Remediation of lignin and its derivatives from pulp and paper industry wastewater by the combination of chemical precipitation and ozonation

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A B S T R A C T

In the present work the degradation of the lignin and its derivatives in the residual water of a paper industry by simple ozonation was investigated. The remediation of lignin was realized using the combination of the pre-treatment with chemical precipitation, using concentrated sulfuric acid (97.1%) at the pH 1 and 3, and of the simple ozonation of the filtered residual water at the pH 1, 3, 8 and 12. Since the high residues content (the initial chemical oxygen demand (COD) is 70,000 mg/L) in the experiments the diluted samples (1:10) were used. The previous precipitation has showed a significant effect on the reduction of the COD (77%) and color (96.1%). The sludge precipitated contents sulfolignin, which in the reaction with sulfuric acid was formed. In ozonation of the filtered residual water during 25 min at the pH 1, 3, 8 and 12 the follows by-products were formed: fumaric, maleic, malonic and formic acids. The biodegradability of the treated water in ozonation increases up 0.067–0.29. The effect of the precipitation and the ozonation conditions on the decolorization kinetics was evaluated.

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1. Introduction

The pulp and paper industry has been considered as one of the biggest consumers of natural resources (wood, water) and energy (fossil fuels and electricity) and as a significant taxpayer of discharge of pollutants to the environment [1–4]. The wood pulping and production of the paper products generate a considerable amount of pollutants characterized by biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), toxicity, and color when untreated or poorly treated effluents are discharged to receiving water. Pulp and paper mills generate varieties of pollutants depending upon the type of the pulping process [5]. This is made from cellulose fibers, carbohydrates as sugar and lignin, and is adhesive substance for the cellulose fibers [4]. The current environmental limitations have caused the decrease of the consumption of the natural resources for this industrial use. So, in this industry the recycling of fibrous raw materials and/or alternative is [6,7]. The high water usage, between 20,000 and 60,000 gallons/t of products [8], results in large amounts of wastewater generation. The water consumption dependents on the technology and the product obtained [9,10]:

- Carton: $3–8 \, m^3/t$ of product.
- Newspaper: $10–15 \, m^3/t$ of product.
- Papel tisú: $15–20 \, m^3/t$ of product.
- Writing paper: $10–20 \, m^3/t$ of product.

The sources of the contamination of the circuits of water in the production of the paper and cardboard are as follows: the fibrous raw materials, the additives and the feeding water, which provide a lot of pollutants such as resinic acids, wax, as well as lignin and their derivates, organic chlorides, dioxins, benzophenils, etc. It is well known that the process of paper production generates a high grade of contamination on the environment [1–4,11], so much for the discharge volumes like for its content. This process has limited ability to provide effluents of high-quality conforming to stringent regulations, since large amounts of lignin and lignin-derived compounds remain in the wastewater. These effluents are characterized of high coloration, suspended solids, unstable pH, high COD and DBO_5, besides chlorides, sulfate, etc. [11–15]. On the other hand, these pollutants can be carcinogenic, due to the chlorine lignin and chlorine phenols that are formed along the process [15–17]. The chemical structure of lignin as the principle residue is not defined. It is known that it is a natural irregular biopolymer, which consists of phenyl propane units with various substitutes ($-OCH_3$, $-OH$, $-COOH$) combined with bonds of different types [18,19]. An important group of compounds is responsible for the toxicity of this residual water and may adversely affect the microbial systems in the bioreactors [14,15,20–22]. These compounds are

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Table 1
Some characteristics of native wastewater.

Parameter	Wastewater
pH	9.0
Color (Pt–Co)	109,284
COD, mg/L	70,000
BOD$_5$, mg/L	503
Suspended solids, g/L	91.5

