Toxic Metal Contamination In Cotton Based Paper Mill Effluent

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ABSTRACT

A number of studies have already been carried out for the metal analysis of paper mill effluents which are generally using wood and non-wood (bamboo, baggase etc.) as fibrous raw material for paper manufacturing process. This study deals with a paper mill which is using cotton comber and cotton linter as raw material for paper manufacturing process. Effluents generated in the paper mill at different stages were sampled and analyzed. The fibrous sludge samples recovered in different sections of mill were also collected. Heavy metal content of the untreated, treated effluents and the sludge samples were determined in the atomic absorption spectrophotometers. Heavy metal analysis results were interpreted and compared with the permissible limits.

Keywords: heavy metals, AOX, TOCl, effluents, white water, black liquor, yellow liquor.

Introduction

Environment as well as clear water is precious and are essential natural resource. Everybody has a duty to keep them clean and pollution free. It is now universally realized that any future developmental activity has to be viewed in the light of its ultimate environmental impact. The tremendous increase in industrial activity during the last few decades and the release of obnoxious industrial wastes into the environment, have been of considerable concern in recent years from the point of view of environmental pollution. There are several factors that cause water pollution. Water pollution causes approximately 14,000 deaths per day, mostly due to contamination of drinking water by untreated sewage and mill discharges in developing countries [6].

Paper mills are generating large quantity of effluents as a consequence of pulping and bleaching processes. Most of the paper mills are using non-wood (bamboo, baggage and straw etc.), hard wood (balsa, Eucalyptus etc.) and soft wood (pine etc.) fibrous raw material; for paper manufacturing. [5]

The paper mills extract cellulose fibre from the above raw materials in the pulping process by using caustic to break the bond between cellulose and lignin. During this pulping process a large quantity of black liquor is generated. The main component of which is the sodium lignite macromolecule, which is the cause for the coloration of water, higher Biochemical Oxygen Demand and Chemical Oxygen Demand of the effluents. Paper mills use bleaching chemicals generally chlorine based compound to improve brightness of paper.[2] The effluent generated from the bleach plant, therefore having more Adsorbable Organic Halide (AOX) and Total Organic Chloride (TOCl) [2]. Hence conventional paper mill effluents even after proper treatments cause more pollution to the nearby water bodies due to more lignin content. At the same time it adds more quantity of organic and inorganic chemicals into the water bodies. Wastes from paper and pulp mills undergo degradation and decomposition by

Table 1: Fibre dimensions of non-wood plant fibres

Non-wood fibre	Average length *(mm)*	Average diameter *(microns)*
Abaca (Manila hemp)	6.0	24
Bagasse (depithed)	1.0-1.5	20
Bamboo	2.7-4	15
Com stalk and sorghum (depithed)	1.0-1.5	20
Cotton fibre	25	20
Cotton stalks	0.6-0.8	20-30
Crotalaria sp. (sun hemp)	3.7	25
Esparto	1.5	12
Flax straw	30	20
Hemp	20	22
Jute	2.5	20
Kenaf bast fibre	2.6	20
Kenaf core fibre	0.6	30
Rags	25	20
Reeds	1.0-1.8	10-20
Rice straw	0.5-1.0	8-10
Sisal	3.0	20
Wheat straw	1.5	15
Wood fibres		
Temperate zone coniferous woods	2.7-4.6	32-43
Temperate zone hardwoods	0.7-1.6	20-40
Mixed tropical hardwoods	0.7-3.0	20-40
Eucalyptus sp.	0.7-1.3	20-30

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bacterial activity in presence of dissolved oxygen, more dissolve oxygen is required to degrade the macro lignin components. This results in depletion of Dissolved oxygen and ultimately affects aquatic life. In brief, such wastes make the receiving water unfit for any use, spoil the sewer fabric and damage the working of treatment plants. The major components of the paper mill effluent thus classified as:

1. Pulp mill effluent is very dark in colour. The major portion of which is Sodium Lignate as lignin in the form of Sodium lignite breaks all bonding from the cellulose and dissolves in water.
2. The washing of bleaching process which generally contains Chloro-lignin, Adsorbable organic halides (AOX), total organic chloride (TOCl), which is very much hazardous and carcinogenic.[2]

The effluents analyzed and estimated in this study, are found to be different from the effluents as discussed above. Because here the raw material used are cotton comber and cotton linter, which generates less impurities.

