

Photo-Fenton process of oxidative destruction of rice husk alkaline hydrolysates lignin

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Abstract

The present work studies the destruction of a silica-free solution of alkaline hydrolysate of rice husk (pH 7.25, COD = 22.80 g·L⁻¹) using the photo-Fenton process in the UV layer at a wavelength of 365 nm. Oxidation of lignin was carried out at a constant mass ratio of COD:H₂O₂ = 1:2 in the solutions with different dilution times (1:10, 1:50) and with varying iron(II) concentrations in the range from 10 to 100 mg·L⁻¹. It was established that the oxidative degradation of alkaline lignin effectively proceeds in the UV layer when the solution is diluted 50 times, at an iron(II) concentration from 50 to 70 mg·L⁻¹. Color, the content of polyphenols and chemical oxygen demand in the silica-free solution with a dilution ratio of 1:50, after oxidation, is reduced by several tens of times. The products of lignin degradation were identified using gas chromatography.

Key words: alkaline hydrolysate, lignin, photo-Fenton, rice husk

INTRODUCTION

The main industrial consumer of plant raw materials is traditionally the pulp and paper industry, which mainly uses various woods. In recent years, there have been many proposals in the literature to involve non-wood plant raw materials into the production of fibrous materials – e.g., multi-tonnage wastes from crops of annual crops, such as rice husk and straw. The main advantage of such raw materials is its annual reproducibility and possibility of processing by alkaline delignification methods. When processing rice husks with sodium hydroxide, alkaline hydrolysates are formed, which contain a high amount (up to 45.15% by weight) of various water-soluble organic (including phenolic) and inorganic substances (Zemnukhova *et al.* 2011, 2013). The main inorganic element in the alkaline hydrolysate is silicon extracted from the husk in the form of sodium silicate, and the desiccated residue of rice husk can serve as a raw material for the production of cellulose materials (Vurasko *et al.* 2006). However, it should be considered that in the process of alkaline hydrolysis wastewater is formed, which is characterized by significant color and increased biochemical oxygen demand (BOD) (Zemnukhova *et al.* 2011). Such waters contain a high amount of alkaline lignin, which is a mixture of toxic or dangerous organic aromatic substances with different molecular weights and their discharge into water bodies is prohibited.

The traditional method of lignin-containing wastewater treatment is biological, but during the treatment process the soluble part of lignin does not degrade and can enter water bodies (Raj *et al.* 2007).

Recently, various physicochemical methods have been studied to treat lignin-containing wastewater: coagulation and flocculation (Dzyuvina 2011), membrane (Zemnukhova *et al.* 2014), and electrochemical (Zayas *et al.* 2011; Zodi *et al.* 2011).

The most promising technologies for the destruction of a wide range of toxic chemicals are the technologies of non-reagent water treatment based on efficient oxidation processes ('Advanced Oxidation Processes', AOPs) (Herrmann *et al.* 1993). These processes include the formation of a highly reactive hydroxyl radical (HO[•]), which is one of the strongest oxidizing agents (Khataee *et al.* 2012). Among the various AOPs technologies, those based on the use of hydrogen peroxide in the variant of the Fenton reagent are promising for wastewater treatment from organic pollutants (Esplugas *et al.* 2002; Khataee *et al.* 2014).

In the Fenton process, the formation of hydroxyl radicals HO[•] occurs as a result of catalytic decomposition of H₂O₂ in an acidic medium (pH 2.8–4.0) in the presence of dissolved Fe²⁺ ions (Walling & Goosen 1973):



According to the data (Lam & Hu 2007; Amorim *et al.* 2013) the speed of the Fenton process increases significantly under the action of visible or ultraviolet (UV) radiation due to the decomposition of photoactive Fe(OH)²⁺ particles promoting additional generation of HO[•] radicals in solution:



The main organic pollutants 'target' of the Fenton's reagent are soluble substances, aromatic nucleophilic compounds (Dogruel *et al.* 2009), and polyphenols such as lignin (Passauer *et al.* 2011). A few works studied the possibility of treatment of lignin-containing wastewater from pulp and paper industries, that is, wastewater generated during the processing of wood raw materials (Pérez *et al.* 2002; Torrades *et al.* 2011). There is no information in the literature devoted to the use of the Fenton process for the destruction of lignin-containing wastewater generated during the processing of non-wood raw materials, in particular, rice production waste (rice husk and straw).

