Removal of Colouring Substances in Wood Based Integrated Pulp and Paper Mills Through External Treatment of Effluent by Coagulation-Flocculation Method

S.K.Chakrabarti, Sanjeev Gupta, K.D.Sharma, Amandeep Kaur and R. Varadhan[1]

The colouring substances present in the pulp and paper mill wastewater are mainly due to high molecular weight lignin substances or its chloro-derivatives. Colour is an aesthetic nuisance and hinders penetration of light in the aquatic body creating disturbance in the aquatic life. Regulatory agencies and public at large are becoming increasingly sensitive towards the release of colouring substances in pulp and paper mills wastewater. Amongst the non-destructive and physico-chemical methods coagulation-flocculation technique is a highly efficient, easy to operate and less capital intensive one. Present paper deals with colour removal by coagulation of the colouring substances with polyaluminum chloride and cationic polydadmac as coagulant followed by flocculating the destabilized mass with high molecular weight polyacrylamide flocculating aid. The system under study can remove 25-70 % coloring substances, 26-75% COD and 15-35% organochlorine substances depending upon the chemical addition and nature of the wastewater. The method is equally suitable either as a pretreatment to or post treatment of secondary biological treatment and can be applied to the mill condition depending upon the facility available.

Key words : Bleach plant effluent, coagulation- flocculation, polyaluminium chloride, colouring substances, COD, AOX, particle charge

INTRODUCTION

The major source of organic compound in the integrated pulp and paper industry wastewaters is degraded products of hemicelluloses and cellulose, and lignin and its chloro-derivatives. Whereas the carbohydrates are easily biodegradable and impart negligible amount. of colour, lignin and its derivatives impart colour due to phenolic and quinone chromophoric groups. These compounds are mostly resistant to conventional aerobic treatment in activated sludge process or aerobic lagoon. Only low molecular weight lignin derivatives are partially degraded by biological treatment. In a pulp mill having well function chemical recovery, lignin compounds come to the effluent treatment plant from three sources; bleaching plant, open washer (decker) in pulp mill and black liquor evaporation plant. 3.5-4% residual lignin in the unbleached pulp which gets removed during multistage bleaching is the largest contributor of lignin compounds in the effluent. Oxygen delignification process followed by ECF bleaching can not completely eliminate the problem of colour in the pulp and paper mill effluent (Lombardo et el. , 1998).

Colour is an aesthetic nuisance and hinders penetration of light in the receiving water body creating disturbance in the aquatic life. Its inhibits self purification capacity of natural water during stagnation low flow condition. Though the intensity of pulp and paper mills in India is very thin as it is too scattered throughout the country, the coloring substances in the discharged effluent are a serious cause of concern to the industry and the regulatory agencies particularly during summer months when low to very low flow of water exists in the water bodies. Public at large are becoming sensitive and critical of the pulp and paper industry. Since the promulgation of comprehensive

Research and Competency Division in Pulp & Paper

Thapar Centre for Industrial Research & Development, Patiala- 147 004, Punjab, India.

1 Corporate Research & Development, Ballarpur Industries Limited, First India Place, Gurgaon - 122 002, Haryana, India

Table 1

Characteristics of different streams of wastewaters of bleach plant in Mill A

Stream	Colour (PCU)	COD (mg/l)	AOX (mg/l)	Particle charge (meq/l)
C_D	1305	805	86	0.04
E_{OP}	12050	2270	158	5.65
H_1	260	725	75	0.62
H_2	280	805	20	0.42
D	75	360	13.8	0.21

Table 2

Characteristics of different streams of wastewaters of bleach plant in Mill B

Stream	Colour (PCU)	COD (mg/l)	AOX (mg/l)	Particle charge (meq/l)
C	2230	1595	144	0.10
E_P	13350	3140	164	5.73
H_1	198	905	102	0.59
H_2	200	835	36,7	0.29
D	25	180	7.4	0.02
Combined bleach stream	1455	1005	68	0.56
Unbleached stream	4760	1425	-	0.94

legislation in 1986 more and more stringency is being imposed on the industry to conserve the resources and reduce the environmental emission (CPCB 2003) in line with the policy followed in the western world. The industry and regulatory agencies have mutually accepted a time bound programme to conserve water and regulate the release of pollutants, work for finding a techno-economic solution at the earliest for controlling the colour. It has become difficult to comply the COD discharge parameter in the treated effluent with the conventional treatment process arising out of more and more water conservation.