resistant to the biodegradation, because generally they are toxic products with the most complex structures [7,18,23]. Makris and Banerjee [24] studied the fate of the resinic acids in the secondary treatment system. The resinic acids are toxic components with securities of 0.4–1.1 mg/L [15]. Many authors reported the presence of toxic species in fish or toxic effects on fish such as respiratory stress, mixed function oxygenase activity, toxicity and mutagenicity, liver damage, or genotoxic effects, and lethal effects on the fishes exposed to pulp and paper mill wastewaters [25–27]. Since described before, in certain cases novel treatment technologies or the combination of different alternative methods for the remediation of contaminated water are necessary [18,19,21,23]. Exist alternatives methods to treat the waste water of paper industry like catalytic process, bio-catalysis, membranes, water treatment with high temperatures and pressures [1–4,9], but these processes are not very efficient and its operations is very costly. Ozonation [6,14,27,28] and advanced oxidation processes (AOPs) including photocatalitic oxidation and catalytic ozonation [29–33] are the alternative to degrade lignin and their derivatives in water, but the efficiency of the treatment depends on the real practice of the operation process and the quality of the treated water. The very interest aspect has the combination of two or more processes. So, a combination of coagulation and wet oxidation [34,35], of ozonation and biofilm reactor [36] and biodegradation [37], etc., have shown high removals of COD and total organic carbon (TOC) and the acute toxicity reduction.

The objective of this work was to improve the treatment performance of pulp and paper mill effluents by the combination of the chemical precipitation and the simple ozonation. The wastewater, which contains considerable amounts of high-molecular-weight pollutants, was pre-treated separately by precipitation with sulfuric acid at the initial pH 1 and 3, then by the simple ozonation at the pH 1, 3, 8 and 12 in order to reduce color, decompose dissolved contaminants and increase the biodegradability (BOD$_5$/COD) of the final compounds composition. The effect of the precipitation conditions and of the ozonation time on the decolorization kinetics and on the composition of the ozonation products has been evaluated.

2. Materials and methods

2.1. Chemical precipitation of lignin by sulfuric acid

In all experiments the samples of original wastewater from the paper plant "Kimberly Clark" of Orizaba City, Veracruz, Mexico were used. Table 1 depicts some characteristics of this wastewater that coincides with the reported in the references [38,39]. The lignin precipitation in the diluted samples (1:10) was carried out using the concentrated sulfuric acid (97.1%, FERMONT) with the magnetic agitation. The acid concentration varies from 1.025 to 2.25 vol% at the initial pH 3 and 1, correspondingly. The treatment of samples during 24 h for the sulfolignin formation was carried out. The acid dose effect on the efficiency of the precipitation degree and the color decrease was determined by the UV–vis spectrophotometry.

2.2. Ozone generation and ozone consumption control

Ozone was generated from dry oxygen by the ozone generator (corona discharge type) HTU500G ("AZCO" INDUSTRIES LIMITED, Canada). The Ozone Analyzer BMT 963 (BMT Messtechnik, Berlin) provides the ozone detection in the gas phase in the reactor outlet for the ozone monitoring to control the ozonation degree, the ozone consuming and the ozone decomposition as well. Data acquisition from the ozone analyzer was performed on line by connecting a computer to the ozonation device, to be processed by means of a program "MATLAB-7.0".

2.3. Ozonation procedure

All ozonation experiments were carried out at room temperature ($23 \pm 3\,^\circ$C) in a semi-continuous glass reactor (230 mL) with the initial ozone concentration of 30 mg/L during 60 min. The ozone/oxygen mixture, with the gas flow of 0.5 mL/min, by the porous ceramic in the inferior part of the reactor was distributed. The ozonation of the diluted and filtered samples after precipitation was carried out at the initial pH 1, 3, 8 and 12. In Fig. 1 the experimental set-up is shown.

2.4. Samples analysis

To control the dose of sulfuric acid, the filtered solution was analyzed by a spectrophotometer UV–vis (PerkinElmer-Lambda 2B). The dynamics of the lignin decomposition in ozonation, as well as the decolorization degree, by the same team was carried out using the wavelength 254 and 465 nm, respectively. The precipitated samples of sludge, after their filtration and draying, by a Fourier-transform infrared spectroscopy (FTIR) technique using the spectrophotometer (PerkinElmer 1600 Series FTIR) with a KBr cell were analyzed. The intermediates and final products formatted in the lignin ozonation were identified by the high performance liquid chromatography (HPLC) using the liquid chromatograph PerkinElmer series 200 coupled with a automatic UV/vis detector accompanied by the chromatographic column Nova Pack C-18, 250 mm × 4.6 mm with a mobile phases of water:acetonitrile:phosphoric acid (79.9:20:0.1) with the flow 0.5 mL/min. The injected sample volume was 30 μL and the used wavelength was 210 nm.

BOD$_5$ and COD of the samples were determined according to the Standard Methods [40].

