

## Selective Removal of Soluble Lignin from Pre-hydrolysis Liquor of Bamboo Willow Dissolving Pulp

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The selective removal of lignin can be a profitable value-added utilization for the pre-hydrolysis liquor (PHL) produced during kraft-based dissolving pulp production. In this work, the soluble lignin was removed from PHL using  $\text{CaCl}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$ , cationic polyacrylamide (CPAM), and a CPAM/ $\text{Al}_2(\text{SO}_4)_3$  dual-system treatment. The results of zeta potential recording revealed that 8.86% of soluble lignin was removed by  $\text{CaCl}_2$  treatment through charge neutralization and adsorption, and 13.1% soluble lignin was removed by CPAM through charge neutralization and flocculation bridging. The optimal dosages of  $\text{CaCl}_2$ , CPAM,  $\text{Al}_2(\text{SO}_4)_3$ , and CPAM/ $\text{Al}_2(\text{SO}_4)_3$  dual-system treatments were 2.0 wt%, 30 ppm, 300 ppm, and 60/300 ppm respectively, at which the soluble lignin removals were 8.09%, 9.24%, 18.3%, and 25.0%, respectively. Additionally, the total sugar loss by the CPAM/ $\text{Al}_2(\text{SO}_4)_3$  dual-system treatment was higher than that by other individual systems; however, the soluble lignin selective removal by the  $\text{CaCl}_2$  treatment was the highest, at over 80%.

*Keywords:* Pre-hydrolysis liquor; Soluble lignin;  $\text{Al}_2(\text{SO}_4)_3$  or CPAM; Removal mechanism

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### INTRODUCTION

The biorefining concept has attracted increasing attention in recent years (Reardon 2014), particularly from the pulping and papermaking industry. Biorefining can transform lignocellulose waste from the pulping process into high-value-added products, thereby adding additional revenue to the pulping and papermaking industry.

The pre-hydrolysis kraft-based dissolving pulp production process accords well with the concept of biorefining (Shen *et al.* 2013). Pre-hydrolysis is a critical step in the production process of kraft-based dissolving pulp, aiming to remove as much hemicellulose as possible from the lignocellulosic material while protecting the cellulose. The pre-hydrolysis liquor (PHL) produced in the pre-hydrolysis process contains a large number of organics, including saccharides derived from hemicelluloses, lignin derivatives, acetic acid, and furfural (Wang *et al.* 2014b). These organics can be separated to produce high-value-added products. For example, the xylose in the PHL can be used to produce xylitol by hydrogenation in the presence of catalysts (Peréz-Bibbins *et al.* 2016), and the glucose in the PHL can be used to produce ethanol by fermentation (Yu *et al.* 2017). Acetic acid is mainly used as a chemical feedstock for the production of vinyl acetate monomer (VAM) and terephthalic acid (TPA) (Yang *et al.* 2013a).

However, the presence of lignin is detrimental to further value-added utilization of the PHL. In the PHL, lignin has adverse effects on the fermentation of xylose/xylan into ethanol or xylitol (Lee *et al.* 2013). Lignin may hinder the separation and concentration of

acetic acid from the PHL (Yang *et al.* 2013a). Therefore, lignin should be removed specifically and completely when the PHL is further utilized. The removed lignin can serve as raw material for producing biofuel, plastics, phenols, *etc.* (Schorr *et al.* 2014; Khazraie *et al.* 2017).

Various investigations have been conducted concerning the removal of lignin from PHL. In one investigation, chemical flocculation was used, such as by poly-diallyl dimethyl ammonium chloride (p-DADMAC), polyethylene oxide (PEO), chitosan, *etc.* Saeed *et al.* (2011) employed 2.2 mg/g low molecular weight (LMW) chitosan and 1.7 mg/g high molecular weight (HMW) chitosan to treat the PHL. Respectively, 40% and 35% lignin removal was achieved. Shen *et al.* (2013) used physicochemical adsorption, such as with activated carbon and lime mud, and treated the PHL with activated carbon (PHL:Activated carbon = 30:1). The results showed that although approximately 85% of lignin was removed from PHL, due to the lack of selectivity of activated carbon, 65% furfural was also adsorbed by activated carbon. Another investigation, using biological enzyme treatment, showed that the molecular weight of lignin in the PHL treated with 2 U/mL laccase increased 160% from the original weight, and the lignin removal in the PHL increased from 11% to 61% when the amount of laccase was 4 U/mL (Wang *et al.* 2014a). Using other methods, such as acidification or thermal acidification, Chen *et al.* (2019) compared the effect of traditional acidification and hydrothermal acid hydrolysis on the removal of lignin from the PHL. The results showed that when compared with the lignin removal rate of 26.8 to 32.7% by the traditional acidification method, a much higher lignin removal rate of 57.1% was achieved by hydrothermal acid hydrolysis. However, there have been few studies on the mechanism of lignin removal.

The objective of the present study was to enhance the soluble lignin removal from the PHL and further explore the mechanism of soluble lignin precipitation. In this paper, the PHL of bamboo-willow dissolving pulp was treated by calcium chloride (CaCl<sub>2</sub>), aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>), cationic polyacrylamide (CPAM), and a CPAM/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> dual-treatment system to promote lignin precipitation. The effect of the treatment methods on saccharide components was also studied. Additionally, the mechanism of soluble lignin precipitation was explored by recording the change of the zeta potential of the PHL.

## EXPERIMENTAL

### Materials

The fast-growing bamboo willow (*Salix* sp, or *zhuliu* in Chinese) was provided by Tianshan Forestry Center in the Xinjiang autonomous region of Wulumuqi, China. The contents of holocellulose,  $\alpha$ -cellulose, pentosan, acid-insoluble lignin, and acid-soluble lignin of bamboo willow were 77.2%, 40.4%, 24.1%, 20.3%, and 3.46%, respectively, as mentioned in the authors' previous research (Zhang *et al.* 2019). Chipped bamboo willow was screened to obtain chips with the dimensions 15 mm to 20 mm (L)  $\times$  10 mm to 20 mm (W)  $\times$  3 mm to 5 mm (H) for subsequent experiments.

