

REVIEW

Ligninolytic enzymes: Versatile biocatalysts for the elimination of endocrine-disrupting chemicals in wastewater

Ayodeji O. Falade^{1,2}  | Leonard V. Mabinya^{1,2} | Anthony I. Okoh^{1,2} | Uchechukwu U. Nwodo^{1,2}

¹SA-MRC Microbial Water Quality Monitoring Centre, University of Fort Hare, Alice, Eastern Cape, South Africa

²Department of Biochemistry and Microbiology, Applied and Environmental Microbiology Research Group (AEMREG), University of Fort Hare, Alice, Eastern Cape, South Africa

Correspondence

Ayodeji Osmund Falade, SA-MRC Microbial Water Quality Monitoring Centre, University of Fort Hare, Alice, Eastern Cape, South Africa.

Emails: 201508654@ufh.ac.za; ayodeji.falade@yahoo.com

Funding Information

We gratefully acknowledge the financial support from the National Research Foundation (NRF) under the South Africa/Tunisia bilateral collaboration (grant number: 95364) and the South African Medical Research Council (SAMRC).

Abstract

Direct municipal wastewater effluent discharge from treatment plants has been identified as the major source of endocrine-disrupting chemicals (EDC) in freshwaters. Consequently, efficient elimination of EDC in wastewater is significant to good water quality. However, conventional wastewater treatment approaches have been deficient in the complete removal of these contaminants. Hence, the exploration of new and more efficient methods for elimination of EDC in wastewater is imperative. Enzymatic treatment approach has been suggested as a suitable option. Nonetheless, ligninolytic enzymes seem to be the most promising group of enzymes for EDC elimination, perhaps, owing to their unique catalytic properties and characteristic high redox potentials for oxidation of a wide spectrum of organic compounds. Therefore, this paper discusses the potential of some ligninolytic enzymes (laccase, manganese peroxidase, and versatile peroxidase) in the elimination of EDC in wastewater and proposes a new scheme of wastewater treatment process for EDC removal.

KEYWORDS

endocrine-disrupting chemicals, laccases, ligninolytic enzymes, manganese peroxidase, versatile peroxidase, wastewater

1 | INTRODUCTION

EDC are chemical substances that impede the endocrine system leading to negative reproductive, developmental, and neurological impacts in both human and animal (NIEHS, 2010). There exist about eight hundred (800) chemicals suspected to have the capability to interfere with the endocrine system (UNEP/WHO, 2012). Our understanding of endocrine disruption is dependent on clear understanding of the endocrine system (ES). ES is a collection of glands that produce hormones directly into the circulatory system to be transported to target organs, where normal hormonal effects are produced through unified complex signaling pathways involving hormone receptors. The system controls a vast number of biological

processes ranging from developmental to functional processes. Any interference in the system will, therefore, result in abnormal hormonal effect, consequently, affecting the development, behaviour, and reproductive system of the organisms (Caliman & Gavrilescu, 2009; You et al., 2015).

EDC either act as agonists or antagonists by their interactions with the hormone receptor. Their mechanisms of action include: mimicking the actions of physiologic hormones, by producing similar physiologic effects; and competitively binding to the hormone receptor, thus, preventing the naturally occurring hormones from binding and, consequently, leading to inactivation and disruption of the hormone synthesis, transport, metabolism, and their corresponding endocrine functions. Major classes of EDC include but not limited

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2018 The Authors. *MicrobiologyOpen* published by John Wiley & Sons Ltd.

to pharmaceuticals and personal care products (PPCPs), phthalates, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs), alkylphenol ethoxylates (APEs), pesticides including dichlorodiphenyltrichloroethane (DDT), and plastic additives such as bisphenol A (BPA) (Annamalai & Namasivayam, 2015).

Runoff and discharge of treated wastewater effluents into freshwaters are the main sources of EDC contamination, perhaps, due to partial elimination of EDC during wastewater treatment. The receiving waterbodies, which serve as the main sources of portable water, are also used for various domestic and agricultural purposes including irrigation, thus exposing the public to biochemical hazards resulting from poor quality wastewater effluents. The U.S. Environmental Protection Agency has described EDC discharged from wastewater treatment plants (WWTPs) as “contaminants of emerging concern with potentially widespread environmental effects.”

This concern has, consequently, motivated research into EDC including their detection and occurrence in the environment, as well as development of effective method for their elimination in freshwater

and wastewater. Recent studies have detected EDC in wastewater (Table 1) and the receiving waterbodies in many countries (Barber, Loyo-Rosales, Rice, Minarik, & Oskouie, 2015; Komesli, Muz, Ak, Bakirdere, & Gokcay, 2015; Noutsopoulos et al., 2015; Vajda et al., 2015). The micropollutants have also been detected in drinking water and sediments (Liu, Kanjo, & Mizutani, 2009). Some examples of EDC detected in water sediments are nonylphenols (NP), bisphenols, hexestrol (HEX), Diethylstilbestrol (DES), dienestrol, androsterone, *trans*-dehydrotestosterone (DEHA), 4,5- α -dihydrotestosterone (DHT), estrone (E1), 17 β -estradiol (E2), trenbolone, 19-norethindrone, and 17 α -ethinylestradiol (EE2) (Yuan et al., 2015).

The effect of EDC on the biochemical and physical integrity of water, as well as their impacts on the flora and fauna that depend on freshwaters, has been reported. These effects are profound in fish, wildlife, and humans. Some of the adverse effects in humans include infertility, increase in natal defects, alteration in sexual expression, and cancer (Jobling et al., 2013). Given the ecological risk and adverse health effects associated with exposure of humans to EDC, their removal from the environment should be the utmost priority of stakeholders.

TABLE 1 Detection of EDC in water

Water source	EDC detected	Concentration	Country	Reference
Surface water	Polycyclic aromatic hydrocarbons (PAHs)	Winter: 582.8–2208.3 ng/l Summer: 952.4–1201.7 ng/l	China	Li et al. (2015)
Groundwater and surface water	PAHs	–	Bangladesh	Mandal et al. (2015)
Surface water	Polychlorinated biphenyls (PCBs)	0.93–13.07 ng/l	China	Yang, Xie, Liu, and Wang (2015)
Wastewater and surface water	Alkylphenolic chemicals (APs)	–	USA	Barber et al. (2015)
Wastewater	Pharmaceutical residues	117 μ g/l	South Africa	Matongo, Birungi, Moodley, and Ndungu (2015)
Surface water	Pharmaceutical residues	84.60 μ g/l		
Surface water	Nonylphenol	694.6 \pm 248.7 ng/l	China	Wang et al. (2015)
Groundwater	Nonylphenol	244.4 \pm 230.8 ng/l		
Surface water	Nonylphenol (NP)	0.1–6.2 μ g/l	Argentina	Babay, Itria, Ale, Becquart, and Gautier (2014)
	Mono-ethoxylate (NP1EO)	0.1–9.2 μ g/l		
	Di-ethoxylate (NP2EO)	0.1–5.2 μ g/l		
Wastewater	Pharmaceuticals and personal care products (PPCPs)	Influent: 7.26 μ g/l Effluent: 6.72–940 ng/l	Spain	Carmona, Andreu, and Picó (2014)
Wastewater	Phthalate esters (PAEs)	6.95–61.49 ng/ml	China	Gao, Li, Wen, and Ren (2014)
Surface water	PAEs	9.93–45.55 ng/ml		
Drinking water sources	Di-2-ethylhexy phthalate (DEHP)	128.9–6570.9 ng/l	China	Liu, Chen, and Shen (2013)
	Di-butyl phthalate (DBP)	52–4498.2 ng/l		
Freshwater	Dichlorodiphenyltrichloroethane (DDT) and its metabolites	Fall: 0.29 \pm 0.69 ng/l Spring: 0.36 \pm 0.91 ng/l	China	Wang et al. (2013)
Wastewater	Bisphenol A	0.07–1.68 μ g/l	Canada	Mohapatra, Brar, Tyagi, and Surampalli (2011)
Surface water	PPCPs	56–1013 ng/l	South Korea	Yoon, Ryu, Oh, Choi, and Snyder (2010)
Surface water	Bisphenol A	Up to 330 ng/l	Netherlands	Belfroid, van Velzen, van der Horst, and Vethaark (2002)

Unfortunately, removal of EDC by most wastewater treatment plants seems to be inefficient as there is no specific unit designed to eliminate EDC in the present wastewater treatment technology (Zhang, Li, Wang, Niu, & Cai, 2016). Auriol, Filali-Meknassi, Tyagi, Adams, and Surampalli (2006) made the following observations with the use of some conventional treatment processes for removal of EDC in wastewater: Coagulation with the use of “iron and aluminum salts” did not support any EDC removal; however, coagulation involving powdered activated carbon (PAC) removed a significant amount of “small-sized contaminants” including EDC, while filtration processes, which allowed quite high EDC removal, are costly and involve a substantial maintenance in order to prevent membrane clogging. These and some other challenges have led to the development of different treatment methods for EDC removal employing the advanced oxidation processes such as photocatalysis, ozonation, the use of hypochlorites, and chlorine oxides (Silva, Otero, & Esteves, 2012; Taboada-Puig et al., 2015). Although the advanced oxidation processes have recorded high EDC removal efficiency, they also present some challenges such as increased prices, narrow specificity, and generation of intermediates with unknown or higher estrogenic activity compared to their precursors (Oller, Malato, & Sanchez-Perez, 2011; Silva et al., 2012; Taboada-Puig et al., 2015). It is obvious that most of the conventional treatment methods are characterized by one challenge or the other. Consequently, research efforts should be channeled toward addressing these challenges and developing new wastewater treatment technologies that will effectively remove EDC and other emerging pollutants even at very low concentrations in wastewater. Hence, this paper discusses the potential of ligninolytic enzymes in the elimination of EDC in wastewater and proposes a new scheme of wastewater treatment process for EDC removal. Details of some reported methods of EDC removal are given in the succeeding section.

2 | CONVENTIONAL METHODS FOR REMOVAL OF EDC IN WASTEWATER

Research efforts toward complete removal of EDC in wastewater have continued to increase, and these had led to appreciable progress in recent years. A major progress made so far include the development of new methods for removal of EDC in wastewater. Some of these methods include but not limited to adsorption, electrochemical oxidation, chemical advanced oxidation, photocatalysis, biodegradation, and enzymatic treatment. Details of these methods are presented as follow:

2.1 | Adsorption by activated carbon

Adsorption by activated carbon is one of the most effective techniques for removal of EDC in wastewater (Jeirani, Niu, & Soltan, 2016; Nam, Choi, Kim, Her, & Zoh, 2014). This technique is based

on hydrophobic interaction, which is determined by the nature of functional groups on the adsorbent and the adsorbates (Moreno-Castilla, 2004). More so, formation of electron donor–acceptor complex and hydrogen bonding, as well as π – π dispersion interactions, are the major mechanisms reported for adsorption of organic pollutants by carbon in aqueous solutions (Li, Lei, & Huang, 2009; Lladó et al., 2015; Moreno-Castilla, 2004). Jeirani et al. (2016), in a recent review, gave a concise documentation of the major mechanisms involved in adsorption of emerging pollutants on activated carbon.

A major progress in adsorption technique is the exploration of cheap adsorbents for adsorption of emerging organic pollutants. Ifelebuegu, Lester, Churchley, and Cartmell (2006) exploited coconut, wood, and coal-based carbons for the removal of EE2 in wastewater final effluent with 99.3%, 96.4%, and 98.6% removal efficiency achieved, respectively. Krupadam, Sridevi, and Sakunthala (2011) employed crab shell chitin as a biosorbent for the removal of some EDC including benzo (a) anthracene, β -estradiol, and BPA in contaminated groundwater. The use of chitin has, therefore, been suggested as a cost-effective adsorbent for EDC elimination in aqueous solutions. Furthermore, Loffredo and Castellana (2015) conducted a comparative study on the efficiency of low-cost adsorbents (almond shells and green compost) and ligninolytic fungi (*Pleurotus ostreatus* and *Sterenum hirsutum*) to remove organic pollutants (xenoestrogens and pesticides) from a landfill leachate. The study concluded that combined adsorption and biodegradation is suitable for the removal of xenoestrogens (BPA, ethinylestradiol, and 4-n-NP) and pesticides. Also, Saucier et al. (2015) assessed the use of microwave-assisted carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide (anti-inflammatory drugs) in aqueous effluents. The study suggested that MWCS-1.0 [a mixture of cocoa shell and inorganic components (CSC-1.0) acidified with HCl] is capable of efficient removal of sodium diclofenac and nimesulide in simulated hospital effluents. Furthermore, Qin, Jia, Liu, Li, and Wu (2015) suggested metal-organic frameworks with high porosity and large pore size as potential adsorbents for the removal of EDC in contaminated water.

2.2 | Electrochemical oxidation

This approach combines electro-enzymatic catalysis and electro-coagulation as a novel electrochemical approach for the removal of EDC in wastewater, with horseradish peroxidase (HRP) immobilized on graphite felt of titanium electrode as cathode and aluminum plate serving as anode of the working electrode (Zhao et al., 2015). Electrochemical approach has been used to remove BPA and reduce the total organic carbon (TOC) of wastewater. By this approach, Zhao et al. (2015) achieved 94% BPA removal and 52% TOC reduction in real wastewater upon sequencing treatment. The electro-enzymatic process mediated polymerization of BPA and incorporation of BPA into humic acid (HA), thereby, transformed BPA. It also altered the chemical/structural features of HA, and this gave rise to a form more prone to electrocoagulation.

