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Research Article

Aqueous Photocatalytic Oxidation of Lignin: The Influence of Mineral Admixtures

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The photocatalytic oxidation (PCO) of UV-irradiated aqueous solutions containing lignin on TiO_2 was studied for the influence of ferrous ions. The addition of Fe^{2+}, up to 2.8 mg L^{-1}, to the acidic lignin solution leads to the drastic, for about 25%, increase in PCO efficiency. A further increase in ferrous ion concentration results in a decrease in PCO efficiency of lignin. The maximum PCO efficiency, up to 9.2 mg $W^{-1}h^{-1}$, was observed in neutral and slightly basic media: the oxidation mechanism with OH-radicals seems to prevail. Also, the difference in the PCO performance with a different attachment mode of titanium dioxide on the catalyst support was observed. Sprayed catalyst exhibited 1.5 times higher efficiency than the one attached by submersion, although sprayed one was easily resuspended in acidic lignin solutions. The efficiency of the N-doped photocatalyst active in visible light was observed to be negligible with lignin.

1. INTRODUCTION

The paper industry is under constant environmental pressure in regards to the air and water pollution. Lignin presence in paper may contribute to chemical degradation of paper and thus should be removed during paper manufacturing. Lignin and its fragments of complex aromatic structure are resistant to biological degradation and other conventional treatment [1]. Natural decomposition of lignin results in formation of toxic phenolics, aldehydes, ketones, methanol and carbonic acids [2]. This toxic behaviour is suspected of being a reason for the depressed immunity of human populations consuming water from polluted sources, especially in the vicinity of pulp and paper plants, and, as a result, for the two-fold increase in endocrine systematic diseases observed for population consuming the polluted water even after it has passed conventional water treatment procedure [3]. Besides, the residual lignin gives the effluent an intense brown colour. Typically, pulp and paper mill effluent is treated by biological oxidation, which does not significantly decrease the colour of the effluent [4]. White rot fungi-based biological oxidation is problematic due to its application in sterile conditions [5]. The wastewater treatment, such as coagulation, is ineffective against lignin: only large molecules of lignosulfonates, but not their fragments, can be removed with coagulants [6]. Concerning potable water treatment, more toxic chlorinated substances could be formed during the disinfection of raw municipal drinking water by chlorination [7].

Advanced oxidation technologies, including photocatalytic oxidation (PCO), have been proposed as an alternative for the reduction of lignin due to extra-cheap solar energy source and freedom of the drawbacks such as selectivity of treatment with coagulants, provision of sterile conditions, the formation of dangerous chlorinated compounds, and high capital investment costs. Advanced oxidation technologies are attractive also due to their combination with subsequent biological treatment of wastewater. Several procedures, such as UV/H_2O_2-oxidation and ozonation, are increasingly used in order to transform recalcitrant compounds into more biodegradable residues, some with success, but they are not widely implemented due to their high installation and operation costs [1, 8].

Most of the following references dealt mostly with the studies of lignin substitutes, such as phenolics; little may be found concerning the oxidation of lignin itself. PCO of lignin substitutes TiO_2-catalysed under artificial and solar radiation was studied in [9, 10]. They found that phenolic compounds yield to PCO forming by-products and showing oxidation

efficiency dependent on treatment conditions. A major role in the degradation process was attributed to $OH^{\cdot}$-radicals and $O_2^{\cdot -}$-ion-radicals. Hydroxyl-radical plays a fundamental role in transformation of nonphenolic molecules into phenolic ones; $O_2^{\cdot -}$ reacts with phenoxyl radicals opening aromatic rings and reacting directly with the intermediate radical cations. The role of the electron scavengers O_2, $K_2S_2O_8$, and N_2O on the degradation process as well as the influence of pH has been studied [7, 9, 11]: the oxidation was observed to better proceed under acidic pH. The addition of $K_2S_2O_8$ may totally substitute O_2, while N_2O, an excellent hydrated electron scavenger, seems to be a very poor electron scavenger under the heterogeneous conditions. The addition of hydrogen peroxide leads to the increase in PCO efficiency, whereas hydrophosphate anion did not influence the PCO [11]. Tanaka et al. [12] and Chang et al. [7] studied UV/TiO_2 oxidation process of different lignin-containing wastewaters searching for optimum TiO_2 dosages. The span as wide as from 1.5 to 10.0 g L^{-1} was reported for wastewaters of different compositions. Ksibi et al. [1] identified some PCO products for lignin such as vanillin, coniferylic alcohol, highly oxidised phenols like syringaldehyde, palmitic, vanillic and the *p*-coumaric, and other carbonic acids.

