Impact of Continuous Electrochemical Degradation of Eucalyptus Alkaline Peroxide Mechanical Pulping Wastewater

Ming Li *

Levels of pollutants in pulp and papermaking wastewater are an important issue for environmental protection. High concentrations of contaminants can seriously affect the environment if they are not processed. Therefore, treating paper wastewater is a necessary option for governments to select appropriate treatment methods to remove the multi-component pollutants. In this study, the impact of continuous electro-degradation of eucalyptus alkaline peroxide mechanical pulping wastewater was studied. An electrolytic treatment method performed at a low voltage was used. Through the electrolysis method, the wastewater chemical oxygen demand was decreased by 98%, and color-generating groups were nearly all destroyed. During the electrolysis process, the pH value of wastewater continuously decreased and finally reached 2.5. Lowering the pH of the waste solution will help increase the electrolysis efficiency of the wastewater. A total of 5.8 g of alkali was obtained. The wastewater precipitation before and after electrolysis was analyzed by X-ray photoelectron, Fourier transform infrared, and energy-dispersive X-ray spectroscopies.

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Contact information: Faculty of Light Industry, State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology (Shandong Academy of Sciences), Ji’nan City 250353 PR China; *Corresponding author: mingliscut@hotmail.com

INTRODUCTION

Paper is an important product for humans, and pulp and paper is a water-consuming industry (Jaafarzadeh et al. 2017). It is usually hard to remove the high-level pollutants of COD in wastewater (Garg et al. 2005; Liang et al. 2021). Water is a precious resource for human survival and an indispensable resource for human production (Mwangi et al. 2021). The quantity of wastewater discharged by the paper industry is large (Carvalho Neves et al. 2020; Mainardis et al. 2020). Therefore, the pollution problem of pulping wastewater is always a main issue of environmental protection (Shojaei et al. 2021). The paper manufacturing process is the conversion of wood or other biomass into paper products, of which the key steps are pulping and bleaching. Overall, the essence of pulping is the removal of lignin, some hemicellulose (Haq et al. 2020), and the retention of a maximum amount of cellulose (Li et al. 2019). The composition from different pulping raw materials and pulping methods varies greatly, containing both organic and inorganic components. The inorganic parts mainly refer to the residual chemicals, the metal salts produced by the chemicals added, and the inorganic parts carried by the raw materials themselves. The organic parts mainly contain degradation products and leachates of wood, such as lignin,
hemicellulose, starch, resin, pigment, and organic acids (Carvalho Neves et al. 2020). The pulp and papermaking industry has been constantly improving its technology in an attempt to further reduce its impact on the environment. Wastewater treatment technologies are not a single technology but a combination of technologies. The conventional treatment technologies for pulp and paper wastewater include electrolysis (Mwangi et al. 2021; Sivaranjani et al. 2021), adsorption, membrane separation (Poojamnong et al. 2020), biological treatment technologies (Sharma et al. 2021), advanced oxidation technologies (Pierpaoli et al. 2021; Ribeiro et al. 2020; Palmas 2021), etc. However, there still exists a high energy consumption issue (Chen et al. 2020). Electrolysis is a typical wastewater treatment technology. In traditional electrolysis, the anode is soluble, meaning that it is constantly oxidized and corroded under the power of electricity to produce free radicals, which oxidize and reduce the organic matter and various color-forming groups in the wastewater to degrade the organic matter and remove the color-forming groups. With the continuous development of electrolysis technology, electrolysis can be performed at low voltages and can reduce costs. It can be powered by solar panels, giving the possibility to treat wastewater with clean energy.

Titanium (Ti) is a widely distributed element. Ti plays an irreplaceable role in many fields (Jiao et al. 2020). The surface of Ti metal, under typical conditions, will consist of Ti oxides. The oxide film, though very thin, can contribute strong resistance of the metal to corrosion. Ti is often used as an electrode matrix because of its good conductivity and stability (Du et al. 2022). Ghimire et al. (2019) used electrochemistry with a Ti anode to remove ammonia nitrogen and COD from domestic sewage. Safwat (2020) used electrocoagulation process with titanium to treat real printing wastewater for removal of COD. In this study, a Ti plate was combined with electrolysis to treat APMP wastewater.

Alkaline peroxide mechanical pulping (APMP) process has obvious advantages such as high yield, good pulp strength, less pollution, and low energy consumption (Chen et al. 2021; Zhao et al. 2004). Usually, the APMP wastewater is treated by biological method. Liu et al. (2020a) used Aspergillus niger S13 aerobic fermentation to treat APMP pulping effluent. Yang et al. (2019) selected Phanerochaete chrysosporium to treat APMP wastewater. The biological treatment process is relatively complex.

