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Treatment of combined bleaching effluent by membrane filtration technology for system closure in paper industry

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ABSTRACT

This study has been carried out for the treatment of combined bleaching effluent of an Indian pulp and paper mill. The Chlorination, extraction, Hypo-1 & Hypo-2 (CEHH) sequence is being used for the bleaching of hardwood pulp in the mill. Effluent was treated by the Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO). Thin film composite spiral-wound modules, having crass flow membranes made-up by polysulphone and polyamide were used in the study. Three initial inlet pressures were 6.8 bar, 10.3 bar and 13.7 bar for UF and NF. For RO initial inlet pressures of 10.3 bar, 13.7 bar and 17.2 bar, were taken in different trials. Retentate of each experiment was recycled back to the feed and retreated till the inlet pressure increased up to the maximum cut-of pressure for each membrane. Ultrafiltration permeate was fed to the nanofiltration, and permeate of nanofiltration was again fed to the reverse osmosis. Variations in Trans Membrane Pressure (TMP) and permeate flux were assessed. Pollutants removal and fouling indexes were obtained for each membrane at each initial inlet pressure.

Keywords: Membrane filtration; Bleaching plant effluent; Paper industry; Closed water circuits

1. Introduction

The fresh water consumption of a paper mill can be reduced significantly by recycling suitable process water and effluents. Prior to reuse, these water fractions must be sufficiently treated in order to avoid different kinds of problems in paper making. This internal treatment can be done by membrane filtration which is one of the most competitive and environmentally friendly techniques available and has already been proven to be successful in various different pulp and paper industry applications even on mill scale [1].

Application of membrane technology is one such option which can improve the recycled water quality by removal of chemical oxygen demand (COD), total dissolved solids (TDS), Adsorbable organic halides (AOX) and color. The major restraints, however, in applying membrane filtration to applications in which large volumes of water are treated are the need for large membrane area and the flux decline due to fouling, both of which directly affect the economics of a membrane plant. The membrane module used in such an application in the pulp and paper industry should be small in size and still capable of economically producing fluxes high enough to satisfy the fresh water need. The reported studies on the applications of membrane filtration in the pulp and paper industry have mainly been focused on pulp mill effluent, pulp bleaching and coating color effluents [2–4]. Also some studies on membrane fouling with the pulp mill

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effluents have been done [5,6]. Rune Glemenius [7] observed that the total solids in the bleach effluent are normally around 0.7% and the liquor can be concentrated up to 25–50 times by UF. Even if only 50% of the total solids are kept in the concentrate, 90% of the color is retained. Zaidi et al. [8], Afonso and Pinho [9], Falth [10], compared the efficiency of (i) ultrafiltration and (ii) ultrafiltration plus dissolved air flotation for bleach plant effluent. The results showed 54%, 88%, 100% removal of TOC, color, and SS, respectively by ultrafiltration alone. Ultrafiltration plus dissolved air flotation resulted in 65%, 90% and 100% removal of TOC, color, and SS, respectively. Merry Alan [11] achieved 50% of the target reduction in the COD with a 98% reduction in volume of combine bleach plant effluent of the soft wood pulp, with a polyethersulphone ultrafiltration membrane. Meuller et al. [12] concluded that about 50% of the bleach plant COD, BOD and color will be returned to the recovery system, but less than 20% of Ba, Ca, Fe, Mg, and Mn and about 35% of the oxalate will be recirculated after using ultrafiltration. Also only about 5% of the total chloride will be returned and with the eucalyptus effluents AOX and COD reductions of about 80% and 70% respectively were obtained. Anna-Karin et al. [13] observed that the change in original design parameter can improve the performance of membrane and increase the flux. It was observed that increasing the inlet pressure from 0.7 MPa to 1.1 MPa in the last stage would increase the average flux in the last stage around 2.5 times.

Present study is mainly focused on membrane filtration of combined bleaching effluent of an Indian integrated paper mill employing conventional CEHH sequence for bleaching of hardwood pulp, using thin film composite spiral wound membrane modules in series (UF, NF, RO). Effect of pressure on pollutants removal efficiency, permeate flux and fouling of membranes were studied. Attempt has been made to treat the effluent in recycling mode to recover as much as possible water, and obtain the minimum concentrate after treatment.