Calcium chloride (CaCl<sub>2</sub>) and aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) of analytical reagent grade were purchased from Tianjin Kemiou Chemical Reagent Factory (Tianjin, China). Cationic polyacrylamide (CPAM) with a molecular weight of 12 MDa was provided by BASF (Ludwigshafen, Germany).

## Methods

### *Pre-hydrolysis of wood and PHL preparation*

Pre-hydrolysis was performed in an electrically heated stainless-steel digester with a 15-L capacity at a reaction temperature of 160 °C for 90 min, using 1 kg of oven-dried bamboo willow chips. Deionized water was added to reach a 6:1 liquid-to-wood ratio. The dosage of phosphoric acid was 0.5% (based on the oven-dried weight of the materials). Upon completion of pre-hydrolysis, the digester was cooled naturally to room temperature, which subsequently separated the PHL from the solid mass. The collected PHL was filtered using two tiers of slowly quantitative filter paper and kept refrigerated for experimental use.

### *PHL treatments*

For an individual system treatment, 25 mL PHL was placed in a 100-mL Erlenmeyer flask and then added with the specified dosage of CaCl<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and CPAM. The mixture was stirred for 60 min at 300 rpm and at 25 °C. After the reaction was completed, the treated PHL was filtered on a filter membrane (nylon, 0.45-μm pore size).

For a CPAM/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> dual-treatment system, the desired dosages (15, 30, 45, 60, 75, and 90 ppm) of CPAM were added to the PHL, which was stirred for 10 min at 300 rpm and a temperature of 25 °C. Subsequently, the above optimal dosage of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was added to the system, which was again stirred for 10 min at 300 rpm. The subsequent procedures were the same as above.

### *Analytical methods*

The soluble lignin content in the PHL was measured *via* ultraviolet visible (UV-vis) spectroscopy (Agilent 8453; Agilent Technologies Inc., Palo Alto, CA, USA) at a wavelength of 205 nm, according to TAPPI um 250 (2000) (Wang *et al.* 2014a).

The sugars content in the PHL was measured using an indirect method based on quantitative acid hydrolysis of the liquid sample. To convert the oligomeric sugars in the PHL to monomeric sugars, the PHL was acid hydrolyzed using 4 wt% sulfuric acid at 121 °C for 1 h in an oil bath according to a technical report from the National Renewable Energy Laboratory (NREL) (Sluiter *et al.* 2006; Shen *et al.* 2011). The acid-hydrolyzed PHL was then diluted, and the content of monomeric sugars was measured. The monomeric sugars were measured using high-performance anion-exchange chromatography coupled with a pulsed amperometric detector (HPAEC-PAD) and an HPAEC-PAD system (ICS-5000; Thermo Fisher Scientific, Sunnyvale, CA, USA) equipped with a CarboPac PA20 analytical column (3 mm × 150 mm) (Thermo Fisher Scientific, Sunnyvale, CA, USA) and guard column (3 mm × 30 mm). The samples were filtered through 0.22-μm syringe filters prior to injection. The concentration of the sugars after this additional hydrolysis stage reflected the total sugars content of the PHL (Shen *et al.* 2011).

The zeta potential of the PHL was determined by the zeta potential and nanoparticle size analyzer (ZS90; Malvern Instruments, Malvern, UK). The measuring temperature was 25 °C, and the dispersion system was deionized water. The sample was diluted 10 times before measurement. All samples were analyzed in duplicates.

The lignin precipitates produced by the CPAM/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> flocculation treatment of the PHL were observed under a scanning electron microscope (SEM; EM-30 plus+; COXEM, Daejeon, South Korea), and images were taken under several magnifications.

### Definitions

The soluble lignin removal was calculated according to Eq. 1,

$$R (\%) = \frac{l_o - l}{l_o} \times 100 \quad (1)$$

where  $R$  is the soluble lignin removal (%),  $l_o$  is the soluble lignin content in the original PHL (g/L), and  $l$  is the soluble lignin content in the treated PHL (g/L).

The total sugar removal was calculated according to Eq. 2,

$$R_S (\%) = \frac{C_o - C}{C_o} \times 100 \quad (2)$$

where  $R_S$  is the total sugar removal (%),  $C_o$  is the total sugar content in the original PHL (g/L), and  $C$  is the total sugar content in the treated PHL (g/L).

The selective removal of soluble lignin was calculated according to Eq. 3,

$$R' (\%) = \frac{R}{R + R_S} \times 100 \quad (3)$$

where  $R'$  is the selective removal of soluble lignin (%),  $R$  is the soluble lignin removal (%), and  $R_S$  is the total sugar removal (%).

## RESULTS AND DISCUSSION

The compositions and properties of the original PHL are listed in Table 1. The zeta potential is an important index to characterize the stability of a colloidal dispersion system. It can be seen that the zeta potential of the original PHL was -8.56 mV. The number was due to the fact that in the pre-hydrolysis stage, the cleavage of the main interunit  $\beta$ -O-4 aryl ether linkages of lignin exposes some free phenolic hydroxyl groups (Yang *et al.* 2013b). This process resulted in the lignin having negatively charged PHL. Therefore, the soluble lignin was stable in the PHL and difficult to remove. The negative charge of the PHL system was neutralized by adding positively charged ions or electrolytes, thereby eliminating the mutual repulsion between lignin colloidal particles. The lignin colloidal molecules were thus unstable, and condensate was able to succeed in removing the lignin. Tong *et al.* (2016) indicated that the soluble lignin was the main lignin in the PHL, so only soluble lignin was investigated in this experiment.

**Table 1.** Compositions and Properties of the Original PHL

Parameter	pH	Zeta potential (mV)	Soluble lignin (g/L)	Arabinose (g/L)	Galactose (g/L)	Glucose (g/L)	Xylose (g/L)	Mannose (g/L)	Total sugars (g/L)
Content	3.65	-8.56	4.84	0.91	1.00	4.02	8.67	1.17	15.8

### The Effect of CaCl<sub>2</sub> Treatment on the Removal of Soluble Lignin

CaCl<sub>2</sub> is a typical ionic halide. The pH value and zeta potential of the 2% CaCl<sub>2</sub> solution were 8.9 and +3.61 mV, respectively. Therefore, the zeta potential of the PHL could be changed by CaCl<sub>2</sub> treatment, or lignin removal could be achieved by adsorption.