3. Results and discussion

3.1. Effect of the sulfuric acid dose on the lignin precipitation efficiency

In the preliminary study [41] a ferric sulfate as the coagulant has been utilized, which demonstrated good results in the color remove and in the ozonation time reduction, but the sludge formed in coagulation is also toxic and provokes an environment impact. In the present study sulfuric acid was used in the lignin precipitation for the possible sulfolignin formation, since the sulfolignin has an application in the additives and cement production [42]. Based on the obtained results presented in Table 2, we can conclude that the use of sulfuric acid is a good alternative method for the high-molecular-weight pollutants precipitation. So, only one stage of treatment, as precipitation with sulfuric acid, allows a decrease of the initial color in 96% and the precipitate lignin as sulfolignin 89.90% of the initial volume of residual water. However, the acid dose effect on the mass of the precipitated sludge, as well as on the color, COD and BOD$_5$ decreases is less significant. Due to the variation of sulfuric acid percentage from 1.01 to 2.25, slightly changes
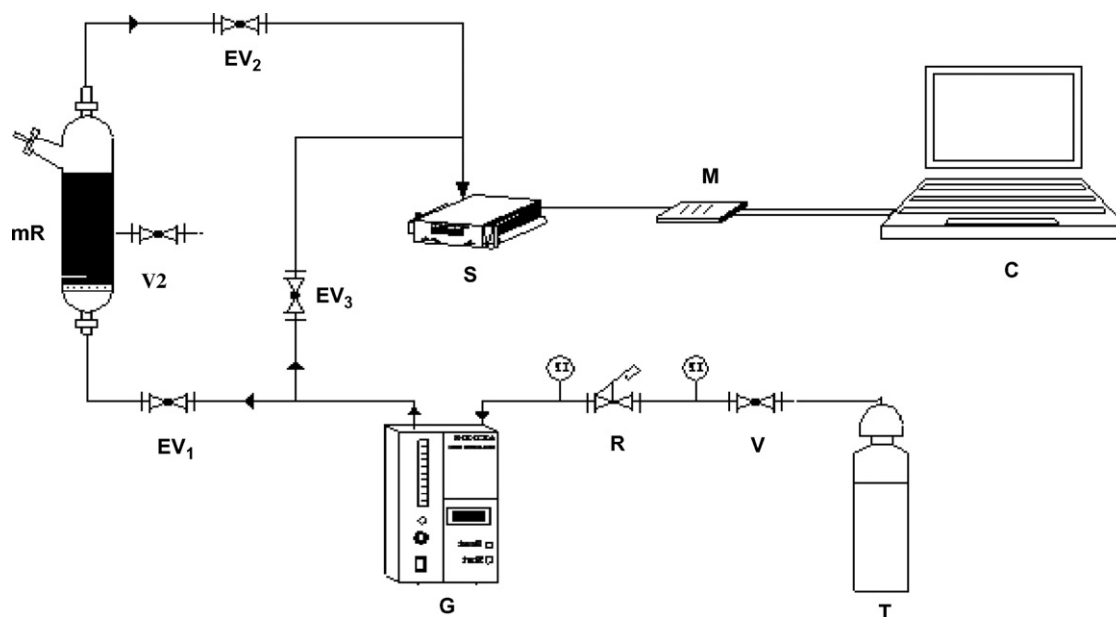
Fig. 1. Schematic diagram of the ozonation apparatus: (R) reactor, (T) oxygen tank, (V) valve, (R) manifold, (G) ozone generator, (EV1, EV2, EV3) bypass system with electrovalves, (S) ozone analyzer, (M) data acquisition system, and (C) PC.

in the mass of the precipitated sludge from 81.80 to 89.90% and of the color from 92.7 to 96.10% were determined.

3.2. Comparison of the sludge structure

The structure of the native and precipitated sludge was analyzed by the IR technique. In Fig. 2(a and b) the corresponded IR spectrums are presented. As it can be seen, spectrums are very similar: so, both spectrums have the characteristic peaks 1131, 1594 and 3415 cm^{-1} that correspond to the lignin. But, in the spectrum of lignin precipitated by sulfuric acid, there are presented the characteristic picks 1116 and 1209 cm^{-1} that are very intense and correspond to the $-S=O$ groups. Based on the IR spectrum comparisons is possible to conclude that the sulfolignin complex was obtained during the precipitation in the presence of sulfuric acid.

