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Degradation of Lignin Derivatives by Photocatalysts

Colin Awungacha Lekelefac and Peter Czermak

Additional information is available at the end of the chapter

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Abstract

Photocatalytic degradation experiments were done with lignin sulfonate in a circulating reactor. Catalysts ($\text{TiO}_2\text{-P25-SiO}_2 + \text{Pt}$, $\text{TiO}_2\text{-P25-SiO}_2$, TiOSO_4 , 30.6 wt%, $\text{ZnO} + \text{TiO}_2\text{-P25-SiO}_2$), synthesized via the sol-gel method, were immobilized on porous glass support material. A comparative study was done regarding morphology of coatings, degradation rates, reaction rates, dissolved carbon (DC), formation of peaks, and fluorescence of products formed from the photocatalytic degradation of lignin sulfonate obtained from a local paper plant. Through simultaneous reaction-extraction pathways applying dialysis filtration and highly porous polystyrene divinylbenzene adsorbent resin (HR-P) for solid-phase extraction (SPE), an attempt was made to isolate smaller molecules produced from photocatalytic degradation. Moreover, relatively high lignin sulfonate (0.5 g/L) concentrations are used in the reactions. UV-Vis spectroscopy revealed a faster reduction in the concentration values for the aliphatic moiety compared to the aromatic moiety. Peaks were observed by both fluorescence spectroscopy and high-performance liquid chromatography (HPLC), suggesting the production of new substances and fluorophores.

Keywords: photocatalysis, lignin degradation, coatings, sintered glass, lignin fluorescence

1. Introduction

There is a growing awareness of the rapid depletion of fossil materials which makes it imperative to think of the development of commercial viable “green products” based on alternatives for fossil fuels. Commercial lignin is a byproduct of the pulp and paper industries, wood hydrolysis industries, and pre-treatment technologies to obtain cellulosic ethanol and biodiesel. More than 70 million tons of various types of lignin are produced as a waste material by the paper industry yearly [1, 2]. Coupled to that, lignin and its degradation products cannot be

completely decomposed by sludge processes and are the source of chemical oxygen demand (COD) of waste water from pulp and paper mills [3]. Lignin is primarily a structural material to add strength and rigidity to cell walls and constitutes between 15 and 40 wt% of the dry matter of woody plants. After cellulose, it is the most abundant renewable carbon source on earth. Lignin can be available through various sources and biomass transformation technologies [4].

Photocatalysis, belonging to the so-called advanced oxidation processes (AOPs) [5], is a potential new transformation technology for lignin to value-added products, for example, phenol, benzene, toluene, and xylene [6]. One of such transforming methods is the heterogeneous procedure in which a photocatalytically active layer is immobilized on a support material. In such a system, both adsorption and photocatalysis take place which have major advantages such as reuse of catalyst; minimization of catalyst leaching or resistance to extreme physical and chemical conditions is exploited. Most publications treating lignin photocatalysis describe suspension systems [7] with the disadvantage that catalyst particles have to be recovered after reaction through downstream processes such as ultrafiltration, which bring along additional process steps and higher cost. Besides photocatalysis, lignin can be degraded by other ways such as biochemical degradation through microbial/enzymatic attack [8–10], thermal degradation [11, 12], and electrochemical oxidation [13].

For a good catalytic efficiency in an immobilized catalytic system, a good hydrodynamic design of the system and modifications involving the utilization of the visible light spectrum by catalyst doping can be of great importance. The selection and design of the supporting material influences both the fluidic design as well as the available catalyst surface. The photocatalytic efficiency increases with an increase in active surface. This means that the carrier material has to provide a high surface to volume ratio. Also, the materials used as supports for photocatalytic purposes must also fulfill stringent optical properties such as transparency to UV-A light, in order to achieve high photonic efficiencies and to minimize the energy consumption required for the illumination.

Stable catalytic coatings produced on porous glass material and their photocatalytic activity studied by degradation experiments of lignin under UV light illumination is described by Awungacha et al [2, 14]. Sintered glass particles were coated to exploit the advantages of a heterogeneous system, and a good fluidic design was assumed by the porosity of the glass particles. Moreover, parameters such as flow characterization and irradiance which are required for the rigorous design and scaling-up of a photocatalytic reactor in order to accomplish a commercial application were reported. Additionally, a simultaneous reaction–extraction pathway, applying dialysis filtration, and highly porous polystyrene divinylbenzene adsorbent resin (HR-P) were applied. Awungacha et al. [2] used a relatively high concentration of lignin sulfonate (0.5 g/L) obtained from a local paper company.

The reaction design introduces a method which can remediate the pollution problem in waste water discharged from pulp and paper mills on the one hand, and on the other hand, it gives room to further exploit the degradation of lignin as an alternative chemical source. Peaks observed by both high-performance liquid (HPLC) and fluorescence chromatograms suggest the production of new substances and fluorophores [2].

1.1. Degradation and mineralization of lignin

Lignin degradation is generally in the range of lower energy (between 300 and 400 nm) because of its multifunctional character [15–17]. For a better illustration, **Figure 1** shows the structure of a softwood lignin fragment containing all prominent linkage types. During the photodegradation process of lignin, radical sites and excited α -carbonyl are involved. Excited α -carbonyl groups are able to abstract hydrogen from some lignin units, preferably phenolic hydrogen, initiating an oxidative chain reaction with the participation of ground-state oxygen, leading to the fragmentation and the formation of new chromophores, dimers, and sometimes oligomers as major products [18]. The action of hydroxyl radicals can induce the formation of radical sites on a substrate, thus inducing further oxidation or disproportionation reactions. The process can be accelerated by oxygen [19]. Machado et al. [20] report a rapid initial decrease of phenolic hydroxyl groups followed by a clear tendency of increasing explained as an effect of incorporation of hydroxyl groups on aromatic rings, occurring by hydroxylation and/or demethoxylation [19]. **Figure 2** summarizes the formation of radicals under photocatalytic conditions [21, 22]. S stands for the lignin substrate, while $\text{TiO}_2 (h^+)$ and $\text{TiO}_2 (e^-)$ represent the electron deficient and electron-rich parts in the structure of TiO_2 , respectively [7].

