Application of Membrane Filtration for Reuse of Bleaching Plant Effluent in the Process

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Abstract:

Membrane filtration technology is 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 of an integrated paper mill employing CEH bleaching sequence for bleaching of hardwood pulp was treated in the Ultrafiltration (UF), Nanofiltration (NF) and Reverse osmosis (RO) in series. Concentrate of each stage is recycled back and permeate of ultrafiltration is fed to nanofiltration, and permeate of nanofiltration is fed to RO. Molecular weight cut-of (MWCO) were 1000, 300 and 50 Dalton, for UF, NF and RO respectively. Initial inlet pressure was 6.8 bar for UF, NF and 10.3 bar for RO. All membranes performed well as per expectation and water recovery was 86.4 %, 95.28 % and 95.95 % for UF, NF and RO membrane respectively.

Key Words: Membrane Filtration; E-stage Effluent; System Closure, Bleaching plant Effluent

1. Introduction:

The water processed in pulp and paper industries cannot be recycled, because some of its components are enriched, causing either direct or indirect problems. Slime and deposit formations, which affect the paper quality, are some of these problems. Therefore, specific purification technologies are required (J. Nuortila-Jokinen, M. Nyström, 1996). Membrane filtration is being adopted increasingly in the paper mills for closing their mill process water. Application of membrane technology is one such option which can improve the recycled water quality by removal of heavy metal contaminates, COD, TDS, AOX (Adsorbable organic halides) and color.

This shall reduce the load on conventional recovery evaporation system with no significant loss of inorganic compounds.

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 H. et. al. (1980) found total removal of color 90%, 40%, reduction in COD, and 10% reduction in BOD_7. M. 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 bleach process.

Jansson, A. S. (1987, 1989) observed that ultrafiltration of plant E- stage effluent contribute 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 efficiency 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. Richard Greaves (1999) achieved 50% reduction in COD in oxygen bleaching by ultrafiltration in the pilot scale study. De Pinho M.N. et. al (2000) carried out flotation / ultrafiltration experiments to treat E_1 stage effluent and achieved the removal efficiencies in terms of conductivity, TOC, color, TSS, 40%, 65%, 90%, and 100% respectively. Fredrik Filth, et. al. (2001) found that the retention of the substances causing the COD is approximately 40%. Dube et al. (2000) reported that 88% and 89% removal of BOD, and COD, respectively was achieved 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), Nanofiltration (NF) and Reverse osmosis (RO). The extraction -stage bleaching plant effluent was taken from an integrated paper mill. The CEH sequence is being used 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 for UF, NF and polyamide used in RO. The molecular weight cut-off (MWCO) is 1000 Dalton for UF, 300 Dalton for NF, and 50 Dalton for RO.

2. Material and Methods:

In the present study extraction- stage bleaching effluent was taken from an integrated paper mill employing conventional CEH sequence for bleaching of hardwood pulp Effluent was treated in a system consisting of Ultrafiltration (UF), Nanofiltration (NF) and Reverse osmosis (RO) membrane modules in series, specifications are given in Table 1. Before introducing the effluent to the ultrafiltration membrane, some primary treatments were applied as coagulation, bag filtration and microfiltration. Scheme of the treatment is given in Fig.1.

2.1 Pre treatment:

In most cases when membrane filtration is used it cannot be used without some kind of pretreatment of the feed. The reason is that the feed channels in the modules get blocked in most types of elements. Especially spiral modules are very sensitive to this type of blocking. In order to avoid this different types of pretreatments or pre-filters have to be used, (Cactus 1, 1998-2000). 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 adsorbable 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, electrosystems Pvt. Ltd. Naroda, Ahmedabad 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 scale on surface of membranes anti-scalant is used. In the present study 6 ml/100L sodium-hexa-meta-phosphate was used while adding coagulants.

2.1.3 Bag filtration and microfiltration:

The solid particles are harmful to the membrane process. They are removed by the pretreatment screen filters like bow screen, multilayer filter, sand filter, bag filter (MF). 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 Membrane experiments:

Membrane treatment experiments were performed for the similar kind of effluent at room temperature. For ultrafiltration and nanofiltration treatment, initial inlet pressure was 6.8 bar and for reverse osmosis treatment 10.3. Retentate of each experiment was recycled back to the feed and retreated till inlet pressure increased up to the maximum cut-of pressure for each membrane (indicated by the manufacturer). Ultrafiltration permeate was fed to the nanofiltration, and permeate of nanofiltration was again fed to the reverse osmosis as shown in Fig 1.

2.3 Water quality assessment:

Feed wastewater samples, the retentate samples and the permeate samples of the UF, NF and RO were collected in clean and dry canisters. All samples were analyzed for their ionic content (pH, Conductivity), total dissolved solids (TDS), total suspended solids (TSS), chemical oxygen demand (COD, Hach reactor**,** dichromate oxidation method), Color (Hach DR/4000) and adsorbable organic halides (AOX analyzer ECS 1200 using column method).

