Application of Ultrafiltration and Nanofiltration Treatment for the Closure of E- Stage Bleaching Plant Effluent

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ABSTRACT

Pulp and paper industry is facing a major problem on account of increasing scarcity of water and stringent discharge norms introduced by Central Pollution Control Board (CPCB) in the form of CREP (Corporate Responsibility for Environmental Protection). Large proportion of water being discharged presently will have to be recycled back into the system at the appropriate intake points with/without treatment. Membrane filtration technology, particularly Ultrafiltration and Nanofiltration are being adopted increasingly in the paper mills for closing of process water streams. E- Stage bleaching effluent is very well suited for ultrafiltration process, because of its comparatively small volume and high molecular weight substances in it. In the present study, extraction stage (E- stage) bleach plant effluent was treated in the Ultrafiltration (UF) and Nanofiltration (NF) from the point of view of system closure. Concentrate of each stage is recycled back and permeate of ultrafiltration is fed to nanofiltration. Spiral wound polysulphone membranes were used for the purpose. The total membrane area was 2.51 m2. Molecular weight cut-off (MWCO) were 1000 Dalton and 300 Dalton, for UF and NF respectively. Inlet pressure was 200 psi for each membrane. Variation in inlet pressure and its relation with flow rate was also stabilized. Significant removal of COD, TDS, Color, AOX and Heavy Metals (Fe, Cu, Co, Cr, Ni, and Zn) was observed. The color removal is very high and permeate from nanofiltration can be recycled back in the system at appropriate point.

Key Wards: Membrane Filtration; Paper Mill Effluent; System Closure, Bleaching plant Effluent

Introduction

Paper mill effluent carries high pollution load in terms of suspended solids, COD, BOD, absorbable organic halides (AOX), toxicity, color and high concentration of nutrients that cause eutrophication in receiving water [Kunai et. al., 1986; Alvares et. at., 2001]. In view of the new stringent environmental norms from Central Pollution Control Board (CPCB) in the form of CREP (Corporate Responsibility for Environmental Protection), large proportion of water now being discharged will have to be recycled back in to the system at the appropriate in take points with/without treatment in paper industries. System closure in paper mill increases the concentration of suspended, dissolved and colloidal materials, which can affect the product quality and can cause operational problems. Hence, to close the water system, it is necessary to make water free from color, AOX, heavy metals and chemicals to the acceptable limits. Conventional end of the pipe line treatment consist of primary treatment based on sedimentation or flotation in clarifiers, followed by biological treatment, usually aerobic as secondary treatment.

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It results in high removal of SS and medium removal of BOD and COD [Thompson et al., 2001]. However, secondary treatment effluents still contain bio-refractory organic matter whose further removal requires a tertiary treatment. Application of ultrafiltration membrane technology is one such option which can improve the recycled water quality by removal of heavy metal contaminates, COD, TDS, AOX (Absorbable organic halides) and color.

E- Stage effluent is very well suited for ultrafiltration process because of its comparatively small volume and high molecular weight substances in it . Some extensive work has been done in removal of impurities from E- stage effluent through membrane filtration. Lundahl et. al. (1980) found 90% removal of color, 40% reduction in COD, and 10% reduction in BOD_7. Nystrijm et. al (1988) observed that sufficient chlorolignin removal can be achieved if ultrafiltration is carried out at pH 10, which is approximately the pH of the first caustic stage in the bleaching process. Jansson, A. S. (1987, 1989) observed that ultrafiltration of E- stage effluent can reduce TOCl (Total organic chlorides) by 60-80%, COD by 50-80%, AOX (absorbable organic halides) by 90%, color by 90%, BOD_7 by 25-50%. Rosa et. al. (1995) studied color removal experiment of E-stage effluent through ultrafiltration, and found 85% color removal by the ultrafiltration with a thin- film composite (TFC) membrane of 10.8 kDa, while total color removal was achieved using a TFC Nanofiltration membrane of poly (transe-2,5-dimethyl) piperazinthiofurazanamide. Greaves R., (1999) achieved 50% reduction in COD in oxygen bleaching by ultrafiltration in the pilot scale study. De Pinho et. al (2000) carried out flotation / ultrafiltration experiments to treat E1 stage effluent and achieved the removal efficiencies in terms of conductivity, TOC, color, TSS, 40%, 65%, 90%, and 100% respectively. Fredrik et. al. (2001) found that the retention of the substances causing the COD is approximately 40%. Dube et al. (2000) reported 88% and 89% removal of BOD and COD respectively by reverse osmosis (RO). Merrill et al. (2001) stated that membrane filtration (MF) and granular membrane filtration (GMF) was suitable for removing heavy metals from the pulp and paper mill wastewaters.