The catalyst commonly used in PCO studies is TiO_2 due to its good activity, chemical stability, and commercial availability [13]. However, the recovery of fine TiO_2 powder is a key issue in industrial implementation. Lignin tends to form stable suspensions with TiO_2, which are hard to separate even by centrifugation. Therefore, in this study, TiO_2 was attached by different methods to a glass plate, where the catalyst mass and the surface were known.

The objective of the research was to clarify the potential of PCO in lignin degradation. In the present study, the photocatalytic oxidation of UV-irradiated aqueous solution of lignin under variable media conditions and with the addition of ferrous ions was studied. Also different methods of attachments of titanium dioxide on the surface of the catalyst support were observed to determine the viability of this photocatalyst application method. Besides, the experiments with the N-doped catalyst active in visible light were carried out to observe its effect on lignin degradation.

The influence of the ferrous [14–16] and some other multivalent cations [17, 18], abundantly present in groundwaters and landfill leachate, on the PCO rates of various pollutants was performed in previous studies. The data available from published sources showed the reduction of decomposition rate with the increase of multivalent metallic ions concentration. However Klauson and Preis [19] observed an increased efficiency of PCO of methyl *tert*-butyl ether and 2-ethoxyethanol at low concentrations of ferrous ions. The role of ferrous ions in the PCO efficiency was studied here.

2. EXPERIMENT

Two 200-mL simple batch reactors with inner diameter 100 mm (evaporation dishes), aperture 40 m^2m^{-3}, thermostatted at 20 ± 1°C, and mechanically agitated with magnetic stirrers were used in the PCO experiments: the reactor

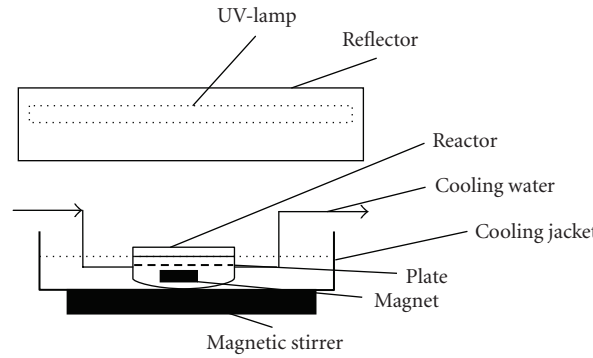

Figure 1: The photocatalytic oxidation experimental setup.

used for the PCO was called "active" and the other, containing no photocatalyst, was called "reference." The reactors were only surface aerated, since the oxygen shortage was not observed even in the PCO experiments with concentrated phenolic solutions [20]. Both reactors were exposed to identical experimental conditions. The samples from the active reactor were compared to the reference samples to avoid complications caused by water evaporation. A UV-light source, Phillips TLD 15W/05 low-pressure luminescent mercury UV-lamp with the emission maximum at 360-nm, was positioned horizontally over the reactors (Figure 1), providing irradiance of about 0.7 mW cm^{-2} measured by the optical radiometer UVX at a distance corresponding to the level of the free surface of the reactor. Phillips TL-D 15W/33–640 luminescent lamp was chosen as visible light source with the irradiance on the reactor' plane surface corresponding to 0.54 mW cm^{-2} at 683 nm.

3. MATERIAL AND METHODS

The experiments were conducted with synthetic solutions of lignin, which was purchased from Aldrich and used as received. The working solution was prepared in concentration of 100 mg L^{-1} of lignin by direct dissolution in distilled water, having final pH around 8.0. The pH of solutions treated in PCO experiments was adjusted with 2-M sodium hydroxide or sulphuric acid. Sulphate ion was chosen as a counterion due to its abundant character in groundwater and due to its known nondramatic effect on the PCO performance [21]. Ferrous sulphate was used for experiments with iron ions. The treatment time in PCO experiments was 24 hours if not specified otherwise. All the experiments were carried out three times under identical conditions; the average deviation of data in parallel experiments did not exceed 5%.