The purpose of this work is to select the conditions for efficient oxidation of lignin in the silica-free solution of alkaline hydrolysate of rice husks using a photo-Fenton process.

METHODS

Obtaining alkaline hydrolysate and silica-free solution

The object of the research was rice husk sampled in Krasnodar Krai. Husk sample was sifted through a sieve (2 mm particle size) to remove tiny fractions (bran siftings, dust). Then, raw materials were washed in distilled water and air dried. Raw materials were hydrolysed by 1 mol·L⁻¹ sodium hydroxide when heated to 90 °C within an hour in a laboratory reactor. The temperature was controlled using thermocouple EKT Hei Con. Mass ration solid to liquid was 1:13. The hydrolysate developed was filtered through synthetic fabric with pore size 15 μm and alkaline hydrolysate was obtained (S1).

Silica-containing substances in the form of silicic acid were obtained from S1 with simultaneous neutralization of alkaline solution. With that purpose, alkaline hydrolysate (S1) was mixed with concentrated hydrochloric acid to reach pH = 6. Silicic acid was filtered through filter paper with pore size 2–3 μm and silica-free solution was obtained (S2). The characteristic of these solutions is presented in Table 1.

Table 1 | Quality parameters of alkaline hydrolysate (S1) and silica-free solution (S2) (Arefieva *et al.* 2017)

Solutions	pH	Chloride ion [g L ⁻¹]	Color [degree]	Turbidity [mg L ⁻¹]	COD [mgO L ⁻¹]	BOD ₅ [mgO ₂ L ⁻¹]	Polyphenols [mg L ⁻¹]
S1	13,90	—*	95,000	3,205	50,804	34,317	1,833
S2	7,25	40	14,500	769	22,813	5,673	1,393

* - the parameter was not determined.

Reagent solutions

All the reagents were of analytical grade. Stock solution of the iron(II) with a concentration of 1.25 mgFe·ml⁻¹ was prepared by dissolving (NH₄)₂Fe(SO₄)₂·6H₂O in distilled water. As the oxidizer, we used a hydrogen peroxide solution with a concentration of 12.05 mol·L⁻¹.

A procedure for oxidative degradation of lignin using the photo-Fenton process

Oxidative destruction of the silica-free solution (P2) was carried out in the UV and visible layers of the spectrum when diluted with distilled water in the ratio 1:10 and 1:50. Concentration of hydrogen peroxide (4.1 and 0.82 g·L⁻¹) and iron (from 10 to 100 mg·L⁻¹) was chosen depending on the chemical oxygen demand (COD) of the test solutions according to (Clarizia *et al.* 2017).

Photocatalytic degradation in the UV layer was carried out in a quartz cell with a volume of 50 ml into which 35 ml of a silica-free solution, hydrogen peroxide and a solution of iron(II) were placed. The irradiation source was a UV irradiator of 100P/F (maximum radiation with a wavelength of 365 nm). The solution was irradiated with constant stirring by a magnetic stirrer (625 rpm) for three hours.

The sunlight photocatalytic degradation of the silica-free solution was carried out in a simple photoreactor. The reactor was a bottle of 100 ml capacity. The photocatalytic degradation was carried out at the same conditions on sunny days between 9 a.m. and 12 a.m. in April. The ambient temperature was 20 °C. The silica-free solution, diluted 1:10 and 1:50 (35 ml), was added into the bottle under the sunlight radiation. Under the similar conditions a control experiment without irradiation (in dark) was conducted.

Waste water quality parameters determination

Color was determined by photoelectrocolorimetric method on spectrophotometer UNICO-1201 (United Products & Instruments Inc., USA). pH was measured by pH-meter FiveEasyPlus 20 (Mettler Toledo) with glass electrode.