The main compositions removals from the PHL treated by  $\text{CaCl}_2$  are illustrated in Fig. 1. As can be seen that with an increase in the dosage of  $\text{CaCl}_2$ , the soluble lignin removal increased first, reaching a maximum rate of 8.86% at 2.5% dosage, and then it began to decline. This may be due to the fact that the dosage of 2.5% is the turning point of the comprehensive effect of  $\text{CaCl}_2$  on the electroneutralization and adsorption of soluble lignin in the PHL. Although the soluble lignin removal by treatment with  $\text{CaCl}_2$  was not high, the selective removal of soluble lignin was considerable, and it remained above 80%. When the dosage of  $\text{CaCl}_2$  was 2.0%, the loss rate of total sugar was the lowest, at 0.44%, and the selective removal of soluble lignin was the highest, reaching 94.8%. At this dosage, the soluble lignin removal was 8.09%, which was 0.77% lower than the maximum removal of 8.86%. Considering that as much as possible of the soluble lignin should be removed, and that the sugars should be kept intact, the 2.0%  $\text{CaCl}_2$  dosage can be considered the optimal condition for PHL treatment.

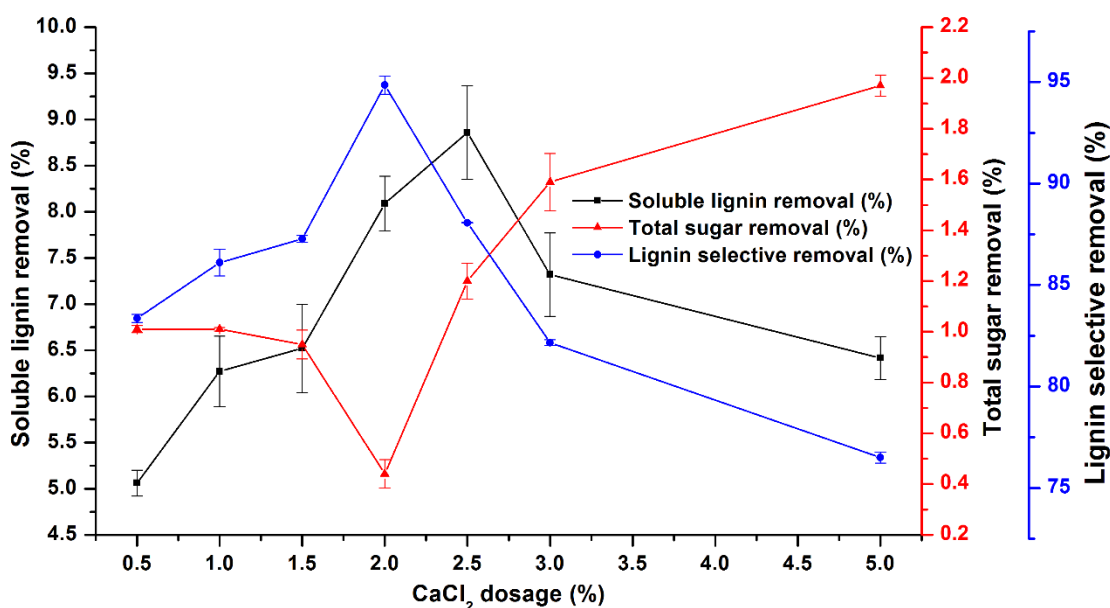


Fig. 1. The effect of  $\text{CaCl}_2$  dosage on the soluble lignin and total sugar removal from the PHL

As shown in Fig. 2, with an increase in the  $\text{CaCl}_2$  dosage, the zeta potential of the PHL first increased to  $-0.23$  mV at a 1.5% dosage, and then it began to decrease, which may be caused by an increase in the pH value of the PHL (Wang *et al.* 2014b). There was a competitive relationship between zeta potential and pH value of PHL. At a dosage of 1.5%, the zeta potential vanished, indicating the isoelectric point for the PHL. After exceeding this dosage, the PHL tended to be stable, but some soluble lignin was removed. This removal indicated that in the initial stage of  $\text{CaCl}_2$  addition, lignin removal was achieved by neutralizing the negatively charged soluble lignin colloid particles and destabilizing the precipitation. In the later stage, soluble lignin removal was achieved by the adsorption of  $\text{CaCl}_2$ . As shown in Fig. 3, when  $\text{CaCl}_2$  was added to the PHL, a Ca cation would adhere to the surface of the soluble lignin colloidal particles, and the repelling force continuously decreased. This process destroyed the electric double-layer structure and the colloid stability. As a result, the attraction between the soluble lignin colloidal particles was dominant, resulting in precipitation. Wang *et al.* (2014b) showed that calcium ions can electrostatically bind to phenolic lignin under alkaline conditions.

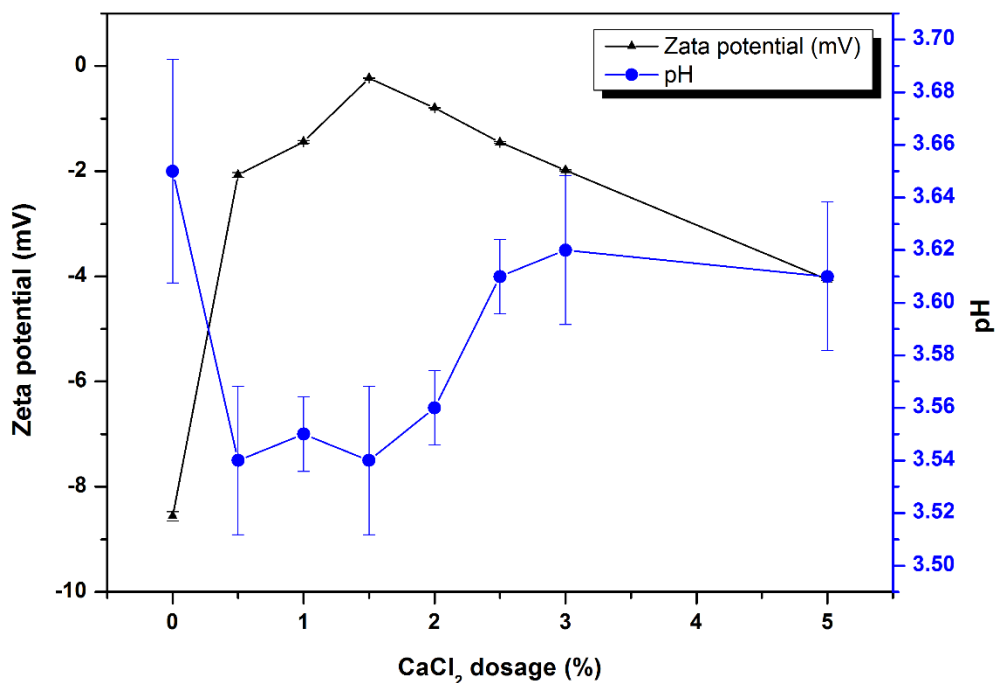


Fig. 2. Effect of CaCl<sub>2</sub> dosage on the zeta potential and pH value of the PHL

