Ferrous Chloride & Hydrated Titania - A Cost Effective Option For Treatment Of Mill Effluent For Colour & Aox Removal

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ABSTRACT

Inspite of the rapid advances in technology related to pollution abatement as well as environmental management , the pulp & paper mills in India are still in search of a suitable techno economically viable colour removal technique in order to address public concerns. Till this search ends the mills will have to continue to rely on chemical treatment for colour removal which is a common practice. The chemicals generally used for colour removal are Lime & Alum. In this perspective a product comprising of 20% Ferrous Chloride + 20gpl Hydrated Titania developed by Cochin Minerals & Rutile Ltd, Cochin was evaluated by CPPRI for its efficiency & merits as well as techno-economics in reducing colour both at lab scale and mill scale. The paper highlights the results & findings of lab scale & mill trials.

INTRODUCTION

Treating the waste water to prescribed discharge norms has always been a challenge for most of the industries and pulp & paper industry is no exception. Though the pulp and paper mills have adequate facility (primary & secondary) in general , to treat the effluents, the efficiency of treatment especially with respect to colour is generally not much effective. Though color itself is not a toxic pollutant and moreover there is no national discharge standards for colour in India , the issue has been included as one of the major agenda to be addressed by the mills under **Charter of Corporate Responsibility for Environmental Protection (CREP)** mainly due to public concern related to it **.** The high color in pulp and paper mill effluents has been a case of serious public issue from aesthetic point of view and many a mills in India, today are involved in legal tussles due to colour problem in their waste water even though it is meeting all the other stipulated discharge standards. Further removal of color from mill effluent increases the possibility of its reuse & recycle back into the process thus reducing water consumption.

The reported impacts caused to the receiving stream due to discharge of effluent with high level of color in effluents include reduction in light penetration, photosynthetic activity of aquatic plants, oxygenation capacity thus affecting aquatic life systems as well as aesthetic quality & recreational use of the water body .

Further , the chlorinated organics compounds or **Adsorbable Organic halides (AOX)** formed during bleaching of pulp with chlorine and chlorine based chemicals are partly responsible for contributing effluent colour, acute / chronic toxicity, mutagenicity and carcinogenicity. The chlorinated organic compounds present in alkali extraction stage (E) bleach effluent are found more toxic and contributes more than 90% of acute toxicity and colour as well.

In small scale agro based pulp and paper mills without chemical recovery or alternate treatment options the environmental problems are compounded due to the discharge of black liquor along with other waste water leading to loss of valuable organic biomass and chemicals in addition to creating adverse environmental impact due to high pollution load. The discharge of black liquor in small scale agro based mills is a major pollution stream due to lignin which contributes 70 -80 % of the total pollution load.

All these three issues viz colour removal , AOX and black liquor treatment have been included among the major agenda in **Charter for Corporate Responsibility for Environment Protection (CREP).**

GENESIS OF COLOUR

The extractives are major sources of colour in the mechanical pulping effluent while lignin is the major source in chemical pulping effluent . These colour bodies are formed due to condensation and oxidation reactions taking place during pulping and bleaching process. These compounds are known to carry bulk of light absorbing materials or **chromophores.** The lignin derivatives are highly coloured and resistant to biological attack and thus remain in the environment. The extractives include mainly aliphatic compounds , terpenes / terpenoids and poly phenolic compounds. Apart from chemical pulping effluent , during bleaching process oxidative degradation of lignin leads to formation of Hydroxy-Quinones during alkali extraction which is the major contributor to colour formation. The major contributor to colour formation in pulp and paper making process include : ***Chemical Pulping- Extent of delignification,Mechanical Pulping - Wood extractives (tannins and polyphenols),Pulp washing,Pulp bleaching, Spills and leaks (Pulp mill & Evaporaters).***As per a rough estimate colored waste water from kraft mills constitutes 20-30% of total waste water.