3.3. Ozonation of residual water at the different pH after the precipitation stage

The residual water after the precipitation and filtration was ozonated at the different initial pH 1, 3, 8 and 12 in order to compare the pH effect on the decoloration and decomposition dynamics, takes in the account that the color reduction does not necessarily mean that total decomposition of the pollutants and, in some cases, the color reduction is related to the production of highly toxic intermediates. The samples precipitated at the pH 1 were ozonated at the pH 1, 8 and 12, (Figs. 3 and 4) and the samples precipitated at the pH 3 were ozonated at the pH 3, 8 and 12, (Figs. 5 and 6) but pH was not controlled during the process. In Figs. 3 and 4 the dynamics of the residuals decomposition (254 nm) and decolorization (465 nm) was presented. As it can be seen, the decolorization dynamics was more rapidly compared with the residuals decomposition (the removal of 85% during 30 min, and of 70% during 60 min, respectively), but

the final results of the residuals remove in ozonation was the same (see Tables 3 and 4) without the significant effect of the pH.

Among those proposed in literature, the BOD$_5$/COD ratio is commonly used as a biodegradability measure [41–44]. The effect of ozonation to the biodegradability of dissolved contaminants by the determination of the BOD$_5$/COD ratio before and after the ozonation was investigated. An increase of the BOD$_5$/COD ratio after ozonation would indicate an increase in the proportion of COD amenable to biodegradation.

In Table 3 the variation of COD, BOD$_5$ and biodegradability in ozonation during 25 and 60 min were presented. As it can be observed, the precipitation conditions influence on the initial biodegradability of residual water. So, the change of the precipitation pH from 3 to 1 provokes the increase of the initial biodegradability from 0.067 to 0. 11, this value is in agreement with the one reported by [33]. Nevertheless, the final biodegradability of the treated water after the ozonation during 25 min has, practically, the same values (0.25–0.29 or 0.24–0.31) that independent on the precipitation conditions, and in the prolonged time of ozonation up to 60 min also it was not changed. Based on the results presented above, we can conclude that the precipitation conditions were not influenced on the final biodegradability of water treated by ozone. In this particular case, the lignin and their derivates are destroyed in ozonation during 25 min with the total decolorization.

3.4. Identification of the products formed in ozonation

In Table 4 the products formed in ozonation were presented. As it can be seen, the main compounds were fumaric, maleic, malonic and formic acids, the last acid may be interpreted as the final ozonation product. This mixture of simple's acids is biodegradable and not toxic. The maximum concentration of formic acid was formed in ozonation at pH 1 during 25 min that corresponds the

Table 2
Effect of the sulfuric acid concentration on the precipitation efficiency for diluted samples (1:10).

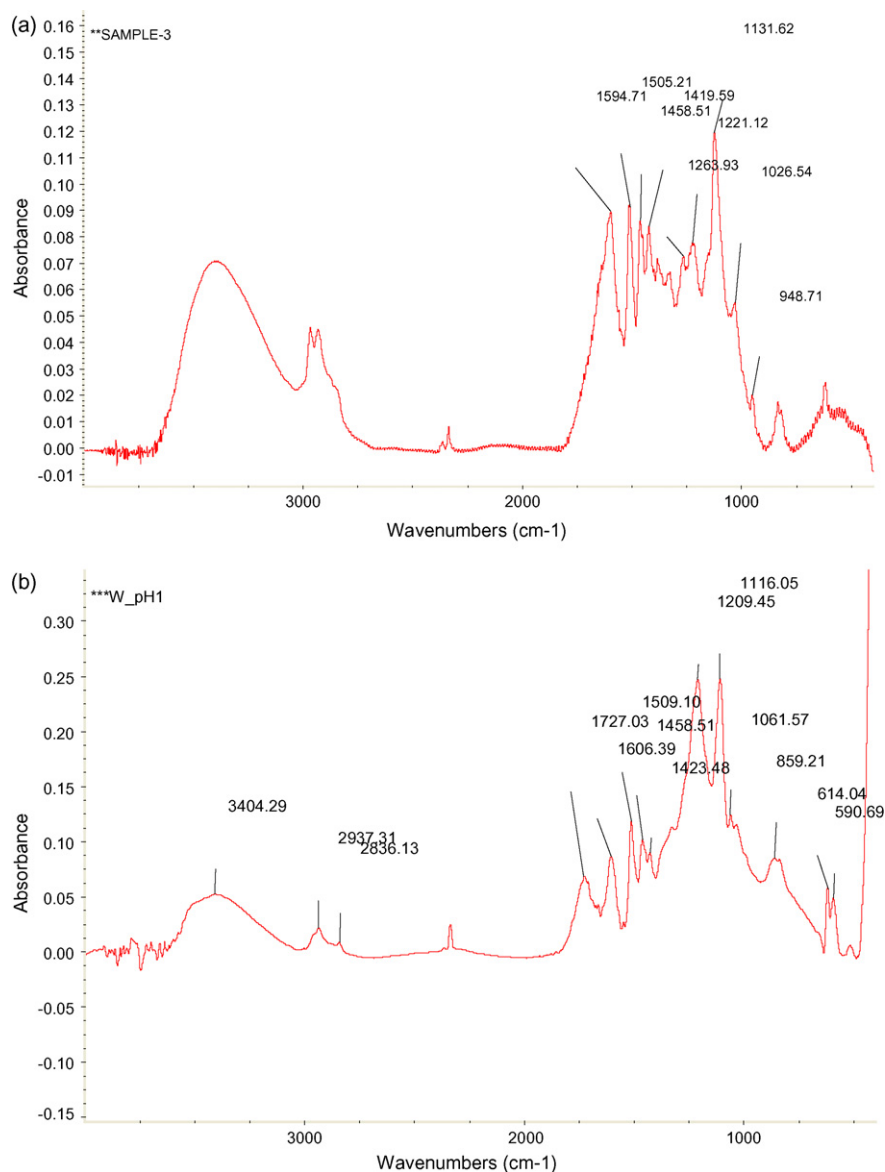| Acid concentration (vol%)	pH	Color	COD (mg/L)	BOD$_5$ (mg/L)	Color decrease (%)	Sludge precipitation (%)
2.25	1.00	430	1599	175	96.1	89.9
1.01	3.0	800	1819	123	92.67	81.80

