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Review

Applications of Biocatalysts for Sustainable Oxidation of Phenolic Pollutants: A Review

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Abstract: Phenol and its derivatives are hazardous, teratogenic and mutagenic, and have gained significant attention in recent years due to their high toxicity even at low concentrations. Phenolic compounds appear in petroleum refinery wastewater from several sources, such as the neutralized spent caustic waste streams, the tank water drain, the desalter effluent and the production unit. Therefore, effective treatments of such wastewaters are crucial. Conventional techniques used to treat these wastewaters pose several drawbacks, such as incomplete or low efficient removal of phenols. Recently, biocatalysts have attracted much attention for the sustainable and effective removal of toxic chemicals like phenols from wastewaters. The advantages of biocatalytic processes over the conventional treatment methods are their ability to operate over a wide range of operating conditions, low consumption of oxidants, simpler process control, and no delays or shock loading effects associated with the start-up/shutdown of the plant. Among different biocatalysts, oxidoreductases (i.e., tyrosinase, laccase and horseradish peroxidase) are known as green catalysts with massive potentialities to sustainably tackle phenolic contaminants of high concerns. Such enzymes mainly catalyze the *o*-hydroxylation of a broad spectrum of environmentally related contaminants into their corresponding *o*-diphenols. This review covers the latest advancement regarding the exploitation of these enzymes for sustainable oxidation of phenolic compounds in wastewater, and suggests a way forward.

Keywords: biocatalysts; horseradish peroxidase; laccase; phenolic pollutants; sustainable oxidation; tyrosinase

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1. Introduction

The increment in the human population, along with the global economic development, has created a remarkable demand for petrochemical products and energy, which is expected to grow up to a further 37% over the next two decades [1]. Different processes such as thermal cracking, exploration, desalting, catalytic treatment, isomerization and distillation are involved in the petroleum refinery and petrochemical industry to produce useful products like gasoline, liquefied petroleum gas and petrochemical feedstock [2,3]. Accordingly, a large volume of water is needed in each one of these processes, making these industries among the most water-consuming establishments. The average volume of wastewater generated by these processes is almost 0.4–1.6 times higher than the volume of the produced crude oil [4]. It is anticipated that the world demand for oil will reach 107 million barrels per day in 2030 [5]. In 2018 alone, around 6500 million liters of wastewater were generated per day, as a result of an approximately 99.93 million barrels per day world oil consumption, according to the Energy Information Administration (EIA)

report [6]. The increasing demand for petrochemical products, the limitation of hydric sources and the negative effects of the contaminated wastewater on the environment and health of living species are nowadays undeniable worldwide issues that have directed a lot of attention towards the safety of the ecosystem. Among them, the wastewaters discharged from petroleum refining industries and petrochemical plants are composed of various toxic organic components with significant potential threats to the environment. In general, the pollutants appearing in the petroleum refinery wastewaters can be classified into inorganic and organic matters [7]. Thus, the efficient treatment of wastewater generated by these industries should be considered as a strategic approach to sustained water resources management across the world [8]. The quality of the crude oil defines the composition of the generated wastewater by the petroleum refining industry, and it differs with the operating conditions [9]. Petrochemical wastewater is considered a major source of aquatic environmental pollution, comprising large amounts of aliphatic and aromatic hydrocarbons such as toluene, xylenes, benzene and phenolics with potential hazards to the ecosystem [10]. Among different contaminants present in petroleum refinery wastewater, ammonia nitrogen and organic compounds (such as phenols) are known as the principal chemical characteristics of environmental concern in the effluent [7]. Introducing these types of wastewaters into the aquatic ecosystem causes a significant reduction of the normal dissolved oxygen (DO) level (2 mg/L) of the water, which can increase the mortality rate of the living species in that environment [11]. In previous literature, the effect of petroleum refinery wastewater on the quality of Ubeji Creek water in the Niger Delta of Nigeria was studied, and the results suggested that the mixing of brackish waters with the discharged effluent had detrimental impacts on the aquatic life [12]. Moreover, chronic or high exposure to these toxic hydrocarbons and compounds (i.e., phenols) can be carcinogenic, and cause many severe health issues to human beings such as lung, liver, kidney and vascular system infection [10,13]. These pollutants are persistent and highly soluble in water, which can migrate into the groundwater [13]. Phenolic compounds are one of the most concerning persistent pollutants originating mainly from crude oil fractionation and catalytic/thermal cracking in petroleum refineries [14]. Furthermore, the other sources of total phenolic compounds in the petrochemical effluents are the tank water (~11.8 ppm), the desalter effluent (~1.4 ppm) and the neutralized spent caustic waste streams (~234 ppm) [15]. It has been reported that more than ten million tons of phenolic compounds are discharged into the environment every year [16]. Depending on the industrial source of wastewater, the typical concentration of phenols in the discharged waste streams can range between 100 and 1000 ppm [17]. This is while that the discharge of untreated effluents containing phenols contaminants into the environment, even at low concentrations, can lead to threatening the aquatic lives and harmony of the ecosystem as well as contaminating soil, groundwater and surface water [18]. Based on their harmful health impacts, the required standards for the discharge of phenolic wastewaters have been becoming increasingly restrictive, and these pollutants are known as priority pollutants, according to the Water Quality standards issued by USEPA [19]. Therefore, elimination of such pollutants is considered as a major importance, and there has been a growing demand for enhanced techniques of effective treatments.

A combination of different techniques, including chemical, biological and physical treatments, have been studied to eliminate such toxic pollutants from petrochemical industrial wastewaters [20]. In this regard, various types of oxidation (chemical and catalytic oxidation e.g., photocatalysis and Fenton and Photo-Fenton oxidation), biological processes (i.e., activated sludge process and anaerobic membrane bioreactors) and coagulation have been utilized for the treatment of such wastewaters [8,21]. However, most conventional wastewater treatment methods cannot efficiently eliminate the persistent aromatic organic and hydrocarbon compounds, i.e., phenols, due to their several inherent drawbacks such as technical complexity, incomplete removal of the pollutants, formation of hazardous by-products with more toxicity comparing with the original phenolic compounds and high capital and maintenance/operation costs [22,23]. These constraints adversely affect

the economic viability and technical feasibility of the treatment processes. Among the aforementioned treatment techniques, biological treatment is considered one of the most effective methods for the elimination of persistent pollutants. In such a technique, a limited number of microbial species can degrade the recalcitrant pollutants. For phenols, it is done by opening the aromatic rings, while microbes derive carbon and energy from the contaminants [23]. In most cases, however, a long retention time is needed for biological degradations, while the variation of the operating conditions, such as pH and temperature, can easily influence the process performance [14]. Furthermore, biological wastewater treatment methods suffer from other serious disadvantages as well. Firstly, the control of the optimum level of microbial growth conditions is always challenging. Thus, specific conditions might have a significant impact on the survival rate of microbes within the system leading to inefficient wastewater treatment [24]. Secondly, some of the bioproducts of biological treatment processes (i.e., the generated sludge) can be toxic [25]. Thirdly, microbes are mostly ineffective when the pollutants exist at very low concentrations. To overcome this issue, surfactants and organic co-solvents are usually added to improve the bioavailability of the pollutants. This process might have negative economic and technical effects on microbial wastewater treatment efficiency. Therefore, cost-effective, eco-friendly, easy-to-operate and novel wastewater treatment technologies are required to efficiently remove various phenolic compounds from different effluents without producing harmful metabolites and sludge.

Accordingly, a relative novel trend has been introduced in recent years on employing extracellular enzymes, rather than whole microbial cells for eliminating phenols and some other organic pollutants from industrial wastewaters. Enzymes selectively catalyze reactions under moderate conditions [26], and their corresponding process can be considered as a feasible alternative to the other traditional treatment methods [14]. The use of enzymes for wastewater treatment purposes was first suggested in the 1930s [17]. Nonetheless, the concept of utilizing enzymes to eliminate individual contaminants in wastewater streams was not fully developed until the 1970s [17]. Over the past decades, the application of enzymatic wastewater treatment processes has been investigated based on oxidoreductive enzymes, especially polyphenol oxidases and peroxidases. In this process, the enzyme catalyzes the oxidation of phenols and catechols, and generates reactive radicals [27]. Enzymatic processes offer more valuable advantages over microbial treatment. Enzymes can retain their activities and effectiveness over a wide range of environmental conditions [28]. Moreover, they are capable of converting the substrate with reasonably high selectivity over a wide range of pollutant concentrations [26]. It has been reported that the phenolic compounds with concentrations higher than 100–200 mg/L can be toxic to some of the species utilized in biological wastewater treatment, modifying the microbial structure and negatively affecting microbial growth [17,29]. Compared to the other conventional catalytic techniques, enzymatic systems produce less waste and consume less water. On this account, enzymatic wastewater treatment processes are progressively becoming an attractive sustainable alternative and environmentally friendly approach. Moreover, the possibility of the production of enzymes on a higher scale with improved activity and stability at a lower cost using the recombinant-DNA technique further encourages the usage of enzymes in wastewater treatment processes [30]. However, more cost-effective approaches for even the enzymatic wastewater treatments are yet to be discussed.

Since the removal of phenolic contaminants from industrial wastewaters using peroxidase and polyphenol oxidase enzymes has been scarcely discussed in the previous literature reviews, the main purpose of this study is to demonstrate a general picture of the obtained results in this research field, as well as those parts which are still uncovered. In this regard, the ability of the aforementioned enzymes in catalyzing the reactions for removing phenols from the wastewater is thoroughly investigated. This can be helpful to determine the feasibility and applicability of biocatalytic processes for the elimination of phenolic compounds from the petroleum refinery wastewaters. After proving the feasibility of this technique, it would be possible to conduct further research and development

studies in this field in order to considerably lower the cost of the application. Justifying the replacement of current wastewater treatment technologies with enzymatic treatment techniques is not the scope of this current study. Rather, the intention is to provide a clear insight into the future potential feasibility of enzymatic treatment methods for treating real wastewater samples under certain conditions.

2. PRPP Wastewater Characteristics and Disposal Standards

The characteristics and total volume of the generated wastewater in an oil refinery plant heavily depend on the quality of the crude oil, the final products and the process's complexity and configuration. The general characterization of these types of effluents is presented in Table 1. The generated wastewater by different processes is mainly characterized by a high COD [31], which is mostly due to the overall contribution of several inorganic substances (i.e., cyanides, sulfides and ammonia), emulsified oil and aromatic and aliphatic hydrocarbons (especially up to C_{10}) such as ethylbenzene, benzene, methyl tertiary butyl ether, polycyclic aromatic hydrocarbons (PAHs), toluene and phenolic compounds [31]. In addition, high concentrations of total dissolved solids (TDS), phenol, benzene, xylene, heavy oil, total suspended solids (TSS) and toluene in different petroleum and petrochemical wastewater were observed in the previous literature [32]. Most of the pollutants present in the petrochemical effluents are persistent in nature, and considerably increase the chemical oxygen demand level and toxicity of the produced wastewater streams. Heavy oil is known as a key pollutant in the petrochemical effluents, which can contaminate the groundwaters and water bodies through oil discharge and spills. They are large hydrocarbons consisting of a higher number of carbon atoms with high chemical stability and viscosity, together with low water solubility and biodegradability [33]. Polycyclic aromatic hydrocarbons are considered as another major component of petroleum refinery wastewater, belonging to the polycyclic aromatic hydrocarbon groups with more than one benzene ring. They are almost colorless, hydrophobic, and with higher boiling and melting points along with comparatively less vapor pressure [34]. These compounds are also very toxic and can undergo bioaccumulation. A remarkable amount of phenolic compounds, along with high levels of COD, Total Organic Carbon (TOC) and BOD, can be detected in the wastewater treated by the conventional methods, which confirms the incompetence and low efficiency of these techniques [35,36]. Due to the presence of the noticeable amount of various persistent and toxic pollutants, such as phenols, in the effluent of the petroleum refinery industry and their detrimental and toxicological impacts on the ecosystem, many existing environmental agencies provide standard limits for each contaminant in the wastewaters before disposing them into the marine water and environment or in the agricultural field. For example, the World Bank Group (WBG) and USEPA set the concentration of 10 ppm as the limits for total nitrogen in the treated effluent [37]. However, some of these regulated standards are challenging to be met by conventional treatment techniques. Thus, this creates opportunities for developing novel, eco-friendly and efficient technologies.