In the present study E- stage bleach plant effluent was treated in the Ultrafiltration (UF) and Nanofiltration (NF).The extraction -stage bleaching plant effluent was taken from an integrated paper mill employing conventional CEHH bleaching sequence for bleaching of hardwood pulp. Spiral wound membranes were used for the purpose. Total membrane area is 2.51 m^2. Membrane material is polysulphone/polyamide blend for both UF and NF. The molecular weight cut-off (MWCO) is 1000 Dalton for UF and 300 Dalton for NF.

2. Material and Methods:

Fresh samples were collected from E-stage bleaching plant effluent of an integrated paper mill and treated through membrane treatment plant. Pilot membrane treatment plant consists of Ultrafiltration and Nanofiltration membranes in series. Before introducing to ultrafiltration membrane, some primary treatments were applied as coagulation, bag filtration and microfiltration. The scheme is given in Fig 1.

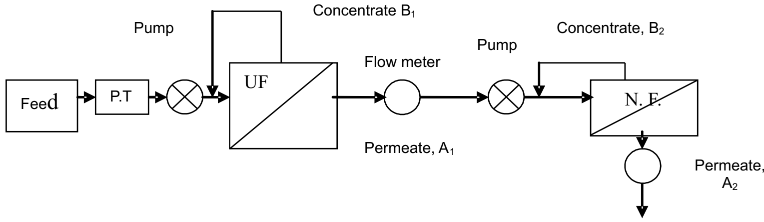

Fig:-1 Scheme of Pilot membrane treatment Plant

2.1 Pre treatment:

To minimize blocking of pores following pretreatment were applied before feed to UF.

2.1.1 Coagulation:

Coagulation and flocculation is normally employed in the tertiary treatment in the case of pulp and paper mill wastewater treatment and not commonly adopted in the primary treatment. Tong et al. (1999) and Ganjidoust et al. (1997) carried out a comparative study of horseradish peroxide (chitosan) and other coagulants such as ($Al_2(SO_4)_3$), hexamethylene diamine epichlorohydrin polycondensate (HE), polyethyleneimine (PEI), to remove absorbable organic halides (AOX), total organic carbon (TOC), and color. The authors indicated that modified chitosan was far more effective in removing these pollutants than other coagulants. Dilek and Gokcay (1994) reported 96% removal of COD from the paper machine, 50% from the pulping, and 20% for bleaching effluents by using alum as a coagulant. For the purpose 0.5 g/l coagulant ASCP (Trade name, procured from Aastropure, Electrosystes Pvt. Ltd. Naroda, Ahamedabad INDIA) was used and retention time given was 20 minutes. After the settling of solids for 20 minutes, effluent was fed to bag filtration and micro filtration.

2.1.2 Anti scaling agents:

For prevention of scale on the surface of membranes, antiscalant is used. In the present study, 6 ml/100 L sodium-hexa-meta-phosphate was used while adding coagulants.

2.1.3 Bag filtration and microfiltration:

After coagulation effluent was passed through bag filter and micro filter. Micro filtered water was collected in a tank and was fed to UF membrane plant.

2.2 Performance assessment of the membrane:

For the present study, polysulphone/polyamide blend thin film composite spiral bound membrane modules were used for ultrafiltration and nanofiltration. Detailed specifications are given in Table 1. Initial inlet pressure was 13.7 bar for both the membranes, while the feed temperature was 45 0C for UF and 40 0C for NF membrane experiment. Retentate of each experiment was recycled back to the feed and retreated till inlet pressure reached up to the maximum cut-off pressure for each membrane (indicated by the manufacturer). Ultrafiltration permeate was fed to the nanofiltration. After starting of the pilot plant, inlet pressures and outlet pressures were measured at every 5 minutes interval, and their corresponding permeate flow rates were also noted.