The choice of treatment technologies for colour removal depends on their potential for removing high molecular weight lignin and lignin derivatives which attribute colour. The technologies tested are of three different types; (i) physico-chemical which includes foam floatation, chemical precipitation, electro flocculation, activated carbon adsorption, ultrafitration, (ii) oxidation which includes H_2O_2, UV and ozone treatment and (iii) fungal biooxidation with active organism (Gautam et al., 1987; Amoth et al., 1992). In India very limited study has so far been carried out on the colour removal processes. Sharma et al., in 1987 carried out the study with various flocculanting chemicals like alum, suflocs, lime and degrading agents like $Ca(OCl)_2$ and reported that the latter one reduces the colour to an appreciable extent. Bleach plant effluent was treated with fly ash followed by coagulation of the whole effluent with alum in the primary treatment (Sahu and Patel). Chakrabarti et al., in 2004 reported that lime treatment of bleach plant effluent reduces colour and AOX by a significant extent. Panwar et al. in 2004 reported that electroflocculation removes the colour, COD, AOX appreciably.

Among the three types of treatment options stated above biooxidation with fungal microorganisms is confined to the laboratory scale and other ones except chemical precipitation require capital investment in plant and machineries. Chemical precipitation with coagulation- flocculation can be applied for colour control in the existing plant conditions. Findings of the current research work are presented here to explore if it can serve the desired objective with a reasonable cost.

MATERIALS & METHODS

Materials

Coagulation- flocculation studies were carried out with 500 ml effluents in polyethylene beakers with regulated agitation with mechanical stirrers. Effluents were collected from two integrated pulp and paper mills which follow $C_D E_{op} H_1 H_2 D$ and $CE_p H_1 H_2 D$ bleaching sequences. The wastewaters

Table 3

Colour, COD and AOX load from different streams in

Stream	Colour load (%)	COD load (%)	AOX load (%)
Unbleached	34.1	13.8	-
C_D	22.7	40.5	54.9
E_{OP}	40.3	21.9	19.3
H_1	2.3	18.2	23.9
H_2	0.6	5.1	1.6
D	Traces	0.5	0.2

Colour, COD and AOX load in the Mill B: 183, 63 and 5.0 kg per tonne of unbleached pulp

Table 4

Colour, COD and AOX load from different streams

Stream	Colour load (%)	COD load (%)	AOX load (%)
Unbleached	58.3	37.8	-
Bleached	41.7	62.2	100

Colour, COD and AOX load in the Mill B: 204, 94 and 4.0 kg per tonne of unbleached pulp

were preserved at temperature below 4°C

Poly aluminium chloride with 18% Al_2O_3 content was procured from commercial source. Polydadmac type low molecular weight and highly cationic coagulant, and polyacrylamide type high molecular weight and anionic flocculant were collected from Ciba.

A laboratory scale treatment system was developed consisting of primary clarifier of 2.5 litre, aeration reactor of 2.25 litre and secondary clarifier of 0.9 litre. The wastewater was fed and sludge was recycled by Masterflex peristaltic pumps.

Analytical Methods

Adsorbable Organic Halides (AOX) was determined as per ISO Method No.9562: 1989 using Euroglas make AOX analyzer (Model No. ECS 2000). p-chlorophenol (SD Fine Chemicals, India) was used as the standard.

Chemical Oxygen Demand (COD) was determined by open reflux method as per APHA method No. 5220D.

Colour was determined by spectrophotometric technique as per Hach method No.8025. The pH of the wastewater was first adjusted to 7.6 by using H_2SO_4 or NaOH solution and filtered through Whatman filter No.1.

Particle charge was analysed by Mutek pcd 03 PH model using Polydadmac as cationic titrant and sodium polyethylenesulphonate as anionic titrant.

