Influence of Residual Black Liquor in Pulp on Wastewater Pollution after Bleaching Process

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The influence of residual black liquor in pulp on wastewater pollution after the bleaching process was studied. The results show that the COD_{Cr} in bleaching effluent has a remarkable linearity with bleaching loss of pulps without residual black liquor. For pulps with some residual black liquor, more than 34% of the overall COD_{Cr} is produced by the residual black liquor. It follows that more effective washing to reduce the residual black liquor is an appropriate way to control the pollutant discharges from pulp and paper mill industry.

Keywords: Residual black liquor; Bleaching loss; COD_{Cr}; Wastewater pollution

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INTRODUCTION

In terms of fresh water usage, the pulp and paper mill industry is a water-intensive industry; it is ranked third in the world after metals and chemical industries (Merayo *et al*. 2013). Wood preparation, pulping, bleaching, and coating operations are the main sources of pollution (Mahesh *et al*. 2016). Effluents of the pulp and paper industry contain a number of toxic compounds. The rejection of this effluent in nature without any treatment is responsible of serious damage for the environment and constitutes a threat for human health (Lara *et al*. 2003).

Kraft (or sulfate) and soda are the two major alkaline processes to produce chemical pulps (Cardoso *et al*. 2009). Cellulose fibers are disassociated from lignin by chemical reactions, which occur in a pressurized digester where wood chips or fibers are heated and cooked with the cooking liquor, composed basically of NaOH (sodium hydroxide), and in the case of the kraft process, also sodium sulfide (Cao *et al*. 2011; Zheng *et al*. 2012). The products from the digester reactions are fibers and black liquor. Black liquor is one of the main by-products of pulp paper industry, which is considered a pollutant because it contains about 50% of lignin (Zaied and Bellakhal 2009).

Some new methods for the treatment of black liquor have been researched, such as the oxidizing action of the Fenton reagent in the presence of solar UV irradiation (Fe^{2+} /H_2O_2 /UV) (Torrades *et al*. 2003), ultra-filtration for the recovery of lignin starting from black liquor (Wallberg *et al*. 2005; Wallberg and Jönsson 2006; Wallberg *et al*. 2003), and the electrocoagulation method (El-Ashtoukhy *et al*. 2009; Khansorthong and Hunsom 2009; Zaied and Bellakhal 2009). But none of them is widely used industrially due to high cost. At present, soda recovery units (Licursi *et al*. 2015) have been mainly applied for the treatment of black liquor. However, limitations of equipment lead to only about 85% recovery ratio for black liquor. This means that more than 15% of the black liquor remains in the pulp, and unfortunately it will be passed forward into the bleaching process.

Bleaching of pulp using chlorine-based agents is still practiced in China and in other developing countries (Deshmukh *et al*. 2009). Due to the presence of chlorinated organic compounds, wastewater from bleaching units is toxic (Savant *et al*. 2006). These organochlorine compounds are collectively termed as adsorbable organic halides (AOX). AOX is a general parameter determining the total amount of organically bond halogens in wastewater. Many AOX compounds are persistent in the environment and show a significant toxic effect on human beings (Höfl *et al*. 1997; Barroca *et al*. 2001). About 500 different chlorinated organic compounds have been identified in paper mill effluent (Savant *et al*. 2006). Due to the universal harmful effect of organic halogens, many countries including China have a series of discharge standards for industrial wastewater (Xie *et al*. 2016). There are a number of approaches that have been explored to reduce the AOX level in paper mill effluent, which can be categorized as physic-chemical and biological (Kumar 2013). Physic-chemical approaches include adsorption, ultrafiltration, nanofiltration, and reverse osmosis (Patel and Suresh 2008). Biological techniques involve the use of diverse kinds of micro-organisms like bacteria, fungi, algae, and microbes of extreme habitats for reducing AOX and chromophores in pulp mill effluent (Belmonte *et al*. 2006; Ruggaber and Talley 2006; Morales *et al*. 2015). Although these methods of treatment seem effective for the wastewater of pulp industry, they present the disadvantage of being expensive because of their operating cost and the high cost for the chemical reagents used. How to reduce pollution emissions in the production process has become urgent for the pulp and paper industry.

