POM-ASSISTED ELECTROCHEMICAL DELIGNIFICATION AND BLEACHING OF CHEMICAL PULP

HÉLÈNE LAROCHE*, MOHINI SAIN, CARL HOUTMAN*** and CLAUDE DANEAULT***

**Pulp and Paper Research Centre, University of Quebec, Trois-Rivières, Canada G9A 5H7*

***Pulp and Paper Research Centre, University of New Brunswick, NB, Canada*

**** USDA Forest Product Laboratory, University of Wisconsin, Madison, Wi, USA*

Received May 8, 2000

A polyoxometalate-catalyzed electrochemical process has shown good selectivity in delignifying pulp. This breakthrough in redox catalysis shows promise for the development of a new environmentally benign technology for pulp bleaching. The electrochemical process. applied with a mildly alkaline electrolyte solution containing trace amounts of a vanadium-based polyoxometalate, $K_5[SiVW_{11}O_{40}]$, decreased the kappa number of a softwood Kraft pulp by about 40% without significant change in the viscosity of the pulp. In a similar electrochemical process, a softwood semi-bleached Kraft pulp was further bleached to a high brightness pulp, above 85% ISO, by electrolysing a borax-based electrolyte activated with tetraacetylethylenediamine in a pulp suspension.

Key words: delignification, bleaching, chemical pulp, electrochemistry, wood pulp.

INTRODUCTION

Electrochemical bleaching of wood pulp is one of the priority research areas in transforming lignin containing wood pulp into value-added paper. Earlier work in this area has indicated that poor mass transfer and lack of reaction selectivity are the two major causes for the slow technological development in this area. Most of the research works in the past years showed that the selectivity of electro-catalytic delignification reaction is limited. In one of our recent publications, we have demonstrated that delignification reaction selectivity of a ferrocyanide-based redox catalyst in an electrolytic cell is relatively poor. In general, the kinetics of cellulose degradation reaction is the dominant reaction once the extent of delignification

reaches above 25%. Two approaches are used in our laboratory to improve selectivity of the delignification reaction. Firstly, an increase in the pulp viscosity was obtained by incorporating an electrochemically active viscosity protector during electrochemical reaction. Secondly, use of a new generation of catalysts, such as engineered polyoxometalates, appears to be more promising. Although the electrochemistry of polyoxometalates has been investigated for several decades. exploitation of their electrochemical reactions has only recently begun. It has been reported that heteropolytungstates demonstrate coalescence of two one-electron reactions into a single two-electron step in aqueous media containing hydrogen ions.[1] It is therefore not unlikely that polyoxometalates can be excellent electrocatalysts because of their chemical stability and capacity to undergo multi-electron charge transfer reactions in the presence of the hydrogen ion. Thus, an efficient electro-catalytic bleaching technology, based on the use of polyoxometalate (POM) salts and oxygen, is being developed to delignify wood pulp in a short time period.

Although good delignification selectivity is one of the major challenges for chemical pulp production, the urge to reduce the number of bleaching stages and bleach chemical consumption also drew attention in years. It is not unlikely that, in an electrochemical process, an in-situ generated oxidant can be a more effective means to oxidize residual lignin and/or to discolour lignin chromophores. Exploring the electrochemical reaction of delignified chemical pulp selectively for high brightness, bleaching is expected to bring some positive contribution. Tetraacetylethylenediamine (TAED) is a known bleach activator. It has been reported earlier that electrolytic perborate bleaching of pulp requires higher temperature[2] for chemical pulp bleaching. Our preliminary investigations also demonstrated that addition of this activator during in-situ generation of perborate in an electrochemical cell could reduce bleaching temperature and improve brightness.

In this work, we describe the incorporation of an electrolyte solution containing trace amounts of a vanadium-based polyoxometalate, $K_5[SiVW_{11}O_{40}]$, as an electrochemical bleaching catalyst. The effect of the hydrogen ion addition in an aqueous solution of the above mentioned heteropolytungstates has been also described. Finally, we presented our recent findings on the effect of electrochemically generated oxidation species with TAED activated-borate on the bleaching of high brightness Kraft pulp.

EXPERIMENTAL

Electrochemical cell: The electrochemical reactor used in the present work is a bench scale apparatus. The reactor was designed and built in our laboratory. It essentially consists of an electrolytic cell having two rectangular carbon electrodes and a rectangular stainless steel electrode placed in between two carbon electrodes. The distance between the carbon electrodes and the stainless steel electrode can be suitably adjusted by moving the electrodes on a teflon base fined at the bottom of the cell. The reactor is fitted with a pump to circulate thick pulp slurry continuously inside the cell. The

electrochemical reactor is also fitted with inlet, outlet and bi-pass valves to allow easy handing of the pulp slurry and also to facilitate intermittent sample collection. The maximum pumping limit is restricted to 5% of dry pulp consistency. For higher consistency pulps, other pumps are recommended. A schematic diagram of the electrochemical reactor used in this study is shown in Figure 1.

