

Electrochemical degradation of industrial alkali lignin

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Abstract. At present, the wastewater, produced in pulp and paper industry, which contains lignin molecules, is still difficult to treat due to the structure complexity of lignin. In this paper, the industrial alkali lignin (AL) was treated with a Violuric acid(VA)-mediated electrochemical degradation system, and the lignin degradation efficiency at different treatment parameters including temperature, time, VA concentration, electrolyte concentration, voltage and lignin concentration were discussed in detail. The changes of chemical oxygen demand (COD) and total carbon content (TOC) of this lignin-containing solution were also monitored. The results showed that in this electrochemically catalyzed system containing Ti/ Sn-Sb-Ir as anode, the industrial AL can be oxidized into small molecular products. The optimum conditions of electrochemical degradation of AL are time 8 h, voltage 5.5 V, temperature 60 °C, alkali lignin 10 g/L, VA 2 mmol/L and Na₂SO₄ 0.2 mol/L. At this condition, higher than 70 % AL can be oxidized and become water soluble, the COD and TOC of this AL-containing solution reduced by 45 % and 20 % respectively. The color of the solution changed from dark to light yellow. This process offered a new process of treating/oxidizing AL-containing wastewater in pulp and paper industry.

Introduction

Lignin is the second most abundant biopolymer after cellulose content on earth, constituting 30% of the dry weight of softwood and 20% of hardwood [1]. However, due to heterogeneity, relative molecular mass polydispersity, water insolubility, separation and purification is difficult. So it has not been put into good use in industry. Most of it was discharged into rivers or burned in the form of black liquor directly, causing a great deal of environmental pollution and waste of resources [2]. On the other hand, in pulp and paper mills, water recycling is difficult because that the accumulation of lignin and derivatives in the recycled water can cause a drop such as sheet forming, sizing, yellowing in paper quality. Fortunately, the lignin molecules containing a variety of reactive groups, such as carbonyl, methoxy, hydroxy, benzene, etc., have the possibility to participate in various reactions, so utilizing it becomes possible. Thus, there is a great interest in lignin oxidization to make it soluble or make the wastewater containing AL meet effluent discharge standards and water saving requirements. Therefore, an effective lignin removal approach with low cost and non-secondary pollution is desired.

Electrochemical oxidation has been expected as an fantastic alternative in polymer modification and wastewater treatment attribute to its easy operation, wide range of treatment conditions and environmental friendliness[3–9]. On the other hand, in the paper industry, electrochemical bleaching technology is a promising approach for the development of environmentally friendly processes in pulp bleaching. This technology is relative clean, compared with traditional pulp

bleaching process[10,11]. In this paper, this electrochemical oxidization/degradation system was applied to AL to degrade it. The influences of electrochemical degradation conditions on degradation effectiveness were discussed in detail.

Experimental

Chemicals. Violuric acid monohydrate was purchased in analytical grade from Fluka-Sigma-Aldrich and used without further purification. Sodium sulfate was in analytical grade. Industrial alkali lignin of poplar came from a pulp mill in Jinan.

Electrochemical mediated degradation system. The electrode cell consists of a titanium anode coated with Stannum/Stibium/ iridium and a stainless steel cathode. The distance between the anode and cathode is 5 cm and the effective electrode surface is $3.5 \times 4 \text{ cm}^2$. The electrochemical treatment process is as follows, lignin and sodium sulfate were added into the electrolytic cell, and then added a certain amount of water. Finally, violuric acid was added into the suspension solution. The electrolytic cell was put into a water bath which was set at required temperature. When temperature of this system was increased to the required temperature, the cathode and anode were inserted into the suspension, and switch the power on to start the electrochemical degradation. After the degradation, some amount of solution was taken out for measuring the UV absorbance.

Analysis of the reaction mixture. UV spectrophotometer(845x, Agilent) was used for measuring the content of benzene derivatives in aqueous solution, as a result of process optimization. Each sample was diluted 500-fold. Lignin has a strong absorption peak at 205 nm of the ultraviolet region. According to this, the transmittance at this wavelength was used to calculate the lignin degradation ratio according to the formula (1).

$$D = \frac{A(D)}{A(AL)} \times 100\% \quad (1)$$

D-degradation ratio

A(AL)- absorbance of AL solution before degradation at 205 nm

A(D)- absorbance of AL solution after degradation at 205 nm

COD(KDB-III) and TOC(TOC-LCPH) were used to characterize the treatment effect for lignin-containing wastewater under optimal process conditions. COD_{cr} adopted the national standard (GB11889-11915-89).

