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Influence of H_2SO_4 as Activator to ClO_2 on the Bleaching Effects

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Abstract: In this study, we show that chlorine dioxide activated by 4% Hydrochloric Acid Solution (HCl) has the same bleaching effects as that by sulfuric acid (H_2SO_4). Chlorine dioxide is an important bleaching agent in ECF bleaching. Stable chlorine dioxide in conjunction with Hydrochloric Acid Solution (HCl) activation in a certain proportion can be applied in the process of pulp bleach with a bleaching result of environment friendly, positive brightness stability, low pollutant bleach and pulp brightness stability, not easy to reverse. By experiment of OD, ODED, ODQP bleach Triploid of Populus Tomentos with stable chlorine dioxide activated by sulfuric acid (H_2SO_4). Moreover, the result of the experiment can prove that principle of activation of HCl to ClO_2 is similar to H_2SO_4 to ClO_2, that is, to provide an acid environment for ClO_2.

Keywords: Triploid of populus tomentos, soda-AQ pulp, chlorine dioxide activated by H_2SO_4, chlorine dioxide activated by HCl, bleaching effects

INTRODUCTION

Chlorine dioxide, one of the most important bleaching agents in ECF bleach, is a high efficiency bleach agent with oxidative ability, whose chemical property is different from elemental chlorine (Lao *et al*., 2001). Chlorine dioxide can choose oxidative lignin and pigment with little damage to fiber. Pulp after chlorine dioxide has high brightness, strength and little reversion. Meanwhile, the role of chlorine dioxide in pulp bleach is to discompose oxide lignin, making benzene ring ruptured and oxidative degradation to hydroxyl acids (Hans and Chreeson, 2005; Ji *et al*., 2005). Therefore, it is rare to form chloride aromatic compounds. What's more, elemental chorine in ClO_2 restore to chloride ion with oxidative valence +5. ClO_2 per mol is equivalent to 2.5 moL of C_{l2}, which significantly lowered the use of elemental chlorine and elemental chlorine does not react and substitute during the process of oxidation lignin. Organic chlorine formation dosage is far less than H stage or CEH bleaching. Therefore, chlorine dioxide bleach technique is a high efficiency and environmental friendly pulp bleach. In recent years, chlorine dioxide bleaching technique has developed very fast and played a more and more important role in pulp bleaching (Zhao *et al*., 2011; Cui *et al*., 2010; Pang, 2011).

Chlorine dioxide is very unstable and easy to decompose, which, to some extent, limit its use and development. Now imported chlorine dioxide generators are applied to produce chlorine dioxide for pulp bleach in large-scale pulp and paper plants in our country. According to preparation principle of stable chlorine dioxide, we respectively choose H_2SO_4 and HCl as the activation of stable ClO_2 through experiments to compare whether the bleaching effects are equivalent, activation of HCL to ClO_2 is similar to H_2SO_4 to ClO_2, thus prove medium ClO_2 generator with reaction principle (1):

$$2NaClO_3+2H_2SO_4+H_2O_2 = 2ClO_2+2NaHSO_4+2H_2O$$

Preparing ClO_2, the rest aid solution can be directly used for adjusting pH valence of pulp and save production cost without separation of the rest H_2SO_4. In the format (1) above, in the process of ClO_2, $NaHSO_4$ and water are synthesized, as well as the excessive H_2SO_4 left. In addition, NaH SO_4 can be ionized in water and the excessive H_2SO_4 influences the ClO_2 bleaching effects. Therefore, H_2SO_4 was chosen as the activation of stable ClO_2 for the pulp bleaching experiment and at the same time the activation effect of H_2SO_4 could be conducted through comparison experiment with normal activation of HCl. It was conjectured that in the equation above of ClO_2 preparation, reflection raffinate is not separated, ClO_2 can be directly used for the pulp bleaching after proper pH value is adjusted and simple reflection principle in (1) can be used for ClO_2 preparation in the medium pulping enterprises. Environmental friendly ECF bleaching can be

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applied for bleaching production line ClO_2 of with high quality and low investment.

