



Effect of pH on Calcium Removal in Dissolving Pulp in The First Stage of Bleaching

Valentina Mailita^{1,*}, Joko Wintoko¹, and Indra Perdana¹

¹ Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Jl. Grafika No.2 Yogyakarta, 55281, Indonesia

Corresponding author's email: valentinamailita@mail.ugm.ac.id

Abstract. Dissolving pulp (DP) has a high cellulose content and low chemical components and is obtained from wood through PHK. It is a raw material for various cellulose products, such as viscose fibers, cellulose esters, and ethers. More than 70% of dissolving pulp is utilized in viscose fiber production. Rayon fibers, including viscose and lyocell, are regenerative cellulose fibers produced from natural cellulose that are chemically dissolved after spinning. The lyocell production process requires dissolving pulp with higher cellulose content and lower impurities such as hemicellulose, lignin, extractives, and metal ions like calcium, iron, and copper. Calcium ion reduction is related to the leaching mechanism from a solid, where the solid in question is the pulp itself. This research aims to analyze the effect of the first-stage bleaching pH and process temperature on calcium reduction in the first stage of bleaching. Unbleached dissolving pulp pH with an initial 9.8 was adjusted to a target range of 1.5 to 3.5 using hydrochloric acid, significantly affecting the process outcomes. The findings indicate that while a pH of 1.5 achieved the highest calcium removal (approximately 80.24%), this lower pH slightly compromised delignification efficiency compared to pH levels between 2.5 and 3.5.

Keywords: Rayon fibers, Calcium content, Calcium leaching, Dissolving pulp bleaching, Bleaching pH.

1 INTRODUCTION

Viscose and lyocell are classified into rayon fibers (viscose and lyocell), which are regenerated cellulose fibers derived from natural cellulose that have been chemically dissolved after spinning and are based on natural polymers[1]. The requirement for rayon fibers has increased due to the growing global population, rising affluence, and demand for fashion and related consumer products[2]. These natural polymers are obtained from wood through a pulping process with prehydrolysis kraft pulp or are defined as dissolving pulp (DP).

Dissolving pulp (DP) is fiber pulp identified by a high cellulose content and low levels of other chemical components. Dissolving pulp is produced using wood as raw material and through pulping processed using the kraft pre-hydrolysis method. This process starts with a hydrolysis step to remove hemicellulose under acidic conditions. The hydrolysis process generally processes with steam and is called autohydrolysis. After the hydrolysis step, hot caustic extraction using white liquor to eliminate lignin generally known as kraft pulping process 3. The pulp then goes through a separation

and washing process. At this stage, there is a separation between fully cooked and partially cooked pulp, along with a lignin removal process through a reaction with oxygen. In the final stage of the pulping process, the Elemental Chlorine Free (ECF) bleaching process is applied to reduce the remaining lignin content and achieve the targeted brightness¹. Generally, the bleaching process is carried out in four stages: D0, EOP, D1, and D2. In stage D0, residual lignin is reduced using Chlorine dioxide as a solvent under acidic conditions. Chlorine dioxide is also used in stages D1 and D2. The brightness of the pulp is further enhanced during the EOP stage through extraction with NaOH, oxygen as an oxidizer, and peroxide, bringing the brightness closer to the target level.

