SPH) (Singh et al. 2015; Selvaraj et al. 2021).

Laccase mediators and their role in dye degradation

Laccase owing to its wide range of substrate specificities, and ability to mediate coupling reactions have significantly attracted the attention in dye remediation. However, the degradation of some structurally stable dyes has been hampered due to the low oxidation–reduction potential of laccase (0.3–0.8 V) (Du et al. 2020). The combination of mediators with laccase (Fig. 5) overcomes the space barrier and also mediates the oxidation process between the substrate and laccase enzyme resulting in a high oxidation potential of laccase and further expanding the range of substrates for laccase. Mediators are small organic compounds involved in the formation of highly active radical cations, and the latter are in turn responsible for the oxidation of non-phenolic compounds which are usually resistive to laccase oxidation through the normal electron transfer from the substrate to the enzyme (Kyomuhimbo and Brink 2023). Immobilization of enzyme and redox mediator system provides better operational stability and reusability, thus reducing the manufacturing cost, which is a prime concern for the continuous industrial-scale process (Gu et al. 2021). The addition of mediators such as violuric acid (VIO), HBT (1-Hydroxybenzotriazole), 2,2′ -azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), and 2,2,5,5-tetramethyl-4-piperidine-1-oxyl radical (TEMPO) to increase the range of laccase oxidizable compounds has been reported in the literature. Himanshu et al. (2023) used a laccase enzyme isolated from *Ganoderma lucidum* in the presence of an ABTS mediator for the decolorization of 0.1 mg/ml malachite green. The decolorization efficiency of laccase was reported to be 91% and 65% within 3 h of incubation in the presence and absence of a mediator respectively. Similarly, in another study, authors investigated the effect of mediators such as HBT, VIO, and ACE (Acetosyringone) for the degradation of Alizarin red, Fuchsin acid, and Congo red dyes. Different mediators had different decolorization efficiency depending upon the mediator's redox potential, incubation time, and dye structure. The degradation rate of Alizarin red dye increased by 26.3% and 30.8% in the presence of 0.1 mM ACE after 3 h and 24 h of incubation respectively, in comparison to the control (laccase-only system). HBT was able to degrade 33% Fuchsin acid after 3 h of incubation in comparison to 13% by ACE thus acting as a better mediator for the dye than the ACE. Of the three mediators used, the synthetic mediator (laccase-VIO) enhanced the dye degradation by 82.8% and 57.1% for the Alizarin Red and Congo Red dyes respectively after 24 h of VIO addition. The high degradation was mainly due to the electron and hydrogen atom transfer mechanism (Du et al. 2020). Shan and co-workers co-immobilized laccase and ABTS mediator on geo-polymer microspheres pre-embedded with amino acids histidine (His) and cysteine (Cys) (Lac-ABTS@GM-H_2C_1). The prepared composite biocatalyst demonstrated high decolorization efficiency (94.78%) of the congo red dye which was superior in comparison to the enzyme-mediator system (Lac-ABTS) (79.23%) and enzyme-microsphere system (Lac@GM-H_2C_1) (53.82%). The enhanced degradation via (Lac-ABTS@GM-H_2C_1) system was due to increased electron transfer and shortened mass transfer distance. Additionally, the composite biocatalyst had a good pH tolerance and competitive storage stability (Shan et al. 2022). Salami and co-authors used sequestered laccase for the degradation of some textile dyes and a higher dye decolorization ranging from 98 to 100% with the mediator 3,4-dimethoxy-5-hydroxybenzoic acid (DMHBA) was observed, however in absence of mediator 43–57% was reported (Salami et al. 2018). Due to the spatial configuration of laccase, some of the free amino acid groups are inaccessible for sequestration, but the use of a mediator can increase the immobilization yield (Zhang et al. 2022). Laccase isolated from *Trametes maxima* IIPLC-32 was efficiently able to degrade 92.3% of RBBR dye without the use of a mediator, indicating that the laccase obtained from the fungus had a high