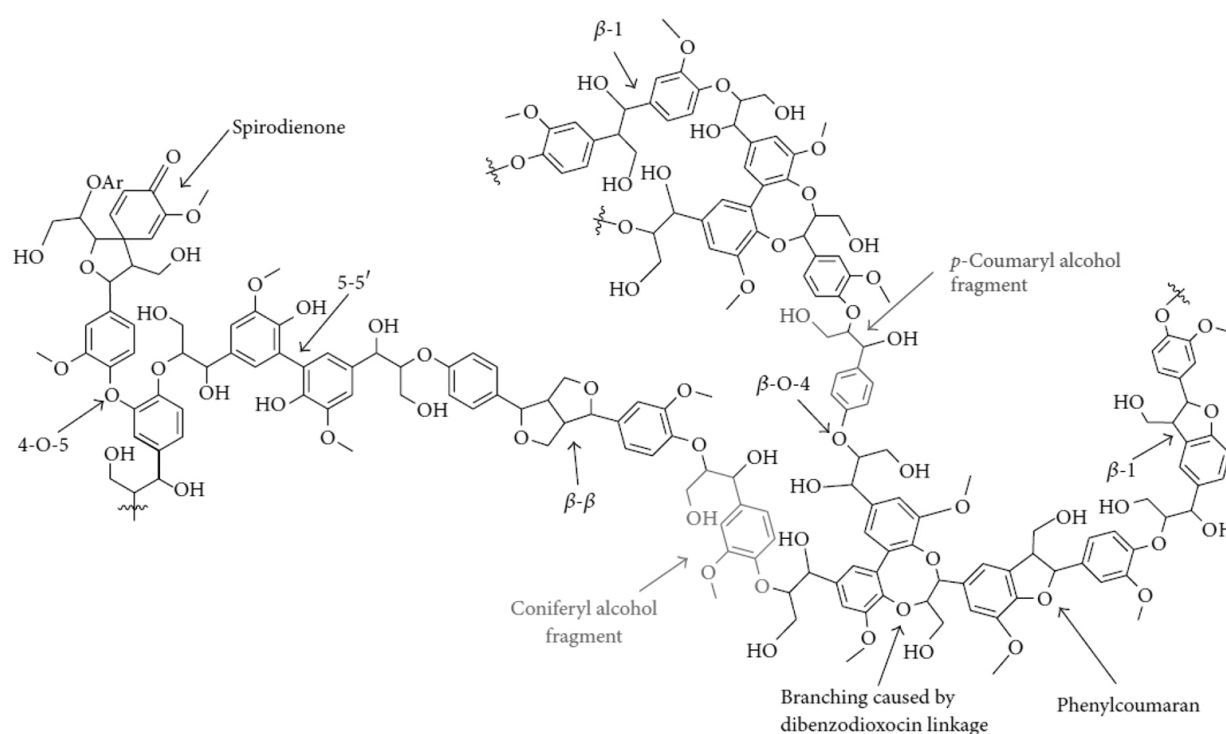


Figure 1. Structure of a softwood lignin molecule showing the prominent linkage types. Reproduced with the permission from Awungacha Lekelefac et al [7].

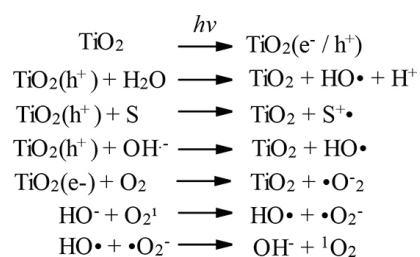


Figure 2. Formation of singlet oxygen, hydroxyl, and superoxide radicals as principal reactive species in a photocatalytic process [21, 22].

From investigations carried out by Mazelier et al. [18], (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, thus forming of new dimers or oligomers (**Figure 3**) [7, 18].

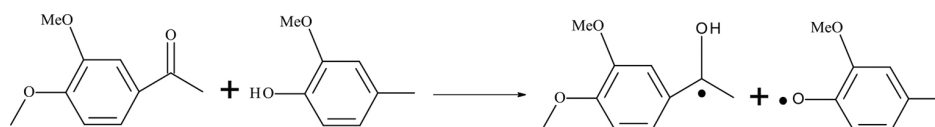


Figure 3. Formation of phenoxy radicals by intermolecular abstraction of phenolic hydrogen by carbonyl groups [7, 18].

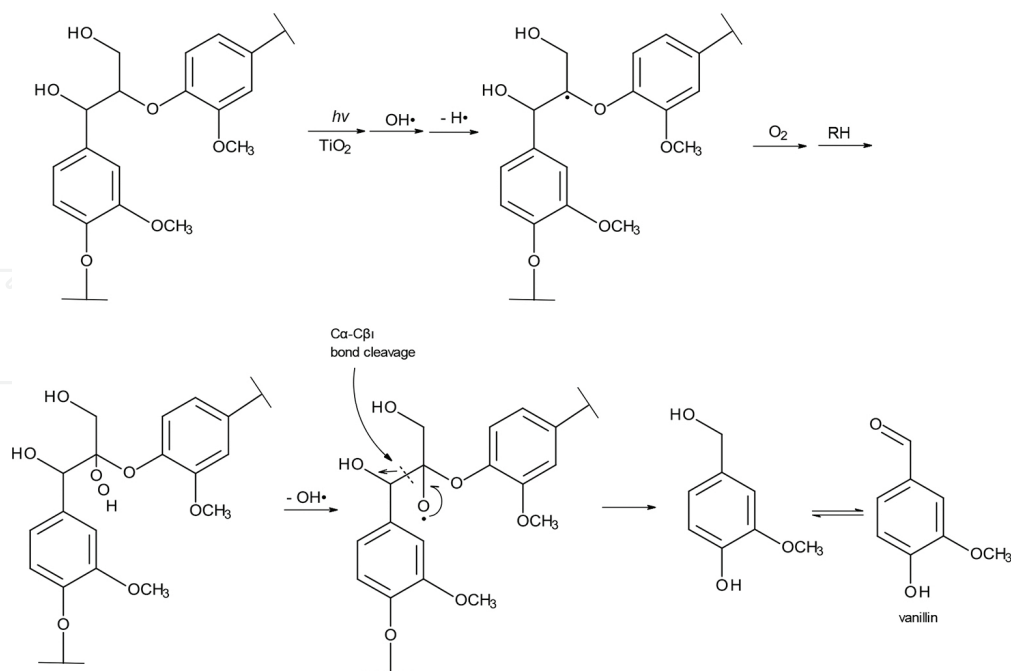


Figure 4. Supposed lignin degradation scheme by auto-oxidation induced by TiO_2 /Poly (ethylene oxide) [23].

Miyata et al. [23] proposed a cleavage mechanism for the $C\alpha-C\beta$ bonds which lead to the formation of small fragments such as vanillin as shown in **Figure 4**.