Performance of each membrane was assessed for each inlet pressure on the basis variation with respect to the time (increasing concentration of pollutants because of recycling) in trans-membrane pressure (Eq.no1) and permeate flux (Eq.no2).

Trans-membrane pressure in (bar)

$$= ((P_i + P_o)/2) \quad P_p \qquad (1)$$

Where Pi is inlet pressure, Po is outlet pressure, Pp is permeate pressure

Permeate Flux ($L\ m^{-2}\ h^{-1}$) = volume of permeate in the given time/ membrane area (2)

2.3 Water quality assessment:

Feed wastewater samples, the retentate samples and the permeate samples of the UF and NF were collected in clean and dry cans. All samples were analyzed for their ionic content (pH, Conductivity), total dissolved solids (TDS), chemical oxygen demand (COD, Hach reactor, dichromate oxidation method), Color (Hach DR/4000) and adsorbable organic

Table 1 Specifications of the membranes used in the study

Module	Membrane	Membrane material	MWCO	Area(m^2)	Manufacturer
UF, spiral bound	AP-01	Thin film polyamide/ polysulphone blend	1000 Da	2.51	Aastropure, India
NF, spiral bound	AP-02	Thin film polyamide/ Polysulphone blend	300 Da	2.51	Aastropure, India

halides (AOX analyzer ECS 1200 using column method), heavy metals i.e. Fe, Cu, Co, Cr, Ni, Zn (Atomic absorption spectrophotometer).

3. Results and Discussion:

3.1. Effect of inlet concentration:

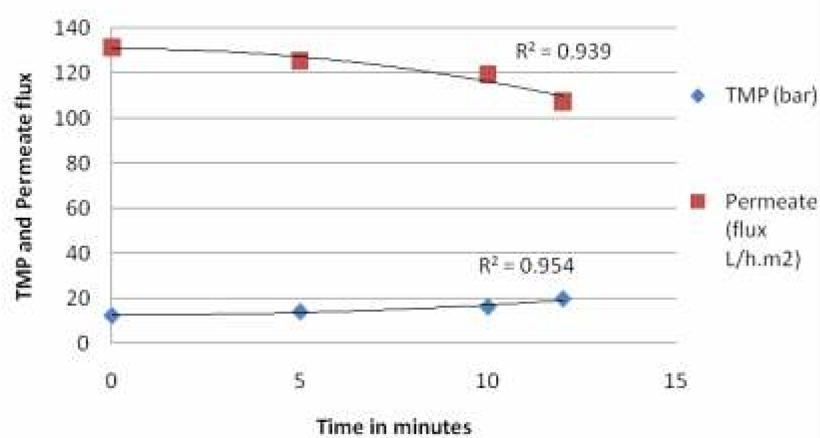

Fig:2 Variation in TMP and Permeate flux in UF

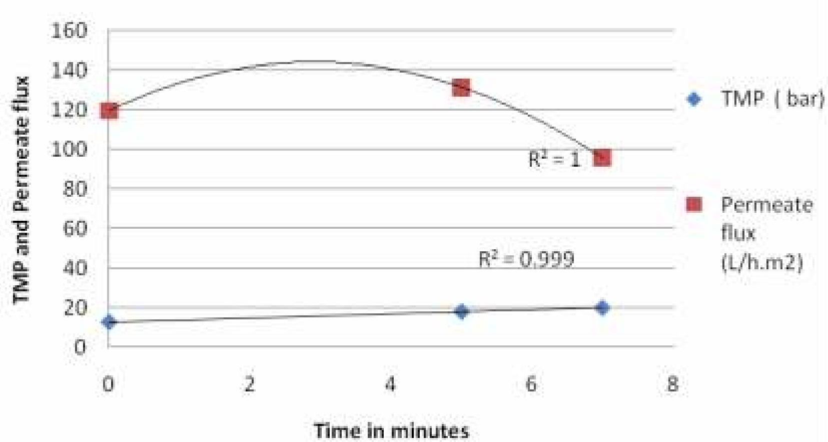

Fig:3 Variation in TMP and Permeate flux in NF

During the course of study, it was found that inlet pressure increases, while flow rate decreases with time for ultrafiltration. Trans membrane pressure increases slowly in the beginning then increases sharply, similarly permeate flux decreases slowly at the beginning afterwards sharp decline was observed as shown in Figure 2. This may be due to rise in the concentration of total dissolved solids due to recycling of concentrate. It shows that concentrate stream from ultrafiltration can not be recycled completely and part of it has to be purged.