Fig. 2. IR spectrums of the native (a) and precipitated sludge (b).

minimum maleic acid concentration (29.42 ppm). By this reason, we may conclude that the best conditions for the lignin precipitation and posterior ozonation were curried out at pH 1.

3.5. Estimation of the lignin decoloration constants

The kinetics of ozonation of the model compounds as guayacol, maleic acid, phenol derivatives has been studied by several researchers [46–48]. In this study the decoloration rate constants were estimated realizing the numerical calculations based on the simplified mathematical model, which have been used in the previous investigation [45,49,50] for the kinetic constants calculation, using the gas phase ozone concentration variation in the reactor outlet and the lignin decoloration dynamics. The differential neural networks (DNN) approach can be used to estimate on-line the ozonation kinetic parameters by the analytical analysis described

Table 3
Variation of COD, BOD$_5$ and biodegradability (BOD$_5$/COD) of treated water during ozonation.

pH	COD$_i$ (mg/L)	BOD$_{5i}$ (mg/L)	(BOD$_5$/COD)$_i$	COD$_{25}$ (mg/L)	BOD$_{5,25}$ mg/L	(BOD$_5$/COD)$_{25}$	COD$_{60}$ (mg/L)	BOD$_{5,60}$ (mg/L)	(BOD$_5$/COD)$_{60}$
Precipitation at pH 1									
1	1599	175	0.11	1400	336	0.24	1290	298	0.23
8	1599	175	0.11	1240	295	0.24	810	306	0.38
12	1599	175	0.11	1150	358	0.31	1115	343	0.31
Precipitation at pH 3									
3	1819	123	0.067	1226	350	0.29	1019	328	0.31
8	1819	123	0.067	1153	293	0.25	1186	306	0.26
12	1819	123	0.067	1139	298	0.26	1066	306	0.29

Table 4
Products formed in ozonation of lignin and its derivatives.

pH of ozonation	Ozonation time (min)	Concentration (ppm)				
		Maleic acid	Malonic acid	Formic acid	Fumaric acid	Catechol
1	25	29.42	17.80	407.00	26.30	5.90
	60	32.17	ND	375.70	21.00	1.80
8	25	39.02	ND	ND	12.50	0.61
	60	46.42	ND	ND	6.10	ND
12	25	50.41	ND	ND	5.40	ND
	60	50.44	ND	ND	4.00	ND
3	25	13.20	ND	326.60	38.80	ND
	60	14.89	ND	239.40	23.80	ND
8	25	20.67	37.20	ND	12.00	ND
	60	19.80	41.20	ND	6.40	ND
12	25	4.44	8.80	ND	4.10	ND
	60	20.91	47.80	ND	3.90	ND

by DNN:

$$\frac{d}{dt}\hat{c}_t^i = -\frac{k_i \hat{c}_t^i \hat{Q}_t}{v^{liq}} \quad (i = 1, 2, \ldots, n) \tag{1}$$