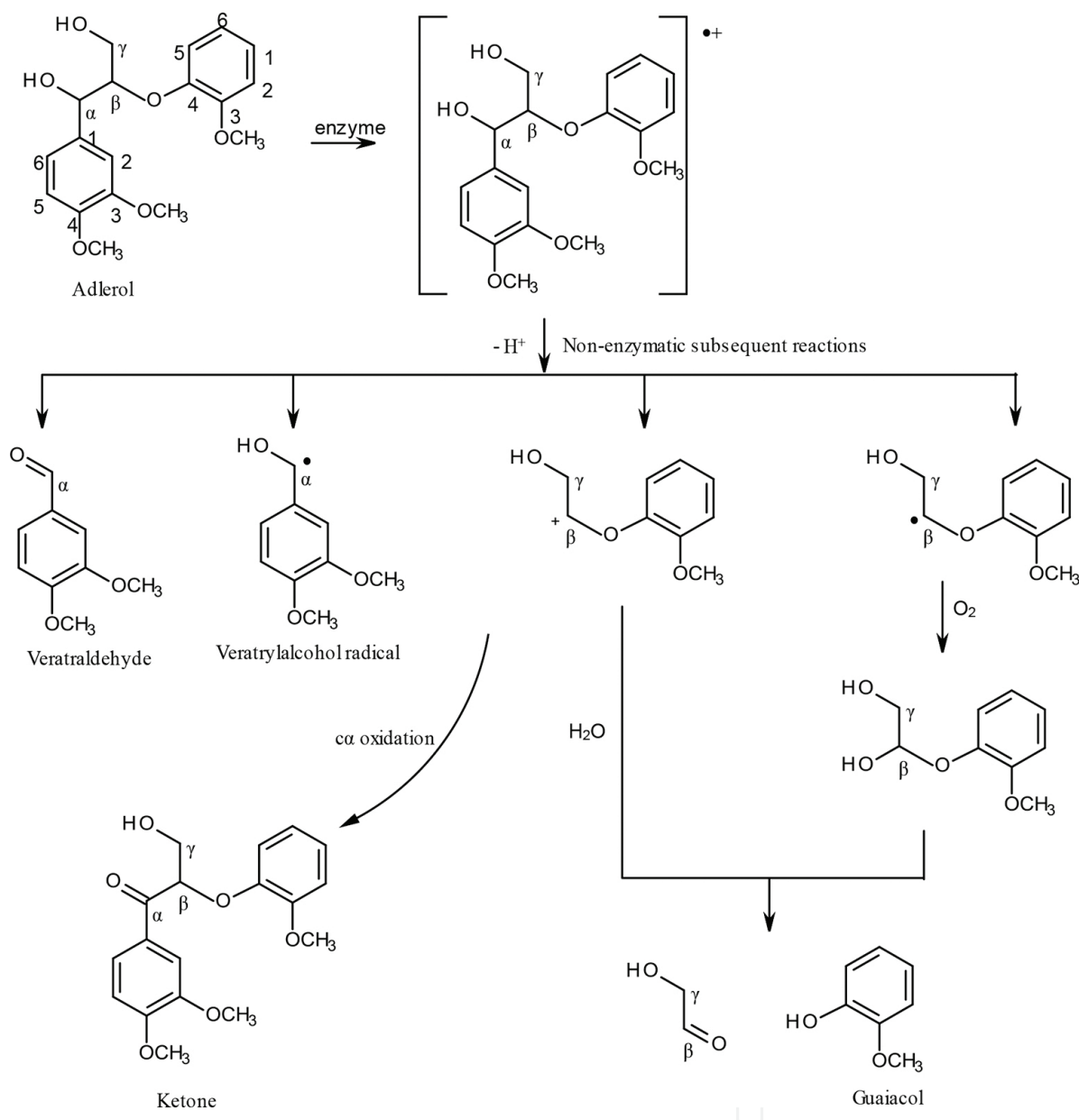


Figure 5. Proposed radical reaction scheme initiated by enzyme (Lignolytic Heme Peroxidase) for the conversion of adlerol possessing $C\beta-O-4$ bonds into smaller units, summarized by Busse et al. [7, 10], Abstracted from Tien and Kirk [24], Kirk et al. [25], Lundell et al. [26], Schoemaker et al. [27], and Palmer et al. [28].

Figure 5 illustrates the formation of a radical cation formed as a result of enzyme (lipase)-mediated reaction of adlerol. Adlerol is characterized by a $C\beta-O-4$ bond and considered to be a lignin model compound. With the formation of the radical species, subsequent non-enzymatic reactions such as radical reactions can take place, generating a wide variety of products and complex compounds.

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 [7]. 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 [7].

2. Experimental

2.1. Photocatalytic experiments

The degradation experiments of lignin sulfonate were carried out with a starting concentration of 0.5 g/L in 200 mL deionized water. The reaction design consisted of TiO_2 coatings on sintered glass (150–250 μm nominal pore size), packed in a borosilicate tube 26 cm long, 1 cm outer diameter, and 6 mm internal diameter. Glass particle grain size was between 200 and 400 μm . The following catalysts were synthesized as follows: $\text{TiO}_2\text{-P25-SiO}_2 + \text{Pt}$, $\text{TiO}_2\text{-P25-SiO}_2$, $\text{ZnO} + \text{TiO}_2\text{-P25-SiO}_2$, and TiOSO_4 30.6 wt%. A detail description of the catalysts synthesis and coating has been described elsewhere [14].

The tube was placed between two planar dielectric barrier discharge lamps. The broad surface of the light source insured incident light to be well distributed all over the surface of the glass tubes. **Figure 6** depicts the reaction setup, while **Figure 7** illustrates the reactor used for the experiments.

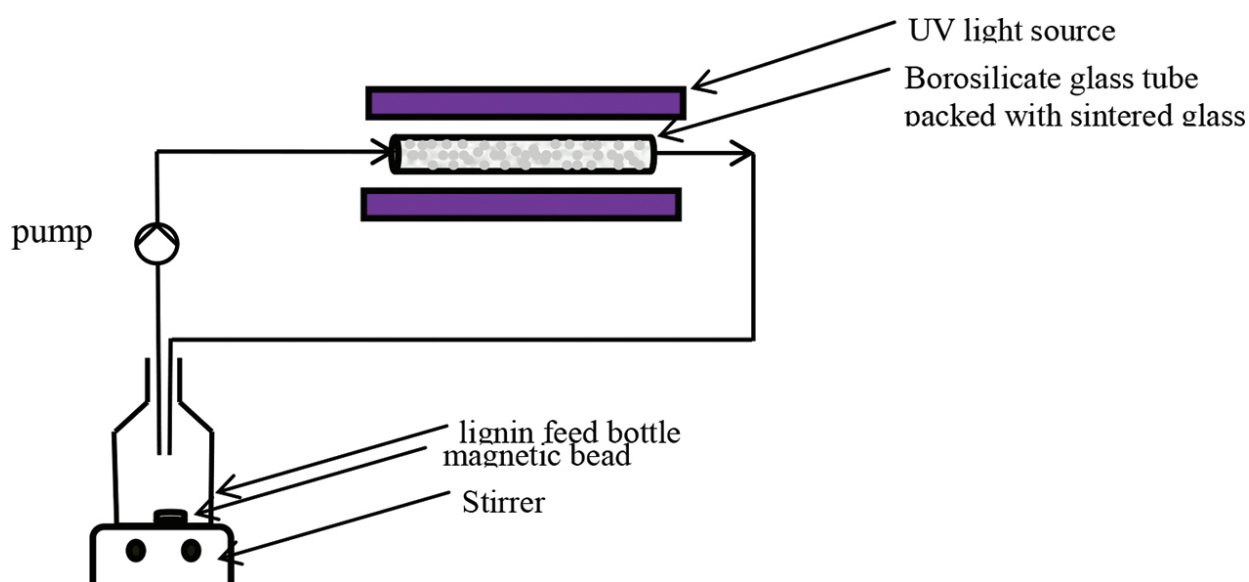


Figure 6. Experimental setup for the photocatalytic degradation of lignin.