RESULTS & DISCUSSIONS

Major raw material in the two mills are bamboo; in the Mill A it is about 60% whereas in Mill B it is about 40%. There is also some difference in the chemicals used in the bleaching; in Mill A 18% chlorine is substituted by ClO_2 in the chlorination stage and extraction stage is O_2 reinforced. ClO_2 in the ultimate stage is used for brightness enhancement. The major colour contributing stage is E_{op}/E_p (Table I, 2). H stages though contribute less colour but generate large amount of COD and AOX compounds due to hemicelluloses/cellulose degradation

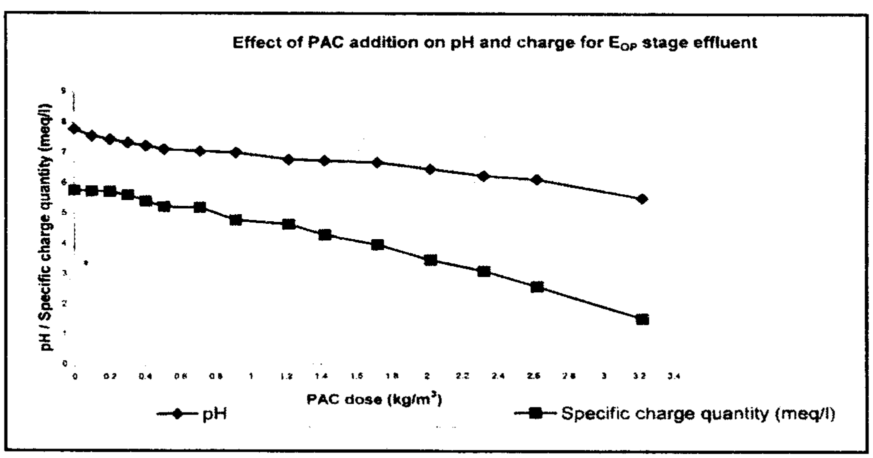


Fig. 1 Effect of PAC dose on charge and pH of E_{OP} stage of Mill A.

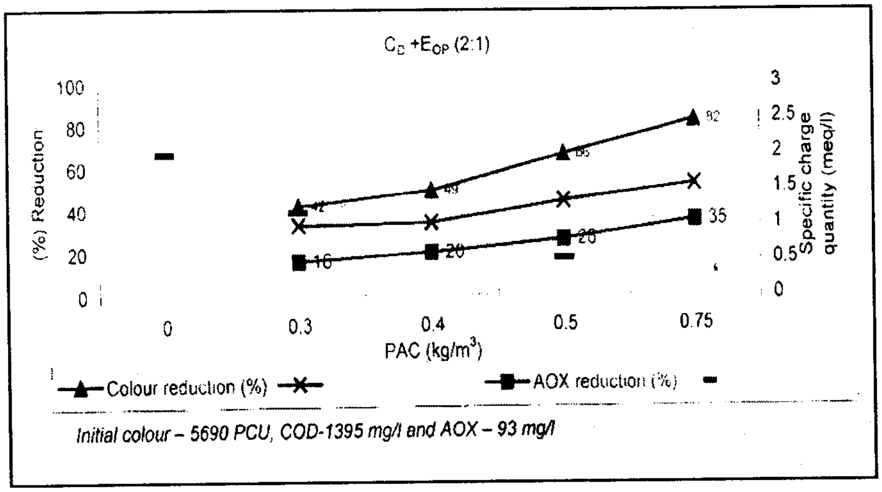


Fig. 2 Effect of coagulation-flocculation with PAC and synthetic polymers in C_D+E_{OP} stage effluent (proportion of mixing: 2 : 1:)

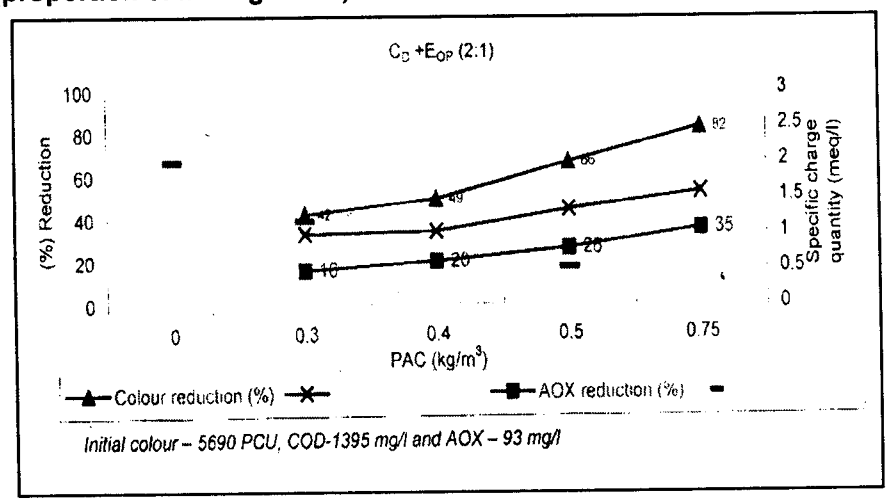
and chloroderivatives formation.

