Properties of Stratified Alkaline Precipitate Isolated from Red Liquor of Acidic Magnesium Sulfite Pulping

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Alkaline precipitate isolated from red liquor of acidic magnesium sulfite pulping exhibited obvious stratification. The properties of the stratified alkaline precipitate were investigated via infrared spectroscopy, ion chromatography, thermogravimetric analysis, and high efficiency liquid chromatography. The sulfonic group of lignosulfonate showed a characteristic absorption peak from 1210 cm^{-1} to 1170 cm^{-1}. There were no significant differences between the structures of the functional groups of the upper and lower layers of the precipitate. The peak time of the sulfonic group was 6.350 min, as measured by ion chromatography. Compared with the upper precipitate, the lower precipitate had more groups with high carbon and low oxygen contents and did not easily decompose. The relative molecular weight of the lower precipitate was greater than that of the upper precipitate. The difference in relative molecular weight of the precipitates gave rise to the observed stratification.

Keywords: Alkaline precipitation; Magnesium lignosulfonate; Ion chromatography; Thermogravimetry

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INTRODUCTION

Lignosulfonate is usually obtained as a by-product of pulping processes (Ouyang *et al.* 2010). The basic components of lignosulfonate are benzyl propane derivatives. Lignosulfonate is an anionic surfactant and has a C6-C3 hydrophobic skeleton, a sulfonic group, and other hydrophilic groups that make up a surfactant structure. It has a molecular weight of 5,000 to 60,000 g/mol and consists of cross-linked phenylpropanoid monomers (Richardson *et al.* 2004). Because of its good wetting, emulsifying, and dispersing properties, it is widely used in dispersants (Yang *et al.* 2007), sand fixation (Ye *et al.* 2012), phenol-formaldehyde resins (Alonso *et al.* 2005), and the construction field (Ouyang *et al.* 2006; Hu *et al.* 2013).

To improve its performance and to study its structure, isolation and purification of lignosulfonate is necessary. However, red liquor from acidic sulfite pulping is soluble over the entire pH range. Thus, isolation and purification of lignosulfonate from red liquor is difficult. Common isolation and purification methods include the ionic-resin method, ultrafiltration, long-chain aliphatic amine extraction, and liquid membrane and solvent extraction (Chakrabarty *et al.* 2009a; Chakrabarty *et al.* 2009b; Chakrabarty *et al.* 2010). However, these methods have shortcomings, such as high energy requirements, that do not benefit industrialization.

The red liquor from acidic magnesium sulfite pulping contains a large amount of lignosulfonate, producing precipitate under alkaline conditions with obvious stratification and a clear interface layer at different pH values (Yang *et al.* 2013). Magnesium lignosulfonate from acidic magnesium sulfite pulping has good solubility under acidic conditions, but precipitation would be produced with the quaternary ammonium salts, calcium, and alkaline conditions. In the preliminary study, the magnesium lignosulfonate isolated from red liquor was found to produce stratified precipitation under alkaline conditions. The alkaline precipitates as two separate layers by centrifugation, with an interface between different layers. So the upper and lower layers of precipitate may have different properties. The composition of the two layers has great potential significance with respect to the efficient recovery and isolation of magnesium lignosulfonate. In this work, the Mg/lignin ratio and average molecular weight of the upper and lower precipitations were investigated. Infrared spectroscopy, ion chromatography, and thermogravimetric analysis (TGA) were conducted with the upper and lower layers of precipitate. The difference between the upper and lower precipitations was also investigated. The aim of this study was to investigate the properties of magnesium lignosulfonate precipitates for their utilization in heavy metal wastewater treatment. Meanwhile, the results will provide a theoretical basis for isolation and purification of magnesium lignosulfonate from the red liquor of acidic magnesium sulfite pulping using the alkaline precipitation method in further work.

EXPERIMENTAL

Materials

The red liquor was obtained from Yingkou Paper Mill, Liaoning Province, China. The raw material was reed, and cooking was performed with acidic magnesium sulfate. The solids content in the red liquor was 10.96% (w/w), the pH was 5.56, and the ash content was 0.154% (w/w). Commercial sodium lignosulfonate was purchased from Sigma-Aldrich Trading Co. Ltd. (Shanghai). The reagent grade was 97%. The molecular formula was $C_{20}H_{24}Na_2O_{10}S_2$, and the molecular weight was 534.51 g/mol.

Isolation of Stratified Alkaline Precipitation from Red Liquor

Samples of red liquor were titrated with 5 mol/L NaOH until the pH was 10, 11, 12, or 13, and then stirred for 10 min. The mixture was centrifuged at 4500 rpm until solid-liquid separation occurred. The precipitate was stratified into upper and lower portions. The upper and lower precipitates at pH 10, 11, 12, and 13 were washed with deionized water and centrifuged. The stratified upper and lower layers of precipitate were separated and then dried for 48 h at 50 °C in a vacuum dryer.