There is a lack of literature about effects of remained black liquor entering the bleaching system on the COD_{Cr} of wastewater. This paper investigated the effects of residual black liquor in pulp on COD_{Cr} after the H-bleaching process, which is supposed to bring about fundamental changes in pollution control and treatments for pulping and paper-making industry in China.

EXPERIMENTAL

Raw Materials

Pinus koraiensis was used as the raw material, with alkaline cooking. The total solids content of the black liquor was 194.3 g/L. The three-stage adverse current washing method was adopted to wash the black liquor out of the pulp at 60 °C to simulate industrial washing. A stock suspension having 35% (or alternatively 30%) consistency has 0.72 (or alternatively 3.71) g of black liquor residual solids in the pulp suspension. As shown in Table 1, four samples were selected according to different degrees of cleanliness for further analysis. The No. 1 pulp was thoroughly washed without any residual black liquor (ideal condition) and has a Kappa index of 27.58, whiteness of 34.32 % ISO, and viscosity of 474 mL • g^{-1}. There are different amounts of black liquor in the No. 2, No. 3, and No. 4.

Table 1. Main Components and Cleanness in 20 g Slurry of Different Pulps

Slurry	No. 1	No. 2	No. 3	No. 4
Dry pulp (g)	20	19.6	18.2	16.1
Black liquor (g)	0	2.4	10.8	23.52
Solids (g)	0	0.4	1.8	3.9

Bleaching Process of Pulp

In the pulp bleaching section, the amount of pulp was 20 g on a dry solids basis. Prior to experiments, these samples had been equilibrated to 10%. The runs were carried out with different doses of active chlorine (4%, 7%, 10%, 13%, 16%) and the other parameters were kept fixed. Single stage hypochlorite bleaching was adopted at 52 °C for 25 min in a water bath. Mixing was accomplished by means of stirring every 10 min in order to make the bleaching reaction better; 8% sodium hydroxide was applied to adjust the pH, and the pH values of the bleaching solution were measured before the reaction, during bleaching, and after the reaction (Diel *et al.* 2016).

Bleaching effluent was collected and the pulp was washed thoroughly with enough water to remove suspended matter and particles for the future study.

Bleaching Process of Black Liquor

To study the effects of residual black liquor on pollution loads in the bleaching process, the amount of black liquor of No. 1 (2, 3, 4) was 0 (2.4, 10.8, 23.5) g and the amount of solids of No. 1 (2, 3, 4) was 0 (0.4, 1.8, 3.9) g. The same bleaching method was applied to bleaching process of black liquor.

Other Analytical Method

Prior to experiments, all liquid effluent samples were filtered with a membrane filter (pore size 0.45 μm) to remove suspended matter and particles. The determination of the COD_{Cr} was carried out using a Hach spectrophotometer (DR2800, Hach, Loveland, CO, USA), according to standard methods (Karichappan *et al*. 2014). The pH was measured with a Sartorious PB-10 (Sartorius, Germany) pH meter.

RESULTS AND DISCUSSION

Kappa Index and Bleaching Loss of No. 1 and COD_{cr} of No. 1 after Bleaching

The No. 1 pulp sample without residual black liquor was H-bleached at different amounts of available chlorine of 4%, 7%，10%, 13%, and 16%, and Kappa index and bleaching loss of No. 1 and COD_{cr} of No. 1 after bleaching are shown in Table 2.

Table 2. Kappa Index and Bleaching Loss of No. 1 and COD_{cr} of No. 1 after Bleaching

Available Chlorine Content	4%	7%	10%	13%	16%
Kappa index	14.24	8.94	8.64	6.06	4.85
Bleaching loss (%)	3.00	4.80	5.70	6.10	7.15
CODcr ($mg \cdot L^{-1}$)	2823.1	4497.6	5274.5	5617.2	6150.0

As is shown in Table 2, with the increase of available chlorine, the kappa index of pulps decreased, indicating that lignin was disassociated from fibers. When the available chlorine was 16%, the removal rate of lignin was about 82.4%. The bleaching loss and COD_{cr} increased with the increase of the available chlorine. A linear relationship between bleaching loss and COD_{cr} was obtained, as is shown in Fig. 1.