2.3 | Chemical advanced oxidation

This approach involves the use of chemical oxidants for the removal of EDC in a process called advanced oxidative process (AOP), which is characterized by the generation of reactive oxygen species (ROS), primarily, hydroxyl radicals ($\cdot\text{OH}$) that, subsequently, oxidize organic pollutants to carbon dioxide (CO_2) and inorganic ions (Esplugas, Bila, Gustavo, Krause, & Dezotti, 2007) in wastewater. Another mechanism employed in this approach is the transformation of pollutants to some other metabolic products by some strong oxidizing agents such as chlorine (Cl_2), chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), and ozone (O_3) through oxidation–reduction reactions (Liu et al., 2009). The promising potentials of manganese oxide (MnO_2) and calcium peroxide (CaO_2) as oxidizing agents for EDC removal in wastewater have also been reported (Jiang, Huang, Chen, & Chen, 2009; Zhang, Wang, & Li, 2015). Han, Zhang, Zhao, and Feng (2015) synthesized a new class of stabilized MnO_2 nanoparticles known as carboxymethyl cellulose-stabilized MnO_2 nanoparticles with potential for in situ “oxidative degradation of several emerging contaminants in soil and groundwater” (Han et al., 2015). More so, CaO_2 oxidation has also been employed for effective removal of EDC including E1, E2, EE2, estriol, BPA, and 4-NP in waste-activated sludge (Zhang et al., 2015). However, the performance of CaO_2 at removing the EDC was dose-dependent (Zhang et al., 2015). In other words, the efficiency of EDC removal increased with CaO_2 dosage. The ROS released during CaO_2 oxidation have been identified as the major factor responsible for EDC removal, with hydroxyl radicals ($\cdot\text{OH}$) playing the most significant role. Interestingly, EDC products from CaO_2 oxidation have shown less estrogenic activity than their precursors, which is an advantage over other advanced oxidation processes that may likely release by-products with higher estrogenic activity than their precursors. CaO_2 treatment has, therefore, been suggested as a promising technology for the removal of EDC in wastewater (Zhang et al., 2015).

Fenton oxidation is another chemical advanced oxidation employed for removal of EDC in wastewater. Fenton oxidation involves the use of ferrous salt and H_2O_2 to generate hydroxyl radicals with high redox potential for oxidation of a broad range of organic pollutants (Klavarioti, Mantzavinos, & Kassinos, 2009) including EDC. The effectiveness of this process is enhanced by ultraviolet irradiation in a photo-Fenton reaction, which leads to generation of more hydroxyl radicals (Ifelebuegu & Ezenwa, 2011). Several studies have reported the use of Fenton oxidation in the degradation of organic compounds including pharmaceutical products (Mendez-Arriaga, Esplugas, & Gimenez, 2010; Xu, Wang, Li, & Gu, 2004). Despite the effectiveness of Fenton oxidation, it is characterized by some major setbacks, which include narrow pH range of operation (pH 2–4) and recovery of dissolved ions from treated solutions, which require additional treatment step (Klavarioti et al., 2009). Furthermore, Fenton-like oxidation has been employed for the removal of EDC in wastewater (Ifelebuegu & Ezenwa, 2011). Fenton-like oxidation is the reaction of ferric ion generated from Fenton oxidation with H_2O_2 to generate ferrous ion and hydroxide radical, which is able

to attack aromatic compounds that are protected against hydroxyl radical attack due to the natural organic matters that are present in the treatment plant (Lindsey & Tarr, 2000). Several studies have also reported the use of ozonation in the removal of EDC in water (Bila, Montalvao, & Dezotti, 2005; Huber, Canonica, Park, & von Gunten, 2003; Ternes et al., 2003; Vogna, Marotta, Napolitano, Andreozzi, & d’Ischia, 2004).

2.4 | Photocatalysis

This mechanism removes EDC in a photochemical reaction catalyzed by semiconductor metal oxides known as photocatalysts such as titanium dioxide (TiO_2), zinc oxide (ZnO), zinc sulfide (ZnS), ferric oxide (Fe_2O_3), and tin oxide (SnO_2). During photocatalysis, photon energy absorbed by the catalyst produces an electron excitation, which leads to a change of level from valence to conduction band (Dalrymple, Yeh, & Trotz, 2007). Consequently, an electron–hole is created in the valence band. Therefore, the electron–hole moves to the surface of the catalyst, where it takes part in an oxidation–reduction reaction with the EDC or other emerging pollutants that are adsorbed on the catalyst. The hole may further interact with water (H_2O) or H_2O_2 to produce hydroxyl radicals, which, subsequently, facilitate degradation of EDC or other micropollutants (Dalrymple et al., 2007; Wong & Chu, 2003) in an indirect photolysis. However, the efficiency of photocatalytic degradation is dependent on the absorbance spectrum of the pollutants, quantum yield of photocatalysis, concentration of H_2O_2 , and the water matrix (Klavarioti et al., 2009). Recent studies have reported the efficiency of photocatalytic degradation of EDC. Arlos et al. (2016) investigated the photocatalytic degradation of some target EDC including EE2, E2, E1, estriol, and BPA and their estrogenic activity by UV-LED irradiated TiO_2 . All the compounds except E2 were efficiently degraded at a wide pH range as a significant reduction in the total estrogenic activity was also observed. Furthermore, previous studies have also reported reduction and removal of estrogenic activity by photocatalytic treatment with TiO_2 (Coleman, Routledge, Sumpter, Eggins, & Byrne, 2004; Ohko et al., 2001, 2002).

2.5 | Biodegradation

Biodegradation involves the use of microbes including fungi and bacteria for degradation of EDC and other environmental pollutants. Biodegradation has been described as a major removal mechanism that is capable of affecting the fate of EDC in the environment (Yu, Deeb, & Chu, 2013). Over the years, several studies have reported the degradation of various EDC by different microorganisms (Ahuactzin-Perez et al., 2018; Cajthaml, 2015; Combalbert & Hernandez-Raquet, 2010; Husain & Qayyum, 2012; Yu et al., 2013; Zhang et al., 2016; Zhao et al., 2016). Lignolytic organisms, predominantly, white rot fungi (WRF), have received increased attention for degradation of various emerging micropollutants. There are quite a number of reviews on the potential of ligninolytic fungi in the efficient removal of EDC in the environment. Cabana, Jones,

and Agathos (2007a) gave a comprehensive review on the capability of WRF to effectively eliminate EDC in various environmental matrices. In the review, the authors suggested the need to develop "robust and reliable biotechnological processes for the treatment of EDC-contaminated environmental matrices" (Cabana, Jones, and Agathos, 2007a). Cajthaml (2015), in another review, reported the versatility of ligninolytic fungi in the degradation of EDC using the lignin-modifying enzymes system and cytochrome P-450. EDC degradation by ligninolytic fungi occurs through polymerization of the micropollutants or degradation of the original structure by extracellular enzymes system (Cajthaml, 2015). It is worthy of note that ligninolytic fungi are among the very few microbes with the ability to degrade EE2 and PCBs efficiently (Cajthaml, 2015).

Ligninolytic bacteria are also promising candidates for degradation of EDC, perhaps, because of their dexterity in the degradation of recalcitrant compounds and their abilities to produce some lignin-modifying enzymes including laccase and manganese peroxidase, which are mostly responsible for the EDC degradation proficiency manifested by WRF. Bacteria seem to hold stronger potential for EDC degradation, given their striking resilience in diverse environments and the maneuverability of their genome. Furthermore, bacterial degradation has been suggested as an easy way to remove EDC in wastewater (Husain & Qayyum, 2012). To justify this claim, Zhang et al. (2016) gave a succinct documentation on the bacterial degradation of EDC and classified EDC-degrading bacteria into the following: Proteobacteria, Firmicutes, Actinobacteria, and Bacteroidetes.

On the other hand, the combination of bacteria and physical methods such as adsorption is a novel technique with excellent potential for EDC elimination in an aqueous environment (Zhang et al., 2016). Nevertheless, a major concern on the adoption of biodegradation for EDC removal is the likely introduction of pathogenic microorganisms into the environment, which may also contribute to the problem of antibiotic and multiple drug resistance via horizontal gene transfer. Therefore, enzymatic treatment, involving the use of ligninolytic extracellular enzymes rather than the whole cell culture, will be a suitable alternative.

3 | PROMISING LIGNINOLYTIC ENZYMES FOR EDC ELIMINATION

Laccases (EC 1.10.3.2), manganese peroxidase—MnP (EC 1.11.1.13), and versatile peroxidase—VP (EC 1.11.1.16) are ligninolytic enzymes (LEs) with promising potential for the removal of EDC in wastewater. The resourcefulness of LEs in the elimination of EDC is, perhaps, due to their high redox potentials for oxidation of a wide spectrum of organic compounds. Besides the lignin degradation activity of LEs, their potentials for bioremediation and wastewater effluent treatment have been reported (Husain, 2010; Mehta, 2012; Rajasundari & Murugesan, 2011). Furthermore, they have shown great potentials for the transformation of several types of recalcitrant aromatic compounds with known or suspected endocrine-disrupting properties such as PAHs, PCBs, APs, and pesticides (Davila-Vazquez,

Tinoco, Pickard, & Vazquez-Duhalt, 2005; Garcia-Morales et al., 2015; Mao, Lu, Gao, & Huang, 2010; Suzuki, Hirai, Murata, & Nishida, 2003; Taboada-Puig et al., 2011; Touahar, Haroune, Ba, Bellenger, & Cabana, 2014).

The potential of laccase and MnP for removal of EDC in wastewater has been well studied (Auriol et al., 2008; Ba, Jones, & Cabana, 2014; Cabana, Jones, & Agathos, 2007b, 2009; Kim, Yeo, Kim, & Choi, 2008; Lloret et al., 2012; Sei, Takeda, Soda, Fujita, & Ike, 2007). However, there is dearth of information on the use of VP for EDC elimination. Among the LEs, VP seems to be the most promising for the elimination of EDC in wastewater, given its peculiar attribute of hybrid molecular architecture. Besides, unlike laccase, VP is not dependent on redox mediators for degradation of micropollutants (Ravichandran & Sridhar, 2016). Summary of EDC removal by LEs is presented in Table 2.

3.1 | Laccases (EC.1.10.3.2)

Laccases are multicopper oxidases (MCOs) that oxidize a wide range of aromatic compounds using molecular oxygen in a radical-catalyzed reaction (Strong & Claus, 2011). Usually, their molecular weights (MW), optimal pH, and temperature fall within 58–90 kDa, 2–10, and 40–65°C, respectively (Quarantino, Federici, Petruccioli, Fenice, & D'Aannibale, 2007; Zouari-Mechichi et al., 2006).

They are the largest member of MCOs family, with wide distribution in eukaryotes and prokaryotes (Sirim, Wagner, Wang, Schmid, & Pleiss, 2011). However, microbial laccases have attracted much interest, probably, owing to their low substrate specificity and capability to oxidize different compounds (Gasser, Ammann, Shahagaldian, & Corvini, 2014). Other MCOs include ferroxidases, ascorbate oxidase, and ceruloplasmin (Strong & Claus, 2011). MCOs oxidize their substrates with a concomitant four-electron reduction of molecular oxygen to water (Sirim et al., 2011). They are divided into three classes, based on their copper centers: type 1 (blue), type 2 (normal), and type 3 or coupled binuclear (Messerschmidt & Huber, 1990; Ouzounis & Sander, 1991). Type 1 (T1) and type 2 (T2) have one Cu atom each, while type 3 (T3) has two Cu atoms (Wong, 2009).