The experiments were performed using titanium dioxide as Degussa P25. In the supported catalyst experiments, TiO_2 was attached to the surface of the glass plate (one side) in approximately equal amounts either by multiple submerging of the plates in the TiO_2 suspension with subsequent drying after each submersion, or by spraying the TiO_2 suspension over the surface of the plates and drying. Before the attachment of titanium dioxide to the surface of the plate,

the latter was treated with 4-M NaOH and rinsed with water. The glass plate surface area was 63 cm^2. The glass plates were submerged horizontally in the solution to be treated at a depth from 5 to 10 mm. The results were compared to the data obtained earlier for the photocatalyst attached to hollow glass microspheres [22]. The experiments with visible light were carried out with the suspended TiO_2-N catalyst made after Gandhe and Fernandes [23]. With this catalyst, calculated titanium to nitrogen ratio was 1 : 5.

The lignin concentration was measured with photometric method developed by Hach Company Solutions of sodium carbonate and tannin-lignin reagent, containing sodium molybdate and sodium tungstate (VI), react with lignin forming blue-coloured intermediates. After 25 minutes of reaction time, the colour intensity was measured at 700 nm. Additionally, the UV-absorbance of treated samples at 280 (A_{280}) nm was measured by Spectronic Unicam spectrophotometer (Heλios β), which was correlated with the content of lignin by calibration line. The A_{280} measurement is an effective parameter to indicate the efficiency of lignin decomposition. The time-dependent variation of absorbance in oxidation experiments was observed by Ksibi et al. [1]. The gradual reduction of the intensity of the absorbance proves that deterioration of chromophores groups of the lignin occurs on course of oxidation.

Aldehydes, as PCO by-products of lignin, were quantitatively determined by the methods described by Evans and Dennis [24]. The analysis was performed by measuring an optical density at 630 nm of 5 mL of centrifuged sample, to which 0.5 mL of sulphuric acid, 1 mL of sodium arsenite solution, and 1 mL of 3-methylbenzolthiazol-2-one hydrazone hydrochloride (MBTH) solution were added. Samples were immersed in a boiling water bath for 6 minutes. Following that, samples were cooled to room temperature and 1 mL of iron (III) chloride-sulphamic acid reagent was added. Samples were allowed to stand for 20 minutes before measurements. Calibration was made with acetaldehyde.

The concentration of phenol, another PCO by-product of lignin, was measured by colorimetric method with p-nitroaniline: to the 100-mL sample of treated solution, 2 mL of 5% sodium carbonate and 4 mL of diazotizated p-nitroaniline were added; after 15 minutes of the reaction the optical density at 570 nm was measured. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) were measured by standard procedures [25].

4. RESULTS AND DISCUSSION

The performance of PCO with artificial radiation sources was characterised by the process efficiency E. The efficiency E is defined as the decrease in the amount of lignin divided by the amount of energy reaching the surface of the treated sample:

$$E = \frac{\Delta c \cdot V \cdot 1000}{I \cdot s \cdot t}, \quad (1)$$

where E is the photocatalytic oxidation efficiency in mg $W^{-1}h^{-1}$; Δc denotes the decrease of pollutants concentration in mg L^{-1}; V depicts the volume of the sample to be treated in L; I is irradiation intensity in mW cm^{-2}; s denotes the solution irradiated plane surface area in cm^2; and t depicts the treatment time in h.

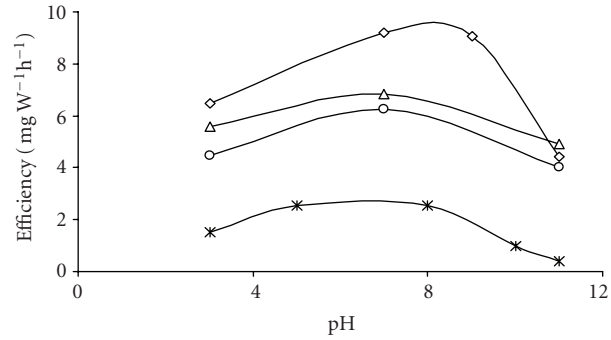

Figure 2: The dependence of PCO efficiency of lignin on pH with different photocatalyst application mode: plate 0.75 mg cm^{-2} (spraying) ($\diamond$), plate 0.7 mg cm^{-2} (submersion) (Δ), plate 0.3 mg cm^{-2} (submersion) ($\circ$), micro-spheres 25 g m^{-2} ($*$); initial concentration of lignin 100 mg L^{-1}.