It can be seen from Figure 3, that permeate flux increases first and then decreases very sharply, while the TMP increases steadily with time for nano filtration. As concentrate is recycled, it increases the TMP which initially improves the recovery but as the concentration increases beyond a certain limit, it offers resistance for filtration. The reason behind increasing initial permeate flux with increasing pressure may be deformation of pores too. Due to the initial pore blocking, inlet pressure increases and because small pore size has less capability to bear stress, pore size get changed, that shows initial increasing in permeate flux. After some time due to further increase in concentration of recycled feed, blockages increase again and permeate flux decreases.

3.1.2 Removal efficiency:

In the present study, COD and color removal by the ultrafiltration is 71% and 81% respectively as shown in the Figure 4. TDS removal was just 40.53 % which may be due to the fact that ultrafiltration removes high fraction. The color imparting high molecular weight dissolved organic compounds. AOX removal was 61.91%, while heavy metals Fe, Cu, Co, Cr, Ni and Zn removal were 63.21%, 59.45%, 39.47%, 95.45%, 38.29% and 43.39% respectively (Figure 4), Chromium removal after UF treatment was 95.45% and only 0.002 mg/l of Cr metal was observed in permeate (Table 2). Final concentration of Zn and Cu were also very less, that can be said encouraging.

Figure 5 shows that COD and color removal after the nanofiltration is 78.58% and 95.78% respectively, TDS removal was also 52%. AOX removal was 78.39%, while heavy metals Fe, Cu, Co, Cr, Ni and Zn removal was 71.78%, 81.08%, 51.31%,100%, 65.95% and 66.03% respectively, that can be said quite significant. It may be due to the fact that nanofiltration removes lower fraction than ultrafiltration. Cr and Cu removal were observed higher than other metals and in permeate of NF only 0.007 mg/l Copper and 0.00 mg/l Chromium were found, that is good indication for reusability of permeate (Table 3). The color removal is very high and permeates seams literally colorless. **4.**

Conclusion:

From the above discussion, it can be concluded that for both the membranes, trans-membrane pressure increases while permeate flux decreases with time, as the inlet concentration of the membrane is continuously increasing because of continuous recycling of concentrate. Therefore 100% recycling and complete recycling without any intermediate treatment stage closure of the bleach plant is not possible. During the course of study, removal efficiency of UF was 71% and 81% for COD and color respectively. AOX removal was 61.91%. COD and color removal after the nanofiltration was 78.58% and 95.78% respectively, TDS removal was also 52%. AOX removal was 78.39%, while heavy metals Fe, Cu, Co, Cr, Ni and Zn removal were 71.78%, 81.08%, 51.31%,100%, 65.95% and 66.03% respectively. Cr and Cu removal were observed higher than other metals and