The catalytic efficiency of laccases is dependent on the redox potential of the active site type 1 (T1) copper ion (Eldridge et al., 2017), where substrate oxidation occurs in a one-electron reaction. Usually, microbial laccases exhibit higher redox potential than laccases of plant origin (Gasser et al., 2014). This indicates that laccases from microbes may probably have higher activity and catalytic efficiency when compared to plant laccases. In the other, T2 and T3 form a trinuclear cluster, T2/T3, where molecular oxygen is reduced to water through the electrons transferred from T1 site to the trinuclear site (Gasser et al., 2014; Wong, 2009). Generally, the catalytic reaction of laccases involves oxidation of four molecules of substrate and reduction of molecular oxygen to two water molecules (Gasser et al., 2014). The use of atmospheric oxygen as electron acceptor in a laccase-catalyzed reaction is an advantage over the use of hydrogen peroxide by peroxidases. Nonetheless, laccases depend on redox mediators such as 2,2'-azino-bis (3-ethylbenzthiazoline-6-

TABLE 2 EDC removal by ligninolytic enzymes

Reaction matrix	Classes of EDC	Removal efficiency (%)	Enzyme used	References
Aqueous system	Bisphenol A	≈100	Immobilized laccase	Zdarta et al. (2018)
	Bisphenol F	≈100		
	Bisphenol S	>40		
Aqueous system	Acetaminophen	90	Immobilized laccase	Garcia-Morales et al. (2018)
	Diclofenac	68		
Aqueous system	Bisphenol A	90	Immobilized laccase	Ji et al. (2017)
	Carbamazepine	40		
Aqueous system	Bisphenol A	100	Crude laccase	de Freitas et al. (2017)
Aqueous system	Bisphenol A	100	Laccase with mediator (Hydroxybenzotriazole)	Daasi et al. (2016)
Wastewater	Bisphenol A (BPA)	100	Versatile peroxidase using two-stage system (TSS)	Taboada-Puig et al. (2015).
	Triclosan			
	Estrone (E1)			
	17β-estradiol (E2)			
	17α-ethinylestradiol (EE2)			
Synthetic and groundwater	Bisphenol A	89	Free laccase cocktail	Garcia-Morales et al. (2015)
	4-nonylphenol	93		
	17α-ethinylestradiol	100		
	Triclosan	90		
Wastewater	Nonylphenol	99.2	Versatile peroxidase using TSS	Mendez-Hernandez et al. (2015)
Aqueous system	Nonylphenol and triclosan	>95%	Laccase	Ramírez-Cavazos et al. (2014)
Wastewater	Acetaminophen	93	Cross-linked laccase aggregates and polysulfone hollow fiber microfilter membrane	Ba et al. (2014)
	Mefenamic acid			
	Carbamazepine			
Aqueous system	Bisphenol A	100	Immobilized laccase	Debaste et al. (2014)
	Nonylphenol			
	Triclosan			
Wastewater	Estrone	83.6	Laccase using enzymatic membrane reactor (EMR)	Lloret, Eibes, Moreira, Feijoo, and Lema (2013)
	17β-estradiol (E2)	94		
	17α-ethinylestradiol (EE2)	93.6		
Water	Bisphenol A	90	Encapsulated ligninolytic enzymes (Manganese peroxidase, lignin peroxidase, and laccase)	Gassara et al. (2013)
Aqueous system	Bisphenol A	80	Immobilized laccase	Songulashvili et al. (2012)
	Nonylphenol	40		
	Triclosan	60		
Aqueous system	Estrone	65	Immobilized laccase in a packed-bed reactor	Lloret et al. (2012)
	17β-estradiol (E2)	80		
	17α-ethinylestradiol (EE2)	80		
Aqueous system	Diclofenac and estrogen hormones	100	Versatile peroxidase	Eibes, Debernardi, Feijoo, Moreira, and Lema (2011)
	Sulfamethoxazole and Naproxen	80		

(Continues)

TABLE 2 (Continued)

Reaction matrix	Classes of EDC	Removal efficiency (%)	Enzyme used	References
Wastewater	Bisphenol A, B, F	100	Immobilized laccase	Diano and Mita (2011)
Aqueous system	Triclosan	99.4	Manganese peroxidase	Inoue et al. (2010)
Wastewater	Estrone Estriol 17 β -estradiol (E2) 17 α -ethinylestradiol	100	Laccase	Auriol et al. (2008)
Simulated wastewater	Nonylphenol Bisphenol A Triclosan	100 100 65	Laccase	Cabana, Jiwan, et al. (2007)
Simulated wastewater	Nonylphenol Bisphenol A Triclosan	100	Immobilized laccase in fluidized bed reactor	Cabana, Jones, and Agathos (2007b)
Aqueous system	Natural steroidal hormone, estrone	98	Manganese peroxidase and laccase	Tamagawa et al. (2006)
Aqueous system	Genistein	93	Manganese peroxidase and laccase	Tamagawa, Hirai, Kawai, and Nishida (2005)
Aqueous system	Bisphenol A Nonylphenol	100	Manganese peroxidase and laccase-1-hydroxybenzotriazole (laccase-HBT) system	Tsutsumi et al. (2001)

sulfonic acid) for degradation of nonphenolic compounds. Despite this shortcoming, laccases have attracted considerable attention in the last one decade, probably, owing to their potential applications in various biotechnological processes such as biopulping, biobleaching, bioremediation, juice/wine clarification, textile dye decolorization, degradation of xenobiotics, and effluent treatment (Afreen, Anwer, Singh, & Fatma, 2016; Chandra & Chowdhary, 2015; Couto & Toca Herrera, 2006). Interestingly, there has been a drastic shift from the conventional application of laccases in lignin modification to degradation of emerging micropollutants.

3.2 | Manganese peroxidase (EC.1.11.1.13)

MnP was discovered by Kuwahara, Glenn, Morgan, and Gold (1984) and is the most common ligninolytic peroxidase produced by microbes (Hofrichter, 2002). Its participation in lignin modification has been documented and studied extensively in fungi (Hofrichter, 2002). Nevertheless, there is rarity of information on MnP-producing bacteria. MnP catalytic reaction involves oxidation of Mn²⁺ to Mn³⁺, which then oxidizes a broad spectrum of phenolic substrates including phenolic lignin monomers (Tuor, Wariishi, Schoemaker, & Gold, 1992). The Mn³⁺ formed from the oxidation of Mn²⁺ present in lignocellulosic materials is stabilized by reacting with a carboxylic acid such as tartrate which serves as ion chelator. The resultant complex will in turn oxidize the phenolic component of lignin structure which leads to generation of unstable radicals that may breakdown naturally (Hofrichter, 2002). However, MnP is also capable of oxidizing nonphenolic compounds, but with the involvement of redox mediators such as

thiyl or lipid radicals (Abdel-Hamid, Solbiati, & Cann, 2013; Reddy, Sridhar, & Gold, 2003). More so, the ability of MnP to oxidize and degrade lignin and other recalcitrant compounds has been reported (Bogan, Lamar, & Hammel, 1996; Dehorter & Blondeau, 1993; Hofrichter, 2002; Hofrichter, Steffen, & Hatakka, 2001; Hofrichter, Ullrich, Pecyna, Liers, & Lundell, 2010). Generally, MnP has a MW ranging from 38 to 62.5 kDa, with most purified MnPs having MW of about 45 kDa (Hatakka, 1994). About 11 various isoforms of MnP have been identified in *Ceriporiopsis subvermisporea* (Lobos, Larram, Salas, Cullen, & Vicuna, 1994) with variations in the isoelectric point of the different isoforms.

3.3 | Versatile peroxidase (EC.1.11.1.6)

VP belongs to the group of enzymes called ligninases, which are microbial extracellular enzymes capable of degrading lignin. Generally, ligninases are characterized by high redox potential for oxidation of phenolic and nonphenolic compounds. As well, they have shown capability for degradation of some recalcitrant compounds including "chlorophenols, polycyclic aromatic hydrocarbons (PAHs), organophosphorus compounds, and phenols" (Wesenberg, Kyriakides, & Agathos, 2003), thus informing their potentials for diverse industrial and biotechnological applications (Falade et al., 2017; Husain, 2010; Mehta, 2012; Rajasundari & Murugesan, 2011).

VP is a relatively new and unique lignin-modifying heme peroxidase belonging to the same class (class II of peroxidase-catalase superfamily) with lignin peroxidase (LiP) and MnP. It is also referred to as "hybrid peroxidase" or "lignin-manganese peroxidase" and is largely produced by ligninolytic fungi belonging to certain genera:

Bjerkandera (Heinfling, Martinez, Martinez, Bergbauer, & Szewzyk, 1998), *Pleurotus* (Palma, Lloret, Sepulveda, & Contreras, 2016; Ruiz-Duenas, Martinez, & Martinez, 1999), and *Lepista* (Zorn, Langhoff, Scheibner, Nimtz, & Berger, 2003). Its production by *Phanerochaete chrysosporium* has also been reported (Coconi-Linares et al., 2014). Nonetheless, there is limited information on its production by bacteria. Thus, exploitation of bacteria and other fungal genera for VP production is imperative.

The uniqueness of VP is manifested in its hybrid molecular architecture, which combines different substrate binding and oxidation sites (Camarero, Sarkar, Ruiz-Duenas, Martinez, & Martinez, 1999). Its characteristic oxidation of high and low redox potential substrates motivates for its potential application in the elimination of EDC in wastewater. Furthermore, the enzyme has the ability to combine the substrate specificity of two ligninolytic peroxidases (MnP and LiP) and one other fungal peroxidase family, *Coprinopsis cinerea* peroxidase (CIP) (Perez-Boada, Ruiz-Duenas, Pogni, Basosi, & Choinowski, 2005). Consequently, it is capable of oxidizing a wide range of substrates such as Mn^{2+} , phenolic and nonphenolic lignin model dimers, α -keto- γ -thiomethylbutyric acid (KTBA), veratryl alcohol (VA), dimethoxybenzenes, synthetic dyes, substituted phenols, and hydroquinones (Caramelo, Martinez, & Martinez, 1999; Perez-Boada et al., 2005). It employs the MnP pathway by oxidizing Mn^{2+} to Mn^{3+} with H_2O_2 as electron acceptor (Figure 1); however, Mn^{3+} is highly reactive, but has a very short half-life. Thus, when VP is utilizing the MnP pathway, a dicarboxylic organic acid such as oxalate, tartrate, or malonate is required to form a stable complex with Mn^{3+} (Mn^{3+} -oxalate, Mn^{3+} -tartrate, or Mn^{3+} -malonate). With the utilization of this mechanism, VP is capable of oxidizing pollutants situated far away from it by the action of the metallic ion complex (Taboada-Puig et al., 2015). The utilization of MnP pathway by VP commits it to oxidation of phenolic substrates as it is also able to oxidize nonphenolic compounds and other typical substrates of LiP using the normal LiP catalytic reaction mechanism. However, LiP is able to oxidize veratryl alcohol, a typical LiP substrate more effectively than VP. The variation in the catalysis of LiP and VP has been attributed to the variation in the tryptophan environment of the enzymes (Khindaria, Yamazaki, & Aust, 1996).

VP also employs the "long-range electron transfer (LRET) mechanism in the oxidation of high redox potential aromatic compounds" (Perez-Boada et al., 2005; Ruiz-Dueñas et al., 2009). Specifically, three possible LRET pathways for the oxidation of high redox potential aromatic compounds have been revealed in two VP isozymes (VPL and VPS 1) of *Pleurotus eryngii* (Caramelo et al., 1999; Perez-Boada et al., 2005; Ruiz-Duenas et al., 1999). The pathways start at either Trp 164 or His 232 of VPL and at His 82 or Trp 170 of VPS 1, which is homologous to Trp 164 in VPL (Perez-Boada et al., 2005; Ruiz-Dueñas et al., 2009). Furthermore, the involvement of Trp 164 in the oxidation of veratryl alcohol and reactive black 5 has been reported. However, the other two pathways (His 232 and His 82) were not involved in LRET (Perez-Boada et al., 2005). Therefore, the ability of VP to oxidize high redox potential compounds could, perhaps, be linked to an exposed

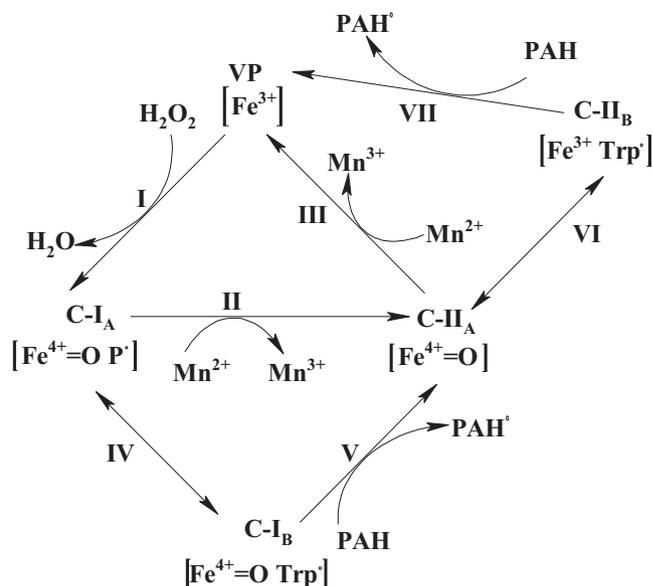


FIGURE 1 Exploitation of the VP catalytic cycle for EDC removal. The VP catalytic cycle is adapted from Perez-Boada et al. (2005) with permission from Elsevier (license number: 4365891195222). C-I_A (Compound I_A, containing Fe⁴⁺-oxo and porphyrin cation radical), C-II_A (Compound II_A, containing Fe⁴⁺-oxo after reduction in porphyrin), C-I_B (Compound I_B, containing Fe⁴⁺-oxo and tryptophanyl (Trp¹⁶⁴) radical), C-II_B (Compound II_B, containing Fe³⁺ and tryptophanyl (Trp¹⁶⁴) radical), and PAH (polycyclic aromatic hydrocarbons). I-III: Reactions involved in Mn²⁺ oxidation mechanism for EDC removal. Mn³⁺ generated in step III forms a complex with a dicarboxylic acid such as oxalate/malonate/tartrate, which is responsible for subsequent degradation of EDC. I, IV-VII: Reactions involved in long-range electron transfer mechanism proposed for EDC removal. The tryptophanyl radical generated on the surface of C-II_B could be exploited for degradation of EDC such as PAH in step VII

catalytic tryptophan: Trp-164, which forms a radical on the surface of the enzyme through a LRET to the heme (Ruiz-Dueñas et al., 2009; Saez-Jimenez et al., 2015). Hence, LRET could suffice as a novel mechanism for EDC removal by VP.