Results and discussion

Effect of time on lignin degradation. Fig.1. shows the effect of treatment time on lignin degradation. From Fig. 1, it can be seen that prolonging the electrochemical treatment time improves the lignin degradation. The degradation ratio was increased from 30 % at 4 h to 62 % at 10 h. When the treatment time is longer than 8 h, the increase of degradation ratio is marginal. One interesting thing in Fig.1 is that the degradation ratio decreased when the time increased from 2 h to 4 h. The reason here might be some lignin polymerization took place at this period, as reported by Qiu et al.[12]. Therefore, the optimal time was 8 h.

Effect of temperature on lignin degradation. The effect of temperature on lignin degradation was shown in Fig. 2. Fig. 2 shows that when the temperature is lower than 50 °C, the degradation ratio was less than 40 %. When the temperature reached 60 °C, the degradation was obviously increased, reached around 60 %. Further increase the temperature to 80 °C, the increase of lignin

degradation ratio was not obvious. Higher temperature benefits the lignin degradation shows that this oxidization reaction for degrading lignin might be an endothermal reaction. Considering the economic and energy issues, the optimal temperature 60 °C was chosen.

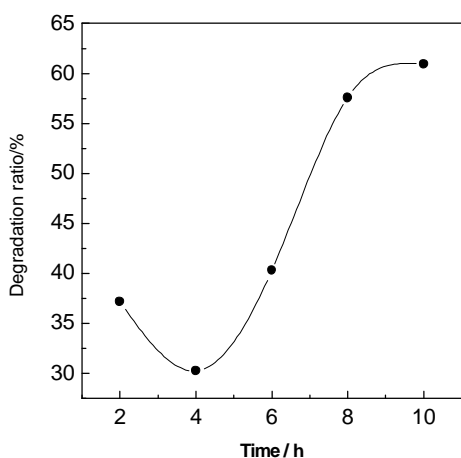


Fig.1. Effect of time on AL degradation
(voltage4.5 V, temperature 60 °C, AL 10 g/L,
VA 3 mmol/L ,Na₂SO₄ 0.2 mol/L.)

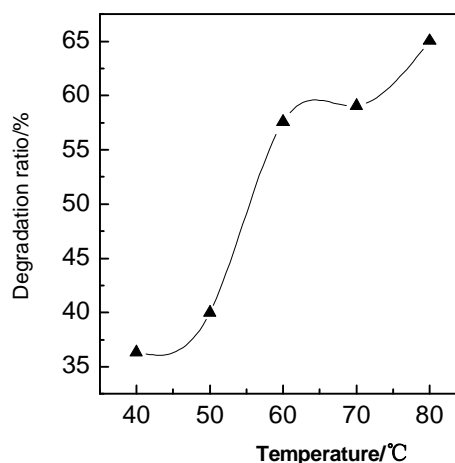


Fig.1. Effect of temperature on AL degradation
(time 8 h, voltage 5.5 V, AL 10 g/L,
VA 3 mmol/L, Na₂SO₄ 0.2 mol/L.)

Effect of voltage on lignin degradation. The effect of voltage on lignin degradation was shown in Fig.3. As can be seen from Fig.3., with the increasing of voltage the degradation ratio of lignin increased. As we all know the higher electrode voltage, the stronger oxidation ability of the electrode . The data in Fig.3 also indicate that when the voltage is higher than 5.5 V, the increase of lignin degradation ratio is marginal. Since at 5.5 V the degradation ratio reached a ceiling level, combined with energy conservation considerations, the optimize voltage was 5.5 V.

Effect of VA concentration on lignin degradation. Fig.4. shows the effect of VA concentration on lignin degradation. The data in Fig. 4 shows that increasing the VA concentration in electrolytic solution firstly improved the lignin degradation, and when the concentration was at around 2.0 mmol/L, the degradation ratio reached the maximum value, around 68.5 %. After that, the degradation ratio decreased to 62 % at 3.0 mmol/L. The optimal amount of VA in electrolytic solution was 2 mmol/L.

