

Fenton Depolymerization of Cellulosic Biomass in Modified Cuprammonium Solution

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This preliminary study developed a novel cellulose pretreatment method for cost-effective cellulosic utilization using a modified cuprammonium solution as a solvent to dissolve cellulose followed by molecular oxygen/Fenton depolymerization. The modified cuprammonium solution is composed of cuprammonium solution and a special catalyst that could efficiently enhance cellulosic oxygen sensitivity and therefore improve cellulosic depolymerization. The molecular oxygen depolymerization and Fenton depolymerization of cellulosic biomass dissolved in the modified cuprammonium solution were investigated. The results demonstrate that the Fenton reaction efficiently depolymerized the cellulose dissolved in the modified cuprammonium solution and reached the monomers with no loss of organic carbon, and almost all the cellulose maintained solubility without reagglomeration after cuprammonium was removed. Molecular oxygen oxidation reduced the cellulose average degree of polymerization (DP) to approximately 4 with less cost, and the oxygen pre-oxidation increased the H₂O₂ utilization in the Fenton depolymerization and remarkably reduced the H₂O₂ requirement.

Keywords: Cellulosic biomass; Fenton reaction; Depolymerization; Modified cuprammonium solution; Cellulosic pretreatment; Cellulosic ethanol

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INTRODUCTION

Because of concerns about the non-renewability of petroleum and pollution from petroleum energy, the exploitation of cellulosic biomass, including woody and herbaceous plants, has attracted worldwide attention. One ton of cellulosic biomass can produce about three times as much energy as one barrel of petroleum. The Earth can annually supply cellulosic biomass with an energy content equivalent to 34 to 160 billion barrels of oil, more than the world's current consumption of 30 billion barrels of oil per year. Cellulosic biomass is the only large-scale sustainable source for producing alternative liquid fuels for vehicles. It is a potential solution to the petroleum oil problems.

Recently, biofuel generation from cellulosic biomass has been focused primarily on four pathways: (1) Solidification, including biomass pellets, high-density pellets and particulates, and high-carbon charcoal; (2) Gasification of biomass to syngas, which is purified to be used or fermented into ethanol or other alcohols; (3) Liquidation of biomass by high temperature and pressure into a "crude-oil-like" product, which is distilled to different grades; and (4) Fermentation of cellulosic biomass into ethanol or other alcohols.

Solidification of biomass is a simple and traditional method. The solidified biomass can be used in boilers and furnaces. During the gasification process, tar is

difficult to remove from the system because of its sticky character and high viscosity. Liquidation of biomass by high temperature and pressure is a process with high energy input, and the purification and distillation of the “crude-oil-like” product is another challenge. Fermentation of cellulosic biomass can be used to convert sugars to ethanol or other alcohols and is a recognized approach for producing liquid biofuel. The United States has identified the production of ethanol from cellulosic biomass as vital to overcoming the “addiction” to oil, and has set a target of producing 16 billion gallons of cellulosic ethanol annually by 2022 (Stubbs 2010).

The critical step in fermenting cellulose is the depolymerization of cellulose molecules into small molecules. Current cellulosic depolymerization approaches mainly focus on acid-catalyzed hydrolysis (Qian *et al.* 2004; Deguchi *et al.* 2008), base-catalyzed hydrolysis (Silverstein *et al.* 2007; Zhao *et al.* 2007), and enzyme-catalyzed hydrolysis (Peri *et al.* 2007; Merino and Cherry 2007; Yeh *et al.* 2010; Levine *et al.* 2010). Due to the recalcitrant crystalline structure of cellulose, the cellulosic hydrolysis rate is severely limited. The highly-ordered cellulose chains make the hydrolysis rate rather slow.

Ionic liquids (ILs) have recently received a great deal of research interest (Kamiya *et al.* 2008; Zhao *et al.* 2009; Li *et al.* 2009; Kim *et al.* 2010; Dee and Bell 2011) because of their ability to dissolve lignocellulose to facilitate the depolymerization of the cellulose. However, the relatively high costs limit their practical application for biomass pretreatment (Zheng *et al.* 2009; Kuo and Lee 2009; Brodeur *et al.* 2011).