Analysis Methods

The magnesium content of the upper and lower layers of precipitate was analyzed by atomic absorption spectroscopy (HITACHI, 180-80, Japan). The lignin content was determined by ultraviolet (UV) spectrophotometry (Varian, Inc Cary 300, USA). All experiments were repeated three times. Fourier transform infrared (FT-IR) analysis was performed on the samples using a Spectrum One-B FT-IR spectrometer. Infrared spectra were obtained with a resolution of 0.5 cm^{-1} ranging from 400 cm^{-1} to 4000 cm^{-1}. Ion chromatography (IC) was performed on an ICS-5000 ion chromatograph (Dionex, USA) at a set temperature of 30 °C, a flow rate of 1.0 mL/min and IonPac^{TM} AS11-HC chromatographic column, 30 mM NaOH (Dionex, USA) and Watsons water as the leacheate. Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (TGA-Q50, TA Instrument Co., USA), in which samples weighing between 3 and 7 mg were heated from room temperature to 700 °C at a rate of 20 °C/min. Differential thermal analysis (DTA) was performed on a simultaneous thermal analyzer. The apparatus was continually flushed with a nitrogen flow of 30 mL/min at a rate of 20 °C/min. The relative molecular weight was characterized by high performance liquid chromatography (HPLC) (Shimadzu, Japan) at a set temperature of 35 °C, a flow rate of 0.5 mL/min, G3000SWXL chromatographic column, and phosphate buffered saline (PBS, 0.1M, pH6.8) as the mobile phase.

RESULTS AND DISCUSSION

Mg/Lignin Ratio of Stratified Alkaline Precipitation

Mg/lignin ratios were used as a variable for discussion. The aim was to investigate whether the precipitations phenomenon was due to flocculation of magnesium lignosulfonate or to the deposition of lignin caused by magnesium. The trend of the Mg/lignin ratio was obtained as shown in Fig. 1.

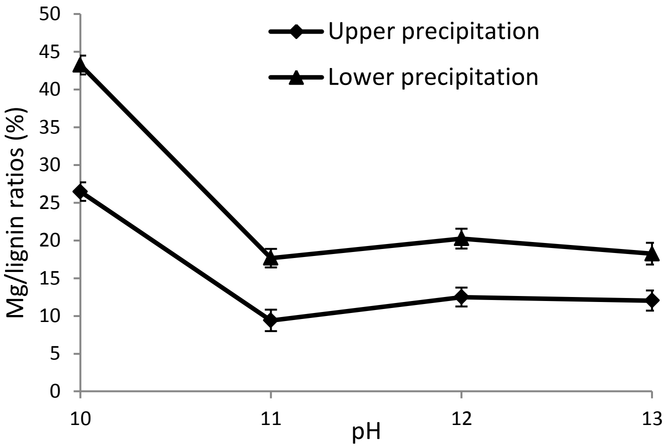

Fig. 1. Mg/lignin ratios of stratified alkaline precipitate

As Fig. 1 shows, the Mg/lignin ratios of the upper and lower layers of precipitate had similar tendencies: a maximum at pH 10, a minimum at pH 11, and mild variations from pH 12 to 13. However, between pH 10 and 13, the Mg/lignin ratio of the lower layer of precipitate was higher than that of the upper layer of precipitate.

Functional Groups of Stratified Alkaline Precipitation

The infrared spectrograms of the upper and lower layers of precipitate at different pH values were obtained as shown in Fig. 2. Both layers obtained under the four pH conditions all had absorption peaks between 1500 and 1600 cm^{-1}, which is the characteristic absorption range for lignin. Compared with acid-insoluble lignin, the upper and lower layers both had an absorption peak at 1200 cm^{-1} to 1170 cm^{-1}. In addition, all precipitates exhibited a weak absorption peak at 1040 cm^{-1} except acid-insoluble lignin, which instead exhibited absorption in the range 1200 cm^{-1} to 1170 cm^{-1}. The absorption at 1040 cm^{-1} was attributed to the sulfonic group in lignin sulfonate. As FT-IR shows, the structure of the functional group of the upper precipitation was similar to that of the lower layer of precipitate.