2. Material and methods

In the present study combined bleaching effluent was taken from an integrated paper mill employing conventional CEHH sequence for bleaching of hardwood pulp. Characteristics of the combined bleaching effluent are given in Table 1. Raw effluent shows lot of variation in terms of pollutants. COD varies between 2,500 and 4,761 mg/l; AOX varies between 26.67 and 43.39 mg/l, all other parameters have also show remarkable variation. Variation in the pollutants in the effluent is depends on raw material, process of operation and climatic condition. In India majority of integrated paper mills use eucalyptus, bamboo and popular as raw material. Physico-chemical properties of wood depend on climatic condition and geography of the region, where they grow. Being a tropical country, India has wide variation in climate and weather condition that affects quality of wood and ultimately quality of effluent. In India majority of mills are applying conventional CEHH sequence for bleaching. So, Studies of other countries cannot be applied in Indian mill without any pre-analysis. Present study was done in the Indian conditions so it can be more useful for the Indian pulp and paper mills. This is the soul of this study.

Table 1
Characteristics of the combined bleaching effluent

Effluent	Raw effluent	After pre-treatment
pH	6.66–6.88	6.37–6.6
TDS, mg/l	3,000–4,800	2,100–3,900
COD, mg/l	2,500–4,761	1,369–976
Color, Pt-Co unit	1,180–1,330	170–580
AOX, mg/l	26.67–43.39	14.43–29.66

Effluent was treated in a system consisting of Ultrafiltration (UF), Nanofiltration (NF) and Reverse osmosis (RO) membrane modules in series with 1,000 Da, 300 Da and 50 Da molecular weight cut-off (MWCO) respectively. Membrane specifications are given in Table 2. 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 pre-treatment of the feed. The reason being 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 pre-treatments or pre-filters have to be used [14]. In the present study following pretreatments were applied before feed to the 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. [15] and

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	1,000 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

Ganjidoust et al. [16] 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 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 [17] 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 of 20 min was used. After the settling of solids for 20 min, effluent was fed to bag filtration and micro filtration.

2.1.2. Anti scaling agents

For the prevention scale on the surface of membranes, anti-scalant is used. In the present study 6 ml/100 L sodium-hexa-meta-phosphate was used as anti-scalant and added with coagulants.

2.1.3. Bag filtration and microfiltration

After coagulation effluent was passed through bag filter and micro filter (pore size 2 micron). Micro filtered water was collected in a tank and was fed to UF membrane plant.

2.2. Membrane experiments

Three experiments were performed for the similar kind of effluent at room temperature. Three experiments were performed for the combined bleach effluent at room temperature. Each membrane was stabilized with fresh water for 30 min before treatment. For ultrafiltration and nanofiltration treatment, initial inlet pressure was varied from 6.8 bar, 10.3 bar and 13.7 bar for 1st, 2nd and 3rd experiments respectively. 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. For reverse osmosis treatment inlet pressure