An October 2011 National Research Council (US) report to Congress states that “Absent major technological innovation or policy changes, the mandated consumption of 16 billion gallons of ethanol-equivalent cellulosic biofuels is unlikely to be met in 2022.” The technological innovation in cellulosic depolymerization is still a big challenge in this area.

This preliminary study proposed a cost-effective modified cuprammonium solution-based cellulosic depolymerization method. The modified cuprammonium solution, composed of copper hydroxide, ammonium hydroxide, and a special catalyst, was used as a solvent to dissolve lignocellulose and to further depolymerize the lignocellulose into oligomers or monomers *via* oxidation. The special catalyst could efficiently enhance cellulosic oxygen sensitivity and therefore improved cellulosic depolymerization. In this study, the lignocellulosic depolymerization by molecular oxygen and Fenton reaction were investigated and the conditions of depolymerization were optimized.

EXPERIMENTAL

Methods

Experimental apparatus and procedure

The modified cuprammonium solution was prepared by mixing copper hydroxide (7.7%, w/w), concentrated ammonium (8%, w/w), and the special catalyst (a polyelectrolyte PolyWeb P30, provided by Tri-Y Environmental Research Institute, Vancouver, Canada). Pulp was added to the modified cuprammonium solution to form a cuprammonium cellulose solution. A magnetic mixer was used for mixing. The weight percentage of the pulp was 3.1%.

Oxygen Depolymerization of Cellulose

Bench-scale experiments were done to examine the cellulosic depolymerization in the modified cuprammonium solution under the Fenton reaction conditions. Molecular oxygen depolymerization was performed in a 250-mL graduated cylinder filled with 200 mL of the cuprammonium cellulose solution by aerating to the bottom of a graduated cylinder. The air flow rate was controlled to be about 0.05 L/min.

Fenton Depolymerization of Cellulose

A 200-mL reactor was used as the Fenton reactor. The reactor was sealed, air-tight, and kept dark during the reaction. All Fenton reactions were conducted at room temperature, *i.e.*, 25 ± 1.5 °C. Every 1.5 h, 0.5 mL of 30%-concentration of hydrogen peroxide was added to the cuprammonium cellulose solution stepwise. After Fenton reaction, NH₃ was stripped with nitrogen gas and recovered with dilute H₂SO₄, and Cu²⁺ was recovered from the cuprammonium cellulose solution by adding NaOH dilute solution to pH value of 8–9 to form Cu(OH)₂ sedimentation.

Analysis and reagent

The variation of the average molecular weights of cellulose molecules was measured to assess the cellulosic depolymerization under different conditions. The average molecular weights were determined from intrinsic viscosity by Eq. 1 (Mark 1999),

$$[\eta] = 1.01 \times 10^{-3} M^{0.661} \quad (1)$$

where M is the average molecular weight of cellulose and $[\eta]$ is the intrinsic viscosity (cp) of the cuprammonium cellulose solution.

Gel permeation chromatography (GPC) was not used in the tests because GPC may not achieve much precision in the case of such a low molecular mass. To the extent of this study, average molecular weight of cellulose determined by intrinsic viscosity was sufficient to identify the trend of reactions.

The reagglomeration of the depolymerized cellulosic fragments was examined by measuring the turbidity and suspended solids formed from the acidified cellulosic fragments solution. In addition, chemical oxidation demand (COD) and total organic carbon (TOC) variations were investigated to evaluate the degradation process of cellulose dissolved in the cuprammonium solution.

