

Bleaching of Kraft Bagasse Pulp in Presence of Polyoxometalate Catalyst

A. A. Ibrahim[†], Mohamed El-Sakhawy and Samir Kamel

(Received on December 6, 2004; Accepted on November 15, 2005)

ABSTRACT

The catalytic effect of molybdovanadophosphate heteropolyanion (HPAs) on the delignification of kraft bagasse pulp by hydrogen peroxide has been investigated. Very small amounts of the catalyst (0.05–0.3 mM/l) gave convenient results. Partial reduction of the catalyst was also studied. The effect of reaction medium (water, ethyl alcohol and acetone) on the bleaching was also studied. The results obtained show that the optimum condition for bleaching in presence of polyoxometalate were 0.05 mM/l catalyst concentration at 70°C reaction temperature and 7 % consistency at pH 2 in aqueous medium. The ratio of water to solvent of 60 : 40 from acetone gives higher brightness than ethyl alcohol. The catalyst solution can be reused for 5 times without any reduction in brightness. ESR for the blank and exhausted solutions under different conditions was also carried out to find the relation between reduced metals and pulp brightness.

Keywords: bleaching, bagasse pulp, polyoxometalate, catalyst, brightness functional group

1. Introduction

The conventional industrial pulping technologies deal mainly with sulphur based reagents while the bleaching reagents are mainly chlorine based. Both have negative impacts on the environment. Recently a great effort has been directed to develop of new approaches for non-pollutant delignification.

A class of inorganic metal-oxygen cluster anions (polyoxometalate) was proposed as reagents and or catalysts for the pulp delignification. Polyoxometalates oxidize residual lignin with high selectivity and may be easily reused in the bleaching process. Vanadium (V) peroxo complexes transfer oxygen to aromatic hydrocarbon at room temperature. In bleach liquor it improve the

• National Research Center, Cellulose & Paper Department, El-Tahrir St., Dokki, Cairo, P O 12622, EGYPT

† Corresponding author : E-mail : aakishar@hotmail.com

delignification efficiency and pulp brightness. Practically, the heteropolyanion such as hepta-molybdopentavanadophosphate anion (HPA-5) was suggested as an efficient catalyst for oxygen and ozone bleaching of kraft pulp. Also an important protective effect against oxidative depolymerization of polysaccharides through the scavenge of the hydroxyl radicals was attained.

Oxidation of organic substrates in the presence of (HPA-5) occurs due to the ability of V^V (in the form of HPA or VO_2^+ produced via dissociation of HPA) to accept electrons from organic substrates. The reduced V^{IV} can be oxidized back to V^V via reaction of HPA with molecular oxygen.

2. Experimental

2.1 Material

Unbleached Kraft bagasse pulp, obtained from Egyptian Sugar Company, Edfo Mill was used in this work.

2.2 POM preparation

The (HPA-5) sodium heptamolybdopentavanadophosphate $Na_8[PMo_7V_5O_{40}]$ solution was prepared by reacting MoO_3 , V_2O_5 , Na_2CO_3 and $NaH_2PO_4 \cdot H_2O$ in stoichiometric proportions according to a previously published procedure. The partially reduced form of HPA-5 (0.2 electron/mol) was obtained by reaction of its sodium salt with an equimolar amount of hydrazine sulphate in the presence of sodium hydrogen sulphate. Finally, aqueous solutions of molybdovanadophosphates in its oxidized or reduced forms were mixed with an appropriate volume of bleaching solutions.

2.3 Bleaching

Bleaching was carried out at controlled thermostatic water bath on a polyethylene bags. The time required to reach the final temperature (70-90°C) was 20-30 min. The bleaching solution was mostly 2 mM/l aqueous solution of partially (0.2 e/mol) reduced HPA-5 at pH 2. At the end of the reaction the bleaching mixture was cooled quickly. The pulps were filtered and washed with distilled water.

3. Results and Discussion

3.1 Effect of POM concentration and type

The amounts of POM, as it is or after partially reduced, were studied on bleaching efficiency. POM (0.2 mM/l) was used in all experiments either reduced or not.