In this study, we show that chlorine dioxide activated by 4% Hydrochloric Acid Solution (HCl) has the same bleaching effects as that by sulfuric acid (H_2SO_4). Moreover, the result of the experiment can prove that principle of activation of HC_l to C_lO_2 is similar to H_2SO_4 to C_lO_2, that is, to provide an acid environment for C_lO_2.

MATERIALS AND EXPERIMENTS

Materials: Triploid of Populus Tomentos in this experiment is provided by Sun Paper, Shandong Province, China, chipped and cooked with soda-AQ (anthraquinone) method in our laboratory. The property of Soda-AQ pulp was kappa number 17.4, viscosity 839 mL/g, yield rate of 54.1% and brightness 35.1% ISO.

Oxygen delignification: Oxygen delignification was done in JF-DSTE polymerizing-kettle with the function of stirring and automatically constant temperature.

Conditions of oxygen delignification are: pulp consistency 10%, alkali dosage 2.5%, oxygen pressure 0.5~0.6 MPa, temperature 100ºC, time 60 min, $MgSO_4$ 0.5%, brightness of pulp after oxygen delignification 55.4% ISO and viscosity 757 mL/g.

Bleaching liquid preparation: Stable ClO_2 is respectively activated by 4% HCl and 5% H_2SO_4 (the dosage of excessive H_2SO_4 is around 5% in a small ClO_2 preparation facility) according to the proportion of 1:1, malonic acid-iodimetry method is used for the calibration of ClO_2 after both activation.

Bleaching method: Bleaching sequence of OD, ODED, ODQP are, respectively applied for the pulp bleaching experiment. Reaction is done in the polythene bags with the temperature controlled by constant water bath pot. The pulp can be even mixed by kneading after reaction every 15 min.

Chelating treatment: Dilute sulfuric acid solution is used to adjust the pH valence during chelation.

Analysis method: Determination of viscosity: Cupriethylenediamine method is used according to the stipulation of national criteria GB1548-1989. Determination of Kappa value: according to the criteria of GB1546-1989. Determination of brightness: brightness meter YQ-Z-48B is applied (Liu, 2004).

RESULTS AND DISCUSSION

Generally in laboratory, HCl is used as activators for stable ClO_2, in this experiment, both HCl and H_2SO_4 were chosen as the activators for stable ClO_2 with an activation volume proportion 1:1; 10% NaOH solution and 5% H_2SO_4 were used for the adjustment of pH valence of the two bleaching solution; bleaching effects of three bleaching sequence of OD, ODED and ODQP were applied for the comparison of the activation effects. In the following bleaching, the chosen pulp was obtained by oxygen delignification under same conditions, the property of the pulp is the same and that is, the brightness is 55.4% ISO, viscosity 757 mL/g.

Comparison of the results of OD bleaching: In this experiment, two OD bleaching sequences are applied for bleaching. The bleaching conditions for D stage were: pulp consistency 8%, initial pH valence controlled to be around 4, temperature 60ºC, reaction time 120 min; under which conditions, experiments were done to the pulp of oxygen delignification and the results were in the Table 1. Table 1 indicates the different result of using 4% HCl and 5% H_2SO_4, respectively for pulp bleaching with the same ClO_2 dosage. When ClO_2 dosage was 0.4%, the brightness of using ClO_2 activated by HCl was lower than that activated by H_2SO_4, but the viscosity of the former was higher than the latter; When ClO_2 dosage was 0.7%, the brightness of using ClO_2 activated by HCl was a little higher than that activated by H_2SO_4, but the viscosity was equivalent; When ClO_2 dosage was 1.0%, the brightness of using ClO_2 activated by HCl was lower than that activated with H_2SO_4, but the viscosity was the same. From the pulp yield of the bleached pulp, yield of using ClO_2 activated by HCl was a little higher than that activated by H_2SO_4.

