Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2015, Article ID 137634, 18 pages
http://dx.doi.org/10.1155/2015/137634

Review Article

Photocatalytic Based Degradation Processes of Lignin Derivatives

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Received 8 August 2014; Accepted 13 October 2014

Academic Editor: Elisa Isabel Garcia-Lopez

Photocatalysis, belonging to the advanced oxidation processes (AOPs), is a potential new transformation technology for lignin derivatives to value added products (e.g., phenol, benzene, toluene, and xylene). Moreover, lignin represents the only viable source to produce aromatic compounds as fossil fuel alternative. This review covers recent advancement made in the photochemical transformation of industrial lignins. It starts with the photochemical reaction principle followed by results obtained by varying process parameters. In this context, influences of photocatalysts, metal ions, additives, lignin concentration, and illumination intensity and the influence of pH are presented and discussed. Furthermore, an overview is given on several used process analytical methods describing the results obtained from the degradation of lignin derivatives. Finally, a promising concept by coupling photocatalysis with a consecutive biocatalytic process was briefly reviewed.

1. Introduction

In October 2014 the price of crude oil was 85 dollars per barrel and the forecast for next year is 98 dollars per barrel [1]. This is a symbolic indicator for the decreasing availability of conventional nonrenewable energy sources due to the global economy growth coupled with frequent political instability. According to the World Energy, Technology and Climate Policy Outlook of the European Commission [2], the world total energy consumption levels will rise from 12.1×10^9 tons oil equivalent (toe) (2010) to 14.5×10^9 toe (2020) to 17.1×10^9 toe by 2030. As a result, the world carbon dioxide emission from the combustion of fossil fuels will increase from 29.3×10^9 tons (2010) to 36.7×10^9 tons (2020) to 44.5×10^9 tons (2030). That means the world carbon dioxide emission will be almost doubled by 2030. Also, less than 1% of the 300×10^6 tons of plastic produced per year are natural polymers [3]. Thus, there is a need for the development of biobased macromolecular materials which would reduce the consumption of fossil resources and hence reduce CO_2 emission.

The major option is a gradual replacement of these fossil resources by renewable alternatives, for example, wind, sun, water, and biomass. Ligneous biomass also known as lignocellulosic biomass is of great interest for industries (chemistry, biotechnology, and fuel) and biorefineries converting sustainable materials [5]. This is due to the biomass's high value-added compounds: cellulose (40–50%), hemicellulose (24–35%), and lignin (18–35%) [6]. Furthermore, biomass is inexpensive and available in large amounts [7] as well as being CO_2 neutral [8]. Nevertheless, just 3–3.5% of the yearly produced biomass ($170–200 \times 10^9$ tons) is utilized by nonfood applications [5] because of reasons related to the lignocellulosic structure per se and its processability.

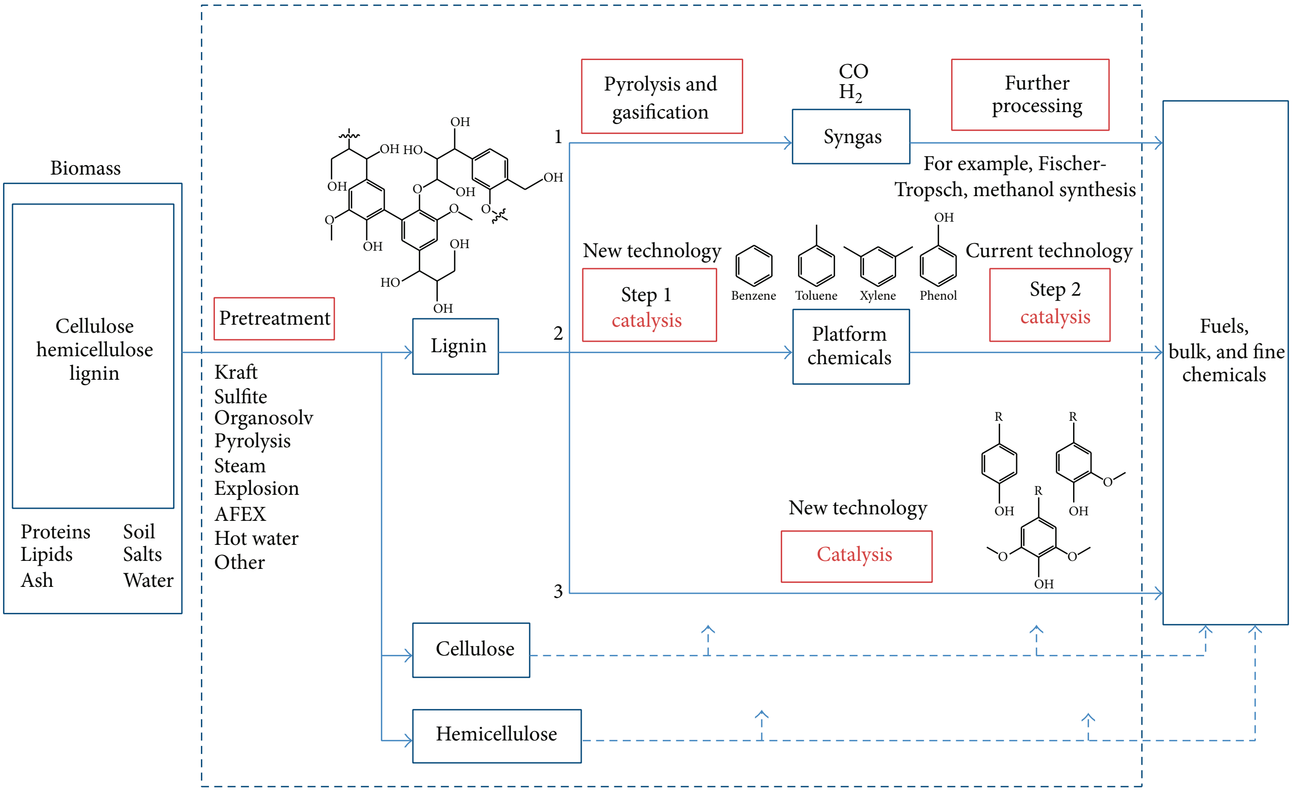

Figure 1: Lignocellulosic biorefinery scheme with particular emphasis on the lignin stream, reprinted with permission from Zakzeski et al. [4], copyright (2010), American Chemical Society.

Figure 1 depicts an exemplary lignocellulosic biorefinery scheme with emphasis on the lignin stream. For separation purposes, several pretreatment procedures are currently applied in order to generate lignin derivatives (modification in lignin structure) which can be differentiated on the basis of their isolation method and their origin since their physical and chemical properties differ [9–11]. The most industrial/technical lignins (>70 million tons per year) are obtained as waste material by the pulp and paper industry [12] mainly from the kraft process as noted by Kamm et al. [5]. 98% is burnt for energy recovery in the paper mills [13] while less than 2% is sold primarily in formulation of dispersants, adhesives, and surfactants [14]. Lignin is an aromatic biopolymer of high potential fission products for a wide range of sectors and it is thus gaining attention, for example, for the production of platform chemicals (Figure 1). Nonetheless, lignin is still underutilized and fundamental research and development are needed [5]. This is explained by lignin's complex nature, its recalcitrance to degradation, and the difficulty to analyze its numerous degradation products. Therefore, intensive research goes on both sides: process engineering and development (homogeneous, heterogeneous catalysis, thermal, electrochemical, and/or hybrid procedures) and process analytics.

Photocatalysis is an advanced oxidation process (AOPs) [15], with the potential to transform lignin to value added products such as phenol, benzene, toluene, and xylene [4]. In this context, it can be applicable as stand-alone unit or it can be coupled with other AOPs (e.g., Fenton's reagent, ozone, electrochemical oxidation) as well as biocatalysis [15] (e.g., hydrolysis through ligninolytic enzymes).

This paper is aimed at reviewing photocatalysis of industrial lignins in connection with evaluating the effects of basic operating parameters such as catalyst loading, illumination intensity, integration of metal ions, and other additives, pH, and initial lignin concentration. Furthermore, analytical techniques used by different researchers are discussed. Finally, a brief overview concerning the suitability of photocatalysis as a pretreatment method for subsequent biocatalysis by ligninolytic systems, for example, fungal heme peroxidases and/or laccases, is highlighted.

2. Lignin as Raw Material: Chemical Structure and Sources

Lignin is the only naturally synthesized aromatic biopolymer [16] and, after cellulose, the most abundant renewable carbon source on earth [17]. In addition, native lignin is a polydisperse 3D macromolecule with an undefined molecular mass. The biopolymer is made up of randomly arranged phenylpropane units, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol as depicted in Figure 2 contributing to an irregular structure [11].

An overview of the common interunit linkages and its estimated proportions are shown in Table 1. For a better

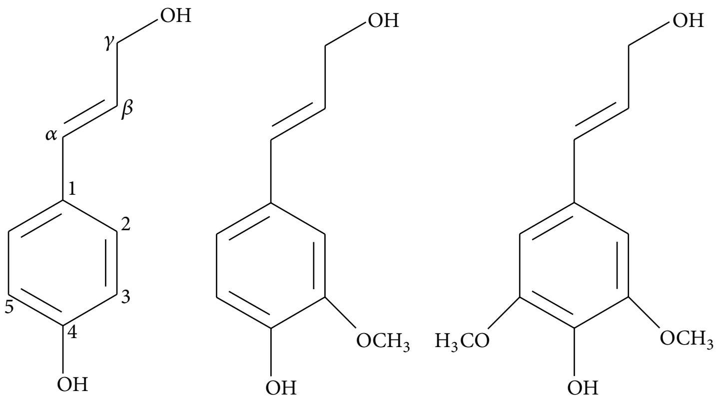

Figure 2: Monomer structures of lignin [18].

