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Bleaching of Agro Raw Material Pulps by Chlorine free Bleaching Sequence: The "Brand Green Bleaching" Concept for Indian Agro Pulp and Paper Industry

Abstract: *The Indian Pulp and paper industry has travelled a long path and has come across with a number of issues related to the production of bleached pulp maintaining the quality of pulp while addressing the environment challenges adequately. Starting with the conventional CEpHH bleaching to now O-DEpD sequence the 50 years of span is remarkable in many ways.*

The Indian agro based raw materials are the biggest example of converting the waste into wealth. Overall process of converting agro residual raw materials into quality product has many challenges which has been very effectively addressed by Indian paper industry. There is, however, great potential for both improving efficiency and moving towards sustainability in this industrial sector.

Being low in lignin content, the agro residual raw materials are low in cooking and bleaching chemical consumption. The post digester kappa number of agro residual raw material which ranges from 10-12 can be easily bleached without chlorinated oxidative chemicals i.e. chlorine dioxide, chlorine, hypo, by replacing these chemicals with environment friendly oxygen, hydrogen peroxide and ozone. Combination of these three green oxidising bleaching chemicals has been tries in short bleaching sequences , the TCF short sequence bleaching is termed as Green Bleaching sequence. The concept of brand green bleaching and its prospects of adoption by Indian agro based Industry has been discussed in the present communication. This paper details the state of current research and technological development in the field of ecologically responsible bleached pulp manufacturing from agro residues like bagasse and wheat straw.


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Introduction:

The Indian Agro Pulp and Paper Industry which covers a substantial share of agroresidue based production of virgin pulp , itself holds brand of tree free manufacturing. Approximately 10% of the total pulp production is sourced by agro residual raw materials.

Pulp and paper Industry is considered one among the highest effluent generating industries. The effluent generated in bleach plant carry maximum load, specially the load of CEop or DEop stage effluent. The bleaching of unbleached pulp is always considered as the biggest area of concern with reference to total production of paper under various stages. The conventionally used bleaching sequence O-DEpD is not only costly but also not a clean process. The disposal of highly concentrated sulphuric acid, high cost of chemical, maintenance and storage of chlorine dioxide plant etc require lot of efforts for a consistent operation of pulp mill. The pulp bleaching technology since past is mainly based on chlorinated compounds. Started with chlorine, gas, calciumhypochlorite, and chlorine dioxide all three oxidents are considered as environment hazards because of carcinogenic byproducts generated during the reaction of these chemicals with lignin.In the beginning years the focus was economy and chlorine being the cheapest chemical was used without any concern towards effluent load of liquid discharge.

Agroresidual raw materials contributes ~10-12% of total pulp production. The agro residues like wheat straw and bagasse are low in lignin and at present pulp bleaching to 82-85% is produced by CEpHH or DEpD bleaching sequence.(1-3)

Green chemistry is the design of chemical products and processes that reduce or eliminate

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the use or generation of hazardous materials. The principles of benign design, selective catalysis, energy efficiency, and pollution prevention are all incorporated into the design of this greener bleaching agent. (2-4). The three green oxidation agent which has developed technology and efficiently used in pulp and paper industry are oxygen, hydrogen peroxide and ozone.Agro residual raw materials like bagasse and wheat straw are the commonly used raw materials in medium or large paper mills. Many pulp and paper mills are using both raw materials where pulp of two different stream are mixed before the bleaching stage. The existing role of the green oxidants is as explored here:

Oxygen:

Oxygen is treated to pulp in gaseous form. It is manufactured at the mill site or supplied in cylinder too.

Oxygen Treatment in Pre bleaching stage:

Oxygen gas is a very well-established green bleaching agent, used in pulp and paper industry for more then last 30 years. The post digester oxygen pre-treatment help in reduction of bleach chemical requirement. The post digester oxygen treatment reduces unbleached pulp kappa number by ~ 50%. The technology was earlier single stage which output into reduction of unbleached pulp kappa number by 35-40%. After introduction of two stage ODL technology the unbleached pulp kappa number reduction crossed to 50%. This has further reduces the bleach chemical demand by 50% and so the generation of load of bleach plant effluent. The oxygen applied at this stage is 2.5-3% at pressure of 5-6 kg , pH 12-13 maintaining temperature 90-95oC at medium consistency.

Extraction stage oxygen fortification:

Oxygen on pulp is also applied during alkaline extraction stage after first stage chlorine dioxide treatment. The oxygen pressure of 2.5 to 3 is maintained during EO stage. This helps in reduction of extraction stage kappa number.

Hydrogen Peroxide:

Hydrogen peroxide (H2O2) is a greener alternative to chlorine (Cl2), chlorine dioxide (ClO2) and sodium hypochlorite (NaOCl)that are traditionally used for bleaching of fabric or pulp.