At first we study the effect of H_2O_2 where used alone in the second step of bleaching of the unbleached bagasse pulp (Table 1, samples 1-6). When we use 0.2 mM/l POM in the first step then H_2O_2 in the second step, we found that increasing the concentration from 1.5 to 2.5 % decrease the degree of polymerization (D.P.) from 717 to about 692, and increasing the H_2O_2 after that to 4 % nearly has no effect on the D. P. Regarding the brightness it increased from about 60 at 1.5 % H_2O_2 to about 69 % at 4 % H_2O_2 . The yield increased from 87.4 at 1.5 % H_2O_2 to 92 % at 2.5 % H_2O_2 then decreased again to 89.8% at 4 % H_2O_2 due to the carbohydrate degradation. When H_2O_2 were used in the two steps of bleaching (Table 1, samples 7-11), it could be noticed that dividing H_2O_2 charge between the two steps decreases the brightness and yield (samples 7, 10,11), even when extra H_2O_2 charge was used on first step it causes also brightness and yield decrease (sample 9), but the time required for bleaching is decreased.

Table 1 shows the effect of time during second H_2O_2 bleaching step (samples 12-17), it is clear that as the time increase the brightness increase while the yield and viscosity slightly decreased.

The partially reduced HPA-5 displays better catalytic activity towards lignin oxidation than the oxidized species (Table 1, samples 18-21). Better results obtained with the partially

reduced HPA-5 could be explained by the scavenging of oxygen radical species by HPA-5 in the initial stages of the process, preventing lignin cross linking, caused by radical coupling reactions. Reduced HPA-5 becomes less stable under the acidic conditions than the oxidized species. In this way, the probability of HPA dissociation with release of VO_2^+ (or VO_2^{2+}) increases, which have higher

Table 1. Effect of different parameters on bleaching

Sample no.	Activation 0.2 mM	H_2O_2 % in 1 st step	H_2O_2 % in 2 nd step	Time, h	Yield %	Viscosity	Brightness %
1	POM	---	1.5	2	87.4	717	60.5
2	POM	---	2.0	2	87.5	696	64.8
3	POM	---	2.5	2	92.0	692	66.7
4	POM	---	3.0	2	89.8	690	68.7
5	POM	---	3.5	2	88.8	693	69.5
6	POM	---	4.0	2	89.8	692	69.2
7	POM	0.25	2.25	2	91.3		62.2
8	POM	0.50	2.5	2	92.1		65.5
9	POM	0.50	2.0	2	91.6		63.0
10	POM	1.25	1.25	2	90.8		57.9
11	POM	1.75		2	88.8		52.8
12	POM	---	2.5	0.25	92.1	721	61.3
13	POM	---	2.5	0.50	90.2		61.7
14	POM	---	2.5	1.0	88.5	657	65.4
15	POM	---	2.5	1.5	88.5		65.0
16	POM	---	2.5	2.0	88.2	690	68.0
17	POM	---	2.5	2.5	86.9		68.2
18	RPOM	---	2.5	0.25	92.0	626	64.4
19	RPOM	---	2.5	0.50	91.4	632	68.0
20	RPOM	---	2.5	1.0	88.4	593	68.3
21	RPOM	---	2.5	1.5	85.3		68.9
22	POM	0.25	2.5	0.25	89.3	584	65.9
23	POM	0.25	2.5	0.50	89.9		64.8
24	POM	0.25	2.5	1.0	90.6	608	65.2
25	RPOM	0.25	2.5	0.25	89.6		61.1
26	RPOM	0.25	2.5	0.50	92.3		64.0
27	RPOM	0.25	2.5	1.0	90.1	583	65.3
28	----	---	2.5	---	93.6	725	58.0
RM						982	36.9

1st step: 0.2 mM/l RPOM, consistency 3%, and pH 2 for 0.5 h at 90°C

2nd step: 2.5 % H_2O_2 , 0.1 % DTPA, and pH 12 at 8% consistency for 2h at 70°C

oxidation potential than that of HPA-5 (7).

Samples 22-28 (Table 1) shows that reduced POM gave pulp of higher viscosity and it require less time to reach same brightness as compared with POM without reduction.

It could be concluded that the addition of $\text{Na}_8[\text{PMo}_7\text{V}_5\text{O}_{40}]$ (HPA-5) sodium heptamolybdopentavanadophosphate as 2 mM/l solution increases lignin oxidative destruction substantially as compared to control experiments (sample 27) without catalyst.