Table 1. Characterization of petroleum refinery and petrochemical effluents.

Parameter	Typical Value Range(s)	Environmental Standards *	References
BOD (mg/L)	718 90–685 3378 8000	30	[10,37]
TSS (mg/L)	28.9–950 2580	30	[31,37,38]
Conductivity (ms/cm)	5.2–6.8	-	[31]
COD (mg/L)	3600–5300 300–800 550–1600 7896	125	[10,31,37]
Total phenol (mg/L)	10–233	0.35	[10,31,39]
pH	6.5–10.8	6–9	[37,38,40]
Heavy metals (mg/L)	0.01–100	-	[10,37]
Sulfide (mg/L)	142 1222 15–30	0.5	[39,41]
Temperature	23.9 °C **	<3 °C at edge of mixing	[15,37]
Benzene (mg/L)	-	0.1	[39]
Mercury (mg/L)	-	~0.03	[37]
SO_4 (mg/L)	14.5–16	-	[31]
o-Cresol (mg/L)	14–16.5	-	[31]
Phenol (mg/L)	11–14	-	[31]
Total dissolved solid (mg/L)	3800–6200 1200–1500	1500–2000	[31,42]
n-Hexane (mg/L)	1.8–1.85	-	[31]
Grease and oil (mg/L)	12.7–3000	10	[10,39,43]
Total organic carbon (mg/L)	220–265 119 398	50–75	[42,43]
Ammonia (mg/L)	4.1–33.4 69	15	[40]
2,5 and 2,4- Dichlorophenol (mg/L)	28–32	-	[31]

* The values are according to the environmental protection agencies. ** Discharged from neutralized spent caustic.

3. Impacts of PPRP Wastewater on Environmental Health

In addition to human activities, due to insufficient treatment, the wastewater released to the environment by the petrochemical industry has become harmful to both the ecosystem and other life forms. The corresponding contaminants are highly toxic and hazardous, and negatively influence different components of the environment such as drinking water, groundwater resources, air and crop production [39]. Different environmental impacts of some of the main pollutants present in petroleum refinery wastewater, especially phenol, were mentioned in Table 2. For example, heavy oil can create a toxic environment for aquatic organisms by forming a layer on the water surface. Accordingly, an abnormal neural development, along with a late head formation, was found in the embryo of *Verasper variegatus* fish, as a result of the existence of these compounds on the surface of seawater. In addition, aromatic hydrocarbons, such as benzene, toluene and xylene, may act

as a mutagen, and the USEPA listed some of these pollutants as a class-A carcinogenic contaminant [44]. They can readily be absorbed by the gastrointestinal system, reach the nervous tissues shortly after being ingested, and subsequently may damage the nervous system [45].

Phenol and its derivatives can penetrate ecosystems as the result of the drainage of the effluents to the environment and surface waters. Even at low concentrations, these pollutants can affect the enzymatic and metabolic mechanisms of the aquatic microorganisms, and modify the biota of the environment based on their high degree of toxicity [46]. Due to the bio-refractory properties of the phenols, the degradation of these compounds is a lengthy process. Thus, phenolic compounds can accumulate in the tissue of aquatic organisms and cause biomagnification. Previous studies introduced phenols as genotoxic, carcinogenic, haematologically toxic, teratotoxic and physiologically toxic compounds with deleterious impacts on different organs of a human body such as kidneys, heart, the nervous system and liver [46]. The toxicity of phenol toward different plants has also been investigated. In this regard, a relevant study showed that the willow trees exposed to phenol with a concentration of 1000 ppm wilted and eventually died. These compounds can stop the preparation of DNA in diploid human fibroblasts, confirming the inhibitory effect of this compound on the replication and synthesis of DNA in cells [46]. Moreover, phenols can penetrate a cell and rupture the internal membranous structure. PAHs compounds are the other contaminates found in petroleum refinery wastewater that may cause genotoxicity among the aquatic living species [47]. Increasing the concentration of PAHs in different sources, such as drinking and ground waters, can negatively affect human life as the overall concentration of these chemicals may exceed the allowable levels reported in the Excess Lifetime Cancer Risk standards set by USEPA for the carcinogenic compounds [48].

Table 2. Major pollutants found in petrochemical and refinery wastewaters and their adverse impacts on the environment and human health.

Wastewater Pollutants	Adverse Health Effects	References
Bisphenols	• Causing abnormalities and metabolic disorders in human infants • Leading to disruption and mutations in animals' reproduction systems • Ability to cause cancer in prostate glands and breast	[49]
Toluene	• Negatively influencing the central nervous system, respiratory system, kidney, liver and eyes • Leading to fatigue, ataxia, cerebral atrophy and drowsiness • Leading to moderate acute toxicity on aquatic species • Leading to detrimental impacts on the leaves in plants	[44]
Nitrophenols	• Inducing changes in testicular tissues • Remarkably decreasing the hormones' plasma levels • Suppressing transcription process and affecting the number of genes in the thyroid system	[50]
Benzene	• Being carcinogenic in nature • Decreasing the production of white and red blood cells • Negatively influencing the central nervous lymphatic system	[44]
Polycyclic aromatic hydrocarbons	• Being mutagenic, carcinogenic and genotoxic in nature	[47]

Table 2. *Cont.*

Wastewater Pollutants	Adverse Health Effects	References
Chlorophenols	• Ability to disturb the endocrine system in aquatic creatures • Inducing genetic mutations or negatively impact cell growth in fishes • Ability to induce asthma, digestive tract infections and heart diseases to human beings	[51,52]
Heavy oil	• Being toxic in nature • Causing growth retardation	[53]
Cresols	• Causing abnormalities in adherens junction, as well as gap junction • Hindering the blood clots formation • Leading to bleeding disorders by producing reactive oxygen species in a human body	[54]
Phenols	• Ability to induce diarrhea, skin rashes and muscle fatigue • Altering the aquatic biota • Leading to detrimental impacts on rats and human lungs • Being ecotoxic and carcinogenic	[55,56]
Xylene	• Modifying enzymatic activity in the human body • Ability to cause skin inflammation • Ability to adversely affect kidneys	[44]
Aminophenols	• Reducing the volume percentage of red blood cells and haemoglobin level in fish • Causing malfunctioning in the respiratory and reproductive system of humans • Damaging kidneys and ability to cause premature death of liver cells	[57,58]
Ethylbenzene	• Adverse effects on the nervous and respiratory systems	[44]
Triclosan	• Causing malfunctioning in the cardiovascular system and adversely impacting the immune system • Inducing noxious effects on cells	[59]
Alkylphenols	• Causing damage to the sustentacular cells • Disturbing the secretion of androstenedione and progesterone in humans (males)	[60]

4. Treatment Technologies

Different treatment processes, including physical treatment (pre-treatment), secondary treatment (biological treatment) and tertiary treatment (polishing), are involved in the treatment of petroleum refinery and petrochemical wastewater [37]. These processes mainly target a multifaceted approach for the elimination of hydrocarbons, oil, sulfates, the trace of metals and other persistent organic pollutants simultaneously. The primary wastewater treatment can be divided into two sub-stages: primary and secondary oil/water separations. Gravity separation, such as corrugated plate interceptor separator, American Petroleum Institute (API) separator and hydro cyclone separators are the most common technologies

utilized in primary water and oil separation. For the secondary separation process, some other techniques with similar principles (i.e., dissolved gas flotation) are employed [61]. The primary treatment is pivotal for the prolonged and efficient performance of the secondary treatment unit (biological treatment), as it reduces the turbidity, heavy oil and suspended solids, which can impact the functioning of different microbes used in the biological treatment stage [62].

The secondary treatment aims at the decomposition of the remaining dissolved oil, a fraction of recalcitrant organic contaminants, degradable organic compounds and trace metals by using microbial activities [63]. In the secondary treatment stage, recalcitrant organics and dissolved oil are oxidized into more simple final products (i.e., CH_4, H_2O and CO_2) under anaerobic, aerobic or semi-aerobic conditions. A broad range of technologies, such as continuous stirred tank bioreactor, activated sludge process and membrane bioreactors can be employed in the secondary treatment step [64]. The application of membrane bioreactors for petrochemical wastewater treatment purposes faces some serious challenges, as they are not considered a cost-effective approach comparing with some existing technologies. However, their applications in wastewater treatment can experience an increasing trend, as a result of providing cost-effective membranes [37]. It has been reported that the combination of two or more biological techniques can be more effective in treating different petroleum refinery wastewater [65]. Regardless of the process utilized in the secondary treatment stage, the performance of the biological treatment can be heavily impacted by various factors such as the aeration rate, sludge loading, sludge retention time and sludge volume index [37]. In addition, most of these technologies require highly skilled labor, generate a huge volume of sludge and require regular maintenance. Operating time is another important factor in the treating of industrial wastewater. In this regard, most of these techniques need a significantly high hydraulic retention time, as shown in Table 3, which is considered as an inherent disadvantage to these technologies, along with some other limitations such as the inhibition of the microorganisms at high concentrations of toxic substances [31]. Furthermore, conventional biological techniques are incapable of completely eliminating the recalcitrant organic pollutants mostly seen in petrochemical wastewater [31].

A tertiary treatment process, or polishing step, is required to further reduce the concentration of the recalcitrant pollutants with bio-refractory characteristics in the discharged effluents to meet the necessary standards. This step usually takes place downstream of the secondary treatment, and can be traditionally achieved through chemical oxidation, activated carbon filtration and sand filtration. Other advanced wastewater treatment approaches such as electrodialysis, ion exchange and electrodialysis reversal were applied for treating effluents on small scales [37]. Membrane separation technologies were also employed recently to treat phenolic wastewater, and improve the quality of the effluents for reuse and discharge purposes. For instance, the separation and transport characteristics of some composite membranes, such as Poly(ether block amide) and PERVAP-1070 membranes, in pervaporative removal of phenol from a wastewater sample were investigated previously. The outcome of this study indicated that Poly(ether block amide) membrane could remove phenol from the samples effectively, and it had the highest phenol removal efficiency in comparison to other membranes [66]. However, the application of most of the advanced oxidation processes and other technologies involved in the tertiary treatment stage on a large-scale level is limited, since they require expensive reactants. Moreover, the efficiency of these processes significantly decreases with the increasing COD level in the wastewater [67]. Table 3 presents some of the conducted studies and employed techniques for the removal of some commonly found pollutants in wastewaters, especially phenols, along with their major drawbacks.