Table 1: Overview of most frequent bond types found in lignin.

Model linkage[a]	W. G. Glasser and H. R. Glasser [19]	Erickson et al. [20]	Nimz [21]
β-Carbon-oxygen-4-aromatic carbon	55	49–51	65
α-Carbon-oxygen-4-aromatic carbon	—	6–8	—
β-Carbon-5-aromatic carbon	16	9–15	6
β-Carbon-1-aromatic carbon	9	2	15
5-Aromatic-carbon-5-aromatic carbon	9	9.5	2.3
4-Aromatic-carbon-5-aromatic carbon	3	3.5	1.5
β-Carbon-β-carbon	2	2	5.5
β-Carbon-β-carbon forming furanic structure	—	—	2
α-Carbon-γ-carbon-oxygen-γ-carbon	10	—	—

[a] % of total phenylpropane units.

illustration, Figure 3 shows the structure of a softwood lignin fragment containing all prominent linkage types.

Native lignin cannot yet be isolated. Contrary, many modified lignins of great variety are available through biomass transformation technologies [17]. Depending on the used isolation method, lignosulfonate, alkali lignin, sulfate lignin, hydrolytic lignin, steam exploded lignin, and organosolv lignins can be derived [31]. The kraft and soda pulping processes generate liquors referred to as black liquor containing alkali lignin also called kraft or sulfate lignin [31]. Although, the kraft process is the dominant process (89%), lignosulfonates attract more attention for the application of lignin as industrial products. This is probably because of advantages such as its solubility properties and relatively lower mass range. Moreover, lignosulfonates are the only commercial lignins which are water soluble. Their average molecular weight varies from 400 Da up to 150 kDa or even 17.000 kDa (taken from Goring [9]), determined by process conditions and applied analytical methods [11].

3. Photocatalysis of Lignin

In this section, the reaction principle for the photocatalytic degradation of lignin is described. After that, the most important operating parameters and their impacts are discussed.

3.1. On the Reaction Pathways for Photocatalytic Lignin Degradation.

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In other words, it involves the initial absorption of photons by a molecule or substrate to produce highly reactive electronically excited states.

Lignin degradation is generally in the range of lower energy (between 300 and 400 nm) because of its multifunctional character [32–34]. This region falls within the UV-light region. TiO_2 is the most applied photocatalyst and its energy band gap is approximately 3.2 e.V [35].

In photogenerated catalysis, the photocatalytic activity depends on the ability of the catalyst to create electron-hole pair which generates free radicals (e.g., hydroxyl radicals: $^{\bullet}OH$) enabling secondary reactions [36]. Other aspects include the rate of electron transfer, the rate of charge recombination, crystal structure, surface area of catalyst, porosity, and surface hydroxyl group density [37].

In what follows, equations summarizing the formation of radical species under photocatalytic conditions shall be described. S stands for the lignin substrate while TiO_2 ($h^+{}_{VB}$) and TiO_2 ($e^-{}_{CB}$) represent the electron deficient (valence band) and electron-rich (conduction band) parts in the structure of TiO_2, respectively.

The initial photocatalytic process involves the generation of electron-hole pair in the semiconductor particles as a result

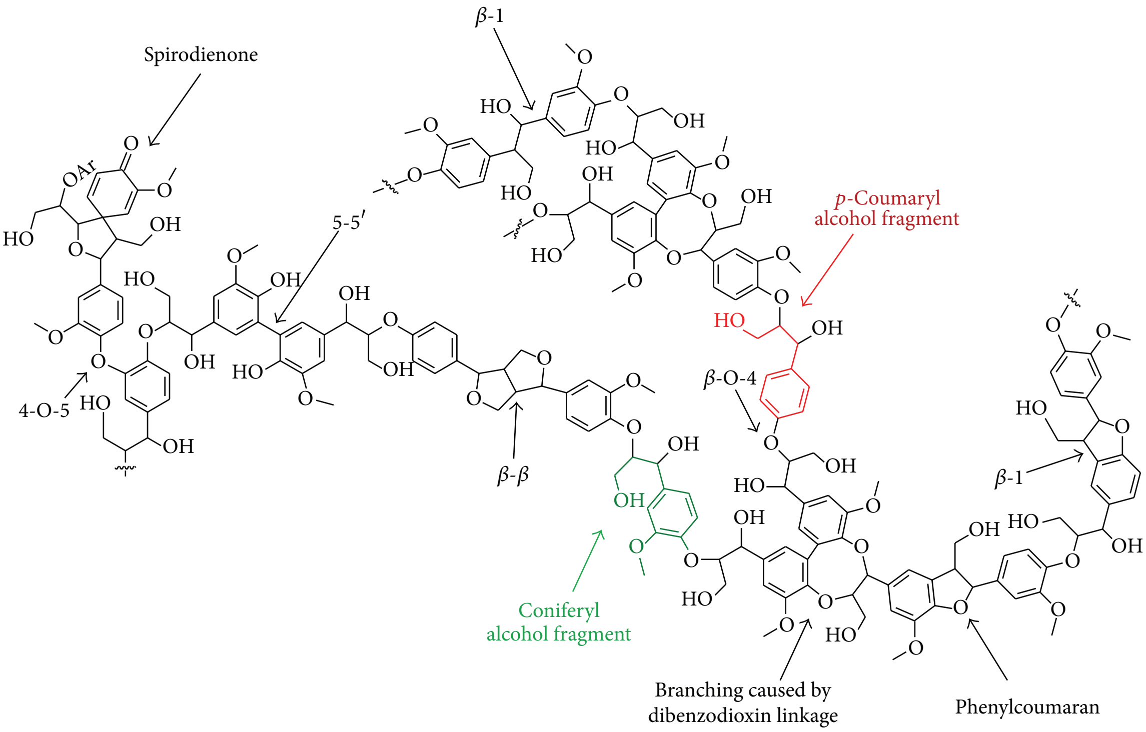

Figure 3: Structure of a softwood lignin fragment showing the prominent linkage types, reprinted with permission from Zakzeski et al. [4] and Evtuguin et al. [22].

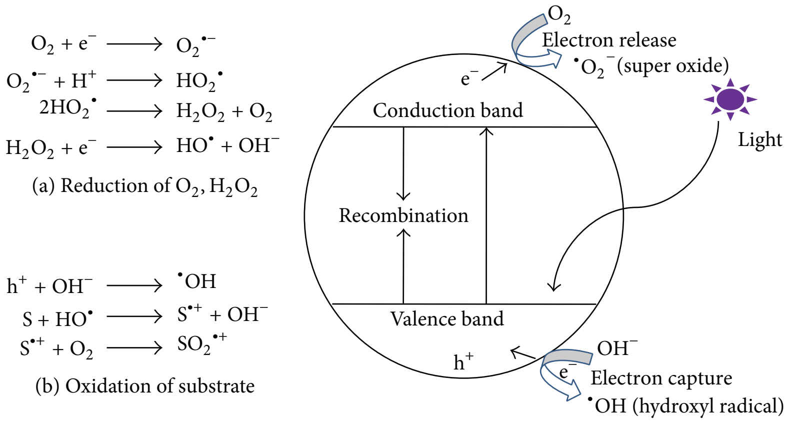

Figure 4: Photocatalysis principle, adapted from Linsebigler et al. [23].

of UV radiation [38, 39]. Figure 4 shows the excitation of an electron from the valence band to the conduction band initiated by light absorption with energy equal to or greater than the band gap of the semiconductor. This is expressed by (1).

Upon excitation, the fate of the separated electron and hole can follow several pathways. Electron or holes can then react with hydroxyl ions (OH^-) or H_2O producing hydroxyl radicals (${}^{\bullet}OH$) as shown in (2). Jaeger and Bard [40], Matthews [41], and Machado et al. [42] report that ${}^{\bullet}OH$ is the main oxidizing agent in the photocatalytic oxidation because of the unpaired electrons. Therefore, it can react fast and unspecifically with almost all organic compounds (S) [43] abstracting an electron with the formation of a radical organic species as shown in (3) [44].

Formation of singlet oxygen, hydroxyl, and superoxide radicals as principal reactive species in a photocatalytic process [38, 39] is as follows:

$$TiO_2 \xrightarrow{hv} TiO_2 \left(\frac{e^-{}_{CB}}{h^+{}_{VB}} \right) \quad (1)$$

$$TiO_2 \left(h^+\right) + H_2O \longrightarrow TiO_2 + HO^{\bullet} + H^+ \quad (2)$$

$$S + HO^{\bullet} \longrightarrow S^{\bullet +} + OH^- \quad (3)$$

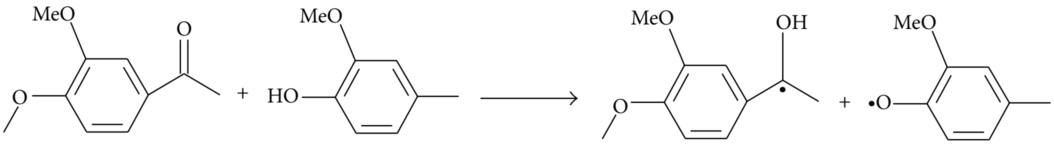

Figure 5: Formation of phenoxyl radicals by intermolecular abstraction of phenolic hydrogen by carbonyl groups.