Measurements of COD were carried out by a method based on the treatment of a water sample with sulfuric acid and potassium dichromate at a temperature of (150 ± 5)°C in the presence of a silver sulfate oxidation catalyst and by the addition of mercury(II) sulfate used to reduce the effect of chlorides. The COD value was determined on a pre-calibrated Fluorat-02 fluid analyser (Russia). When calibrating the analyser and all measurements in the range from 10 to 160 mgO·L⁻¹ we used a light filter at a wavelength (440 ± 20) nm in the excitation channel.

The polyphenols were determined photometrically using the Folin reaction with the phenolic reagent Folin-Ciocalteu. A phenol solution in water was used as the standard solution for the determination of the polyphenols. The optical density of the solution was determined on a UNICO-1201 spectrophotometer at a wavelength of 650 nm. A blank sample was used as the reference solution.

Chromato-mass-spectrometric analysis

The analysis of volatile compounds in the extracts obtained from wastewater after oxidative degradation using the photo-Fenton process according to (Abrahamsson & Xie 1983) was carried out on

a GCMSQP5050A (Shimadzu, Japan) equipped with a SLB-5 ms column (30 m × 0.25 mm in diameter, 0.25 μm film thickness, Supelco, USA). Helium was used as the carrier gas.

Analysis parameters: The separation of substances was carried out at a temperature gradient: 45 °C - 1 min → 280 °C, 6°/min, 280 °C - 25 min. The carrier gas flow rate is 1 ml/min, the split mode is 1/7. The temperature of the injector is 220 °C, the temperature of the ion source is 200 °C. The scanning was performed in the range of 50–600 m/z.

Identification of organic compounds of extract components was carried out on the basis of comparison of mass spectra with the spectra of the NIST library. Identification was considered reliable at a degree of convergence of the working spectrum with a library one of at least 90%.

RESULTS AND DISCUSSION

Preliminary studies showed that neutral silica-free solutions of lignin (pH 7.25, Table 1) are sufficiently stable in time, regardless of the degree of dilution, because they contain very strong organic compounds, represented mainly by low molecular weight soluble lignin, consisting of substances of an aromatic nature. In this paper, the experiments were carried out at a constant mass ratio of COD:H₂O₂ = 1:2 in the solutions with varying degrees of dilution and varying the concentration of iron(II) in the range from 10 to 100 mg·L⁻¹.

The control experiments showed that after placing the dilute solutions (1:10 and 1:50) with hydrogen peroxide and iron(II) of different concentrations in the dark or in the light (in the visible layer of the spectrum) for almost three hours there are practically no changes in the color of the solution.

Figure 1 shows the results of the evaluation of the oxidative degradation of alkaline lignin in a silica-free solution by the effectiveness of its discoloration at different iron(II) concentrations under the influence of UV irradiation (dilution 1:10; COD: H₂O₂ = 1:2). At iron(II) concentrations of up to 30 mg·L⁻¹ the decolorization efficiency is ~1%, which means that practically nothing happens in the solution. A further increase in the concentration of iron(II) to 90 mg·L⁻¹ leads to an increase in the color of the test solution and as a consequence to a negative efficiency of discoloration. This fact indicates that the solution due to the destruction of lignin under these conditions produces the formation of organic substances with stronger chromophore groups, the presence of which causes an increase in the intensity of the solution color. In fact, the effectiveness of the discoloration becomes positive only at an iron(II) concentration of 100 mg·L⁻¹ and does not exceed 10%. That is, in the given conditions (dilution 1:10; COD:H₂O₂ = 1:2; C (Fe²⁺) = 100 mg·L⁻¹), the application of the photo-Fenton process to destroy the complex organic molecules contained in the lignin-containing silica-free solution was not sufficiently effective.