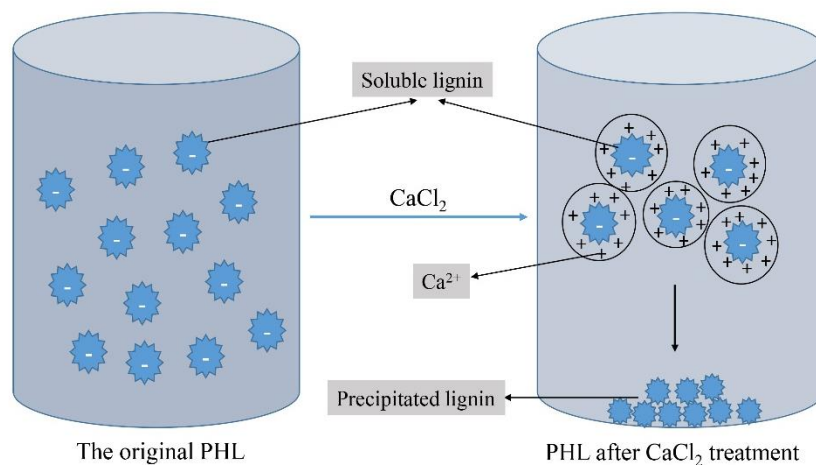


Fig. 3. Mechanism of precipitating soluble lignin by CaCl<sub>2</sub> treatment

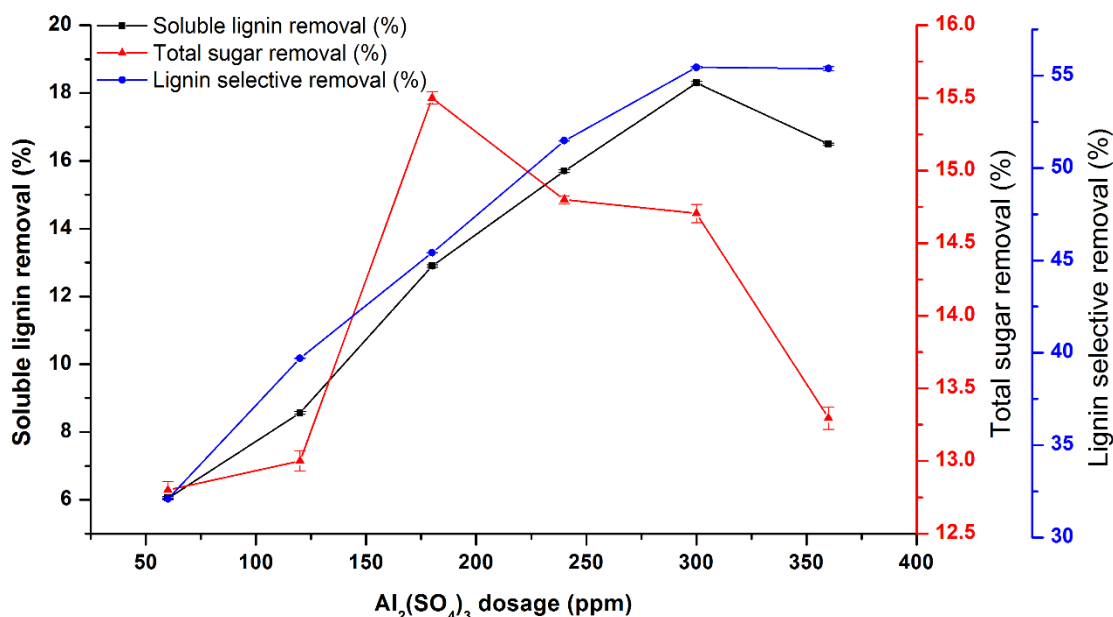
### The Effect of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> Treatment on the Removal of Soluble Lignin

The most common use of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is as a precipitant for rosin rubber, wax emulsion, and other rubber compounds in the papermaking industry; followed by flocculants in drinking water, industrial water, and industrial wastewater treatment. The pH value and zeta potential of the 2% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution were 3.65 and +3.61 mV, respectively. Table 2 shows the pH value of the PHL decreased gradually with the increase of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> dosage, but the range was slight. Decreasing pH value of solution leads to increase of zeta potential.

**Table 2.** The Effect of  $\text{Al}_2(\text{SO}_4)_3$  Dosage on the pH Value and Zeta Potential of the PHL

$\text{Al}_2(\text{SO}_4)_3$ Dosages (ppm)	60	120	180	240	300	360
pH	3.62	3.54	3.46	3.44	3.39	3.36
Zeta potential (mV)	-7.26	-4.26	-2.25	-2.64	-3.05	-3.67

The main compositions removals from the PHL treated by  $\text{Al}_2(\text{SO}_4)_3$  are presented in Fig. 4. As can be seen, the soluble lignin removal from the original PHL increased with the increase of  $\text{Al}_2(\text{SO}_4)_3$  dosage. When the dosage was 300 ppm, the removal reached the maximum of 18.3%, and then it slightly decreased. This may be due to the hydrolysis of aluminum ions in water to produce aluminum hydroxide precipitation ( $\text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3 \downarrow + 3\text{H}^+$ ), which leads to the weakening of aluminum sulfate flocculation. The loss rate of total sugar increased first and then decreased, reaching the maximum of 15.5% at the  $\text{Al}_2(\text{SO}_4)_3$  dosage of 180 ppm. The selective removal of soluble lignin increased continuously, reaching the maximum of 55.5% at the dosage of 300 ppm. The soluble lignin removal and its selective removal were highest, at 18.3% and 55.5%, respectively, with the  $\text{Al}_2(\text{SO}_4)_3$  dosage of 300 ppm; the loss rate of total sugar was not high (14.7%) at this dosage. Therefore, the  $\text{Al}_2(\text{SO}_4)_3$  dosage of 300 ppm was considered the optimum condition for PHL treatment.