The reagents were ACS-grade, purchased from Sigma-Aldrich (Montreal, Canada), and used as received. All water used was distilled water. The pulp used was Bleaching Kraft North Pulp (from Tembec Inc., Canada), which contained 90% cellulose. Viscosity was measured using a Cannon-Fenske glass capillary viscometer (Cannon Instrument Co. USA). The HACH colourimeter (DR/850, a multiparameter clourimeter) was used for suspended solids (SS), TOC, and COD analysis (EPA-approved). Nephelometric turbidity unit (NTU) was measured using a HACH (USA) 2100P turbidimeter. Water was examined by a YSI 9300 photometer (YSI, USA), and the pH value measured using a HANNA HI 8424 pH meter (Hanna Instruments, USA).

RESULTS AND DISCUSSION

Fenton Depolymerization of Cellulose

Fenton depolymerization of cellulose was conducted to explore the possibility of reaching a monomer level. Since copper ions can also efficiently decompose hydrogen peroxide to generate hydroxyl radicals, this study mainly investigated the copper-based Fenton depolymerization by directly adding hydrogen peroxide to the cuprammonium cellulose solution. However, a set of copper-based Fenton depolymerizations with additional iron ions was conducted for comparison. Ferrous ions were provided by ferrous sulfate at a concentration of 182 mg/L.

As shown in Fig. 1, the Fenton reaction could efficiently depolymerize the cellulose dissolved in the modified cuprammonium solution to a level of monomers. In the initial reaction phase, the cellulosic DP was remarkably reduced. However, when the average DP was less than 20, the depolymerization rates of the cellulosic fragments were much slower.

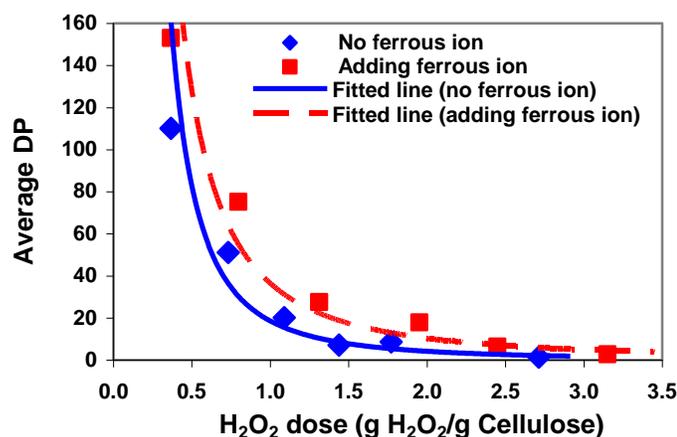


Fig. 1. Variations of the average molecular weight with differing H₂O₂ doses

Figure 1 also illustrates that the addition of ferrous ions did not speed up the depolymerization rates, and on the contrary, Fenton depolymerization of cellulose with ferrous ions was slightly slower. This indicates that the copper-based Fenton reaction worked well on cellulosic depolymerization. In previous studies, similar results were also obtained. The Cu²⁺ ion was more active in decomposing H₂O₂ than the Fe²⁺ ion (Strlic *et al.* 2003), and the Cu²⁺ ion effectively decomposed H₂O₂ under alkaline conditions (Skounas *et al.* 2010). Not requiring ferrous ions would significantly simplify depolymerization, as well as reduce operational cost. Therefore, the subsequent Fenton depolymerization experiments with cellulose were conducted with a copper-based Fenton reaction by adding only hydrogen peroxide to the modified cuprammonium cellulose solution.

Oxygen Depolymerization of Cellulose

Taking advantage of the high oxygen sensitivity of the cellulose dissolved in the modified cuprammonium solution, this study also investigated the depolymerization of cellulose in the modified cuprammonium solution using natural oxygen aeration. As shown in Fig. 2, cellulose with high molecular weights was easily depolymerized by molecular oxygen oxidation. It took only 3.2 days to depolymerize cellulose to average

degree of polymerization (DP) of about 20, with an initial average DP of 2,679. For the sake of clarity, these data were not shown in Fig. 2. However, when the average DP of cellulosic fragments was below 20, the decrease in the average DP was much slower. It would take 6 days to depolymerize cellulose from average DP of 20 to 4. This result suggested that molecular oxygen oxidation could remarkably reduce the DP of cellulose dissolved in the modified cuprammonium solution, but it is difficult to obtain cellulose monomers. It can be inferred that molecular oxygen oxidation is suitable for the pretreatment of cellulosic depolymerization because of its low cost.