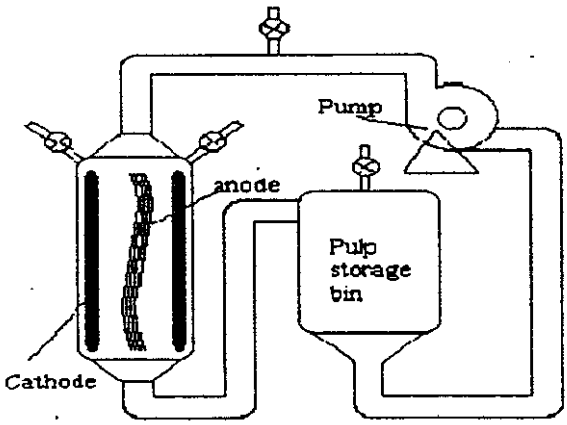

Fig. 1. – Electrochemical reactor.

MATERIAL

Unbleached softwood Kraft pulp obtained from Abitibi-Consol Inc., Waggamack was used for the delignification experiments. The pulp contains about 80% spruce and 20% birch. The hardwood pulp was obtained from Domtar. The initial pulp viscosity and kappa number of pulp were given in Table 1. The polyoxometalate catalyst used in this set of experiments was a heteropolytungstate, $K_5[SiVW_{11}O_{40}]$, The activator used for electrolytic borate bleaching was tetraacetylethylenediamine (TAED). Borax was used to generate bleaching chemical-electrochemically.

TABLE 1

Initial pulp properties

Properties	Softwood
Viscosity, cP	28.7
Kappa	26.5
ISO, %	27.5

METHODOLOGY

Pulp consistency was adjusted to 3% before experimentation with an electrolyte solution, which was a suitable mixture of alkali, acid and catalysts. Catalysts concentration was varied within a suitable concentration range. Viscosity,

kappa number and pulp brightness were measured after a given time interval. Current density was also varied by changing the input current and by maintaining the effective electrode surface area constant. Electrode passivation was performed before each set of experimentation.

Cell reactions: The electrochemical reaction of polyoxometalates has been studied recently. In aqueous solution of a heteropolytungstate salt of Keggin $SiVW_{11}O_{40}^{-5}$ anion can undergo electron transfer reaction at anode, according to the following reaction:

In anode:

$$SiVW_{11}O_{40}^{6-} \text{ (a)} \longrightarrow SiVW_{11}O_{40}^{5-} \text{ (b)} + e^-$$

Electrochemical data indicate that the above reaction should be favourized by 12.5 kcal/mole (taking E (b/a) as 0.68 V and the reduction of oxygen to water at pH 7 as 0.815 V.[3]

The oxidized form of polyoxometalates can then react with pulp lignin.

Oxidized pulp was then removed from the cell at predetermined intervals and the electrolyte was recycled into the system with further addition of fresh pulp.

RESULTS AND DISCUSSION

The first electrolysis experiment was carried out in an alkaline electrolyte containing 1 mmol/L of vanadium catalyst. The pH of the solution was adjusted to 12 and the electrolysis was carried out for 30 min at 25° with a current density of 12.5 mA/cm^2. Results are shown in Table 2. There is hardly any change in the kappa number during electrolysis. On the other hand, the pulp viscosity decreased by few centipoises and pulp brightness increased proportionaly. It was suggested that the Keggin anion used in this electrochemical process was not sensitive to alkaline pH condition. The little change in viscosity and brightness was attributed to the electrochemical generation of active oxygen, in the presence of atmospheric oxygen and alkali. However, this treatment had little effect on delignification and was dropped in later work.

TABLE 2

Effect of POM under alkaline condition

Condition	viscosity	Kappa	ISO %
12.5mA/c^2, 30 min pH–12	24.5	25	31.2

Furthermore, the results of alkaline electrolytic treatment of pulp with a Keggin anion were also compared with a ferrocyanide catalyst, under the same reaction condition. Although ferrocyanide was an effective delignification catalyst

under alkaline condition, selectivity was very poor. A decrease in kappa number by 50% within 30 min resulted in a proportionate loss of pulp viscosity. These results are shown in Figure 2.

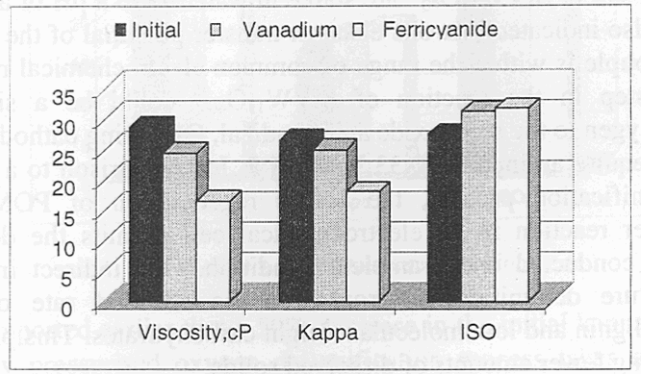

Fig. 2 – Effect of the catalyst type.

