Short Communication

Flocculation of high purity wheat straw soda lignin

G.J. Piazza,1, J.H. Lora,2, R.A. Garcia1

U.S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, Biobased and Other Animal Coproducts Research Unit, 600 East Mermaid Lane, Wyndmoor, PA 19038, USA

HIGHLIGHTS

- Action of flocculants on nonsulfonated lignin solutions was tested for the first time.
- Out of five flocculants, only pDADMAC and bovine blood (BB) were effective.
- Zeta potential with BB was always negative.
- Spectroscopic measurements showed 87–92% flocculation by BB and pDADMAC.
- Nitrogen analysis showed that BB was associated with flocculated lignin.

ARTICLE INFO

Article history:
Received 24 September 2013
Received in revised form 11 November 2013
Accepted 14 November 2013
Available online 23 November 2013

Keywords:
Bovine blood
Cationic polyacrylamide
Chitosan
Lignin
Poly(diallyldimethylammonium chloride)

ABSTRACT

In industrial process, acidification causes non-sulfonated lignin insolubility. The flocculants poly(diallyldimethylammonium chloride) (pDADMAC) and bovine blood (BB) also caused lignin insolubility while cationic polyacrylamide, chitosan, and soy protein PF 974 were ineffective. Turbidity determined optimal flocculant, but turbidity magnitude with BB was greater than expected. pDADMAC caused negative lignin Zeta potential to became positive, but BB-lignin Zeta potential was always negative. Insoluble lignin did not gravity sediment, and flocculant–lignin mixtures were centrifuged. Pellet and supernatant dry mass and corrected spectroscopic results were in good agreement for optimal pDADMAC and BB. Spectroscopy showed 87–92% loss of supernatant lignin. Nitrogen analysis showed BB concentrated in the pellet until the pellet became saturated with BB. Subtracting ash and BB mass from pellet and supernatant mass confirmed optimal BB. Low levels of alum caused increased lignin flocculation at lower levels of pDADMAC and BB, but alum did not affect optimal flocculant.

Published by Elsevier Ltd.

1. Introduction

About one-third of biomass is composed of lignin, and most lignin is burned to produce heat or electricity and regenerate process chemicals used in pulping (Varanasi et al., 2013). Economic and environmental concerns about the use of petroleum and natural gas are promoting increasing interest in biofuels (Amidon et al., 2008; Yuan et al., 2013) which produce cellulose and hemicelluloses for biofuel production and a lignin-rich stream as a major co-product. This lignin can be converted to substitutes for petrochemicals (Bos and Sanders, 2013; Rahimi et al., 2013; Varanasi et al., 2013) and biofuels (Beauchet et al., 2012).

Aqueous alkaline treatment of biomass is the most popular delignification technology currently practiced industrially (Shatalov and Pereira, 2013; Lora and Glasser, 2002). Most industrial delignification operations associated with the paper industry incinerate the alkaline extract. High purity lignin is being used in some industrial and consumer applications, and new uses have been proposed (Bos and Sanders, 2013; Yuan et al., 2013). Recovery of processed lignin uses acidification to promote lignin insolubility. The insoluble acidified lignin may be recovered on an industrial scale with filtration. The filter cake is washed with water to reduce the content of impurities such as acid, hemicellulose, sugars, and salts.

There is little information on the effect of flocculants on the lignin recovery process. There are several studies in which flocculant was used to treat wood hydrolysates containing biomass-derived components and relatively small amounts of lignin (Burke et al., 2011; Duarte et al., 2010; Yasarla and Ramarao, 2012). However, there have been no published studies of the influence of flocculants...
on solutions of lignin which had been largely freed of cellulose, hemicellulose, and other biomass components.

Recently it was shown that some purified proteins are active flocculants (Piazza and Garcia, 2010), and that animal blood is a remarkably effective and economically competitive flocculant (Piazza et al., 2011; Piazza and Garcia, 2012). Three active flocculant proteins in blood were identified (Piazza et al., 2012). Here it is reported that bovine blood (BB) and the synthetic flocculant poly(diallyldimethylammoniumchloride) (pDADMAC) act as flocculants on high purity lignin solutions.