Table 1: Bleaching results of od bleaching sequence

				Brightness % ISO		
Acid for activation	ClO_2 dosage/%	Initial pH valence	Yield/%	Front	Back	Viscosity/mL/g
4% HCl	0.4	3.85	98.10	70.6	70.2	752
	0.7	4.10	97.36	72.8	72.3	746
	1.0	3.67	97.41	74.8	74.5	730
5% H_2SO_4	0.4	4.05	97.94	71.4	71.1	751
	0.7	4.06	97.38	71.8	71.4	748
	1.0	3.19	96.17	75.0	74.6	727

1: Volume proportion 1:1 for ClO_2 activation. Stable ClO_2 for the experiment was supplied by Shangdong University Huate Company; 2: The pulp yield was the last bleaching yield in the Table 1

Table 2: Bleaching results of ODED bleaching sequence

Acid for activation	ClO_2 dosage for the 1st D stage/%	Initial pH valence	ClO_2 dosage for the 2nd D stage/%	Initial pH valence	Yield/%	Brightness % ISO Front	Brightness % ISO Back	Viscosity/ mL/g
4% HCl	0.3	3.55	0.4	3.75	97.3	81.8	82.2	729
	0.5	4.13	0.5	3.80	97.2	82.9	84.0	720
	0.7	4.21	0.3	3.85	96.9	82.9	83.9	702
5% H_2SO_4	0.3	3.98	0.4	3.86	97.4	81.3	81.8	734
	0.5	4.05	0.5	3.81	97.3	82.2	83.1	729
	0.7	4.01	0.3	3.79	96.8	83.2	83.9	704

1: Volume proportion 1:1 for ClO_2 activation. Stable ClO_2 for the experiment was supplied by Shangdong University Huate Company; 2: The pulp yield was the last bleaching yield in the Table 2

Table 3: Bleaching results of odqp bleaching sequence

Acid for activation	ClO_2 dosage/%	Initial pH value	Yield /%	Brightness % ISO Front	Brightness % ISO Back	Viscosity/mL/g
4% HCl	0.3	4.05	97.66	85.2	86.1	726
	0.5	3.61	96.50	84.5	85.8	720
	0.7	3.80	96.00	85.2	86.4	712
5% H_2SO_4	0.3	4.01	98.27	83.8	85.1	728
	0.5	3.57	97.73	85.0	85.8	725
	0.7	3.68	96.44	85.5	86.0	711

1: Volume proportion 1:1 for ClO_2 activation. Stable ClO_2 for the experiment was supplied by Shangdong University Huate Company; 2: The pulp yield was the last bleaching yield in the Table 3

Comprehensive consideration from the brightness of bleached pulp, viscosity and yield, probably the reason that the result was obtained was: Firstly, part of ClO_2 was lost for the different time of adjusting of the pH valence of the bleaching solution. Second, it was difficult to adjust pH valence at one consistent value. Table 1 showed that the smaller the pH valence was, the higher brightness of the pulp was and the lower the viscosity was, which is the same with the bleaching result when HCl works as the activating agent. Third, there possibly were some differences between the properties of ClO_2 activated by HCl and H_2SO_4.

Comparison of ODED bleaching results: To further prove the bleaching effect of ClO_2 activated by HCl and H_2SO_4, ODED bleaching sequence with better bleaching effect to NaOH-AQ pulp of triploid of Populus Tomentos was used for the pulp bleaching. On stage D, the pulp consistency were both 8%, time 120 min, the first stage D, reaction temperature 60ºC, the second stage D reaction temperature 70ºC. On stage E, 2% NaOH solution was used for alkaline extraction, time 60 min, pulp consistency 10%, the experiment results were Table 2.

Table 2 indicates that under the conditions of the same ClO_2 dosage and ODED bleaching sequence, 4% HCl and 5% H_2SO_4 were respectively used to bleach pulp, when ClO_2 dosage was the same, the brightness and viscosity of pulp were slightly different between ClO_2 activated by HCl and H_2SO_4 and the pulp yield is equivalent. Generally, the brightness of the pulp slightly increased, HCl and H_2SO_4 dosage from 0.7 to 1.0%; on stage D, ClO_2 dosage was over 0.5%, brightness didn't increase, while the viscosity decreased considerably, which matched the experiment result of ECF high brightness bleach of low hardness NaOH-AQ pulp of Triploid of Populus Tomentos.