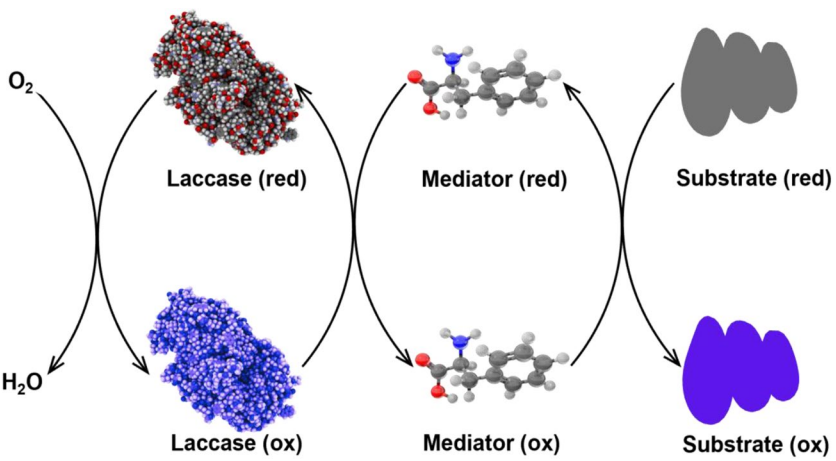


Fig. 5 Laccase-mediator system

redox potential (Suman et al. 2021). Most of the synthetic mediators due to their toxic nature could result in secondary pollution of the natural environment. Additionally, LMS produces strong oxidation intermediates known as co-mediators which reduce the catalytic activity of laccase by interacting with the active groups present on the laccase surface, leading to its passivation. Reduced concentration of mediators and proper reaction temperature could help in minimizing the effects of synthetic mediators. Many natural environment-friendly compounds such as vanillin (Va), syringaldehyde (Sa), and acetosyringone (As) have been investigated to be used as natural mediators. Natural mediators have a low free radical activity after oxidation which results in reducing the attack probability of sensitive amino groups present on the laccase surface, thus improving the stability of laccase and the ability to treat wastewater (Gu et al. 2021).

Immobilized laccase in dye degradation

Laccase in its free form gets easily denatured in harsh operating conditions and thus lacks stability during the dye degradation pathway. Additionally, free laccase has a high solubility in water and is difficult to separate from the substrate molecules, thus reducing its reusability for further reactions (Gu et al. 2021). Therefore, to overcome these shortcomings, immobilized laccase has been extensively used in the degradation and detoxification of a large number of acidic, direct, sulfur, and dispersive dyes such as Reactive blue, Malachite green, Congo red, Crystal violet, Acid orange, Reactive red, and Brilliant blue (dos Santos et al. 2022; Zhu et al. 2022; George et al. 2023). Table 3 represents the degradation efficiency of different industrial dyes by immobilized laccase obtained from different sources.

Nguyen and co-authors demonstrated the effect of immobilized laccase on the degradation of sulfur dyes. Laccase immobilized on chitosan beads with an initial activity of 2.24 UL^{-1}, degraded 98% of sulfur blue 15 and 49.5% of sulfur green dye after 12 h of reaction time (Nguyen et al. 2016). Laccase immobilized on $CuFe_2O_4$ nanoparticles was studied for the degradation of direct red 23 (DR 23) dye. HPLC analysis showed a peak reduction of the treated dye solution using laccase immobilized on nanoparticles at the same retention time (0.96 min) as that of the control dye solution along with the emergence of a new peak at a retention time of 1.73 min. Immobilized laccase showed a higher degradation of DR 23 dye than the free laccase which was due to the presence of Cu ions in the carrier material which stimulated the laccase activity (Alsaiari et al. 2021). An eco-friendly and highly efficacious technology was developed by Gao and co-authors for the biodegradation and detoxification of anthraquinone and azo dyes using vault-encapsulated laccase (vlaccase). Vlaccase efficiently degraded 72% and 80% of dyes in comparison to free laccase which degraded 40% and 32% of reactive blue 19 and acid orange 7 dyes respectively. The effect of detoxification by vlaccase on synthetic dye solutions was supported by the reduced toxicity on Sf9 cells (derived from the ovaries of fall armyworm moths) and an increase in mitochondrial dehydrogenase activity which is pivotal in physiological functions. The bacterial species such as *E. coli* and *Staphylococcus epidermidis* exposed to the treated dye solutions with vlaccase demonstrated reduced cytotoxicity than the control dye solution. Additionally, on exposure to vlaccase, the inhibition of chlorophyll synthesis by the green algal cells *Chlorella vulgaris* was significantly decreased to 18% in comparison to 52% of the untreated sample (Gao et al. 2022b). The practical applicability of laccase immobilized on 2,3-epoxypropylmethacrylate Fe_3O_4 nanoparticles towards catalytic degradation of azo dye was demonstrated using acid blue 193 (AB 193). Over 95% dye degradation was achieved within a period of 4 h and the immobilized laccase retained > 90% of its activity after 10 cycles of dye degradation (Rawat et al. 2022). Laccase immobilized on chitosan beads achieved maximum immobilization yield from 1% glutaraldehyde solution after 1 h of incubation by the cross-linking method. The immobilized enzyme was efficiently able to degrade different reactive and disperse dyes such as Drimaren red, Drimaren yellow, Drimaren black, Drimaren turquoise, Foron turquoise, and Foron blue in the range of 86.19% to 91.01%. The immobilized system efficiently removed 92.25–96.55%, 91.90–94.94%, and 77.01–93.29% BOD, COD, and TOC levels, respectively, from the dye solution, thus playing a significant role in improving the water quality parameters (Aslam et al. 2021). Khakshoor and coworkers co-entrapped laccase isolated from bacterial spores on TiO_2 nanoparticles for enhancing dye degradation. The entrapped laccase resulted in 69.3% degradation of Indigo carmine dye in the laccase/TiO_2 two-step remediation process (Khakshoor et al. 2021). Laccase immobilized on pine needle biochar was efficiently able to degrade malachite green from wastewater. FTIR, HPLC, and GC–MS analysis confirmed the degradation of malachite green into lesser toxic metabolites such as leuco malachite green, methanone, phenyl, and 3-dimethyl-phenyl amine. The phytotoxicity test of the treated dye samples, performed on *Vigna radiatae* indicated a higher root-shoot ratio than those of the untreated samples. This indicated the presence of lesser toxic metabolites during the degradation pathway than the original dye, thus posing the capacity for dye removal from wastewater (Pandey et al. 2022). Similarly, Bagewadi and co-authors confirmed the degradation of azo dyes (Malachite green and Methylene blue) by the occurrence of new peaks and the disappearance of control peaks in HPLC analysis. The phytotoxicity test of the degraded