Table 3. Some of the conventional processes to treat phenolic wastewaters along with their main drawbacks.

Treatment Techniques	Targeted Pollutants	Wastewater Origin	Treatment Time (h)	Major Drawbacks	References
Activated sludge process	COD	Petroleum refinery	4.19	Aerobic or Anaerobic bioremediation: ♦ Hard to maintain the optimal level of growth media ♦ May produce toxic by-products ♦ Low efficiency at high or very low phenol concentrations ♦ Produce secondary pollution such as sludge	[29,68]
Activated sludge process	COD	Petrochemical plant	24–96		[69]
Upflow anaerobic sludge blanket	Toxic phenolics	Synthetic	7.92–18		[70]
Anaerobic expanded granular sludge bed bioreactor	COD and petrochemical pollutants	Petrochemical plant	62.8		[65]
Anaerobic packed-bed biofilm reactor	COD	Synthetic from a Fisher-Tropsch process	33–100		[35]
Upflow anaerobic sludge blanket	Phenols	Synthetic	48–72		[71]
Biological aerated filter and upflow anaerobic sludge blanket	Ammonium and COD	Heavy oil	12		[72]
Membrane bioreactor	Heavy metals	Petrochemical plant	>24		[73]
Microaerobic hydrolysis-acidification-anoxic-oxic processes	COD and ammonium	Petrochemical plant	20		[74]
Anaerobic-aerobic biofilm reactor	Total nitrogen and COD	Petroleum refinery	36–50		[75]
Microbial fuel cell	COD	Petrochemical plant	264		[76]
Immersed membrane process	Grease and oil	Petroleum refinery	-	Membrane-based separation techniques: ♦ The short lifetime of membranes ♦ Low pollutant removal efficiency when operating under harsh conditions or subjected to elevated temperatures ♦ Require considerably high energy	[77]
Membrane sequencing batch reactors	Hydrocarbon pollutants	Petroleum refinery-synthetic effluent	8–24		[78]
Membrane sequencing batch reactors	COD	Petroleum refinery	24		[79]
Polyvinylidene fluoride (PVDF)/ multi-walled carbon nanotube (MWCNT) nanocomposite membranes	Grease and oil—organic pollutants	Petroleum refinery	6		[80,81]
Membrane sequencing batch reactors	Phenol and COD	Petroleum refinery	8		[82]
Polyaluminium chloride for coagulation treatment	COD, TOC and Turbidity	Petrochemical plant	0.5	Coagulants treatment: ♦ The salts can cause several environmental and health issues such as Alzheimer's disease causativeness, reduction in treated water pH due to the reaction between alum and natural water alkaline ♦ Low coagulation efficiency in cold water ♦ High sludge production and non-biodegradability of the reagents	[83]

Table 3. *Cont.*

Treatment Techniques	Targeted Pollutants	Wastewater Origin	Treatment Time (h)	Major Drawbacks	References
Adsorption by organoclay	Organic substances	Petroleum refinery	-	Adsorption: ♦ The complex process for regeneration of the adsorbents ♦ The regeneration procedure can generate new phenolic pollutants ♦ Some chemicals used in this method can be toxic ♦ In some cases, it requires a large amount of adsorbent due to low adsorption capacity	[84]
Ozone-Photocatalytic oxidation (O_3/UV/TiO_2)	Phenol, Sulfide, ammonia and COD	Petroleum refinery	1	Photo-oxidation: ♦ Not economical due to the utilization of the UV light ♦ Hard to achieve effective charge separation ♦ Not always applicable to synthesis or regenerate the photocatalysts effectively	[81,85]
Bismuth oxybromide/oxyiodide photocatalysts	Phenolic pollutants and TOC	Synthetic	1.33		[86]
Phenol-formaldehyde resin-coupled TiO_2 photocatalysts	Phenol	Synthetic	7.5		[21]
Fe_2O_3/RGO nanocomposite photocatalysts	4-Nitrophenol	Synthetic	0.83		[87]
TiO_2@graphene nanocomposites	Phenol	Synthetic	60		[21]
ZnO nanoparticles—photocatalysis treatment	COD	Petroleum refinery-oily effluent	3		[88]
Boron-graphene oxide-TiO_2 photocatalysts	4-Nitrophenol and COD	Petrochemical plant	3		[89]
Photochemical treatment (UV/H_2O_2)	TOC	Petrochemical plant	4		[45]
Two-stage wet-air oxidation	COD, grease and oil	Oily sludge frompetrochemical plant	2.5	Wet air oxidation: ♦ High hydraulic retention time ♦ To achieve a desired level of oxidation, it requires high pressure and temperature	[84,85,90]
Fenton process	Phenol, COD and TOC	Petroleum refinery	10	Chemical Oxidation: ♦ Some of the required agents (i.e., ozone) can be expensive, ineffective to oxidize phenolic pollutants and not very soluble in water ♦ May produce secondary recalcitrant chemicals ♦ Safety issues due to working with noxious compounds	[84,85]
Electro-Fenton treatment	TOC, phenol and COD	Synthetic	0.5		[63]
Iron-nickel foam (Catalytic ozonation)	COD and dissolved total organic carbon (DOC)	Petrochemical	2		[91]
Fe/ZrO_2 and Fe/sulfonated- ZrO_2 catalysts	Phenol	Synthetic	6		[21]
MoO_3/V_2O_5/MCM-41 catalysts	Dibenzothiophene	Synthetic	1.25		[21]
Catalytic cracking catalysts (Catalytic ozonation)	COD	Petrochemical plant	0.5		[92]

Table 3. *Cont.*

Treatment Techniques	Targeted Pollutants	Wastewater Origin	Treatment Time (h)	Major Drawbacks	References
Bioelectrochemical systems	COD and diesel range organics	Petroleum refinery	96	Electrochemical oxidation: ♦ Require a large amount of energy and expensive equipment ♦ Safety issues due to working with noxious compounds ♦ Low processing capacity	[85,93]
Electrochemical advanced oxidation	1,2-Dichlorobenzene and TOC	Synthetic	3		[94]
Electrochemical treatment	Phenol	Petroleum refinery	2		[95]
Electrochemical catalytictreatment	Phenol and COD	Synthetic	0.67		[96]
Electrochemical oxidation treatment	COD and organic pollutants	Petrochemical plant	8		[21]
Electro-Fenton process	COD	Petrochemical plant	~1.31		[21]

Enzymatic Treatment

Enzymatic wastewater treatment refers to the processes using naturally occurring enzymes in plants or microorganisms to reduce or degrade recalcitrant, harmful and undesirable water pollutants such as phenolic acids. These biocatalysts can facilitate a complete and quick breakdown of the substrates by lowering the required activation energy [97]. The enzymatic wastewater treatment approaches have evolved during recent years, in order to deal with slow growth-dependent microbial remediation and minimize, or even eliminate in some cases, the toxic organic pollutants. In comparison with the traditional chemical and biological treatments, this technology is more environmentally friendly with the advantage of superior and selective degradation capabilities, no shock loading or delay impacts associated with the plant start-up or shut-down, and improved action on the compounds of interest. Moreover, the smaller size of enzymes compared to the microbial cells enable these biocatalysts to contact pollutants easily, and have quicker mobility. Furthermore, biocatalysis facilitates more targeted rapid and effective reduction or elimination of the pollutants to a less or even admissible harmful state. Various enzymes, such as oxidoreductase enzymes (i.e., peroxidases, laccases and tyrosinase), oxygenases, haloalkane dehalogenases and lipases have been reported to be effective in wastewater treatment processes for degrading and eliminating a wide range of organic pollutants such as phenolic compounds [98]. In the following section, the focus was directed toward biocatalysis for wastewater treatments, and more details were discussed regarding this comparatively novel technology.

5. Oxidoreductase Enzymes and Their Mechanisms of Action

Pioneering applications of oxidoreductive enzymes (such as peroxidases and polyphenol oxidases) have gained tremendous interest in the last few decades [99]. These enzymes can participate in the removal/degradation of many aromatic pollutants present in various industrial wastewaters, and also catalyze the oxidation of different phenolic compounds [19]. Peroxidases (EC 1.11.1.x) are hemoproteins that are broadly distributed in nature, especially in fungi, microbes and plants, with the ability to efficiently oxidize a wide range of substrates in the presence of hydrogen peroxide (H_2O_2). The biological functions of peroxidases differ within organisms, and some members of this group have considerably high redox potential and thermal stability [100]. Theoretically, peroxidases are considered the most oxidizing enzymes available in nature, due to their redox potential of H_2O_2 [101]. The classic mechanism of action for these types of enzymes is depicted in Figure 1. These enzymes showed remarkable performances in oxidizing pesticides, dioxin, phenols, polycyclic PAHs, polychlorinated biphenyls and other xenobiotics, directly or through co-oxidation. A 3D structure of horseradish peroxidase [102], as a member of the peroxidases group, was obtained from the RCSB protein data bank (PDB ID: 1W4Y), processed by discovery studio and Visual Molecular Dynamics (VMD) software [103], and visualized in Figure 2. Horseradish peroxidase, as a heme protein, consists of about 308

amino acid residues and the N-terminal residue of this protein is blocked by pyrrolidone carboxyl residuals. The structure of horseradish peroxidase predominately comprises α-helix contents. However, requiring the oxidizing agent (H_2O_2) and suicide inactivation of peroxidases by hydrogen peroxide are the weakest points for utilizing these biocatalysts in the bioremediation processes [101].

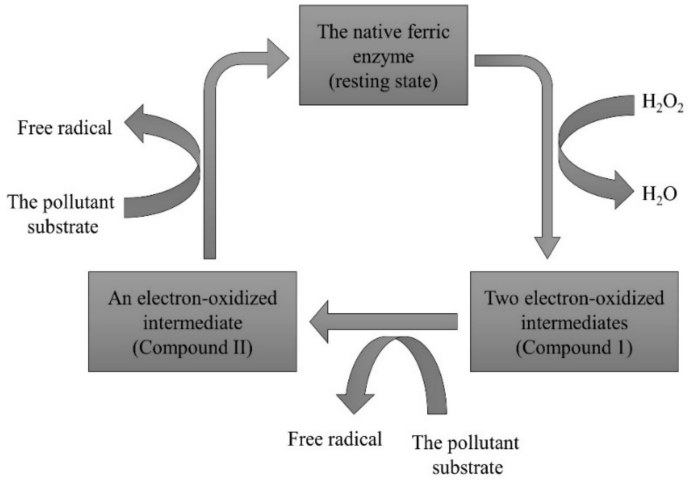

Figure 1. Schematic representation of the catalytic cycle of peroxidases.