It was found that the PCO provided the decrease of lignin concentrations in time. The catalyst presence was essential, since the decrease of lignin concentration in absence of titanium dioxide was not observed.

The effect of pH

In the present research, two ways of attachment of the TiO_2-catalyst to the surface of plates were used: submersion to the TiO_2-suspension (0.3 and 0.7 mg cm^{-2} were attached) and spraying of the latter over the surface (0.75 mg cm^{-2}) with subsequent drying. In both cases, the maximum PCO efficiency was observed in neutral and slightly basic media (Figure 2), which confirms that the oxidation mechanism with OH-radicals derived from OH-ions may prevail. As was established previously [22], the acidic media were most favourable for lignin adsorption, although are not the best for PCO: the surface concentration at 25°C decreased from 140 to 30 mg g^{-1} TiO_2 with the pH increasing from 3.0 to 7.0; at pH 9.0 and above the adsorption of lignin was not observed. As one can see, the PCO efficiency of the attached catalyst behaved consistently with the previous observations made with the TiO_2 attached to buoyant hollow glass microspheres, although reached greater numbers: the PCO efficiency increased, for example, in neutral solutions for about 3.5 times from 2.5 to 9.2 mg $W^{-1}h^{-1}$. The increased efficiency with the plate-attached catalyst may be explained by the increased irradiated surface: the catalyst on the microspheres works under ineffective irradiation conditions; the irradiated part of the microsphere has poor contact with treated water.

The decrease of PCO efficiency under strong alkaline conditions is explained by the effect of charges repulsion between both negatively charged lignin molecules and TiO_2 particles. Since the isoelectric point pHzpc for TiO_2 is around 6.3, its surface is positively charged in acidic media

and negatively in alkaline [26]. Molecules of lignin are deprotonated and negatively charged in alkaline solutions, being repelled from the catalyst surface; this dramatically reduces their adsorption. Also the accumulation of bicarbonate and carbonate ions, the well-known OH-radical scavengers, could be the reason of decreased efficiency at alkaline pH.

Figure 2 shows that the TiO_2 attachment mode to the glass plates makes a difference in the PCO efficiency: the spraying attachment appeared to be more effective. This may be explained by the uneven relief and porosity of the catalyst surface and, thus, a larger contact surface resulted from the nonuniform spray attachment. Within the tested limits of the photocatalyst surface concentration, the increased efficiency was observed for the increased amount of the catalyst. This could be explained by the UV-light penetration to a certain depth of the TiO_2 layer, which is active in PCO reactions. A similar phenomenon was observed earlier with the photocatalyst attached to the microspheres: the oxidation efficiency increased with increased thickness of the catalyst layer until a certain limit, above which the PCO efficiency did not increase further [27].

Under acidic conditions, the washing-off of titanium dioxide from the plate made by spraying was observed as the decrease in the PCO efficiency of lignin: the oxidation result decreased in repetitive experiments. No washing-off was observed neither under acidic conditions from the plates made by submersion, nor from any plate under neutral and alkaline conditions. This difference is explained by the difference in porosity and, thus, the strength of the catalyst layer, since lignin exhibits the property to form stable suspensions with TiO_2.

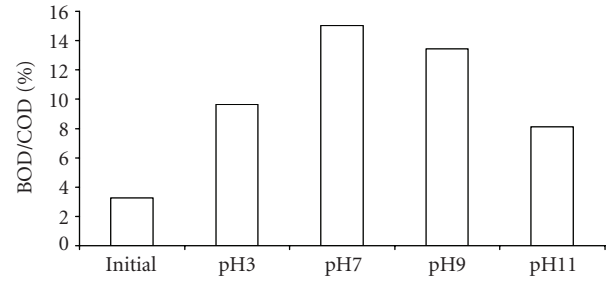

Figure 3: The increase of BOD/COD ratio in PCO treatment time at different pH: initial concentration of lignin 100 mg L^{-1}; plate 0.75 mg cm^{-2} (spraying), treatment time 24 hours.