2. Methods

2.1. Lignin solution and coagulation–flocculation

Finely divided purified soda lignin (5.88 g, GreenValue Enterprises, Media, PA) was dissolved in 350 mL NaOH (3 g/100 mL) by stirring with a magnetic stirrer for 1 h at 22 °C. The pH was reduced to 5.5 with sulfuric acid. In specified trials, 1.35 mL aluminum sulfate (alum, 20 g/110 mL) was added when the lignin pH was 6.5, and then sulfuric acid was added to reduce the pH to 5.5. Lignin concentration was determined from absorbance at 205 nm. A typical coagulation–flocculation experiment contained 21.9 mL pH 5.5 soluble lignin, 0–4.5 mL flocculant, and NaOH (3 g/100 mL), adjusted to pH 5.5 with sulfuric acid to maintain a constant volume of 25.4 mL in capped glass vials (12 × 950 mm). The vials were placed on a vertically rotating wheel (diameter 17 cm; 17 rev./min) to provide constant gentle mixing.

2.2. Distribution of soluble and insoluble mass

An 8 mL portion of the mixture was removed to a weighed, capped Corning disposable polypropylene 50 mL centrifuge tube. Centrifugation was conducted for 30 min at 12,000g. One mL of the supernatant was removed to a weighed vial for dried weight determination. The remainder of the supernatant was removed for nitrogen and ash determination. Residual moisture in the pellet was determined from absorbance at 205 nm. A typical coagulation–flocculation experiment contained 21.9 mL pH 5.5 soluble lignin, 0–4.5 mL flocculant, and NaOH (3 g/100 mL), adjusted to pH 5.5 with sulfuric acid to maintain a constant volume of 25.4 mL in capped glass vials (12 × 950 mm). One mL of the supernatant was removed by placing the centrifuge tube in a 50 °C oven for 8 h, and then into a vacuum oven for 12 h. After cooling, the pellet dry weight was determined.

2.3. Supernatant absorbance

The wavelength which is most sensitive to lignin is 205 nm (Shi et al., 2011), and absorbance at this wavelength was used to measure supernatant lignin as pDADMAC was added. Absorbance by BB gave significant interference with lignin measurement at 205 nm. Simultaneous measurements at 205 and 280 nm were used to calculate the lignin concentration in the presence of BB using four linear calibration curves: \( A_{205} = C_1e^{C_2} + e; \) \( A_{280} = C_3e^{C_4} + e; \) \( A_{205} = C_5e^{C_6} + e; \) \( A_{280} = C_7e^{C_8} + e; \) where \( A_{205}, A_{280}, A_{205}, \) and \( A_{280} \) are the absorbance of lignin and BB solutions at 205 nm and 280 nm, respectively. \( C_1 \) and \( C_2 \) are the concentration of lignin and BB, respectively. \( C_3, C_4, \) \( C_5, \) and \( C_6 \) are the extinction coefficients that relate absorption to concentration. The constants, \( a, b, c, \) and \( d \), are determined empirically by linear least squares fit of the calibration data. The concentration of lignin was calculated by \( C_2 = (e^{A_{205}} - e^{A_{280}} + e^{280} - e^{205})/ \) \( (e^{C_1} - e^{C_2}) \) where \( e = a + c \) and \( f = b + d \).

2.4. Turbidity, Zeta potential nitrogen, and ash determinations

Turbidity measurements (Hach 2100AN IS Turbidimeter, ISO method 70270, Loveland, CO) were made at 2 h after adding flocculants on high purity lignin solutions. Recently it was shown that some purified proteins are active flocculants (Piazza and Garcia, 2010), and that animal blood is a remarkably effective and economically competitive flocculant (Piazza et al., 2011; Piazza and Garcia, 2012). Three active flocculant proteins in blood were identified (Piazza et al., 2012). Recent work showed that bovine blood (BB) and the synthetic flocculant poly(diallyldimethylammoniumchloride) (pDADMAC) act as flocculants on high purity lignin solutions.