3.2 Effect of temperature

Table 2 shows the effect of temperature on the bleaching of bagasse using reduced POM 0.2 mM/l for 30 minutes at pH 1.5 and 3 % consistency. As it can be seen from the table, raising the temperature from 60°C to 70°C give some improvement in the brightness. Raising the temperature after that lower the brightness until it reaches 66.5 at 100°C. The yield of the

bleaching slightly lowered from 92.9 to 91.4 % by raising the temperature from 60 to 100°C. So we can conclude that 70°C is the optimum temperature to carry the treatment with reduced POM.

3.3 Effect of consistency

The effect of solution consistency during the reduced POM treatment is shown in Table 3. From the table it can be seen that as the consistency increased from 1 to 7 % both the brightness and the yield of the process increased. So the higher consistency is more suitable for this treatment.

3.4 Effect of RPOM concentration

The effect of reduced polyoxometalate (RPOM) in the activation step can be found in Table 4. As the concentration of the RPOM increased from 0.05 to 0.3 mM/l we found that both yield and brightness of bleached bagasse

Table 2. Effect of temperature during activation on bleaching

Sample no	Temperature	Yield	Brightness
29	100	91.4	66.5
19	90	91.4	68.0
30	80	92.2	69.3
31	70	92.9	71.3
32	60	92.9	69.8

Bleaching conditions as on table 1 caption

Table 3. Effect of consistency during activation on bleaching

Sample no	Consistency %	Yield	Brightness
33	7	93.6	71.9
34	5	94.3	70.7
19	3	91.4	68.0
35	2	91.8	69.2
36	1	95.4	68.2

Bleaching conditions as on table 1 caption

Table 4. Effect of RPOM concentration during activation on bleaching

Sample no	RPOM, mM/l	Yield	Brightness
37	0.05	96.1	73.8
38	0.1	93.5	70.7
39	0.15	96.0	70.7
19	0.2	91.4	68.0
40	0.3	94.1	67.3

Bleaching conditions as on table 1 caption

decreased. This indicates that the use of only 0.05 mM/l is sufficient for the bleaching and give best results than higher concentration of RPOM. This finding is with good agreement with that found with Patt (8), which indicate, that only 20 ppm of the catalyst is sufficient for the process.

The decrease in oxidizing ability at HPA-5 concentrations above 0.05 mM (at constant pH) is probably a consequence of an increase in ionic strength in solution due to addition of NaOH for pH adjustment. This may disturb the appropriate equilibrium between the different molybdovanadophosphate species in solution and change their redox properties.

3.5 Effect of pH

Table 5 illustrates the effect of changing pH of the treatment from 1.5 to 4. From that table we can see that pH 2 is the most suitable pH since at this pH the highest brightness and also the highest yield were obtained. The pH has

a pronounced effect on delignification. The delignification rate increases in the pH range 3.5 to 2.0 due to the increasing HPA-5 dissociation followed by the appearance of free VO_2^+ . Delignification rate slows down in the pH range 2.0 to 1.0 because the HPA re-oxidation rate decreases and the rate of lignin condensation reactions catalyzed by acid increases (11).

3.6 Effect of bleaching solution contents

Tables 6 and 7 show the effect of using ethyl alcohol or acetone with water at different concentrations ranging from 0 to 60 %. The use of a mixture containing 60 % water and 40 % ethyl alcohol or acetone give the best results for brightness and yield also. Also from the results we can say that the use of ethyl alcohol with water give better results than using acetone, where with 40 % ethyl alcohol a brightness of 73 were obtained and 93.1 % yield, with 40 % acetone the brightness

Table 5. Effect of pH during activation on bleaching

Sample no	pH	Yield	Brightness
19	1.5	91.4	68.0
41	2	95.8	71.4
42	3	95.4	70.1
43	4	96.0	67.8

Table 6. Effect of ethanol as medium during activation

Sample no	EtOH : H ₂ O	Yield	Brightness
44	0 : 100	93.5	67.3
45	40 : 60	93.1	73.0
46	50 : 50	97.4	71.0
47	60 : 40	96.3	68.2