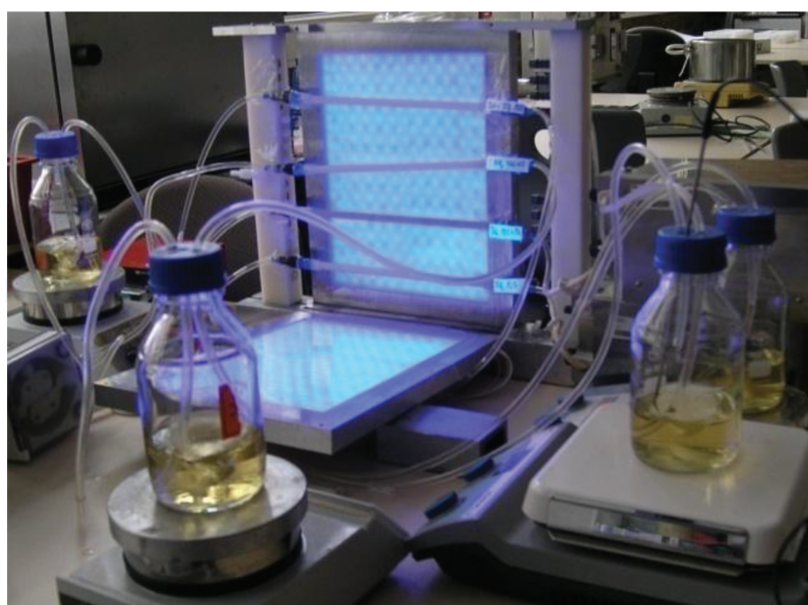


Figure 7. Photocatalytic reactor.

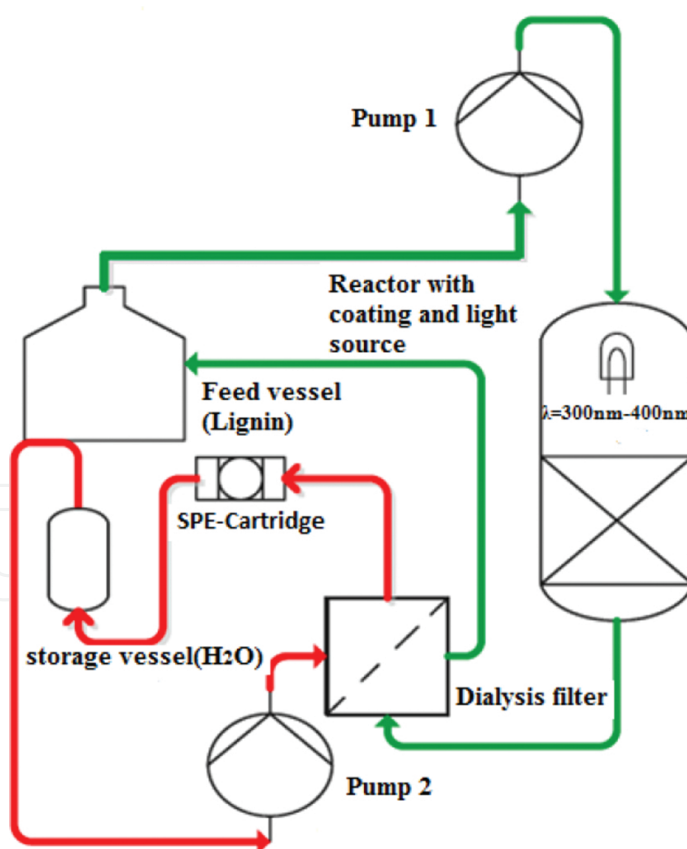


Figure 8. Photocatalytic cycle process with integrated solid-phase extraction and dialysis membrane.

The reaction procedure involved 03 pathways. In the first one, lignin sulfonate solution was pumped through the reactor using roller pumps in a continuous manner with a flow rate of 22.5 mL/min. Samples were collected at intervals up to a period of 20 h reaction time. Reactions were carried out at room temperature. Blank experiments were performed in the absence of UV light illumination as well as with uncoated sintered glass tubes. For all experiments, lignin was recirculated through the reactor for 60 min before UV light was put on. This was to ensure uniform wettability within the packed bed and same starting reaction conditions for all experiments. The second procedure involved a reaction–extraction pathway in which extraction followed after reaction with the use of highly porous polystyrene divinylbenzene adsorbent resin (HR-P). In the third procedure, the reactor was connected to a dialysis filter fitted with a HRP extraction column operating in a cycle process, and this is depicted in **Figure 8**. Its aim was to directly extract smaller molecules produced and preferably aromatic and phenol like compounds from aqueous the medium.

3. Results and discussion

3.1. Degradation experiments

Figure 9 shows time-dependent UV–Vis spectra of lignin sulfonate. Absorption peaks were observed at 203 and 280 nm, while a shoulder at around 230 nm was observed. Lignin absorbs UV light with high molar extinction coefficients because of the several methoxylated phenylpropane units of which they are composed of [29]. The absorption peaks decrease gradually, indicating the decomposition of lignin sulfonate and hence deterioration of the chromophor groups present. Peaks around 203 nm correspond to portions of unsaturated chains [29, 30], while those around 280 nm correspond to unconjugated phenolic hydroxyl groups [31] and aromatic rings [30] of lignin sulfonate [2]. Ohnishi et al. [30] report the absorption tailing arising from the color of lignin.

Preliminary reactions carried out involved in lignin sulfonate degradation experiments performed on uncoated glass in the presence of UV light as well as on coated glass particles in the absence of UV light. Results obtained revealed no significant change in absorbance over a 20 h period, indicating no major degradation and adsorption. Houas et al. [32] note that at catalytic surfaces experiencing unfavorable conditions such as repellent interactions, there may be no adsorption. It can further be argued that because of the nature of lignin used in this work (lignin sulfonate), the sulfonate groups attached to lignin render it anionic. Likewise, because of the basic nature of the reaction medium (pH 9) and the negatively charged hydroxyl (OH^-) ions generated from photochemical reactions, adsorption conditions do not prevail [2].