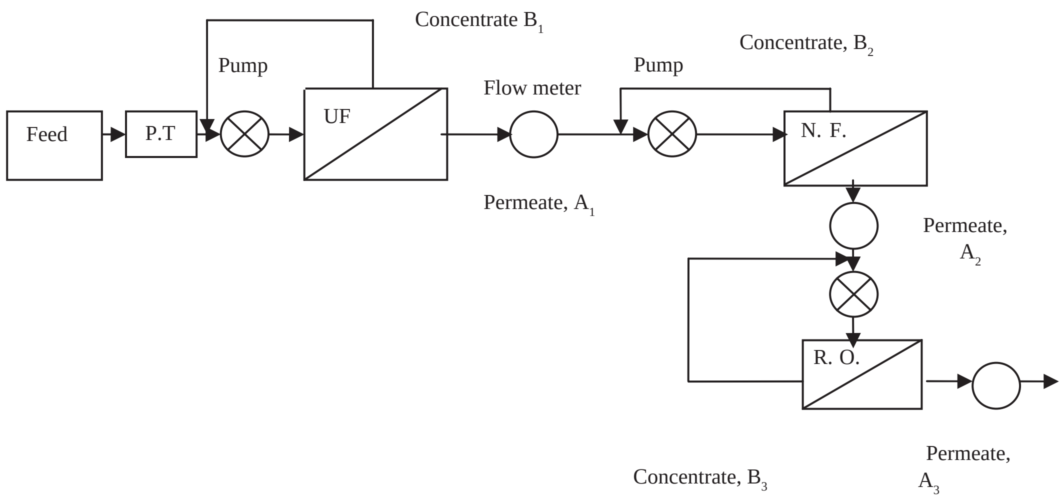

Fig. 1. Scheme of Pilot membrane treatment plant. Abbreviations: P.T.: primary treatment unit, UF: ultrafiltration, NF: nanofiltration, RO: reverse osmosis.

was taken 10.3 bar, 13.7 bar and 17.2 bar for I, II and III experiments respectively. All other conditions remained same as UF and NF treatment.

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), TDS, 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. (1)), permeate flux (Eq. (2)) and fouling index (Eq. (3))

$$\text{Transmembrane pressure in (bar)} = [(\text{Pi} + \text{Po})/2] - \text{Pp} \tag{1}$$

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

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

$$\text{Fouling index } J_t = J_0 e^{-bt} \tag{3}$$

Where b is the fouling index (min^{-1}), J_0 is the initial permeate flux (L m^{-2} h^{-1}) and J_t is the permeate flux at time *t* (L m^{-2} h^{-1})

3. Results and discussion

3.1. Membrane performance

The performance of ultrafiltration membrane is better at low initial inlet pressure. It can be seen from Fig. 2 that at low pressure (6.8 bar) increase in TMP is very small in comparison to the higher pressures (10.3 and 13.7 bar). Although permeate flux is almost double at high pressure (13.7 bar), in comparison to low pressure (6.8 bar) initially, but at low pressure permeate flux remains almost constant, while it decreases rapidly at higher pressure. It can be seen that after some time of operation, permeate flux at low pressure becomes equal or even more than permeate flux at high pressure (Fig. 3). Nanofiltration shows increase in the TMP in the beginning and almost stable permeate flux at all studied initial inlet pressures (Figs. 4 and 5). In the reverse osmosis rapid advancement in TMP and fall in the permeate flux was observed at all the three initial inlet pressures i.e. 10.3 bar, 13.7 bar, 17.2 bar (Figs. 6 and 7). In the RO permeate flux at low pressure becomes equal to the permeate flux at higher pressure after some time of operation. As RO has small MWCO of 50 Da and retentate is completely recycled with 100% TDS removal, rapid increase in TMP and rapid decrease in permeate flux results.

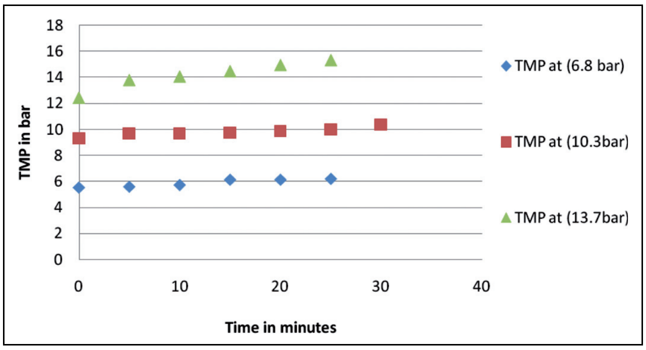

Fig. 2. Pattern of TMP in different initial inlet pressure (UF).