The wavelength which is most sensitive to lignin is 205 nm (Shi et al., 2011), and absorbance at this wavelength was used to measure supernatant lignin as pDADMAC was added. Absorbance by BB gave significant interference with lignin measurement at 205 nm. Simultaneous measurements at 205 and 280 nm were used to calculate the lignin concentration in the presence of BB using four linear calibration curves: \( A_{205} = C_1e^{C_2} + e; \) \( A_{280} = C_3e^{C_4} + e; \) \( A_{205} = C_5e^{C_6} + e; \) \( A_{280} = C_7e^{C_8} + e; \) where \( A_{205}, A_{280}, A_{205}, \) and \( A_{280} \) are the absorbance of lignin and BB solutions at 205 nm and 280 nm, respectively. \( C_1 \) and \( C_2 \) are the concentration of lignin and BB, respectively. \( C_3, C_4, \) \( C_5, \) and \( C_6 \) are the extinction coefficients that relate absorption to concentration. The constants, \( a, b, c, \) and \( d \), are determined empirically by linear least squares fit of the calibration data. The concentration of lignin was calculated by \( C_2 = (e^{A_{205}} - e^{A_{280}} + e^{280} - e^{205})/ \) \( (e^{C_1} - e^{C_2}) \) where \( e = a + c \) and \( f = b + d \).

3. Results and discussion

3.1. Treatment by flocculants

Lignin solutions were prepared in aqueous NaOH. The pH was lowered to 5.5 with sulfuric acid, and flocculants were tested for their ability to promote lignin insolubility. Cationic polyacrylamide (Superfloc C-494 from Cytec), chitosan (75–85% deacetylated) and soy protein PRO-FAM 974 showed little lignin flocculation activity, but pDADMAC (MW 240,000) and BB were effective lignin flocculants. In some experiments discussed below, 0.042 g alum per g lignin was added along with pDADMAC (pDADMAC-Al) and BB (BB-Al). The purpose of adding low level alum and flocculant together was to ascertain whether their interaction was synergistic.

3.2. Turbidity of lignin–flocculant mixtures

Fig. 1A shows 2 h turbidity measurements for four different flocculation treatments. The highest turbidities were obtained at the following flocculant/lignin ratios: pDADMAC, 0.066–0.37 mg/mg; pDADMAC-Al, 0.080–0.36 mg/mg; BB, 0.89–1.7 mg/mg; BB-Al, 0.87–1.7 mg/mg. Thus alum does not significantly affect optimal flocculant/lignin ratios. The maximum turbidity magnitude for BB was about twice as large as that for pDADMAC. Subsequent data showed that the degree of lignin flocculation with optimal BB was about the same as that with optimal pDADMAC. Turbidity from BB can account for only 1.3% of the observed turbidity of the lignin–BB mixture, and thus the high magnitude turbidity in BB–lignin mixtures results from an interaction of BB with lignin.

3.3. Zeta potential readings

As the amount of pDADMAC was increased, the Zeta potential also increased, and an imaginary curve drawn through the Zeta potential values gives an interpolated zero Zeta potential value at the following flocculant/lignin ratios: pDADMAC/lignin, 0.24 mg/mg; pDADMAC-Al/lignin, 0.20 mg/mg (Fig. 1B). These pDADMAC/lignin ratios are slightly lower than the high end of the range of pDADMAC/lignin ratios observed at the highest turbidity readings (Fig. 1A). At still higher pDADMAC/lignin, Zeta potential readings became positive which correspond to lower turbidity readings.

Zeta potential readings with BB became progressively less negative as the flocculant/lignin ratio was increased (Fig. 1B). However, the Zeta potential with BB and BB-Al never became more negative than about –5 mV. The excess negative charges in the BB–lignin system are likely due to negative charges in the interior regions of the BB proteins or negative charges associated with specific proteins that do not interact with the lignin. At pH 5.5 most proteins in blood have a net positive charge, but some proteins in blood such as bovine serum albumin have isoelectric points less than 5.5 and thus have a net negative charge.

3.4. Percent of pellet mass

Lignin mixtures were centrifuged, and the supernatant and pellet were separated. The percent pellet mass is the ratio of the mass of the centrifugation pellet to the mass of the dried flocculant–lignin mixture times 100 (Fig. 1C). The higher mass in some
alum-containing trials at lower flocculant concentrations shows that alum is binding to lignin. The loss of influence of alum at higher flocculant concentrations shows that lignin-alum binding is diminished by displacement of the alum from the lignin by the flocculant. The highest percent pellet mass values were at the following flocculant/lignin ratios: pDADMAC, 0.066–0.37 mg/mg; pDADMAC-Al, 0.048–0.36 mg/mg; BB, 0.33–1.2 mg/mg; BB-Al, 0.30–1.1 mg/mg.