Ep stage

During bleaching of pulp hydrogen peroxide is applied in many different ways. During alkaline extraction hydrogen peroxide is applied along with oxygen and enhance the effectivity of extraction stage by lowering the post Eop stage kappa number and increasing the brightness. Another mode is as sole bleaching agent after DEpD or older CEpHP bleaching sequence.

PO Stage:

This stage is known as pressurized peroxide stage. Themost effective use of peroxide is along with oxygen under mild pressure and high temperature of around 120-130oC, results into significant gain in brightness and reduction of PC number. The effluent properties are also improved by applying PO stage. This is an essential stage for TCF bleaching technology. A metal extraction stage either chelation or acid pretreatment is essential before PO stage.

Ozone Stage:

The ozone bleaching is the stage which can be applied in many different ways either as a single stage or in combination with chlorine dioxide. After the introduction of ozone bleaching technology it was considered as a replacement of first stage chlorination or dioxide stage. The efficacy of ozone is depends on the initial kappa number. Though ozone has high oxidation potential and 4.43 times stronger then chlorine its potential for particle bleaching is less effective than chlorine dioxide. That is the reason that light ECF sequences ZDEpD are becoming the choice of many Pulp and paper mills.(4-5)

Ozone as a sole bleaching stage can be used as first stage bleaching and also in the final stage. The ozone stage followed by pressurized peroxide stage is capable to bleach the agroresidue pulp to brightness similar to DEpD, up to 84-85%ISO.

Role of Ozone in Bleaching Of Pulp by Green Bleaching Sequences:

For decades chlorine and chlorinated bleaching chemicals based technologies has been the option before pulp and paper industries. The ozone as bleach chemical came in existence during decade 1990 and pulp and paper mills has installed ozone in the bleaching sequence. Though oxygen and and hydrogen peroxide are also potential oxidents but their impacts and efficiency is limited. In order to replace the chlorine and chlorine dioxide from the system it was necessary to replace these chemicals with very fast and effective oxidative agent which is ozone. Since the first commercial ozone bleaching installation was started, enhancements to the ozone bleaching process have been conducted jointly by laboratories on the chemical side and by both the industry and equipment suppliers on the operational and technical sides. With developed and new technology It is now possible to adjust very precisely the ozone dosage, the pH, the retention time and the temperature in the Z-stage. These improvements now fully guarantee the pulp quality after ozone bleaching. (3-5)

The efficacy of ozone bleaching is much better when pulp kappa number is low. The efficacy is more in case of bleach plant entering pulp has kappa number below 10, which is attained by the hardwood after two stage ODL treatment technology. Yet many pulp producers still believe that the quality of ozone bleached pulps, especially softwood ones, is lower than traditional ECF bleached pulp quality. Since most of the mills using ozone are producing hardwood pulps, some people even believe that this evidence sustains the alleged lower strength of softwood ozone bleached pulps(4-5)

On the other hand, numerous studies carried out during the 90's and in the more recent years have shown that the selectivity of ozone against lignin is very high. It is now established that the reaction rate of ozone with lignin is 1,000 times higher than the rate of cellulose oxidation or depolymerisation by ozone .This means that as long as there is some remaining lignin a well-operated ozone bleaching process does not impact the cellulose more than any other bleaching stage.(4-5)

Ozone Generation

Ozone generation is a pure on site technology requiring only energy and oxygen (usually also produced on site from a VPSA plant). Ozone (O3) is produced from oxygen (O2) in an electrical field at a concentration of 12% by weight.(3)

Modern ozone generators are 50% more efficient than the ones used in the first ozone pulp bleaching applications. Compact and modular ozone plants were specially designed for the pulp and paper industry and they are able to produce up to 250 kg O3/h (6 tons per day).

Agroresidual Pulp Bleaching with Ozone:

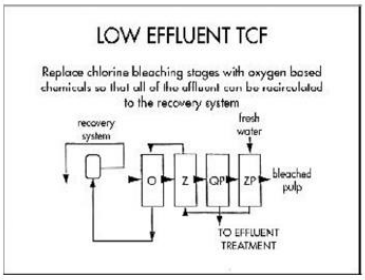
The unbleached pulp of wheat straw and bagasse has separate technology for pulping then the hardwoods. As proven by the comparative statement on efficacy of ozone bleaching on hardwood pulp is better than softwood pulp. The

outcome of the ozone bleaching technology is effective for hardwood pulp has a valid reason as the unbleached pulp kappa number of hardwood pulp reduced to 8-9 after oxygen pre-treatment. As a number of studies carried out by CPPRI on ozone pretreatment also resulted that pulp kappa number for ozone treatment has better efficacy if it is below 10. Agroresidues pulp post ODL kappa number is 7-8 which help in better efficacy of ozone treatment in agroresidues.