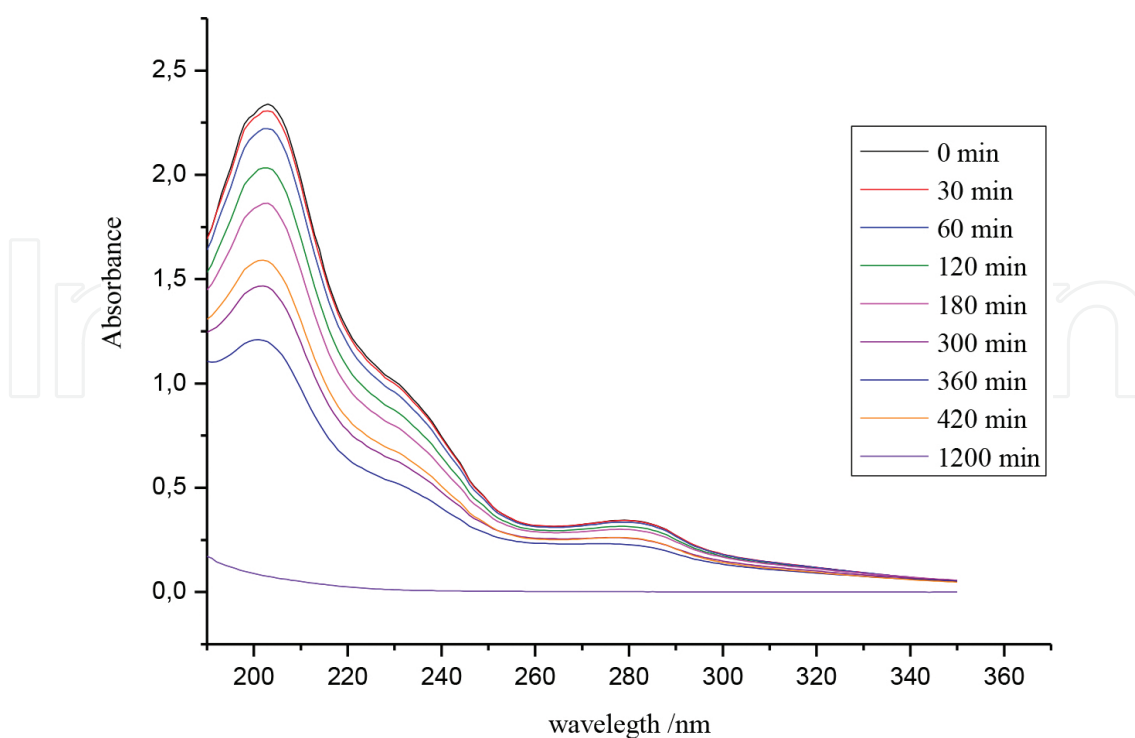


Figure 9. Time-dependent UV-Vis absorption spectra of aqueous lignin sulfonate solution. Concentration: 0.5 g/L in 200 mL, reaction time: 20 h, catalyst: sol-gel derived $\text{TiO}_2\text{-P25-SiO}_2$, reaction at room temperature, UV radiation (280–420 nm) [2].

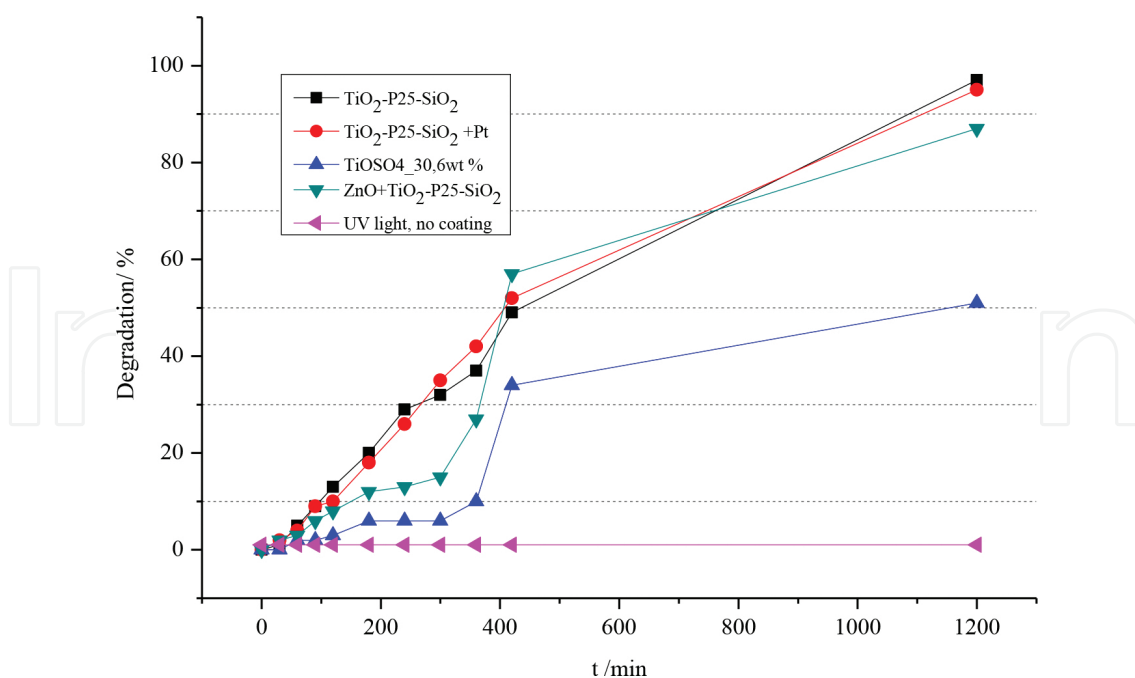


Figure 10. Effect of different catalyst on percentage degradation of lignin sulfonate under UV light at wavelength 203 nm (lignin sulfonate concentration: 0.5 g/L in 200 mL, reaction time: 20 h, reaction at room temperature, UV radiation (280–420 nm) [2].