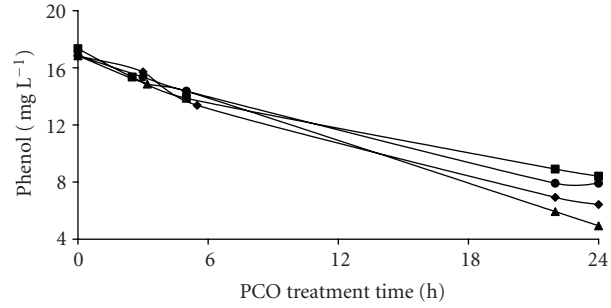

Figure 4: The decrease of phenol concentration in PCO treatment time at different pH: pH 3 (■), pH 7 (◆), pH 9 (▲), pH 11 (•); initial concentration of lignin 100 mg L^{-1}; plate 0.75 mg cm^{-2} (spraying).

Oxidation by-products

The lignin solutions were PCO-treated for the lignin concentration reduced to 50%. These solutions were analysed for free phenols, aldehydes, and the biodegradability expressed as the BOD_5/COD ratio. The initial concentration of free phenols in the solution containing 100 mg L^{-1} of lignin, measured by the standard method, was found to be 16 mg L^{-1}. As a result of 24-hour PCO under neutral media conditions, 80% of free phenols were removed, that is, their concentration decreased five times; the final concentration of phenols was 3.25 mg L^{-1}. The biodegradability of this sample increased from 3 to 15%, that is, also five times. The analogous effect was observed for the samples PCO-treated under different pH (see Figure 3), although the neutral media was the most beneficial for the increased biodegradability. It may be interesting to notice that the five-fold decrease in phenols' concentration resulted in five times increased biodegradability, indicating possible correlation between these two parameters.

The PCO treatment never resulted in an increased phenols concentration to any extent (Figure 4). This may be explained by the degradation of phenolic compounds exceeding the degradation of lignin by its rate: the free phenols degraded for about 80%, whereas lignin degradation did not exceed 50%. The reduced concentration of toxic free phenols together with the formation of biodegradable oxidation by-products may be the reason for increased biodegradability of the lignin solutions.

During the PCO of lignin the formation of aldehydes, another PCO by-product of lignin, was observed (Figure 5); unlike polydisperse lignin concentration expressed in mg L^{-1}, the aldehyde concentration is expressed in μM L^{-1}. The neutral pH was the most beneficial for the aldehyde formation similar to the lignin oxidation rate and the growth of biodegradability. However, one can see that, in contrast to the oxidation of phenol and lignin, acidic medium was favourable for aldehydes formation. In general, the rate of aldehyde accumulation, determined by the balance between the formation and oxidation of aldehydes, increased with the pH increasing from 3 to 7 and decreased with the further increasing pH, having the maximum rate at pH 7.

There is an observation made during the study, which cannot be easily explained by the authors at this stage of the research: aldehydes observed as PCO by-products of lignin were not traced in PCO treated solutions of lignin in presence of ferrous ions. This may indicate the difference in oxidation pathways in presence and absence of Fe^{2+}. The authors suggest that aldehydes were not observed due to either the oxidation of lignin and/or its fragments directly to carbonic acids or the fast oxidation of aldehydes to carbonic acids enhanced with some additional oxidant. One of the options could be

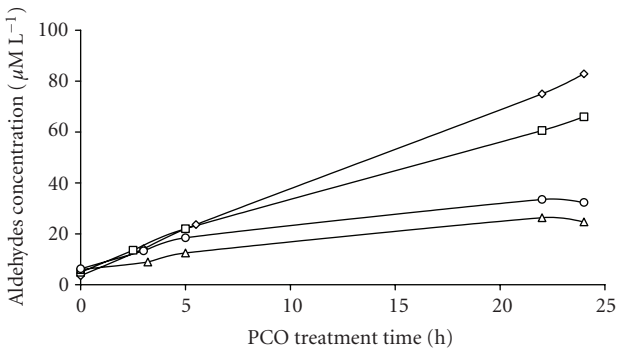

FIGURE 5: The increase of aldehydes concentration in PCO treatment time at different pH: pH 3 (□), pH 7 (◇), pH 9 (△), pH 11 (○); initial concentration of lignin 100 mg L^{-1}; plate 0.75 mg cm^{-2} (spraying).