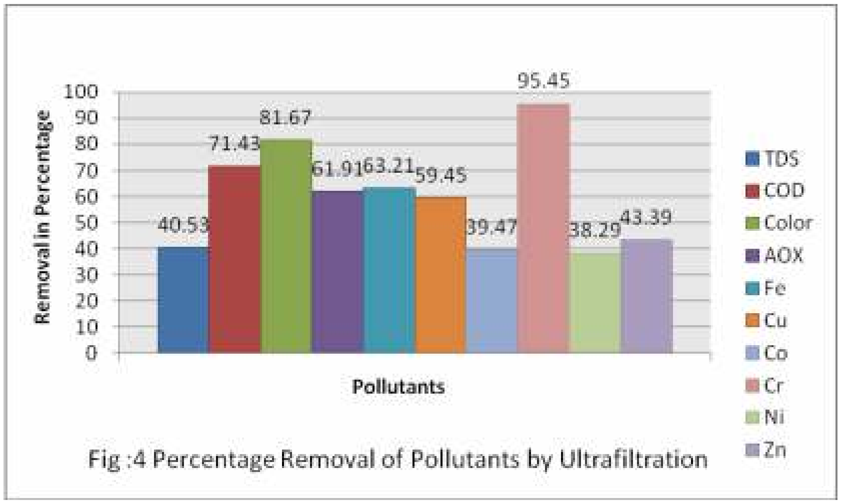

Fig :4 Percentage Removal of Pollutants by Ultrafiltration

Table: 2 Variation in different parameters in treatment of E-stage effluent through Ultrafiltration Treatment

Pollutants	Feed (UF)	Permeate (UF)	Concentrate (UF)
pH	10.96	10.96	10.84
Conductivity (m.mho)	3.75	2.23	9.5
TDS (mg/l)	3750	2230	9500
COD (mg/l)	4166	1190	9523
Color (mg/l)	442	81	1123
AOX (mg/l)	33.37	12.71	77.64
Fe (mg/l)	0.528	0.194	0.774
Cu (mg/l)	0.037	0.015	0.069
Cr (mg/l)	0.044	0.002	0.021
Co (mg/l)	0.076	0.046	0.119
Ni (mg/l)	0.047	0.029	0.062
Zn (mg/l)	0.106	0.06	0.203

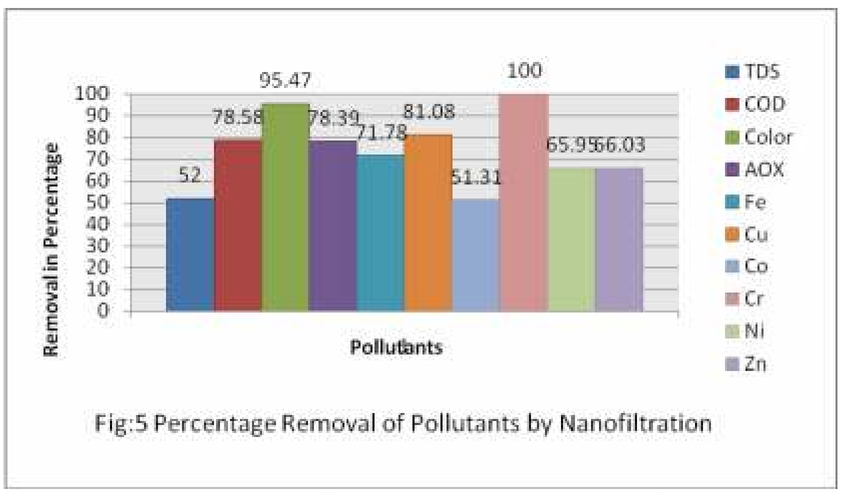

Fig:5 Percentage Removal of Pollutants by Nanofiltration

Table: 3 Variation in different parameters in treatment of E-stage effluent through Nanofiltration Treatment

Pollutants	Feed (NF)	Permeate (NF)	Concentrate (NF)
pH	10.96	11.01	10.89
Conductivity (m.mho)	2.23	1.8	4.3
TDS (mg/l)	2230	1800	4300
COD (mg/l)	1190	892	3273
Color (mg/l)	81	20	234
AOX (mg/l)	12.71	7.21	82.09
Fe (mg/l)	0.194	0.149	0.395
Cu (mg/l)	0.015	0.007	0.051
Cr (mg/l)	0.002	ND	0.038
Co (mg/l)	0.046	0.037	0.192
Ni (mg/l)	0.029	0.016	0.063
Zn (mg/l)	0.06	0.036	0.092

in permeate of NF only 0.007 mg/l Copper and 0.00 mg/l Chromium were found, that is a good indication for reusability of permeate. Though results are encouraging but as at 13.7 bar initial inlet pressure membranes shows rapid increase in TMP and decline in permeate flux, so further studies are needed at lower pressures to stabilize optimum initial inlet pressure for long run of system.

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