

Evaluation of Pretreatments for Removing Metal Ions from Industrial Grade Magnesium and Its Application during the Alkaline H₂O₂ Bleaching Process of Poplar Chemi-thermomechanical Pulp (CTMP)

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Abstract. The objective of this work is to evaluate the effect of applying industrial grade MgO with different grades of metal impurity partially substituting NaOH as the alkali source on the hydrogen peroxide bleaching process. In this study, the effects of pretreatments, such as washing in deionized water, washing in deionized water combined with chelating by EDTA, grinding by grinding machine, and grinding by grinding machine combined with chelating by EDTA pretreatments, on the removing of metal impurity from the industrial grade MgO were investigated. The residual H₂O₂ of bleaching effluent and the bleached pulp properties were determined. The results showed that pretreatments had positive effects on the removal of metal ions from industrial grade MgO, but there were no obvious effects on pulp properties. The bleached pulp applied MgO that was pretreated by washing in deionized water combined with chelating by EDTA had a similar brightness (75.91%) with control sample (75.41%), but which could cut 16.73% of H₂O₂ consumption during the bleaching.

Introduction

Sodium hydroxide is widely used as the alkali source in the high yield pulp (HYP) peroxide bleaching[1-3]. The chromophoric groups, which are associated with lignin, can be oxidized by the perhydroxyl ion resulted from the decomposed hydrogen peroxide, thus increasing the pulp brightness[4].

However, the strong alkalinity of NaOH can result in the dissolving of hemicelluloses and lignin, thus resulting in the decrease in the bleached pulp yield and increase in the amount of dissolved and colloidal substances (DCS). The DCS will increase the loading of bleaching effluent, such as the biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Further more, the excess alkalinity causes alkali-induced darkening of the pulp, due to the generation of new chromogenic groups, which limits the brightness ceiling[5-8].

Mg(OH)₂ or MgO partially substituting NaOH is used as alkali source in alkaline peroxide bleaching process, due to its weaker alkali and lower solubility[9,11], the celluloses could also be shielded by Mg²⁺ in bleaching[10]. Zeinaly F et al[11] reports that the total peroxide consumption in the Mg(OH)₂-based process is inferior to that of the NaOH-based peroxide process. There are some advantages in the MgO or Mg(OH)₂ bleaching such as lower effluent BOD/COD, lower anionic trash, higher bleached pulp yield, less oxalate scaling, and higher bulk[11-14].

But the high metal impurity content of Industrial grade MgO has a negative effect on the alkaline H₂O₂ bleaching process. Transition metal ions, such as iron, copper, and manganese ions, especially manganese and iron ions, can result in the decomposition of hydrogen peroxide[15-17], increasing the radical coupling reaction rate and further affecting pulp bleaching[18].

Many studies have also been focused on the combination of the metal ions with the lignin model compounds, which would also decrease the pulp brightness, due to its stronger colour and higher absorbance in visible light region complex. The metal ions in the pulp could decrease the paper brightness by the order of Al³⁺ < Mn²⁺ < Cu²⁺ < Fe³⁺ < Fe²⁺[18-20].

In this study, industrial grade MgO were pretreated with four different kinds of pretreatments: washing with deionized water (Pretreatment 1), washing with deionized water combined with chelating by EDTA (Pretreatment 2), grinding by grinding machine in the deionized water (Pretreatment 3), grinding by grinding machine in the deionized water combined with chelating by EDTA (Pretreatment 4) followed by immediately centrifuging, which were used in alkaline peroxide bleaching process of poplar CTMP under constant proportion of industrial grade MgO partially substituting NaOH. The evaluations of industrial grade MgO pretreatments on the bleached pulp properties and the residual H₂O₂ of bleaching effluent were studied.

Experimental

Materials. The poplar CTMP (15 °SR, initial ISO brightness of 50.02%), as raw materials, were purchased from a paper mill in Shandong Province, China. Industrial grade MgO (86.92% of MgO, 1.42% of CaO, 0.35% of Fe, 0.07% of Mn, 0.9 ppm of Cu) supplied by a magnesite mill in Liaoning province, China, was dried at 105±5°C to constant weight. All other chemicals (analytical grade) were purchased from a chemical company in Tianjin, China. Deionized water was used in the experiment, and the particle size of industrial grade MgO, determined by alaser diffraction particle size analyzer (model LS 13320, Beckman Coulter, U.S.A.), was 18.10 μm.

Pretreatment 1. The desired amount of industrial grade MgO were mixed with deionized water in conical flask and stirred with an electric blender at 1000 rpm under the water bath. The effects of reaction conditions, such as washing temperature, washing time and MgO suspension concentration on the metal ions extraction, were investigated.

