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MINI REVIEW

Review on Total Chlorine Free Bleaching Sequences of Wheat Straw Pulp

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Wheat straw is one of the important non-wood natural fibers being used by many pulp and paper mills around the globe to make the quality paper. Pulp and paper making offers various challenges ranging from raw material to finish products. Besides customers' demand, satisfying environmental regulatory is another obligation for mill owners since last few decades. To look for environmentally benign processes without compromising pulp fibre's physical and chemical properties is today's practical consideration. In this review, only those total chlorine free bleaching sequences for wheat straw pulp developed during 1994 to 2009 are presented which yielded brightness more than 80 % ISO/SBD.

Key Words: Wheat straw, Total chlorine free bleaching, Pulp and paper industry, Cellulose, Delignification.

INTRODUCTION

Wheat straw is non-wood agricultural waste which is serving as an excellent fiberous material to recycle into quality paper in many parts of the globe.

The two major constituents of the wheat straw are the celluloses and lignin (Table-1). The chemical composition of which vary according to the wheat straw genetics, geographic conditions[1] and/or pulping/cooking condition to pulp straw. Other constituents are the silica, ashes and extractive.

TABLE-1
CELLULOSES AND LIGNIN CONTENTS
OF WHEAT STRAW PULP

Country of origin of wheat straw	Celluloses			Lignin
	α-Cellulose	Holocellulose	Hemicellulose	
Pakistan[2]	33.7	58.5	25.0	16-17
India[3]	–	–	28.9	23.0
USA[4]	39.9	–	28.2	16.7
Dennmark[4]	41.6	72.9	31.3	20.5

The main purpose of bleaching pulp is to increase its brightness level to obtain white paper. Conjugated double bonds present in the structure of residual lignin imparts colour to the pulp. So the bleaching process is either to stabilize or solubilize to wash away the lignin contents while cellulose contents remains intact in the pulp fiber. Thus bleaching can be done in two different ways[5]: (i) Removing the residual lignin of chemical pulps (delignification). (ii) Lignin-preserving or retaining bleaching: in which chromophoric groups of mechanical pulp are converted or stabilized without loss of substance.

Delignifying and/or bleaching chemicals can be classified into three groups[6] according to the particular groups they prefer to react with.

Group I: The pulping and /or bleaching chemicals of group I react with all aromatic lignin units, with phenolic groups and their double bond (Fig. 1) *e.g.*, chlorine, ozone, peroxy acids, *etc*.

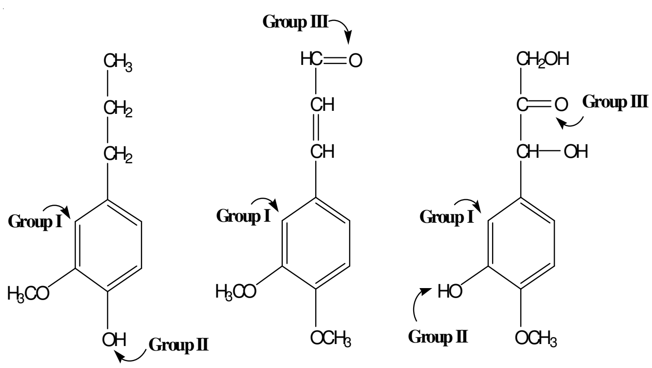

Fig. 1. Possible attacking site of group I, group II and group III bleaching chemicals[6] at three typical monomers of lignin molecule

Group II: The pulping and/or bleaching chemicals of group II reacts mainly with free phenolic hydroxyl group (Fig. 1) *e.g.*, oxygen, chlorine dioxide.

Group III: The pulping and/or bleaching chemicals of group III reacts mainly with certain functional conditions groups in lignin, *e.g.*, carbonyl group (Fig. 1) *e.g.*, hydrogen peroxide in alkaline media.