The maximum influence of each flocculant upon the percent pellet mass was obtained by subtracting the percent pellet mass of controls without flocculant from the highest percent pellet mass obtained with flocculant. The resulting increases in percent pellet masses were pDADMAC, 59%; pDADMAC-Al, 51%; BB, 61%; and BB-Al, 44%. The lower net increases obtained with flocculant in the presence of alum is caused by higher alum control values.

3.5. Supernatant absorbance measurements

The lowest supernatant lignin concentrations were found at the following flocculant/lignin ratios: pDADMAC, 0.068–0.37 mg/mg; pDADMAC-Al, 0.048–0.36 mg/mg; BB, 0.33–1.2 mg/mg; BB-Al, 0.30–1.1 mg/mg.

The maximum influence of each flocculant upon the percent pellet mass was obtained by subtracting the percent pellet mass of controls without flocculant from the highest percent pellet mass obtained with flocculant. The resulting increases in percent pellet masses were pDADMAC, 59%; pDADMAC-Al, 51%; BB, 61%; and BB-Al, 44%. The lower net increases obtained with flocculant in the presence of alum is caused by higher alum control values.

3.6. Distribution of BB

The nitrogen contents of samples of the supernatant and pellet were compared to that of BB (15.9 ± 0.8%) with a correction for lignin nitrogen (0.62 ± 0.03%) to get the amount of BB in each fraction. The highest percent of pellet BB was found at the following flocculant/lignin ratios: BB, 0.61 mg/mg; BB-Al, 0.37–0.59 mg/mg (Fig. 2A and B). Insight into the distribution of blood is shown by plotting the data as the percent ratio of BB mass to the dry mass of the pellet or supernatant fraction. The amount of supernatant BB relative to the supernatant mass remained relatively low until the BB/lignin ratio reached 0.61 mg/mg with BB or 0.59 with BB-Al (Fig. 2C and D). Thus at lower BB, most BB congregated with the lignin in the pellet fraction. At values of the BB/lignin higher than 0.61 mg/mg or BB-Al/lignin higher than 0.59 mg/mg, the amount of supernatant BB rose considerably because the BB-saturated pellet lignin could absorb no more BB. The observation that BB is strongly absorbed by lignin is consistent with research demonstrating that proteinaceous enzymes are strongly adsorbed by lignin (Pareek et al., 2013). Hemoglobin, the major protein in BB, is a good flocculant for kaolin (Piazza et al., 2012) and may contribute to lignin flocculation by BB.

3.7. BB pellet mass without ash and BB

Ash mass measurements of the supernatant and pellet fractions were made. These masses, as well as those of BB, were subtracted from the pellet and supernatant masses to directly give the mass of lignin. Because the pellet masses, supernatant masses, BB masses,
and ash masses each have associated measurement errors, the calculated errors in the calculated lignin masses are fairly high. Nevertheless, at the optimal flocculant/lignin range, the pellet mass values are high whilst those of the supernatant are low. The highest lignin pellet masses given by BB and BB-Al were at the flocculant/lignin ranges of 0.46–1.7 mg/mg and 0.45–1.7 mg/mg, respectively (data not shown). These ranges are similar to the optimal flocculant/lignin ranges given by the turbidity measurements (Fig. 1A).

4. Conclusion

The flocculants BB and pDADMAC caused lignin insolubility without high acid, but flocculant–alum synergism was not evident. Measurements by turbidity, pellet mass, spectroscopy, and lignin mass gave similar ranges for optimal BB and pDADMAC. BB turbidity magnitude was not a reliable indicator of the degree of flocculation, and BB removed no more lignin from solution than pDADMAC. Zeta potential was a poor predictor of BB induced lignin flocculation, as it was always negative. The dependence of BB protein net charge upon pH possibly gives BB an advantage over pDADMAC in schemes to disrupt the lignin–flocculant complex in lignin processing after flocculation.

Acknowledgement

Technical assistance was provided by F. Fox.

References


Fig. 2. Influence of the flocculant/lignin ratio on the percent distribution of BB in the supernatant and pellet for BB (A) and BB-Al (B). The influence of the flocculant/lignin ratio on the mass of BB in the supernatant and pellet divided by the dried mass the supernatant and pellet for BB (C) and BB-Al (D). Legend: BB or BB-Al in the supernatant (s); BB or BB-Al in the pellet (d).