4 | POTENTIAL OF LEs IN THE ELIMINATION OF EDC IN WASTEWATER

The high environmental and health risk posed by exposure of human to EDC and the inefficiency of the conventional treatment approaches for complete removal of EDC in wastewater, as well as some challenges that characterized the conventional treatment processes, have led to an increased interest in the exploration of alternative treatment processes for elimination of EDC in wastewater. Therefore, enzymatic treatment process, involving the use of ligninolytic oxidative enzymes for EDC removal, has recently attracted attention as an environmentally friendly alternative. The potential of some LEs including laccase, MnP, and VP for efficient removal of EDC in water has recently been reported (Diano & Mita, 2011;

Garcia-Morales et al., 2015; Ramírez-Cavazos et al., 2014; Taboada-Puig et al., 2011; Touahar et al., 2014; Wen, Jia, & Li, 2009, 2010; Zhang & Geissen, 2010).

Immobilized laccase from *Cerrena unicolor* C-139 eliminated 80% of BPA, 40% of NP, and 60% of triclosan from solutions that contained 50 μmol of each endocrine disruptor, respectively (Songulashvili, Jimenez-tobon, Jaspers, & Penninckx, 2012). Also, Debaste, Songulashvili, and Penninckx (2014) reported total removal of BPA, 4-NP, and triclosan by immobilized laccase from *Cerrena unicolor*. The authors, therefore, suggested the potential application of the immobilized enzyme for elimination of harmful micropollutants industrially and domestically. On the other hand, Eldridge et al. (2017) have attributed the efficient removal of EE2 by *Lentinula edodes* (Shiitake) to laccase as the induction of laccase production in the organism increased the removal efficiency of the pollutant from 50% to 80%. More so, Zdarta et al. (2018) reported approximately 100% removal of BPA and bisphenol F (BPF) by *Trametes versicolor* laccase immobilized on *Hippospongia communis* spongin scaffolds. However, the removal efficiency of the enzyme on bisphenol S (BPS) was only greater than 40%. The removal efficiency of the enzyme was optimal at slightly acidic pH (4–5), while the optimum temperature ranged from 30 to 40°C.

A new approach for elimination of EDC in wastewater is the immobilization of LEs on nanoparticles. Garcia-Morales et al. (2018) reported 90% and 68% biotransformation of acetaminophen and diclofenac by *Pycnoporus sanguineus* laccase immobilized onto titania nanoparticle, respectively. Likewise, *Pleurotus ostreatus* crude laccase immobilized on functionalized TiO_2 nanoparticles attained 90% BPA degradation within 6 hr of treatment, while only about 10% degradation efficiency was recorded with carbamazepine after 48 hr (Ji, Nguyen, Hou, Hai, & Chen, 2017). The poor elimination of carbamazepine in the study was attributed to the high redox potential of the compound, which hampered its oxidation by the enzyme (Hata, Shintate, Kawai, Okamura, & Nishida, 2010; Ji et al., 2017). Nevertheless, degradation of carbamazepine was enhanced in the presence of BPA, with 40% elimination attained after 24 hr reaction. The authors, therefore, concluded that oxidative products of BPA had a redox mediator effect on the degradation of carbamazepine. The findings from the study suggested that the “presence of more reactive micropollutant can promote the removal of the more recalcitrant pollutants” in a cocktail (Ji et al., 2017). Also, crude laccases from *P. ostreatus* and *P. pulmonarius* were able to degrade BPA in aqueous solution, with 100% and 85% degradation efficiency achieved, respectively, within 1 hr (de Freitas et al., 2017). Moreover, *P. ostreatus* laccase reduced BPA toxicity from 85% to less than 5%, but there was no decrease in toxicity when treated with laccase from *P. pulmonarius*. The study indicated that degradation of BPA by *P. pulmonarius* laccase, probably, generated metabolites with the same toxicity as the parent compound (de Freitas et al., 2017). Therefore, crude laccase from *P. ostreatus* was recommended as an efficient degrader of EDC. Besides the use of laccase alone for EDC elimination, Gassara, Brar, Verma, and Tyagi (2013) assessed the effectiveness of free LEs (Laccase, MnP and LiP) and encapsulated LEs in the degradation of BPA. The authors recorded higher degradation

efficiency (90%) when the three LEs were encapsulated on polyacrylamide hydrogel and pectin, while only 26% efficiency was observed with the free enzymes.

MnP is another ligninolytic enzyme that has shown effectiveness for elimination of EDC (Inoue, Hata, Kawai, Okamura, & Nishida, 2010; Tamagawa, Yamaki, Hirai, Kawai, & Nishida, 2006; Tsutsumi, Haneda, & Nishida, 2001). In a study by Tsutsumi et al. (2001), BPA and NP were treated with MnP and laccase from ligninolytic fungi. MnP was able to completely remove the target compounds in an aqueous solution after 1 hr of treatment, but not without estrogenic activities. Upon extension of treatment time to 12 hr, the observed estrogenic activities were totally removed. Similarly, Inoue et al. (2010) treated triclosan with MnP from *P. chrysosporium*, *T. versicolor* laccase, and the laccase (0.5 and 2.0 nkat/ml) with 1-hydroxybenzotriazole (0.2 mM) as mediator. The authors observed 99.4% triclosan removal by MnP after 1 hr of treatment, while 10.2% and 29% elimination were observed with the use of laccase and laccase–mediator system, respectively. The ability of MnP to almost remove the target compound completely within a short period indicates its potential for degradation of other classes of EDC.

VP has recently emerged with promising potential for elimination of EDC in wastewater. One of the few reports that implicated VP in EDC removal is the work of Taboada-Puig et al. (2011). They produced a combined cross-linked enzyme aggregate from VP and glucose oxidase (combined CLEA) and investigated its ability to eliminate the following endocrine disruptors: BPA, NP, triclosan, EE2, and E2. Coaggregation of VP with glucose oxidase resulted in an increased activity recovery of 89% from the initial activity of 67% and an increased stability of VP against H_2O_2 . The combined CLEA was able to remove all the target pollutants except triclosan, while the removal of their estrogenic activities was more than 55% for all the EDC except triclosan. The exploration of other H_2O_2 -producing enzymes with more appropriate substrates in water treatment rather than glucose in the case of glucose oxidase has been suggested as glucose may support the unwanted growth of microorganisms. Adoption of this concept (coaggregation of glucose oxidase with other ligninolytic peroxidases) is desirable for EDC removal and other applications as this will nullify the cost of H_2O_2 . Likewise, Touahar et al. (2014) investigated the ability of a combined cross-linked enzyme aggregate (combi-CLEA) {comprising laccase, VP, and glucose oxidase} to transform a cocktail of pharmaceutically active compounds (PhACs) in a mixed solution and synthetic wastewater. The free enzymes and combi-CLEA showed the ability to efficiently transform nonsteroidal anti-inflammatory drugs (acetaminophen, naproxen, mefenamic acid, diclofenac, and indometacin) in a mixed solution and eliminate acetaminophen in municipal wastewater. However, combi-CLEA exhibited more improved removal efficiency. The study also demonstrated that VP had a wider removal spectrum than laccase. Furthermore, Taboada-Puig et al. (2015) utilized the oxidant, Mn^{3+} -malonate generated by VP in a two-stage (TS) system for continuous removal of the following EDC: BPA, triclosan, E1, E2, and EE2 from synthetic and real wastewaters at degradation rates ranging from 28 to 58 $\mu\text{g/L min}$, with little enzyme inactivation observed. Interestingly, a 14-fold increase in the

EDC removal efficiency of VP in a TS system was observed when compared with a regular enzymatic membrane reactor (EMR) system. Also, some of the operational challenges encountered during EDC removal in an EMR system were prevented, as the TS system was able to separate the complex formation stage from the contaminant oxidation stage. It is noteworthy that VP in a TS enzymatic system exhibited 100% removal efficiency for all the EDC studied, therefore demonstrating the practicability of this approach for removing EDC at both high and environmental concentrations.

5 | PROPOSED SCHEME OF WASTEWATER TREATMENT PROCESS FOR EDC REMOVAL BY LEs

The present wastewater treatment technology involves three different stages including primary, secondary, and tertiary treatments. Each stage has specific units for specified treatment (Figure 2a). In most cases, the tertiary wastewater treatment stage involves disinfection and probably, nutrient removal (optional). However, no

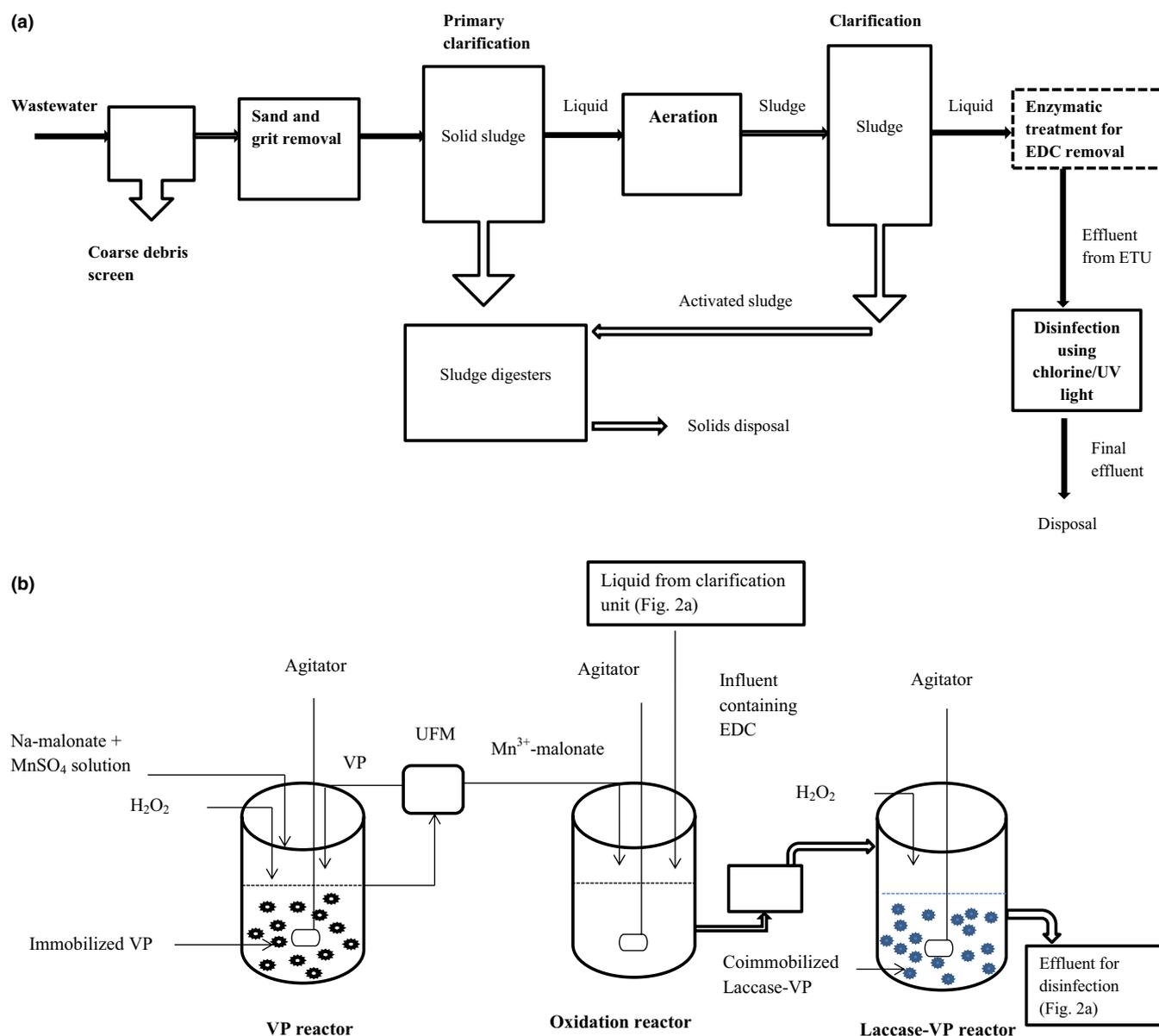


FIGURE 2 (a) Proposed scheme of wastewater treatment process for EDC removal by LEs. Adapted from <https://www.britannica.com/technology/wastewater-treatment>. Primary Treatment Stage: coarse debris screen, sand and grit removal, and primary clarification. Secondary Treatment Stage: aeration and clarification. Tertiary Treatment Stage: enzymatic treatment for EDC removal and disinfection. Solid lines: conventional treatment units; broken lines: proposed additional treatment unit. ETU: enzymatic treatment unit. (b) Proposed treatment stages for EDC elimination by LEs using continuous stirred tank reactors. Stage I (VP reactor): generation of Mn^{3+} -malonate complex by immobilized VP via the MnP mechanism. Stage II (oxidation reactor): oxidation of EDC by Mn^{3+} -malonate complex. Stage III (laccase-VP reactor): treatment of residual EDC with coimmobilized laccase-VP. Stages I and II are adapted from Mendez-Hernandez et al. (2015). UFM: ultrafiltration membrane

specific unit is designed to remove EDC during wastewater treatment process. This deficiency has, perhaps, resulted in the occurrence of EDC in wastewater treatment plant effluents (Huang et al., 2014; Ifelebuegu, 2011; Martín, Camacho-Munoz, Santos, Aparicio, & Alonso, 2012; Pessoa et al., 2014; Ra et al., 2011; Zhang et al., 2016).