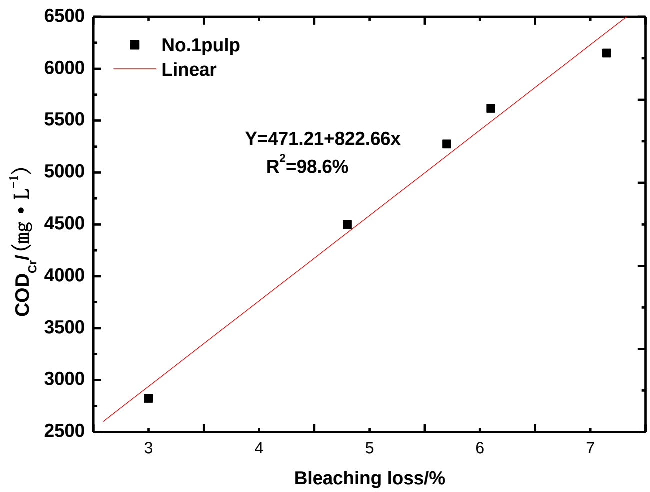

Fig. 1. Relationship between bleaching loss and COD_{cr} in effluents for pulps without residual black liquor

For pulps without residual black liquor, the COD_{cr} in the wastewater are contributed to lignin and carbohydrates that are disassociated from the cellulose fibers (solid phase lignin). For the same fiber materials with the same bleaching conditions, the COD_{cr} contributed to solid phase lignin is calculated as COD_1 in the next experiments.

Kappa Index and Bleaching Loss of Pulp with Residual Black Liquor and COD_{Cr} of Pulp with Residual Black liquor after Bleaching

H-bleaching was applied to the No. 2, No. 3, and No. 4 pulp samples under different available chlorine dosages of 4%, 7%, 10%, 13%, and 16%. The kappa index and bleaching loss of No.2 (3, 4) and COD_{Cr} of No.2 (3, 4) are shown in Tables 3, 4 and 5, respectively. The COD_0 is the actual determination values in bleaching effluents, which is composed of COD_1 produced by solid phase lignin, and COD_L originated from the theoretical residual black liquor. According to Fig. 1, COD_1 can be calculated with bleaching loss.

To test the reliability of the results obtained by calculating the COD_L from COD_0 and COD_1, different amounts of black liquor were H-bleached in the same bleaching conditions, and the determination of COD_{Cr} in bleached residual black liquor was obtained as COD_2, as shown in Tables 3, 4, and 5.

The relative standard deviation (RSD) of the COD_L and COD_2 ranged from 0.10% to 3.15%. Thus, the calculated values were in good agreement with the measured values, and it was feasible to calculate the COD_1 by Fig. 1 to determine the pollution load from solid phase lignin. For all pulp samples, with increasing available chlorine content, the kappa index decreased gradually.

For the same slurry, the COD_L from residue black liquor had a greater effect on the wastewater pollution load than COD_1 from solid phase lignin without No.2 pulp, but

COD_L from residue black liquor in the wastewater pollution load of No.2 was still evident. This is because the residual black liquor mainly includes the small molecule lignin compounds, hemicellulose, and some organic degradation of sugars after cooking (Sun *et al.* 1999; Mussatto *et al.* 2007). However, with the increase of available chlorine, the increase of the COD_L is smaller than that of COD_1 in wastewater, because the amount of residue black liquor in the slurry is certain. Another possible reason is that aldehyde or alcohol organics in the black liquor are oxidized to the acid organics by adding one more oxygen, resulting in a smaller COD_L change.

Table 3. No. 2 Pulp Properties and Pollution Load after H-Bleaching

Available Chlorine Content	4%	7%	10%	13%	16%
Kappa index	16.64	12.82	10.42	9.28	7.57
Bleaching loss (%)	2.43	3.48	5.22	5.97	6.84
COD_0 ($mg \cdot L^{-1}$)	4360.5	5436	7506.6	8470	9182
COD_1 ($mg \cdot L^{-1}$)	2470.3	3334.1	4765.5	5382.5	6098.2
(COD_1/COD_0) (%)	57	61	63	64	66
COD_L ($mg \cdot L^{-1}$)	1890.2	2101.9	2741.1	3087.5	3083.8
COD_2 ($mg \cdot L^{-1}$)	1882.4	2238.6	2610.8	3147.5	3189.3
*COD_L=COD_0-COD_1					