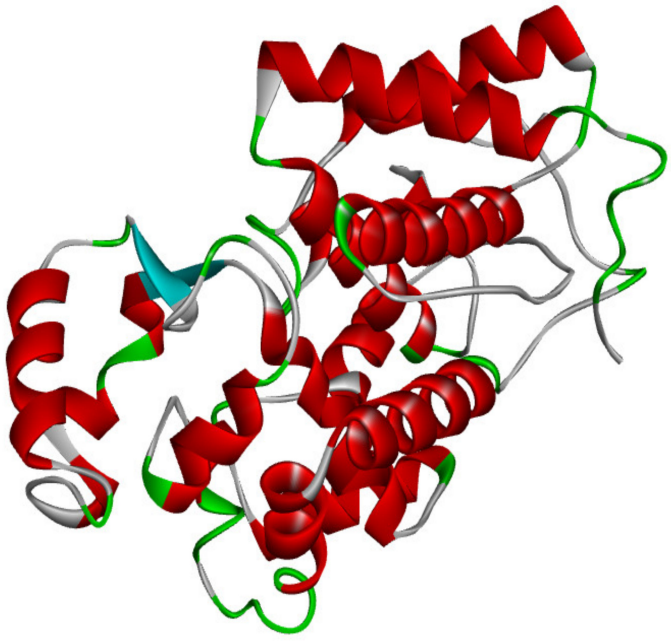

Figure 2. Conformational structure of horseradish peroxidase as a member of peroxidases.

Polyphenol oxidases (PPOs) are copper-containing enzymes that are almost ubiquitous among plants [104]. Among the oxidoreductases, the copper-containing enzymes are of particular interest based on their unique advantages over the peroxidases. For instance, these biocatalysts do not require hydrogen peroxide for their reactions, and this property makes them more practical for different industrial processes such as wastewater treatment. In the literature, the designation "polyphenol oxidases" is sometimes used for both tyrosinase and laccase enzymes. These enzymes react with oxygen atoms, and catalyze the oxidative transformation of several phenols and non-phenolic compounds to their corresponding *o*-quinones (which are insoluble and less toxic) without requiring any additives [27,83].

Tyrosinase (E.C. 1.14.18.1, monophenol monooxygenase) is extensively distributed throughout the phylogenetic scale from mammals to bacteria [27]. Tyrosinase extracted from different mushrooms (i.e., edible mushrooms) are the most commercially available polyphenol oxidase enzymes for various industrial processes, such as wastewater water treatments [101]. This enzyme catalyzes two various oxygen-dependent reactions occurring consequently. As shown in Figure 3, in the first reaction, the *o*-hydroxylation of monophenols occurs, which yields the generation of *o*-diphenols (also known as cresolase activity), while the second reaction involves the oxidation of the produced *o*-diphenols to *o*-quinones (known as catecholase activity) [27]. The products of catalytic activity (*o*-quinones) are highly unstable in the aqueous solution, and tend to react either with other nucleophilic or themselves to form oligomers and insoluble polymers, which can be easily separated from the reaction solution by simple conventional technologies such as simple filtration, sedimentation and coagulation processes [101]. Spectroscopic and chemical studies of tyrosinase indicated that the active site of this enzyme contains coupled binuclear copper complex, as shown in the 3D representation of tyrosinase in Figure 4 (PDB ID: 5M6B) [27,105]. As represented in this figure, the crystal structure of tyrosinase depicts that the residual architecture of this protein predominately consists of α-helix and random coil structures. The central domain of tyrosinase is composed of six conserved histidine residues, and it contains the CuA and CuB oxidizing ions. Among them, the CuB site exhibits higher conservation than CuA [27,105].

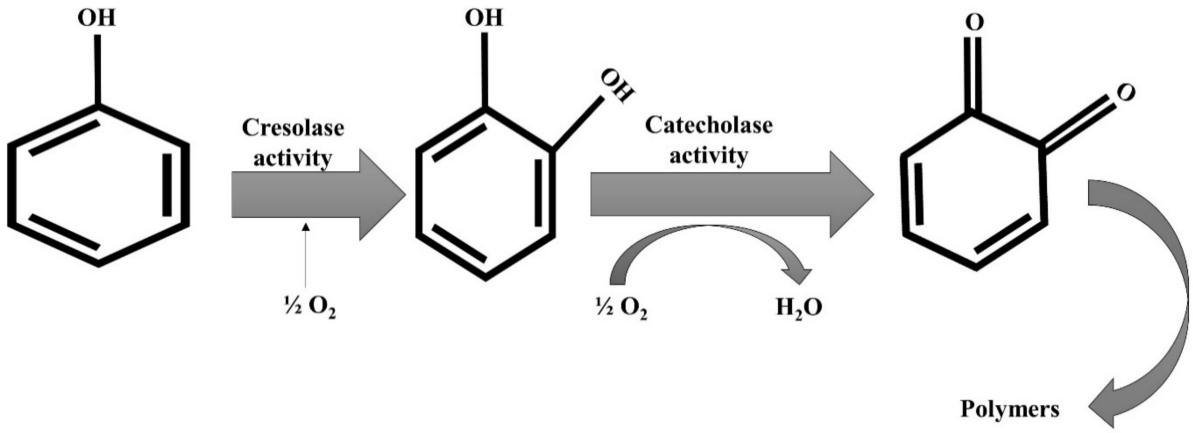

Figure 3. Schematic depiction of the catalytic mechanisms of tyrosinase (polyphenol oxidase); the final products of the biocatalytic process evolve towards the formation of the insoluble polymers.

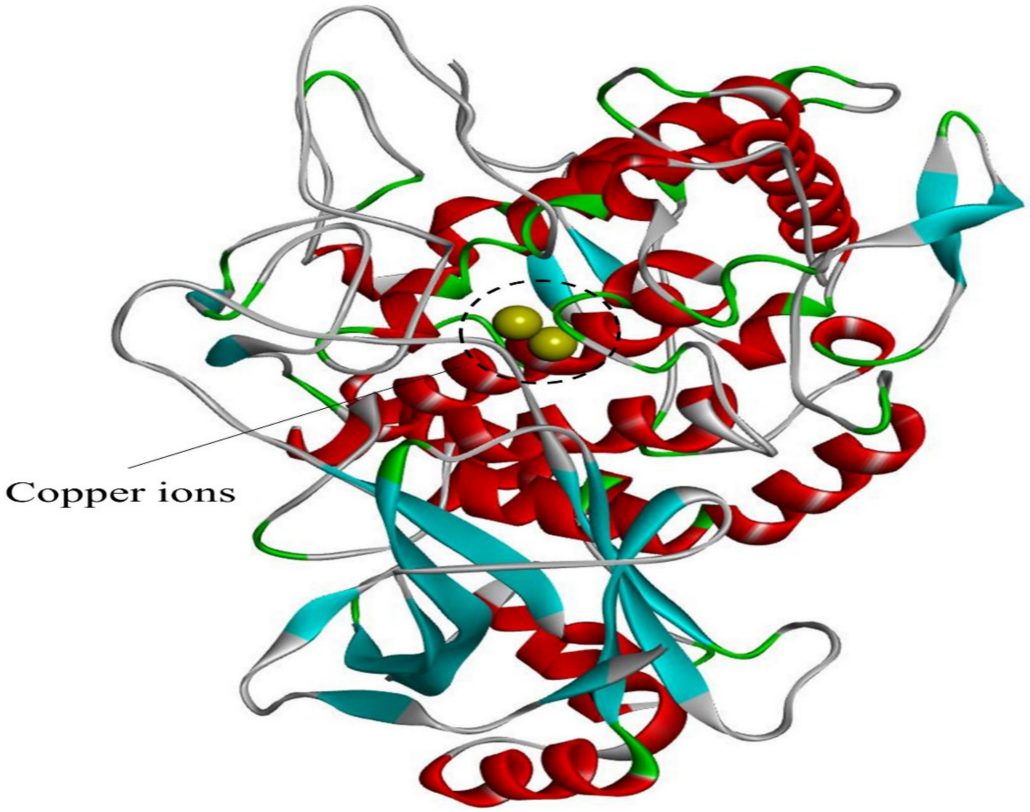

Figure 4. 3D structure of tyrosinase containing two copper ions.

On the other hand, laccases (EC 1.10.3.2) are multicopper blue oxidases broadly found in different sources including bacteria, plants, selected fungi and insects [101,106]. This enzyme accommodates four copper ions within its structure as illustrated in Figure 5, based on the PDB ID: 1Gw0 [107]. Fungal laccases are known as monomeric and extracellular glycoproteins with a molecular weight of about 60–70 kDa and ~520–550 amino acid residues in their glycosylated form. These laccases contain three tightly arranged cupredoxin-like domains, with each one possessing β-barrel symmetry [107]. Recently, many research interests in the field of wastewater treatment have been attracted to the laccase family, due to their exceptional abilities to effectively catalyze the one-electron oxidation of a significant number of non-aromatic and aromatic chemicals and degrade them. Some examples of the substrate for the laccase family include triclosan [108], bisphenol A, chlorophenols, phenols, aminophenols and phenolic dyes [84,101]. Molecular oxygen is the only co-substrate required for laccases, and similar to tyrosinases, these enzymes offer significant advantages over peroxidases. Almost similar to tyrosinases, the final products of the enzymatic reaction in the presence of laccases are water and the phenoxy radicals which can also form insoluble polymers [84]. The stoichiometry of the enzymatic reactions for laccases is 1 mol O_2 per 4 mol substrate as shown in Figure 6. In general, copper-containing enzymes have a Cu^{2+}/Cu^{+} redox system, in which the copper ion can change its valency from Cu^{+} to Cu^{2+} during the first complexation step, and then this generated complex possesses a polarized O-O bonding. The whole process results in the hydroxylation of the substrate to form *o*-diphenols, and the cycle is completed by the oxidation of the produced *o*-diphenols to *o*-quinones [27,101,107].

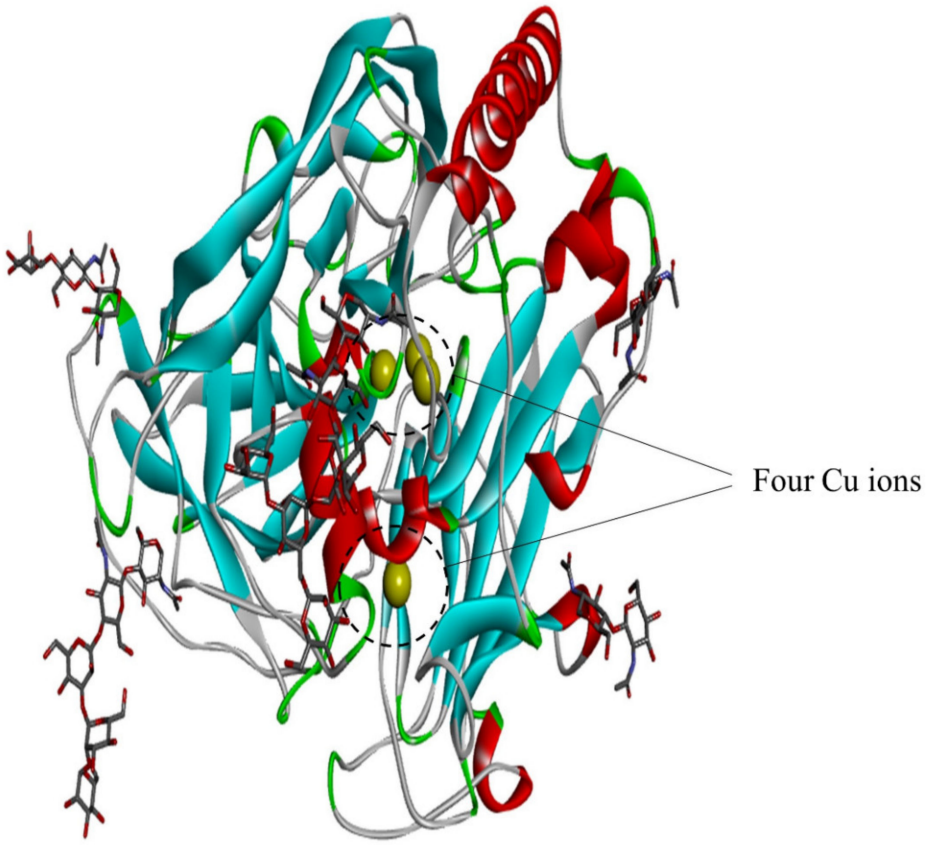

Figure 5. The 3-dimensional structure of the laccase enzyme showing the four copper ions.