**Fig. 4.** Effect of  $\text{Al}_2(\text{SO}_4)_3$  dosage on the soluble lignin and total sugar removal from the PHL

### The Effect of CPAM Treatment on the Removal of Soluble Lignin

The linear polymer CPAM has a high-charge density and relative molecular weight ( $M_r$ ). Its aqueous solution is a polymer electrolyte with positive charge, and can effectively flocculate suspended organic colloids and organic compounds, as well as strengthen the solid-liquid separation process. As a flocculant, the use of CPAM with high  $M_r$  is advantageous because it requires a smaller dosage, exhibits rapid and thorough flocculation, and has loose precipitation and fast filtration (Mai *et al.* 2012).

The main compositions of removals from the PHL treated by CPAM are presented in Fig. 5. It can be seen that with the increase of CPAM dosage, the soluble lignin removal remained between 7.10% and 13.1%. The lignin removal was not as regular as in alkaline environment (Wang *et al.* 2015). An obvious fluctuation of soluble lignin removal could be observed, which may be attributed to the acidic environment (Original PHL without pH adjustment), which is not conducive to the flocculation of soluble lignin in the PHL by CPAM (Yasarla and Ramarao 2012). The lowest lignin removal was 7.10% at the dosage of 45 ppm, and the highest was 13.1% at 90 ppm. The total sugar loss rate increased with the increase of CPAM dosage, and the selective removal of soluble lignin showed a downward trend, indicating that the increase of CPAM dosage is detrimental to the further value-added utilization of the PHL. When the CPAM dosage was 30 ppm, the soluble lignin removal was 12.1%, which was only 1.05% lower than the highest 13.1%. At this dosage, the total sugar loss rate was 4.63%, which was 1.02% higher than the lowest 3.61%, and the selective removal of soluble lignin was 72.2%, which was also considerable. Therefore, the optimal amount of CPAM for PHL treatment was considered to be 30 ppm.

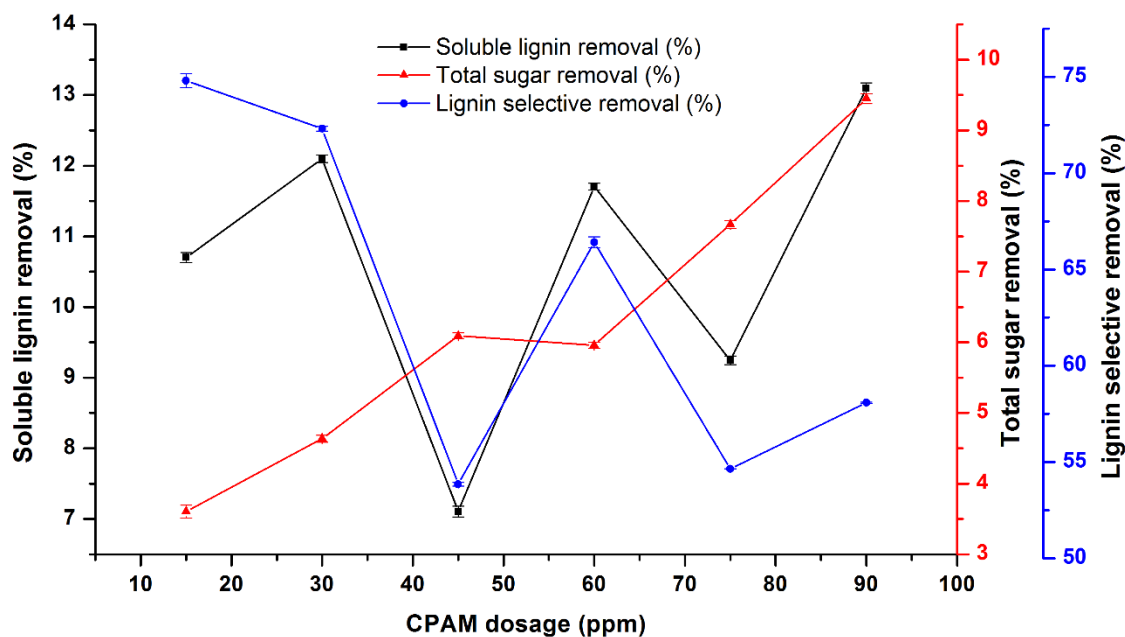


Fig. 5. Effect of CPAM dosage on the soluble lignin and total sugar removal from the PHL

As shown in Fig. 6, the addition of CPAM had a negligible effect on the pH value of the PHL, whereas it had a great influence on the zeta potential. The zeta potential of PHL increased with the increase of CPAM dosage as a whole. This result was different from that of the slight change of zeta potential obtained by Yasarla and Ramarao (2012), which can be explained by the different molecular weights of the CPAM employed. However, at higher CPAM dosages, the zeta potential became positive due to the charge reversal caused by cationic charges (Yasarla and Ramarao 2012), leading to the re-dispersion of soluble lignin as well as the removal of soluble lignin. This result indicated that CPAM mainly formed precipitation by charge neutralizing and destroying the stable electric double layer in the early stage of treatment. In the later stage, soluble lignin molecules were flocculated together by bridging, thus removing the soluble lignin colloidal particles from the PHL. The precipitation mechanism in Fig. 7 shows that, due to the



positive charge of CPAM, the original PHL stable system was destroyed. Together with the bridging flocculation of CPAM, a bridge was formed between the soluble lignin molecules to cause flocculation.