COLOUR REMOVAL TECHNIQUES

Though various physico-chemical treatment techniques and technologies

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like ultra filtartion , reverse osmosis, electrofloculation carbon adsorption , photo oxidation etc are available in context of color removal. Only chemical treatment so far has been used in Indian scenario due to its time tested efficiency & ease in handling and applications Lime & Alum are the major chemicals used for reduction in pollution load particularly suspended solids including colour to some extent in pulp & paper mill effluent. **Cochin Minerals & Rutile Ltd, Cochin** has recently introduced a product comprising of **20% Ferrous Chloride + 20gpl Hydrated Titania** as an alternative to lime & alum with major emphasis on higher reduction efficiency at reduced treatment cost.

Ferrous chloride is a powerful coagulant for suspended and colloidal impurities and act as a good adsorbent for dissolved colouring matter. The mechanism of treatment includes formation of Ferrous Hydroxide on addition of Ferrous Chloride to water which further gets oxidized to Ferric hydroxide .The Ferric Hydroxide is a bulky voluminous precipitate having fast settling properties. Suspended matter color bodies present in the effluent are adsorbed by the precipitate and settle out thus reducing the color of the effluent. The chloride ions formed during the dissociation , reacts with alkali/ other metal ions present in the effluent to form respective chlorides which are harmless to aquatic flora &

Table -1

Treatment of Bleach Plant Effluent with Ferrous Chloride + Hydrated Titania

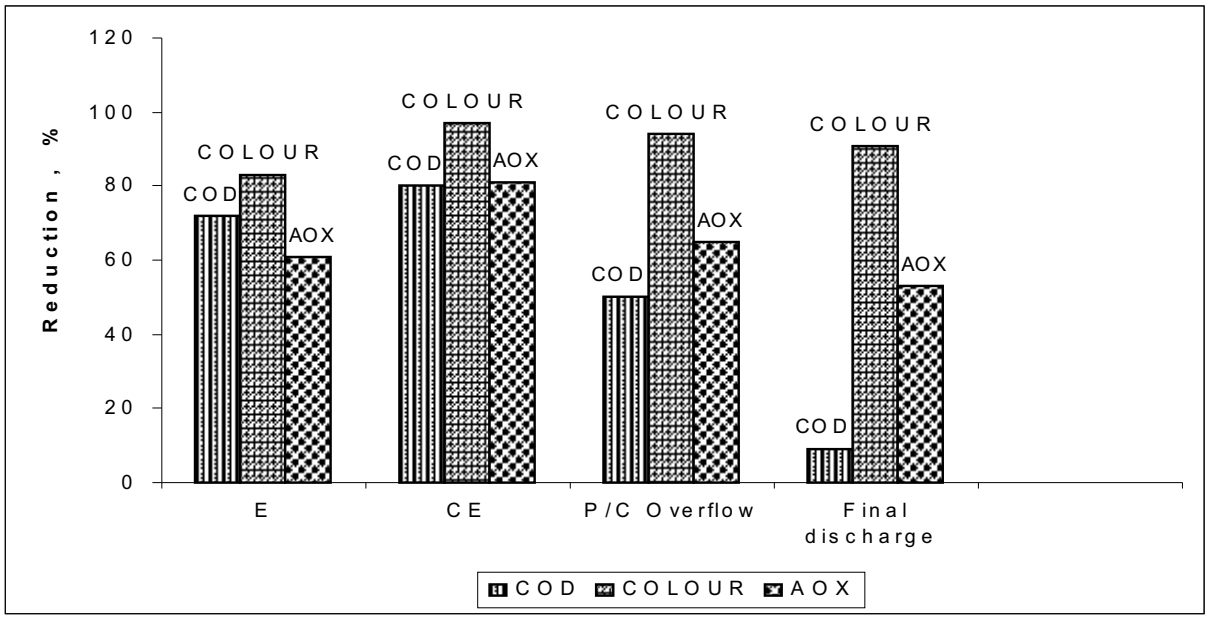
Bleach Effluent	Bleach Plant Effluent –Wood Based Mill							
	E				CE (1:3)			
Parameters	pH	COD,mg/l	Color. PCU	AOX mg/l	pH	COD,mg/l	Color. PCU	AOX mg/l
Initial Characteristics	11.5	1031	478	38	11.2	1007	394	65.50
Final Characteristics (After Treatment)	7.5	606	71	26	7.3	618	48	28.90
Removal efficiency %	-	41	85	32		39	88	60