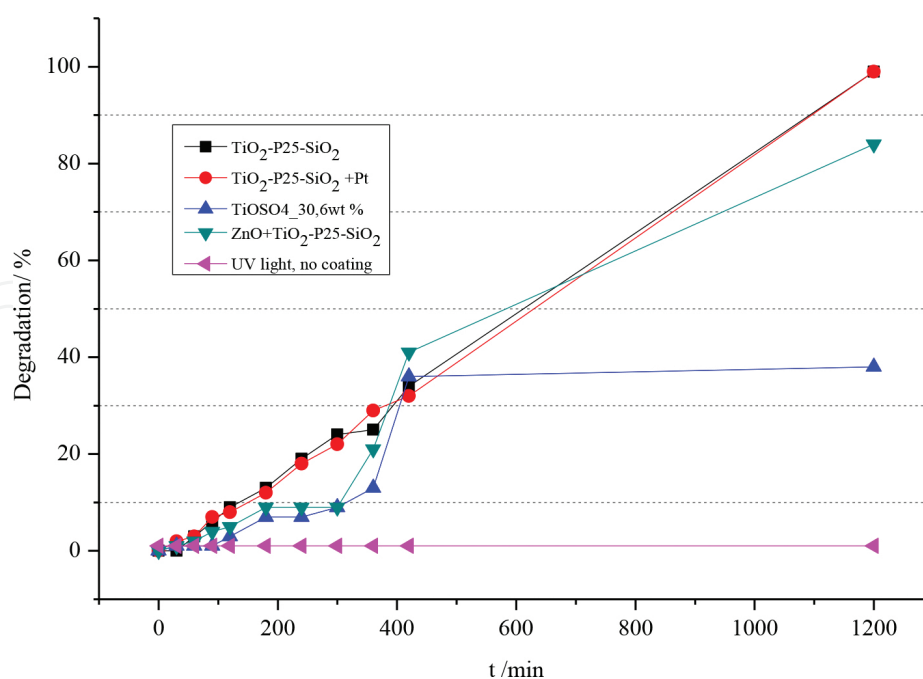


Figure 11. Effect of different catalyst on percentage degradation of lignin sulfonate under UV light at wavelength 280 nm (lignin sulfonate concentration: 0.5 g/L in 200 mL, reaction time: 20 h, reaction at room temperature, UV radiation (280–420 nm) [2].

Figure 10 depicts the degradation of lignin sulfonate by different catalyst at wavelength 203 and 280 nm, respectively. Degradation of lignin sulfonate prevailed in the presence of a catalyst. An abrupt degradation increase was observed for TiOSO_4 _30.6 wt% and $\text{ZnO} + \text{TiO}_2$ -P25-SiO₂ catalysts between 240 and 300 min. Here, the slow reaction at the beginning is the rate-determining step [33]. In this step, processes such as absorption of photons of light by catalyst, production of electrons, and other oxidizing species among other take place before a faster reaction takes place [34]. An almost linear degradation pattern was noted for TiO_2 -P25-SiO₂ + Pt and TiO_2 -P25-SiO₂ throughout the complete reaction time. Degradation rates of 97, 95, 87, and 51% were attained by coatings TiO_2 -P25-SiO₂ + Pt, TiO_2 -P25-SiO₂, $\text{ZnO} + \text{TiO}_2$ -P25-SiO₂, and TiOSO_4 _30.6 wt%, respectively, after 20 h reaction time for the straight chain lignin sulfonate moiety (**Figure 11**). Similar degradation values are also observed for the aromatic moiety after 20 h (**Figure 11**). TiOSO_4 _30.6 wt% catalyst was less reactive compared with the others because of the relatively low degradation values it produced. Less than 40% degradation was achieved after 420 min for both the aromatic and aliphatic moiety. Comparing the degradation rates of the aromatic moiety against that of the straight chain moiety after 420 min, it was observed that higher degradation values were attained by the aliphatic moiety. In detail, for the aliphatic moiety, degradation rates of 49, 52, 57, and 34% were noted, while for the aromatic moiety, degradation rates of 34, 32, 41, and 36% were observed for TiO_2 -P25-SiO₂ + Pt, TiO_2 -P25-SiO₂, $\text{ZnO} + \text{TiO}_2$ -P25-SiO₂, and TiOSO_4 _30.6 wt%, respectively. This suggests a faster transformation of the aliphatic side chains as compared to the aromatic species. A similar conclusion was arrived at by Tanaka et al. [35], whereby FTIR measurements were applied.

Comparing the degradation values of lignin sulfonate by using plain TiO_2 -P25- SiO_2 and that of the combination between ZnO and TiO_2 -P25- SiO_2 , a higher degradation rate was observed for ZnO and TiO_2 -P25- SiO_2 after 420 min, both for the straight chain moiety and aromatic moiety. However, after 20 h reaction time, TiO_2 -P25- SiO_2 had a higher degradation value, both for the straight chain moiety and aromatic moiety. Degradation rates of 49 and 57% were observed after 420 min for TiO_2 -P25- SiO_2 and $\text{ZnO} + \text{TiO}_2$ -P25- SiO_2 catalysts, respectively. Meanwhile, after 20 h reaction time, values of 97 and 87% are attained by TiO_2 -P25- SiO_2 and $\text{ZnO} + \text{TiO}_2$ -P25- SiO_2 catalyst, respectively. This means that $\text{ZnO} + \text{TiO}_2$ -P25- SiO_2 catalyst was more active during the first 420 min and its activity decreased in the proceeding time.

Adding (doping) Pt as metal ion to TiO_2 -P25- SiO_2 slightly improved the degradation values compared with that of plain TiO_2 -P25- SiO_2 catalyst. Values of 49 and 52% are attained after 420 min reaction time for TiO_2 -P25- SiO_2 and TiO_2 -P25- $\text{SiO}_2 + \text{Pt}$ catalyst, respectively, whereas after 20 h reaction time, values of 97 and 95% are attained by TiO_2 -P25- SiO_2 and TiO_2 -P25- $\text{SiO}_2 + \text{Pt}$ catalyst, respectively. These results indicate that Pt contributed little or no change in degradation rate which is contradictory to some published results on the effect of doping [36, 37]. However, for reactions in which doping enhances degradation, a threshold dosage has to be considered [37].

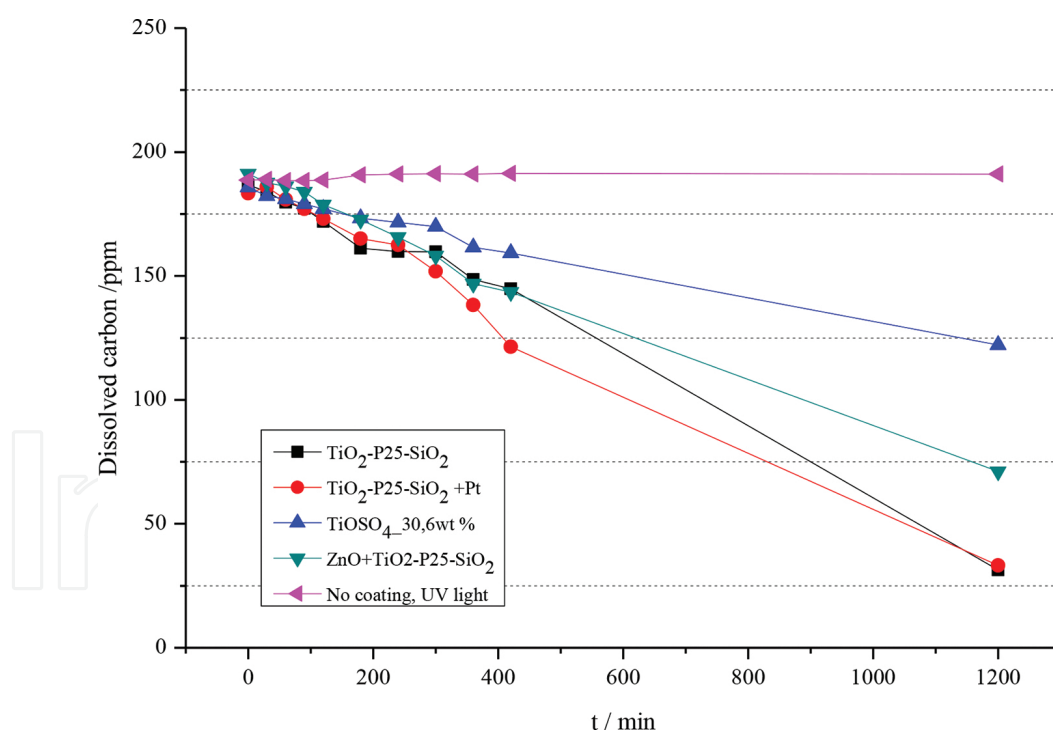


Figure 12. Removal of dissolved carbon in lignin sulfonate. Concentration: 0.5 g/L in 200 mL, reaction time: 20 h, reaction at room temperature, UV radiation (280–420 nm) [2].