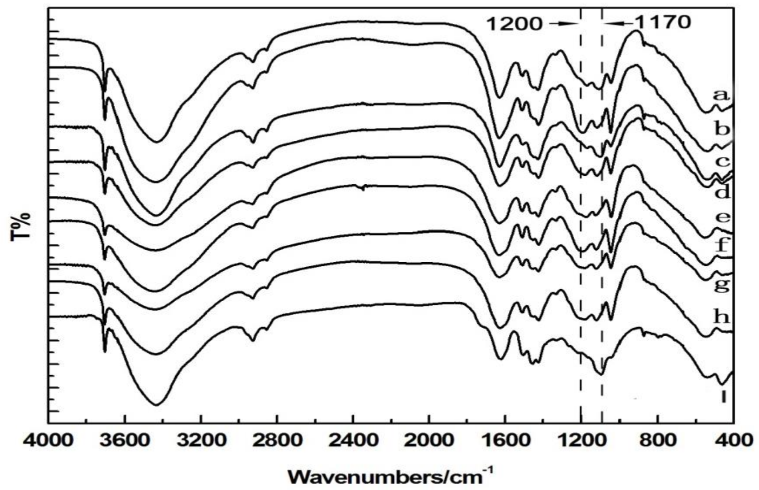

Fig. 2. FT-IR spectra of stratified alkaline precipitates and acid-insoluble lignin. (a-d) upper layer of precipitate at pH 10,11,12,13, respectively; (e-h) lower layer of precipitate at pH 10,11,12,13, respectively; (I) acid-insoluble lignin

Anion Species of Stratified Alkaline Precipitation

The alkaline precipitate of red liquor in sulfuric acid solution was determined by ion chromatography for anions with sodium lignosulfonate as a standard. To eliminate the interference of SO_3^{2-} and SO_4^{2-}, the peak times of SO_4^{2-} and SO_3^{2-} were determined under the same conditions for comparison. The ion chromatograms of SO_4^{2-} and SO_3^{2-} are shown in Fig. 3. The results of anions in the upper and lower precipitations at different pH values are shown in Fig. 4.

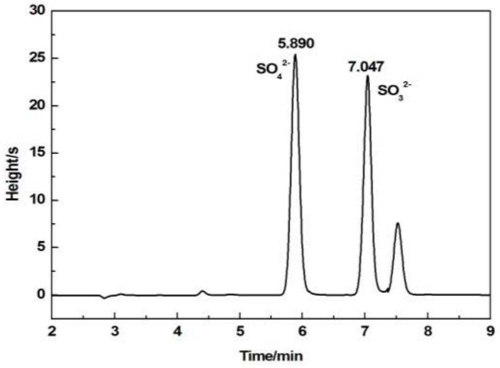

Fig. 3. Ion chromatogram of SO_4^{2-} and SO_3^{2-}

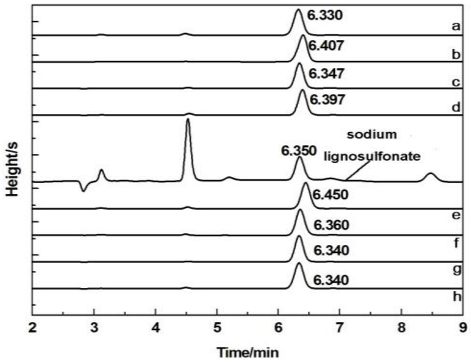

Fig. 4. Ion chromatogram of stratified alkaline precipitate and commercially available sodium lignosulfonate:(a-h); see Fig. 2.

As shown in Fig. 3, the peak times of SO_4^{2-} and SO_3^{2-} were 5.890 and 7.047 min, respectively, which differed from lignosulfonate as well as from the upper and lower layers of precipitate, as shown in Fig. 4. The ion peaks of sodium lignosulfonate appeared at 4.530 and 6.350 min. In order to confirm the peak at 4.53 min in Fig. 4, IC of phenol was performed. The peak time of phenol was found to be 4.61 min, which is close to 4.53 min. The deviation may be caused by the branched carbon of lignin. Therefore, the peak at 4.53 min may be generated by the phenolic structure of lignin. The peak time of the sulfonic group in the determined conditions was 6.350 min. All of the precipitate samples exhibited an ion peak near 6.350 min, and only this large ion peak was observed. The results showed that all of the precipitates had a sulfonic group and that the anionic species in the upper and lower layers of precipitate were similar.

TGA and DTA of Stratified Alkaline Precipitation

The thermal properties of stratified alkaline precipitate are very important with respect to thermochemical conversion into chemicals and energy. TGA is a useful method for the quantitative determination of degradation behavior. The magnitude and location of peaks found in the DTA curve also provide information on the chemical composition of the compound. Therefore, both TGA and DTA were used to study the thermal degradation behavior of the stratified alkaline precipitation. The degradation behavior of the precipitates is greatly influenced by their complicated structures. This behavior can also indirectly reflect the molecular weight of the stratified alkaline precipitation. The results are shown in Fig. 5.