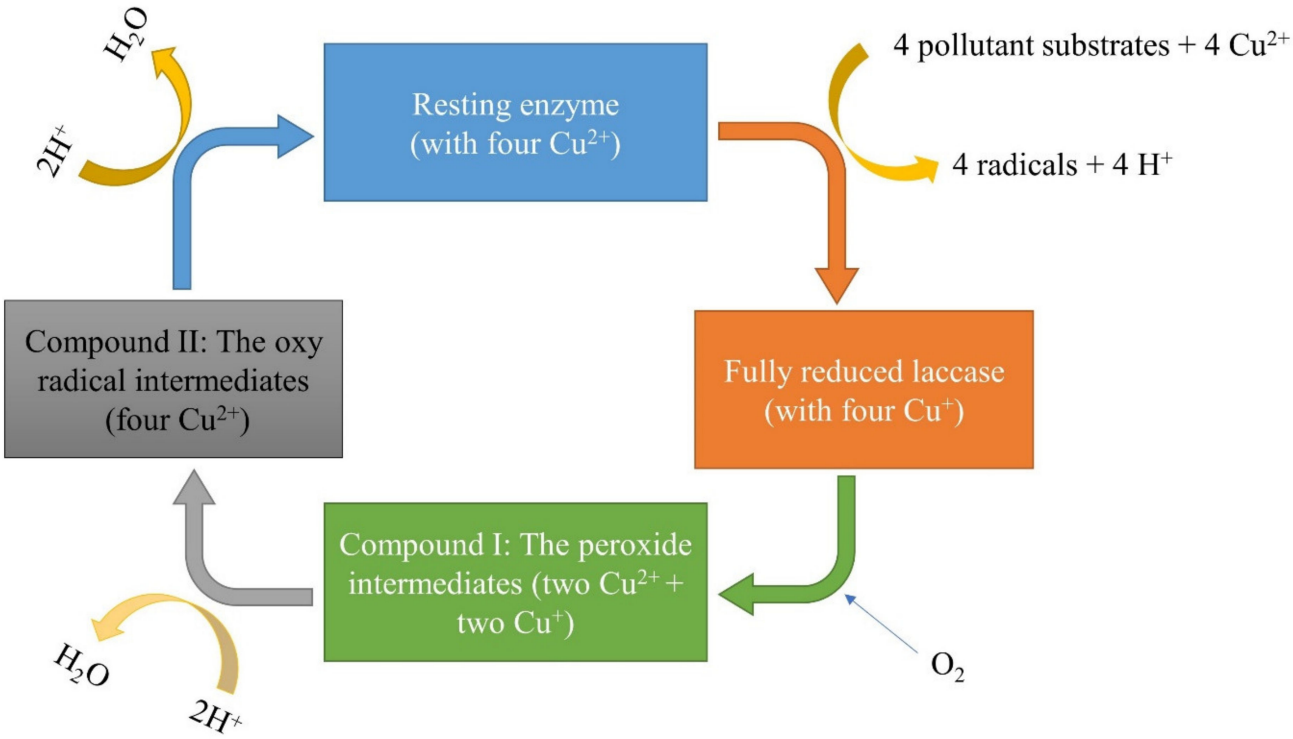

Figure 6. Catalytic cycle of laccase-catalyzed oxidation of an organic pollutant.

Modern directed molecular evolution technologies seem to be an interesting technique that is currently being evaluated, and has yielded promising outcomes to obtain laccase variants with better redox capability, improved stability under different harsh operating conditions and enhanced specific activity towards phenols and non-phenolic compounds [101].

5.1. Biochemical Properties of Polyphenol Oxidase (PPO)

The positive cooperativity of polyphenol oxidases (including laccases), in addition to the sigmoidal relationship between the substrate concentration and the reaction rate with a high Hill coefficient value, was reported previously [27]. On the other hand, Ricquebourg et al. [109] showed the allosteric behavior of polyphenol oxidases with positive cooperativity and conformational alteration. Laccases and tyrosinases have the capability of oxidizing phenolic compounds in broad ranges, although the enzyme activity may vary depending on the type of substrate. In this regard, it has been suggested that these enzymes offer higher activities in reaction with diphenols compared to that of monophenols. Polyphenol oxidases are mostly present in latent form in several plants, and this may be transformed into its active form by treating with some compounds, known as the activators, such as trypsin, salts, fatty acids and Triton-X114. On the contrary, some chemicals like dithiothreitol, EDTA, cysteine and Tris are considered inhibitors for polyphenol oxidases. The enzymes belonging to this group possess the potential of oxidizing a wide range of phenolic pollutants efficiently over a broad range of operating conditions (such as temperature and pH) [27].

5.2. Homogeneous Enzymatic Reactions for the Remediation of Phenolic Wastewaters

Homogenous enzymatic treatments are defined as the utilization of dissolved biocatalysts in the effluent samples to catalyze the degradation of the phenolic pollutants (some relevant studies are presented in Table 4). As explained earlier, peroxidases and polyphenol oxidases are the most prevalent enzymes used for the treatment of different synthetic and industrial wastewaters. The most extensively used peroxidase for the removal of the phenolic pollutants from the industrial effluents is horseradish peroxidase [110]. One study, for instance, showed that an increase in the concentration of this enzyme resulted in an enhanced bisphenol A elimination up to more than 98% during a treatment period of 3 h [111]. Another study evaluated the degradation of phenols from petroleum refinery wastewater in the presence of horseradish peroxidase, and the results confirmed the removal efficiency of almost 99% after treatment for only 35 min [112]. This level of removal was obtained by using H_2O_2 as a required electron acceptor and the enzyme simultaneously. However, enzyme deactivation and the consequent reduction in the phenolics removal efficiency were observed at high hydrogen peroxide concentration [111]. The application of horseradish peroxidase for industrial wastewater treatment purposes is extremely limited by its vulnerability to deactivation, as well as the costly enzyme production [23].

In this regard, soybean peroxidase can be a proper alternative to horseradish peroxidase, as it has the potential to be produced more cheaply [113]. Moreover, this enzyme has a higher level of catalytic activity in degrading some recalcitrant phenolic compounds, and it offers a lower vulnerability to irreversible deactivation in the presence of high concentrations of H_2O_2 [114]. It was reported that about 98% of was successfully removed by soybean peroxidase within 30 min in comparison, with only 36.5% degrading efficiency achieved by using horseradish peroxidase with the same treatment period [114]. The degradation efficiency of the peroxidases obtained from potato in eliminating 2,4-dichlorophenol from wastewater was also evaluated, and it was revealed that about 98% of the pollutant was removed from the sample with an initial phenolic concentration of 1–3 mM [115]. This study highlighted the potential application of the peroxidases extracted from food wastes in the remediation of the phenols from wastewater. For peroxidases, high or low concentrations of H_2O_2 in the medium can negatively affect the enzymatic reaction rate [116]. In this regard, polyphenol oxidases have been introduced as good alternatives to the peroxidases,

as the functionality of polyphenol oxidases are independent of the presence or absence of hydrogen peroxidase [117]. Due to some exceptional properties of these enzymes, such as their non-specificity, polyphenol oxidases have been widely employed to treat various wastewaters – particularly phenolic effluents [118].

The separation of bisphenol A and phenol from wastewater was conducted using a polyphenol oxidase enzyme. The initial concentrations of the enzyme and each pollutant used in this study were 5 U/mL and 4 mM, respectively. The treatment was carried out for 30 min, and after that the removal efficiencies for bisphenol A and phenol reached 60% and 80%, respectively. Within the same reaction period, further optimization in the operating conditions caused a significant increase in the degradation rates of phenol and bisphenol A to 88% and 96%, respectively [106]. The aforementioned reports showed almost the same removal efficiency for bisphenol A, but with a different treatment time. Despite the fact that the initial pollutant concentration utilized in the second study was 90 times higher than the one used in the first study [106], a comparatively higher enzyme concentration used in the latter one can be considered as an explanation for the faster pollutants degradation rate in the second observation. In addition to that, the operating conditions, such as temperature, presence of inorganic/organic co-pollutants and pH, along with the purity and source of the enzyme, can significantly affect the removal efficiency and required treatment time. Polyphenol oxidases were also reported to be effective in the removal of about 90% of phenol found in the refinery wastewater sample using the enzyme, with a concentration of 0.12 U/mL [119]. Although this pollutant can be degraded easier than bisphenol A, another study showed that the same concentration of the enzyme could effectively and almost completely degrade bisphenol A from synthetic wastewater in a considerably short treatment period (~3 h) [111]. This observation and higher degradation rate obtained for bisphenol A than that one reported for phenol could be due to the complexity of the refinery wastewater sample, and the presence of other pollutants.

A laccase produced by *Coriolopsis gallica*, a fungus species, showed a 100% degradation efficiency for bisphenol A in a wastewater sample after 4 h treatment [120]. However, the same enzyme obtained from the other fungi (*Bjerkandera adusta* and *Tinea versicolor*) was found to be less effective against this pollutant, highlighting the impact of the enzyme source on the degradation of phenolic contaminants from different wastewaters [120]. Other pollutants than phenol, such as chlorophenols, have also been reported to be effectively removed by the polyphenol oxidases. For instance, laccase was used in order to treat a mixture of different chlorophenols with the initial concentration of 15 mg/L during 4 h treatment. After this period, the enzyme with the activity of 10 U/L could entirely remove 2,4-dichlorophenol and 2-chlorophenol from the wastewater [121]. In another study, a wastewater sample containing 2,4-dichlorophenol, 4-chlorophenol and 2-chlorophenol pollutants with the initial concentration of 50 mg/mL (for each pollutant) was treated by laccase enzyme (80 mg/mL). The process continued for almost 10 h, and the obtained results suggested the removals of 94%, 69% and 75% for 2,4-dichlorophenol, 4-chlorophenol and 2-chlorophenol, respectively [122]. The better degrading efficiency reported in the former study may correspond to both the lower concentration of the pollutants in the wastewater sample, as well as the usage of a crude enzymatic extract that contained two laccase isoenzymes. This finding further emphasizes the significant impacts of some operating conditions – such as the treatment conditions and the presence of co-pollutants in the wastewaters – on the phenolic compounds degradation rate. Moreover, polyphenol oxidases were also employed in order to entirely degrade four different phenolic compounds, namely tyrosol, hydroxytyrosol, p-coumaric acid and guaiacol, within 1 h of enzymatic reaction. However, it was found that the same enzyme obtained from the same source was less effective in removing catechol within 1 h of treatment [123], but could completely degrade the pollutant after 2 h of reaction. The variation in the structures of these chemical compounds could be the main reason for the slower degradation rate of catechol in comparison to the other four phenolic pollutants, as discussed in this literature. In connection with this, a study showed that more than 40% catechol removal can be

achieved by using laccase after treating it for only 72 s [124]. Contrary to the earlier study, these results suggested that the prolonged reaction times, such as 1h, might be enough for the complete degradation of this compound. However, no further investigations were reported in these two studies, thus it is difficult to correlate the differences observed in the removal efficiencies with only the variations in the phenolic compound structures.