Table - 2

Treatment of Combined Mill Effluent with Ferrous Chloride + Hydrated Titania

	Combined Effluent –Wood Based Mill							
Bleach Effluent	Combined Effluent				Final Discharge			
Parameters	pH	COD,mg/l	Color. PCU	AOX mg/l	pH	COD,mg/l	Color. PCU	AOX mg/l
Initial Characteristics	7.5	509	808	6.30	7.6	315	870	8.0
Final Characteristics (After Treatment)	7.2	250	77	2.9	7.3	287	81	3.8
Removal efficiency %	-	51	90.47	54.0	-	9	91	53

Fig . 1 Chemical Treatment with Ferrous Chloride + Hydrated Titania of Wood Based Mill Effluent



fauna.

The treatment efficiency of the product was evaluated & verified by CPPRI both at laboratory scale for individual effluent streams and combined effluent as well as black liquor (in case of agro based mills).

LABORATORY STUDIES CARRIED OUT BY CPPRI ON CHEMICAL TREATMENT WITH CMRL PRODUCT

Bleach Plant Effluent Stream, Combined Effluent & Final Discharge

Laboratory studies were carried out by CPPRI to evaluate the impact of CMRL product for treatment of bleach plant effluent stream, combined effluent, and finally treated effluent collected from wood based & agro based mills producing different grades of paper The results obtained after optimisation of dosages are indicated in **Table 1 & 2 and Fig 1.**

Black Liquor Treatment

Black liquor were collected from two agro based mills producing writing & printing paper but using different raw material. In this case the pH of the black liquor was lowered up to 6.5 when the lignin separation occurs. After lignin separation the pH was again raised to 7.5 with lime the results of the same are indicated in **Table 3& 4 as well as in Fig 2 & 3**

MILL SCALE TRIAL FOR LIGNIN SEPARATION FROM BLACK LIQUOR

The **Lignin Separation Technology** has recently been employed as an

Table - 3

Chemical Treatment of Agro Based Black Liquor

(Raw Material Furnish : Bagasse & Wheat Straw)

S. No.	Parameters	Black Liquor	Treated Black (pH 8.6 to 6.5 with Ferrous Chloride & 6.5 to 7.5 with Lime)	% Red.
1.	pH	8.6	7.5	-
2.	T.D.S. , mg/l	20500	16350	20.24
3.	COD, mg/l	19846	4794	75.84
4.	BOD, mg/l	10808	5576	48.41
5.	Color, PCU	**32500**	**2710**	**91.66**
6.	Lignin, mg/l	**5342**	**687**	**87.14**
7.	Organic, mg/l	**12900**	**3770**	**70.78**

Table 4
Chemical Treatment of Agro Based Black Liquor
(Raw Material Furnish : Bagasse & Rice Straw)

S. No.	Parameters	Black Liquor	Treated Black ((pH 8.6 to 6.5 with Ferrous Chloride & 6.5 to 7.5 with Lime)	% Red.
1.	pH	8.0	7.0	-
2.	T.D.S. , mg/l	11520	9320	19.1
3.	COD, mg/l	10500	2400	77.1
4.	BOD, mg/l	2210	1308	40.8
5.	Color, PCU	24500	1300	94.7
6.	Lignin, mg/l	3100	485	84.3
7.	Organic, mg/l	6860	1826	73.4

Fig 2 Performance Efficiency of Chemical Treatment Of Black Liquor Using CMRL'S 20% Ferrous Chloride + 20gpl Hydrated Titania (Raw Material Bagasse & Wheat Straw)