This paper, therefore, proposes a scheme of wastewater treatment process that includes a specific unit for EDC removal at the tertiary treatment stage (Figure 2a). Upon clarification, the liquid is passed through enzymatic treatment unit (ETU) for EDC removal: a three-stage continuous stirred tank reactor (Figure 2b). The first stage is the VP reactor, where Mn^{3+} -dicarboxylic acid complex (Mn^{3+} -malonate, Mn^{3+} -tartrate, or Mn^{3+} -oxalate) is generated by immobilized VP, while the second stage (oxidation reactor) involves the oxidation of EDC by the complex generated in stage I (Mendez-Hernandez et al., 2015). In the third stage (laccase-VP reactor), effluent from the oxidation reactor is further treated with laccase coimmobilized with VP to eliminate any residual EDC before passing the effluent through disinfection unit and subsequent disposal. During the treatment process, the VP reactor will be fed with two different peristaltic pumps. One will be used for the enzyme activator, H_2O_2 , while the other will be used for the solution of sodium malonate and $MnSO_4$ (Mendez-Hernandez et al., 2015) at predetermined feeding rates. Another peristaltic pump will be used to feed the laccase-VP reactor with H_2O_2 . However, further research is required to optimize the concentrations of H_2O_2 , Mn^{2+} , and sodium malonate required by VP. It is also imperative to regulate the concentration of H_2O_2 in the laccase-VP reactor to ensure that laccase activity is not adversely affected as increase in H_2O_2 may inhibit the enzyme activity (Milton, Giroud, Thumser, Minteer, & Slade, 2013). However, addition of H_2O_2 may also increase laccase activity during oxidation of some phenolic compounds (Min, Kim, Kim, Jung, & Hah, 2001). Although both enzymes usually perform optimally in slightly acidic pH region (Jarosz-Wilkolazka, Luterek, & Olszewska, 2008; Min et al., 2001; Zdarta et al., 2018), it is important to determine the pH requirements of the enzymes to ensure best performance during application. Likewise, efforts should be geared toward assessing the potential toxicity of Mn^{2+} and malonate in the effluent and the chance of recovering them after the enzymatic treatment.

The use of immobilized enzymes is suggested for the proposed technology as immobilization increases enzyme stability and allows the enzymes to be reused in subsequent treatment (Zdarta et al., 2018). A three-stage reaction system is necessary to ensure high efficiency in the elimination of EDC during treatment process. One of the benefits of separating the oxidation process from the Mn^{3+} complex generation system is that it allows recirculation of the immobilized enzyme into the VP reactor for reuse (Taboada-Puig et al., 2015). Also, it prevents some operative challenges that characterize conventional enzymatic reactors such as decrease in enzyme activity against time (Rios, Belleville, Paolucci, & Sanchez, 2004; Taboada-Puig et al., 2015). Moreover, a second enzymatic reactor with coimmobilized laccase and VP is essential for complete EDC removal as there is possibility that some more recalcitrant EDC,

which may resist oxidation by Mn^{3+} complex in stage II (Figure 2b), are present. However, coimmobilized laccase-VP will have a wider EDC removal spectrum through combined advantages. At this stage, VP will catalyze EDC removal in Mn-independent reaction through LRET mechanism, a typical LiP catalytic pathway. Exploitation of the LiP catalytic mechanism by VP will ensure degradation of nonphenolic micropollutants.

6 | CONCLUSION

Indeed, LEs have shown great potential for degradation of EDC and other emerging organic micropollutants in wastewater, hence their potential applications in bioremediation and the water sector. More so, a new design of wastewater treatment technology that includes a three-stage continuous stirred tank reactor for EDC removal should be adopted as this will prevent discharge of the micropollutants directly into freshwater environment. Furthermore, coimmobilization or combined cross-linking of laccase and VP will be a promising approach for complete elimination of EDC and other emerging organic pollutants in wastewater as this will provide leverage for laccase in the degradation of nonphenolic pollutants and, consequently, nullifying the cost of redox mediators required by laccase for degradation of nonphenolic compounds.

CONFLICT OF INTEREST

Authors declare that there is no conflict of interests.

AUTHORS' CONTRIBUTIONS

Ayodeji O. Falade conceptualized the manuscript and wrote the first draft. Leonard V. Mabinya, Anthony I. Okoh, and Uchechukwu U. Nwodo contributed to the conception of the manuscript and thoroughly reviewed the manuscript. All authors approved the final version of the manuscript.

DATA ACCESSIBILITY

No new data were generated in support of this review article.

ORCID

Ayodeji O. Falade  <http://orcid.org/0000-0001-9548-5749>

REFERENCES

- Abdel-Hamid, A. M., Solbiati, J. O., & Cann, I. K. O. (2013). Insights into lignin degradation and its potential industrial applications. *Advances in Applied Microbiology*, 82, 1–28.
- Afreen, S., Anwer, R., Singh, R. K., & Fatma, T. (2016). Extracellular laccase production and its optimization from *Arthrospira maxima* catalyzed decolourization of synthetic dyes. *Saudi Journal of Biological Sciences*, <https://doi.org/10.1016/j.sjbs.2016.01.015>.

- Ahuactzin-Perez, M., Tlecuitl-Beristain, S., Garcia-Davila, J., Santacruz-Juarez, E., Gonzalez-Perez, M., Gutierrez-Ruiz, M. C., & Sánchez, C. (2018). A novel biodegradation pathway of the endocrine-disruptor di (2-ethyl hexyl) phthalate by *Pleurotus ostreatus* based on quantum chemical investigation. *Ecotoxicology and Environmental Safety*, 147, 494–499. <https://doi.org/10.1016/j.ecoenv.2017.09.004>
- Annamalai, J., & Namasivayam, V. (2015). Endocrine disrupting chemicals in the atmosphere: Their effects on humans and wildlife. *Environment International*, 76, 78–97. <https://doi.org/10.1016/j.envint.2014.12.006>
- Arlos, M. J., Liang, R., Hataat-Fraile, M. M., Bragg, L. M., Zhou, N. Y., Servos, M. R., & Andrews, S. A. (2016). Photocatalytic decomposition of selected estrogens and their estrogenic activity by UV-LED irradiated TiO₂ immobilized on porous titanium sheets via thermal-chemical oxidation. *Journal of Hazardous Materials*, 318, 541–550. <https://doi.org/10.1016/j.jhazmat.2016.07.048>
- Auriol, M., Filali-Meknassi, Y., Adams, C. D., Tyagi, R. D., Noguero, T. N., & Pina, B. (2008). Removal of estrogenic activity of natural and synthetic hormones from a municipal wastewater: Efficiency of horseradish peroxidase and laccase from *Trametes versicolor*. *Chemosphere*, 70, 445–452. <https://doi.org/10.1016/j.chemosphere.2007.06.064>
- Auriol, M., Filali-Meknassi, Y., Tyagi, R. D., Adams, C. D., & Surampalli, R. Y. (2006). Endocrine disrupting compounds removal from wastewater, a new challenge. *Process Biochemistry*, 41, 525–539. <https://doi.org/10.1016/j.procbio.2005.09.017>
- Ba, S., Jones, J. P., & Cabana, H. (2014). Hybrid bioreactor (HBR) of hollow fiber microfilter membrane and cross-linked laccase aggregates eliminate aromatic pharmaceuticals in wastewaters. *Journal of Hazardous Materials*, 280, 662–670. <https://doi.org/10.1016/j.jhazmat.2014.08.062>
- Babay, P. A., Itria, R. F., Ale, E. E. R., Becquart, E. T., & Gautier, E. A. (2014). Ubiquity of endocrine disruptors nonylphenol and its mono- and diethoxylates in freshwater, sediments, and biosolids associated with high and low density populations of Buenos Aires, Argentina. *Clean: Soil, Air, Water*, 42, 731–737.
- Barber, L. B., Loyo-Rosales, J. E., Rice, C. P., Minarik, T. A., & Oskouie, A. K. (2015). Endocrine disrupting alkylphenolic chemicals and other contaminants in wastewater treatment plant effluents, urban streams, and fish in the Great Lakes and Upper Mississippi River Regions. *Science of the Total Environment*, 517, 195–206. <https://doi.org/10.1016/j.scitotenv.2015.02.035>
- Belfroid, A., van Velzen, M., van der Horst, B., & Vethaark, D. (2002). Occurrence of bisphenol A in surface water and uptake in fish: Evaluation of field measurements. *Chemosphere*, 49, 97–103. [https://doi.org/10.1016/S0045-6535\(02\)00157-1](https://doi.org/10.1016/S0045-6535(02)00157-1)
- Bila, D. M., Montalva, A. F., & Dezotti, M. (2005). Ozonation of the endocrine disruptor 17β estradiol and estrogenic activity evaluation. IOA 17th World Ozone Congress, Strasbourg.
- Bogan, B. W., Lamar, R. T., & Hammel, K. E. (1996). Fluorene oxidation in vivo by *Phanerochaete chrysosporium* and in vitro during manganese peroxidase-dependent lipid peroxidation. *Applied and Environmental Microbiology*, 62, 1788–1792.
- Cabana, H., Jiwan, J. L. H., Rozenberg, R., Elisashvili, V., Penninckx, M., Agathos, S. N., & Jones, J. P. (2007). Elimination of endocrine disrupting chemicals nonylphenol and bisphenol and personal care product ingredient triclosan using enzyme preparation from the white rot fungus, *Coriopsis polyzona*. *Chemosphere*, 67, 770–778. <https://doi.org/10.1016/j.chemosphere.2006.10.037>
- Cabana, H., Jones, J. P., & Agathos, S. N. (2007a). Elimination of endocrine disrupting chemicals using white rot fungi and their lignin modifying enzymes: A review. *Engineering in Life Sciences*, 5, 429–456. [https://doi.org/10.1002/\(ISSN\)1618-2863](https://doi.org/10.1002/(ISSN)1618-2863)
- Cabana, H., Jones, J. P., & Agathos, S. N. (2007b). Preparation and characterization of cross-linked laccase aggregates and their application to the elimination of endocrine disrupting chemicals. *Journal of Biotechnology*, 132, 23–31. <https://doi.org/10.1016/j.jbiotec.2007.07.948>
- Cabana, H., Jones, J. P., & Agathos, S. N. (2009). Utilization of cross-linked laccase aggregates in a perfusion basket reactor for the Continuous elimination of endocrine-disrupting chemicals. *Biotechnology and Bioengineering*, 102, 1582–1592. <https://doi.org/10.1002/bit.22198>
- Cajthaml, T. (2015). Biodegradation of endocrine-disrupting compounds by ligninolytic fungi: Mechanisms involved in the degradation. *Environmental Microbiology*, 17, 4822–4834. <https://doi.org/10.1111/1462-2920.12460>
- Caliman, F. A., & Gavrilescu, M. (2009). Pharmaceuticals, personal care products and endocrine disrupting agents in the environment- a review. *Clean.*, 37, 277–303.
- Camareo, S., Sarkar, S., Ruiz-Duenas, F. J., Martinez, M. J., & Martinez, A. T. (1999). Description of a versatile peroxidase involved in the natural degradation of lignin that has both manganese peroxidase and lignin peroxidase substrate interaction sites. *Journal of Biological Chemistry*, 274, 10324–10330. <https://doi.org/10.1074/jbc.274.15.10324>
- Caramelo, L., Martinez, M. J., & Martinez, A. T. (1999). A search for ligninolytic peroxidases in the fungus *Pleurotus eryngii* involving α-keto-γ-thiomethylbutyric acid and lignin model dimers. *Applied and Environmental Microbiology*, 65, 916–922.
- Carmona, E., Andreu, V., & Picó, Y. (2014). Occurrence of acidic pharmaceuticals and personal care products in Turia River Basin: From waste to drinking water. *Science of the Total Environment*, 484, 53–63. <https://doi.org/10.1016/j.scitotenv.2014.02.085>
- Chandra, R., & Chowdhary, P. (2015). Properties of bacterial laccases and their application in bioremediation of industrial wastes. *Environmental Science: Processes & Impacts*, 17, 326–342.
- Coconi-Linares, N., Magana-Ortiz, D., Guzman-Ortiz, D. A., Fernandez, F., Loske, A. M., & Gomez-Lim, M. (2014). High yield production of manganese peroxidase, lignin peroxidase and versatile peroxidase in *Phanerochaete chrysosporium*. *Applied Microbiology and Biotechnology*, 98, 9283–9294. <https://doi.org/10.1007/s00253-014-6105-9>
- Coleman, H. M., Routledge, E. J., Sumpter, J. P., Eggins, B. R., & Byrne, J. A. (2004). Rapid loss of estrogenicity of steroid estrogens by UVA photolysis and photocatalysis over an immobilized titanium dioxide catalyst. *Water Research*, 38, 3233–3240. <https://doi.org/10.1016/j.watres.2004.04.021>
- Combalbert, S., & Hernandez-Raquet, G. (2010). Occurrence, fate, and biodegradation of estrogens in sewage and manure. *Applied Microbiology and Biotechnology*, 86, 1671–1692. <https://doi.org/10.1007/s00253-010-2547-x>
- Couto, S. R., & Toca Herrera, J. L. (2006). Industrial and biotechnological applications of laccases: A review. *Biotechnology Advances*, 24, 500–513. <https://doi.org/10.1016/j.biotechadv.2006.04.003>
- Daasi, D., Prieto, A., Zouari-Mechichi, H., Martinez, M. J., Nasri, M., & Mechichi, T. (2016). Degradation of bisphenol A by different fungal laccases and identification of its degradation products. *International Biodeterioration and Biodegradation*, 110, 181–188. <https://doi.org/10.1016/j.ibiod.2016.03.017>
- Dalrymple, O. K., Yeh, D. H., & Trotz, M. A. (2007). Removing pharmaceuticals and endocrine-disrupting compounds from wastewater by photocatalysis. *Journal of Chemical Technology and Biotechnology*, 82, 121–134. [https://doi.org/10.1002/\(ISSN\)1097-4660](https://doi.org/10.1002/(ISSN)1097-4660)
- Davila-Vazquez, G., Tinoco, R., Pickard, M. A., & Vazquez-Duhalt, R. (2005). Transformation of halogenated pesticides by versatile peroxidase from *Bjerkandera adusta*. *Enzyme and Microbial Technology*, 36, 223–231. <https://doi.org/10.1016/j.enzmictec.2004.07.015>
- Debaste, F., Songulashvili, G., & Penninckx, M. J. (2014). The potential of *Cerrena unicolor* laccase immobilized on mesoporous silica beads for removal of organic micropollutants in wastewaters. *Desalination and*