Table 4. No. 3 Pulp Properties and Pollution Load after H-Bleaching

Available Chlorine Content	4%	7%	10%	13%	16%
Kappa index	18.57	16.62	14.13	12.29	11.72
Bleaching loss (%)	1.21	1.87	2.91	3.79	4.67
COD_0 ($mg \cdot L^{-1}$)	9828.5	10709	12263	12998	13852
COD_1 ($mg \cdot L^{-1}$)	1465.6	2008.0	2866.9	3590.1	4313.33
(COD_1/COD_0) (%)	15	19	23	28	31
COD_L ($mg \cdot L^{-1}$)	8362.9	8701.0	9396.1	9407.9	9538.7
COD_2 ($mg \cdot L^{-1}$)	8209.4	8924.1	9262.0	9346.2	9621.8
*COD_L=COD_0-COD_1					

Table 5. No. 4 Pulp Properties and Pollution Load after H-Bleaching

Available Chlorine Content	4%	7%	10%	13%	16%
Kappa index	22.27	18.94	17.27	15.45	12.12
Bleaching loss (%)	0.56	1.11	1.67	1.98	2.65
COD_0 ($mg \cdot L^{-1}$)	21062	23085	23837	24664	26706
COD_1 ($mg \cdot L^{-1}$)	931.93	1385.3	1842.3	2096.2	2654.8
(COD_1/COD_0) (%)	4.4	6.0	7.7	8.5	9.9
COD_L ($mg \cdot L^{-1}$)	20130	21700	21995	22568	24051
COD_2 ($mg \cdot L^{-1}$)	20110	21550	21894	23013	24610
*COD_L=COD_0-COD_1					

For different slurries at the same amount of available chlorine, with the increase of residual black liquor in the pulp, COD_0 and COD_L gradually increased and bleaching losses and COD_1 decreased. Thus, the liquid organics are more likely to react with bleaching agent than solid phase lignin; in a bleaching process for pulps with residual black liquor, most of bleaching agents react with the solubilized organics first. This reaction weakens the bleaching efficiency and wastes bleaching agents. A decrease in residual black liquor can reduce the dosage of bleaching agent, which may lessen the production of AOX and decrease the toxicity of wastewater (Rey *et al.* 2013; Kumar

Chenna *et al.* 2016).

Contribution of Residual Black Liquor to COD_{cr} in Bleaching Effluents

The contribution of residual black liquor to COD_{cr} after H-bleaching is shown in Fig. 2. As shown in Fig. 2 and Tables 3, 4, and 5, for different slurries in the same amount of available chlorine, a greater amount of residual black liquor resulted in a greater COD_{Cr}. For the same slurry, with the increase of available chlorine content, the contribution of residual black liquor to COD_{cr} in the wastewater decreased gradually. But all COD_L/COD_0 ratio values were more than 34%. This result reveals that COD_{cr} from the residual black liquor was greater.

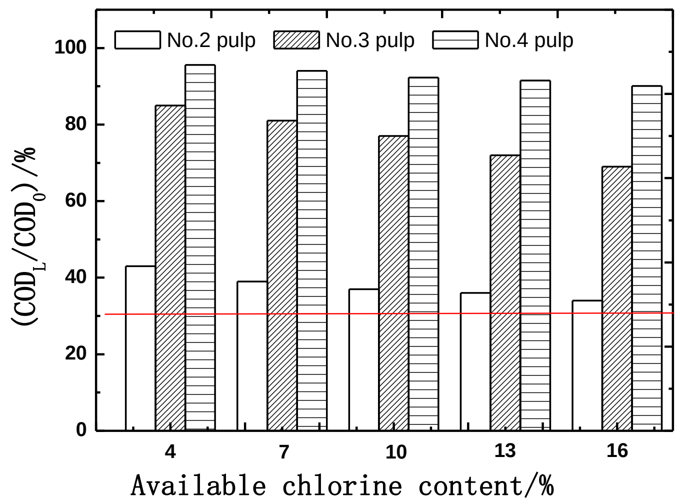

Fig. 2. Effect of black liquor on wastewater

CONCLUSIONS

1. In the H-bleaching process, the relationship of bleaching loss and COD_{Cr} in bleaching effluents is remarkably linear for pulps without residual black liquor.
2. For pulps with residual black liquor in H-bleaching process, most of bleaching agent reacts with residual black liquor in the pulp first. The results show that the COD_{Cr} produced by residual black liquor accounted for more than 34% of the overall COD_{Cr}.

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