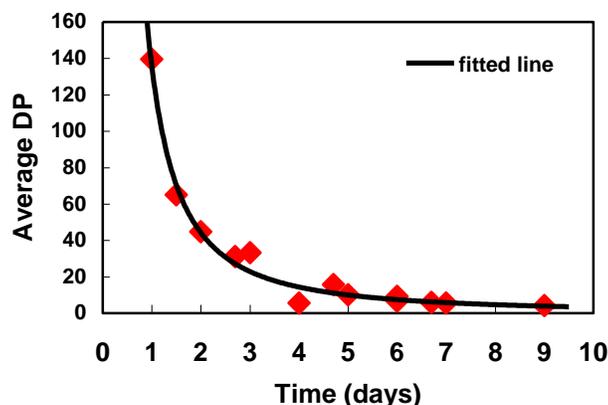


Fig. 2. Variations of the average molecular weight with oxidation reaction time

Fenton Depolymerization with Pretreatment of Molecular Oxygen Depolymerization

An experiment of the Fenton depolymerization with the molecular oxygen pretreatment was conducted to optimize the cellulosic depolymerization process. The hydrogen peroxide doses required for depolymerizing cellulose molecules into monomers was sharply reduced with increased pre-aeration time (Fig. 3). The requirements for H_2O_2 to reach the cellulosic monomers were estimated through interpolation or extrapolation methods. After 1.5 days of aeration, about 2.71 g of H_2O_2 /g cellulose was required to obtain cellulosic monomers. The hydrogen peroxide required with pre-aeration periods of 2.7 days and 4.7 days were about 1.96 and 1.18 g of H_2O_2 /g cellulose, respectively. However, with 6.7-day aeration pretreatment, only about 0.19 g of H_2O_2 /g cellulose was required.

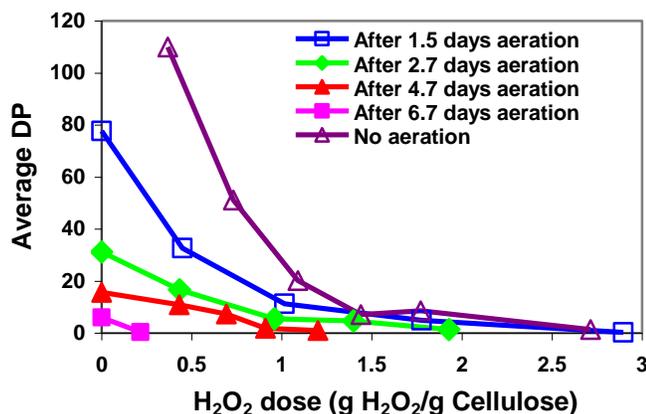


Fig. 3. Variations of the average molecular weight with differing H_2O_2 doses with molecular oxygen depolymerization pretreatment

To evaluate the H₂O₂ utilization efficiencies with different pre-aeration times, the actual requirements and theoretical demands of hydrogen peroxide are compared in Table 1. The theoretical demands of hydrogen peroxide can be calculated according to Eq. (2), assuming that each H₂O₂ molecule forms one hydroxyl radical, and one hydroxyl radical is required for breaking one β-1,4 glycosidic linkage,

$$W_{H_2O_2} / W_{cellulose} = 34 (MW_1 - MW_2) / (MW_1 \cdot MW_2) \quad (2)$$

where $W_{H_2O_2}/W_{cellulose}$ denotes the H₂O₂ demands for depolymerization per unit weight cellulose from molecular weight M_1 to molecular weight M_2 (g of H₂O₂/g cellulose).