3.2. Fouling index

Fouling indexes were calculated for each membrane at all the three inlet pressures and are shown in Table 3. Fouling indexes are found to be higher at higher pressures for all the membranes except NF. At higher pressure more effluent is passed through the membrane in a particular time, which increases concentration polarization on the membrane surface and shows higher fouling index. Nanofiltration showed negative fouling index at the highest pressure, may be due to the fact

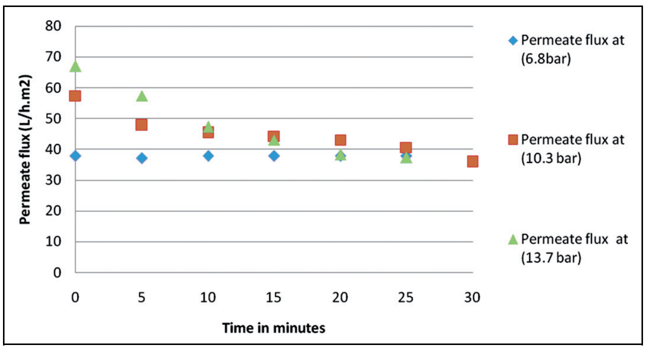

Fig. 3. Pattern of permeate flux in different initial inlet pressure (UF).

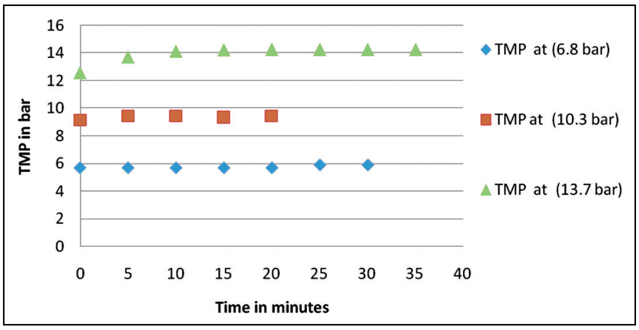

Fig. 4. Pattern of TMP in different initial inlet pressure (NF).

that at very high pressure some blockage which might have been present initially have been removed and this results in slight increase in flux. Among all three membranes, fouling indexes were found to be more in RO and least in NF.

3.3. Pollutants removal

During the course of study, individual removal of pollutants in ultrafiltration at 6.8 bar pressure was 14.2% for TDS, 80% for COD, 52.9% for color and 10.46% for AOX as shown in Fig. 8. At 10.3 bar initial inlet pressure, removal was 12% for TDS, 66.6% for COD, 22.41% for color, and 15.77% for AOX (Fig. 8). At the initial inlet pressure of 13.7 bar, pollutants removal was 7.8% for TDS, 24.98% COD, 25.45% color and 3.43% AOX as illustrated in Fig. 8. Results show that though removal of all pollutants decrease with increase in the pressure. Individual removal in nanofiltration is 33.33% for TDS, 50% for COD, 25% for color and 48.37% for AOX was observed at 6.8 bar initial inlet pressure (Fig. 9). At 10.3 bar initial inlet pressure, TDS removal was 23%, 25.0% for COD, 73.3% for color and 41.4% for AOX observed (Fig. 9). At 13.7 bar initial inlet pressure removal was 20% for TDS, 66.6% for COD, 92.68% for color, 62.7% for AOX observed (Fig. 9). Results show that removal of pollutants increases as

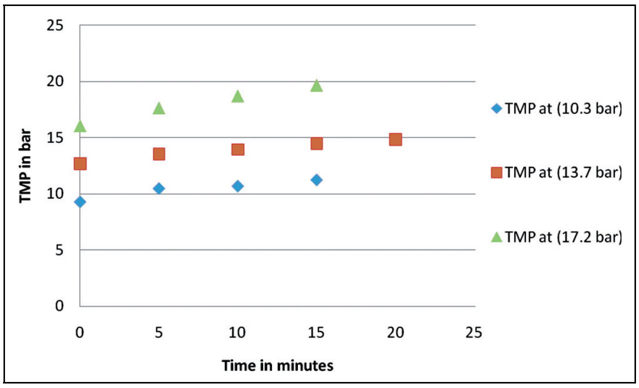

Fig. 6. Pattern of TMP in different initial inlet pressure (RO).

pressure increases except for TDS in the case of nanofiltration treatment. As far as removal in RO is concerned TDS and color removal was 100% in all the three experiments (At initial inlet pressure 10.3 bar, 13.7 bar and 17.2 bar, respectively). Whereas COD removal was 89.91%, 56.25%, 50% for all the three pressures respectively. AOX removal was 70.16%, 98.0% and 83.7% for all the three pressures (Fig. 10). Water recovery was found to be 94.4% for UF, 92% for NF and 90% for RO at lowest pressure, At 10.3 bar pressure for UF water recovery was 91.58%, at 10.3 bar pressure in NF water recovery was 90.96% and at 13.7 bar pressure for RO water recovery of 88.5% was observed. However at initial inlet pressure of 13.7 bar, water recovery was 86.36% for UF; 81.03% for NF and at 17.2 bar initial pressure, water recovery was 87.5% in the case of RO membrane. As results show, water recovery is high at low initial inlet pressure and less at high initial inlet pressure for each membrane.

