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Effect of magnesium-salts on hydrogen peroxide bleaching of non-wood pulps

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Abstract

Transition metal ions present in pulp, cause wasteful decomposition of hydrogen peroxide, a pulp brightener, and thus significantly affect the delignification selectivity of hydrogen peroxide bleaching. The metal ions also affect the brightness and optical properties of pulp. The free radicals generated during the decomposition degrade carbohydrates resulting in lower viscosity and yield.

It is reported in the literature that magnesium sulfate successfully adsorbs transition metal ions and thus decrease their activity. This study dealt with the effect of Mg salts in hydrogen peroxide bleaching of jute caddies pulp. It was observed that prior bleaching treatments like chelation and acid washing of pulp were efficient in removing transition metal ions as indicated by lower consumption of hydrogen peroxide. However EDTA chelation seemed better compared to acid washing. The inclusion of Mg salts improved pulp brightness. The pulp viscosity was the highest with 0.3% Mg addition for both treated kraft and soda-AQ pulps. Considering both pulp viscosity and pulp brightness, it appeared that a 0.3% Mg dose on EDTA chelated pulp, was enough in hydrogen peroxide bleaching of pulps obtained from jute caddies.

Keywords: Jute caddies fibers; Hydrogen peroxide bleaching; Kraft; Magnesium salt; Soda-AQ

Introduction

The conservation of forests and growing environmental awareness has increased research interest in new renewable resources for pulp and paper mills. Bangladesh, a densely populated country, is already in short supply of forest resources in pulp mills, and is depending to a large extent on its non-wood fibre sources. A wide variety of non-wood plants, i.e., bamboo, bagasse, and straw, are used for paper making in many countries of the world. In Bangladesh extensive research on papermaking potential of jute fibre (Akhtaruzzaman, 1998; Akhtaruzzaman *et al.*, 1988; Shafi *et al.*, 1997) has identified the material as a promising pulp fibre source for various end uses.

Jute, a cheap, strong, durable fabric eminently suited for making sacks, bags, carpets, etc. has played a long historical role in the socio-economic development of Bangladesh. There is huge accumulation of unwanted waste during different production stages of the items from jute. This waste is a natural by-product of the industry. It is estimated that the loss in the shaker dust stage is about 6-9% of the total pro-

duction of the industry. This shaker dust is a mixture of short unspinnable fibers and dust with high oil content (jute batching oil). The droppings in the stages like under-card-draw from frames and looms are known as jute caddies, which are about 2-4% of the total production of the jute industry (Roy, 1982). There are about 105 jute mills (including 34 Twine mills) in Bangladesh (Anon, 1988). These mills are producing a large amount of jute caddies which is mainly used as fuel for generating steam in the boilers, and in making cheaper cushions.

According to FAO there is a considerable scope for utilization of the waste generated during processing of jute, kenaf, coir and sisal (Anon, 1994). There is a high demand of packaging paper in the country. Jute caddies, a by-product of jute fibre, is already being used for the manufacture of the mid layer of a 3 ply duplex board. This potential fibre source could also be used for the manufacture of the top and bottom layers. The pulp produced from this fibre source is a bit darker in colour due to the presence of dirt and oily substances.

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The colour of pulp could be improved with the use of hydrogen peroxide, a pulp brightener.

Previously, considerable research with hydrogen peroxide, but almost all of them dealt with either hardwood or softwood pulps (Loureiro, 2012; Lipierre *et al.*, 2000; Lizi *et al.*, 2011). There is not much study with non-wood fibres, especially jute caddies. It is well established that transition metals cause wasteful decomposition of hydrogen peroxide (Wojciak, 2006; Lizi *et al.*, 2011). The free radicals generated during the decomposition degrade carbohydrates resulting in lower viscosity and yield. It is reported that sodium silicate and magnesium sulphate combination adsorbs transition metals and decrease their activity (Bose *et al.*, 1998; Lipierre *et al.*, 1995; Potucek and Milichovsky, 2000). It is, therefore, imperative to study the effect of magnesium salts on deactivation of metal ions during peroxide bleaching of non-wood pulps and to optimize the Mg doses for maximum brightness and pulp viscosity.

Materials and methods

Pulping experiments

The air-dried (85.5% dry moisture content) jute caddies fibers equivalent to 250 g oven dried was cooked in small stainless steel autoclaves (2L) heated in a temperature controlled air bath. Analytical grades of NaOH, Na₂S, and AQ were used. The following pulping parameters were maintained:

- Liquor to fiber ratio, 7:1
- Rise of temperature from room temperature to 80°C in 30 min and from 80 to 170°C in 60 min;
- Cooking at maximum temperature (170°C)
- Active alkali, 14 - 18% as NaOH in kraft and soda -AQ;
- A total H-factor of 2000 was used for pulping.