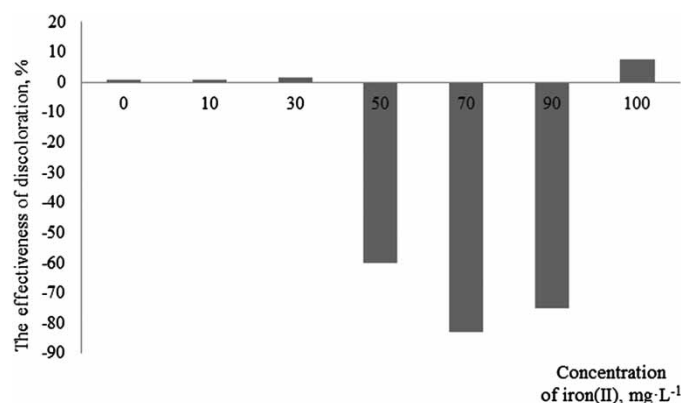


Figure 1 | The effectiveness of discoloration of desilicized solution diluted 10-fold, depending on the concentration of iron(II) cations.

It is known that an increase in the degree of destruction of organic substances in lignin-containing solutions by electrochemical methods can be achieved by diluting them with water and as a consequence by reducing the concentration of lignin in them (Kovshun *et al.* 2014).

In connection with this the dilution of the test solution with distilled water was increased from 1:10 to 1:50 with a constant COD:H₂O₂ ratio 1: 2. After irradiation of the studied solutions with a dilution ratio of 1:50 containing from 0 to 30 mg·L⁻¹ iron(II) an increase in their color occurred, so a negative efficiency of decolorization was observed (Figure 2). The obtained results obtained show that a higher dilution rate of the lignin-containing solution even without the addition of iron(II) or with the addition of an insignificant amount, already led to the fact that chemical processes begin to occur in the solution, leading to a change in its qualitative composition. When the concentration of iron(II) in the solution is increased up to 50 mg·L⁻¹ and above, the decolorization process acquires a positive tendency and the efficiency of decolorization is 92–97%. The color of the test solution (dilution 1:50; COD:H₂O₂ = 1:2, C (Fe²⁺) = 50–100 mg·L⁻¹) after its irradiation with UV light for three hours was ~ 16 degree (Table 2), which satisfies requirements of wastewater discharge into water bodies.

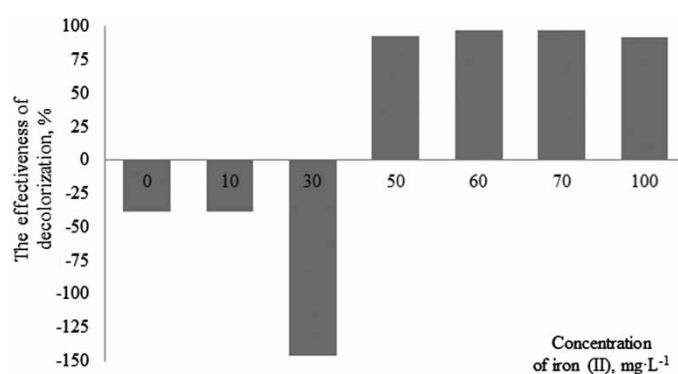


Figure 2 | The effectiveness of decolorization of a desiliconized solution diluted 50-fold, depending on the concentration of iron(II) cations.

Thus, it has been established that a high dilution rate and an iron(II) concentration of 50 to 100 mg·L⁻¹ are required to reduce the color of lignin-containing solutions and, consequently, to increase the efficiency of their destruction by the photo-Fenton reaction.

Table 2 summarizes the data on color, COD and polyphenols content in solutions with a dilution ratio of 1:10 and 1:50 with the addition of 100 and 60 mg·L⁻¹ of iron(II), respectively.

The color in the solution diluted 10 times after UV irradiation for three hours was half that of the original solution, and the content of polyphenols was reduced 1.5 times. The value of COD increased 4-fold, which is apparently due to the fact that hardly-oxidizable organic compounds decompose to compounds capable of being oxidized by potassium dichromate.