As far as cumulative removal of pollutants after each treatment is concerned, removal at two pressures i.e. 6.8 bar and 13.7 bar for UF, NF, and 10.3 and 17.2 bar for RO were studied. After ultrafiltration treatment 40% TDS, 87.4% COD, 93.2% color and 51.5% AOX removal

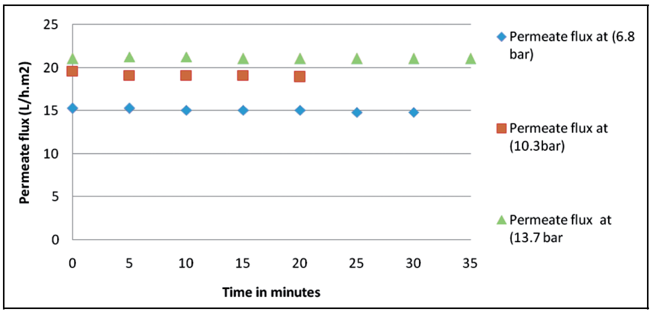

Fig. 5. Pattern of permeate flux in different initial inlet pressure (NF).

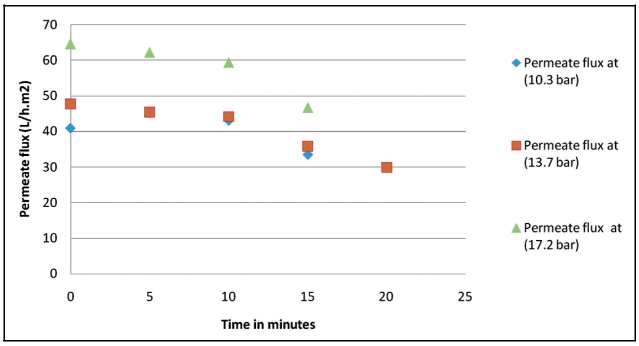

Fig. 7. Pattern of permeate flux in different initial inlet pressure (RO).

Table 3
Fouling indexes (Min^{-1}) for each membrane in each initial inlet pressure

Module	Initial inlet pressure in bar			
	6.8	10.3	13.7	17.2
UF, AP-01	0.01×10^{-2}	1.57×10^{-2}	1.73×10^{-2}	–
NF, AP-02	0.10×10^{-2}	0.18×10^{-2}	-0.062×10^{-2}	–
RO, AP-03	–	1.33×10^{-2}	2.35×10^{-2}	2.17×10^{-2}

was observed when initial inlet pressure was 6.8 bar, as shown in Table 4. At initial inlet pressure of 13.7 bar, pollutants removal was 27% for TDS, 62.5% for COD, 69.1% for color and 30.2% for AOX, as illustrated in Table 4. After nanofiltration 53.3% TDS, 93.7% COD, 94.9% color and 74.9% AOX removal was observed at the initial inlet pressure of 6.8 bar (Table 4). At the initial inlet pressure of 13.7 bar, 41.66% of TDS, 87.5% COD, 97.7% color, 74% AOX removal was observed (Table 4). As far as removal in RO is concerned TDS, and color removal was 100% at both the initial pressures i.e. 10.3 bar, and 17.2 bar, whereas COD removal was 99.3% and 93.7% for both the pressures respectively. AOX removal was 92.5%, and 95.7% at 10.3 bar and 17.2 bar pressures respectively (Table 4).