Here $(\hat{c}_t^i)$ is the numerical estimate (as a result of DNN application) of contaminant concentration during the overall reaction ($\mathrm{M\,L^{-1}}$), while $(\hat{Q}_t/v^{liq})$ is the estimate of the "DNN-liquid phase ozone concentration" ($\mathrm{M\,L^{-1}}$), $\hat{Q}$ is the estimate of the total ozone amount into the liquid phase and (v^{liq}) is the total liquid phase volume (L).
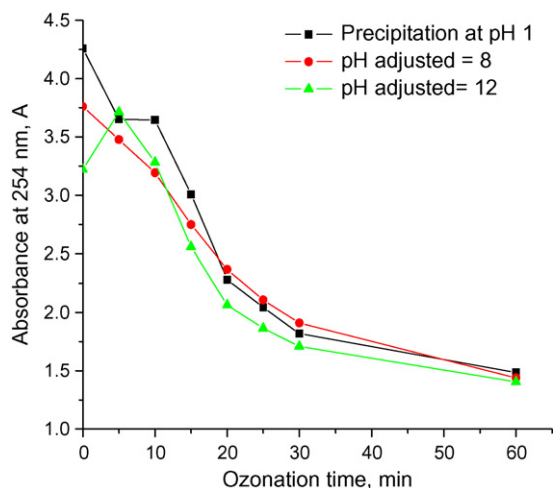
The technique, based on DNN, is usually used to obtain the physical "model-free" representation of some dynamics as it was mentioned before [28]. Observe that $\hat{c}_t$, $\hat{Q}_t$ as well as $(d/dt)\hat{c}_t$ are available. It is possible to define the LS (least square) estimates of $k_i(t)$ as the solution of the following optimization problem:

$$k_{i,t}^* = \arg\min_{k_t} \int_0^t \left(\frac{d}{d\tau}\hat{c}_\tau^i + k_i \frac{\hat{c}_\tau^i \hat{Q}_\tau}{v^{liq}} \right)^2 d\tau \tag{2}$$

The solution is as follows:

$$k_{i,t}^* = -\frac{v^{liq} \int_0^t \hat{c}_\tau^i \hat{Q}_\tau (d/d\tau)\hat{c}_\tau^i d\tau}{\int_0^t \left(\hat{c}_\tau^i \hat{Q}_\tau \right)^2 d\tau} \tag{3}$$

With the experimental data of the lignin decoloration (Figs. 4 and 6), the corresponded ozonograms and the equation set (3) the decoloration rate constants for the diluted sample of the pre-treated

effluent was calculated. In Table 5 the calculated constants were presented. In the base of the obtained results, it was been observed the significant effect of pH in precipitation as well as in ozonation. So, with the pH decrease up 3 to 1 the decoloration constants
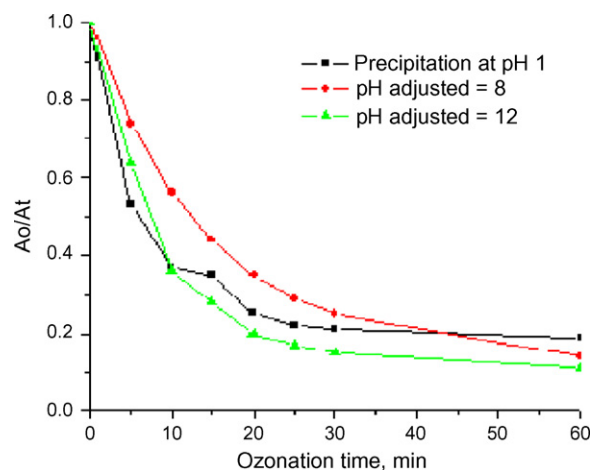
Fig. 4. Lignin decoloration in ozonation at different pH (465 nm): at pH 1 (■), at pH 8 (●) and at pH 12 (▲). The precipitation pH is 1.
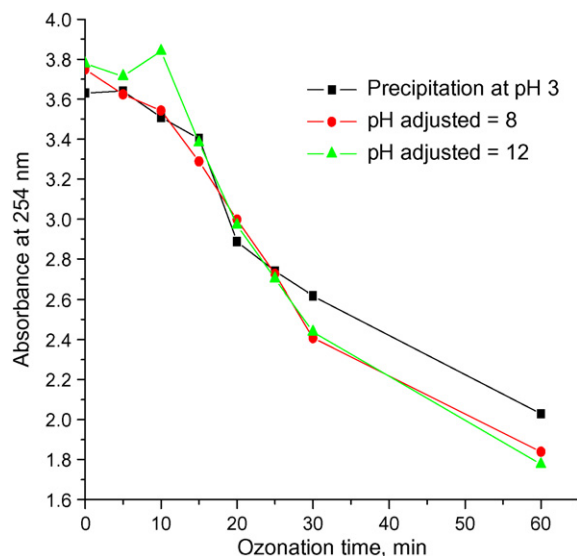
Fig. 5. Lignin decomposition in ozonation at different pH (254 nm): at pH 3 (■), at pH 8 (●) and at pH 12 (▲). The precipitation pH is 3.