At the same time, bleaching results of ODED bleaching sequence indicates that the bleaching effect of ClO_2 activated by HCl is equivalent to that activated by H_2SO_4. The fact shows that when HCl was used as activator to ClO_2, HCl possibly worked as an acid to supply a proper acid bleaching environment for the bleach of ClO_2, which was not like that HCl can offer more auxiliary Cl- as was imagined. This can better explain H_2SO_4 as activator to ClO_2 has the same bleaching effect. However, whether the principles are the same or not needs further study.

Comparison of ODQP bleaching effect: In the experiment of low kappa number NaOH-AQ pulp of high brightness of Triploid of Populus Tomentos, the pulp could be bleached to 86% ISO with ODQP sequence. Therefore, it is necessary to conduct comparison experiments of 4% ClO_2 activated by HCl and ClO_2 activated by H_2SO_4. In the experiment, bleaching conditions of stage D were: temperature 60ºC, time 120 min; on stage Q, 0.3% of DTPA were used for chelating process, time 60 min, temperature 60ºC, pulp consistency 8%, when chelating, the initial pH value was controlled in 4±0.3; on stage P were: the bleaching pulp consistency 10%, H_2O_2 dosage 2%, $MgSO_4$ dosage 0.5%, $NaSiO_3$ dosage 4%, temperature 70ºC, pH Value 12 and time 90 min; under this conditions, bleaching results were obtained as follows in Table 3.

From Table 3, under the same ClO_2 dosage, using ClO_2 activated by 4% HCl and ClO_2 5% activated by

H_2SO_4, there is big difference in brightness of the pulp with ODQP bleaching sequence and that of OD and ODED bleaching sequence: brightness of ClO_2 activated by 4% HCl can reach 85% ISO with small changes of viscosity, which is better than that of ClO_2 activated by 5% H_2SO_4. from the analysis of the viscosity and yielding of the pulp, the viscosity and yield of ClO_2 activated by 4% HCl was higher than or equivalent to ClO_2 activated by 5% H_2SO_4, which was possibly because of the adjustment of the initial pH valence. It was likely that ClO_2 activated by HCl was more suitable for the ODQP bleaching than ClO_2 activated by H_2SO_4. From the analysis of yield and viscosity, the yield and viscosity of ClO_2 activated by 4% HCl was higher than that of ClO_2 activated by H_2SO_4, which was consistent with normal pulp bleach.

In addition, from Table 3, when ClO_2 dosage was 0.3 and 0.5%, there was no big difference of the final bleaching brightness of ClO_2 activated by 4% HCl and ClO_2 activated by H_2SO_4. That is, in ODQP bleaching sequence, the bleaching effect was not determined by ClO_2. We should consider from the facet of production cost and the optimum dosage of bleaching agent and choose reasonable ClO_2 dosage.

The experiment above showed that there was no big difference in brightness, yield and viscosity of the obtained pulp using ClO_2 activated by HCl and ClO_2 activated by H_2SO_4. We can thus conjecture: the working principle of ClO_2 activated by HCl and ClO_2 activated by H_2SO_4, that is, to provide an acid environment, which is not like that HCl can offer more auxiliary Cl^- as was imagined. Therefore, the excessive H_2SO_4 in the preparation of ClO_2 can be used for activator and directly used for the bleaching of pulp without separation.

Summary: OD, ODED, ODQP bleaching experiments indicate that 4% HCl activated ClO_2 and 5% activated ClO_2 have equivalent bleaching effect. The experiment results can prove that principle of ClO_2 activated by 4% HCl and ClO_2 activated by 5% H_2SO_4 are similar, that is, to offer an acid environment for ClO_2.

By this experiment, it can be conjectured that ClO_2 produced by medium sized ClO_2 preparation device with $NaClO_3$ as the raw materials can be directly used for the bleaching and production of pulp after the adjustment of pH valence without separation of ClO_2 from its residual liquid.

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