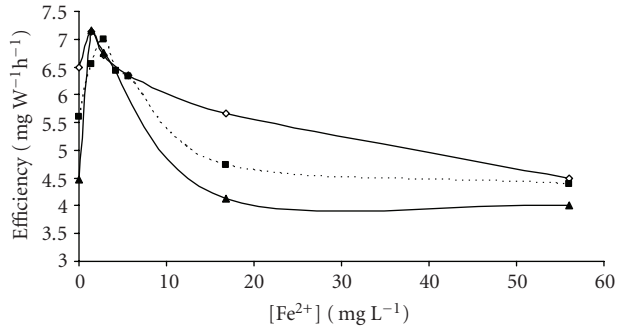

FIGURE 6: The dependence of PCO efficiency of lignin on the ferrous ion concentration: initial concentration of lignin 100 mg L^{-1}, pH 3; plate 0.75 mg cm^{-2} (spaying) (◇), plate 0.7 mg cm^{-2} (submersion) (■), plate 0.3 mg cm^{-2} (submersion) (▲).

hydrogen peroxide formed in photocatalytic reactions, which in presence of ferrous/ferric ions works as the Fenton reagent. This reagent may easily oxidize aldehydes in the bulk solution to acids. However, further research is necessary to explain the observation in details.

Influence of ferrous ions

The addition of ferrous ions to the lignin solution in acidic media leads to the sharp increase of PCO efficiency at low concentrations of iron (Figure 6). This fact could be explained by the decrease in recombination rate between positively charged holes and conductivity band electrons, which is considered to be the PCO limitation stage. Conductivity electrons may be scavenged by ferric ions adsorbed on the titanium dioxide surface, extending the lifetime and thus the oxidation performance of positively charged holes, which dominate in oxidation mechanism under acidic media conditions. The ferric ions appear as the product of ferrous ions oxidation with the ferrous/ferric ions equilibrium established in the PCO-treated solutions [28]. The peak in PCO efficiency was observed at the concentrations of ferrous/ferric ions between 1.4 and 2.8 mg L^{-1}. The decrease in PCO efficiency with further increase in the ferrous/ferric ions concentration is, presumably, caused by the blockade of absorption sites by metallic ions. This presumption was confirmed earlier by Klauson et al. [28] for the oxygenated hydrocarbons: the minimum PCO efficiency was observed around the maximum adsorption of Fe^{2+} on the TiO_2 surface.

Testing the N-doped catalyst

Recently, many attempts have been made in the direction of N anion-doped TiO_2 photocatalysis because it has good potential for the utilization of the solar energy to eliminate environmental pollutants in water [23, 29, 30]. According to Asahi et al. [29] the doped nitrogen atoms narrow the band-gap of TiO_2 and thus make it capable for visible light driven photocatalysis. In our experiments of lignin oxidation under visible irradiation with N-doped catalyst synthesized after Gandhe and Fernandes [23], no degradation of lignin was observed in wide range of pH conditions, catalyst, and lignin concentration, although the catalyst was effective against, for example, methyl *tert*-butyl ether (MTBE) and tert-butyl alcohol (TBA). The reason for this inefficiency was found in zero adsorption of lignin on the N-doped catalysts. The detailed explanation of this observation was given in [31]: the zero adsorption with a good PCO performance with MTBE and TBA indicated the prevailing radical oxidation, ineffective against unadsorbable lignin. In fact, the catalyst synthesized according to [23] did not even form the stable suspensions with lignin solutions like Degussa P25 did.

5. CONCLUSIONS

The highest photocatalytic oxidation efficiency for lignin was observed in neutral and slightly basic media also with the photocatalyst attached to the glass plates, which showed 3.5 times higher efficiency in oxidation of lignin than the photocatalyst attached to buoyant hollow glass microspheres.

The difference in the procedure of TiO_2 attachment to the glass plates makes a difference in the PCO efficiency: the spraying attachment appeared to be more effective. However, under acidic conditions, the washing-off of titanium dioxide from the plate made by spraying was observed in presence of lignin.

PCO of lignin resulted in degradation of toxic free phenols and the drastically increased biodegradability of lignin solutions indicating possible correlation between these parameters.

The addition of ferrous ions, up to 2.8 mg L^{-1}, to the lignin solution leads to the drastic increase in PCO efficiency. A further increase in ferrous ion concentration results in a decrease in PCO efficiency of lignin.

No lignin degradation was observed in experiments with N-doped catalyst under visible light.

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