In order to effectively quantify lignin degradation, dissolved carbon (DC) measurements were done (**Figure 12**). DC describes the amount of carbon bound in a compound. DC in lignin sulfonate of initial concentration 500 mg/L decreased from 185 to 144 ppm, 121, 159, and

143 ppm after 420 min for the catalyst $\text{TiO}_2\text{-P25-SiO}_2$, $\text{TiO}_2\text{-P25-SiO}_2 + \text{Pt}$, $\text{ZnO} + \text{TiO}_2\text{-P25-SiO}_2$ and $\text{TiOSO}_4\text{-30.6 wt\%}$, respectively. This value further decreased to 31, 33, 122, and 71 ppm making a DC removal of 84, 82, 61, and 34% for $\text{TiO}_2\text{-P25-SiO}_2$, $\text{TiO}_2\text{-P25-SiO}_2 + \text{Pt}$, $\text{ZnO} + \text{TiO}_2\text{-P25-SiO}_2$, and $\text{TiOSO}_4\text{-30.6 wt\%}$ respectively. Hence, TC removal was in the order: $\text{TiO}_2\text{-P25-SiO}_2 + \text{Pt} \sim \text{TiO}_2\text{-P25-SiO}_2 > \text{ZnO} + \text{TiO}_2\text{-P25-SiO}_2 > \text{TiOSO}_4\text{-30.6 wt\%}$. Decrease in DC has been reported to generate carbon dioxide and a small amount of carbon monoxide as the main gaseous products [2, 30].

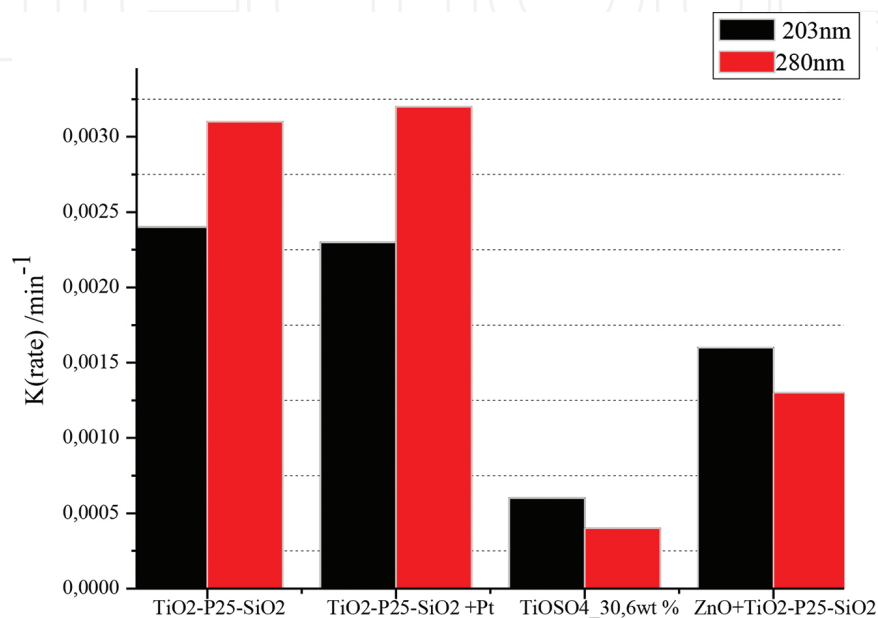


Figure 13. Reaction rates of the photocatalytic degradation of lignin sulfonate (500 mg/L) under UV light on immobilized catalysts. Concentration: 0.5 g/L in 200 mL, reaction time: 20 h, reaction at room temperature, UV radiation (280–420 nm) [2].

The rate constant values for the different catalyst are shown in **Figure 13**. Reaction rate was in the order: $\text{TiO}_2\text{-P25-SiO}_2 + \text{Pt} \sim \text{TiO}_2\text{-P25-SiO}_2 > \text{ZnO} + \text{TiO}_2\text{-P25-SiO}_2 > \text{TiOSO}_4\text{-30.6 wt\%}$ for both the aromatic and aliphatic side chain wavelength regions.

Comparing $\text{ZnO} + \text{TiO}_2\text{-P25-SiO}_2$ and $\text{TiO}_2\text{-P25-SiO}_2$, adding ZnO to $\text{TiO}_2\text{-P25-SiO}_2$ had an adverse effect to reaction rate probably because ZnO occupies some of the active sites on the catalyst support and it does not optimally absorb UV light in the domain of the wavelengths transmitted by the photo reactor ($280 < \lambda < 420 \text{ nm}$), and as a consequence, limitations in electron transfer between the band gap [2, 38].

3.2. Fluorescence and HPLC results

Fluorescence spectroscopy was used as a means to identify non-aliphatic component in the complex mixture of lignin degradation products. Fluorescence emission in lignin is attributed to aromatic structures such as conjugated carbonyl, biphenyl, phenylcoumarone, and stilbene groups [39, 40]. New fluorophores were detected in the time ranging from 10 min to around 40 min (Figure 14) with application of $\text{TiOSO}_4\text{-30.6 wt\%}$ catalyst. With the use of $\text{TiO}_2\text{-}$

P25-SiO₂ catalyst, new fluorophores were detected as soon as 5 min to around 55 min (**Figure 14**) [2].

