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RESEARCH ARTICLE

TANNERY WASTEWATER MANAGEMENT AND SALT RECOVERY BY REVERSE OSMOSIS SYSTEM

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ABSTRACT

The attitude of an industry towards environment protection is influenced by the manner its constituents are organized. Dominated by small-scale units, with limited technical expertise and financial resources, the tanning industry is insular by nature. To address these issues, a study with pilot plant results were addressed to identify the reasons for high organics, particularly, the COD in the treated effluent remaining higher than the desired limits of membrane manufactures. Also understand the effectiveness of various tertiary treatment systems on different types of tannery effluents to produce the effluent with characteristics fit for the RO membranes. Based on the results the effectiveness and impact of varying operational parameters of different RO membranes are discussed

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INTRODUCTION

In arid countries and specifically in the tropical zone of South and East Asia scarcity of fresh water of good quality is emerging as a major challenge. Ever dwindling reserve of surface and groundwater on hand and exponentially increasing demand for water due to population explosion and per capita water usage increase on the other present a bleak picture. When whatever little reserve available gets contaminated and become unusable due to discharge of polluted industrial effluents into it, the situation becomes catastrophic (Subramanian 2000; James *et al.*, 2006). Unlike organic contamination which indeed has a potential to redeem itself through inherent microbial activity, salinization of water is irreversible and therefore warrant urgent attention. Tannery effluent, even after treatment, contains TDS at levels in the range 8,000 mg/l to 18,000 mg/l, often with chloride 2000 mg/l-8000 mg/l and sulphates around 2000 mg/l. When it is discharged to the surface it contributes to degradation of soil and ground water quality (Strathmann 1990). Membrane technologies are increasingly applied to process saline water where the demand for fresh water is high. Since the beginning of 1990's, 70% of the newly built desalination plants are using the reverse osmosis (RO) technology. The wider adoption of this technology has contributed to reduce the cost of the membranes (Gabelich *et al.*, 2007). It was thus worthwhile to test the viability of the RO for primary and biologically treated tannery effluent. One of the key issues in employing the RO technology is the satisfactory disposal of the saline reject from the system (Ahmed *et al.*, 2001). It was therefore considered

essential that while assessing the feasibility of the RO system for treating salinity in tannery effluent an appropriate course of action for dealing with the reject must also be specified. The leather industrial sector in India has been posting significant rate of growth in the past 15 years. The growth of this industrial sector owes a great deal to its export thrust. Export from this sector has grown from Rs. 7.8 billion in 1985 to an estimated Rs. 90 billion in 2000-01. That the share of value added products in the export basket of this industry has risen from less than 40% in 1985 to more than 85% in 2000 is a testimony to the structural transformation that this industry has undergone in the intervening years (Tiwari *et al.*, 2006). Pollution control and treatment did not directly enhance the value of products at the same time these increased cost of production. Reliable and tested pollution treatment technologies were not readily available in the country. This was an emerging field, with only a few private sector companies active in it. Till the end of 1980's, the governments at the center and the states were also not very proactive in enforcement of environmental laws. In such an apathetic state of affairs, the attitude of industry varied from state to state. The key issues in employing the RO technology is the satisfactory disposal of the saline reject from the system (Amiri and Samiei 2007). It was therefore considered essential that while assessing the feasibility of the RO system for treating salinity in tannery effluent an appropriate course of action for dealing with the reject must also be specified.

MATERIALS AND METHODS

A variety of chemicals - both common and special - are used in tanning. Some of the chemicals widely used in tanneries are: Sodium chloride, Sodium sulphide, Calcium oxide / calcium hydroxide, Ammonium sulphate / chloride, