Effect of Hydroxymethylated Experiment on Complexing Capacity of Sodium Lignosulfonate

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Abstract. Influence of hydroxymethylated reaction in different conditions on complexing capacity of sodium lignosulfonate (SL) with Cu(II), Zn(II) and Mg(II) was investigated. By single factor experiment, the optimal reaction conditions were as follows: dosage of formaldehyde was 0.22 g·(g SL)$^{-1}$, temperature was 60~70˚C, pH was 11.0. Under the optimum condition, the amount of complexed Cu, Zn and Mg of hydroxymethylated sodium lignosulfonate (HSL) increased by 34.9%, 23.3% and 18.9% respectively, compared to the original SL. Moreover, the total hydroxyl group content of SL increased after reaction, which suggested that the main contributor to complexing capacity improvement was total hydroxyl content.

Introduction

Sodium lignosulfonate (SL), the waste of acid pulping, has good water solubility and complexing capacity because of the large amount of hydrophilic and chelating groups, which can complex polyvalent metal ions to form water-soluble chelates. The complexing property of lignin and its derivatives can be used as water treatment agent, chelated fertilizer and flocculants. So it's important to investigate the complexing capacity of SL and find ways to increase its complexing capacity.

Many factors can affect complexing capacity of SL, for example, the most important factor affecting complexing capacity of massoniana alkali lignin with metal element was hydroxyl group content [1]. Adilson R[2] also found that the complexing capacity of lignin increased with hydroxyl and carbonyl content. Some chemical reactions were used to increase the complexing capacity of raw SL, for instance, the methylol content of lignin model compound increased after hydroxymethylated reaction[3]. Based on it, I try to increase the hydroxyl group content to improve complexing capacity of SL by hydroxymethylated modification, and then optimal reaction conditions can be obtained.

Experimental

Reagents. Sodium lignosulfonate (SL), supplied by Tongdao Paper Making Co. Ltd., Hunan, China, was purified by ion exchange and ultrafiltration. Formaldehyde (37%), NaOH, $MgCl_2·6H_2O$, $ZnSO_4·7H_2O$ and $CuSO_4·5H_2O$ used in this paper were of recognized analytical grade.

Hydroxymethylated experiment of SL. A certain amount of SL was dissolved in deionized water and the mass concentration made up to 25 wt %, then the solution was transferred to a 250 ml flask. Sodium hydroxide was added in it to adjust the pH, and then formaldehyde was dropped in the solution and reacted for 2 hours at a set temperature. Lastly, the product was dried at 50˚C and named hydroxymethylated sodium lignosulfonate (HSL).

Intrinsic viscosity measurement of SL. The intrinsic viscosity measurement of SL in deionized water was performed with an Ubbelohde viscometer at 25℃. The time of deionized water and tested SL flowing through capillary column was recorded. Each measurement conducted three continuous tests, which should be repeated until the relative standard deviation for any sample was within 5%. The intrinsic viscosity formula was shown in Eq. 1 and Eq. 2.

$$[\eta]=\frac{\sqrt{2\eta_r-2-2\ln\eta_r}}{c} \quad (1)$$

$$\eta_r = \frac{\rho t}{\rho_0 t_0}. \quad (2)$$

Where, $[\eta]$ was intrinsic viscosity of SL, mL/g, η_r was reduced viscosity, c was the mass concentration of SL solution, g/mL, t was the time of SL solution flowing through capillary column, s, t_0 was the time of deionized water flowing through capillary column, s, ρ was density of SL at 25℃, g/mL, ρ_0 was density of deionized water at 25℃, which was 1.00 g/mL.

Content determination of phenolic hydroxyl and carboxyl in SL. The phenolic hydroxyl and carboxyl content of SL were measured by an automatic potentiometric titrator (Type 809 Titrando, Metrohm Corp., Switzerland) [4].

Complexed metal analysis[5]. This method is based on AOAC Official Method 983.03 (1986). In brief, Mg(II)SL, Zn(II)SL and Cu(II)SL complexes were prepared from SL and the addition of appropriate amount of metal solution ($MgCl_2 \cdot 6H_2O$ or $ZnSO_4 \cdot 7H_2O$ or $CuSO_4 \cdot 5H_2O$). In complexes, the mass ratio of SL to Mg(II), Zn(II) and Cu(II) were all 1:0.05. Each complex sample was adjusted to pH 6.0 with 0.1M HCl and the volume made up to 100 mL with deionized water. At this time, the concentration of SL was c_0, g/L. Then the solution was transferred to a stoppered erlenmeyer flask and shaken for 12 hours at 25˚C in an oscillator (THZ-C-1). 20 mL of sample solution was pipetted into a beaker and two drops of H_2O_2 were added in it. Then the pH increased to a given value (the pH value of Mg(II)SL, Zn(II)SL and Cu(II)SL were 11.0, 10.0 and 9.0, respectively). The pH was increased again to the above value after 30 min and the solution was allowed to stand for 24 hours. Then samples were centrifuged at 5000 r/min at 25˚C for 30 min. The supernatant was collected and diluted n times with deionized water. The complexed metal element was determined after the removal of organic compound by FAAS (Z-2300, Hitachi Corp., Japan). The formula was shown in Eq. 3.

$$\Gamma(\mathrm{mg}/g) = \frac{n c_t}{c_0}. \quad (3)$$

Where, Γ was the content of metal ions complexed by SL or HSL, mg·(g sample)$^{-1}$, c_0 was the concentration of the original SL solution, g/L, c_t was the concentration of metal ion measured by FAAS, mg/L.

Results and Discussion

Effect of the content of formaldehyde on hydroxymethylated experiment of SL. When temperature was 70˚C, pH was 11.0, the influence of different concentration of formaldehyde on the molecular conformation of HSL was studied. The dosage of formaldehyde were 0.15, 0.22, 0.30 g·(g SL)$^{-1}$ in this experiment. When the content of formaldehyde was 0.30 g·(g SL)$^{-1}$, the FTIR spectrum (Tensor 27 Infrared Spectrometer, Bruke Corp., Germany) of SL and HSL were shown in Fig. 1.

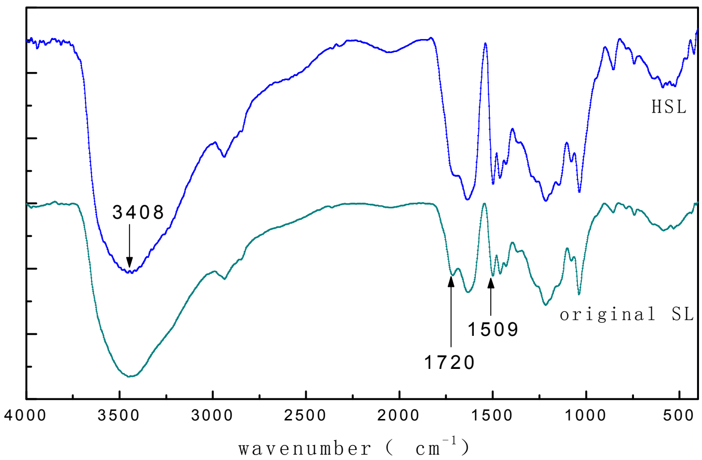


Fig. 1 FTIR spectrum of SL and HSL

As shown in Fig. 1, compared to SL, the absorbed vibration of HSL increases at 1509 cm^{-1}, which means that the content of aromatic ring structure in lignin increased. This result may be caused by the polycondensation reaction between SL and formaldehyde in alkali condition[6]. Moreover, the absorption peak strength at about 1720 cm^{-1} is almost the same before and after reaction, which indicates that the carbonyl content substantially unchanged. The peak area of band at 3408 cm^{-1} and 1509 cm^{-1} are compared in order to determine the total hydroxyl content of SL and HSL, and results are given in Table 1.

Table 1 IR peak area of lignosulfonates at the wave numbers 3408 cm^{-1} and 1509 cm^{-1}

lignosulfonates	Peak area		S_{3408}/S_{1509}
	S_{1509}	S_{3408}	
Original SL	6.94	264.97	38.18
HSL	3.35	184.81	55.17

It can be seen from Table 1, the total hydroxyl content of SL increases after hydroxymethylated experiment. Moreover, phenolic hydroxyl and carboxyl content and intrinsic viscosity of SL were measured and results were given in Table 2.

Table 2 Effect of the dosage of formaldehyde on the molecular conformation of HSL

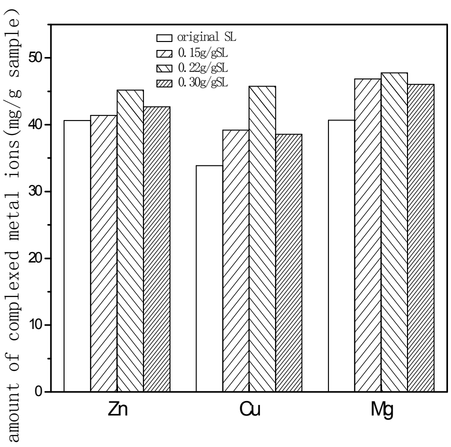
dosage of formaldehyde （g·(g SL)$^{-1}$）	carboxyl content (mmol/g)	phenolic hydroxyl content (mmol/g)	intrinsic viscosity （mL/g）
0	2.02	0.98	5.29
0.15	2.00	0.60	5.81
0.22	2.04	0.64	5.60
0.30	2.01	0.76	5.75

As shown in Table 2, intrinsic viscosity slightly increases after modification, which indicates that the relative molecular weight of SL is increased, inferring that polycondensation reaction between SL and formaldehyde occurres in alkali condition. The carbonyl content substantially unchange after reaction, which is similar to the results of FTIR spectrum measurement. The phenolic hydroxyl content decreased and total hydroxyl content increases, indicating that alcoholic hydroxyl content of SL increases after reaction.

Fig. 2 shows that the complexing capacity of different SLs with Mg, Zn and Cu. The complexing capacity of SL is different with different metal ions. The complexing capacity of HSL with Mg, Zn and Cu are all higher than that of SL. The total hydroxyl content increases, relative molecular weight of SL slightly increases and carbonyl content substantially unchange, so it can be inferred that the increasing total hydroxyl group content of SL is the main contributor to complexing capacity improvement.

The maximum values of HSL complexed with Zn, Mg and Cu are 45.18, 47.77 and 45.72 mg·(g sample)$^{-1}$, which increases by 11.9%, 17.5% and 34.9% respectively, compared to the original SL. The complexing capacity of HSL with the above three metal ions firstly increases and then decreases with the dosage of formaldehyde, and it come to a head when the dosage is 0.22 g·(g SL)$^{-1}$. The more the formaldehyde, the easier Cannizzaro reaction and aggregation of SL occurres, which hinder the development of hydroxymethylated experiment. Thus, excessive dosage of formaldehyde goes against complexing capacity improvement of SL, and the optimum content of formaldehyde is 0.22 g·(g SL)$^{-1}$.

Effect of temperature on hydroxymethylated experiment of SL. When the dosage of formaldehyde was 0.22 g·(g SL)$^{-1}$, pH was 11.0, the influence of temperature on the complexing capacity of HSL was studied and results were shown in Fig. 3. It can be seen from Fig. 3, the maximum values of HSL complexed with Zn, Mg and Cu are 47.25, 48.33 and 45.72 mg·(g sample)$^{-1}$, which increases by 23.3%, 18.9% and 34.9% respectively, compared to the original SL. The complexing capacity of HSL with Mg changes very little with changing temperature, and it reaches maximum at 60˚C. But temperature has great impact on the complexing capacity of HSL with Zn and Cu. The complexing capacity of HSL with Zn and Cu firstly increases and then decreases with temperature and come to a head at 60°C and 70°C respectively. So the optimum temperature is 60~70°C.



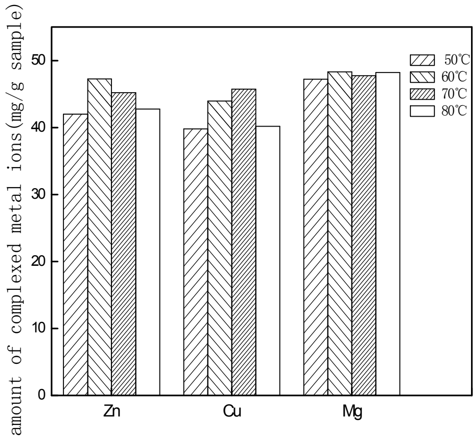


Fig. 2 Influence of the content of formaldehyde on the chelating capacity of HSL

Fig. 3 Influence of the temperature on chelating on the chelating capacity of HSL

Effect of system pH on hydroxymethylated experiment of SL. When the dosage of formaldehyde was 0.22 g·(g SL)$^{-1}$, temperature was 60°C, the change of system pH before and after reaction was investigated. When the initial system pH is 9～11, the decrement of pH is about 1.0, and the pH value decreases by 1.8 when original pH is 12. It indicates that the lager the initial pH, the more of pH decrement after reaction. The result infers that it is easy for formaldehyde to produce formic acid and methanol under high alkali condition due to the Cannizzaro reaction.

Effect of pH on complexing capacity of HSL is further studied and results are shown in Fig. 4. The maximum values of HSL complexed with Zn, Mg and Cu are 47.25, 48.85 and 43.95 mg·(g sample)$^{-1}$, which increases by 23.3%, 20.1% and 29.6% respectively, compared to the original SL. The pH has little impact on the complexing capacity of HSL with Zn, Mg and Cu. When pH value is 11.0, the amount of complexed Zn and Cu reaches maximum. The amount of complexed Mg is 48.33 mg·(g sample)$^{-1}$ at pH 11.0, which is close to 48.85 mg·(g sample)$^{-1}$ at pH 9.0. Thus, the optimum reaction pH value is 11.0.

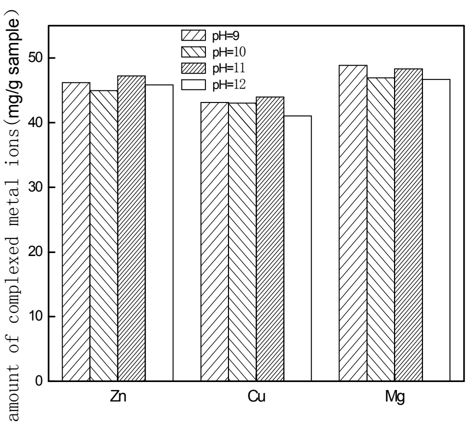


Fig. 4 Influence of the pH on the chelating capacity of HSL

Conclusions

The complexing capacity of SL with metal ions is improved after hydroxymethylated reaction. Results suggest that the superior reaction conditions are as follows: the dosage of formaldehyde is 0.22 g·(g SL)$^{-1}$, temperature is from 60 to 70°C, pH is 11.0. Under this optimum condition, the complexing capacity of HSL with Zn, Mg and Cu respectively increases by 23.3%, 18.9% and 34.9%. Furthermore, the total hydroxyl group content and intrinsic viscosity of HSL are increased, the carbonyl content remains almost the same after reaction. This study shows that the main contributor to complexing capacity improvement is increasing total hydroxyl group content of SL.

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