4. Conclusion

As shown by the results, almost all the pollutants removal is high in the low pressure and less in the higher pressure in ultrafiltration, which shows higher removal at higher pressure. Permeate flux and TMP is almost stable at 6.8 bar pressure, whereas initial higher permeate flux was obtained by applying high pressure which comes similar to low pressure after some time of operation. In the case of NF and UF, more removal in pollutants was observed at high pressure. COD removal decreases at high pressure in the case of RO. Among all membranes, NF has shown most stable water flux, and TMP and RO have shown least stable water flux, and TMP. By comparison of the performance of all the membranes, fouling indexes were found to be higher in RO and least in NF. As far as removal of

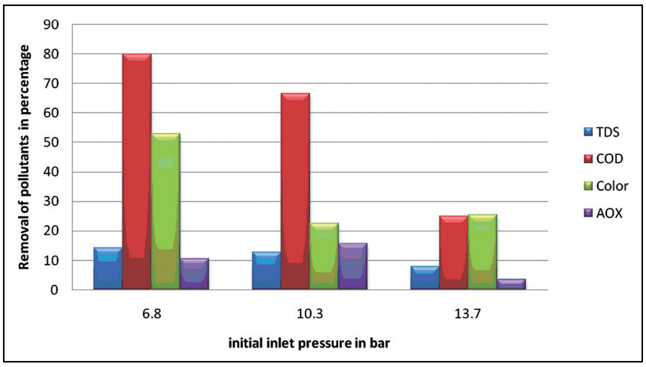

Fig. 8. Percentage removal of pollutants at different initial inlet pressure in the ultrafiltration treatment of combined bleach plant effluent.

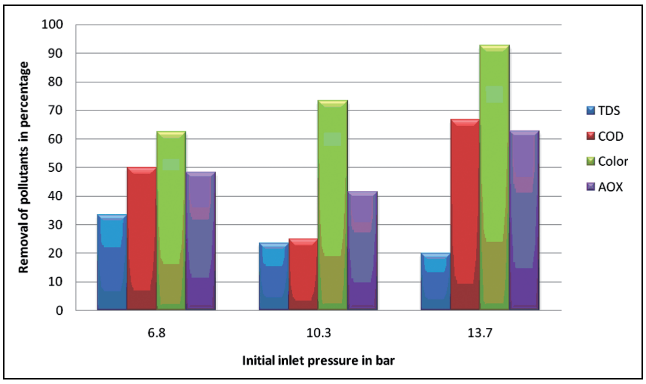

Fig. 9. Percentage removal of pollutants at different initial inlet pressure in the nanofiltration treatment of combined bleach plant effluent.

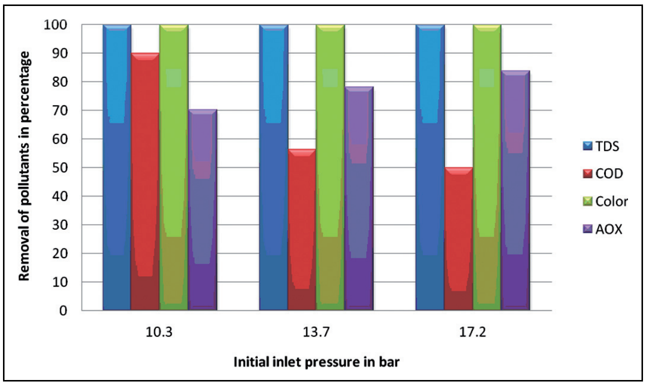

Fig. 10. Percentage removal of pollutants at different initial inlet pressure in the reverse osmosis treatment of combined bleach plant effluent.

Table 4
Cumulative removal of pollutants in percentage after each treatment for each pressure

Treatment	Pre-treatment		Ultrafiltration		Nanofiltration		Reverse osmosis	
Pressure (bar)	–	–	6.8	13.7	6.8	13.7	10.3	17.2
TDS	30	20.8	40.0	27	53.3	41.6	100	100
COD	37.4	50	87.4	62.5	93.7	87.5	99.3	93.7
Color	85.5	58.6	93.2	69.1	94.9	97.7	100	100
AOX	45.8	27.8	51.5	30.2	74.9	74	92.5	95.7

pollutants by the membrane treatment is concerned, it depends on the membrane pore size, concentration of pollutants in the feed as well as operating pressure. More water recovery was also observed at low initial inlet pressure than at high initial inlet pressure.

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