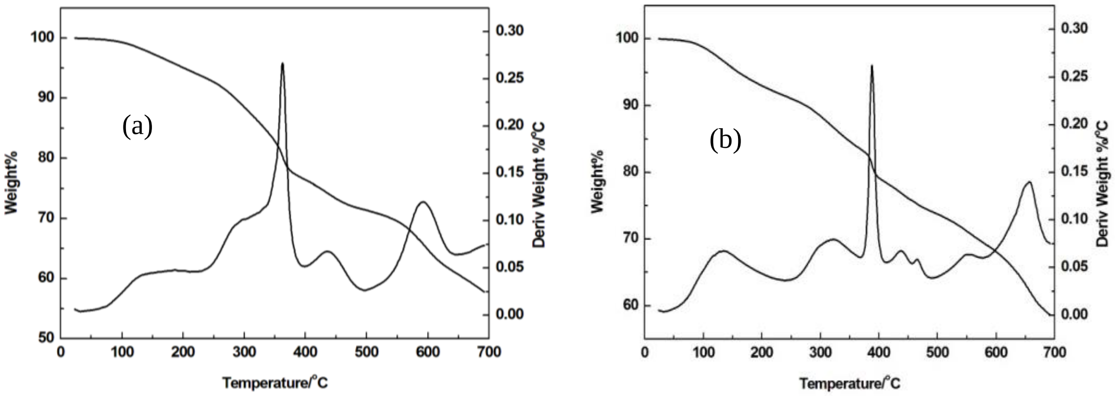

Fig. 5. TGA and DTA of stratified alkaline precipitation: (a) upper layer of precipitate; (b) lower layer of precipitate

As Fig. 5(a) shows, the upper layer of precipitate exhibited two main thermal decomposition processes: the first stage occurred at 340 °C to 400 °C and was attributed to the thermal decomposition of sodium sulfonate groups. The second stage occurred at 500 °C to 640 °C because lignin contains numerous radical groups with high carbon and low oxygen contents and is therefore difficult to decompose. The pyrogenation of these radical groups occurs at a relatively high temperature. However, from Fig. 5(b), TGA of the lower sediment also showed two different thermal decomposition processes: the first stage, similar to that of the upper precipitation, occurred at 360 °C to 400 °C because of the thermal decomposition of sodium sulfonate groups. The second stage occurred at 600 °C to 700 °C, which was higher than that of the upper layer of precipitate, showing that the lower precipitate layer had more radical groups with high carbon and low oxygen contents than the upper layer of precipitate, causing pyrolysis to occur at a somewhat higher temperature.

Relative Molecular Weight of Stratified Alkaline Precipitation

In order to investigate the reasons for the stratification of the precipitation, the relative molecular weight was evaluated by HPLC. Figure 6 shows the pH-dependency of the relative molecular weight of the upper and lower layers of precipitate. In Fig. 6, the relative molecular weight of the upper precipitation was the largest at pH 10, and the relative molecular weight tended to be consistent at about 8000 g/mole within the pH range 11 to 13. The relative molecular weight of the lower layer of precipitate was decreased slightly but did not change significantly with increasing pH increased; the relative molecular weight was 9500 to 10000 g/mole. These results show that the relative molecular weight of the lower precipitate layer was higher than the upper layer within the pH range of 10 to 13. Therefore, it appears that the difference in relative molecular weight of the precipitations gave rise to the observed stratification.

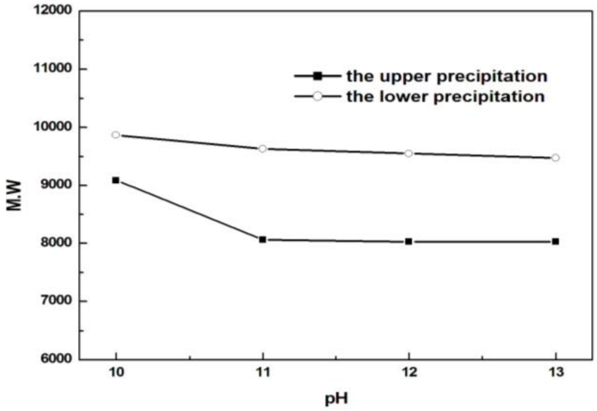

Fig. 6. Relative molecular weight of stratified alkaline precipitation

CONCLUSIONS

1. The precipitate obtained by centrifugation of red liquor of acidic magnesium sulfite pulping was stratified.
2. The sulfonic acid of lignosulfonate had a characteristic absorption peak from 1210 cm^{-1} to 1170 cm^{-1}. The structure of the functional groups of the upper and lower precipitations showed no significant difference.
3. The peak time of sulfonic groups in the upper and lower precipitations was 6.350 min, as measured by ion chromatography.
4. The relative molecular weight of the lower layer of precipitate was higher than that of the upper layer of precipitate. The difference in relative molecular weight of the precipitations caused stratification.

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Article submitted: April 19, 2013; Peer review completed: June 5, 2013; Revised version received: July 31, 2013; Accepted: August 31, 2013; Published: September 4, 2013