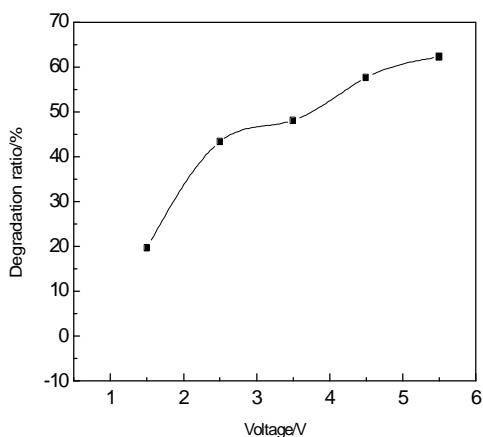


Fig.3.Effect of voltage on AL degradation
(time8h,temperature6 °C,AL10g/L,VA
mmo/L , Na₂SO₄ 0.2 mol/L)

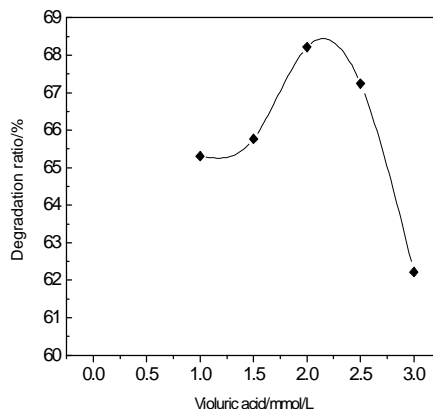


Fig.4.Effect of VA on AL degradation
3 (voltage5.5 V, temperature60 °C, AL10 g/L,
Na₂SO₄ 0.2 mol/L)

Effect of lignin concentration on lignin degradation . The effect of lignin concentration on lignin degradation was shown in Fig.5. It can be seen from Fig.5 that at lignin concentration of 10 g/L in electrolytic solution, the degradation ratio can reach 68.2 %. Lower or higher than this concentration, 10 g/L, decreased the degradation ratio. The reason for this is that when lignin concentration was very low, the contact opportunities between lignin molecules and anode were very less. When the concentration is too high, the lignin in the electrolytic solution would cover the anode surface, which hampered the electrochemical oxidization. Therefore, the optimal lignin concentration was 10 g/L in the electrolytic solution.

Effect of sodium sulfate concentration on lignin degradation. Fig.6 shows the effect of sodium sulfate concentration on lignin degradation. As can be seen from Fig. 6, the lignin degradation ratio obviously increased when the concentration of sodium sulfate increased from 0.1 mol/L to 0.25 mol/L. Further increasing the concentration didn't improve the degradation ratio and the degradation ratio reached a ceiling level, around 72 %. The optimum concentration of sodium sulfate was 0.2 mol/L.

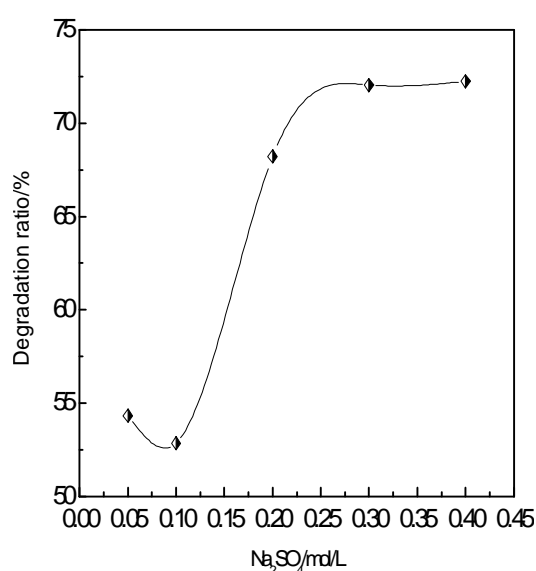
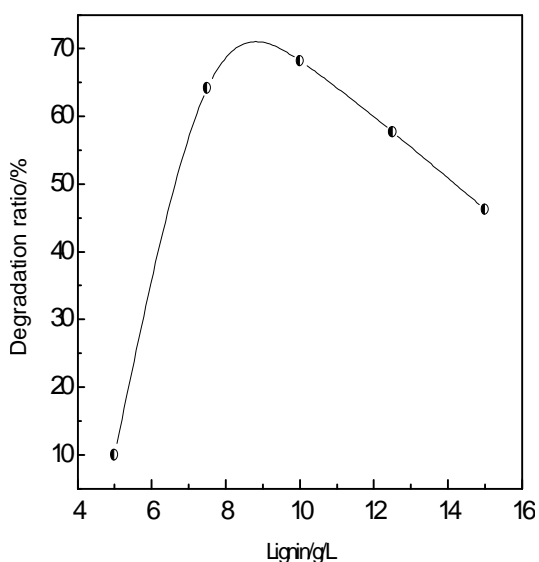