Electrochemical processing has been shown to be technically and economically suitable for large-scale wastewater treatment (Coimbra et al. 2021). It is a suitable choice to use low-pressure electrolysis to treat APMP wastewater to comply with the concept of green development. In this work, the eucalyptus APMP wastewater was investigated and the depolymerization phenomenon during the electrolysis process was analyzed.

**EXPERIMENTAL**

**Materials**

The eucalyptus APMP wastewater was obtained from Guangxi Jingui Pulp & Paper Co., Ltd. (Qinzhou, Guanxi, China). The chemical oxygen demand (COD), solid content, inorganic content, organic content and pH value of the collected APMP wastewater were 13,199 mg/L, 22.73g/L, 9.11%, 13.62%, and 7.5, respectively. Ammonium iron (II) sulfate, potassium dichromate, and potassium bromide were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Potassium bromide was of spectral purity. The other chemicals were of analytical grade and from commercial sources.
Methods

A 500-mL glass beaker was used as an electrolytic cell. The Ti plate (10 cm × 6 cm) was put into the beaker as an anode, and the cathode was a Ni-chrome (Cr) alloy electrode tube inside a PVC pipe with a cation exchange membrane. Finally, wastewater was added to the beaker as an electrolyte, wired, and connected to the power supply (5.0 V). The device is shown in Fig. 1(a). Alkali will be generated in the cathode chamber of the PVC pipe, and Na⁺ will enter the cathode PVC pipe through a cation exchange membrane to generate sodium hydroxide with OH⁻. A small amount of hydrogen may be produced during the reaction. Therefore, the work should be kept ventilated.

The CODs of APMP wastewater were measured based on Standard Methods for Examination of Water and Wastewater (APHA 1985) with slight modification. The COD (mg/L) was calculated using Eq. 1,

\[
COD_{(mg/L)} = \frac{C \left( \text{NH}_4 \right) \text{Fe} \left( \text{SO}_4 \right) \cdot 6 \text{H}_2 \text{O} \left( V_1 - V_2 \right) \times 8000}{V_0}
\]

where \( V_0 \) is mL of original sample; \( V_1 \) represents mL of ferrous ammonium sulphate for blank titration; \( V_2 \) represents mL of ferrous ammonium sulphate for sample titration; \( C \) is normality of ferrous ammonium sulphate; and 8000 is the unit conversion value.

Characterization

The FTIR spectra of the samples were acquired using 32 scans on a Vector 33 spectrometer (Tensor 27; Bruker Corporation, Ettlingen, Germany) in the range of 400 to 4000 cm⁻¹. The samples were mixed with KBr and pressed. X-ray photoelectron spectroscopy (XPS) (Axis Ultra DLD, Kratos Analytical Ltd., Manchester, UK) was used to analyze C and O. The pH value was tested using a pH meter (PHS-25, Leici, Shanghai, China). Energy dispersive X-ray (EDX) (Shimadzu SS-550, Shimadzu Corporation, Kyoto, Japan) spectrometry was used to analyze the elements of filtering precipitate from APMP wastewater.

RESULTS AND DISCUSSION

The EDX results showed that carbon (40.10%) and oxygen (36.78%) were the major components of the APMP wastewater filtration precipitates. The third-largest component was sodium at 16.50%, which provided confirmation of the collected alkali. The content of other elements, such as magnesium, aluminum, silicon, and phosphorus, were less, as shown in Table 1. In the electrolysis process of 500 mL wastewater, alkali was collected from the cathode chamber of PVC pipe every day. A 5.8 g alkali could be collected per 500 mL of APMP wastewater.

Table 1. Elements of the Filtration Precipitates from APMP Wastewater

<table>
<thead>
<tr>
<th>No.</th>
<th>Element</th>
<th>wt%</th>
<th>No.</th>
<th>Element</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>36.78</td>
<td>6</td>
<td>Si</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>40.10</td>
<td>7</td>
<td>P</td>
<td>0.46</td>
</tr>
<tr>
<td>3</td>
<td>Na</td>
<td>16.50</td>
<td>8</td>
<td>S</td>
<td>0.72</td>
</tr>
<tr>
<td>4</td>
<td>Mg</td>
<td>0.16</td>
<td>9</td>
<td>Cl</td>
<td>1.46</td>
</tr>
<tr>
<td>5</td>
<td>Al</td>
<td>0.16</td>
<td>10</td>
<td>K</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>100.02</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The COD is an index to measure the relative content of organic matter in wastewater, and the change in COD value can reflect the effectiveness of wastewater treatment. Figure 1(b) shows the influence of reaction time on the APMP wastewater with respect to COD. After 264 h of electrolysis, the wastewater COD decreased from 13,200 mg/L to 251 mg/L. The color in the wastewater was attributed mainly to lignin-based substances. Under the electrolysis, free radicals reacted with such groups in a series of reactions, unsaturated groups were destroyed, and the color of wastewater was diminished or even disappeared.