Table 1. Comparison of Actual and Theoretical Demands for H₂O₂

Experiments	Estimated Actual Consumption of H ₂ O ₂ (g H ₂ O ₂ /g cellulose)	Theoretical Demands for H ₂ O ₂ (g H ₂ O ₂ /g cellulose)	Initial Average Molecular Weight	Target Molecular Weight
No Pre-aeration	2.75	0.189	434,023	180
Pre-aeration for 1.5 days	2.71	0.186	12,604	180
Pre-aeration for 2.7 days	1.96	0.182	5,062	180
Pre-aeration for 4.7 days	1.18	0.176	2,562	180
Pre-aeration for 6.7 days	0.19	0.155	998	180

As shown in Table 1, the estimated actual consumption of H₂O₂ was far higher than the theoretical demands for shorter pre-aeration periods. However, for long pre-aeration times such as 6.7 days, the estimated actual requirements (0.19 g H₂O₂/g cellulose) could be close to the theoretical demands (0.155 g H₂O₂/g cellulose). The reason for this may be that ammonia can react with H₂O₂ and therefore waste H₂O₂. The pre-aeration process stripped off the ammonia in the cuprammonium cellulose solution and thereby lowered the ammonia concentrations and reduced the useless consumption of H₂O₂.

In this work, the utilization of H₂O₂ was determined via measuring the variation of the average DP of the cellulose, which reflected the effective utilization of H₂O₂ for the cellulosic depolymerization. Such an approach would be more accurate than the utilization of H₂O₂ *via* chromatography analysis because the latter is the total utilization of H₂O₂, including not only the effective utilization for the cellulosic depolymerization but also the ineffective utilization caused by side reactions.

COD and TOC Variations of Fenton-depolymerized Cuprammonium Cellulose

During the process of the Fenton depolymerization preceded by 4.7 days of aeration, the COD of the cellulose in the cuprammonium solution was gradually reduced from 41.4 g/L to 30.0 g/L as the DP was reduced from 15.7 to 0.9; the TOC did not show any decrease even at low average DP of 0.9 (Table 2). The variation of COD reflects the degree of cellulose oxidation, and the TOC stands for the content of total organic carbon of the cellulose depolymerized. This result indicated that Fenton depolymerization only made cellulosic molecules smaller, and no organic carbon was further oxidized into inorganic carbon, *i.e.*, there was no organic carbon loss, at least until the average DP had been decreased to 0.9.

Table 2. Variations of COD and TOC of Fenton-depolymerized Cuprammonium Cellulose

Pre-aeration days	4.7		
H ₂ O ₂ dose (g H ₂ O ₂ /g Cellulose)	1.201	0.692	0
DP	0.9	7.3	15.7
COD (g/L)	30.0	33.3	41.4
TOC (g/L)	18.1	17.6	17.6

Reagglomeration of Cellulosic Fragments Depolymerized

The cellulosic fragments depolymerized tended towards reagglomeration when copper and/or ammonium in the modified cuprammonium solution were removed or reduced to some extent. This study examined the reagglomeration of the cellulosic fragments by diluting 1 mL of the cuprammonium cellulose solution in 50 mL of distilled water, acidifying the dilute solution until colourless (at a pH of about 5), and then testing SS and turbidity of the dilute solution at 10 minutes after acidification. The variations of SS and turbidity of the acidified dilute solution are shown in Table 3. It can be seen that the SS and turbidity were reduced with decreasing DP. This implies that large cellulosic fragments are more inclined to agglomerate than the small ones. The reason for this reagglomeration is that the hydrogen bond force between cellulosic fragments causes agglomeration of the fragments, which is similar to the reagglomeration of large cellulosic molecules. Larger fragments formed bigger particulates.

Table 3. SS and Turbidity of Acidified Dilute Solution of Depolymerized Cuprammonium Cellulose

DP	2.6	5.7	16.3	21.2	60.5	112.4
SS (g/L)	5.0	8.0	26.8	102.0	178.0	241.0
Turbidity (NTU)	1.75	2.75	42.3	151.0	210.0	211.0

The reagglomeration of cellulosic fragments increased with increased aging time, as shown in Fig. 4. The aging-increased reagglomeration depended on the DP of the cellulosic fragments depolymerized. The smaller the average DP, the less the increase in aging. However, only the cellulosic fragments of the average DP < 1.0 had insignificant aging reagglomeration, and their acidified dilute solution remained transparent. Even the cellulosic fragments with less than average DP of 2 displayed obvious aging reagglomeration. Consequently, the initial transparent acidified dilute solution became turbid after a few days. The reason for this is probably because there were some larger fragments, even though the average DP was small.