Fig. 3. Lignin decomposition in ozonation at different pH (254 nm): at pH 1 (■), at pH 8 (●) and at pH 12 (▲). The precipitation pH is 1.

Fig. 6. Lignin decoloration in ozonation at different pH (254 nm): at pH 3 (■), at pH 8 (●) and at pH 12 (▲). The precipitation pH is 3.
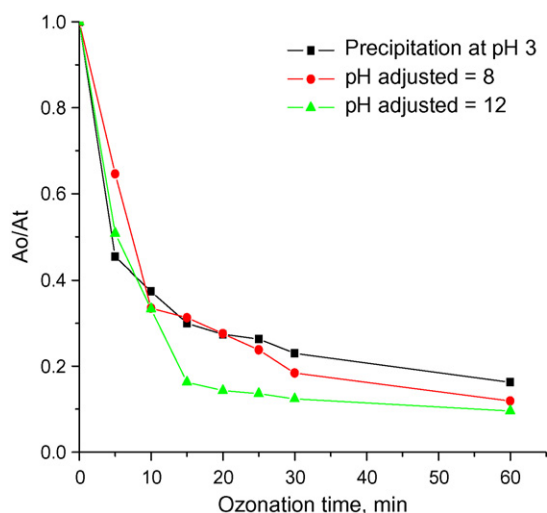
Table 5
Effect of pH on the lignin decoloration in ozonation.

pH of precipitation	pH of ozonation	Decoloration constant, k (M^{-1} seg^{-1})
	1	2.98×10^2
1	8	2.14×10^2
	12	4.32×10^2
	3	6.75×10^2
3	8	10.46×10^2
	12	5.45×10^2

increase. On the other hand, if the ozonation pH was changed, the mayor constant at the pH 12 (4.32×10^2 L/mol s) was obtained for the first case, and at the pH 8 (10.46×10^2 L/mol s) for second case. It is can be observed, the lignin decoloration kinetics has the follow order:

- pH 12 > pH 1 > pH 8 for the precipitation at pH 1.
- pH 8 > pH 3 > pH 12 for the precipitation at pH 3.

The possible explanation of the precipitation conditions effect on the decoloration kinetics is the variation of the composition of contaminants dissolved in water after the precipitation with sulfuric acid.

4. Conclusions

The following conclusions may be done based of the results of this study:

1. The previous precipitation of the diluted samples with sulfuric acid decreases the initial color in 96% and the formed sludge in 90%.
2. The coagulated sludge contains sulfolignin complex, which may be obtained during the precipitation in the presence of sulfuric acid.
3. In the decomposition of the lignin derivatives dissolved in the filtered water after the precipitation with ozone during 25 min are formatted the simple acids mixture (formic, maleic and malonic).
4. The precipitation pH has significant effect on the efficiency of sulfolignin formation as well as on the lignin decolorization kinetics. It very probable, that the different composition of the dissolved contaminants were formed in the precipitation stage depend-

ing on pH. By this reason, the decolorization rate has the follows order:
- pH 12 > pH 1 > pH 8 for the precipitation at pH 1.
- pH 8 > pH 3 > pH 12 for the precipitation at pH 3.
5. The biodegradability of the lignin decomposition products was increased in ozonation at the four pHs (1, 3, 8 and 12) to 0.24–0.29 during 25 min.

Acknowledgements

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