There is a striking similarity in the particle charge behaviour in the bleach plant effluents of both the two mills; Eop/Ep stage effluent is highly anionic; it might be that in the alkaline pH of Eop/Ep stage particles lose H ion and acquire negative surface charge. Surface charge of particles in all other stages is low to moderate. In the mill A black liquor spill control is well organized which results in lower colour and COD discharges in unbleached streams (Table 3,4). Though Eop/Ep stage contributes larger amount of colour contributing substances Co/C stage generates larger share of AOX compounds and COD compounds. (Table 2).

The demand of PAC to bring the isoelectric point is extremely high; 3.5 kg of PAC is required per m^3 of the effluent to bring down the particle charge from 5.8 to 1.5 meq (Fig.1). It shows that if Eop/Ep effluent is exclusively treated for colour removal PAC requirement will be extremely high and cost prohibitive.

To reduce the cost of the treatment and to make the process viable different proportion of Co stage effluent were mixed with Eop stage effluent in the ratio of 2: 1 to consume part of the CD stage effluent with Eop stage effluent (Fig 2). In case of 2:1 mixed effluent 42 to 82% colour, 33 to 52% COD and 16 to 35% AOX compounds can be removed with PAC dose of 0.3 to 0.75 kg per m^3 of the effluent (Fig. 2). The treatment cost for chemicals per m^3 of the effluent will be Rs. 2.9 to 6.0 culminating a cost impact of Rs. 53 to 110 per tonne of paper (Table 5).

Two other experiments were carried out to see the impact of pretreatment on 2.5 times diluted 2:1 mixed effluent of C_D and E_{OP} stages with coagulating flocculating chemicals and similar treatment with biologically treated effluent as tertiary treatment as dilution waters could be available from paper machine effluent. In case of the former 39 to 68% colour 28 to 43% COD and 26 to 36% AOX compounds can be removed with PAC dose of 0.2 to 0.4 kg per m^3 of the effluent (Fig. 3). The treatment cost for chemicals per m^3 of



C_D+E_{OP} (2:1)
Colour reduction (%)
AOX reduction (%)
Initial colour – 5690 PCU, COD-1395 mg/l and AOX – 93 mg/l

Fig. 2 Effect of coagulation-flocculation with PAC and synthetic polymers in C_D+E_{OP} stage effluent (proportion of mixing: 2 : 1:)

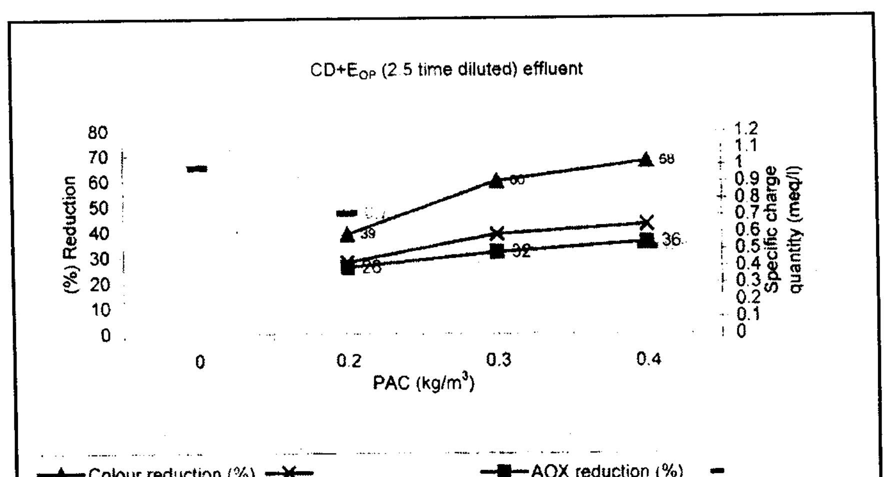


Fig. 3 Effect of coagulation-flocculation with PAC and synthetic polymers in C_D+E_{OP} 2.5 times diluted effluent (proportion of mixing : 2: 1)