In the next set of experiments, the electrolysis reaction parameters were changed. The pH of the solution was adjusted to near neutral condition by adding alkali at pH 7.6, current density was decreased to 2.5 mA/cm^2, and electrolysis time was increased to 60 minutes. The results are shown in Table 3. It is evident that, there is practically no change in viscosity, kappa or brightness under the given electrolysis condition. Therefore, it is concluded that the presence of trace amounts of hydroxyl anion under neutral pH condition has no effect on delignification. The obvious reason is the absence of electrolyte in the system. Therefore, in the third phase of electrolysis, an additional hydrogen ion was introduced

TABLE 3

Effect of POM under neutral condition

Condition	Viscosity *c*P	Kappa number	ISO %
pH ~ 7.6 60 minutes	28.4	24.2	28.8

was about 10% within the stipulated electrolysis period. This selectivity of the electrochemical reaction is not surprising.

It has been already demonstrated by Weinstock et al.[4] that selective POM salts such as K-salt of $SiVW_{11}O_{40}^{-5}$ are stable in water up to a pH of approximately 8. They have also indicated that one electron transfer potential of the $SiVW_{11}O_{40}^{-5}$/ $SiVW_{11}O_{40}^{-6}$ couple is within the range of common electrochemical reactions. The rate limiting step in the reaction of $SiVW_{11}O_{40}^{-6}$ could be a single-electron reduction of oxygen to the superoxide anion radical, O_2 during cathodic reduction.' which would require an input of 0.33 V at pH 7. In comparison to a conventional catalytic delignification process, the in-situ regeneration of POM_{oxd} via one electron transfer reaction in an electrochemical cell permits the delignification reaction to be conducted under ambient condition. One indirect implication of room temperature delignification process is the retarded rate of hydrolytic dissociation of lignin and low molecular weight carbohydrates. This process would help in generating fewer amounts of dissolved solids.

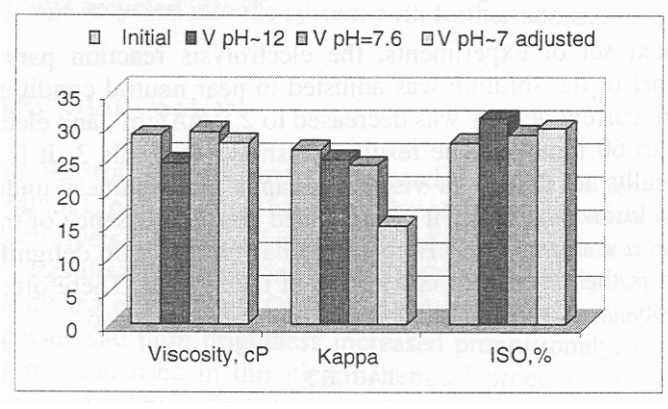

Fig. 3 – Effect of pH and electrolyte composition.

We have recently investigated this wet oxidation process and the results will be published in one of our future communications.

Effect of Electrolyte Recirculation

After 30 min of electrolysis, the fibre was separated from the electrolyte by filtration under vacuum and the recovered electrolyte was used for further electrolysis. The results of electrolyte recycling reveal that the recovered electrolyte is a very effective delignifying chemical. The results in Figure 4 indicate that there is only a marginal loss in the delignification efficiency after a two time recirculation. Kappa no. of the pulp reached 17 and 18 in two successive recirculation processes compared to a kappa no. of 15, achieved with a fresh electrolyte solution. A similar effect was also observed for viscosity and brightness.

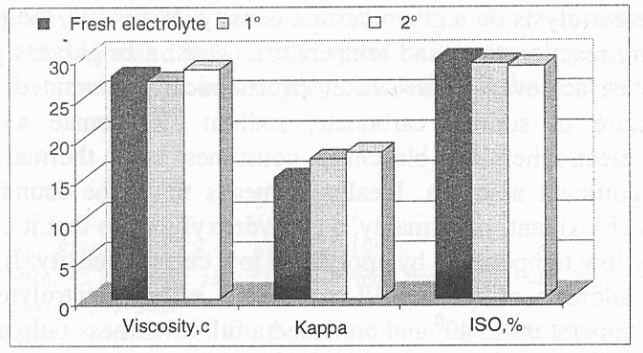

Fig. 4 – Effect of electrolyte recirculation.