Table 3 Laccase isolated from different sources and their dye degradation ability

Source of laccase	Dyes	Initial dye amount	Degradation efficiency	Activity retention	References
Trametes versicolor	Malachite Green	100 ppm	97.70%,	50%, 10 cycles	(Wang et al. 2022b)
Aspergillus	Direct red 23 Acid blue 92	10 ppm	88.7% 48.7%	75%, 6 cycles	(Kashefi et al. 2019)
N. A	Eriochrome Black T Acid red 88 Reactive black 5 dye	40 ppm	99%, 3.5 h 98%, 3.5 h 66%, 3.5 h	87%, 10 cycles	(Habimana et al. 2021)
Pleurotus florida	Reactive blue 5	50 ppm	47%	67%, 10 cycles	(Sathishkumar et al. 2014)
Methylobacterium extorquens	Congo red Crystal violet	80 ppm	100%,10 h 51%, 10 h	80%, 10 cycles	(Ainiwaer et al. 2022)
Alcaligenes faecalis XF1	Textile dyes	5 mL	78%	40%	(Mehandia et al. 2022)
Trametes versicolor	Acid orange 52	54 mL	73%	50%, 10 cycles	(Koklukaya et al. 2016)
Ganoderma sp. KU-Alk4	Malachite green Congo red Direct blue 15 Direct red 23	3 mL	82%, 2 h 64%, 2 h 54%, 2 h 22%, 2 h	80%, 4 cycles	(Teerapatsakul et al. 2017)
Pleurotus nebrodensis WC 850	Reactive blue 171	100 mL	85%	84.2%, 3 cycles 54.21%, 8 cycles	(Aslam et al. 2021)
Trametes versicolor IBL-04	Remazol brilliant blue R Crystal violet Reactive black 5	10 ppm	94.57% 90.63% 78.72%	60%, 8 cycles	(Bilal et al. 2021)
T. trogii	Reactive blue 171 Reactive blue 198	3 mL	78%, 1 h 61%, 1 h	56.5%, 12 cycles	(Birhanlı et al. 2022)
Trametes versicolor	Direct red 31 dye	N. A	92%, 6 h	70%, 10 cycles	(Jiang et al. 2022)
N. A	Malachite green	20 ppm	94.2%, 6 h	51%. 7 cycles	(Zhang et al. 2018)
Trametes versicolor	Crystal violet	10 ppm	88%, 5 h	50%, 10 cycles	(Dai et al. 2010)
Pleurotus ostreatus	Malachite green Reactive blue 2	500 ppm 500 ppm	91%, 1.5 h 30%, 2 h	95%, 6 cycles 12%, 6 cycles	(George et al. 2023)
Trametes versicolor	Reactive deep green Reactive deep blue Acid red 18	50 ppm	73%, 4 h 68.3%, 4 h 85.7%, 4 h	68.1%, 5 cycles 52.3%, 5 cycles 40%, 5 cycles	(Yang et al. 2023)
Trametes versicolor	Direct red 23	10 mg/ml	95%, 1 h	84%, 6 cycles	(Alsaiari et al. 2021)
Trametes versicolor	Malachite green Brilliant green Azophloxine Procion red-MX5B Reactive blue 19 Alizarin red	400 ppm 200 ppm 100 ppm 40 ppm 400 ppm 400 ppm	99.6%, 1 h 99.5%, 1 h 94.2%, 1 h 89.4%, 1 h 94.6%, 1 h 79.3%, 1 h	98.7%, 10 cycles 99.3%, 10 cycles 79.0%, 10 cycles 78.7%, 10 cycles 88.8%, 10 cycles 64.4%, 10 cycles	(Zhu et al. 2022)
Coriolus versicolor	Acid brilliant scarlet GR Reactive blue 19	15 ppm	95%, 3.3 h 92%, 3.3 h	70%, 10 cycles	(Huang et al. 2023)