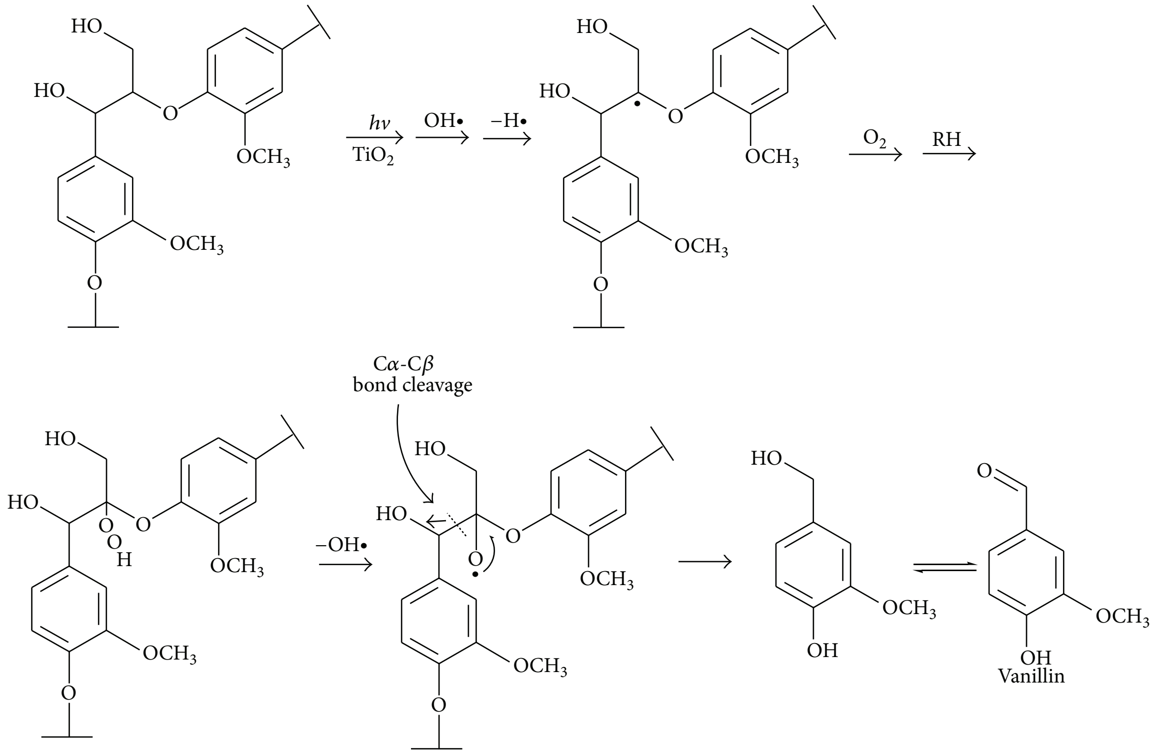

Figure 6: Supposed lignin degradation scheme by autoxidation induced by TiO_2/poly (ethylene oxide) [24].

$$S^{\bullet +} + O_2 \longrightarrow {SO_2}^{\bullet +} \tag{4}$$

$$TiO_2\left(h^+\right) + S \longrightarrow TiO_2 + {}^{\bullet}S^+ \tag{5}$$

$$TiO_2\left(e^-\right) + O_2 \longrightarrow TiO_2 + {}^{\bullet}{O_2}^- \tag{6}$$

$$HO^{\bullet} + {}^{\bullet}{O_2}^- \longrightarrow OH^- + {}^1O_2 \tag{7}$$

$$TiO_2\left(e^-\right) + TiO_2\left(h^+\right) \longrightarrow \text{heat} \tag{8}$$

The organic radicals and radical cations can, for example, react with molecular oxygen, to form organic peroxy radicals and peroxy radical cations respectively (4). The holes can oxidize organic compounds by electron abstraction to form organic cationic radicals (5) [42]. Superoxides can be formed by the reaction of electrons with electron acceptors such as O_2 (6). Meanwhile the formation of singlet oxygen can be from the reaction of hydroxyl radical and superoxide (7) [42]. Moreover, there is a possibility that electrons and holes recombine if electron acceptors are limited. In this case, recombination can take place in the volume of the semiconductor particle. When recombination takes place, radiation energy is lost or converted into heat (8) [45].

From investigations caried out by Mazellier et al. [46], (photochemistry of 2,6-dimethylphenol), it was postulated that hydrogen can be abstracted by α-carbonyl groups. In the same context, lignin derivatives having similar functionality can follow a similar pathway. In addition, oxidative chain reactions with the participation of ground-state oxygen can be initiated leading to fragmentation and combination reactions and thus the formation of new dimers or oligomers (Figure 5).

Miyata et al. [24] proposed a cleavage mechanism for the Cα–Cβ bonds which leads to the formation of small fragments such as vanillin as shown in Figure 6.

Figure 7 [25] illustrates the formation of a radical cation formed as a result of enzyme (lipase) mediated reaction of adlerol. Adlerol is characterized by a Cβ–O–4 bond and considered to be a lignin model compound. With the formation of the radical species, subsequent nonenzymatic reactions such as radical reactions can take place generating a wide variety of products and complex compounds.

It is widely assumed that the photocatalytic degradation of lignin follows a radical reaction pathway which is similar to that considered in thermal, electrochemical, and biochemical

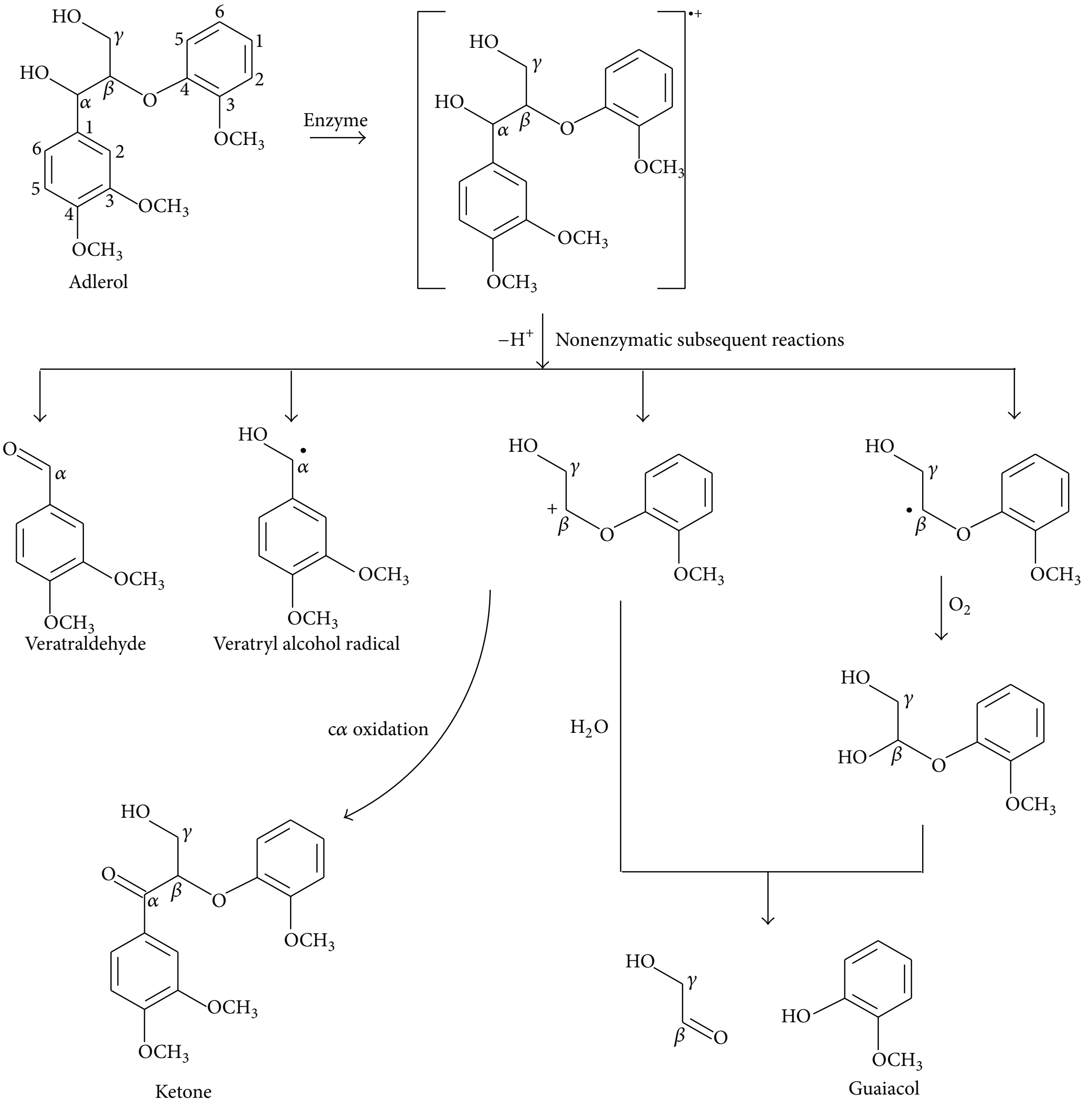

Figure 7: Proposed radical reaction scheme initiated by enzyme lignolytic heme peroxidase for the conversion of adlerol possessing Cβ–O–4 bonds into smaller units, summarized by Busse et al. [25] and abstracted from Tien and Kirk [26], Kirk et al. [27], Lundell et al. [28], Schoemaker et al. [29], and Palmer et al. [30].

processes. However, reporting on the degradation pathway of lignin derivatives and even that of lignin model compounds is still a major challenge. This is probably due to the complex nature and variety of possible degradation products. Indeed the mechanism is far more complex considering other factors such as type of lignin, type of catalyst, pH, illumination source, and additives.