Different stages of delignification were achieved by varying the amount of effective alkali (14%, 16%, 18%) both in kraft and soda-AQ pulping. The amount of AQ used in soda-AQ cooks were 0.1% calculated on oven dry material. The cooked material was washed with fresh water and then disintegrated. Screening was done on a flat vibratory screen with 0.38 mm slot. The screened pulp was pressed to remove excess water and stored in a refrigerator in polythene bags.

Pulp analysis

The yield and kappa number of pulp samples were determined (TAPPI Test Methods T236 cm-85). The percentage of lignin content in pulp was determined by multiplying the kappa number of pulp by a factor 0.15 (Toven *et al.*, 2006)

Preparation of pulps for hydrogen peroxide bleaching

Two types of treatments likely acid treatment and chelation were given to reduce the free metal ions contents on the pulp prior hydrogen peroxide bleaching.

a. Acid treatment of pulp

30 g of pulp on OD basis was taken in a stainless steel container and a sufficient amount of water was added so that the disintegrator moved freely in the slurry. The pH was then adjusted to 2.0 by adding H₂SO₄, to the continuously stirred pulp slurry. The slurry was stirred for an hour. Thereafter, the water was drained out and the pulp was washed thoroughly with distilled water.

b. Chelation of pulp

30 g of pulp on OD basis was taken in a stainless steel container and a certain amount of water was added so that the disintegrator moves freely in the slurry. The pH was then adjusted to 4.3 with the addition of H₂SO₄ solution. Then 0.5% EDTA, based on OD pulp was added to the slurry maintaining the temperature at 60°C and stirred continuously for an hour. At the end of an hour the water was drained out and the pulp was washed thoroughly with fresh distilled water.

Hydrogen peroxide bleaching

The acid treated and the chelated pulps were taken in a poly bag. Then additional amount of water was added to have the slurry with 10% consistency. The pH of the slurry was adjusted to 11.0 with addition of NaOH solution. The different doses of MgSO₄·7H₂O followed by 2% H₂O₂ solution, (all based on OD pulp) were added to the pulp which was then mixed thoroughly. The poly bag was then sealed and placed in a water bath maintained at 80° C for 2 hours with occasionally mixing. At the end of the reaction, the poly bags were taken out. The liquor was titrated to measure the residual H₂O₂. A portion of the liquor was used to measure the end pH. Thereafter, the water was drained out and the pulp was washed thoroughly with distilled water. The viscosity

and brightness of pulps were determined according to Tappi test methods T230 om-89 and T452 om-92 respectively.

Estimation of residual H₂O₂

20 mL of 4N sulfuric acid was taken in a 250 mL conical flask and 25 mL 10% KI solution was added to it. 5 mL of the spent liquor sample was added and titrated against 0.1 N Na₂S₂O₃ solution using starch as the indicator.

Results and discussion

Pulp yield

Pulping of jute caddies was done at different total alkali charge to obtain various levels of delignification. The pulping results are shown in Table I. It was found that delignification increased with the increase of alkali charge. The delignification was slightly better with soda-AQ compared to kraft at low alkali dose. The pulp yield was even higher with soda-AQ.

Table I. Pulp yield and lignin content of various pulps* #

Pulping processes	Active Alkali (as NaOH) %	AQ %	Kappa No.	Pulp yield %	Lignin content of pulp %	Delignification %
kraft	14.0	0.0	16.9	50.8	2.54	90.6
	16.0	0.0	13.0	50.0	1.95	92.9
	18.0	0.0	11.8	49.7	1.77	93.6
soda-AQ	14.0	0.1	13.7	57.8	2.06	91.3
	16.0	0.1	11.9	55.0	1.78	92.8
	18.0	0.1	11.3	53.9	1.70	93.3

* Lignin content of the original material = 13.7%

Carbohydrate content of the original material = 81.3%

The kappa number of the kraft pulps decreased sharply with the increase of active alkali. However, in case of soda-AQ process the kappa number changes were not that big. This might be due to redeposition of dissolved lignin on residual lignin (Francis *et al.*, 2005). The situation was quite opposite in case of pulp yield. In soda-AQ process the drop in pulp yield with the increase of active alkali was higher than that of kraft process. Various researchers reported the same observation in the past (Shafi *et al.*, 1994; Akhtaruzzaman and Shafi, 1995).

Delignification selectivity

Selectivity is defined as a ratio between the amounts of lignin removed over the amount of carbohydrate removed.