metabolites indicated higher germination of *P. mungo* seeds than the original dyes. However, the seeds germinated in treated samples showed a decreased growth rate than in the control samples (sterilized water) (Bagewadi et al. 2017). Hydrogels prepared by entrapment of laccase in a semi-interpenetrating polymer network decolorized 66% of acid orange 52 dye within 6 h of treatment which was further increased to 75% by the addition of ABTS substrate. The immobilized enzyme showed a lower affinity for the substrate than the free counterpart but had higher storage and temperature stability and better reusability. Heat denaturation of the immobilized enzyme caused the degradation efficiency to be 1.9% in 6 h, which proved that the decolorization was due to enzymatic degradation and not due to adsorption on the hydrogel (Yamak et al. 2009).

Mehandia and group developed a continuous packed bed reactor system (PBRS) by immobilizing laccase on chitosan clay beads and further packing it in the column. PBRS, due to their efficient reusability, cost-effectiveness, and simple design, can efficiently conduct enzymatic reactions. The diminishing of peaks in the UV–VIS Spectrum confirmed the degradation of effluents. The BOD and COD level decreased by 90.98% and 87% compared to the untreated samples. The toxicity of the treated samples was analyzed by studying the growth pattern of different microbial cultures. Untreated textile wastewater resulted in ≤ 90%, ≤ 87%, and ≤ 83% inhibition

of growth *S. cerevisiae*, *E. coli.*, and *Bacillus subtilis* respectively, which was largely terminated by the treated samples. This indicated that the degraded products formed after the treatment were not toxic for the growth of yeast and bacterial species (Mehandia et al. 2022). In another study, the toxicity of dye-degraded water was analyzed by studying the growth pattern of soil microorganisms. Zone formation was not observed with the treated dye samples for the microbial species *R. leguminosarum*, *A. brasilense*, *P. fluorescens*, *B. subtilis*, and *B. megaterium*. In contrast, significant microbial zones were observed in the untreated dye at 500 ppm, thus indicating that the degraded metabolites were non-toxic to the soil microbiota. The authors also illustrated significant detoxification in model plants such as *Triticum aestivum* and *Phaseolus mungo* suggesting the potentiality of the treated dye solution for agronomical purposes (George et al. 2023).

Prospects

Immobilized laccase has a wide application prospect in the treatment of water contaminated with dye effluents.

The necessity for environmental sustainability is the key motive for the development and application of enzyme technology for environmental stewardship. Laccases immobilized on various carrier matrices has promising dye removal potential due to their higher catalytic properties and stability compared to native free laccase. However, the undesirable reactions between the carrier and laccase enzyme, lower enzyme loading efficiency, loss of enzymatic activity as a result of leakage from the support material, low residual activity, high costs related to the production of novel supporting material, enzyme production, and enzyme immobilization are the most significant barriers to scaling up the enzyme technology. Therefore, further research in the bioavailability, biocompatibility, and cost-worthiness of immobilized support involved in industrial use and commercialization needs to be addressed. Future research should be focussed on the cost of the cultivation media for the microbes required for laccase production must be reduced by optimizing the process or developing new technology. The use of recombinant technology and constructing an expression system for heterologous synthesis of extracellular recombinant enzymes can improve the commercial production of laccase. Additionally, genetic engineering can improve laccase stability and reusability. The fabrication of immobilized supporting materials should be cheap and easy to scale up with minimal enzyme loss following immobilization. In this context, the use of natural carriers as immobilized supporting materials should be selected that "comes from nature and returns to nature." Modification of existing immobilization techniques that ensures direct enzyme attachment to safeguard the catalytic site and utilization of integrated remediation treatment strategies, including whole cell–enzymatic, enzymatic–enzymatic, and photocatalytic–enzymatic, needs to be developed. Formulating and implementation of laccase treatment on a large-scale application in different water bodies such as a river, groundwater, and seas under real parameters such as temperature and pH should be focussed.

Conclusion

Laccase immobilization with good removal efficiency offers a promising approach for dye decolorization. Immobilization provides increased stability, reusability, improved operational and process control, and broadened application range. Different immobilization methods and carriers have been utilized for the biodegradation of hazardous industrial dyes by immobilized laccase. However, there is a further need for the development of laccases with higher efficiency, customized immobilization systems, and their integration into wastewater treatment processes. Continued research and development efforts in this area are expected to drive the advancement and widespread application of enzyme immobilization for dye removal in the future.

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