3.2. Influence of Process Parameters in Lignin Degradation. Varying process parameter could either have a positive or negative impact on the photocatalytic efficiency. The basic process parameters, such as catalyst concentration [4, 48, 56], substrate concentration [48, 51], addition of metal ion to TiO_2 catalyst [17, 50, 56–58], pH [47, 48], illumination [33, 48, 49, 59], and their influence shall be discussed in this subchapter. Table 2 gives an overview about starting reaction conditions and catalyst applied by some work groups while Table 3 portrays parameters, analytical methods, and results obtained. It is worthwhile noting that comparing the different photochemical processes poses a big challenge because of the wide variables involved. These discrepancies start already from the source and type of lignin followed by the differences in reactor design, illumination source, intensity of radiation, and different types of TiO_2 catalyst such as Fischer scientific rutile TiO_2 [49], TiO_2 (TiO_2—TP-2 of Fujititan), just to name a few.

Table 2: Summary of starting conditions for the photocatalytic degradation of lignin.

Reference	Lignin source	Catalyst	Reaction conditions
MacHado et al. [42]	Peroxyformic acid lignins from eucalyptus grandis wood (EL1) EL1 + sodium borohydride	TiO_2 and H_2O_2	Lignin concentration: 0.25 mg/mL, $T = 25^{\circ}C$, pH 11, UV Vis radiation $\lambda > 300$ nm, 400 W mercury lamp, cylindrical Pyrex glass reactor, constant oxygen bubbling
Ksibi et al. [47]	Water soluble lignin obtained from black liquor	TiO_2-P25 (Degussa)	Lignin concentration: 90 mg/L, $T = 20^{\circ}C$, pH 8.2, UV-radiation $\lambda > 290$ nm, pyrex reactor open to air, Philips HPK 125 W lamp
Kansal et al. [48]	Lignin from wheat straw kraft digestion	TiO_2-P25 (Degussa) and ZnO	Lignin concentration: 10–100 mg/L in 100 mL, ZnO catalyst dose (0.5–2.0 g/L), pH of the solution (pH 3–11), solar illumination, oxidant concentration: 3.06×10^{-6} M to 15.3×10^{-6} M, thin bed film slurry pond reactor, oxidant: sodium hypochlorite solution (4% available Cl_2)
Dahm and Lucia [49]	Whitewater from industrial process water that exits in paper machines	Fischer Scientific rutile TiO_2	Lignin concentration: 40 mg/L in 500 mL batch reactor, $T = 21^{\circ}C–42^{\circ}C$, Rayonet photochemical chamber, 16 VWR 8-W black light, phosphor (350-nm) lamps, constant oxygen bubbling, power of illumination: 128 to 64 W, light intensity: 223–445 mW/cm^3
Portjanskaja and Preis [50]	Lignin, purchased from Aldrich	TiO_2 P25-N (Degussa)	Lignin concentration: 100 mg/L, pH 8, batch reactor system, reactor open to air, Phillips TLD 15 W/05 low-pressure luminescent mercury UV-lamp, UV-radiation $\lambda > 360$ nm, power density of irradiation = 0.7 mW/cm^2, visible light source
Tanaka et al. [51]	Lignin from coniferous wood	TiO_2 (TiO_2—TP-2 of Fujititan)	Lignin concentration: 0.003 to 0.03%, UV-radiation $\lambda > 310$ nm, cylindrical reaction vessel
Tonucci et al. [33]	Ca^{2+} and NH_4^+ lignin derivatives	TiO_2 as Degussa P25 + polyoxometalates (POM), H_2O_2	Open quartz tubes (20 mL) reactor, $T = 20^{\circ}C$, 1 atm, multirays of ten UV lamps of 15 W power each, UV-radiation $\lambda > 254$ nm
Miyata et al. [24]	Picea glehnii wood flour	TiO_2/polyethylene oxide (PEO)	Reactor: open petri dish, $T = 30^{\circ}C$, $t = 48$ h, 400 W mercury lamp
Shende et al. [17]	Kraft lignin	TiO_2-ZnO-ZrO_2	Lignin concentration: 1 mg/mL in 10 mL, 250 W Xenon lamp and AM 1.5 G lamp filter, power density of irradiation: 100 mW/cm^2, solar lamp simulator
Tian et al. [52] and Pan et al. [53]	Kraft lignin from black liquor	Ta_2O_5-IrO_2 and PbO_2 thin film TiO_2 nanotube/PbO_2	Lignin concentration: 30% (w/w), UV-radiation $\lambda > 365$ nm, $t = 10$ min, power density of irradiation: 20 mW/cm^2, blue wave TM50 AS UV spot lamp, EG&G 2273 potentiostat/galvanostat to apply current, Ti/TiO_2NT/PbO_2 electrode as working electrode and Pt coil as outer electrode and Ag/AgCl as reference electrode
Awungacha Lekelefac et al. [54], [55]	Lignin sulfonate from paper waste water	TiO_2 as Degussa P25 TiO_2 from sol-gel process of $TiOSO_4$, TTIP	Lignin concentration: 500 mg/L in 200 mL, Osram Planon light source, irradiance: 30–40 W/m^2, UV-radiation λ: 280–420 nm, $t = 20$ h, reactor open to air, recirculation system, flow rate 22.5 mL/min

Table 3: Parameters, analytical methods, and results from different work groups.

Reference	Parameter studied	Analytics	Result
MacHado et al. [42]	Role of hydroxyl radicals, irradiation of lignin in the absence and presence of photocatalyst TiO_2 and H_2O_2	Ultraviolet-visible (UV-Vis) spectroscopy, ionization absorption spectroscopy (IAS), size exclusion chromatography (SEC)	A sharp decrease in the phenolic content observed for reactions involving direct photolysis; SEC: a reduction of almost 50% in the average molecular weight of lignin equal to 1.4 kD after 90 min of irradiation
Ksibi et al. [47]	Irradiation of lignin in the absence and presence of photocatalyst TiO_2-P25	UV-Vis spectroscopy, ^{13}C-nuclear magnetic resonance (NMR) solid state, total ion gas chromatography (TIC), induction coupling plasma (ICP), chemical oxygen demand (COD)	56% degradation rate with TiO_2 catalyst after 420 min, reaction time; ethyl acetate-extractable products showed vanillin, vanillic acid, palmitic acid, biphenyl structures, and 3,4,5-trimethoxy benzaldehyde; presence of magnesium and calcium ions; COD removal is higher for the initially low concentrations of lignin solution
Kansal et al. [48]	Catalyst dose, pH, oxidant concentration, initial substrate concentration, ZnO catalyst in slurry and immobilized mode	UV-Vis spectroscopy, COD	Optimum catalyst dose is 1 g/L; optimum oxidant concentration: 2×10^{-6} M; gradual decrease of absorption peak indicating decomposition of organics; COD removal is higher for the initially low concentrations of lignin solution
Dahm and Lucia [49]	Catalyst dose, illumination intensity	UV-Vis spectroscopy, total organic carbon (TOC), capillary ion electrophoresis analysis (CIA)	Gradual decrease in absorption peak indicating decomposition of organics; optimal catalyst dose of 10 mg/m; higher illumination intensities correlated well with higher initial degradation rate; 74% disappearance of TOC
Portjanskaja and Preis [50]	Influence of ferrous ions, N-doped catalyst effect, sprayed catalyst on support and submersed catalyst	COD, UV-Vis spectroscopy, biochemical oxygen demand (BOD), colorimetric measurement at 570 nm	Addition of Fe^{2+}, up to 2.8 mg/L leads to 25% increase in photocatalytic efficiency; sprayed catalyst exhibited 1.5 times higher efficiency than the one attached by submersion; negligible effect of N-doped catalyst; increase of aldehyde concentration over reaction time; neutral media was most beneficial for biodegradability; 80% of free phenols removed under neutral conditions
Tanaka et al. [51]	Catalyst loading, lignin concentration, illumination time	UV-Vis spectroscopy, TOC, gel permeation chromatography (GPC), ^{1}HNMR, Fourier transformation infrared (FTIR) spectroscopy	FTIR measurement revealed a fast transformation of aromatic moiety present in lignin; characteristic bands of aromatic rings, methoxy, and aliphatic side chains; decrease in TOC values over time; decrease in degradation rate with increase catalyst dosage. But after catalyst threshold value is attained, catalyst increase causes a decrease in degradation rates. FTIR peaks are shifted towards lower molecular weight region after photocatalysis
Tonucci et al. [33]	Test of catalytic systems to obtain fractions with reduced degrees of polymerization, comparison of thermal and photochemical reactions	^{1}HNMR, gas chromatography-mass spectroscopy (GC-MS)	POMs are less selective when used as photocatalysts and no appreciable bleaching of the solution was seen when POM was used as thermal catalyst; derived chemicals from experiment: vanillin, hydroxyl methoxy-acetophenone, coniferyl alcohol, coniferyl aldehyde, methanol, formic acid, acetic acid, and sometimes small amounts of C-2 and C-3 alcohols
Miyata et al. [24]	Examination of cell wall structure of lignin (wood flour) before and after photocatalysis	GC-MS, scanning electron microscopy (SEM), ^{1}HNMR	High delignification activity, delignification confined to the surface of lignin; derived chemicals experiment: vanillin
Shende et al. [17]	Test of combined action of bio- and photocatalytic systems	UV-Vis spectroscopy, GC-MS, X-ray dispersive energy spectroscopy and X-ray diffraction analysis (EDX, XRD), SEM	Detection of following chemicals: acetyl guaiacol, 4-ethoxymethyl-2-methoxy phenol, methoxyphenyl oxime, guaiacol, succinic acid, acetyl guaiacol, vanillic acid, and vanillin