2.4 Membrane performance assessment:

Performance of each membrane was assessed with time for each initial inlet pressure on the basis of variation in the three parameters namely, trans-membrane pressure (Eq.no1), permeate flux (Eq.no2).

$$\text{Trans-membrane pressure in (bar)} = Pi + Po/2 - Pp \quad (1)$$

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

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

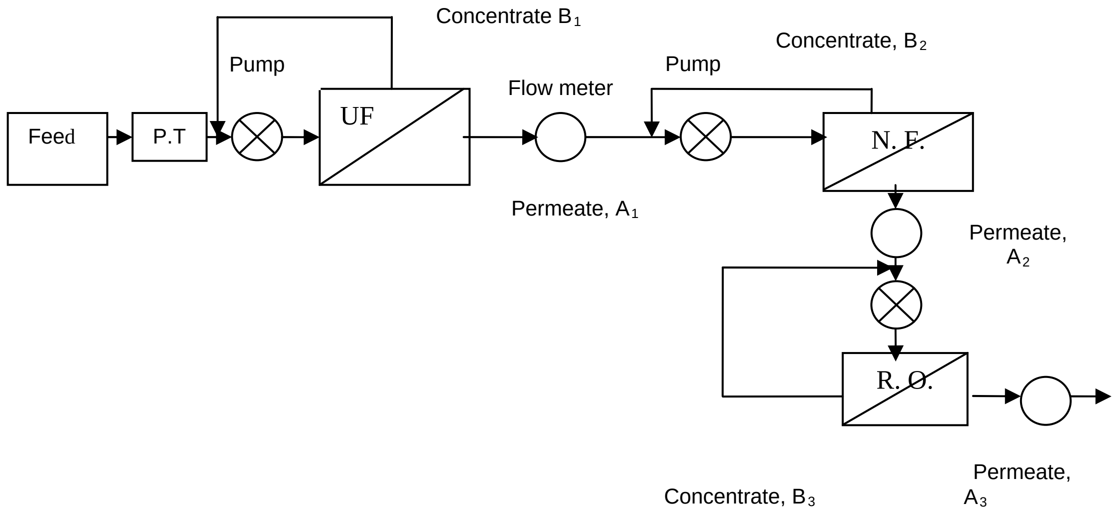

Fig: 1 Scheme of Pilot membrane treatment plant

Abbreviations:
P.T.: primary treatment unit, UF: ultrafiltration, NF: nanofiltration, RO: reverse osmosis

Table 2 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
RO, spiral bound	AP-03	Thin film Polyamide	50 Da	2.51	Aastropure, India

3. Result and Discussion:

3.1. Pollutants removal:

It can be seen from the figure: 2 that COD and color removal from the ultrafiltration is 50% and 84.34% respectively and 86.85% TSS removal was observed which are very good. TDS removal was just 40.05% which may be due to the fact that ultrafiltration removes high fraction. The color importing high molecular weight dissolved organic compounds. AOX removal was 38.62% observed.

It can be seen from the figure: 3 that COD and color removal after the nanofiltration is 77.1% and 96.79% respectively. 95.7% TSS removal was observed, TDS removal was also 70.83 %. AOX removal was 88.94%. The color removal is very high and permeates seams literally colorless.

It can be seen from the figure: 4 that TDS and AOX removal after the reverse osmosis were 99.77% and 98.51% respectively, which is excellent. All other pollutants like TSS, COD and Color removal was found to be 100%. Permeate seems transparent after the treatment, and it can be recycled at adequate point.

3.2 Membrane performance:

During the course of study it was found that TMP increases slowly for each membrane (Fig; 5, 6, 7). In the RO TMP was found more stable than UF and NF at this particular initial inlet pressure. TMP in the membranes shows linear pattern. Permeate flux decreases rapidly in UF treatment and shows linear pattern, in the NF membrane, initially permeate flux was stable, which slowly decreases later, it also shows linear pattern. As far as RO membrane is concerned permeate flux is almost stable initially but after some time of run rapid decrease was observed, and shows polynomial pattern. As retentate is being recycled and mixed to the feed so it increases the trance – membrane pressure, and due to concentration polarization decline in permeate was observed for each membrane.