The wastewater chromaticity was reduced, and the color-generating groups were basically all destroyed. The colorimetric contrast between the wastewater at the beginning of electrolysis and the end of electrolysis was obvious. At the beginning of electrolysis, white foam would accumulate on the surface of wastewater. This was attributed to the process of electrolysis. Carbon dioxide, and possibly a small amount of hydrogen, were generated. A further result of electrolysis was the degradation of organic matter in wastewater degraded by oxidation. The main reasons are as follows: (1) Hydroxyl radicals (Liu et al. 2020b) can directly oxidize the organic pollutants in wastewater under the action of the electric field, thus destroying the color-generating groups and reducing COD and chromaticity. Overall, the color of the wastewater was destroyed; (2) The electric field induces the water to be converted partly into high-energy hydrogen atoms and hydroxyl radicals (Liu et al. 2020b). The hydroxyl radicals can chemically react with the organic pollutants in the wastewater, triggering the polymerization of organic molecules, thus precipitating the unsaturated color-generating groups and reducing the chromaticity (Han et al. 2016). In addition, when the reaction solution remained for 6 to 7 days after electrolysis, its chromaticity would increase.

Although the electrolysis mostly destroyed color-generating groups, some color-generating groups would still recover. When the electrolysis was restarted, the chromaticity decreased again. This shows that the color change of wastewater electrolysis is somewhat reversible. During the electrolysis process, the pH value of wastewater continuously decreased and finally decreased to 2.5, as shown in Fig. 2.

As shown in the figure, the initial pH value of wastewater was 7.5, which was weakly alkaline. The oxygen precipitation reaction was more likely to occur. After 264 h of reaction time, the pH of the electrolyte gradually decreased from 7.5 to 2.5 and remained stable, indicating that the concentration of H+ gradually increased during the reaction process. The pH value of the electrolyte finally reached the minimum value of
approximately 2.5. A dynamic balance was achieved because the OH⁻ was electrolyzed out of the reaction solution to produce H₂O with H⁺. In addition, under acidic conditions, organic acid ions in wastewater can generate organic acids with H⁺ generated by electrolysis.

![Fig. 2. The pH value change of the APMP wastewater](image)

To discuss the influence of pH value on electrolytic wastewater and avoid the interference of other factors, the pH value of the wastewater was changed using acidic wastewater (pH = 2.5) after electrolysis to investigate the effect of pH on the degradation of COD in wastewater. The phenomenon during electrolysis was recorded, as shown in Table 2.

**Table 2. The Effect of the Acid Solution on APMP Wastewater**

<table>
<thead>
<tr>
<th>No.</th>
<th>Wastewater (mL)</th>
<th>Acid Filter Liquor (mL)</th>
<th>Time (h)</th>
<th>pH Value</th>
<th>Reaction Phenomena; Precipitation Stratification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>0</td>
<td>168</td>
<td>4</td>
<td>The color was dark; Precipitation stratification appeared.</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>50</td>
<td>168</td>
<td>4</td>
<td>The color was dark; Precipitation stratification appeared.</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>100</td>
<td>144</td>
<td>3.5</td>
<td>Color changed to yellow; Precipitation stratification appeared.</td>
</tr>
<tr>
<td>4</td>
<td>500</td>
<td>150</td>
<td>120</td>
<td>3.5</td>
<td>Color changed to yellow; Precipitation stratification appeared.</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>200</td>
<td>96</td>
<td>3-2.5</td>
<td>Wastewater became clear; Precipitation stratification was obvious.</td>
</tr>
<tr>
<td>6</td>
<td>500</td>
<td>250</td>
<td>96</td>
<td>3-2.5</td>
<td>Wastewater became clear; Precipitation stratification was obvious.</td>
</tr>
</tbody>
</table>

The original wastewater showed noticeable solid-liquid stratification at 168 h of electrolysis. The lower layer was dark sediments, and the upper layer was brown liquid. With the extension of electrolysis time, the upper layer liquid of electrolyte gradually became clarified and transparent. As the amount of acidic filtrate increased, the stratification became faster. At the acidic filtrate and wastewater addition of 1:2 ratio (v/v), it reduced the electrolysis reaction time 72 h. Compared with Yang et al. (2019), the reaction time of 72 h was shorter than 168 h of Phanerochaete chrysosporium biological
treatment. During the electrolysis, the precipitation stratification appeared and polymers in the wastewater would precipitate under acidic conditions. Therefore, decreasing the pH of the waste solution would help to improve the efficiency of electrolysis. One effective way to accelerate the electrolysis reaction is to recycle the residual acidic solution of the upper layer. The original wastewater showed noticeable solid-liquid stratification at 168 h of electrolysis. The lower layer consisted of dark sediments, and the upper layer was a yellow-brown liquid. With the extension of electrolysis time, the upper layer liquid of electrolyte gradually became clarified and transparent. As the amount of acidic filtrate increased, the stratification became faster. At a ratio of acidic filtrate to wastewater addition of 1:2, the electrolysis reaction time was reduced by 72 h. Therefore, decreasing the pH of the waste solution would help to improve the efficiency of electrolysis. One effective way to accelerate the electrolysis reaction is to recycle the remaining acidic solution. However, the pH would need to be adjusted to neutral pH (pH about 7) before discharging the water.