It was reported earlier that a 50% decrease in the initial kappa number of the same pulp by pressurised oxygen delignification process takes about 150 min. Therefore, it is concluded that POM catalysed electrochemical delignification of a chemical pulp is promising. However, a further study on the understanding of the fundamental electrochemical reaction involving dissolved organic components and related electrochemical oxidation process, as well as a correct evaluation of design efficiency of the electrochemical cell will be required to advance this lab-scale technology to a commercial process.'

Effect of TAED Catalysed Electrolysis

It has been demonstrated earlier that the electrolysis of borax and tetraacetylethylenediamine in alkaline pH condition generates an intermediate (not identified) oxidising agent and improves the in-situ bleaching of a semi-bleached Kraft pulp in an electrochemical cell [as above]. Recently, we have carried out further experimentation in order to optimise bleaching efficiency of borate and TAED activated borate solutions as a function of time, temperature and current density. The results demonstrated that, in the absence of an activator 84 ISO% brightness pulp could be obtained using relatively high current density. Equation (1) gives the regression correlation of electrochemically bleached chemical pulp as a function of electrolysis time, temperature and current density. This correlation is valid for the given pulp having initial brightness of 75% ISO. Other electrolysis conditions are: time interval 60 to 150 min, temperature interval 50 to 80° and current density of 0.12 to 0.18 A/cm^2.

$$\%ISO = 81.2 + 0.91\ (time) + 0.44\ (current\ density) + 1.12\ (temperature);$$

$R^2 = 0.91$ and R^2 (adj.) = 0.82. where R^2 is the correlation coefficient.

The regression equation is presented in coded values with the upper and lower limits −1and +1, respectively. This equation shows the effect of temperature

and time of electrolysis on a given current density. Moreover, the process requires relatively long reaction time and temperature. Thus, a brightness gain of about 9 points has been achieved by in-situ electrochemically generated oxidising agent from a mixture of sodium carbonate, sodium bicarbonate and borax. High temperature electrochemical bleaching consumes both thermal and electrical energy in significant amounts. Ideally, a means might be found to control the action of bleach oxidant, presumably, a perhydroxyl ion, so that it can be generated at a relatively low temperature by applying a low current density. It has been found out that the addition of 30 mmol/L of TAED in the electrolyte decreased the electrolysis temperature to 40° and produced a full brightness pulp above 86% ISO. Table 4 summarises some significant results at two different concentrations of TAED.

TABLE 4

Activated electrochemical bleaching

Temperature (°C)	50.0	50.0
Current density (A/cm2)	0.2	0.2
Time (minutes)	150.0	150.0
TAED , mmol/l	30.0	15.0
Brightness gain*, %ISO	11.6	9.4

*initial brightness 75% ISO.

CONCLUSION

A mildly alkaline electrolyte solution containing trace amounts of a vanadium-based polyoxometalate having the chemical formula $K6SiVW_{11}O_{40}$ decreased the kappa number of a softwood Kraft pulp by about 40%, without significant change in the initial viscosity of the pulp. The process can be either continuous or batch, and a recirculation of pulp and electrolyte in an electrochemical cell is feasible, with insignificant change in the delignification efficiency. Thus, successful pilot scale delignification of a softwood pulp of initial kappa 28, viscosity 27 cP and brightness 27% ISO was achieved at a flow rate of 50 kg/h (o.d), to obtain a delignified pulp with a Kappa number of 15, viscosity 26 cP and ISO brightness 31%.

In addition, the in-situ incorporation of a peroxide bleach catalyst, TAED, in electrochemically generated perborate solution was also found to be effective to bleach a semi-bleached chemical pulp to full brightness. Thus, a bright softwood Kraft pulp of final brightness 86 ISO% has been achieved by TAED activated electrolysis at 50°.

Such electrochemical short sequence delignification and bleaching processes permit consequent counter-current washing, which reduces the cycle time, and

facilitates mill closure. Although more work should be done, our bench scale trial showed excellent promise and this technological development generated optimism in adopting electrochemistry for in-situ pulp processing in the next millennium.

REFERENCES

[1] B. Keita and L. Nadjo, *Electroanal, Chem.*, **217,** 287 (1987).
[2] M.M. Sain, Q.Y. Hu, C. Daneault and J.D. Pellerien, *Proc. Int. Pulp Bleaching Conf.* 1988, Helsinki, Finland, p. 337–342.
[3] J.E. Huheey, "Inorganic Chemistry". 2nd Ed., Harper and Row, New York, 1978, p. 312.
[4] Ira Weinsrock, Rajai Atalla, Richard Reiner, Mark Moen, Kenneth Hammel, Carl Houtman, Craig Hill and Mason Harrup; *J. Molecular Catalysis, A: Chemical,* **116,** 59 (1997).
[5] M. Chanon, M. Julliard. J. Santamaria and F. Chanon, *New J. Chem.* **16,** 171 (1992).