Table 7. Effect of acetone as medium during activation

Sample no	Acetone : H ₂ O	Yield	Brightness
44	0 : 100	93.5	67.3
48	40 : 60	93.0	71.0
49	50 : 50	93.8	67.9
50	60 : 40	90.0	65.5

Bleaching conditions (tables 5-7) as on table 1 caption

obtained is only 71 and 93 % yield. Therefore it is better to use ethyl alcohol as solvent with water to obtain higher yield and brightness. The addition of organic solvents to aqueous solution of molybdovanadophosphates usually increases their structure stability and changes their redox properties. Organic solvent addition may be a useful way of tuning the catalytic activity of HPA-5 and the delignification selectivity. The acidity of HPA-5 and sulfuric acid decreases with the addition of ethanol to the system. This decrease of acidity slows lignin condensation reactions and hydrolytic

degradation of polysaccharides (11).

3.7 Effect of reusing RPOM

We try to use the spent solution after bleaching to bleach another amount of pulp as it was previously tried in bleaching wood pulps and give good results (4-6). For this, we readjust the amount of the liquor produced by addition of fresh POM (if required) and reuse it to bleach another amount of bagasse pulp under the same conditions and this were repeated for five times. Table 8 shows the results obtained. From which we can concluded

Table 8. Effect of RPOM reusing

Sample no	POM	Yield	Brightness
51	Ist time	93.9	71.2
52	2nd time	93.8	71.0
53	3rd time	93.4	71.0
54	4th time	93.2	69.6
55	5th time	93.0	69.6

1st step: 0.3 mM/l RPOM, cons. 7%, and pH 2 for 0.5 h at 70°C

2nd step: 4 % H₂O₂, 0.1 % DTPA, and pH 12 at 8% consistency for 2h at 70°C

that the bleaching solution can be used for several times without affecting the pulp brightness, only the yield of the process was slightly affected.

Literature Cited

1. J. P. Casy, *Pulp and Paper Chemistry and Chemical Technology*, 3rd ed. Vol1, Wiley, New York, p.1610 (1980).
2. K. Kratzl; P. K. Claus; A. Hruschka and F. W. Vierhapper, *Cellulose Chem. Technol.* 12:445 (1978).
3. I. A. Weinstak, R. H. Attalla, R. S. Reiner, M. A. Mone, K. E. Hammel, C. J. Houtman, C. L. Hill and H. K. Harrup, *J. Mol. Cat.* 116:59-84 (1997).
4. I. A. Weinstak, R. H. Attalla, R. S. Reiner, C. J. Houtman and C. L. Hill, *Holzforschung* 52 (3):304-310 (1998).
5. D. V. Evtuguin and C. Pascoal Neto, *Holzforschung* 51 (4) :338-342 (1997).
6. D. V. Evtuguin, C. Pascoal Neto and J. D. Pedropa de Jesus, *J. Pulp and Paper Sci.* 24 (4) :133-140 (1998).
7. D. V. Evtuguin, C. Pascoal Neto, V. M. Marques and F. P. Furtado, *Proceeding of International Pulp Bleaching Conf. June 1-5 Helsinki*, pp. 493-498 (1998).
8. R. Patt, T. Jaschinski and H. J. Mielisch, *Stabilisierte und katalysierte peroxid bleich, Wol fur Paperfabrikation* 124 (17):750-755 (1996).
9. L. I. Kuznetsova, E. N. Yurchenko, R. I. Maksimovskaya, N. P. Kirik and K. I. Matveev, *About State of Phosphomolybdovanadate Heteropolyblues in Aqueous Solutions*, *Koord. Khimia* 3:51-58 (1977).
10. K. I. Matveev, N. B. Shitova, Z. P. Pai, V. F. Odiakov, O. K. Akmalova, L. I. Kuznetsova, T. A. Basalaeva, A. B. Rumiantsev and L. N. Shadrin, *Catalyst for liquid phase oxidation of ethylene in acetaldehyde*. SU Patent 421226, 1972, Int. Cl. B 01 J.37/04.
11. D. V. Evtuguin, C. Pascoal Neto, J. Rocha and J. D. Pedropa de Jesus, *Applied Catalysis A: General* 167:123-139 (1998).