Washed suspension was dumped into a beaker and stirred at 370 rpm, then transferred for centrifuging at 10000 rpm under 20 °C for 20 minutes. The supernatant was collected for the determine of iron, copper, and manganese ions content by inductively coupled plasma source mass spectrometer (ICP-MS 7500cx Aglient Japan).

Pretreatment 2. Different dosages of EDTA were added into the MgO suspension under the optimized washing conditions for pretreatment. The solid-liquid isolation was conducted by following the same procedure as the Pretreatment 1.

Pretreatment 3. The dried industrial grade MgO was ground by a basket mill (model SA II-0.75, Shanghai Suowei Mechanical and Electrical Equipment Co. Ltd., China) with different grinding time under 10% consistency at 510 rpm. The solid-liquid isolation was conducted by following the same procedure as the Pretreatment 1.

Pretreatment 4. Different dosages of EDTA were added to the suspension under the optimized grinding time for pretreatment. The solid-liquid isolation was conducted by following the same procedure as the Pretreatment 1.

Peroxide Bleaching. The bleaching were applied by following the previously reported methods[21]. 40 g of oven-dried poplar CTMP; 3.5% total alkali charge (on NaOH) of which 50% of NaOH was replaced with industrial grade MgO (molar ratio); 0.3% DTPA; 2.0% Na₂SiO₃; 6.0% H₂O₂; 20% pulp consistency; at 80°C for 90 min. All the chemical dosages were based on the dry weight of CTMP. NaOH, MgO, certain amount of the deionized water, and DTPA were mixed thoroughly first with the CTMP by kneading the polyethylene bag with hand. H₂O₂ and the remaining deionized water were then added into the bag. After the pulp and chemicals were well-mixed by hand kneading constantly, the polyethylene bag was sealed and placed into the water bath of 80 °C. The pulp in polyethylene bag was mixed thoroughly by kneading every 20 min. At the completion of the bleaching process, the pulp sample was cooled down to room temperature immediately by tap water.

Preparation of the Bleaching Effluent and Determination of Residual H₂O₂. After bleaching, 2.0 g of oven-dried bleached CTMP was diluted to 1% consistency by deionized water. The well-mixed pulp suspension was then filtered in a Büchner funnel with a 200-mesh screen. In order to determine the residual H₂O₂, the resultant filtrate was further filtered with a filter paper (medium-fast) to remove the residual fines.

Handsheets Preparation and Testing. The well-washed pulp was dispersed to 1% consistency

with deionized water, and the pH of pulp slurry was adjusted to 5.0 (± 0.1) with the diluted sulfuric acid of 0.3% concentration. The handsheets were prepared according to the ISO 5269–1(2005) and ISO 3688(1999), respectively. In addition, brightness, opacity, light-scattering coefficients and physical properties of the handsheets were determined based on the ISO 2470(2009), ISO2471 (2008), ISO 9416(2009), and ISO 5270 (2012), respectively.

Characterization of the pretreated MgO metal ions content in the bleaching process. The residual H_2O_2 resulted from a simulate bleaching experiment without CTMP were determined to evaluate the effect of pretreatments on the extraction amount of metal ions from MgO in the bleaching process. The simulate bleaching condition was same as the above bleaching process, except that the bleaching time was only 30 min. In addition, the activity of applied MgO were also determined.

Results and Discussion

The schematic diagram for the removal of metal ions from MgO by different pretreatments

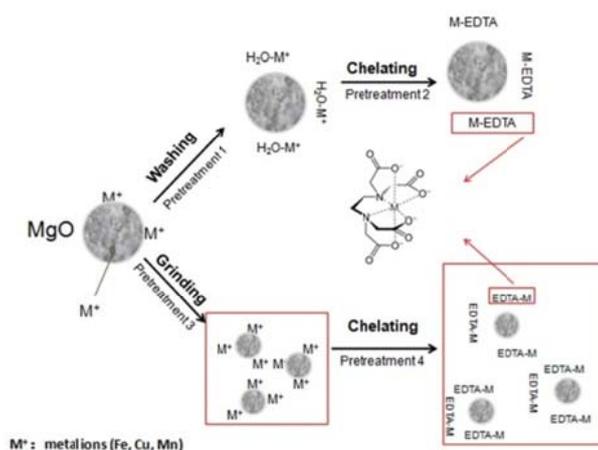


Fig.1 The schematic diagram of pretreating MgO

Fig.1 shows the schematic diagram of pretreating industrial grade MgO. The metal ions of MgO surface were dissolved into water after Pretreatment 1, and would be easier to combine with EDTA in the following process of Pretreatment 2. Meanwhile, the grinding by Pretreatment 3 would facilitate the decrease of MgO particle size and present more particle surface, which is beneficial for the dissolving of metal ions into water after its combination with EDTA during the process of Pretreatment 4.