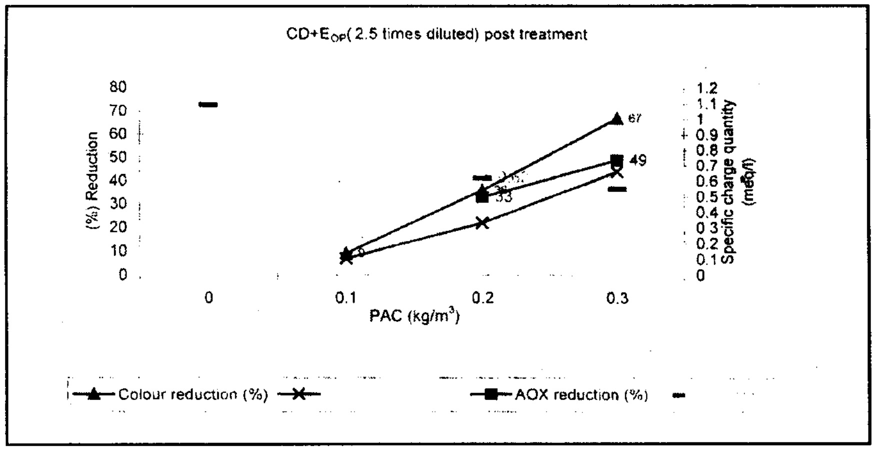


Fig. 4 Effect of coagulation-flocculation with PAC and synthetic polymers in biologically treated 2.5 times diluted C_D+E_{OP} stage effluent (proportion of mixing : 2 : 1:)

Table 5

Cost of pollutants removal in Mill A

PAC dose (kg/m³)	Pollutants removal (kg/m³ of effluent)	Cost of treatment (Rs./m³)	Impact on cost of paper (Rs/t)
a. C_D+E_{OP} stage effluent (proportion of mixing : 2 : 1)			
0.3	2.1416 colour + 0.455 COD + 0.014 AOX	2.9	53
0.4	2.784 colour + 0.469 COD + 0.0183 AOX	3.6	66
0.5	3.756 colour + 0.62 COD + 0.0246 AOX	4.3	79
0.75	4.683 colour + 0.727 COD + 0.0331 AOX	6.0	110
b. 2.5 times C_D + E_{OP} stage effluent (proportion of mixing : 2: 1)			
0.2	0.905 colour + 0.158 COD + 0.0095 AOX	2.2	101
0.3	1.41 colour + 0.220 COD + 0.0120 AOX	2.9	133
0.4	1.585 colour + 0.246 COD + 0.0131 AOX	3.6	165
c. Biologically treated 2.5 times diluted C_D + E_{OP} stage effluent (proportion of mixing : 2 : 1)			
0.1	0.16 colour +0.021 COD +	1.5	69
0.2	0.64 colour + 0.064 COD +0.009 AOX	2.2	101
0.3	1.205 colour + 0.127 COD + 0.0128 AOX	2.9	133
d.Whole mill effluent			
0.1	0.70 colour + 0.21 COD + 0.003 AOX	1.5	192
0.2	0.89 colour + 0.24 COD + 0.004 AOX	2.2	282

the effluent will be Rs. 2.2 to 3.6 culminating a cost impact of Rs. 101 to 165 per tonne of paper (Table 5).In the post biological treatment 9 to 67% colour, 7 to 44% COD can be removed with PAC dose of 0.1 to 0.3 kg per m³ of the effluent (Fig. 4). Tertiary treatment is comparatively less than the pretreatment with respect to colour and COD removal whereas AOX removal is better in case of post treatment. The treatment cost for chemicals per m³ of the effluent will be Rs. 1.5 to 2.9 culminating a cost impact of Rs. 69 to 133 per tonne of paper (Table 5).

The more the dilution of the effluent more the requirement of coagulating-flocculating chemicals; in the whole mill effluent cost of treatment is Rs. 192 to 282 (Table 5) for a colour removal of 53 to 67%, COD removal of 26 to 30% and AOX removal of 17.3 to 22%.