Table 3: Continued.

Reference	Parameter studied	Analytics	Result
Tian et al. [52] and Pan et al. [53]	Test of combined action of electro-and photocatalytic systems	UV-Vis spectroscopy, FTIR, SEM, X-ray (EDX), high performance liquid chromatography (HPLC), COD	Detection of the following chemicals: carbonyl functionality, vanillin, and vanillic acid
Awungacha Lekelefac et al. [54], [55]	Comparison of degradation rates by different catalyst	HPLC, fluorescence and UV-Vis spectroscopy, SEM, TOC	UV-Vis results reveal faster degradation of the aliphatic moiety compared to the aromatic moiety of ligninsulfonate obtained from paper waste water. Peaks observed during HPLC analysis. Some of the peaks produced after photocatalysis had fluorescence signals. This suggests the production of new substances and fluorophores. Coatings produced through Sol-Gel procedures are stable and can be used many times.

3.2.1. Influence of Catalyst. One aspect to successfully implement photocatalysis is the choice of an appropriate photocatalyst. The majority of catalysts used are based on TiO_2 as summarized in Table 2. ZnO has also been applied either as single catalyst [48] or in a combination with other catalyst such as TiO_2 [54]. de Lasa et al. [60] described ZnO as being less active than TiO_2. They add that the use of ZnO is particularly relevant when the oxidative degradation rate becomes limited. This is opposite to what Kansal et al. [48] reported by saying that ZnO is more reactive than TiO_2. However, TiO_2 (mainly anatase) remains the most used catalyst as can be depicted from Table 2. TiO_2 is reported to be favored because of its nontoxic property, cost efficiency, and chemical and biological inertness. Moreover, TiO_2 possesses the most efficient photoactivity and the highest stability, thus making it suitable for industrial use [61].

ZnO has been described to degrade lignin under visible light sources [48, 62], whereas TiO_2 is mostly applied in connection to UV-light sources as highlighted in Table 2. However, both ZnO and TiO_2 possess energy band gap energy of 3.2 e.V. [23].

Additives such as SiO_2 [63], polyethylene oxide (PEO) [24], and polyethylene glycol [64] have been added to TiO_2 catalyst, particularly when applying immobilized catalyst. Addamo et al. [63] noted a high adhesion of TiO_2 to glass support material when precoating was done with SiO_2. Moreover, the precoating might have other advantages such as a hindering diffusion of Na^+ ions from the glass material into the nascent TiO_2 film during heat treatment processes. Analogous to the addition of SiO_2, polyethylene glycol (PEG) has also been introduced to mitigate catalyst surface activity, modify surface hydrophobicity, and also reduce agglomeration tendency of the TiO_2 gel or TiO_2 particles in the suspensions [64]. By a proper surface modification, interaction between catalyst and substrate can be enhanced [55, 63].

Kansal et al. [48] varied catalyst (ZnO) dose from 0.5 g/L to 2.0 g/L for 0.1 g/L kraft lignin solutions and found out that there was an optimum catalyst threshold value at 1 g/L which gives a catalyst to substrate ratio of 1 : 10.

Dahm and Lucia [49] examined catalyst dose from $2 \cdot 10^{-3}$ g/L to $1.2 \cdot 10^{-2}$ g/L for lignin solutions (from white water liner mill) of $4 \cdot 10^{-2}$ g/L (catalyst to lignin ratio: $5 \cdot 10^{-3}$–$3 \cdot 10^{-2}$) at pH 8 and obtained best energy efficiency values and lignin degradation rates with a catalyst loading of $1.0 \cdot 10^{-2}$ g/L.

In contrast, Ma et al. [56] applied far higher catalyst concentration compared to Dahm and Lucia [49]. Catalyst concentration was varied between 1 g/L and 10 g/L Pt/TiO_2. Best catalysis dose with respect to reaction turnover was obtained at 5 g/L Pt/TiO_2. With the increase of catalyst dose at pH 7, the reaction rate increased from $6.1 \times 10^{-3}\ \text{min}^{-1}$ (1 g/L TiO_2) to $7.1 \cdot 10^{-3}\ \text{min}^{-1}$ (5 g/L TiO_2) and $9.9 \cdot 10^{-3}\ \text{min}^{-1}$ (10 g/L TiO_2).

Catalyst effect has been explained on the basis that optimum catalyst loading is dependent on the initial solute concentration. An increase in catalyst dosage leads to a corresponding increase of total active surface area for reactions [65]. To that, at higher TiO_2 concentrations, the photon flux is more easily intercepted by the catalyst before penetrating into the bulk of the system. At the same time, due to an increase in turbidity of the suspension with high dose of photocatalyst, there is a decrease in penetration of UV light and hence photoactivated volume of suspension or solution decreases [66].

In summary, authors have obtained best catalyst to lignin relations for different reaction designs and thus a general recommendation on catalyst dose is not possible. However, when lignin solution is treated with increasing catalyst loads, a corresponding increase in degradation rate is observed until a threshold value is reached [48–50, 56].

3.2.2. Influence of Metal Ion Addition (Doping) and Additives. The purpose of adding metal ion to photocatalyst is to mitigate band gap energy through the introduction of intraband gap states and as a consequence produce a bathochromic shift in the absorption spectrum [37]. Altering the absorption spectral range gives the possibility to exploit both the visible light spectrum and UV light sources. Metal ion doping is also introduced to serve as electron or hole traps in order to minimize recombination between generated electron-hole pairs [37].

Portjanskaja and Preis [50] studied the addition of Fe^{2+} ions to an acidic lignin solution and found an increase in photocatalytic oxidation (PCO) efficiency. The optimum Fe^{2+} ions quantity was 2.8 mg/L while using 100 mg/L lignin solution. Upon further elevation of Fe^{2+} ions concentration, a corresponding reduction of the photocatalytic oxidation efficiency of lignin was noted. Likewise, Ohnishi et al. [57] made a comparative study by doping platinum (Pt), silver (Ag), and gold (Au) ions to TiO_2. In these reactions, 50 mg of catalyst (TiO_2) was used with the addition of an equivalent 1.5 wt% (based on TiO_2) metal ion. The addition of noble metals brought about a faster decolorization of lignin. Au showed better results than Ag, followed by Pt. In the same context, adding sodium hypochlorite as oxidant to Pt/TiO_2 catalyst, an additional fivefold degradation rate was observed compared to that without doping [56]. Contradictory to the results described above, negligible effect of photocatalytic efficiency due to doping has been reported as well. Awungacha Lekelefac et al. [54] obtained little or no change in degradation rate by doping TiO_2-P25-SiO_2 catalyst with Pt ions (1 wt% relative to TiO_2 catalyst). Likewise Portjanskaja and Preis [50] noted a negligible change of photocatalytic efficiency of TiO_2 when doped with nitrogen.

Sarkanen et al. [67] and Gellerstedt and Lindfors [68] reported the bias of peroxides to oxidation with reagents such as permanganate to favor aromatic moieties. Oxidation agents like permanganate oxidizes predominantly aliphatic chains in alkaline and neutral media. However, by the application of H_2O_2 (Fenton system), lignin disappeared completely [33]. Tonucci et al. [33] conclude that, in order to satisfactorily conserve the organic material, the best compromise appears to be the TiO_2 photosystem, which shows low carbon consumption, good preservation of the aromatic rings, and greatly reduced mineralization.

In summary, different results have been obtained concerning the influence of noble metal ion addition. While some authors report an improvement in the photocatalytic efficiency upon their addition, others report their addition as having no considerable influence. However, for reactions in which an improvement in the photocatalytic efficiency was noticed, there was a threshold value to be considered. When the concentration of dopant surpasses this threshold value, electron-hole recombination is favored and this has a negative impact to photocatalysis. In such a case, the space-charge layer gets narrower and p-type dopants attract electrons and by virtue become negative. They would now then act as hole acceptor attracting holes. On the other hand, n-type dopants which act as electron donor centers and possess excess electrons attract holes as well [37].