The effect of Pretreatment 1 on the Extraction Amount of Transition Metal Ions from Industrial Grade MgO.

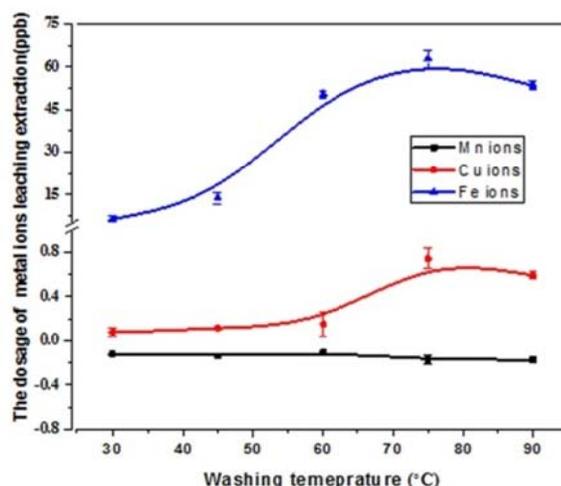


Fig.2 The effect of washing temperature on transition metal ions extraction during Pretreatment 1 (washing time 10 min, MgO suspension concentration 25%)

Fig.2 shows the effects of washing with deionized water pretreatment at varied temperatures on the extraction amount of transition metal ions from industrial grade MgO. The results revealed that the washing time and concentration of MgO suspension have no obvious contribution on this purpose. As seen from Fig.2, the maximum concentration of iron and copper ions from the supernatant were obtained at 75 °C, while the concentration of manganese ions decreased constantly and negative numbers were shown in Fig.2. A feasible explanation was that Mn^{2+} was unstable in the alkaline medium and would turn into Mn^{3+} , then readily disproportionated into Mn^{2+} and Mn^{4+} , thus resulting in the generation of MnO_2 precipitate[22,23], which maybe mixed with MgO after centrifuge.

The Effects of Pretreatment 2 on the Amount of Transition Metal Ions Extraction from Industrial Grade MgO. Hydrogen peroxide is unstable and the presence of transition metal ions heavy metals would accelerate its decomposition. EDTA was commonly used for chelating metal ions, such as Fe^{2+} , Fe^{3+} , Cu^{2+} , and Mn^{2+} , which would decrease the paper brightness by causing the decomposition of hydrogen peroxide.[19]

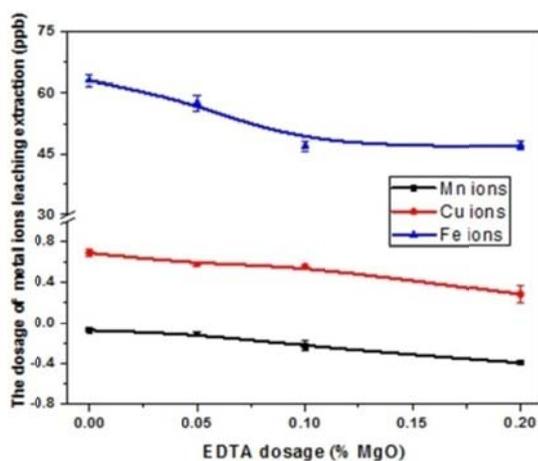


Fig.3 The effect of EDTA dosage on the transition ions extraction during Pretreatment 2 (time 10 min, temperature 75 °C, MgO suspension concentration 25%)

The effect of EDTA dosage on the transition metals extraction from industrial grade MgO was investigated and as shown in Fig.3, the concentration of metal ions decreased as the dosage of EDTA increased from 0 to 0.2%. One possible explanation was that the determined ICP-MS signal of organic macromolecular chelate formed by EDTA and metal ions was weaker than single metal ions. In addition, the decrease of iron when EDTA dosage beyond 0.1% was slighter than the EDTA dosage under 0.1%. The optimal dosage of EDTA was set as 0.1% considering the economically feasible.

The effects of Pretreatment 3 on the Extraction Amount of Transition Metal Ions from Industrial Grade MgO.