Total chlorine free bleaching approaches for wheat straw pulp: Hypochlorite and chlorine are being used for bleaching by pulp and paper industries for many years. These chemicals proved to be highly effective to delignify and/or brighten various pulp varieties. But these chlorine-containing chemicals once released into environment could be potent carcinogenic. Search of environmentally benign bleaching processes for pulp industry has investigated new oxidative, reductive and/or enzymatic chemicals and hence, elemental chlorine free (ECF)[7-10] and totally chlorine free (TCF)[11,12] technologies have evolved. Application of elemental chlorine free and total chlorine agents on pulp posed another challenge and research shows that not a single elemental chlorine free or total chlorine free agent is effective to fully bleach the pulp without compromising pulp properties *i.e.*, brightness reversion, loss in pulp strength, cellulose degradation, *etc*. This difficulty was overcome by using multi-stage sequence of bleaching chemicals. Another point is pulp composition and type varies according to genetic make-up, growing conditions, geographical factors and pulping conditions itself used to cook the raw material. So the bleaching sequences developed for one type of pulp is not equally effective for other type. Thus there is always a need for particular bleaching sequence for a particular pulp type feasible for a particular region and/or mill type.

The following discussions present some of the total chlorine free bleaching sequences reported in literature wherein the brightness gain is greater than 80 % ISO/SBD only.

Pekarovicova *et al.*[13], prepared organocell organosolv straw pulp and developed six different bleaching sequences to bleach it (Table-2). Their work becomes worthful due to the introduction of an enzymatic stage that was included as intermediate to increase the effectiveness of final bleaching stage. They found ligninase and chelation treatment both to be effective in increasing the bleaching capabilities of peroxide.

Chen *et al.*[14] reported another total chlorine free agent potassium permanganate as intermediate bleaching stage between oxygen and peroxide. They worked out OMnP bleaching sequence for soda-AQ pulp. Like Pekarovicova's[13], their work also illustrate that chelation prior to peroxide treatment is helpful to increase brightness to 80 % ISO.

Another efficient study to achieve greater than 80 % SBD brightness was reported in the year 2000. Six total chlorine free bleaching sequences were presented for two types of soda-AQ wheat straw pulp cooked at two different kappa numbers[15]. For improving bleachability and brightness of chemo-mechanical wheat straw pulp Hong *et al.*[16], adopts the method of enzymatic pre-treatment using xylanase prior to bleaching. The increased pulp brightness even at 50 % reduced dosage of hydrogen peroxide proved that xylanase pre-treatment assisted to improve the bleachability of straw pulp.

TABLE-2
TOTAL CHLORINE FREE (TCF) BLEACHING SEQUENCES REPORTED IN LITERATURE

Inventor	Pulp type	Bleaching sequences
Pekarovicova *et al.*[13]	Organocell organosolv straw pulp	O-L-P O-X-P O-P E_{OP}-X-P E_{OP}-L-P E_{OP}-P
Chen *et al.*[14]	Soda-AQ wheat straw pulp	OMnP or OMnQP
Qiao *et al.*[15]	Soda-AQ wheat straw pulp	EApPht ApPht Ap(PO) (Ap-Q)PO (XQ)Pht
Feng *et al.*[16]	Wheat straw chemo-mechanical pulp	XPP
Han *et al.*[17]	Wheat straw pulp pre-treated in laccase-mediator enzyme system	OEPP QPP QPaP
Roncero *et al.*[18]	Wheat straw pulp	XOAZRP
Wang *et al.*[19]	Low kappa number kraft wheat straw pulp	ZpP ZpY ZpEPY ZpEYP
Xu *et al.*[20]	Auto-catalyzed ethanol wheat straw pulp	OOpZP ZOOpP
Cao *et al.*[21]	Low kappa number kraft wheat straw pulp	AQ(PN)P QZEYP
Latibari *et al.*[22]	Soda-AQ wheat straw pulp	OQ(OP) or OQ(OP)P
Tong *et al.*[23]	Wheat straw kraft pulp	AZEYP
Hedjazi *et al.*[24]	Wheat straw soda pulp	O/Q/OP
Niu *et al.*[25]	Soda-AQ wheat straw pulp	(OpQPo)
Hedjazi *et al.*[26]	AS/AQ wheat straw pulp	OQ(OP) or OQ(OP)P

A = Acid treatment, E = Alkaline extraction, L = Ligninase pre-bleaching, Mn = Potassium permanganate, O = Oxygen delignification, P = Hydrogen peroxide, Q = Chelation (with EDTA), R = Reductive bleaching, X = Enzymatic pre-treatment (*e.g.*, xylanase), Y = Bleaching with hydroso/reductive chemical bleaching, Z = Ozone charge, Ap = Pre-treatment with acidic hydrogen peroxide, (PO) = Bleaching with hydrogen peroxide at room temp. under normal atmosphere, Pht = Bleaching with hydrogen peroxide at room temperature, Zp = Ozone charge in atmosphere of hydrogen peroxide.