5.3. Heterogeneous Enzymatic Reactions for the Remediation of Phenolic Wastewaters

Different limitations have been listed for homogenous enzymatic wastewater treatments. Among these, the recovery of the enzymes from the reaction medium is considered as one of the key obstacles to the utilization of biocatalysts for wastewater treatment purposes. However, enzyme immobilization within or on insoluble supports has been introduced as an applicable approach to overcome this issue, which can also facilitate enzyme reusability and recovery [117]. Furthermore, enzyme immobilization techniques and the utilization of the heterogeneous biocatalyst reactions offer more advantages, such as improving the enzyme stability [125]. The immobilization of different enzymes on a wide range of solid carriers using various techniques was investigated to utilize the resultant biocatalysts for the treatment of different phenolic wastewaters, and some of these studies are listed in Table 4. The immobilization of a biocatalyst on an insoluble carrier can be performed by physical or chemical attachments [126]. The chemical immobilization of an enzyme on suitable support can be achieved through the formation of covalent bonds between the biocatalyst and functional groups available on the surface of the solid carrier. On the other hand, the most common physical enzyme immobilization techniques, such as encapsulation, entrapment and physisorption, are defined as the bonding of an enzyme to a carrier via hydrophobic or electrostatic interactions [127]. The covalent attachments mostly provide a robust and effective enzyme immobilization, and enhance the biocatalyst thermal and pH stability significantly. For example, Kujawa et al. used newly synthesized spacer molecules to functionalize ceramic supports (Al_2O_3 powders and membranes) for *Candida antarctica* lipase B enzyme immobilization. The obtained results indicated that the specific enzyme activity was much higher for those samples which were functionalized with longer modifiers. The enzyme loading efficiency was found to depend on different factors, such as type of spacer molecules, their chemical composition and the length of the chains, along with enzyme interactions with the surfaces of the carriers [128]. However, these approaches are usually more expensive and complicated when compared with the physical techniques [117]. Thus, it seems essential to develop cost-effective, applicable and eco-friendly enzyme immobilization techniques with a high immobilization yield to extend the application of enzymatic reactions for treating different industrial wastewaters. In a study, laccase was immobilized on granular activated carbon support for the removal of carbamazepine, sulfamethoxazole, bisphenol A and diclofenac from wastewater samples [129]. The obtained results showed that about 60%, 59%, 98% and 40% of diclofenac, sulfamethoxazole, bisphenol A and carbamazepine were degraded by the insoluble enzyme after 24 h of reactions, respectively. Moreover, it was observed that the phenolic pollutants degradations by the immobilized enzyme were significantly higher than those obtained using the free form of laccase. The higher removal efficiency observed for the immobilized enzyme could be attributed to the simultaneous effects of pollutants adsorption on the solid carrier and the enzymatic reaction. However, the absorption of the pollutants or any products generated as a result of an enzymatic reaction on the support was found to have a significant negative impact on the overall process yield and enzymatic activity [129]. Abdollahi et al. used magnetic nanoparticles functionalized with amine groups and cyanuric chloride agent, as the cross-linker, to covalently immobilize tyrosinase onto them and degrade phenol in both synthetic and real wastewater samples. In this regard, the effect of different operating parameters such as biocatalyst dosage, temperature, pH and initial phenol concentration on the catalytic activity and phenol removal of the immobilized enzyme was studied. The immobilized tyrosinase showed a reasonably high phenol degradation of 70% when a high concentrated substrate (phenol, 2500 ppm) was

subjected to treatment using a comparatively small amount of the biocatalyst. Furthermore, 100% of phenol was removed after reusing the immobilized tyrosinase for three consecutive treatment cycles, and this efficiency dropped to 58% after the seventh reaction cycle. This study also showed that the immobilized enzyme degraded up to 78% of phenol pollutant in a real wastewater sample, with the initial phenol concentration of 250 mg/L within 60 min treatment period [130]. The immobilization of lignin and manganese peroxidases via the encapsulation method within three various polymeric matrices, including carboxymethyl-cellulose, gelatin and pectin, was reported previously for the degradation of bisphenol A from wastewater [131]. In this study, higher pollutant efficiency was obtained for the enzymes immobilized within the pectin polymeric matrix. This difference between the enzymatic activities of the biocatalysts encapsulated by various polymeric matrices could be due to the higher level of protection offered by the pectin polymeric matrix for the enzymes against the inhibitory agents in the medium [131]. Another study reported the immobilization of horseradish peroxidase on a hydrous-titanium surface, instead of the polymeric matrices. It was discussed that the immobilized form of this enzyme can have better stability and phenol removal efficiency from wastewater, compared with the mobile horseradish peroxidase [116]. In this regard, it was observed that the increment in the concentration of hydrogen peroxide from 0.2 to 1 mM did not affect the activity of the immobilized horseradish peroxidase [116]. Similar to the findings reported earlier, the better performance of the immobilized biocatalyst in this study could be attributed to the combined impacts of enzymatic degradation and pollutant adsorption on the support. In physical attachments, the leakage of an immobilized enzyme from the polymeric matrix or a surface of a carrier is possible, and considered as one of the main disadvantages of these techniques, which can also hinder the reusability of the immobilized enzymes. A possible solution to overcome this issue is to form insoluble enzyme aggregates by cross-linking the molecules of multiple enzymes. This approach was utilized to cross-link glucose oxidase with versatile peroxidase for removing bisphenol A from wastewater samples using continuous and batch treatment processes [132]. In both cases, it was shown that the pollutant was completely degraded by the cross-linked enzymes. However, a high amount of enzymes is usually required for degrading and crosslinking the substrates, since the unavailability and deactivation of the enzymes' active site using this method can be higher than that of the other ones; this is known as a potential limitation of using cross-linked enzymes for wastewater treatment. In this regard, covalent immobilization of the biocatalysts onto the surface of appropriate supports or within their pores accessible by the phenolic compounds can be a solution to overcome this limitation. To do this, both the insoluble carrier and the enzyme should offer reactive functional groups suitable for the formation of the covalent bonds. For the non-reactive carriers, this goal can be achieved by using proper chemical coupling techniques to functionalize their surfaces [133]. Accordingly, horseradish peroxidase was immobilized on electrospun microfibrous membranes to remove bisphenol A pollutant from a wastewater sample [134]. The immobilized enzyme showed improved stability, and could degrade 93% of bisphenol A after 3 h of incubation with the pollutant. This removal efficiency was higher than that one obtained for the free enzyme, which was about 61%, within the same reaction time [134]. In another relevant study, silica-coated superparamagnetic nanoparticles were functionalized with N-[3-(trimethoxysilyl)propyl]ethylenediamine agent, and then tyrosinase extracted from edible mushrooms (*Agaricus bisporus*) was immobilized onto them. The obtained nanobiocatalyst was employed for phenol degradation in wastewater. The immobilization of tyrosinase onto these nanoparticles caused a remarkable enhancement in the enzyme thermal and pH stability. Moreover, based on the magnetic properties of the supports, the nanobiocatalysts could be separated from the reaction medium and redispersed (reused) in different treatment cycles. The results indicated that the immobilized enzyme could remove up to 80% of the pollutant within 2 h of treatment, using a relatively small amount of nanobiocatalysts. Furthermore, this study suggested that the ultrasound waves could have a positive impact on the enzymatic activity of the immobilized tyrosinase [133]. Poly-

acrylonitrile (PAN) beads have also been suggested as a suitable support for enzyme immobilization purposes. In this regard, PAN beads were used for the immobilization of laccase, and consequently the removal of three different phenolic pollutants (2,4,6- trichlorophenol, 2- chlorophenol and pentachlorophenol) at the initial concentrations of 1 mM (for each compound) from a wastewater sample [135]. This system showed a degradation yield of 91% for pentachlorophenol, 65% for 2- chlorophenol and 93% for 2,4,6- trichlorophenol within a relatively short treatment period (about 90 min). Furthermore, it was shown in this study that the removal efficiency of pentachlorophenol and 2,4,6- trichlorophenol by the immobilized enzyme were negatively affected by the addition of 2- chlorophenol to the system as a co-substrate [135]. In a similar investigation, tyrosinase was also immobilized onto the PAN beads via covalent attachments, and the immobilized biocatalyst was utilized for the degradation of three different bisphenols (bisphenol A, bisphenol B and bisphenol C) from a wastewater sample [136]. It was observed that the immobilized tyrosinase could degrade up to 90% of the pollutants within 90 min of reaction. Furthermore, the immobilized enzyme showed good storage stability, where it retained more than 80% of its initial activity after incubating at 4°C for 30 days [136]. Zhang et al. activated the surface of chitosan through the chemical treatment with glutaraldehyde before the immobilization of laccase on it [137]. The immobilized biocatalyst was then employed for the remediation of 2,4-dichlorophenol from a synthetic wastewater sample, and a pollutant degradation of about 89% was achieved after 6 h of enzymatic reaction. Furthermore, it was found that the immobilization of laccase resulted in improving the enzyme activity. The immobilized laccase was used in different consecutive treatment cycles, and its activity decreased to less than 50% after the sixth reaction cycle. As stated in this study, this reduction in the activity of immobilized laccase could be due to the adsorption of some reaction products on the surface of the enzyme [137]. By considering the conducted studies in this field, enzyme immobilization techniques are a practical strategy to enhance the enzyme stability, as well as the applicability of different biocatalysts for wastewater treatment purposes.

Table 4. Free and immobilized enzymes are being used for the treatment of different wastewater samples.

Biocatalysts	Forms of the Enzyme *	Targeted Pollutants	Enzyme Carriers	Reaction Time (h)	Reference
Horseradish peroxidase	I	2,4-Dichlorophenol (97.7%)	Nano-spray dried ethyl cellulose particles	2	[138]
Horseradish peroxidase	I	2,4-Dichlorophenol (80%)	Modified magnetic nanoparticles	4.17	[139]
Laccase	I	Carbamazepine (10%) Bisphenol A (~100%)	Titania nanoparticles	24	[140]
Laccase	I	Bisphenol A (85–88%)	Metal-ion-chelated magnetic microspheres	12	[126]
Horseradish peroxidase	F	2-Methoxyphenol Phenol (99%)	-	0.58	[112]
Horseradish peroxidase	I	Phenol (~92%)	Hydrous titanium	0.25	[116]
Laccase	F	Bisphenol A (59.7%) Phenol (80%)	-	0.5	[106]
Soybean hulls peroxidase	F	Triclosan (98%)	-	0.5	[114]
Laccase	F	Bisphenol A (100%)	-	1	[141]

Table 4. *Cont.*

Biocatalysts	Forms of the Enzyme *	Targeted Pollutants	Enzyme Carriers	Reaction Time (h)	Reference
Glucose oxidase and versatile peroxidase	I	Nonylphenol (~100%) Bisphenol A (~96%) Triclosan (~26%)	Enzymes aggregates	0.17	[132]
Horseradish peroxidase	I	Phenol (99.9%)	Polyacrylonitrile (PAN)- based beads	5	[110]
Jicama Skin Peels Peroxidase	F	Phenol (~97%)	-	24	[142]
Laccase	F & I	Bisphenol A (100%) Bisphenol F (100%) Bisphenol S (40%)	*Hippospongia communis* spongin-based scaffold	24 (I*)M 10 (F*)	[99]
Tyrosinase	F	Phenol (90%)		3	[143]
Tyrosinase	I	Phenol (87%) *Para*-cresol (74%) Phenyl acetate (91%)	Modified diatom biosilica	12	[144]
Tyrosinase	F & I	Phenol (>90% by F and >85% by I)	PAN-based beads	6	[145]
Tyrosinase	I	Phenol (100%)	Aminopropyl-controlled pore glass	2.5–5	[146]
Laccase	F	Bisphenol A (>97%)		1	[147]
Laccase	I	2,4-Dichlorophenol (76%)	Chitosan–halloysite hybrid porous microspheres	4	[148]
Laccase	I	Bisphenol A (90%) Nonylphenol (30%)	Silica beads	1	[127]
Laccase	I (entrapment)	Phenol (95%)	Alginate beads	0.5	[149]
Horseradish peroxidase	F & I	2,4-Dichlorophenol (>90% by F and ~80% by I)	Activated beads	7.5	[150]

* I: Immobilized enzyme, F: Free enzyme.