- Water Treatment*, 52, 2344–2347. <https://doi.org/10.1080/19443994.2013.877851>
- de Freitas, E. N., Bubna, G. A., Brugnari, T., Kato, C. G., Noll, M., Rauen, T. G., ... Peralta, R. M. (2017). Removal of bisphenol A by laccase from *Pleurotus ostreatus* and *Pleurotus pulmonarius* and evaluation of ecotoxicity of degradation products. *Chemical Engineering Journal*, 330, 1361–1369. <https://doi.org/10.1016/j.cej.2017.08.051>
- Dehorter, B., & Blondeau, R. (1993). Isolation of an extracellular Mn-dependent enzyme mineralizing melanoidins from the white-rot fungus *Trametes versicolor*. *FEMS Microbiology Letters*, 109, 117–122. <https://doi.org/10.1111/j.1574-6968.1993.tb06153.x>
- Diano, N., & Mita, D. G. (2011). Removal of endocrine disruptors in waste waters by means of bioreactors. In F. S. G. Einschlag (Ed.), *Waste water – treatment and reutilization* (pp. 29–48). Croatia: InTech. Retrieved from <http://www.intechopen.com/books/waste-water-treatment-and-reutilization/removal-of-endocrine-disruptors-in-waste-waters-by-means-of-bioreactors>
- Eibes, G., Debernardi, G., Feijoo, G., Moreira, M. T., & Lema, J. M. (2011). Oxidation of pharmaceutically active compounds by a ligninolytic fungal peroxidase. *Biodegradation*, 22, 539–550. <https://doi.org/10.1007/s10532-010-9426-0>
- Eldridge, H. C., Milliken, A., Farmer, C., Hampton, A., Wendland, N., Coward, L., ... Johnson, C. M. (2017). Efficient remediation of 17 α -ethynylestradiol by *Lentinula edodes* (Shiitake) laccase. *Biocatalysis and Agricultural Biotechnology*, 10, 64–68.
- Esplugas, S., Bila, D. M., Gustavo, L., Krause, T., & Dezotti, M. (2007). Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. *Journal of Hazardous Materials*, 149, 631–642. <https://doi.org/10.1016/j.jhazmat.2007.07.073>
- Falade, A. O., Nwodo, U. U., Iweriebor, B. C., Green, E., Mabinya, L. V., & Okoh, A. I. (2017). Lignin peroxidase functionalities and prospective applications. *MicrobiologyOpen*, 6, e00394. <https://doi.org/10.1002/mbo3.394>
- Gao, D., Li, Z., Wen, Z., & Ren, N. (2014). Occurrence and fate of phthalate esters in fullscale domestic wastewater treatment plants and their impact on receiving waters along the Songhua River in China. *Chemosphere*, 95, 24–32. <https://doi.org/10.1016/j.chemosphere.2013.08.009>
- García-Morales, R., García-García, A., Orona-Navar, C., Osma, J. F., Nigam, K. D. P., & Ornelas-Soto, N. (2018). Biotransformation of emerging pollutants in groundwater by laccase from *P. sanguineus* CS43 immobilized onto titania nanoparticles. *Journal of Environmental Chemical Engineering*, 6, 710–717. <https://doi.org/10.1016/j.jece.2017.12.006>
- García-Morales, R., Rodríguez-Delgado, M., Gomez-Mariscal, K., Orona-Navar, C., Hernandez-Luna, C., Torres, E., ... Ornelas-Soto, N. (2015). Biotransformation of endocrine-disrupting compounds in groundwater: Bisphenol A, nonylphenol, ethynylestradiol and triclosan by a laccase cocktail from *Pycnoporus sanguineus* CS43. *Water, Air, and Soil Pollution*, 226, 251. <https://doi.org/10.1007/s11270-015-2514-3>
- Gassara, F., Brar, S. K., Verma, M., & Tyagi, R. D. (2013). Bisphenol A degradation in water by ligninolytic enzymes. *Chemosphere*, 92(10), 1356–1360. <https://doi.org/10.1016/j.chemosphere.2013.02.071>
- Gasser, C. A., Ammann, E. M., Shahagaldian, P., & Corvini, P. F.-X. (2014). Laccases to take on the challenge of emerging organic contaminants in wastewater. *Applied Microbiology and Biotechnology*, 98, 9931–9952. <https://doi.org/10.1007/s00253-014-6177-6>
- Han, B., Zhang, M., Zhao, D., & Feng, Y. (2015). Degradation of aqueous and soil-sorbed estradiol using a new class of stabilized manganese oxide nanoparticles. *Water Research*, 70, 288–299. <https://doi.org/10.1016/j.watres.2014.12.017>
- Hata, T., Shintate, H., Kawai, S., Okamura, H., & Nishida, T. (2010). Elimination of carbamazepine by repeated treatment with laccase in the presence of 1-hydroxybenzotriazole. *Journal of Hazardous Materials*, 181, 1175–1178. <https://doi.org/10.1016/j.jhazmat.2010.05.103>
- Hatakka, A. (1994). Lignin-modifying enzymes from selected white-rot fungi: Production and role from in lignin degradation. *FEMS Microbiology Reviews*, 13, 125–135. <https://doi.org/10.1111/j.1574-6976.1994.tb00039.x>
- Heinfling, A., Martinez, M. J., Martinez, A. T., Bergbauer, M., & Szewzyk, U. (1998). Purification and characterization of peroxidases from the dye decolorizing fungus *Bjerkandera adusta*. *FEMS Microbiology Letters*, 165, 43–50. <https://doi.org/10.1111/j.1574-6968.1998.tb13125.x>
- Hofrichter, M. (2002). Review: Lignin conversion by manganese peroxidase (MnP). *Enzyme and Microbial Technology*, 30, 454–466. [https://doi.org/10.1016/S0141-0229\(01\)00528-2](https://doi.org/10.1016/S0141-0229(01)00528-2)
- Hofrichter, M., Steffen, K., & Hatakka, A. (2001). Decomposition of humic substances by ligninolytic fungi. 5th Finnish Conf. Environ. Sci., Proceedings, Turku, Finland, pp. 56–60.
- Hofrichter, M., Ullrich, R., Pecyna, M. J., Liers, C., & Lundell, T. (2010). New and classic families of secreted fungal heme peroxidases. *Applied Microbiology and Biotechnology*, 87, 871–897. <https://doi.org/10.1007/s00253-010-2633-0>
- Huang, L. P., Lee, C. C., Fan, J. P., Kuo, P. H., Shih, T. S., & Hsu, P. C. (2014). Urinary metabolites of di (2-ethylhexyl) phthalate relation to sperm motility reactive oxygen species generation and apoptosis in polyvinyl chloride workers. *International Archives of Occupational and Environmental Health*, 87, 635–646. <https://doi.org/10.1007/s00420-013-0905-6>
- Huber, M. M., Canonica, S., Park, G. Y., & von Gunten, U. (2003). Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environmental Science and Technology*, 37, 1016–1024. <https://doi.org/10.1021/es025896h>
- Husain, Q. (2010). Peroxidase mediated decolorization and remediation of wastewater containing industrial dyes: A review. *Reviews in Environmental Science & Biotechnology*, 9, 117–140. <https://doi.org/10.1007/s11157-009-9184-9>
- Husain, Q., & Qayyum, S. (2012). Biological and enzymatic treatment of bisphenol A and other endocrine disrupting compounds: A review. *Critical Reviews in Biotechnology*, 33, 260–292.
- Ifelebuegu, A. O. (2011). The fate and behavior of selected endocrine disrupting chemicals in full scale wastewater and sludge treatment unit processes. *International Journal of Environmental Science and Technology*, 8, 245–254. <https://doi.org/10.1007/BF03326213>
- Ifelebuegu, A. O., & Ezenwa, C. P. (2011). Removal of endocrine disrupting chemicals in wastewater treatment by fenton-like oxidation. *Water, Air, and Soil Pollution*, 217, 213–220. <https://doi.org/10.1007/s11270-010-0580-0>
- Ifelebuegu, A. O., Lester, J. N., Churchley, J., & Cartmell, E. (2006). Removal of an endocrine disrupting chemical (17 α -ethynylestradiol) from wastewater effluent by activated carbon adsorption: Effects of activated carbon type and competitive adsorption. *Environmental Technology*, 27, 1343–1349. <https://doi.org/10.1080/09593332708618748>
- Inoue, Y., Hata, T., Kawai, S., Okamura, H., & Nishida, T. (2010). Elimination and detoxification of triclosan by manganese peroxidase from white rot fungus. *Journal of Hazardous Materials*, 180, 764–767. <https://doi.org/10.1016/j.jhazmat.2010.04.024>
- Jarosz-Wilkolazka, A., Luterek, J., & Olszewska, A. (2008). Catalytic activity of versatile peroxidase from *Bjerkandera fumosa* at different pH. *Biocatalysis and Biotransformation*, 26(4), 280–287. <https://doi.org/10.1080/10242420701830082>
- Jeirani, Z., Niu, C. H., & Soltan, J. (2016). Adsorption of emerging pollutants on activated carbon. *Reviews in Chemical Engineering*, 33, 491–522. <https://doi.org/10.1515/revce-2016-0027>
- Ji, C., Nguyen, L. N., Hou, J., Hai, F. I., & Chen, V. (2017). Direct immobilization of laccase on titania nanoparticles from crude enzyme