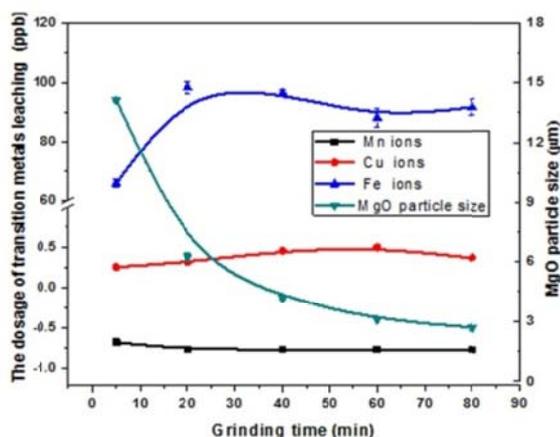


Fig.4 The effect of grinding time on transition ions extraction during Pretreatment 3 (MgO concentration 10%, grinding speed 520 rpm)

As shown in Fig.4, the particle size of industrial grade MgO decreased with the increasing of grinding time. A visible drop in the MgO particle size within the first 20 min of grinding could be observed which followed by a slight decrease in the prolonged 60 min. The particle size of industrial grade MgO at grinding time of 20 min was 6.10 μm .

In addition, there was an obvious increase in the iron concentration at the first 20 min and followed by a slight change in the next 60 min, while the copper ions concentration increased slightly as the grinding time increased from 0 min to 80 min. According to the former study[21], more transition metal ions would be exposed to the interface when the particle size of MgO decreased, thus would be much easier to be extracted into the suspension. Meanwhile, the increase of specific surface area may cause more transition metal ions adsorbed onto the MgO particles[24]. The effect of specific surface area on the promoting of iron extraction would be in dominate at the first 20 min, and then reached equilibrium as the adsorbent effect at the following 60 min. The results in Fig.4 indicated that the optimum grinding time for the pretreatment of industrial grade MgO was 20 min.

The Effects of Pretreatment 4 on the Amount of Transition Metal Ions Extraction from Industrial Grade MgO.

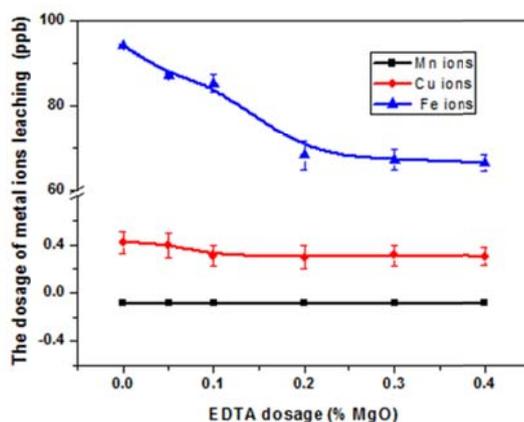


Fig.5 The effect of EDTA dosage on the transition ions extraction during Pretreatment 4 (MgO suspension concentration 10%, grinding speed 520 rpm, grinding time 20 min)

The extracted transition metal ions from centrifugal supernatant by Pretreatment 4 were determined by ICP-MS response curves, and the results was shown in Fig.5 which had a similar trend as the Fig.3, thus well supporting that the optimal EDTA dosage (% MgO) was 0.2%.

The Effects of Different Pretreated MgO as Alkali Sources on the Bleached Pulp Properties and Residual H_2O_2 . As reported in the previous literatures that the transition metals would catalyze the H_2O_2 decomposition[25], which is in good agreement with our results.

The effects of application of different pretreated industrial grade MgO on the residual H_2O_2 from the effluent were investigated, and the results were shown in Table 1. The residual H_2O_2 when applied untreated MgO (control) was 26.54%, which was less than that of Sample 1 (28.21%) and Sample 2 (30.98%) due to the inhibition of H_2O_2 decomposition after the removing of transition metal ions by pretreatments. However, the lower residual H_2O_2 was obtained from Sample 3 (25.72 %) and Sample 4 (28.48%), which may be due to the more exposed metal ions impurity adsorbed on the relatively smaller MgO particle size from Sample 3 and Sample 4, thus negatively affected the H_2O_2 stability. Pretreatment 2, which cut 16.73% H_2O_2 consumption, was a better way for the H_2O_2 saving. In addition, Pretreatment 1 and Pretreatment 4 cut 6.29% and 7.31%, respectively. The highest residual H_2O_2 (36.70 %) was achieved from Sample 5, which maybe attributed to the lower metal impurity in the analytical pure MgO.

The pulp brightness was also shown in Table 1, and the pretreated MgO samples applied in the H_2O_2 bleaching process does have a certain contribution to the increase in pulp brightness comparing with control sample (75.41%), the pulp by applying Sample 1, Sample 2, Sample 3, and Sample 4 obtained a brightness of 75.72%, 75.91%, 76.21%, and 76.34%, respectively. Especially for the Sample 4, which is almost close to the bleaching effect of the application of high purified

analytical MgO (Sample 5, 76.66%)[5].