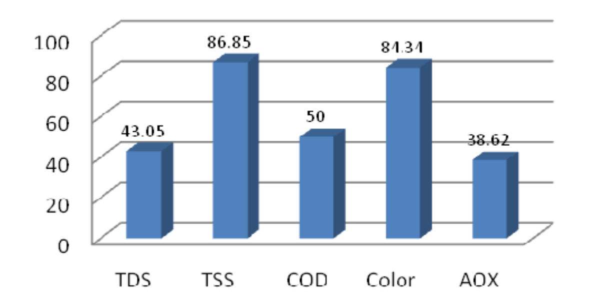

Fig: 2 Percentage removal of pollutants after UF treatment

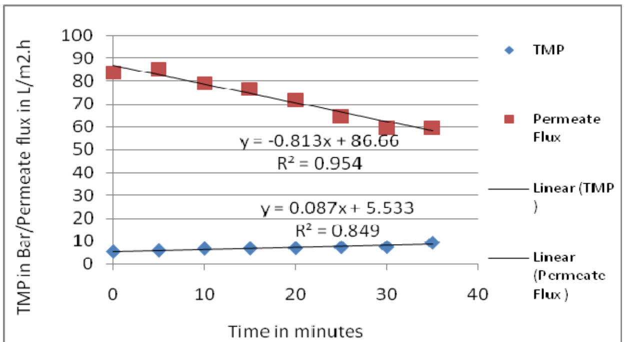

Fig: 5 Variation in TMP and Permeate flux with time in UF membrane

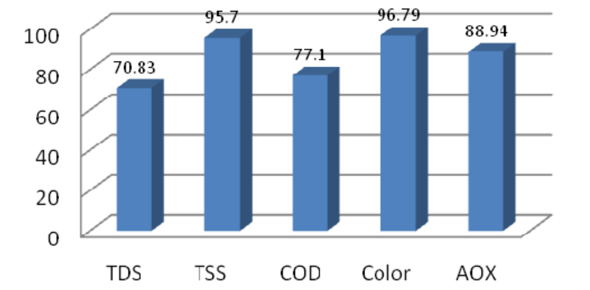

Fig: 3 Percentage removal of pollutants after NF treatment

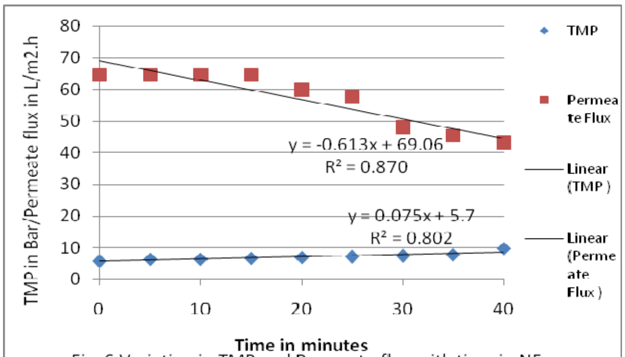

Fig: 6 Variation in TMP and Permeate flux with time in NF membrane

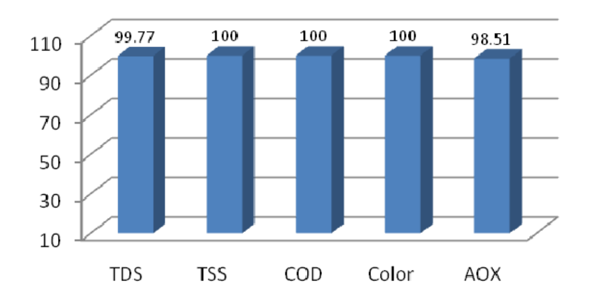

Fig: 4 Percentage removal of pollutants after RO treatment

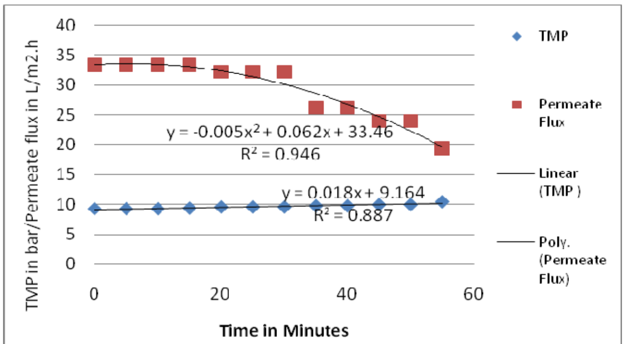

Fig: 7 Variation in TMP and Permeate flux with time in RO membrane

4. Conclusion:

During the course of study removal efficiency of UF, removal of COD, TSS and color was 50%, 86.85% and 84.34% respectively. TDS and AOX removal is not very good in that particular treatment. After NF treatment COD, TSS and color removal was 77.1%, 95.7% and 96.79% respectively. TDS removal was also 70.83 %. AOX removal was 88.94%. Nanofiltration has smaller pore size than UF that is 300 Da make it more efficient for removal of TDS and AOX. Whereas after RO treatment TDS and AOX removal was 99.77% and 98.51% respectively, that can be said excellent. All other pollutants like TSS, COD and Color removal was found to be 100%. TMP in the all studied membranes was found almost stable. Slow decrease in permeate flux was observed at 6.8 bar initial inlet pressure for UF and NF and at 10.3 bar initial inlet pressure for RO. As for as reusability of E- stage treated water is concern membrane treatment is best available process, one hand it removes organic matters like COD and AOX and other hand it removes solid like TDS and TSS significantly. After the treatment water recovery was 86.4 % for UF 95.28 % for NF and 95.95 % for RO membrane respectively. Permeate seems transparent after the treatment, and it can be recycled at adequate point.

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