The degree of reagglomeration of the Fenton-depolymerized cellulose was further examined in terms of COD and TOC. The above cellulosic samples were aged for 39 days under acidic conditions. The percentages of soluble COD (CODs) and TOC (TOCs) were up to 99.7% and 99.9% at the average D of 0.9, as shown in Fig. 5. Almost all the cellulose depolymerized remained soluble. However, for an average DP of 15.7, the percentages of the soluble COD and TOC after an aging time of 39 days were 42.5% and 53.6%, respectively. Just over half of the cellulose depolymerized was soluble.

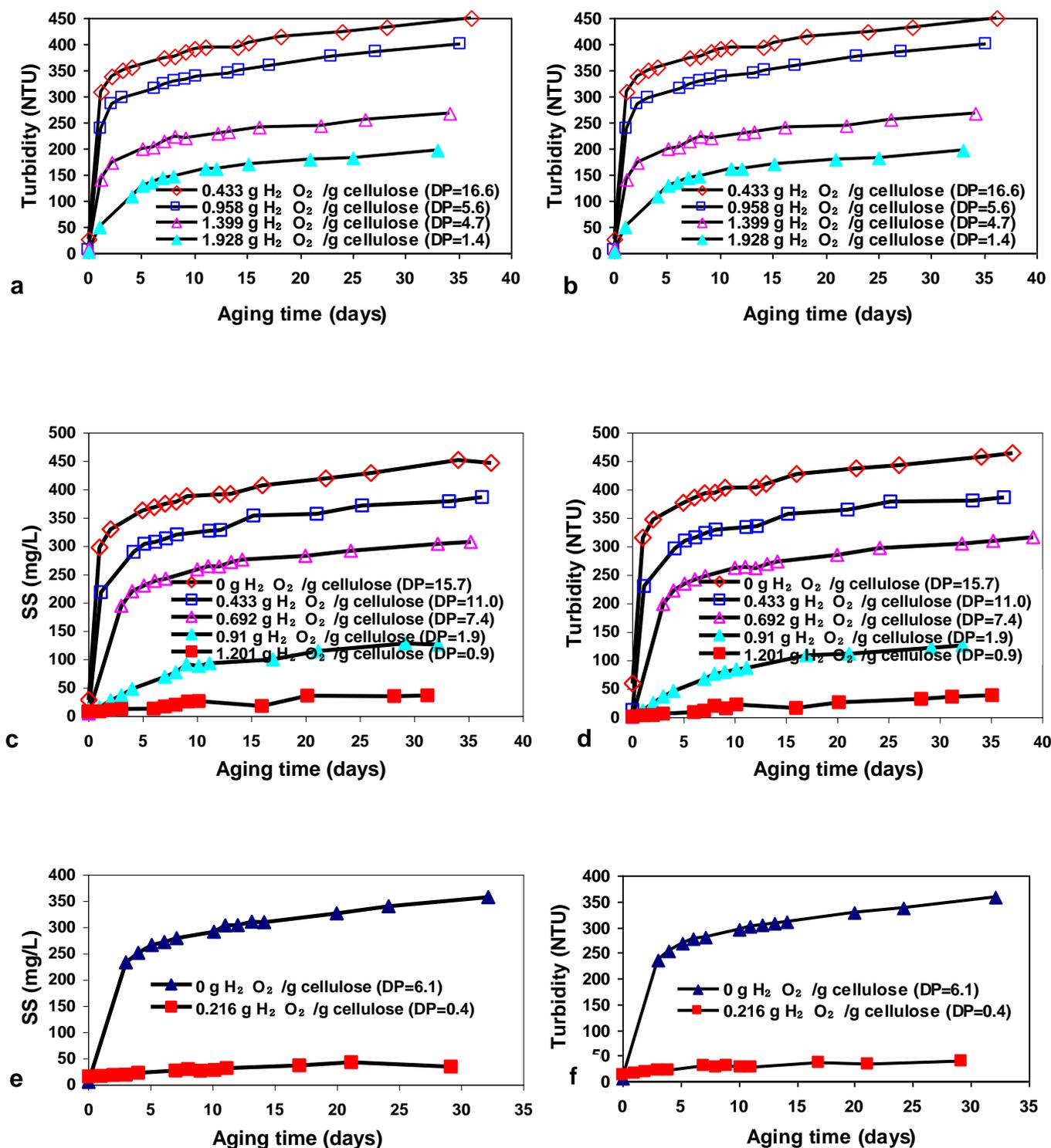


Fig. 4. The effect of aging time on the reagglomeration of cellulosic fragments: (a) 2.7 days pre-aeration, the variations of SS with aging time; (b) 2.7 days pre-aeration, the variations of turbidity with aging time; (c) 4.7 days pre-aeration, the variations of SS with aging time; (d) 4.7 days pre-aeration, the variations of turbidity with aging time; (e) 6.7 days pre-aeration, the variations of SS with aging time, and (f) 6.7 days pre-aeration, the variations of turbidity with aging time