Dissolving pulp is used as the raw material for rayon fibers production that involves dissolving pulp in strong carbon disulfide (CS₂), followed by the regeneration of the cellulose solution in a sulfuric acid bath. Strong acids used by rayon fiber process create a significant environmental burden as impact of low solvent recovery. On the other hand, the lyocell fiber production process uses much milder chemicals compared to the viscose rayon process. Cotton fibers and dissolving pulp are the main basic materials used in the solvent-spinning process to create lyocell fibers. The solvent used in this procedure is N-methylmorpholine-N-oxide (NMMO). These fibers are often known as "21st-century green fibers" due to their reduced use of hazardous chemicals compared to the viscose process, which helps minimize wastewater, harmful gas emissions, and the disposal of toxic waste residues, thus offering a more environmentally sustainable alternative⁴. The lyocell fibers offer excellent quality in addition to their environmental benefit. It has been noted that, when wet, lyocell fibers exhibit great strength and tenacity⁵. Dissolving pulp with high quality, such as high cellulose content and minimal impurities, including hemicellulose, lignin, extractives, and metal ions, such as calcium, iron, and copper, are required for lyocell fibers production. High concentrations of metal ions in dissolving pulp can lead to several issues in lyocell fiber production, such as reduced cellulose solubility, increased NMMO degradation, lower fiber quality, and higher chemical consumption. Specifically, calcium metal ions can cause blockages in the micron-sized spinneret orifices. Additionally, contamination of pulp with inorganic compounds can result in gradual blockages of the spinneret, affecting the uniformity of fiber titers^[6]. Acidic bleaching processes can be employed to remove metal ions from the pulp^[1]. The early study found final pH of a ClO₂ bleaching stage significantly affects the performance of that stage and the optimum pH for D0 stages where delignification is the primary goal, an optimum final pH of 2.8–3.5 was determined to provide the best performance^[7]. Another studies that evaluates the impact of acid washing of chips to reduce metal content before kraft pulp cooking on the bleaching properties and strength of the resulting pulp^{8,9}. Metal ion removal can be optimized in the D0 bleaching stage, which has the most acidic conditions compared to other stages. The mechanism for calcium ion reduction involves a leaching process from the solid material, which in this case is the pulp itself. This research aims to analyze the effects of the pH during the first stage of bleaching on calcium ion reduction.

2 MATERIALS AND METHOD

The raw material for this study is unbleached dissolving pulp that has undergone cooking through the pre-hydrolysis kraft pulping process and has been subjected to the oxygen delignification stage. The unbleached pulp was analyzed to determine its characteristics, as presented in Table 1.

Table 1. Characteristic Unbleached Pulp

Parameter	Uom	Index
Brightness	%ISO	55,8
Viscosity	mL/g	607
Kappa Number	-	6,4
pH	-	9,8
Calcium content	ppm	271,7
Iron content	ppm	188,6
Silica content	ppm	576,8
Magnesium content	ppm	17,5
Copper content	ppm	0,2

This study focuses on the D0 stage to further investigate the relationship between pH and the reduction of metal ions, especially calcium content, and pulp bleachability. The pulps were bleached using a D0 sequence in plastic bags and then reacted in waterbath for 60 minutes at a temperature 80°C. In the initial D0 stage, chlorine dioxide (ClO₂) was applied at 0,6% or 15 kg/Adt as chlorine dioxide. The pH was adjusted following the variance 1,5, 2,5 & 3,5 by adding dilute hydrochloric acid (HCl). Pulp evaluations were performed based on the Standard Methods established by the Technical Association of the Pulp and Paper Industry (TAPPI, Atlanta, GA). The assessments included metal content (T 266 om 06) and, brightness (T 525 om 06 & T 218 SP 02), and viscosity (T 230 om-04) as the main parameters in the bleaching process.

3 RESULTS AND DISCUSSION

3.1 pH Adjustment

Initial pH was 9,8 and needed pH adjustment before entering the D0 stage. Hydrochloric acid was used as pH adjustment to achieve a pH of 1,5 -3,5 for this study. Hydrochloric acid or sulfuric acid was used for pH adjustment to achieve D0 stage pH 2,2 -2,3 for general pulp industries. This adjustment is necessary to prevent the oxidation of non-phenolic lignin groups at high pH, which would otherwise produce chlorite ions instead of hypochlorous acid. The acidity of the chlorine dioxide solution and the acidic byproducts from chlorine dioxide bleaching result in an acidic final pH of the stock under standard Chlorine Dioxide dosages. The pH level without additional acid or caustic is known as the natural pH of the bleaching stage[7].