![Fig. 3. XPS spectra of the APMP wastewater precipitation before (a) and after electrolysis (b)](image)

The wastewater precipitation before and after electrolysis was analyzed by XPS. The XPS spectra of the APMP wastewater precipitation before and after electrolysis are shown in Fig. 3. One absorbance peak near the horizontal coordinate 275 to 285 eV corresponds to the element C. The absorbance peak near the horizontal coordinate 520 to 577 eV corresponds to O. The two elements of carbon and oxygen are the most dominant in the structure of wastewater electrolytic precipitation. The result shows that the O element decreased noticeably, and the C element decreased slightly, with O/C going from 73% to 83%. As inferred, the groups associated with O are more easily degraded during the degradation and oxidation of wastewater precipitation.
FTIR analysis is an effective method for analyzing materials. FTIR spectra of the APMP wastewater precipitation are shown in Fig. 4. The absorbance peak of 3383 cm\(^{-1}\) is related to the -OH stretching vibration (Li et al. 2021). The absorbance peaks located at 2919 and 2849 cm\(^{-1}\) are C-H stretching vibrations of methyl and methylene groups. The absorbance peak at 1724 cm\(^{-1}\) is due to the C=O (unconjugated ketone, carboxyl, and ester) stretching vibrations (Joffres et al. 2014). The characteristic absorbance peak of the C=C vibration of lignin is near 1622 cm\(^{-1}\). The C-C-H (syringyl), and C-O (guaiacyl) stretching vibrations are at 1151 cm\(^{-1}\) (Shi et al. 2019), and 617 cm\(^{-1}\) is the C-H stretching vibration. The results indicate that the main components of APMP wastewater precipitate were lignin-based polymers. From Fig. 4(b), the most disrupted groups were C-H, and C=O, which indicates that the side chains of aromatic rings were more severely damaged by the action of electric field (Li et al. 2016). This was because the wastewater enters the electrolytic reactor. In the presence of H\(^+\), C=O changes from an unsaturated state to a saturated state. Na\(^+\) combines with OH\(^-\) to form NaOH.

In the presence of an electric field, the wastewater undergoes an oxidation reaction. The pollutants and organic matter of wastewater gain and lose electrons directly at the anode/cathode, which causes direct degradation of organic matter through oxidation/reduction reactions. Moreover, the electrolysis process can generate high-energy hydrogen atoms and hydroxyl radicals, which can degrade the wastewater by free radicals. The wastewater in the electrolysis tank contains organic acid sodium salt, and Na\(^+\) is a cation. So, Na\(^+\) can enter the cathode chamber through the cation exchange membrane. Under the effect of the applied electric field, the cations can freely enter the cathode chamber and combine with the OH\(^-\) in the cathode chamber to form NaOH, which can recover alkali. At the same time, the wastewater is continuously oxidized by the anode plate in the electrolytic cell, producing a large amount of H\(^+\). H\(^+\) and organic acid salts can generate organic acid so that the pH value keeps decreasing and the acidity increases. Under the acidic condition, H\(^+\) continuously replaces Na\(^+\) in lignin, which makes part of lignin water-insoluble, so that it precipitates out of solution.
CONCLUSIONS

1. During electrolysis, the lignin-based organic parts in the wastewater completed reactions and formed deposits. The chemical oxygen demand (COD) of alkaline peroxide mechanical pulp (APMP) wastewater decreased by 98%, and color-generating groups were nearly all destroyed. A total of 5.8 g of alkali was obtained.

2. Lowering the pH of the waste solution (acidic environment) at a constant voltage will help increase the efficiency of electrolysis of wastewater and take less time. But the pH would need to be adjusted to neutral pH (pH about 7) before discharging the water.

3. During the process of wastewater electrolysis, hydrogen radicals and hydroxyl radicals are generated. Unsaturated groups, such as carbonyl groups, will undergo hydrogenation with hydrogen radicals under the condition of the applied electric field. Some groups will change from unsaturated carbon-oxygen bonds to saturated states. The lignin-based polymers will precipitate out of solution and settle under acidic conditions.

4. Ti electrodes are not corroded during the electrolysis process. The combination of Ti and electrolysis is an effective way to treat APMP wastewater.

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