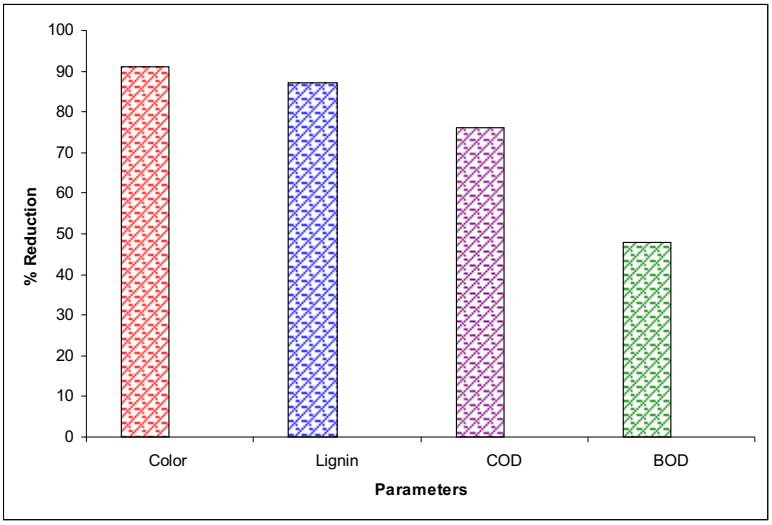
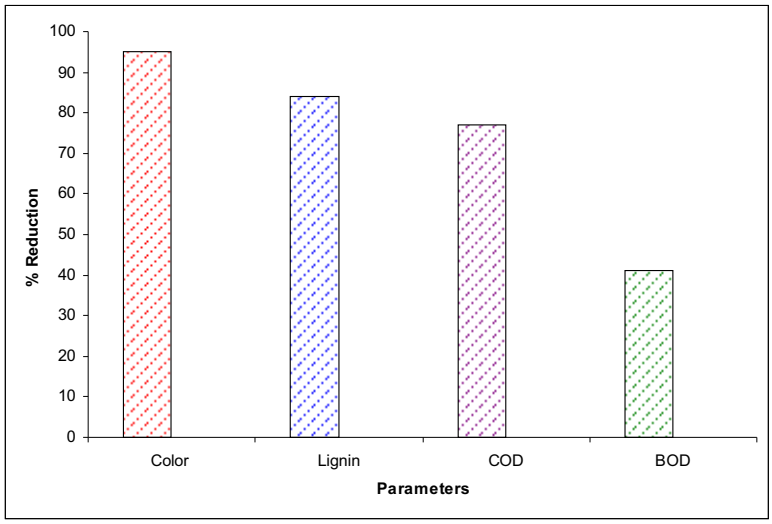


Fig 3 Performance Efficiency of Chemical Treatment Of Black Liquor Using CMRL'S 20% Ferrous Chloride + 20gpl Hydrated Titania (Raw Material Bagasse & Rice Straw)



alternate treatment option by a number of agro based mills producing unbleached variety of paper(below 50 tpd) .The process usually involves use of mineral acid to reduce pH of black liquor for precipitation of lignin followed by separation of lignin using suitable filtration technique.

A full scale trial with CMRL product was carried out in an agro based mill to evaluate its efficiency as an alternative to mineral acid . The mill is producing around 35 tpd of writing & printing paper using 25 % agro chemical pulp & 75 % waste paper. The mill at present produces around 10 tpd chemical pulp from bagasse/rice straw depending on their availability. **The CMRL chemical was effective in precipitating out lignin from black liquor at pH 6.0-6.5 unlike with acid which takes place at pH 2.5-3.0.**

RESULTS & DISCUSSIONS

(I) Lab Scale Studies

The treatment studies carried out using **CMRL chemical i.e. 20% Ferrous Chloride + 20gpl Hydrated Titania** have been found to be quite effective and encouraging in reducing the various pollutional parameters specially **COD , Color & AOX** in bleach plant effluent, combined mill effluent and final discharge of wood based mill producing writing and printing grade of paper. The average reduction in major pollutional parameters depends on the characteristics of the effluent, process followed and dosage of chemicals