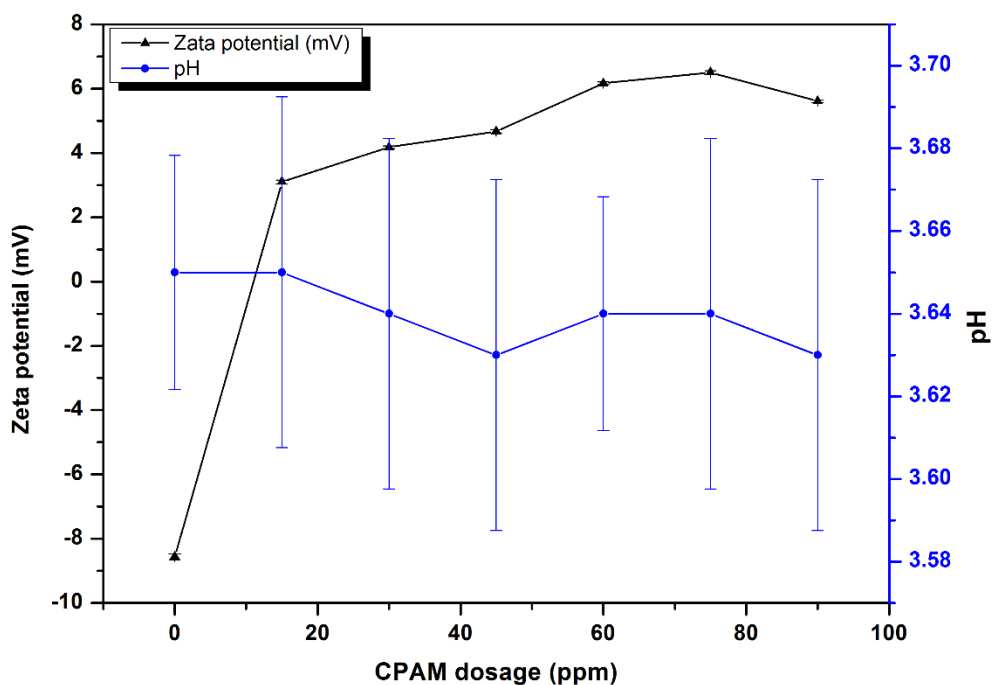


Fig. 6. Effect of CPAM dosage on the zeta potential and pH value of the PHL

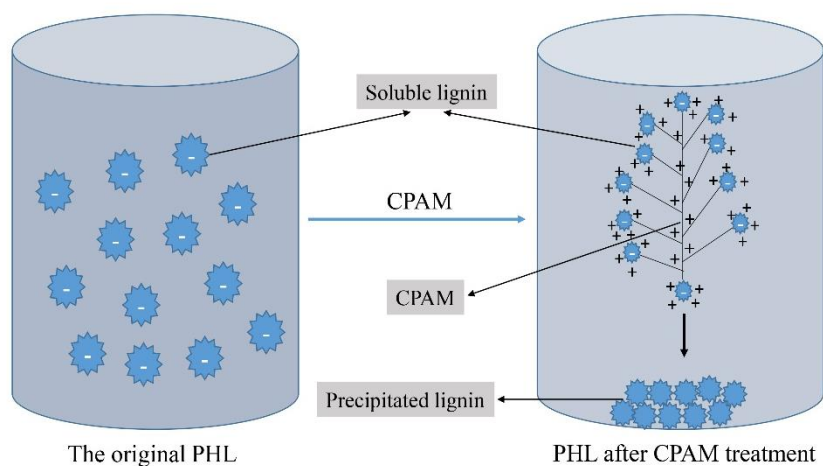


Fig. 7. Mechanism of precipitating soluble lignin by CPAM treatment

### The Effect of CPAM/ $\text{Al}_2(\text{SO}_4)_3$ Dual-system Treatment on the Removal of Soluble Lignin

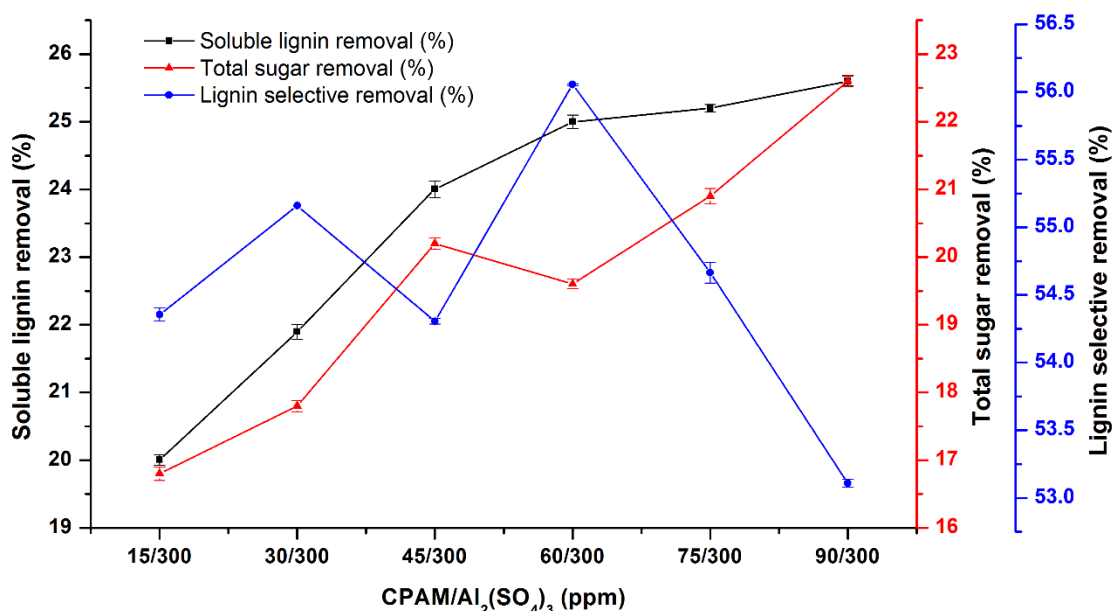
The  $\text{Al}_2(\text{SO}_4)_3$  generally only reacts with soluble lignin colloidal macromolecules. Thus, a flocculant can be added as a coagulant aid to enhance the removal effect of lignin by bridging, and, therefore, a CPAM/  $\text{Al}_2(\text{SO}_4)_3$  dual system can be employed to treat the PHL. In addition, a dual-system treatment has been recognized as an effective coagulation/flocculation process for removing lignin from the PHL (Shi *et al.* 2011, 2012;

Wang *et al.* 2014a). In this set of experiments, different dosages of CPAM were added to the PHL first, followed by the addition of  $\text{Al}_2(\text{SO}_4)_3$ . It can be seen from Table 3 that the CPAM/ $\text{Al}_2(\text{SO}_4)_3$  dual-system treatment had a negligible effect on the pH value of the PHL, though all decreased slightly due to the effect of  $\text{Al}_2(\text{SO}_4)_3$ . The zeta potential of the PHL increased with the increase of the CPAM/ $\text{Al}_2(\text{SO}_4)_3$  dosage, which was the result of the  $\text{Al}_2(\text{SO}_4)_3$  and CPAM double-positive electrolyte.