Pulp samples are alkaline and have a consistency of approximately 29 – 32%. Initially, they are treated with Chlorine dioxide in a waterbath for 1 hour at 80°C.

Subsequently, hydrochloric acid is added to adjust the pH to match the desired chlorine dioxide variations.

Table 2. pH Adjustment with Additional Hydrochloric acid

Parameter	Reaction pH	Hydrochloride acid charge		
		1.5	2.5	3.5
Chlorine dioxide 14 kg/Adt	6.3	60.0	10.0	5.0
Chlorine dioxide 15 kg/Adt	6.0	65.0	10.4	4.9
Chlorine dioxide 16 kg/Adt	5.7	62.0	10.0	4.8

In the initial treatment shown in Table 2, the natural pH of the pulp after reaction with chlorine dioxide ranged from 5.7 to 6.3, indicating that higher doses of chlorine dioxide led to a lower pH. Acid products are produced in significant quantities by the dominating ClO₂ reactions with lignin. As these reactions continue, ClO₂ is transformed into acidic intermediates or reaction products, making the stock more acidic. This observation is consistent with the findings of Hart and Connell[7], which state that chlorine dioxide dosage affects the natural pH of the pulp without additional acid regulators. Based on this reaction pH, adding hydrochloric acid is necessary to achieve the desired pH for the variable being studied. The pulp consistency and the concentration of chlorine dioxide added significantly influence the amount of water required to adjust the pulp consistency to 10%.

3.2 Characterization of Treated Pulp

After treating the pulp with acid and varying the acid conditions of bleaching, the pulp was obtained with more than 64 %ISO, 544 – 564 mLg⁻¹ pulp viscosity, 2.4 – 3.3 kappa number, respectively, with the acid treatment of pulp. Results in detail are given in Table 3.

Table 3. pH Adjustment with Additional Hydrochloric acid

Parameter	Uom	pH		
		1.5	2.5	3.5
Brightness	%ISO	64,0	66,2	65,4
Viscosity	mL g ⁻¹	564	552	544
Kappa number	-	3,3	2,7	2,4
Calcium content	ppm	53,7	68,0	89,6
Iron content	ppm	9,9	10,4	10,9
Silica content	ppm	472,6	462,9	508,3
Magnesium content	ppm	5,9	4,9	5,2
Copper content	ppm	0,71	0,57	0,82

The final pH during chlorine dioxide (Chlorine dioxide) bleaching stages significantly impacts performance[7]. The study found that stages D0, D1, and D2 exhibit optimal pH ranges, varying depending on the material, stage, and chlorine dioxide dosage[7]. Acid or alkali is required to adjust the final pH to the optimal range

found in most study cases. The desired outcomes of the chlorine dioxide bleaching stages vary depending on their position in the bleaching sequence. For the D0 stage, where delignification is the primary goal, the optimal final pH is determined to be between 2.8 and 3.5 for best performance. A lower final pH, specifically below 2.5 at stage D0, results in a slight loss of delignification efficiency but may lead to significant losses of non-process metals. This increased metal removal can reduce scale formation and decrease hydrogen peroxide decomposition in the subsequent EP stage[7].

3.3 Impact on Calcium Content and Other Metal Ions

The evaluation of the effect of pH in the D0 stage on metal ion reduction, as the main purpose of this study, is calcium reduction, as shown in Picture 1. In acidic conditions, metal content from the sulfite pulping process becomes water-soluble and is easily removed during washing⁶.