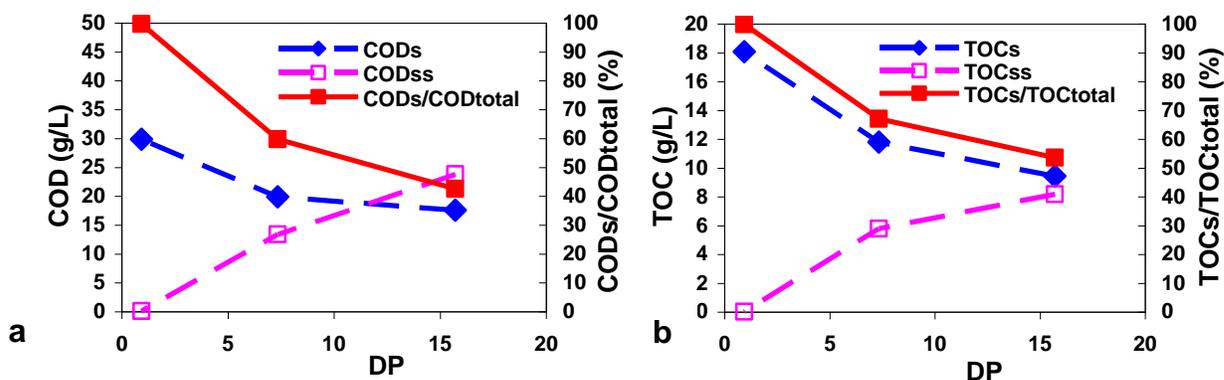


Fig. 5. Variations of the aging reagglomeration of Fenton-depolymerized cellulose with the average DP: (a) COD variation with average DP; and (b) TOC variation with average DP

Degradability of Reagglomeration Particulates

The Fenton results for deagglomerability of the reagglomeration particulates are shown in Fig. 6. The particulates were obtained from reagglomeration of the cellulose depolymerized by molecular oxygen with 8 days aeration. The Fenton deagglomeration was conducted at a pH of 3 with 0.78 of weight ratio of H_2O_2 to the particulates' COD and with 50 mg/L of ferrous ions until the H_2O_2 was depleted. A small amount of COD was removed, and the H_2O_2 consumption was 28.2 times the removed COD. The cellulose in pulp was almost unable to be depolymerized by the Fenton reaction due to its recalcitrant crystalline structure (data not shown). The above result indicates that the reagglomeration particulates were a little easier to deagglomerate than the crystalline cellulose in pulp, but they were still rather resistant to deagglomeration.