Han *et al.*[17], worked out enzymatic applications on increased bleachability of straw pulp. They devised a bio-bleaching laccase-mediator enzyme system followed by peroxide treatment (Table-2). Use of laccase-mediator system not only reduces the consumption of bleaching agents but can also help to reduce the load of effluents on environment with a negligible loss of pulp strength. Roncero and co-workers[18] defined the application of enzyme and ozone in a multistage XOAZRP sequence to fully bleach the wheat straw pulp.

Wang *et al.*, attempted to develop four different bleaching sequences[19]. Their results successfully suggested that the whiteness yield is greater than 80 % SBD for all the developed total chlorine free sequences with kraft wheat straw pulp. They coupled hydrogen peroxide atmosphere with ozone bleaching and achieved 83 % SBD whiteness in a short sequence of ZpP. Inclusion of extraction (E) and reductive (Y) bleaching stages shoot-up the whiteness to > 88 % SBD (Table-2).

Auto-catalyzed ethanol wheat straw pulp was examined for total chlorine free bleaching to yield 80 % SBD by Xu *et al*.[20] and they remained successful in developing two bleaching sequences without any loss of strength properties (Table-2).

Cao *et al*.[21] cooked wheat straw kraft pulp at low lignin contents for total chlorine free bleaching. It was found that AQ(PN)P and QZEYP bleaching sequences are successful in achieving brightness greater than 80 % SBD. Their research findings suggested that cellulose viscosity of bleached pulp and its brightness stability is better than chlorinated bleached pulp using CEH sequence.

One of the other investigations regarding total chlorine free bleaching was for soda-AQ wheat straw pulp. Eco-friendly OQ(OP) or OQ(OP)P bleaching sequences designed yielded the pulp fiber in an acceptable strength with 80+ % ISO brightness[19].

Tong *et al*.[23] highlighted the significance of ozone in AZEYP sequence for wheat straw kraft pulp with a brightness gain of 86.9 % SBD. This sequence combination of oxidative-reductive-oxidative bleaching steps was found to be selective in terms of lignin solubilisation without cellulose degradation, which depicts the chemistry behind true bleaching technology. Hedjazi and co-workers remained successful in yielding greater than 80 % ISO brightness in O/Q/OP sequence[24] (Table-2) using wheat straw soda cooked pulp. Hydrogen peroxide treatment in alkaline media was optimized with different chemical additives. The addition of only 2.0 % sodium silicate was studied to be quite effective both to reduce the peroxide bleach consumption and to achieve the targeted brightness of 80 % ISO.

Bleaching sequence OpQPo was reported by Niu *et al*.[25] for soda-AQ wheat straw pulp. Oxygen treatment coupled with optimized peroxide dosage boost the delignification process in oxygenation stage of pulp. Further chelation and peroxide treatment yielded total chlorine free bleached pulp brightness of 80.2 % ISO.

More recently in 2009[26], sequences OQ(OP) or OQ(OP)P developed previously by similar research group for soda-AQ wheat straw pulp were considered for AS/AQ pulp. Bleaching experiments turned out to be in favour of producing greater yield, increased brightness and high tear strength for AS/AQ pulp fiber as compared to Soda-AQ pulp fiber.

Although these bleaching sequences for both type of pulp are effective to gain 80 % ISO brightness but other pulp properties of commercial importance were sacrificed. This also proves the fact that one sequence developed for particular pulp type may not be fully effective to achieve all the desired pulp properties of industrial significance.

Conclusion

The chemical composition of wheat straw pulp and its pulping conditions may vary according to location and its genetic makeup. It is quite obvious that different pulp types may not behave similarly to a particular bleach sequence. Thus literature reveals quite a varying type of totally chlorine free bleaching sequences for pulp fibers originated and cooked at varied conditions which offers much smaller environmental footprints than conventional bleaching methodologies.

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