The pulp properties with different pretreated MgO as partial alkali source for replacing NaOH in the H₂O₂ bleaching process were shown in Table 1. The resulted pulp bulk of Sample 1 and Sample 2 were 2.39 cm³/g and 2.45 cm³/g, respectively, which were similar as the effect of applying the untreated industrial grade MgO (2.43cm³/g). The Sample 3 (2.30 cm³/g) and Sample 4 (2.28 cm³/g) showed a little lower bulk, so as the light-scattering coefficient and opacity. However, the change in the strength properties is neglectful among different groups.

Table 1. The properties of bleached CTMP handsheets and residual H₂O₂ content of bleaching effluent

	MgO samples					
	Control	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Residual H ₂ O ₂ (%)	26.54±0.9	28.21±0.5	30.98±0.7	25.72±0.6	28.48±0.5	36.20±0.6
Brightness (%ISO)	75.41±0.12	75.72±0.20	75.91±0.21	76.21±0.10	76.34±0.18	76.66±0.14
Bulk (N·m/g)	2.43±0.06	2.39±0.07	2.45±0.06	2.30±0.02	2.28±0.03	2.21±0.03
Opacity (%)	84.22±0.18	84.52±0.42	84.36±0.28	83.81±0.18	83.76±0.25	83.41±0.32
Light-scattering Coefficient (m ² /kg)	38.25±0.16	38.19±0.10	38.40±0.14	37.86±0.19	37.80±0.22	37.04±0.2
Tensile index (N·m/g)	24.1±0.8	24.68±0.3	24.47±0.3	25.0±0.2	24.90±0.3	25.8±0.4
Burst index (kpa·m ² /g)	0.948±0.14	0.932±0.08	0.966±0.07	1.006±0.05	0.979±0.06	0.985±0.09
Tear index (mN·m ² /g)	2.13±0.20	2.21±0.30	2.07±0.10	2.30±0.24	2.27±0.12	2.45±0.18

The characterization of pretreated industrial grade MgO transition metal ions content. In case of the particle size or the activity of industrial grade MgO was similar, the more residual H₂O₂ were determined in this experiment mean that the more metal ions of industrial MgO were removed by pretreatments and centrifuging. Table 2 showed that the residual H₂O₂ of applying Sample 4 (23.70%) was higher than that of applying Sample 3 (19.13%), due to more metal ions were removed by pretreating with EDTA chelating in Sample 4. It means that the application of EDTA as a pretreatment had a positive contribution for the removing of metal impurity ions from industrial grade MgO. The difference were also presented between groups applying Sample 1 (25.84%) and Sample 2 (27.10%), which were higher than Sample 3 and Sample 4, mainly due to the lower MgO activity.

Table 2. The industrial grade MgO activity and residual H₂O₂ of simulate bleaching experiment

	Activity (s)	Residual H ₂ O ₂ (% applied)
Control	223±3	16.35±0.35
Sample 1	213±5	25.84±0.05
Sample 2	210±6	27.10±0.18
Sample 3	135±4	19.13±0.10
Sample 4	141±3	23.70±0.15
Sample 5	–	86.40±0.42

Note: the activity of Sample 5 was could not determined

Conclusions

The four pretreatments for removing the transition metal ions from industrial grade MgO were studied, and the optimum temperature of Pretreatment 1 was 75 °C; the optimum EDTA dosage (%)

MgO) of the chelating Pretreatment 2 and the optimum EDTA dosage (% MgO) of chelating Pretreatment 4 were achieved at 0.1% and 0.2%, respectively; the best effect for removing of metal ions was realized at 20 min of grinding time in the Pretreatment 3.

The industrial grade MgO of pretreating by the four pretreatments had a certain contribution in the increase of bleached CTMP brightness. The bulk, opacity, light-scattering coefficient of bleached pulp were changed accordingly.

The pretreated MgO samples were used as alkali source for the partially substituting for NaOH in the poplar CTMP H₂O₂ bleaching process, and the resulted pulps exhibited the similar properties as the control sample, but the residual H₂O₂ of bleaching effluent was increased. It mean that the required H₂O₂ in the bleaching stage was well-lowered by the pretreatments, and there are 6.29%, 16.72%, and 7.31% cut in the H₂O₂ consumption from Sample 1 (28.21%), Sample 2 (30.98%), and Sample 4 (28.48%), respectively, compared with the control sample (26.54%).

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