5.4. Treatment of Real Wastewater

In addition to the treatment of synthetic wastewaters, which provide precious information on the mechanisms involved in the enzymatic reactions, it is also crucial to investigate the efficiency and treatment mechanisms in the bioremediation of real wastewater samples containing different types of pollutants. It has been reported that natural organic matters can inhibit the oxidative coupling processes of polyphenol oxidases, such as laccase. However, the reaction mechanism was found not to be changed since some dimers were still identified as the products of the catalytic reaction. In this regard, enzymatic treatment of the effluents discharged from an industrial wastewater treatment plant using cross-linked laccase and tyrosinase indicated the high conversion of some organic micropollutants to the oligomers [26]. Several reports are suggesting that polyphenol oxidases can be considered as relatively stable enzymes in treating different industrial real wastewaters, as shown in Table 5. For example, the wastewater of a textile factory located in Cairo, Egypt, was treated by laccase enzyme, and the results showed that about 71% of pollutant degradation was achieved [141]. Moreover, another study reported a noticeably high bisphenol A transformation of up to 95%, after using an enzymatic membrane reactor containing a polyphenol oxidase for the treatment of industrial effluent. The bioremediation of a real wastewater sample containing a wide range of different endocrine-

disrupting chemicals using a laccase-catalyzed treatment approach not only resulted in a high degradation efficiency for most of the pollutants, but also significantly reduced the ecotoxicity of those contaminates. Additionally, this enzyme was also used for the effective removal of chlorolignins and chlorophenols from the kraft bleach wastewaters, and the final results were promising. Some contributory studies reported the feasibility of using the immobilized form of the laccase enzyme in treating some petroleum and petroleum-like wastewater samples containing various organic and oil pollutants. In one of the recent works, laccase was encapsulated in core-shell magnetic copper alginate beads to be utilized for the treatment of a real wastewater sample. The outcome of this investigation confirmed the simultaneous removal of triclosan and some other recalcitrant pollutants from the real effluents [141]. In another study, peroxidases extracted from potato pulp were used for the elimination of phenol from both real and synthetic wastewaters, with the initial pollutant concentration ranging from 0.02 to 0.1 mM. It was found that more than 95% and 90% of phenol were removed from the synthetic and real wastewater samples, respectively [151]. Zeng et al. investigated the effect of the 1-hydroxybenzotriazole-laccase system on isoproturon removal efficiency in real wastewater effluent, and showed that some natural organic matters can serve as an efficient natural mediator [152]. Different characteristics of the optimized and real operating conditions can change the conversion yield of different pollutants in a wastewater sample. For example, some organic micropollutants existing in the wastewater of the pharmaceutical industry, such as diclofenac, are so recalcitrant in the effluents. It was found that almost 90% of this pollutant in synthetic wastewater can be removed by an immobilized polyphenol oxidase. However, the same biocatalyst could degrade only 20% of this compound in real wastewater [26]. On the contrary, the same study suggested that the removal efficiency of bisphenol A compound in the real and synthetic wastewaters can be reached 85% and 90%, respectively, using the aforementioned immobilized enzyme. It has been discussed that it is difficult to gain precise details on the reaction products generated as a result of enzymatic treatment of wastewater, mostly due to the complex measurement methods and ever-changing quality of the real wastewater effluents. However, it is known that the treatment of wastewater samples containing different pollutants by oxidoreductase enzymes could generate oligomers, quinones and dimers instead of simple compounds. This characteristic makes the separation process easier, and allows users to utilize simple conventional processes such as filtration and precipitation to achieve better performance [26].

Table 5. Some oxidoreductase enzymes are being used for the treatment of real wastewater samples.

Biocatalyst	Source of the Effluent	Country	Reference
Laccase	Liquefied petroleum gas station	China	[153]
Immobilized and free manganese peroxidase	Textile factory effluent	Pakistan	[154]
Horseradish peroxidase	Municipal wastewater effluents	South Korea	[155]
Immobilized tyrosinase	Industrial effluent (coal-gas conversion plant)	South Africa	[156]
Soybean peroxidase	Refinery wastewaters	Canada	[119]
Laccase	Chemical plant wastewater	South Korea	[157]
Immobilized lignin peroxidase	Industrial wastewater discharged by a paper industry	Brazil	[158]
Immobilized soybean peroxidase	Coffee processing wastewater	Brazil	[159]
Soybean peroxidase	Alkyd resin manufacturing wastewater containing phenol	Canada	[160]
Laccase	Municipal wastewater	Italy	[161]

5.5. Enzymatic Oxidation Kinetic

The rate of an enzymatic reaction is a function of different parameters such as mass transport effect, temperature and pH of a reaction medium, and the concentrations of the reactants. Mathematical modelling has been developed to effectively investigate the optimal productivity and functioning conditions of enzymatic catalysis by providing precise information on the enzymatic mechanisms, the concentrations of products and reactants and other parameter estimates. The laws of thermodynamics are applied to any enzymatic and chemical reactions. Enzyme kinetic modellings can provide crucial information on the enzymatic reactions through the reactivities of the participating species. These types of information are essential in designing enhanced reaction devices and estimating their performances. Development of proper kinetic equations and the establishment of reacting systems require comprehensive information on mass transfer effects and mass conservation requirements. Moreover, some parameters such as the interfacial tension, the utilization of immobilized biocatalysts, operating conditions (i.e., pH and temperature) and the reaction media composition can heavily affect enzyme kinetic modelling [162].

In 1913, Equation (1) was developed by Michaelis and Menten to establish the relationship between the concentration of the substrate and the velocity of an enzymatic reaction.

$$V_i = \frac{V[S]}{[S] + K_m} \quad (1)$$

In this equation, V_i is the initial velocity which can be defined as the rate of the enzymatic reaction at a given substrate concentration. $[S]$ and V are the substrate concentration and the maximum speed that the biocatalyst can achieve at saturating substrate concentrations, respectively. Finally, K_m is known as the Michaelis–Menten constant reflecting the affinity of the biocatalyst for the substrate. In this regard, the higher K_m values indicate a lower affinity of the enzyme for the substrate. When the reaction rate reaches half of its maximum value, the corresponding concentration of the substrate specifies the K_m value [163].

The initial enzyme kinetic concepts were based on homogeneous systems where the enzyme, the substrate and reaction products can be present in a single phase (the reaction medium). In these systems, the reaction can only be determined by the activity of the enzyme, while the rates of transport of products and substrates are irrelevant. On the other hand, in enzymatic heterogeneous systems developed using enzyme immobilization

techniques, the catalyst phase (mostly solid) differs from the bulk of the liquid phase where the products and substrates are dissolved. Enzyme immobilization can produce both micro-environmental and conformational effects. The former one refers to the mass transfer limitation, while the latter one is attributed to the steric effects due to the proximity of the enzyme to the surface of the carrier and the structural alternation in the biocatalyst molecule. In this scenario, the catalytic potential of an enzyme and the mass transport rate of substrates from the reaction medium to the enzyme can determine the kinetic behavior of the immobilized biocatalysts [164]. In the absence of inhibition, the Michaelis–Menten kinetics model can effectively predict the reaction rates of oxidoreductase enzymes such as horseradish peroxidase, laccase and tyrosinase. However, oxidoreductase enzymes show very complex reaction mechanisms that involve different enzyme forms and intertwined catalytic cycles for the oxidation of monophenols and diphenols. Hence, very complex kinetic situations may arise in presence of inhibitors due to their bindings to one or multiple enzyme forms at the same time. In this case, the classical Michaelis–Menten model may not be applicable to properly investigate the enzyme kinetic. As a result, several models have been developed based on the Michaelis–Menten equation to take the inhibitory effects into account [165].

For example, some studies on the kinetic behavior of horseradish peroxidase at room temperature, and pH 8 showed normal Michaelis-Menten saturation kinetics for the reaction of H_2O_2 with phenol catalyzed by this enzyme [166]. In another study, horseradish peroxidase was immobilized on poly(lactic-co-glycolic acid) fine particles and the kinetics of 2,4-dichlorophenol oxidation by the immobilized biocatalyst was studied. By applying the Michaelis–Menten model, the enzyme kinetic study suggested competitive product inhibition and probable hindrance by the reduction of hydrogen peroxide concentration [167]. A purified laccase was also used to oxidize 2,6-dimethoxyphenol (DMP). Kinetic assays of DMP oxidation using variable initial concentrations of dioxygen were conducted in a closed system, and the depletion rates of dioxygen were measured. As a result, bi-substrate and single-substrate models developed based on the Michaelis-Menten equation were successfully applied to the experimental data [168]. In a similar study, kinetic constants for the oxidation of a homologous series of catechol substrates by tyrosinase have been investigated. Studies of the dependence of catechol oxidation on the concentration of oxygen showed that the Michaelis constant for oxygen can be different based on the nature of the catechol substrate [163].

Generally, the kinetic studies of phenolic compound oxidation by oxidoreductase enzymes immobilized on various carriers require careful consideration of different factors, especially the substrates and products' nature, as well as the inhibitory and mass transfer effects. In this case, the mass transfer rate of substrates from the reaction medium to the biocatalyst and its catalytic activity can represent the kinetic behavior of the immobilized enzymes. As described earlier, this can be due to the fact that enzyme immobilization processes may result in introducing mass transfer limitations, and the steric effects as a result of the proximity of the biocatalyst to the surface of the support, as well as the changes in the structure of the enzyme molecule.