- extracts of *P. ostreatus* culture for micro-pollutant degradation. *Separation and Purification Technology*, 178, 215–223. <https://doi.org/10.1016/j.seppur.2017.01.043>
- Jiang, L. Y., Huang, C., Chen, J. M., & Chen, X. (2009). Oxidative transformation of 17 beta-estradiol by MnO₂ in aqueous solution. *Archives of Environmental Contamination and Toxicology*, 57, 221–229. <https://doi.org/10.1007/s00244-008-9257-8>
- Jobling, S., Bjerregaard, P., Blumberg, B., Brandt, I., Brian, J. V., Casey, S. C., ... Zoeller, R. T. (2013). Evidence for endocrine disruption in humans and wildlife. In A. Bergman, J. J. Heindel, S. Jobling, K. A. Kidd, & R. T. Zoeller (Eds.), *State of the Science of Endocrine Disrupting Chemicals – 2012*. (pp. 23–186). Geneva, Switzerland: UNEP/WHO.
- Khindaria, A., Yamazaki, I., & Aust, S. D. (1996). Stabilization of the veratryl alcohol cation radical by lignin peroxidase. *Biochemistry*, 35, 6418–6424. <https://doi.org/10.1021/bi9601666>
- Kim, Y., Yeo, S., Kim, M. K., & Choi, H. T. (2008). Removal of estrogenic activity from endocrine-disrupting chemicals by purified laccase of *Phlebia tremellosa*. *FEMS Microbiology Letters*, 284, 172–175. <https://doi.org/10.1111/j.1574-6968.2008.01189.x>
- Klavarioti, M., Mantzavinos, D., & Kassinos, D. (2009). Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environment International*, 35, 402–417. <https://doi.org/10.1016/j.envint.2008.07.009>
- Komesli, O. T., Muz, M., Ak, M. S., Bakirdere, S., & Gokcay, C. F. (2015). Occurrence, fate and removal of endocrine disrupting compounds (EDCs) in Turkish wastewater treatment plants. *Chemical Engineering Journal*, 277, 202–208. <https://doi.org/10.1016/j.cej.2015.04.115>
- Krupadam, R. J., Sridevi, P., & Sakunthala, S. (2011). Removal of endocrine disrupting chemicals from contaminated industrial groundwater using chitin as a biosorbent. *Journal of Chemical Technology and Biotechnology*, 86, 367–374. <https://doi.org/10.1002/jctb.2525>
- Kuwahara, M., Glenn, J. K., Morgan, M. A., & Gold, M. H. (1984). Separation and characterization of two extracellular H₂O₂-dependent oxidases from ligninolytic cultures of *Phanerochaete chrysosporium*. *FEBS Letters*, 169, 247–250. [https://doi.org/10.1016/0014-5793\(84\)80327-0](https://doi.org/10.1016/0014-5793(84)80327-0)
- Li, P., Cao, J., Diao, X., Wang, B., Zhou, H., Han, Q., ... Li, Y. (2015). Spatial distribution, sources and ecological risk assessment of polycyclic aromatic hydrocarbons in surface seawater from Yangpu Bay, China. *Marine Pollution Bulletin*, 93, 53–60. <https://doi.org/10.1016/j.marpolbul.2015.02.015>
- Li, B., Lei, Z., & Huang, Z. (2009). Surface-treated activated carbon for removal of aromatic compounds from water. *Chemical Engineering and Technology*, 32, 763–770. <https://doi.org/10.1002/ceat.200800535>
- Lindsey, M. E., & Tarr, M. A. (2000). Quantitation of hydroxyl radical during Fenton oxidation following a single addition of iron and peroxide. *Chemosphere*, 41, 409–417. [https://doi.org/10.1016/S0045-6535\(99\)00296-9](https://doi.org/10.1016/S0045-6535(99)00296-9)
- Liu, Y., Chen, Z., & Shen, J. (2013). Occurrence and removal characteristics of phthalate esters from typical water sources in Northeast China. *Journal of Analytical Methods in Chemistry*, 2013, 1–8.
- Liu, Z., Kanjo, Y., & Mizutani, S. (2009). Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment – physical means, biodegradation, and chemical advanced oxidation: A review. *Science of the Total Environment*, 407, 731–748. <https://doi.org/10.1016/j.scitotenv.2008.08.039>
- Lladó, J., Lao-Luque, C., Ruiz, B., Fuente, E., Solé-Sardans, M., & Dorado, A. D. (2015). Role of activated carbon properties in atrazine and paracetamol adsorption equilibrium and kinetics. *Process Safety and Environmental Protection*, 95, 51–59. <https://doi.org/10.1016/j.psep.2015.02.013>
- Lloret, L., Eibes, G., Moreira, M. T., Feijoo, G., & Lema, J. M. (2013). Removal of estrogenic compounds from filtered secondary wastewater effluent in a continuous Enzymatic Membrane Reactor. Identification of biotransformation products. *Environmental Science and Technology*, 47, 4536–4543. <https://doi.org/10.1021/es304783k>
- Lloret, L., Hollmann, F., Eibes, G., Feijoo, G., Moreira, M. T., & Lema, J. M. (2012). Immobilization of laccase on Eupergit supports and its application for the removal endocrine disrupting chemicals in a packed-bed reactor. *Biodegradation*, 23, 373–386. <https://doi.org/10.1007/s10532-011-9516-7>
- Lobos, S., Larram, J., Salas, L., Cullen, D., & Vicuna, R. (1994). Isoenzymes of manganese dependent peroxidase and laccase produced by the lignin degrading basidiomycete, *Ceriporiopsis subvermispora*. *Microbiology*, 14, 2691–2698. <https://doi.org/10.1099/00221287-140-10-2691>
- Loffredo, E., & Castellana, G. (2015). Comparative evaluation of the efficiency of low-cost adsorbents and ligninolytic fungi to remove a combination of xenoestrogens and pesticides from a landfill leachate and abate its phytotoxicity. *Journal of Environmental Science and Health Part A Environmental Science*, 50, 958–970.
- Mandal, S., Khuda, N., Mian, M. R., Moniruzzaman, M., Nahar, N., Mamun, M. I. R., & Shoeb, M. (2015). Analysis of ground and surface water samples from some area of Dhaka City for polycyclic aromatic hydrocarbons (PAHs). *Dhaka University Journal of Science*, 63, 59–60.
- Mao, L., Lu, J., Gao, S., & Huang, Q. (2010). Transformation of 17β-estradiol mediated by lignin peroxidase: The role of veratryl alcohol. *Archives of Environmental Contamination and Toxicology*, 59, 13–19. <https://doi.org/10.1007/s00244-009-9448-y>
- Martin, J., Camacho-Munoz, D., Santos, J. L., Aparicio, I., & Alonso, E. (2012). Occurrence of pharmaceutical compounds in wastewater and sludge from wastewater treatment plants: Removal and ecotoxicological impact of wastewater discharges and sludge disposal. *Journal of Hazardous Materials*, 239, 40–47. <https://doi.org/10.1016/j.jhazmat.2012.04.068>
- Matongo, S., Birungi, G., Moodley, B., & Ndungu, P. (2015). Pharmaceutical residues in water and sediment of Msunduzi River, KwaZulu-Natal, South Africa. *Chemosphere*, 134, 133–140. <https://doi.org/10.1016/j.chemosphere.2015.03.093>
- Mehta, R. (2012). Bioremediation of textile waste water. *Colourage*, 59, 46.
- Mendez-Arriaga, F., Esplugas, S., & Gimenez, J. (2010). Degradation of the emerging contaminant ibuprofen in water by photo-fenton. *Water Research*, 44(2), 589–595. <https://doi.org/10.1016/j.watres.2009.07.009>
- Mendez-Hernandez, J. E., Eibes, G., Arca-Ramos, A., Lu-chau, T. A., Feijoo, G., Moreira, M. T., & Lema, J. M. (2015). Continuous removal of nonylphenol by versatile peroxidase in a two-stage membrane bioreactor. *Applied Biochemistry and Biotechnology*, 175(6), 3038–3047. <https://doi.org/10.1007/s12010-014-1474-1>
- Messerschmidt, A., & Huber, R. (1990). The blue oxidases, ascorbate oxidase, laccase and ceruloplasmin. Modelling and structural relationships. *European Journal of Biochemistry*, 187, 341–352. <https://doi.org/10.1111/j.1432-1033.1990.tb15311.x>
- Milton, R. D., Giroud, F., Thumser, A. E., Minter, S. D., & Slade, R. C. T. (2013). Hydrogen peroxide produced by glucose oxidase affects the performance of laccase cathodes in glucose/oxygen fuel cells: FAD-dependent glucose dehydrogenase as a replacement. *Physical Chemistry Chemical Physics*, 15, 19371–19379. <https://doi.org/10.1039/c3cp53351d>
- Min, K., Kim, Y., Kim, Y. W., Jung, H. S., & Hah, Y. C. (2001). Characterization of a novel laccase produced by the wood-rotting fungus *Phellinus ribis*. *Archives of Biochemistry and Biophysics*, 392(2), 279–286. <https://doi.org/10.1006/abbi.2001.2459>
- Mohapatra, D. P., Brar, S. K., Tyagi, R. D., & Surampalli, R. Y. (2011). Occurrence of bisphenol A in wastewater and wastewater sludge of CUQ treatment plant. *Journal of Xenobiotics*, 1, e3. <https://doi.org/10.4081/xeno.2011.e3>

- Moreno-Castilla, C. (2004). Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon*, 42, 83–94. <https://doi.org/10.1016/j.carbon.2003.09.022>
- Nam, S., Choi, D., Kim, S., Her, N., & Zoh, K. (2014). Adsorption characteristics of selected hydrophilic and hydrophobic micropollutants in water using activated carbon. *Journal of Hazardous Materials*, 270, 144–152. <https://doi.org/10.1016/j.jhazmat.2014.01.037>
- NIEHS (National Institute of Environmental Health Sciences). (2010). *Endocrine disruptors*. United States of America: National Institute of Health, U. S. Department of Health and Human Services.
- Noutsopoulos, C., Koumaki, E., Mamais, D., Nika, M. C., Bletsou, A. A., & Thomaidis, N. S. (2015). Removal of endocrine disruptors and non-steroidal anti-inflammatory drugs through wastewater chlorination: The effect of pH, total suspended solids and humic acids and identification of degradation by-products. *Chemosphere*, 119, S109–S114. <https://doi.org/10.1016/j.chemosphere.2014.04.107>
- Ohko, Y., Ando, I., Niwa, C., Tatsuma, T., Yamamura, T., Nakashima, T., ... Fujishima, A. (2001). Degradation of bisphenol A in water by TiO₂ photocatalyst. *Environmental Science and Technology*, 35, 2365–2368. <https://doi.org/10.1021/es001757t>
- Ohko, Y., Luchi, K., Niwa, C., Tatsuma, T., Nakashima, T., Iguchi, T., ... Fujishima, A. (2002). 17 Beta-estradiol degradation by TiO₂ photocatalysis as a means of reducing estrogenic activity. *Environmental Science and Technology*, 36, 4175–4181. <https://doi.org/10.1021/es011500a>
- Oller, I., Malato, S., & Sanchez-Perez, J. A. (2011). Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. *Science of the Total Environment*, 409, 4141–4166. <https://doi.org/10.1016/j.scitotenv.2010.08.061>
- Ouzounis, C., & Sander, C. (1991). A structure-derived sequence pattern for the detection of type I copper binding domains in distantly related proteins. *FEBS Letters*, 279, 73–78. [https://doi.org/10.1016/0014-5793\(91\)80254-Z](https://doi.org/10.1016/0014-5793(91)80254-Z)
- Palma, C., Lloret, L., Sepulveda, L., & Contreras, E. (2016). Production of versatile peroxidase from *Pleurotus eryngii* by solid-state fermentation using agricultural residues and evaluation of its catalytic properties. *Preparative Biochemistry & Biotechnology*, 46, 200–207. <https://doi.org/10.1080/10826068.2015.1084513>
- Perez-Boada, M., Ruiz-Duenas, F. J., Pogni, R., Basosi, R., & Choinowski, T. (2005). Versatile peroxidase oxidation of high redox potential aromatic compounds: Site-directed mutagenesis, spectroscopic and crystallographic investigation of three long-range electron transfer pathways. *Journal of Molecular Biology*, 354, 385–402. <https://doi.org/10.1016/j.jmb.2005.09.047>
- Pessoa, G. P., de Souza, N. C., Vidal, C. B., Alves, J. A., Firmino, P. I. M., Nascimento, R. F., & dos Santos, A. B. (2014). Occurrence and removal of estrogens in Brazilian wastewater treatment plants. *Science of the Total Environment*, 490, 288–295. <https://doi.org/10.1016/j.scitotenv.2014.05.008>
- Qin, F. X., Jia, S. Y., Liu, Y., Li, H. Y., & Wu, S. H. (2015). Adsorptive removal of bisphenol A from aqueous solution using metal-organic frameworks. *Desalination and Water Treatment*, 54, 93–102. <https://doi.org/10.1080/19443994.2014.883331>
- Quarantino, D., Federici, F., Petruccioli, M., Fenice, M., & D'Aannibale, A. (2007). Production, purification and partial characterisation of a novel laccase from the whiterot fungus *Panus tigrinus* CBS 577.79. *Antonie Leeuwenhoek*, 91, 57–69.
- Ra, J. S., Lee, S. H., Lee, J., Kim, H. Y., Lim, B. J., Kim, S. H., & Kim, S. D. (2011). Occurrence of estrogenic chemicals in South Korean surface waters and municipal wastewaters. *Journal of Environmental Monitoring*, 13, 101–109. <https://doi.org/10.1039/COEM00204F>
- Rajasundari, K., & Murugesan, R. (2011). Decolourization of distillery waste water – role of microbes and their potential oxidative enzymes (review). *Journal of Applied Environmental and Biological Sciences*, 1, 54–68.
- Ramírez-Cavazos, L. I., Junghanns, C., Ornelas-Soto, N., Cárdenas-Chávez, D. L., Hernández-Luna, C., Demarche, P., ... Parra, R. (2014). Purification and characterization of two thermostable laccases from *Pycnoporus sanguineus* and potential role in degradation of endocrine disrupting chemicals. *Journal of Molecular Catalysis B: Enzymatic*, 108, 32–42. <https://doi.org/10.1016/j.molcatb.2014.06.006>
- Ravichandran, A., & Sridhar, M. (2016). Versatile peroxidase: Super peroxidases with potential biotechnological applications. *Journal of Dairy, Veterinary & Animal Research*, 4(2), 00116.
- Reddy, G. V., Sridhar, M., & Gold, M. H. (2003). Cleavage of non-phenolic β-1 diaryl propane lignin model dimers by manganese peroxidase from *Phanerochaete chrysosporium*: Evidence for a hydrogen abstraction mechanism. *European Journal of Biochemistry*, 270, 284–292. <https://doi.org/10.1046/j.1432-1033.2003.03386.x>
- Rios, G. M., Belleville, M. P., Paolucci, D., & Sanchez, J. (2004). Progress in enzymatic membrane reactors - a review. *Journal of Membrane Science*, 242, 189–196. <https://doi.org/10.1016/j.memsci.2003.06.004>
- Ruiz-Duenas, F. J., Martinez, M. J., & Martinez, A. T. (1999). Molecular characterization of a novel peroxidase isolated from the ligninolytic fungus *Pleurotus eryngii*. *Molecular Microbiology*, 31, 223–236. <https://doi.org/10.1046/j.1365-2958.1999.01164.x>
- Ruiz-Dueñas, F. J., Morales, M., Garcia, E., Miki, Y., Martinez, M. J., & Martinez, A. T. (2009). Substrate oxidation sites in versatile peroxidase and other basidiomycete peroxidases. *Journal of Experimental Biology*, 60, 441–452.
- Saez-Jimenez, V., Baratto, M. C., Pogni, R., Rencoret, J., Gutierrez, A., Santos, J. I., ... Ruiz-Duenas, F. J. (2015). Demonstration of lignin-to-peroxidase direct electron transfer, a transient-state kinetics, directed mutagenesis, EPR and NMR study. *Journal of Biological Chemistry*, 290, 23201–23213. <https://doi.org/10.1074/jbc.M115.665919>
- Saucier, C., Adebayo, M. A., Lima, E. C., Cataluna, R., Thue, P. S., Prola, L. D. T., ... Dotto, G. L. (2015). Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents. *Journal of Hazardous Materials*, 289, 18–27. <https://doi.org/10.1016/j.jhazmat.2015.02.026>
- Sei, K., Takeda, T., Soda, S. O., Fujita, M., & Ike, M. (2007). Removal characteristics of endocrine-disrupting chemicals by laccase from white-rot fungi. *Journal of Environmental Science and Health Part A Environmental Science*, 43, 53–60. <https://doi.org/10.1080/10934520701750397>
- Silva, C. P., Otero, M., & Esteves, V. (2012). Processes for the elimination of estrogenic steroid hormones from water: A review. *Environmental Pollution*, 165, 38–58. <https://doi.org/10.1016/j.envpol.2012.02.002>
- Sirim, D., Wagner, F., Wang, L., Schmid, R. D., & Pleiss, J. (2011). The laccase engineering database: A classification and analysis system for laccases and related multicopper oxidases. *Database*, 6, 1–7.
- Songulashvili, G., Jimenez-tobon, G. A., Jaspers, C., & Penninckx, M. J. (2012). Immobilized laccase of *Cerrena unicolor* for elimination of endocrine disruptor micropollutants. *Fungal Biology*, 116, 883–889. <https://doi.org/10.1016/j.funbio.2012.05.005>
- Strong, P. J., & Claus, H. (2011). Laccase: A review of its past and its future in bioremediation. *Critical Reviews in Environment Science and Technology*, 41(4), 373–434. <https://doi.org/10.1080/10643380902945706>
- Suzuki, K., Hirai, H., Murata, H., & Nishida, T. (2003). Removal of estrogenic activities of 17β-estradiol and ethinylestradiol by ligninolytic enzymes from white rot fungi. *Water Research*, 37, 1972–1975. [https://doi.org/10.1016/S0043-1354\(02\)00533-X](https://doi.org/10.1016/S0043-1354(02)00533-X)
- Taboada-Puig, R., Junghanns, C., Demarche, P., Moreira, M. T., Feijoo, G., Lema, J. M., & Agathos, S. N. (2011). Combined cross-linked enzyme aggregates from versatile peroxidase and glucose oxidase: Production, partial characterization and application for the elimination of endocrine disruptors. *Bioresource Technology*, 102, 6593–6599. <https://doi.org/10.1016/j.biortech.2011.03.018>