Raw material

Cotton linters are generally of different grades. An optimum blend of these grades is used for paper making process. Linter is recovered from the cotton seeds by the process of ginning.[8] The process of converting the linter into pure cellulose pulp require digestion, bleaching and beating with mild treatment of caustic and peroxide.

The average fibre length of different kinds of cotton varies from 20 to 50 mm, the diameter of 18 to 25 mm. The detailed morphological characteristics of cotton along with their raw material are mentioned in the table 1.

NATURE OF CHEMICAL TREATMENT FOR WOOD, NON-WOOD MATERIAL AND COTTON

Basic characteristics of raw materials used for conventional paper making is that they have no free cellulose content. The cellulose remains linked with lignin. The lignin is to be separated from the cellulose by the process of pulping and bleaching. As the lignin is polymeric macromolecules, it requires drastic chemical treatment for the separation of cellulose fibre from the lignin. In spite of that some residual lignin remains inside the bleached pulp.[1][7] Whereas the raw material cotton comber and linter has unique characteristics having almost nil lignin content. So, it requires very less chemical treatment for the pulping bleaching process as compared to the conventional paper making process.

Generally in India most of the paper mills are adopting Kraft process for the pulping of raw material. In the Kraft process chemical called white liquor having composition ($NaOH + Na_2S$) is being used to extract cellulose from the raw material. After pulping the pulp thus formed is bleached to remove the residual lignin and to make the pulp of desired brightness.[7] Different bleaching sequences are being adopted by different paper mills depending on the raw material and the end product. Generally Chlorine, Chlorine dioxide, Hydrogen peroxide and Oxygen are being used for the bleaching process. The pulping and bleaching process are the main process which causes the major component of the water effluent, whereas no separate pulping or bleaching has been used for cotton as raw material. The cooking process adopted in cotton raw material is simultaneously the pulping bleaching process with caustic and hydrogen peroxide. The objective of this is only to remove the impurities like dust, specks and to soften the fibres for any breaking and beating.

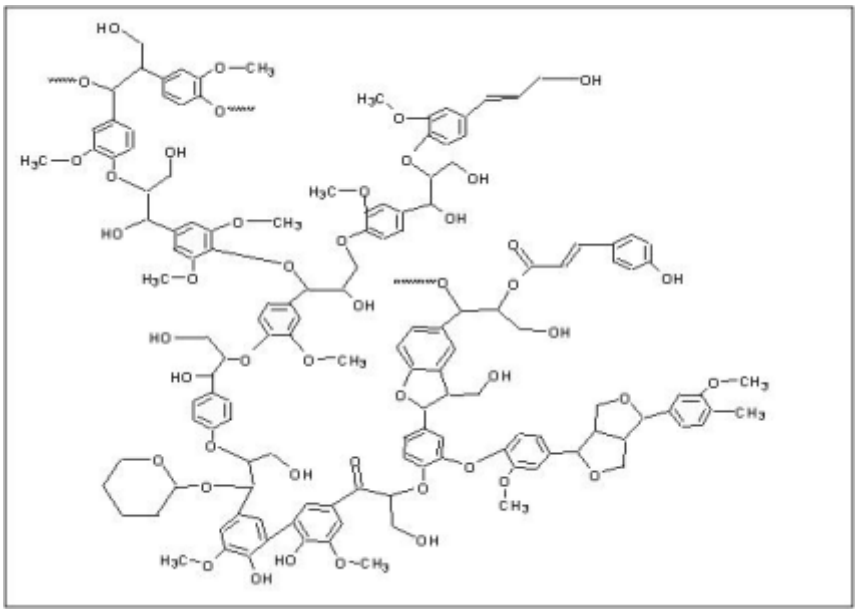
Experimental

The entire water requirement of the mill is received from the river Narmada. Total required quantity of raw water is being pumped from intake well.