The delignification results are given in Table II. The table shows that the amount of lignin removed did not vary either for the change in active alkali or for the change in pulping processes. However, the amount of carbohydrate removed was lower in case of soda-AQ process compared to kraft process. This resulted in higher selectivity ratio for soda-AQ process compared to kraft. The selectivity values remained the same for kraft process. However, it changed in soda-AQ pulping. It was the highest with 14% active alkali. The result was obvious as AQ acted as a nucleophile and thus, enhanced the rate of delignification. This increased delignification reduced the carbohydrate loss that resulted in higher pulp yield.

Hydrogen peroxide bleaching

The pulp was bleached using hydrogen peroxide, as a brightener, at 80°C for two hours. The pulp consistency was 10%. The chemical doses were 0.3, 0.5 and 1.0% of MgSO₄·7H₂O and 2% of H₂O₂, all calculated on oven dry pulp. The results,

for both treated and untreated pulps, were shown in Table III and IV and Fig. 1 and 2.

The bleached pulp yield was the highest with the untreated kraft compared to both chelated and acid washed kraft pulps (Table III and Fig. 1). The bleached pulp yield increased with the increase of Mg doses with the exception of acid washed pulp where the yield decreased by 1.3 percent points. This could be due to the removed of Mg²⁺ during acid treatment and the amount of Mg²⁺ added after words was not enough. The pulp viscosity was the highest with 0.3% Mg charge. Wojciak (2002) reported similar results. The consumption of peroxide was the highest with untreated pulp as it contained higher percentages of metal ions compared to both

Table II. Selectivity of pulping processes

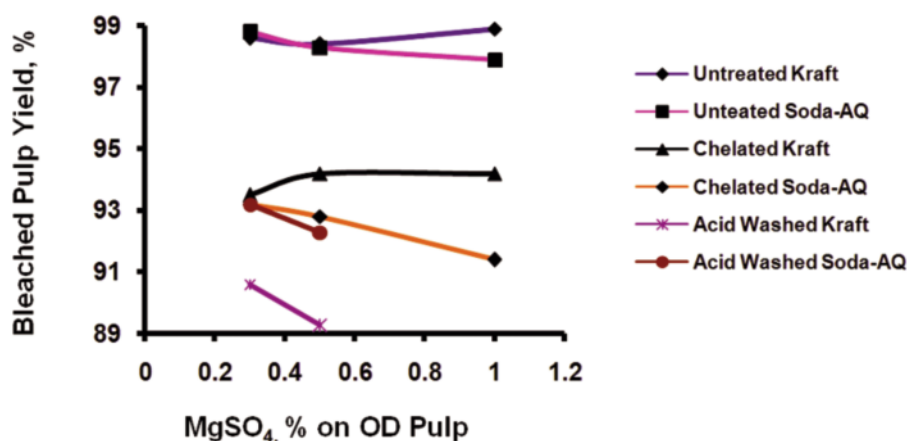
Pulping processes	Active alkali (as NaOH) %	AQ (%)	Kappa no. (%)	Pulp yield (%)	Lignin removed (original raw material basis (g))	Carbohydrate removed (original raw material basis (g))	Selectivity ratio
kraft	14.0	0.0	16.9	50.8	31.0	79.5	0.39
	16.0	0.0	13.0	50.0	31.8	80.7	0.39
	18.0	0.0	11.8	49.7	32.1	81.2	0.39
soda-AQ	14.0	0.1	13.7	57.8	31.3	61.7	0.51
	16.0	0.1	11.9	55.0	31.8	68.2	0.47
	18.0	0.1	11.3	53.9	32.0	75.5	0.42

* g lignin removed/g carbohydrate removed.

Table III. Effect of magnesium sulfate application on hydrogen peroxide bleaching of kraft pulp

	Untreated kraft			Chelated kraft			Acid washed kraft	
MgSO ₄ ·7H ₂ O % on pulp	0.3	0.5	1.0	0.3	0.5	1.0	0.3	0.5
Yield, %	98.6	98.4	98.9	93.5	94.2	94.2	90.6	89.3
Kappa No	12.8	13.0	13.4	11.0	10.0	10.0	11.0	10.0
Viscosity, cp	10.9	7.5	8.3	8.6	6.3	6.5	8.4	7.2
Elrepho Brightness, %	34.3	35.5	33.7	38.4	39.6	41.0	37.4	41.7
Consumption H ₂ O ₂ , %	95.6	97.8	97.8	50.0	56.1	60.5	50.0	47.0
End pH	8.8	9.0	8.8	11.3	10.9	11.3	8.2	8.5

(Unbleached pulp kappa no- 16.9, Elrepho Brightness- 28.5%, kraft pulp viscosity- 17.3)

**Fig. 1. Effect of Mg dose on bleached pulp yield**

chelated and acid washed pulps. There was severe viscosity losses in all the cases. After bleaching untreated pulp brightness was lower compared to the treated pulps.