Table 2 | Characterization of the desiliconized solution before and after oxidative degradation

Solution	pH	Color [degree]	COD [mgO L ⁻¹]	Polyphenols [mg L ⁻¹]
Dilution ratio 1:10				
The stock solution	7,15	1,450	2,281	139,30
After the destruction	7,20	708	8,915	92,64
Dilution ratio 1:50				
The stock solution	6,98	290	456	27,86
After the destruction	7,15	16	79	1,53

At the photocatalytic degradation of the 50-fold diluted solution, color, COD and concentration of polyphenols decrease 180, six and 18 times, respectively, indicating that at such a dilution ratio, the process of mineralization (complete destruction) of lignin takes place. The color of the treated solution achieves regulatory requirements, while the COD value of the solution does not meet the regulatory requirements. Compared with the electrochemical oxidation of a silica-free solution diluted 10-fold, the quality of the treated solution is 10–100 times lower, indicating more effective destruction of lignin (Arefieva *et al.* 2017). But in the extracts after electrochemical treatment of the solution were identified organic compounds classified as structures of a number of organochlorine compounds possessing increased biological activity associated with negative effects on living organisms.

In the extracts isolated from the silica-free solution diluted 10 and 50 times, after oxidative degradation, organic compounds were determined (Table 3).

It can be seen from Table 2 that after destruction with the use of the photo-Fenton process of silica-free solutions, the composition of organic compounds is almost the same. The main components of the mixture of organic compounds are aromatic hydrocarbons and carboxylic acids. It should be noted that the studied solutions contain a high amount of chloride ions (Table 1), capable of forming highly toxic, chloroorganic compounds with lignin degradation products. However, according to the data in Table 3, such compounds were not detected, which is very important from an environmental point of view.

It is known that the photo-Fenton process is a high speed process that takes place in an acidic medium (pH 2.8–3.5) (Clarizia *et al.* 2017; Villegas-Guzmana *et al.* 2017). The studied lignin-containing wastewater is neutral or close to neutral pH (Table 2). Despite such a pH value, an effective degradation of lignin is observed using the photo-Fenton process. Several studies conducted at near neutral pH by harnessing the benefits of natural organic matter on photo-Fenton

Table 3 | Extract components identified by chromatographic-mass spectrometric analysis

Name	Dilution ratio	
	1:10	1:50
Benzoic acid	+	+
Octanoic acid	+	+
Naphthalene	+	+
Benzo[b]thiophene	+	–
Decanal	+	+
Nonanoic acid	+	+
n-Decanoic acid	–	+
4-hydroxybenzaldehyde	+	–
Biphenyl	+	–
Butylated hydroxytoluene	+	+
n-Dodecanoic acid	+	+
Cyclopentaneacetic acid, 3-oxo – 2-pentyl-, methyl ester	–	+
Eicosane	+	+
Squalane	–	+
Tetradecanoic acid	+	+
Pentadecanoic acid	+	+
Oleic acid	–	+
N-phenyl-naphthalenamine	–	+
Squalene	–	+
Stigmast – 4-en – 3-one	+	+

systems were found (Clarizia *et al.* 2017). Such compounds (L) should be able to form stable complexes with Fe(III), which significantly absorb UV-vis light and undergo photochemical reductions leading to Fe(II) ions (Clarizia *et al.* 2017):



According to (Zemnukhova *et al.* 2004), similar solutions contain alkaline extraction polysaccharides, which can form stable complexes with Fe(III), which leads to the degradation of lignin through photo-Fenton process in a neutral medium.

CONCLUSIONS

Thus, we showed the possibility of applying the photo-Fenton process for the destruction of lignin in silica-free solutions of alkaline hydrolysates of rice husk with a neutral pH. It was found that the efficiency of degradation of lignin in a solution with hydrogen peroxide (COD:H₂O₂ = 1:2) increases with an increase in the iron(II) concentration from 10 to 100 mg·L⁻¹ and the dilution ratio. The color, the content of polyphenols and COD in the silica-free solution, diluted 50-fold, after oxidative degradation are reduced by several tens of times. The products of degradation of lignin were identified using gas chromatography.

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