- Taboada-Puig, R., Lu-Chau, T. A., Eibes, G., Feijoo, G., Moreira, M. T., & Lema, J. M. (2015). Continuous removal of endocrine disruptors by versatile peroxidase using a two-stage system. *Biotechnology Progress*, 31, 908–916. <https://doi.org/10.1002/btpr.2116>
- Tamagawa, Y., Hirai, H., Kawai, S., & Nishida, T. (2005). Removal of estrogenic activity of endocrine-disrupting genistein by ligninolytic enzymes from white rot fungi. *FEMS Microbiology Letters*, 244, 93–98. <https://doi.org/10.1016/j.femsle.2005.01.023>
- Tamagawa, Y., Yamaki, R., Hirai, H., Kawai, S., & Nishida, T. (2006). Removal of estrogenic activity of natural steroidal hormone estrone by ligninolytic enzymes from white rot fungi. *Chemosphere*, 65, 97–101. <https://doi.org/10.1016/j.chemosphere.2006.02.031>
- Ternes, A. T., Stuber, J., Herrmann, N., McDowell, D., Ried, A., Kampmann, M., & Teiser, B. (2003). Ozonation: A tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Research*, 37, 1976–1982. [https://doi.org/10.1016/S0043-1354\(02\)00570-5](https://doi.org/10.1016/S0043-1354(02)00570-5)
- Touahar, I. E., Haroune, L., Ba, S., Bellenger, J.-P., & Cabana, H. (2014). Characterization of combined cross-linked enzyme aggregates from laccase, versatile peroxidase and glucose oxidase, and their utilization for the elimination of pharmaceuticals. *Science of the Total Environment*, 481, 90–99. <https://doi.org/10.1016/j.scitotenv.2014.01.132>
- Tsutsumi, Y., Haneda, T., & Nishida, T. (2001). Removal of estrogenic activities of bisphenol A and nonylphenol by oxidative enzymes from lignin-degrading basidiomycetes. *Chemosphere*, 42, 271–276. [https://doi.org/10.1016/S0045-6535\(00\)00081-3](https://doi.org/10.1016/S0045-6535(00)00081-3)
- Tuor, U., Wariishi, H., Schoemaker, H. E., & Gold, M. H. (1992). Oxidation of phenolic arylglycerol β -aryl ether lignin model compounds by manganese peroxidase from *Phanerochaete chrysosporium*: Oxidative cleavage of an α -carbonyl model compound. *Biochemistry*, 31, 4986–4995. <https://doi.org/10.1021/bi00136a011>
- UNEP/WHO. (2012). *State of the science of endocrine disrupting chemicals—2012*. Geneva, Switzerland: United Nations Environment Programme/World Health Organization.
- Vajda, A. M., Kumar, A., Woods, M., Williams, M., Doan, H., Tolsher, P., ... Barber, L. B. (2015). Integrated assessment of wastewater treatment plant effluent estrogenicity in the upper Murray river, Australia, using the native murray rainbowfish (*Melanotaenia fluviatilis*). *Environmental Toxicology and Chemistry*, 34, 1078–1087. <https://doi.org/10.1002/etc.2895>
- Vogna, D., Marotta, R., Napolitano, A., Andreozzi, R., & d'Ischia, M. (2004). Advanced oxidation of the pharmaceutical drug diclofenac with UV/H₂O₂ and ozone. *Water Research*, 38, 414–422. <https://doi.org/10.1016/j.watres.2003.09.028>
- Wang, Y., He, W., Qin, N., He, Q. S., Kong, X. Z., Tao, S., & Xu, F.-L. (2013). Distributions, sources and ecological risks of DDT-related contaminants in water, suspended particulate matter and sediments from Haihe Plain, Northern China. *Environmental Monitoring and Assessment*, 185, 1777–1790. <https://doi.org/10.1007/s10661-012-2667-0>
- Wang, S., Wu, W., Liu, F., Yin, S., Bao, Z., & Liu, H. (2015). Spatial distribution and migration of nonylphenol in groundwater following long-term wastewater irrigation. *Journal of Contaminant Hydrology*, 177–178, 85–92. <https://doi.org/10.1016/j.jconhyd.2015.03.013>
- Wen, X., Jia, Y., & Li, J. (2009). Degradation of tetracycline and oxytetracycline by crude lignin peroxidase prepared from *Phanerochaete chrysosporium*—a white rot fungus. *Chemosphere*, 75, 1003–1007. <https://doi.org/10.1016/j.chemosphere.2009.01.052>
- Wen, X., Jia, Y., & Li, J. (2010). Enzymatic degradation of tetracycline and oxytetracycline by crude manganese peroxidase prepared from *Phanerochaete chrysosporium*. *Journal of Hazardous Materials*, 177, 924–928. <https://doi.org/10.1016/j.jhazmat.2010.01.005>
- Wesenberg, D., Kyriakides, I., & Agathos, S. N. (2003). White-rot fungi and their enzymes for the treatment of industrial dye effluents. *Biotechnology Advances*, 22, 161–187. <https://doi.org/10.1016/j.biotechadv.2003.08.011>
- Wong, D. W. S. (2009). Structure and action mechanism of ligninolytic enzymes. *Applied Biochemistry and Biotechnology*, 157, 174–209. <https://doi.org/10.1007/s12010-008-8279-z>
- Wong, C. C., & Chu, W. (2003). The hydrogen peroxide-assisted photocatalytic degradation of alachlor in TiO₂ suspensions. *Environmental Science and Technology*, 37, 2310–2316. <https://doi.org/10.1021/es020898n>
- Xu, X. R., Wang, W. H., Li, H. B., & Gu, J. D. (2004). Degradation of dyes in aqueous solutions by the fenton process. *Chemosphere*, 57, 595–600. <https://doi.org/10.1016/j.chemosphere.2004.07.030>
- Yang, Y., Xie, Q., Liu, X., & Wang, J. (2015). Occurrence, distribution and risk assessment of polychlorinated bi-phenyls and polybrominated diphenyl ethers in nine water sources. *Ecotoxicology and Environmental Safety*, 115, 55–61. <https://doi.org/10.1016/j.ecoenv.2015.02.006>
- Yoon, Y., Ryu, J., Oh, J., Choi, B. G., & Snyder, S. A. (2010). Occurrence of endocrine disrupting compounds, pharmaceuticals, and personal care products in the Han River (Seoul, South Korea). *Science of the Total Environment*, 408, 636–643. <https://doi.org/10.1016/j.scitotenv.2009.10.049>
- You, L., Nguyen, V. T., Pal, A., Chen, H., He, Y., Reinhard, M., & Yew-Hoong Gin, K. (2015). Investigation of pharmaceuticals, personal care products and endocrine disrupting chemicals in a tropical urban catchment and the influence of environmental factors. *Science of the Total Environment*, 536, 955–963. <https://doi.org/10.1016/j.scitotenv.2015.06.041>
- Yu, C. P., Deeb, R. A., & Chu, K. H. (2013). Microbial degradation of steroidal estrogens. *Chemosphere*, 91, 1225–1235. <https://doi.org/10.1016/j.chemosphere.2013.01.112>
- Yuan, K., Kang, H., Yue, Z., Yang, L., Lin, L., Wang, X., & Luan, T. (2015). Determination of 13 endocrine disrupting chemicals in sediments by gas chromatography–mass spectrometry using subcritical water extraction coupled with dispersed liquid–liquid microextraction and derivatization. *Analytica Chimica Acta*, 866, 41–47. <https://doi.org/10.1016/j.aca.2015.02.011>
- Zdarta, J., Anteck, K., Frankowski, R., Zgola-Grzeskowiak, A., Ehrlich, H., & Jesionowski, T. (2018). The effects of operational parameters on the biodegradation of bisphenols by *Trametes versicolor* laccase immobilized on *Hippospongia communis* spongin scaffolds. *Science of the Total Environment*, 615, 784–795. <https://doi.org/10.1016/j.scitotenv.2017.09.213>
- Zhang, Y., & Geissen, S.-U. (2010). In vitro degradation of carbamazepine and diclofenac by crude lignin peroxidase. *Journal of Hazardous Materials*, 176, 1089–1092. <https://doi.org/10.1016/j.jhazmat.2009.10.133>
- Zhang, C., Li, Y., Wang, C., Niu, L., & Cai, W. (2016). Occurrence of endocrine disrupting compounds in aqueous environment and their bacterial degradation: A review. *Critical Reviews in Environmental Science and Technology*, 46, 1–59. <https://doi.org/10.1080/10643389.2015.1061881>
- Zhang, A., Wang, J., & Li, Y. (2015). Performance of calcium peroxide for removal of endocrine-disrupting compounds in waste activated sludge and promotion of sludge solubilization. *Water Research*, 71, 125–139. <https://doi.org/10.1016/j.watres.2015.01.005>
- Zhao, H., Du, H., Lin, J., Chen, X., Li, Y., Li, H., ... Wong, H. (2016). Complete degradation of the endocrine-disruptor di-(2-ethyl hexyl) phthalate by a novel *Agromyces* sp. MT-O strain and its application to bioremediation of contaminated soil. *Science of the Total Environment*, 562, 170–178. <https://doi.org/10.1016/j.scitotenv.2016.03.171>

- Zhao, H., Zhang, D., Du, P., Li, H., Liu, C., Li, Y., & Huang, Q. (2015). A combination of electro-enzymatic catalysis and electrocoagulation for the removal of endocrine disrupting chemicals from water. *Journal of Hazardous Materials*, 297, 269–277. <https://doi.org/10.1016/j.jhazmat.2015.04.063>
- Zorn, H., Langhoff, S., Scheibner, M., Nimtz, M., & Berger, R. G. (2003). A peroxidase from *Lepista irina* cleaves b, b-carotene to flavor compounds. *Biological Chemistry*, 384, 1049–1056.
- Zouari-Mechichi, H., Mechichi, T., Dhouib, A., Sayadi, S., Martínez, A. T., & Martínez, M. J. (2006). Laccase purification and characterization from *Trametes trogii* isolated in Tunisia: Decolorization of textile dyes

by the purified enzyme. *Enzyme and Microbial Technology*, 39, 141–148. <https://doi.org/10.1016/j.enzmictec.2005.11.027>

How to cite this article: Falade AO, Mabinya LV, Okoh AI, Nwodo UU. Ligninolytic enzymes: Versatile biocatalysts for the elimination of endocrine-disrupting chemicals in wastewater. *MicrobiologyOpen*. 2018;7:e722. <https://doi.org/10.1002/mbo3.722>