**Table 3.** The Effect of CPAM/ $\text{Al}_2(\text{SO}_4)_3$  Dosage on the pH value and zeta potential of the PHL

CPAM/ $\text{Al}_2(\text{SO}_4)_3$ Dosages (ppm)	15/300	30/300	45/300	60/300	75/300	90/300
pH	3.56	3.55	3.56	3.54	3.55	3.54
Zeta potential (mV)	2.90	2.97	4.45	7.19	7.64	10.4

The main compositions removals from the PHL treated by the CPAM/ $\text{Al}_2(\text{SO}_4)_3$  dual-system are illustrated in Fig. 8. The removal of soluble lignin from the PHL by the CPAM/ $\text{Al}_2(\text{SO}_4)_3$  dual system treatment was considerably higher than that of a singular system, but the loss rate of total sugar also increased as a whole. The selective removal of soluble lignin was higher than that of the single-component treatment of  $\text{Al}_2(\text{SO}_4)_3$ , but lower than that of the single-component treatment of CPAM. It is found that the increase of the CPAM/ $\text{Al}_2(\text{SO}_4)_3$  dosage caused the soluble lignin removal to increase gradually. Above a dosage of 60/300 ppm, the increase slowed down. The total sugar loss rate also increased as a whole; above 45/300 ppm, the loss rate decreased slightly and began to increase again above 60/300 ppm.

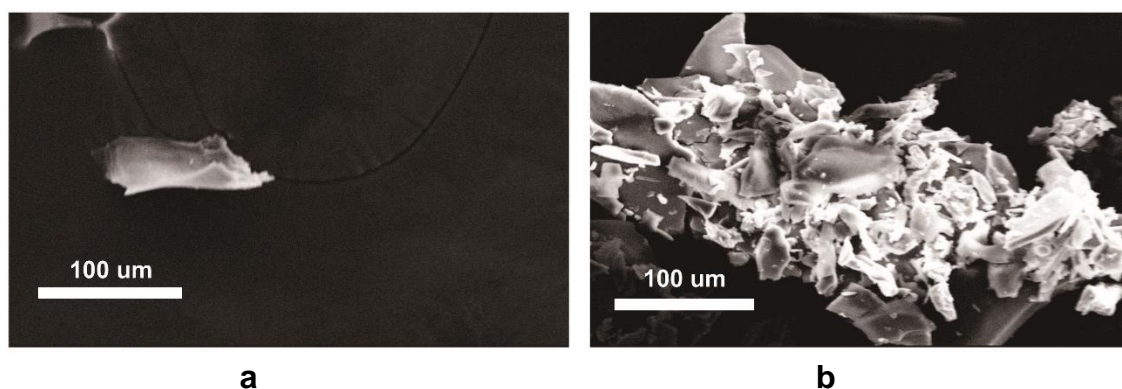


**Fig. 8.** Effect of the CPAM/ $\text{Al}_2(\text{SO}_4)_3$  dosage on the soluble lignin and total sugar removal from the PHL

The selective removal of soluble lignin increased to a maximum of 56.1% at 60/300 ppm, and then began to decline. Considering that the soluble lignin removal was 25.0%, the loss rate of total sugar was 19.6%, and the selective removal of soluble lignin was the

highest at 56.1% at a CPAM/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> dosage of 60/300 ppm, the CPAM/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> dosage of 60/300 ppm was considered the optimal condition for PHL treatment.

To demonstrate the formation of flocculating precipitation of soluble lignin colloidal particles, the PHL was treated with the above optimal CPAM/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> dosage (60/300 ppm), and the precipitation structure was observed by SEM. The SEM images of untreated blank samples and precipitation samples produced by flocculation treatment are shown in Fig. 9. They clearly illustrate that at the same magnification, the particle size of the precipitation samples produced by the flocculation treatment was much larger than that of the blank sample, and many fine particles flocculated together to form large particles with a loose structure. Considering the flocculation state of the precipitates, the precipitation mixtures produced by the CPAM/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> flocculation treatment of the PHL may be used to produce other value-added chemical products.



**Fig. 9.** SEM micrographs of untreated blank samples (a) and precipitation samples (b), produced by flocculation treatment, magnification 500×

## CONCLUSIONS

1. The precipitation of soluble lignin from the pre-hydrolysis liquor (PHL) of the kraft-based dissolving pulp production process was achieved by positively charged ions or electrolytes, namely, CaCl<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and cationic polyacrylamide (CPAM).
2. The CaCl<sub>2</sub> removed soluble lignin from PHL by charge neutralization and adsorption, and the CPAM was removed by charge neutralization and flocculation bridging.
3. The soluble lignin and total sugar removal from PHL by the CPAM/Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> dual-system treatment was higher than that by other individual systems (CaCl<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and CPAM); however, the soluble lignin selective removal *via* the CaCl<sub>2</sub> treatment was the highest, at more than 80%.