Table-5

Parameters	Reduction %
Colour	85-90
AOX	30-60
COD	40-60
BOD	25- 40
Lignin	65- 78

Table-6

Parameters	Reduction %
Colour	92-95
COD	76-77
BOD	41-48
Lignin	84-87

Table-7

Effluent	Consumption ,	
	CMRL product , Liter / m^3	Lime ,kg /m^3
E Stage	8	1.7
Combined Bleach effluent	6.0	1.5
P/C Overflow	1.6	2.0
Final discharge	1..2	1.2
Agro Based Black Liquor	14-15	2. 0 -2.3

Polymer Used : 10 ml / m^3 of 0.2 % solution

applied. The results obtained with effluent collected from wood based large pulp & paper mill are as table-5 **However the product has been found to be most effective in case of treatment of final discharge and as such may be useful option as a tertiary treatment for mill effluent.**

The efficacy of CMRL product was also assessed in context of lignin separation from black liquor and it has been observed that the product is more effective in reducing pollution load especially Colour, COD and Lignin compared to conventional route of lignin removal process. The average reduction in major pollutional parameters observed in the treatment of black liquor from agro based small pulp & paper mill are as table-6

The chemical has been found to be pH sensitive so the pH of the system needs to be critically monitored and maintained to achieve best performance efficiency. Reappearance of colour was observed in cases if the pH of the resultant mixture was not maintained properly. So proper and thorough mixing of the effluent after lime addition at optimal pH is necessary to prevent color reversion after chemical treatment of the effluent. The average consumption figures of the chemicals (CMRL's product and lime) to achieve maximum possible reduction in pollution load is summarised in table-7

The results achieved during the trials for Lignin Separation are as follows:

Parameters	Black Liquor	LRP Filtrate after treatment with CMRL Product #	LRP Filtrate after treatment with H_2SO_4 *	% Reduction	
				CMRL Product	H_2SO_4
pH	9.0	7.3	1.8	-	-
COD,mg/l	61004	11094	15861	82	74
BOD,mg/l	12960	6609	4536	49	65
TSS,mg/l	3700	106	672	97	81
TDS ,mg/l	52860	20538	27288	61	48
Lignin,mg/l	11895	779	1389	93	88
Colour,PCU	147000	4360	13485	97	91

 # at pH 6.5 * at pH 2.0

The results of analysis of lignin sludge separated is as under:

Parameters	Sludge after treatment with CMRL Product at pH 6.5	Sludge after treatment with mineral acid acid at pH 2.5
Moisture , %	78.20	77.86
Organic ,%	54.14	51.95
Inoragnic,%	45.86	48.05
Calorific Value, kcal/kg	4690	4338

(II) Mill Scale Trials For Lignin Separation

As indicated above , **the CMRL product is more effective than the mineral acid in reducing COD, lignin & colour of the black liquor**. **The main advantage of CMRL product is that the above chemical works effectively at about neutral pH. The another advantage of CMRL product is easy handling due to its non corrosive nature compared to sulphuric acid.**

CONCLUSIONS

The high level of colour in mill effluent is now a more important issue before pulp & paper industry. Interestingly the issue has gained prominence not for any adverse impact but because of public perception & objections. The major problem in addressing to the issue of colour is the non availability of any indigenous technology for its removal while those available are prohibitive in terms of capital investment as well as operation & maintenance costs involved. The chemicals like alum & lime widely used by the industry are not very encouraging w.r.t extent of colour removal. The laboratory treatment trials carried out using CMRL's product 20% Ferrous Chloride + 20gpl Hydrated Titania have been found to be encouraging with respect to reduction in Colour, AOX, Lignin ,COD & BOD from combined as well as selected effluent streams including black liquor. The trials carried out with CMRL product have been found very effective in removing colour to maximum extent . **The another advantage of CMRL product is that it acts at neutral pH avoiding need for further correction of pH for making it suitable for reuse/ discharge.** The interested mills may approach CMRL for any further details or mill scale trials etc.

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