TCF Bleaching and Effluent Treatment

In general, treatment of effluent reduces toxicity in the case of all effluents, although toxicity of the effluent can itself influence the effectiveness of biological treatment processes. There are indications that TCF effluents may be simpler to treat. For example, reduction of AOX and chlorate, which are only generated in ECF, but not TCF,bleaching, requires anaerobic conditions, while COD and BOD,produced in both ECF and TCF mills, are most effectively removed in aerobic conditions.Because TCF mills do not produce AOX and chlorate, the treatment systems needed are, therefore, likely to be less complex. A recent study, which contradicts assertions that ECF and TCF effluents have a similar toxicity, demonstrates that Effluents are more toxic to methanogenic organisms than TCF effluents. A greater potential for anaerobic biodegradation was also demonstrated for TCF effluent.

Ozone based TCF Bleaching Sequence and ZLD Of Bleach plant(3)



Experimental:

The experiments on short bleaching sequences with utilizing the oxygen, ozone and hydrogen peroxide. The bagasse and wheat straw pulp samples were bleached following two stage OP-Z sequences. Similar to hardwoods, agro residues also are high in hexenuronic acid. A strong acid treatment help in reduction in hexenuronic acid and also leaches out metal ions. This help greatly in II stage of oxygen treatment. The II stage oxygen pre-treatment is intensifies by addition of additive oxidants hydrogen peroxide. The combination of oxygen and hydrogen peroxide and treatment under pressurized conditions results in higher gain in reduction of kappa number. (Table-1, 2)

The experiments of pressurized peroxide were carried out in oxygen reactor and ozone treatment were carried out in quantum mixture under the optimized conditions as shown below:

Parameters	Pressurized peroxide stage	Ozone stage
Consistency,%	10	8
Temp,oC	120	Ambient
pH	12-13	2-3
Time, min	90	30

Table 1:Unbleached pulp characteristics of wheat straw and bagasse

S.No.	Parameter	Unit	Bagasse pulp	Wheat straw pulp
1.	Chemical applied, AA as Na_2O	%	15	13
2.	Kappa number		11.1	11.6
3.	Viscosity	cm^3/gm	1056	900
4.	Brightness	% (ISO)	31.7	32.0
5.	Screened yield	%	54.3	50.0

Pulping Conditions: Ambient to 100°C - 30 min, 100°C to 160°C - 90 min, At 160°C - 90 min, Bath ratio -1:4.5 in case bagasse, 1:5 in case wheat straw

Table 2:Effect on pulp characteristics after acid treatment

S.No.	Parameter	Unit	Bagasse pulp	Wheat straw pulp
1.	Kappa number		10.2	9.8
2.	Viscosity	cm^3/gm	1005	845
3.	Brightness	% (ISO)	33.7	34.0
4.	Kappa reduction	%	8.1	15.5
5.	Viscosity reduction	%	4.8	6.1

Pulping Conditions: H_2SO_4 applied, 0.5%, Consistency 10%, temp.80oC, Time 60 min

Table 3: Pressurized peroxide (OP) of Acid treated Pulp of wheat Straw and Bagasse

S.No.	Parameter	Unit	Bagasse pulp	Wheat straw pulp
1.	Peroxide charge	%	2	2
2.	Oxygen Pressure	kg	5	5\
3.	Kappa No.		3.0	3.5
4.	Pulp Brightness	% (ISO)	72	61
5.	Pulp Viscosity	cm^3/gm	967	790
6.	Kappa Reduction	%	70.6	58.4
7.	Viscosity Reduction	%	3.78	6.5
8.	Improvement in brightness	%	36.1	25.6

Table4: Result of final Z- stage bleaching of bagasse, wheat straw pulp

S.No.	Parameter	Unit	Bagasse pulp	Wheat straw pulp
1.	Ozone added	%	0.5	0.5
2.	Consistency	%	15	15
3.	Pulp Brightness	% (ISO)	84	82.5
4.	Pulp Viscosity	cm^3/gm	734	632

Conclusions:

- The kraft pulping of bagasse and wheat straw with 15 and 13% alkali(as Na2O) produced unbleached pulp of kappa number 11 of agroresidual raw materials like bagasse and wheat straw is produced with kappa number.
- The short TCF bleaching sequence following OP-Z was applied for bleaching of unbleached pulp.
- Before bleaching acid treatment of unbleached pulp was given for removal of metal ions and hexenuronic acid, which results in better and effective treatment of hydrogen peroxide.
- The pressurized peroxide treatment was carried out under optimized conditions which results in brightness gain of pulp 72 and 61%ISO for bagasse and wheat straw respectively. (Table - 3)
- The final ozone stage was performed after washing of the pulp and OP stage pulp has been bleached to +82 %ISO brightness. (Table - 4)
- The bleaching sequence is closed as all the effluent can be recycled to bsw plant and bleach plant is Z L Dthough the brightness of final bleached pulp is low.
- Since no chlorinated chemical has been used the bleaching is considered as **Green Bleaching Technology.**
- When it comes to developing bagasse and wheat straw as sustainable source of fibre for pulp and paper making, it is shown that adopting a Green bleaching process enables increased environmental compliance, greater operational efficiency and more cost-effective production.

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