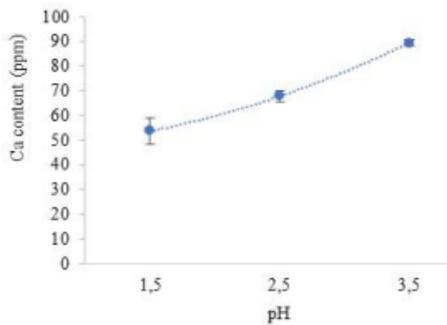


Fig. 1. Calcium content after treatment

Fig. 1. illustrates the effect of pH during the D0 stage on calcium removal following washing. The highest calcium removal, approximately 80.24%, was observed at pH 1.5, while 74.99% and 67.04% removals were noted at pH 2.5 and pH 3.5, respectively. In the kraft pulping process, metal ions are reduced to a low oxidation state and are difficult to remove by washing as they are precipitated as sulfides. The metal ion may become more oxidized and insoluble during the oxygen delignification process. Nevertheless, metal ions can be removed under mild to strong acid conditions. In the conventional ECF bleaching stage, they were removed during acidic bleaching stages or D0 stages[6]. Acid condition below 2.5 can effectively remove calcium content sorbed in the pulp with a proper washing system and adequate purge of D0 filtrate[7].

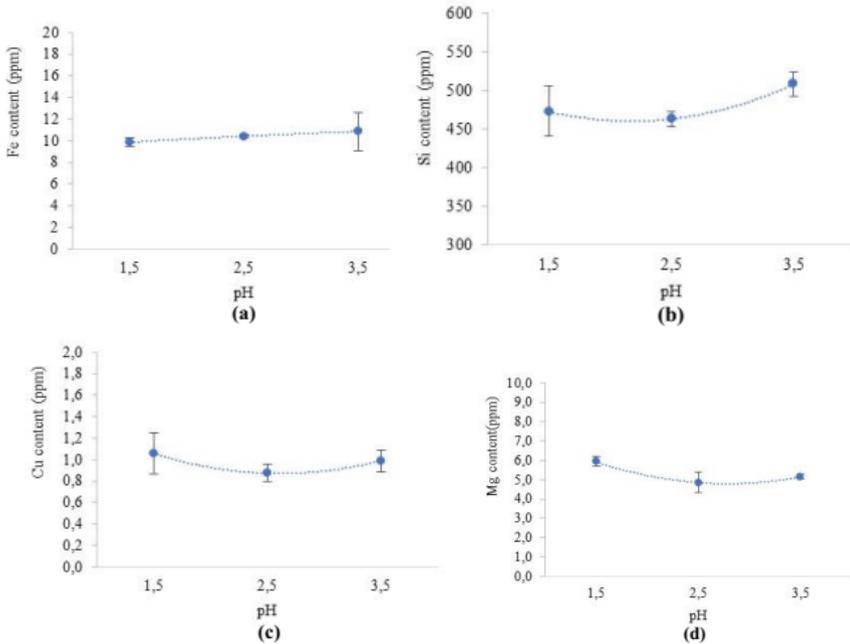


Fig. 2. (a) Iron, (b) Silica as SiO₂, (c) Copper, and (d) Magnesium after treatment

In general, the acidic condition was applied to remove metal ions such as calcium, iron, and magnesium [4]. Lower pH had a strong effect on the desorption process of different metal ions, which vary at different pH values. **Fig. 2.** (a) iron contents, (b) Si as SiO₂, (c) copper and (d) magnesium is shown that pH not affect to this metal ion content removal. Iron content removal was maximum at pH 1.5; meanwhile, for silica, copper, and magnesium, removal was optimum at pH 2.5. Yang et al. mention that iron content removal can be improved with additional chelating agents such as EDTA. At pH 1.5 and an EDTA dosage of 0.4 wt%, the iron content of the pulp reached the target value. Nevertheless, only adding EDTA was not enough to reach the required ash content [10].

3.4 Impact on Delignification Results

The residual lignin from unbleached pulps that the pulping process was unable to remove. For lignin removal, pulp must be treated through oxidative lignin degradation with bleaching reagents such as chlorine dioxide [6]. Bleaching chemical treatments are generally applied to improve pulp quality as raw material high-purity rayon fibers. The bleaching process is the most widely used method by industry to produce a dissolving pulp of such a standard [11].