Fig.5.Effect of lignin concentration on lignin degradation(time8h, temperature60°C, voltage 5.5 V, VA 2 mmol/L ,Na₂SO₄ 0.2 mol/L)

Fig.6.Effect of sodium sulfate on lignin degradation(time8h,temperature 60°C, voltage 5.5 V, VA 2 mmol/L , AL 10 g/L)

UV, COD and TOC change of lignin solution during electrochemical treatment. Fig.7.shows the COD and TOC change during the electrochemical treatment. It is obvious that the COD and TOC of the lignin solution decreased with the prolongation of treatment time. At 8 h treatment time, the COD decreased to around 3000 mg/L, from original 5500 mg/l, reduced by 45 %, and the TOC decreased to 1600 mg/L, from original 2000 mg/L, reduced by 20 %, which illustrates that part of lignin in the electrolytic solution was oxidized completely. Fig. 8 also demonstrated that the characteristic absorbance peak at 205 nm presenting the benzene ring decreased with the increase of treatment time, illustrating some of benzene ring in lignin was opened through this electrochemical technology. Fig. 9 shows the color change of lignin solution before and after the electrochemical treatment. As shown, the solution became clear and the color was changed from dark to light yellow after electrochemical treatment, which illustrated this technology can be potentially used as treatment of wastewater containing lignin or modification of industrial lignin.

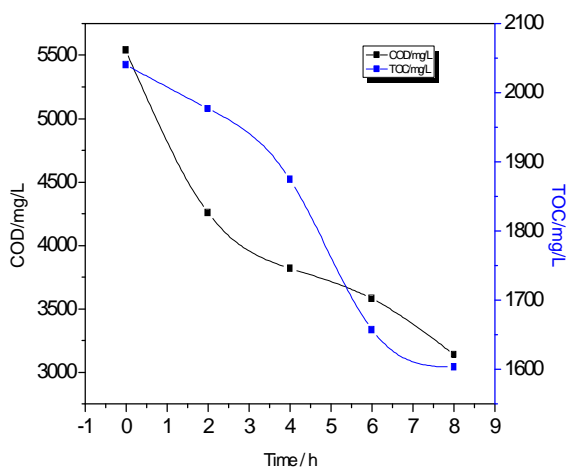


Fig.7.COD and TOC at different time (temperature60°C,AL 10 g/L, VA 2 mmo/L ,Na₂SO₄ 0.2 mol/L, voltage5.5 V)

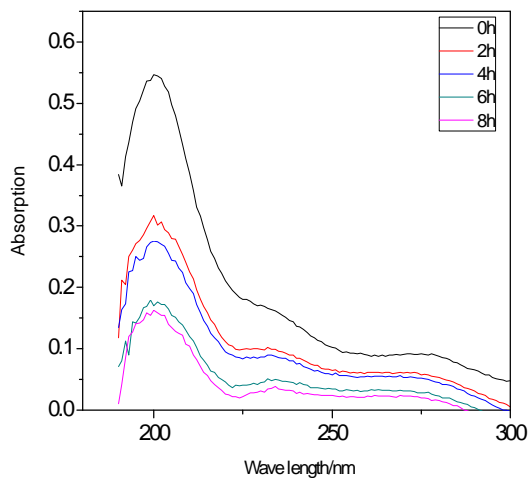


Fig.8. UV absorption at different time (temperature60°C,AL10g/L, VA2 mmo/L ,Na₂SO₄ 0.2 mol/L,voltage5.5 V)



Fig.9.Comparison of the reaction solution

Conclusions

The voluric acid catalyzed electrochemical treatment system can be successfully used to oxidize/degrade the lignin-containing wastewater produced in pulp and paper industry. The optimum treatment conditions of this process are 8 h of treatment time, 5.5 V of voltage, 60 °C of temperature, 10 g/L of alkali lignin, 2 mmol/L of violuric acid and 0.2 mol/L of Na₂SO₄. Under these conditions, 70 % of lignin in the electrolytic solution was degraded, which was confirmed by UV spectrum. After 8 h treatment, the COD and TOC reduced by 45 % and 20 % respectively, which offered a new process of treating/oxidizing AL-containing wastewater in pulp and paper industry.

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