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## REFERENCES CITED

- Chen, X., Cao, X., Sun, S., Yuan, T., Wang, S., Shi, Q., and Sun, R. (2019). "Hydrothermal acid hydrolysis for highly efficient separation of lignin and xylose from pre-hydrolysis liquor of kraft pulping process," *Separation and Purification Technology* 209, 741-747. DOI: 10.1016/j.seppur.2018.09.032
- Khazraie, T., Zhang, Y., Tarasov, D., Gao, W., Price, J., DeMartini, N., Hupa, L., and Fatehi, P. (2017). "A process for producing lignin and volatile compounds from hydrolysis liquor," *Biotechnology for Biofuels* 10, Article Number 47. DOI: 10.1186/s13068-017-0729-9
- Lee, H.-J., Lim, W.-S., and Lee, J.-W. (2013). "Improvement of ethanol fermentation from lignocellulosic hydrolysates by the removal of inhibitors," *Journal of Industrial and Engineering Chemistry* 19(6), 2010-2015. DOI: 10.1016/j.jiec.2013.03.014
- Mai, Y.-F., Zhu, H., Lin, J.-Y., and Qiu, Z.-H. (2012). "Important technical progresses of cationic polyacrylamide," *Polymer Bulletin* 2012(8), 105-110. DOI: 10.14028/j.cnki.1003-3726.2012.08.017
- Peréz-Bibbins, B., Torrado-Agrasar, A., Salgado, J. M., Mussatto, S. I., and Domínguez, J. M. (2016). "Xylitol production in immobilized cultures: A recent review," *Critical Reviews in Biotechnology* 36(4), 691-704. DOI: 10.3109/07388551.2015.1004660
- Reardon, K. F. (2014). "Lignocellulosic biorefineries: Concepts and possibilities," in: *Plants and BioEnergy*, M. C. McCann, M. S. Buckeridge, and N. C. Carpita (eds.), Springer, New York, NY, USA, pp. 255-265.
- Saeed, A., Fatehi, P., and Ni, Y. (2011). "Chitosan as a flocculant for pre-hydrolysis liquor of kraft-based dissolving pulp production process," *Carbohydrate Polymers* 86(4), 1630-1636. DOI: 10.1016/j.carbpol.2011.06.075
- Schorr, D., Diouf, P. N., and Stevanovic, T. (2014). "Evaluation of industrial lignins for biocomposites production," *Industrial Crops and Products* 52, 65-73. DOI: 10.1016/j.indcrop.2013.10.014
- Shen, J., Fatehi, P., Soleimani, P., and Ni, Y. (2011). "Recovery of lignocelluloses from pre-hydrolysis liquor in the lime kiln of kraft-based dissolving pulp production process by adsorption to lime mud," *Bioresource Technology* 102(21), 10035-10039. DOI: 10.1016/j.biortech.2011.08.058
- Shen, J., Kaur, I., Baktash, M. M., He, Z., and Ni, Y. (2013). "A combined process of activated carbon adsorption, ion exchange resin treatment and membrane concentration for recovery of dissolved organics in pre-hydrolysis liquor of the kraft-based dissolving pulp production process," *Bioresource Technology* 127, 59-65. DOI: 10.1016/j.biortech.2012.10.031
- Shi, H., Fatehi, P., Xiao, H., and Ni, Y. (2011). "A combined acidification/PEO

- flocculation process to improve the lignin removal from the pre-hydrolysis liquor of kraft-based dissolving pulp production process,” *Bioresource Technology* 102(8), 5177-5182. DOI: 10.1016/j.biortech.2011.01.073
- Shi, H., Fatehi, P., Xiao, H., and Ni, Y. (2012). “Optimizing the poly ethylene oxide flocculation process for isolating lignin of prehydrolysis liquor of a kraft-based dissolving pulp production process,” *Industrial & Engineering Chemistry Research* 51(14), 5330-5335. DOI: 10.1021/ie300141k
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., and Templeton, D. (2006). *Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples*, U. S. National Renewable Energy Laboratory, Golden, CO, USA. TAPPI um 250 (2000). “Acid-soluble lignin in wood and pulp,” TAPPI Press, Atlanta, GA, USA.
- Tong, R., Wu, C., Zhao, C., and Yu, D. (2016). “Effect of boric acid addition on the prehydrolysis of whangee,” *BioResources* 11(4), 9628-9637. DOI: 10.15376/biores.11.4.9628-9637
- Wang, Q., Jahan, M. S., Liu, S., Miao, Q., and Ni, Y. (2014a). “Lignin removal enhancement from prehydrolysis liquor of kraft-based dissolving pulp production by laccase-induced polymerization,” *Bioresource Technology* 164, 380-385. DOI: 10.1016/j.biortech.2014.05.005
- Wang, Z., Jiang, J., Wang, X., Fu, Y., Li, Z., Zhang, F., and Qin, M. (2014b). “Selective removal of phenolic lignin derivatives enables sugars recovery from wood prehydrolysis liquor with remarkable yield,” *Bioresource Technology* 174, 198-203. DOI: 10.1016/j.biortech.2014.10.025
- Wang, X., Wang, J., Qin, M., and Wang, Z. (2015). “Flocculation-induced enhancement in lignin removal by ion exchange resin from prehydrolysis liquor of poplar,” *Paper Science & Technology* 34(1), 91-95. DOI: 10.19696/j.issn1671-4571.2015.01.023
- Yang, G., Jahan, M. S., Ahsan, L., Zheng, L., and Ni, Y. (2013a). “Recovery of acetic acid from pre-hydrolysis liquor of hardwood kraft-based dissolving pulp production process by reactive extraction with triisooctylamine,” *Bioresource Technology* 138, 253-258. DOI: 10.1016/j.biortech.2013.03.164
- Yang, G., Jahan, M. S., and Ni, Y. (2013b). “Structural characterization of pre-hydrolysis liquor lignin and its comparison with other technical lignins,” *Current Organic Chemistry* 17(15), 1589-1595. DOI: 10.2174/13852728113179990068
- Yasarla, L. R., and Ramarao, B. V. (2012). “Dynamics of flocculation of lignocellulosic hydrolyzates by polymers,” *Industrial & Engineering Chemistry Research* 51(19), 6847-6861. DOI: 10.1021/ie202567c
- Yu, H., Guo, J., Chen, Y., Fu, G., Li, B., Guo, X., and Xiao, D. (2017). “Efficient utilization of hemicellulose and cellulose in alkali liquor-pretreated corncob for bioethanol production at high solid loading by *Spathaspora passalidarum* U1-58,” *Bioresource Technology* 232, 168-175. DOI: 10.1016/j.biortech.2017.01.077
- Zhang, J.-C., Wu, C.-J., and Yu, D.-M. (2019). “Effect of phosphoric acid in the pre-hydrolysis process of dissolving pulp production from bamboo-willow,” *BioResources* 14(2), 3117-3131. DOI: 10.15376/biores.14.2.3117-3131

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