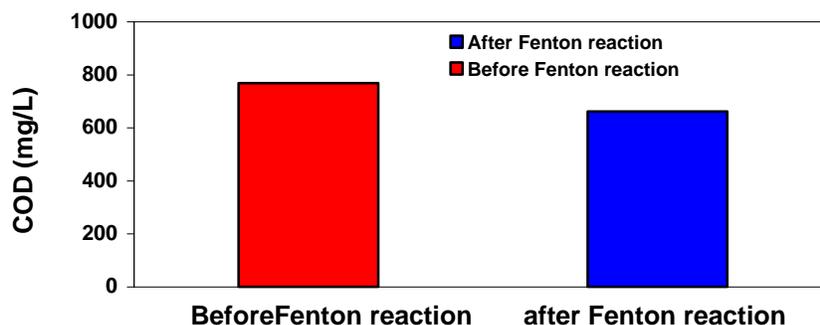


Fig. 6. Fenton deagglomerability of reagglomeration particulates of Fenton-depolymerized cuprammonium cellulose

Compared with the theoretical H_2O_2 requirement of about 2.1 g per g removed COD (Kurt *et al.* 2007), the real H_2O_2 consumption is so high that, like the cellulose in pulp, Fenton depolymerization of reagglomerated particulates is also impractical. The reason for this might be that the reagglomerated particulates still possess a crystalline structure, but were transformed into cellulose II, which is different from the initial natural cellulose I structure. Cellulose II has a much lower DP and X-ray crystallinity as well as higher water absorbency than cellulose I (Sasaki *et al.* 2003), and therefore is slightly easier to deagglomerate.

Mechanism for Fenton Depolymerization of Cellulose Dissolved in Cuprammonium Solution

In the modified cuprammonium cellulose solution, copper ammonium complex displaces the hydrogen bonds between cellulose molecules therefore dissolves the cellulose. This study showed that the Fenton reaction is an efficient method for depolymerizing the cellulose dissolved in the modified cuprammonium solution. The mechanism for the Fenton depolymerization of the dissolved cellulose presumably is that the hydroxyl radical that comes from the Fenton reaction cleaves the β -1,4-linked bond. The hydroxyl radical attack takes place at the anomeric carbon, and can readily break down any encountered glycosidic linkage in cellulose (Guay *et al.* 2002). However, besides cleaving glycosidic linkages, other reactions between hydroxyl radical and cellulose would also take place, especially for very low DP. The products generated need to be investigated in the future.

The mechanism for the molecular oxygen depolymerization of cellulose might involve the special catalyst catalyzing the oxygen reduction reaction to generate active oxygen species (AOS, mainly $O_2^{\cdot-}$), and the strong oxidation capability of the AOS cleaving the glycosidic linkage in celluloses, making the celluloses highly oxygen-sensitive. However, from the above data, it can be seen that the AOS could not efficiently depolymerize the cellulose into monomers.

CONCLUSIONS

It can be concluded from this preliminary study that,

1. The Fenton reaction can efficiently depolymerize the cellulose dissolved in the modified cuprammonium solution. The Fenton depolymerization of the cellulose reached the monomers without loss of organic carbon, and almost all the cellulose depolymerized maintained solubility without reagglomeration after cuprammonium was removed.
2. Molecular oxygen oxidation could reduce cellulose to an average DP of approximately 4 within 6 days, which is suitable for the pretreatment of cellulosic depolymerization because of its low cost. The combination of the Fenton depolymerization and oxygen pre-oxidation *via* aeration is a reasonable and optimal cellulose depolymerization process, which could remarkably increase H_2O_2 utilization of the Fenton depolymerization and correspondingly reduce the H_2O_2 requirements.
3. Under the conditions in this preliminary study, the optimum parameters to obtain cellulose monomers may be about 6 days of oxygen pre-oxidation *via* aeration and about 0.2 g H_2O_2 /g cellulose of H_2O_2 dose.

Further study is required to confirm the accuracy of DP tests and to improve the conditions to shorten reaction time of oxygen pre-oxidation.

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