Table: 2 Average water Consumption at different sections /Day

S. No.	unit	Consumption (KL/ day)
1	Rag Boiler, Hamp breaker, New Digester House, Garage, Boiler, A./C. & Ventilation Plant	1000
2	Breaker Beater House	4000
3	Machine House & Additive Plant	5500
4	Finishing End, Laboratory, Administrative building CISF building and other departments	1600

Fig.1: One type of structure of lignin



The raw water from the river is treated in a conventional Water Treatment Plant (WTP) consisting of alum coagulation, clarification and filtration through the Rapid Sand Filters. At present the total water requirement of the industry is 14,000 m^3/day. Water consumption of different sections were different and presented below.

1. **Collection of sample**

   The present study was carried out by collecting two type of effluent samples. The effluent generated from various processes at the mill is segregated into two streams. One type is generated by the washing of break, beaten, refining and from machine backwater which is generally called white water. The other stream generated from the washing of digester house is called black and yellow liquor. Both the samples were collected separately and also tested

separately. The fibre sample recovered after the treatment of white water and also the sludge generated from the black and yellow liquor plant also collected and tested separately. The effluent samples were collected in the incubated plastic bottles.

2. **Analysis of parameters:**
The heavy metal content of effluent apart from Na^+ and K^+ ions like Iron, Lead, Mercury, Copper, Nickel, Zinc were detected and suitably estimated, using Atomic Absorption Spectrophotometer.

The toxic materials and chemicals generated through the effluent destroy the biological functioning in the streams as well as in the treatment plants. Wastes from paper and pulp mills undergo degradation and decomposition by bacterial activity in presence of dissolved oxygen. This results in depletion of Dissolved oxygen and ultimately affects aquatic life.[9]

Industrial effluent containing As, Pb and other heavy matels cause cerebral degeneration in brain, which results in frigidity, coma, stupor and numbness.[10]

Results

The effluents generated from various process operations are segregated into two streams. One is the process effluent generated from the Machine House, Breaker Beater Section (white water) with a flow rate 8000 to 8500 m^3 /day. The white water received at Effluent Treatment Plant (ETP) is primarily passed through bar screen and sent to two clarifiers followed by equalization tank. The supernatant water from equalization tank is sent to filter drum and the thickened sludge generated from filter drum is sent to drying beds whereas filtered water is discharged in natural drain joining other stream. The effluent containing yellow and black liquor with a flow rate of 200 to 250 m^3 /day is neutralized by dilute Sulphuric Acid in a neutralization tank followed by equalization tank and then treated by Urea and than through the Activatd Sludge Process (ASP) followed by secondary settling tank (clarifier). Sludge from secondary settling tank is sent to sludge drying beds. The heavy metal content of raw water, treated white water, yellow liquor and final discharge from mill has been analysed and the results are produced in table- 3, 4, 5, 6 respectively. The graphs for the same has also been plotted and given in figure 2 to 5.

Table-3 Heavy metal analysis of Narmada river water at Hoshangabad (All values in mg/L)

parameters	Jan 08	July 08
Fe	0.57	1.62
Zn	0.08	0.46
Cu	0.13	0.75
Mn	Nd	1.24
Pb	0.62	1.17
Cd	Nd	0.76
Ni	0.53	1.19
Co	Nd	1.02
Cr	0.26	0.75
Hg	Nd	Nd

Table 4 Heavy metal analysis of treated white water at ETP (All values in mg/L)

parameters	Jan 08	July 08
Fe	0.59	0.74
Zn	0.10	0.08
Cu	0.21	0.34
Mn	0.90	0.65
Pb	0.87	0.84
Cd	0.16	0.25
Ni	1.06	0.62
Co	0.62	0.86
Cr	0.49	0.13
Hg	Nd	Nd