3.2.3. Influence of Lignin Concentration. Once the initial lignin concentration becomes higher exceeding a threshold value, an inhibitory effect on the photodegradation was noted [47–49]. This threshold value varies and depends on the reaction system and reaction parameters such as optical density, catalyst concentration, and reaction volume. From the literature, different authors have implemented varying lignin concentrations probably to suit their reaction design. For example, Ksibi et al. [47] use 90 mg/L and Awungacha Lekelefac et al. [54] use 500 mg/L while Kansal et al. [48] applied 10 mg–100 mg/L.

Explanations arising from the findings are as follows: at low lignin concentrations, the incidental photonic flux irradiated interacts with the catalyst generating radicals (e.g., hydroxyl radicals ($OH^{\bullet}$)) which allow a faster degradation [69]. On the other hand, high initial lignin concentrations may lead to tight adsorption which can suppress CO_2 evolution [51] and hence maintain chemical oxygen demand (COD) values. Moreover, low delignification yields may be due to an inhibitory effect because of autoxidation by low molecular weight lignin degradation products formed [24]. Also, due to the polymer structure of lignin which is cross-linked, this makes it difficult for radical species, acid, and the aldehyde compounds produced to spread into the inner region of the substrate hence limiting autoxidation. As a worst case, this might be the rate-determining step of delignification which is hindered [70–72].

In summary, it can be concluded that the time taken for complete degradation depends on the initial concentration of lignin and faster degradation occurs at low lignin concentrations.

3.2.4. Influence of pH. Varying pH entails an alteration in the properties of semiconductor-liquid interface [73], mainly related to the acid-base equilibrium of the adsorbed hydroxyl group [39]. Furthermore, pH also impacts lignin degradation rates [47, 48, 57]. In this context, several studies were carried out with partly contradictory outcomes.

Kansal et al. [48] made pH investigations 3–11 under solar light illumination using ZnO as catalyst. Maximum degradation was reached in alkaline conditions (pH 11). This is supported by Villaseñor and Mansilla [74] reporting an almost complete decolorization of kraft black liquor from pine wood at pH value of 11.6 in combination with ZnO catalyst. Similar results were achieved by Ohnishi et al. [57] with TiO_2 and ZnO being catalyst for bleaching alkaline lignin in aqueous solution with TiO_2 and ZnO being catalyst. High activities at neutral pH were also reported by Ohnishi et al. [57]. In contrast, Ma et al. [56] observed higher reaction rates and rapid degradation of a synthetic lignin wastewater (prepared by dissolving commercial lignin powder in aqueous solution; pH 11) in acidic solution (pH 3) than in alkaline solutions at pH 11, for either TiO_2 or Pt/TiO_2 catalysts.

Reconsidering the photocatalytic principle, the formed superoxide anion radicals (${}^{\bullet}O_2{}^{-}$) are in a pH-dependent equilibrium with perhydroxyl radicals ($HO_2{}^{\bullet}$) as follows [75]:

$$HO_2{}^{\bullet} \rightleftharpoons H^+ + {}^{\bullet}O_2{}^{-} \quad \text{pKa} \sim 4.8 \tag{9}$$

See [76].

${}^{\bullet}O_2{}^{-}$ undergoes dismutation reaction resulting in H_2O_2 and O_2 competing to any other ${}^{\bullet}O_2{}^{-}$ triggered reaction. In case of low pH operation conditions in aqueous solutions, $HO_2{}^{\bullet}$ becomes dominant whose reactivity is considerably higher compared to ${}^{\bullet}O_2{}^{-}$ [77]. Subsequently, $HO_2{}^{\bullet}$ initiates substrate (S) oxidation to the radical cation ($S^{+\bullet}$) and is itself reduced to H_2O_2 [78]. Thus, increased degradation rates can be reasonably expected supporting the results made by Ma et al. [56] in an acidic environment. ${}^{\bullet}O_2{}^{-}$ is extremely reactive in organic solvents [77]. Another aspect is the solubility of kraft lignin (soluble at pH > 10.5) which reduces with decreasing pH, whereas lignosulfonate should remain unaffected by pH in aqueous solution. Moreover, β–O–4 bonds have been described to be stable at acidic pH [11]. In fact, this could additionally explain the elevated degradation of kraft lignin made by Kansal et al. [48] and Villaseñor and Mansilla [74]. Nevertheless, the contradictory results gained by Ma et al. [56] still exist under the assumption that kraft lignin was used (which would be supported by the high pH of 11, obviously necessary for dissolving the lignin powder). Although most photocatalytic reactions described in the literature are in an aqueous milieu, lignin raw material and its fission products may however vary considerably. Therefore, the optimal pH is most likely to be reaction specific and has to be evaluated experimentally in principle.

3.2.5. Influence of Illumination. Many of the studies found in the literature so far have not dealt on this subject per se. What is found is the use of different illumination sources, each having a specified power and lamp type. However, all tend to emit UV-light between the range 280–420 nm. Table 2 depicts this in detail. Other illumination sources include the visible light spectrum.

In general terms, illumination influences in that it initiates photocatalysis by generating electron-hole pair in the semiconductor particles [38, 39]. Dahm and Lucia [49] altered illumination intensity while observing lignin degradation. In this study, 0.04 g/L lignin was used and light intensity was varied 223–445 mW/cm^3. It was found out that higher illumination intensities correlated well with higher initial degradation rates and hence total lignin degradation [49]. Neppolian et al. [69] report degradation to be proportional to radiation intensity and best results are achieved for low lignin concentrations because of enhanced interaction between catalyst and incidental photonic flux.

In summary, high illumination power causes a corresponding high initial degradation rate at low lignin concentrations because maximum light penetration into the reaction medium is favored.

3.3. Process Analytical Methods. Various analytical techniques have been used to monitor lignin degradation. At the beginning of this subchapter, analytics revealing compounds formed from lignin degradation are treated. This includes, for example, gas chromatography (GC) and ^{1}H NMR (nuclear magnetic resonance). This is then followed by results qualitative analytic measurements such as ultraviolet-visible (UV-Vis) spectroscopy and dissolved carbon (DC). A list of authors, analytical techniques applied, and results achieved are outlined in Table 3.

Portjanskaja and Preis [50] studied lignin degradation by measuring the removal of phenols through colorimetric measurements. As a result of 24 h photocatalytic oxidation under neutral media conditions, 80% of free phenols were removed. Gas chromatography (GC) result from Ksibi et al. [47] attested vanillin, vanillic acid, palmitic acid, biphenyl, and 3,4,5-trimethoxy benzaldehyde structures after the photocatalysis of lignin from black liquor. This is in accordance with the findings of Tonucci et al. [33] reporting the formation of vanillin, hydroxyl methoxy-acetophenone, coniferyl alcohol, coniferyl aldehyde, methanol, formic acid, acetic acid, and small amounts of C-2 and C-3 alcohols as degradation products.

^{1}H NMR spectral analysis of lignin before illumination and after 24 h of illumination showing characteristic bands of aromatic rings, methoxy, and aliphatic side chains was compared with each other. Results revealed that the aromatic ring degraded faster than the aliphatic chain [51]. Fourier transformation infrared spectroscopy (FTIR) showed bands corresponding to CH_3, CH_2, and CH which remained unchanged after illumination while bands corresponding to aromatic rings disappeared as a result of illumination [51, 53].

Results obtained from the combination of photochemical and electrochemical oxidation [52, 53] were similar to those of Tanaka et al. [51]. Here, ^{13}C-NMR confirmed the presence of the carbonyl functionality and the presence of vanillin and vanillic acid after 12 h photochemical-electrochemical oxidation. These results showed that the combination of a photocatalytic and an electrochemical oxidation significantly enhanced the efficiency of lignin degradation. This is because the applied anodic potential bias greatly suppressed the recombination of photogenerated electrons and holes [53].

Ultraviolet spectrophotometry offers a convenient method to qualitatively and quantitatively analyze lignin in solution [79]. This is reflected by the large number of publications using this technique [17, 33, 47–51, 56, 58, 80]. This is most likely due to its simplicity to interpret lignin degradation. Lignins absorb UV light with high molar extinction coefficients because of the several methoxylated phenylpropane units of which they are composed [33]. Figure 8 depicts a series of photometric scans of ligninsulfonate from paper waste water showing a gradual reduction of absorbance during photocatalytic treatment [54]. Here, the absorption peaks are around 210 nm and 280 nm. Absorbance decreases with time implying the decomposition of lignin and the deterioration of chromophore groups [54].