In case of Mill B where there is a separate primary clarifier for pulp mill effluent clarification two experiments were carried out one with unbleached effluent and other one with whole pulp mill effluent. In case of former colour removal of 44 to 63% and COD removal of 35 to 43% were observed with PAC addition of 0.05 to 0.2 kg per m³ of the effluent (Fig4). The treatment coast for chemicals per m³ of the effluent will be Rs. 1.1 to 2.2 cluminating a cost impact of Rs. 26 to 51 per tonne of paper (Table6). In case of whole pulp mill effluent 37 to 68% colour, 20 to 36% COD and 15 to 21% AOX compounds can be removed with PAC dose of 0.1 to 0.3 kg per m³ of the effluent (Fig. 5). The treatment cost for chemicals per m³ of the effluent will be Rs. 1.6 to 3.3 cluminating a cost impact of Rs. 125 to 257 per tonne of

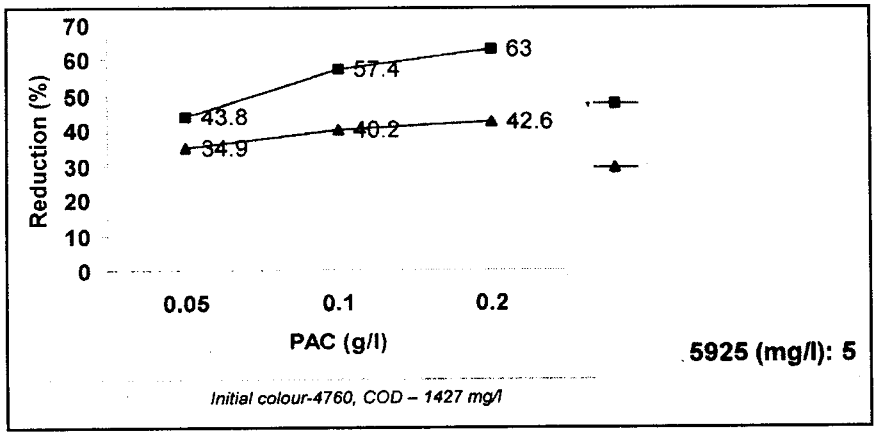


Fig. 5 Effect of coagulation-flocculation with PAC and synthetic polymers in unbleached effluent in Mill B

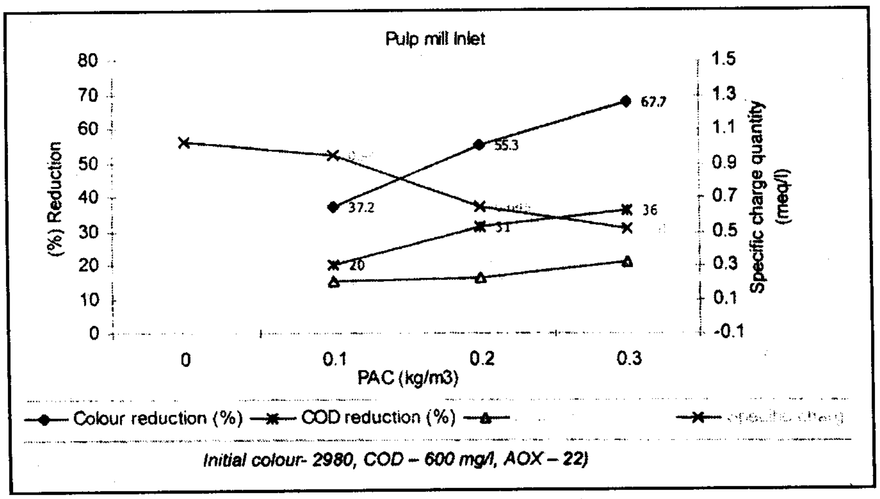


Fig. 6 Effect of coagulation-flocculation with PAC and synthetic polymers in whole pulp mill effluent in Mill B

paper (Table 6).

CONCLUSIONS

Coagulation - flocculation with right chemical can give appropriate solution in reducing the colour, COD and AOX concentration in the final treated effluent with insignificant investment. As it is a physical treatment the pollutants will be transferred from liquid phase to solid phase which needs dewatering and proper disposal.

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Table 6

Cost of pollutants removal in Mill B

PAC dose (kg/m³)	Pollutants removal (kg)	Cost of treatment (Rs./m³)	Impact on cost of paper (Rs/t)
a. Unbleached stream			
0.05	2.08 colour + 0.50 COD	1.1	26
0.1	2.73 colour + 0.57 COD	1.5	35
0.2	3.0 colour + 0.61 COD	2.2	51
b. Whole pulp mill effluent			
0.1	1.11 colour + 0.12 COD + 0.0033 AOX	1.6	125
0.2	1.65 colour + 1.84 COD + 0.0035 AOX	2.45	190
0.3	2.02 colour + 0.216 COD + 0.0046 AOX	3.3	257