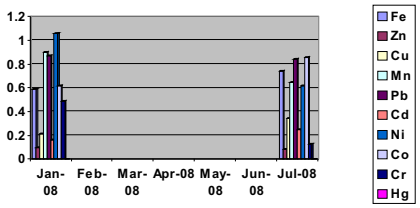


Fig 2: Heavy metal analysis of Narmada river water at Hoshangabad

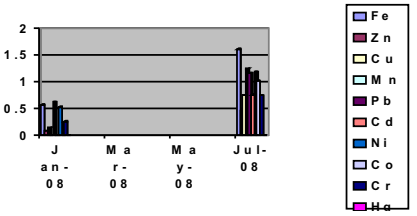


Fig 3: Heavy metal analysis of treated white water at ETP

Table 5 Heavy metal analysis of treated yellow liquor at ETP (All values in mg/l)

parameters	Jan 08	July 08
Fe	0.83	1.54
Zn	0.09	0.26
Cu	0.07	0.12
Mn	0.48	0.52
Pb	0.99	0.74
Cd	0.25	0.36
Ni	0.94	0.90
Co	0.72	0.91
Cr	0.51	0.26
Hg	Nd	Nd

Table 6 Heavy metal analysis of effluent discharged from mill to river Narmada (All values in mg/l)

parameters	Jan 08	July 08
Fe	0.70	0.84
Zn	0.08	0.24
Cu	0.13	0.22
Mn	0.5	0.67
Pb	0.37	0.53
Cd	0.13	0.32
Ni	0.74	0.77
Co	0.48	0.74
Cr	0.55	0.24
Hg	Nd	Nd

Discussion

Results of Table- 3, 4, 5 show that the heavy metals are present in the effluent samples. The results show lower heavy metal content in effluent sample than effluents of conventional paper mills. The result in table 6 indicate that except Cu, Zn and Mn all the heavy metal contents of finally treated discharged sample in less than the water sample of tube well. The low heavy metal content may be due to inherent character of raw material or may also be due to less chemicals used

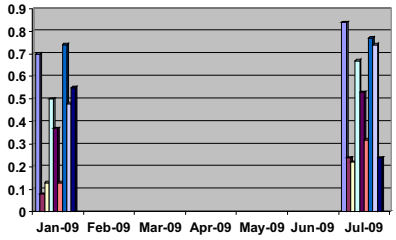


Fig 4: Heavy metal analysis of treated yellow liquor at ETP

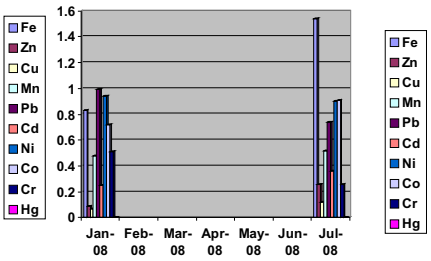


Fig 5: Heavy metal analysis of effluent discharged from mill to river Narmada

during the paper manufacturing process. The concentration of Cu, Ni and Fe is slightly on the higher side as compared to the concentration of these in tube well water. But the quantity found in effluent is same for Cu as in raw water (Narmada water). Higher values of Fe (iron) may be due to the wear and tear or rusting of the equipments of plant. This may be also due to very old and obsolete equipments and machineries.

Hg (mercury) which is one of a harmful metal is non-detectable in all the samples of the effluent from the mill. This is a good sign for the nature of effluent.

Conclusion

The study clearly shows that the effluent is extremely well with respect to the metal content. It concludes that the effluent discharge will not increase the metal content of receiver and will not badly affect the life of the people. The effluent water mixes to the down stream then gets used. Alternate sources of fibres, including non-wood fibres, are being used to an increasing extent by the pulp and paper industry. It is projected that the amount of non-wood fibres employed will increase steadily in countries that are deficient in wood, and parallel trends may also be seen in countries that are rich in forest resources as environmental and social pressures reduce the areas of forest available for wood supply.

The results analyzed that the nature of effluent is totally different from other paper making mills. The heavy metal contents are well within the standard limit. There are no harmful ingredients present in the mill effluent. The only limitation is that the effluent is slightly turbid. From the metal analysis point of view, the effluent sample is tolerable and can be safely used for the irrigation purpose and can also be reutilized in the process of paper making after reducing the turbidity of the water.

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