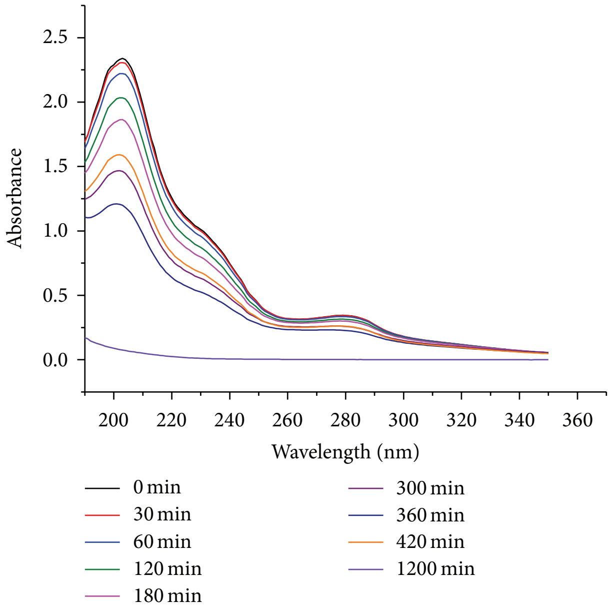

Figure 8: Time dependent UV-Vis absorption spectra of aqueous lignin solution from waste paper water irradiated with UV light (280–420 nm) for different time intervals. The spectra are obtained for sol-gel derived TiO_2 nanocrystalline coating (TiO_2-P25-SiO_2) [54].

Peaks at 210 nm correspond to portions of the unsaturated chains while those at 280 nm correspond to unconjugated phenolic hydroxyl groups [17] and the aromatic moiety [57] of the lignin molecule. The absorption tailing to the long wavelength region arises from the color of lignin [57]. Lignin degradation has been reported either at wavelength around 280 nm corresponding to unconjugated phenolic hydroxyl groups [17, 48, 51, 58] or for both wavelengths (210 nm and 280 nm) [33, 54, 57]. Kobayakawa et al. [81] noted some other absorbance at wavelengths lower than 250 nm and pointed out that this could be due to the modification of lignin fragmentations leading to the formation of transient species like methanol, ethanol, formaldehyde, formic acid, and oxalic acid among others.

Analytical methods to effectively quantify lignin degradation by calculating the oxygen demand by organic substances and remaining organic carbon before and after photocatalysis have been studied. Amongst the methods are dissolved carbon (DC) [49, 51, 58], chemical oxygen demand (COD) [47, 48, 50, 57, 80], biochemical oxygen demand (BOC) [50], dissolved organic carbon (DOC) [56], and American dye manufacture institute value (ADMI) [56]. COD and BOD describe the oxygen demand by organic substances to be

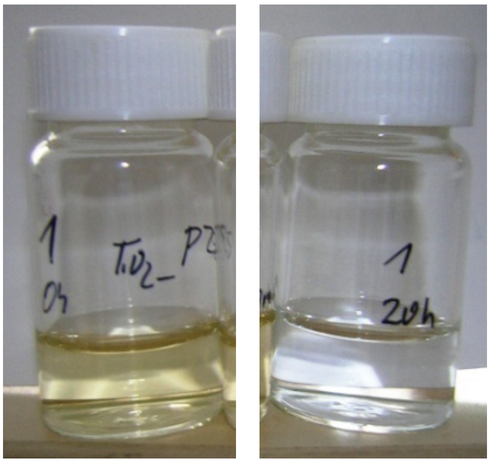

Figure 9: Gradual change from the characteristic yellow lignin sulfonate to a colorless liquid after a period of 20 h. Catalyst: TiO_2-P25 (Degussa) + TEOS, UV-light, 25°C, lignin concentration: 0.5 g/L [54].

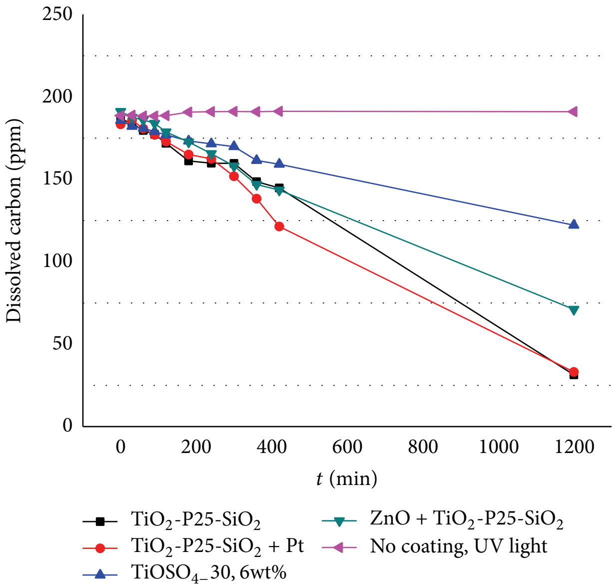

Figure 10: Variation of DC with time of aqueous lignin solution from waste paper water irradiated with UV light (280–420 nm) for different time intervals. The spectra are obtained for sol-gel derived TiO_2 nanocrystalline coatings (TiO_2-P25-SiO_2 + Pt, TiO_2-P25-SiO_2, $TiOSO_4$−30.6 wt%, ZnO + TiO_2-P25-SiO_2) [54].

converted to CO and CO_2 and H_2O and NH_3. Total organic carbon (TOC) describes the amount of carbon bound in an organic compound while DOC describes the dissolved fraction of organic carbon. ADMI measures the amount of dyestuff in water.

Decolorization of lignin solution has been reported to be another parameter observed during photocatalytic degradation. Color is an indirect indicator of the lignin amount. The higher the color intensity of the solution is, the greater the lignin content is (high concentrated lignin solutions, e.g., black liquor, appear dark brown) [82]. Thus, color changes can be interpreted as conversion of lignin to transient species or conversion to CO_2 and H_2O. Awungacha Lekelefac et al. [54] observed a gradual change from the characteristic yellow lignin (when highly diluted) to a colorless liquid after a period of 20 h with sol-gel derived TiO_2 nanocrystalline coatings on sintered borosilicate glass as depicted in Figure 9. A corresponding decrease in DC values close to 82% was observed for TiO_2-P25-SiO_2 catalyst confirming degradation. This is shown in Figure 10.

These findings are analogous to that of Ohnishi et al. [57] who reported the bleaching of lignin when illuminated continuously and that the solution becomes colorless. To that, the chemical oxygen demand (COD) value decreases, generating carbon dioxide and a small amount of carbon monoxide as the main gaseous products. COD removal was reported to be effective at low lignin concentrations as compared to high lignin concentrations [48].

Another applied analytical technique is fluorescence detection directly coupled to a high performance liquid chromatography (HPLC) as a means to identify nonaliphatic component in the complex mixture of lignin degradation products [54]. Fluorescence emission in lignin is attributed to aromatic structures such as conjugated carbonyl, biphenyl, phenylcoumarone, and stilbene groups [83, 84]. Awungacha Lekelefac et al. [54] observed peaks on both HPLC and fluorescence chromatograms suggesting the production of new substances and fluorophores.

Despite developed analytical technologies, analyzing lignin degradation products remains challenging. Proofs such as mass spectroscopy (MS), HPLC, ^{13}C, or ^{1}H-NMR spectra from photocatalytic lignin degradations are not yet established. The setback to qualitatively and quantitatively analyze lignin and its degradation products starts from the native lignin polymer itself with its indefinite polymeric structure and multiple bond types. Also, the influence of different pretreatments additives and the wide variety of compounds obtainable from its degradation makes lignin analysis challenging [85]. Moreover, lignin streams could contain proteins, inorganic salts, and other potential poisons that generally complicate catalysis [4].

The challenge to identify and separate the products streams derived from the photocatalytic degradation lignin is also worth noting. Lignin product stream is highly functionalized and conventional techniques such as gas chromatography have the disadvantage of requiring a time-consuming derivatization step. Also, because of high boiling point of substances arising from lignin degradation, it is not easily applicable. High performance liquid chromatography (HPLC) seems to be the remedy because analysis can be carried out without derivatization but the exact identification of the separated substances is difficult because of the numerous peaks arising from such a chromatogram [87]. Unfortunately, well-established databases such as that of the national institute of standard and technology (NIST) [88] cannot give information on HPLC-MS chromatograms. This is because of the ionization sources such as electrospray ionization (ESI)

Table 4: Main advantages and disadvantages, photocatalysis versus enzymatic biocatalysis.

Lignin degradation process	Advantages	Disadvantages
Photocatalysis (single stage)	(i) Relatively fast degradation of complex as well as nonbiodegradable organic (macro)molecules (ii) Stable catalysts (iii) Moderate reaction conditions	(i) Not selective (ii) Limited selection of operating conditions (iii) Energy costs
Enzymatic conversion (single stage)	(i) More selective (ii) Moderate reaction conditions	(i) High enzyme loads required, otherwise lignin hydrolysis is quite slow [16] (ii) Enzymes are less stable[1] (iii) cost-intensive (POXs)[2]

[1] For example, POXs are sensitive to high H_2O_2 concentrations.

[2] According to Torres and Ayala [86].

and atmospheric pressure chemical ionization (APCI) for LC-MS while GC-MS is based on electron ionization. A remedy to this can be the development of a database of model lignin compounds based on a unanimous HPLC-MS measuring procedure. This would mean much time and cost expensive investments for adequate personnel and material.

Though product identification based on peak superposition gives information on a possible product, this cannot always be true for lignin degradation because of the large number of possible degradation products. In order to properly identify products from lignin degradation, product isolation techniques are to be implemented and further analytic methods such as tandem mass spectroscopy (MS/MS) and other advanced structure enhancing research techniques such as ^{1}H-NMR, ^{13}C-NMR have to be studied extensively.