It is also observed that end pHs were higher with the addition of magnesium salts. Bose *et al.* (1998) reported similar observations. The results suggested that in order to get better

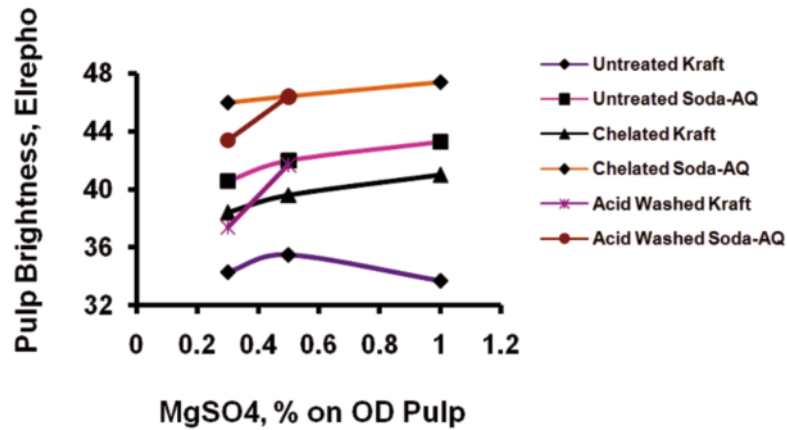
pulp yield with acceptable viscosity MgSO₄·7H₂O dose of 0.3-0.5% (on OD pulp) is beneficial.

In case of soda-AQ pulp the yield and viscosity decreased gradually (Table IV and Fig. 1) with the increase of Mg charge. The pulp viscosity was the highest with 0.3% Mg charge. In all the cases, 0.3% Mg dose showed the best performance.

Table IV. Effect of magnesium sulfate application on hydrogen peroxide bleaching of soda-AQ pulp

	Untreated soda-AQ			Chelated soda-AQ			Acid washed soda- AQ	
MgSO ₄ .7H ₂ O								
% on pulp	0.3	0.5	1.0	0.3	0.5	1.0	0.3	0.5
Yield, %	98.8	98.3	97.9	96.6	92.8	91.4	93.2	92.3
Kappa No	10.6	10.3	10.0	9.4	9.0	9.0	7.8	7.6
Viscosity, cp	11.0	6.2	5.9	10.3	9.2	8.1	6.1	5.0
Elrepho Brightness, %	40.6	43.3	42.0	46.0	46.4	47.4	43.4	46.4
Consumption H ₂ O ₂ , %	98.0	98.0	98.0	87.0	85.0	82.0	47.0	41.0
End pH	9.1	10.3	10.6	11.5	11.3	11.5	8.3	9.0

(Unbleached pulp kappa No 13.7, Elrepho Brightness-31.6%, soda-AQ pulp viscosity- 11.5)

**Fig. 2. Effect of Mg dose on bleached pulp brightness**

The consumption of peroxide was the highest with untreated pulp as it contained higher percentages of metal ions compared to both chelated and acid washed pulps. Presence of higher amount of metal ions resulted in fast decomposition of hydrogen peroxide. On bleaching, untreated pulp brightness was lower compared to the treated pulps (Fig. 2). There was viscosity loss in all the cases (Table III and IV).

Conclusion

The selectivity ratio in kraft and soda-AQ pulp from jute caddies was highest with 14% soda-AQ pulping. The reason was that the amount of lignin removed was almost the same with all alkali doses, but the amount of carbohydrate removed was the lowest with 14% soda-AQ pulping. The result is obvious as AQ acted as a nucleophile and thus, enhanced the rate of delignification. This increased delignification and reduced the carbohydrate loss that resulted in higher delignification selectivity.

Hydrogen peroxide bleaching of kraft and soda-AQ pulps showed that both chelation and acid-treatment of pulps were efficient in removing transition metal ions. However chelation was better in consideration of the pulp viscosity and pulp brightness. The inclusion of Mg salts improved pulp brightness. The brightness was higher with treated pulps. Among the three doses of Mg addition, the pulp viscosity was highest with 0.3% Mg both with kraft and soda-AQ pulps. Considering both pulp viscosity and pulp brightness, it appeared that a 0.3% Mg dose on EDTA chelated OD pulp, was enough for hydrogen peroxide bleaching of pulps obtained from jute caddies.

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