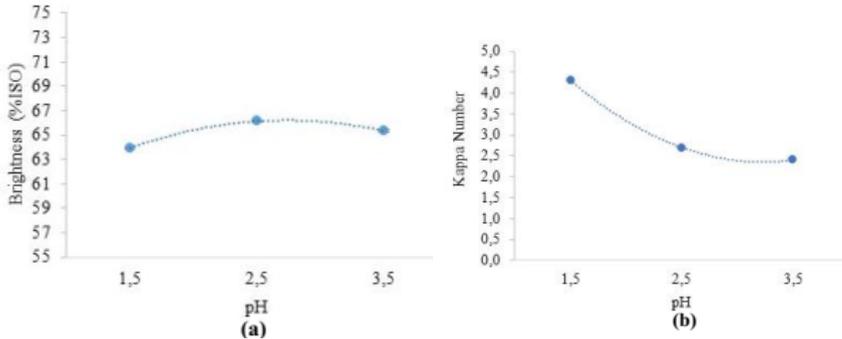


Fig. 3. (a) Brightness and (b) kappa number after treated

The effectiveness of bleaching process measured by brightness. However, the main purpose of D0 stages is delignification. Fig. 3 (b) shown that delignification process optimum at pH 2.5 to 3.5. This observation aligns with Hart and Conell’s findings, which indicate that a lower pH in the D0 stage, significantly below 2.5, may reduce the efficiency of the delignification reaction. A lower pH can lead to chlorate ions' generation, adversely affecting delignification efficiency. Conversely, a higher pH can produce more chlorite, which facilitates the regeneration of active chlorine and thereby maximizes bleaching efficiency[7].

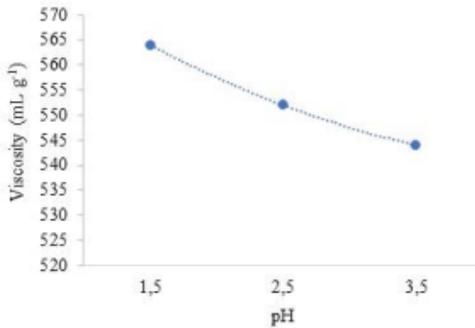


Fig. 4. Pulp Viscosity after treatment

Effect of pH control in D0 stage to viscosity can be seen in Fig. 4. Based on the Fig.4, the pulp viscosity decreased with increasing pH in D0 stage. In high pH conditions, the degradation of cellulose fiber was increased. As mentioned by Matin et al., degraded carbohydrate content (S10/S18) was increased hand in hand with increasing pH 12. High viscosity reduction Low viscosity may have a destructive impact on the viscose rayon process, causing the viscose solution to swell like gel. This gel-like swelling can make the filtration difficult and may also negatively affect the physical strength of the resulting cellulosic fiber; however, if the viscosity is too high, it will cause inhomogeneity for mercerization and xanthation reactions[13]. Uniformity of dissolving pulp viscosity was absolutely essential for the rayon-making process.

4 CONCLUSION

This study aims to know the critical role of precise pH adjustment during the D0 stage of chlorine dioxide bleaching in optimizing both delignification and metal ion removal in pulp processing. Unbleached dissolving pulp pH with an initial 9.8 was adjusted to a target range of 1.5 to 3.5 using hydrochloric acid; the result significantly affected the process outcomes. The findings indicate that while a pH of 1.5 achieved the highest calcium removal (approximately 80.24%), this lower pH slightly compromised delignification efficiency compared to pH levels between 2.5 and 3.5. The study also highlights that higher pH levels lead to increased cellulose degradation and viscosity reduction, which can negatively impact subsequent processing stages, such as viscose rayon production. Thus, careful pH control is crucial for balancing effective delignification, efficient metal ion removal, and maintaining desired pulp viscosity for high-quality end products.

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