5.6. Recent Advances

The application of enzymes in industrial scales required providing enzymes with excellent technical features in a cost-effective manner. Screening of the new enzyme-producing species, developing genetically engineered species and applying different carriers and immobilization techniques are well-known efforts to reach high enzyme production yield, to enhance enzyme stability and reusability, and to reduce the cost of biocatalyst production. Recently, various engineering and recombinant-DNA techniques have been effectively implicated in the bioremediation of different wastewater effluents containing various phenolic and other persistent organic pollutants. These approaches gave rise to the increased production of a wide range of oxidoreductase enzymes, which can enhance the applicability of the biocatalysts in wastewater treatment processes [27]. Due to the ever-increasing

demand for bioremediation of industrial effluents, nanobiotechnology can also play a crucial role. Generally, nanobiotechnology is employed for those processes that require attacking the molecular level of compounds. Different forms of nanomaterials, such as nanoporous zeolites, nanoparticles and nanomembranes, have been employed for the treatment of wastewaters, although the progress was not adequate. On the other hand, nanozyme technology or nanostructure advanced biomaterials showed very promising potential in terms of better performance and applicability for these purposes. A broad range of methods, such as the immobilization of enzymes on nanostructured materials, production of single-enzyme nanoparticles and self-immobilization of enzymes, have been developed and utilized for the production of stable and highly efficient nanobiocatalysts for water and wastewater treatment purposes [117]. High enzyme loading per unit mass, a reduced loss of biocatalyst activity and catalytic recycling can be achieved by the enzyme immobilization on nanoscale supports. Furthermore, the biocatalysts can be stabilized by generating single-enzyme nanoparticles consisting of enzyme molecules surrounded by a porous inorganic-organic network with a thickness of less than a few nanometers [27]. As a result, the novel nanozymes and nanomaterials coupled with enzymes are considered promising and applicable candidates for bioremediation of industrial wastewaters, and they can be employed as a cost-effective technique that is capable of offering better performances and pollutant removal rates than conventional methods [27]. Moreover, many polyphenol oxidase nanozymes or nanostructured compounds (i.e., such as polyphenol oxidase-based nanofiber and nanowires) can be developed for degrading a broad range of persistent organic and phenols pollutants in industrial wastewaters [27].

Bioreactors equipped with immobilized polyphenol oxidases onto the nanomaterials can also be another example of the systems which may be used for the large-scale bioremediation of wastewaters. One of the remarkable achievements in the field of water and wastewater treatment utilizing enzymes-nanomaterials conjugates is the use of immobilized laccase onto the modified surface of silica nanoparticles for the removal of a mixture of micropollutants or recalcitrant pollutants, such as endocrine-disrupting chemicals, from wastewater in a bioreactor [169]. Based on the relevant reports, it is believed that nanozymes and enzyme-nanomaterial technology can be applicable approaches for the advancement of enzymatic wastewater treatment, due to its exceptional advantages such as reusability, the capability of providing better performance and cost-effectiveness over the other conventional methods [130].

6. Unresolved Challenges, Concluding Remarks and Future Outlooks

In the last decade, the use of different enzymes as biocatalysts in large-scale processes has aroused a tremendous research interest, as it can form part of the technology that embraces green chemistry. Under the current and existing legal legislations, different industries require to implement sustainable and eco-friendly processes under non-polluting operating conditions [101]. In this regard, biocatalysts, as environmentally friendly materials, display a large number of advantages over other conventional methods due to their biodegradability, sustainability, natural origin and capability of working under mild temperature and pressure conditions. The biodegradability properties of the biocatalysts eliminate the concern of any secondary contamination encountered with some other wastewater treatment technique. As explained earlier, various well-characterized biocatalysts allow the choice of the most suitable enzymes for the degradation of particular recalcitrant organic matter from industrial origins. However, despite all of these advantages, enzymatic wastewater treatment methods are still expensive, adversely impacting their competitiveness with the currently conventional used techniques.

Most of the biocatalysts reported in the literature for treating phenolic wastewaters are still not commercially available. Thus, this may make the adaption of large-scale enzymatic treatment of industrial wastewaters a considerable economic and technical challenge. To overcome this issue, the bulk productions of biocatalysts using recombinant-DNA technology are required in order to produce enzymes at a lower cost and on a large scale [170].

Even if this technology is proved to be effective for large-scale enzyme production, purification and separation of the produced enzymes will still be challenging. Although pure enzymes are not needed for enzymatic water and wastewater treatments from the economic point of view, a specific level of purity is still required for technical issues. As a result, extensive investigations are required to enhance enzymatic purification and production, in order to be able to make the enzymatic wastewater treatment technology a practical option in the future. Biocatalyst stability and a loss of enzyme activity are other substantial limitations of using enzymatic treatment technology for removing pollutants from real wastewaters. It was reported that under some unfavorable operating conditions, a considerable reduction in enzyme activity was observed as a result of its incubation in an aqueous medium for a short period of time (less than a day) [136]. The presence of inhibitory agents in the reaction medium can also negatively impact enzyme activity and effectiveness. Industrial wastewaters mostly contain a broad range of inorganic and organic compounds, which may affect biocatalyst activity [171]. Similar to what has been reported for biological wastewater treatments, this issue can be rectified by separating the dissolved and suspended inorganic materials using some simple conventional techniques such as precipitation, ion exchange, coagulation-flocculation, filtration, etc. [172–174]. However, it is still more favorable to develop robust enzymatic systems which are tolerant to the presence of some inhibitory compounds, in order to reduce the environmental impact, as well as the cost of the physical treatment processes. Biocatalysts are also needed to be stable at different pH values to be able to effectively eliminate organic, and especially phenolic pollutants from wastewaters under alkaline and acidic environments. In this case, it is possible to reduce or even eliminate the costs associated with the pH adjustment processes before conducting the enzymatic treatments. Advances in protein engineering and enzyme mutation, especially using directed evolution methods, have made it possible to develop highly stable variants of proper enzymes with superior characteristics for numerous industrial applications. In addition, it is well-established that different immobilization and chemical modification approaches can result in a significant enhancement in enzyme stabilities and reusability [125]. Furthermore, enzymes can exhibit extremely high substrate specificities, and thus all pollutions may not be accepted by a single-enzyme biocatalyst. Hence, a combination of chemical and enzymatic wastewater remediation methods was also shown to be effective in further increasing the efficiency of individual treatment approaches, and completely detoxifying and removing different recalcitrant pollutants from the various effluents.

Some studies suggested that homogenous enzymes are more efficient than heterogeneous reaction systems [150], while other investigations reported an opposite observation [126]. These differences in the obtained results might be according to various operating conditions (i.e., enzyme concentration, treatment time and source of enzyme) used in these two studies. As a result, it seems crucial to minimize the variability in these types of studies to achieve a meaningful benchmarking of the effectiveness of a known biocatalyst on a certain phenolic pollutant. This can lead to developing a deep understanding of the potential interactions between a biocatalyst and a given pollutant, and mimicking approaches to select the appropriate enzymes for degrading a specific organic pollutant. By having this understanding, it is possible to even turn the enzymatic reactions in a way that enhance the removal efficiency of many phenolic compounds from the industrial wastewaters.

In some cases, it was reported that the enzyme immobilization process can cause a complete or partial loss of enzyme activity. This might be due to the chemical compounds utilized during biocatalyst immobilization, which can block or completely destroy the active site of the enzymes. A solution is to replace the harsh immobilization conditions with mild ones. In this regard, less damaging reagents must be employed for the enzyme immobilization. However, using such chemical compounds for enzyme immobilization can be more expensive, or in some cases, impossible. As a result, a reversible blockage of the biocatalyst active sites may be considered a good alternative. This blocking reagent can be detached from the enzyme active site after the process. Another limitation of the enzyme

immobilization technique is that sometimes the active sites of an enzyme may be buried as the result of the complexation between the biocatalyst and the carrier. This phenomenon is not desirable, since the active site should be exposed to the reaction medium without any obstacles to accelerate the interaction between the phenolic pollutants and the immobilized biocatalyst. In order to achieve a suitable immobilization, the interaction between the reactive functional group of the carrier should only be taken place with the proper functional groups on the biocatalyst molecule that are located at the longest distance from the enzyme active site [117,175]. With a clear understanding of the biocatalyst-phenolic pollutants interactions, it may be possible to develop the desired enzyme modification without adversely affecting the enzyme activity and stability.

Generally, it is required to develop practical procedures to scale up enzymatic reactions from laboratory scale to pilot plant scale. This translation of bioremediation technique into pilot plants, and finally industrial-scale wastewater treatment plants, should be the focus of the local and international funding agencies. In near future, it is reasonable to expect that a high level of industrial and large-scale applications can be achieved with oxidoreductases, especially laccases and tyrosinases. Emerging trends in treating phenols wastewater, such as the enzyme mimicking approach and the addition of surface-active compounds (to reduce enzyme inhibition), have shown the potential to enhance wastewater treatment. However, they are still surrounded by several limitations and challenges which are required to be addressed properly. Mimicking techniques should be environmentally friendly, economically feasible and robust. Using the surface-active agents, on the other hand, should not add an economic burden to the process or cause secondary pollution. These desired properties are yet to be investigated and established. There is still so much that has not been adequately studied or understood about the enzymatic treatment processes, strongly suggesting that additional investigations are required to gain further understandings of how these versatile biocatalysts can be employed for efficient industrial wastewater bioremediation.

7. Conclusions

In the present review, we highlighted the recent progress regarding the application of biocatalysis to treat phenolic wastewater originated from petrochemical plants and petroleum refineries. As detailed above, the environmental impacts of such wastewaters and strict international standard limits, along with several drawbacks of the conventional technologies, have led to an increased demand for reliable and effective technologies to deal with the global challenges concerning the management of these effluents. As a result, enormous research interests have been directed toward the effective remediation of the petrochemical and petroleum refinery wastewaters. Most studies focused on the reduction of COD levels, while scant attention has been given to the remediation of toxic and persistent organic pollutants in these types of wastewaters. To address the aforementioned challenges, biocatalysis using extracellular enzymes, especially oxidoreductases, has been increasingly viewed as a technology that can contribute to the remediation of organic pollutants such as phenols and PAHs. The sustainability of the process, short treatment time, working under mild temperature and pressure and ability to polish wastewater by oxidation of phenols, even at very low concentrations, are considered the main advantages of biocatalysis. However, different parameters, such as operating conditions, source of the enzyme, the presence of other pollutants in the media and the mobile or immobilized forms of the biocatalyst should be taken into consideration for designing a biocatalytic process to treat phenolic wastewaters. Furthermore, several obstacles have yet to be addressed in order to progress from laboratory-scale experiments to applicable and commercially available biocatalyst-based wastewater treatment technology. Cost-effective production of these enzymes is crucial for this purpose, which can be fulfilled by the exploitation of recombinant-DNA technology and fermentative enzyme production. The activity and stability of the biocatalyst should be promoted to achieve an acceptable degradation yield. Employing protein engineering and different immobilization approaches can affect these

characteristics. However, it is required that many field studies be conducted using real wastewaters to gain a deep understanding of the biocatalysis mechanisms in these effluents, and identify the enzymatic reaction products in the media in order to be able to assess the efficiency of the treatment in realistic circumstances. Moreover, most of the relevant studies performed in this area only focused on employing a specific enzyme to remove one known pollutant at a time. However, such a scenario rarely happens in real conditions, as an industrial wastewater sample contains a broad range of pollutants from extremely recalcitrant compounds to easily biodegradable ones. Therefore, pre-treatment of the wastewater, using hybrid treatment systems, combining multiple enzymes and designing successive biocatalytic processes, can be beneficial to address some of these issues. The current review opens some avenues for the utilization of different mobile and immobilized enzymatic systems for the treatment of phenolic petrochemical and petroleum refinery wastewater, by providing insights into the biochemistry and mechanisms of actions of different biocatalysts appropriate for wastewater remediation purposes.

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