4. Photocatalysis and Its Suitability as Integrated Technology in Multistage Concepts with Biocatalysis

Depending on lignin treatment specification, photocatalysis will find application for complete lignin mineralization to CO_2 and H_2O (single stage) or as integrated technology in a multistage system aiming at partial conversion of lignin macromolecules to organic low molecular weight intermediates for a consecutive biological oxidation, finally generating value added end-products [15].

For biological oxidation of lignin or lignin derivatives, H_2O_2-dependent ligninolytic heme peroxidases (POXs, including lignin peroxidase (LiP, EC 1.11.1.14), manganese peroxidase (MnP, EC 1.11.1.13), versatile peroxidase (VP, EC 1.11.1.16), O_2-dependent laccases (Lac, EC 1.10.3.2), and extracellular enzymes from *Basidiomycetous white-rot fungi* are the most efficient lignin degraders in nature [89]. Thus, such enzymatic systems, especially POXs (with high redox potentials), have attracted much interest as industrial biocatalyst [86, 90]. The enzyme degradation mechanism (in nature) is facilitated by nonenzymatic processes mainly through free $^{\bullet}$OH radicals also generated by the fungus (Fenton-type reaction). Those $^{\bullet}$OH radicals enable the required physical contact between the enzymes and structural units of the lignin molecule due to numerous nonspecific oxidative reactions [91]. Both the photocatalytic (equations (2)–(7)) and the POX reaction mechanism recently reviewed by Busse at al. [25] are quite similar. Consequently a combination of photocatalysis followed by an enzymatic oxidation maybe a promising concept utilizing lignin derivatives, for example, originated from industrial effluents [15, 92]. The advantages forming biobased products are as follows; see also Table 4 in this context. A reduction of the lignin polymerization degree via photocatalysis, at best, in more biodegradable intermediates and a simultaneous detoxification, causes savings in enzyme costs, since it will be expected that less enzyme loads are necessary for sufficiently rapid reaction rates [15, 91]. As a result, hydraulic retention times in bioreactor systems should be diminished. Moreover, the delignification is expected to be enhanced simultaneously, which was in recent years shown in a dual system by Kamwilaisak and Wright [93] using TiO_2/H_2O_2/UV for photocatalytic pretreatment and Lac (from *Trametes versicolor*) in the subsequent biocatalytic step. Within 24 h, they obtained in their dual system an elevation in delignification of 20% (without H_2O_2) up to at least 50% when H_2O_2 was present.

In previous studies, the treatment of lignin (from the pulp and paper industry) containing effluents by fungus as a biological system (excreting appropriate lignin degrading enzyme cocktails) were more focused for posttreatment exclusively (Durán et al. [92], Reyes et al. [94], and González et al. [95]). Shende et al. [17] even examined ligninolytic bacteria, with photooxidized kraft lignin as substrate.

Although POXs are potential industrial biocatalysts [86], no application studies were found for the direct use in such dual systems as described above. The major reason may be the complexity of the reaction mechanism (inclusive lignin derivatives as substrate and their analysis) per se, on the one hand, slowing down research and development processes. On the other hand, POXs are sensitive to their cosubstrate H_2O_2, once it is supplied in excess causing considerable inactivation (for details, refer to Busse et al. [25]). At the present, several studies are carried out modifying these enzymes regarding enhanced stability, activity, and selectivity as well. Hence, it can be expected that their technological applicability will be raised significantly right after successful modification is reached [86].

5. Concluding Remarks

It is widely assumed that the photocatalytic degradation of lignin follows a radical reaction pathway which is similar to that considered in thermal, electrochemical, and biochemical processes. However, reporting on the degradation pathway of lignin derivatives and even that of lignin model compounds are still a major challenge. This is probably due to the complex nature and variety of possible degradation products. Indeed the mechanism is far more complex considering other factors such as type of lignin, type of catalyst, pH, illumination source, and additives.

Generally, comparing the different photochemical processes poses a big challenge because of the wide variables involved. These discrepancies start from the source and type of lignin followed by differences in reactor design, illumination source, intensity of radiation, and different types of catalyst. An idea would be to have a specific reference reaction with well-defined starting parameters which include lignin type, source, and purity, catalyst specifications, illumination source, and intensity so as to ease comparison of results.

Basic process parameters, such as catalyst concentration, substrate concentration, addition of metal ion to catalyst, pH, and illumination, have been discussed.

Despite developed analytical technologies, analyzing lignin degradation products remains challenging. Proofs such as mass spectroscopy (MS), HPLC, ^{13}C, or ^{1}H-NMR spectra from photocatalytic lignin degradations are not yet established.

In order to properly identify products from lignin degradation, product isolation techniques are to be implemented and further analytic methods such as MS/MS and other advanced structure enhancing research techniques such as ^{1}H-NMR and ^{13}C-NMR have to be studied extensively. A remedy to this can be the development of a databank of model lignin compounds based on a unanimous HPLC-MS measuring procedure. This would mean much time and cost expensive investments for adequate personnel and material.

Photocatalysis is denoted as the most popular lignin pretreatment technology, besides ozonation [96]. Photocatalyzed lignin may be an appropriate substrate for a consecutive biocatalytic process using ligninolytic enzymes (POX and/or Lac) as supported by experimental results of Kamwilaisak and Wright [93]. Combining the advantages of both catalytic processes savings in the overall process costs will be expected in addition to elevated lignin conversion. Nonetheless, extensive research work including POX modifications is still required.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Authors' Contribution

Colin Awungacha Lekelefac and Nadine Busse contributed equally to this work.

Acknowledgments

The authors gratefully thank the Federal Ministry of Education and Research (BMBF) for funding (FKZ17N0310). The researchers also thank the Hessen State Ministry of Higher Education, Research and Arts for the financial support within the Hessen initiative for scientific and economic excellence (LOEWE).

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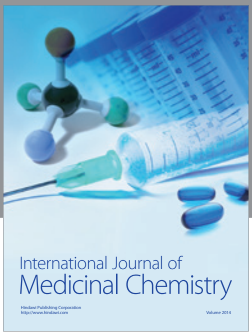
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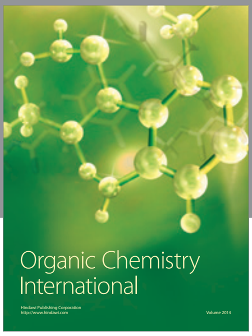
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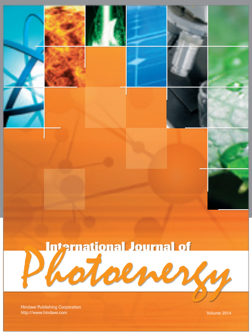
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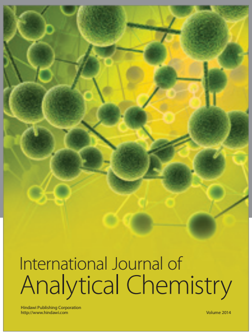
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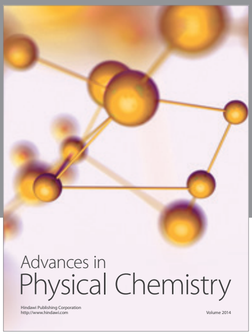
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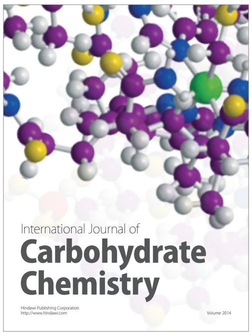
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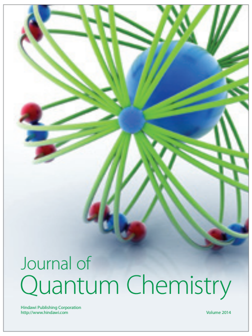
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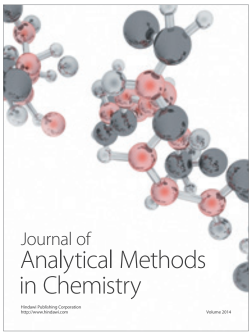
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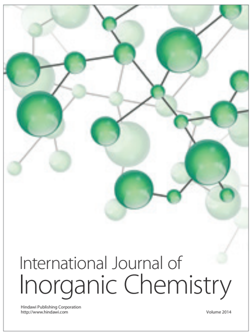
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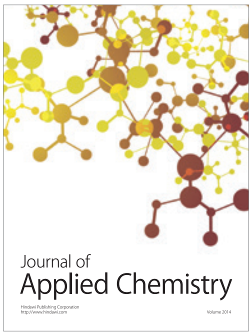
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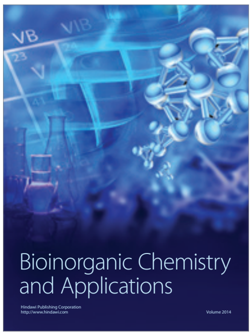
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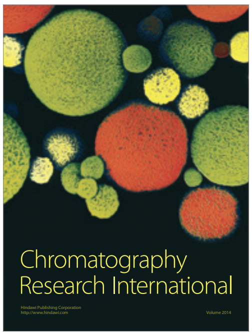
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