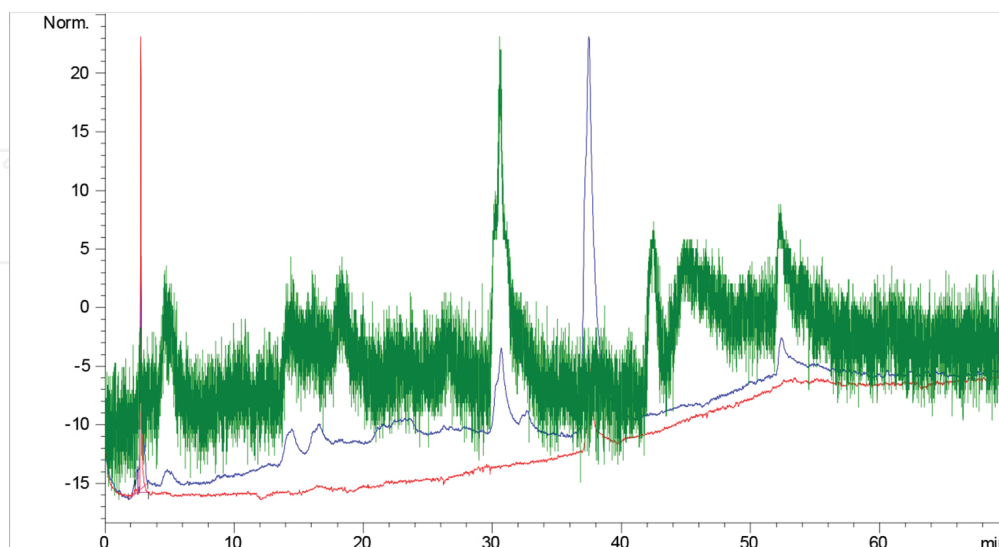


Figure 14. HPLC chromatogram and fluorescence peaks of lignin sulfonate solution. Concentration: 200 mL of 0.5 g/L, reaction time: 4 h, catalyst: TiO₂-P25-SiO₂, reaction at room temperature, presence of UV radiation, simultaneous reaction, dialysis filter, and SPE with HP-R cartridge during reaction [2].

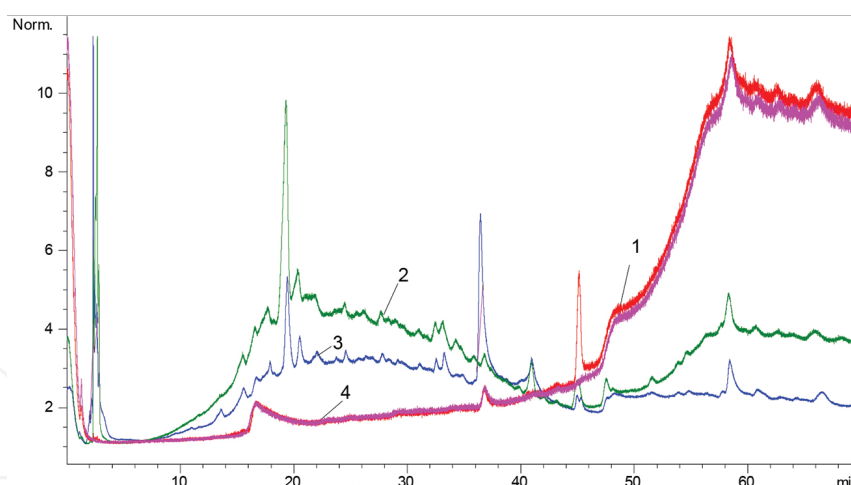


Figure 15. Fluorescence chromatogram of lignin sulfonate degradation product. Emission spectrum, λ_{em} : 240 nm, λ_{ex} : 330 nm, concentration: 100 mL 0.5 g/L, reaction time: 20 h, catalyst: TiOSO₄_30.6 wt%, reaction at room temperature.

(1): absence of UV radiation, SPE with HP-R cartridge after reaction suspended in methanol.
 (2): presence of UV radiation, SPE with HP-R cartridge after reaction suspended in methanol.
 (3): presence of UV radiation, simultaneous SPE with HP-R cartridge during reaction. (4): presence of UV radiation, aqueous raffinate from continuous extraction.

Comparing pathway (2) and pathway (3) from **Figure 15**, it was observed that the fluorophores produced had similar retention times and similar peak areas. This indicates that it did

not matter whether the extraction was done after the reaction or during the reaction. No peaks were observed for (1) reinforcing the necessity of UV light for lignin sulfonate degradation. The absence of peaks for (4) suggests that the degradation was complete and the all-produced substances were adsorbed on the SPE cartridge. Moreover, tailing was observed for samples (1) and (4) that did not contain degradation products dissolved in it [2].

Figure 14 depicts an HPLC and fluorescence chromatogram in which both measuring apparatus were coupled. The peak at around 2 min retention time arises from methanol used as eluting agent during SPE. Peaks were observed on both chromatograms, suggesting the production of new substances in which some generated fluorescence peaks. However, some fluorescence peaks appear only on the fluorescence chromatogram. Also broad peaks were found on the both HPLC and fluorescence chromatograms. During measurements, diode array detector (DAD) wavelength was set at 240 nm and not all degradation products could be detected at this particular wavelength. In fact, one of the challenges to analyze lignin through HPLC is to set the DAD wavelength for maximum detection. An analogous scenario was observed during fluorescence in which emission wavelength was set at 240 nm and excitation wavelength set at 330 nm. These difficulties arise because of the vast range of possible products arising from lignin degradation. Because of that, distinct emission decay peaks cannot be produced due to superimposition of the different fluorophores [2].

4. Conclusion

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. Indeed, the mechanism is far more complex considering other factors such as type of lignin, type of catalyst, pH, illumination source, and additives [7].

Despite developed analytical technologies, analyzing lignin degradation products from photocatalysis remains challenging. Proofs such as mass spectroscopy (MS), HPLC, ^{13}C , or ^1H -NMR spectra from photocatalytic lignin degradations are not yet established. This is probably due to the complex nature and variety of possible degradation products [7].

The reactor design reported here effectively degraded relatively high concentration of lignin sulfonate solutions (500 mg/L) from paper waste water. UV-Vis spectroscopy revealed a faster transformation of the aliphatic side chains as compared to the aromatic species. Adding Pt as metal ion to $\text{TiO}_2\text{-P25-SiO}_2$ catalyst showed a negligible effect on degradation rates. The reaction rate of the catalytic systems was in the order: $\text{TiO}_2\text{-P25-SiO}_2 + \text{Pt} \sim \text{TiO}_2\text{-P25-SiO}_2 > \text{ZnO} + \text{TiO}_2\text{-P25-SiO}_2 > \text{TiOSO}_4\text{-30.6 wt\%}$ [2].

Peaks were observed on HPLC and fluorescence chromatograms, suggesting the production of new substances and fluorophores. Through simultaneous reaction-extraction pathways applying dialysis filtration and highly porous polystyrene divinylbenzene adsorbent resin (HR-P), an attempt has been made to isolate smaller molecules produced from photocatalytic degradation [2].

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Author details

Colin Awungacha Lekelefac^{1,2,3} and Peter Czermak^{1,2,3*}

*Address all correspondence to: peter.czermak@kmub.thm.de

1 University of Applied Sciences Mittelhessen, Institute of Bioprocess Engineering and Pharmaceutical Technology, Giessen, Germany

2 Department of Chemical Engineering, Faculty of Engineering, Kansas State University, Manhattan, NY, USA

3 Faculty of Biology and Chemistry, Justus-Liebig-University, Giessen, Germany

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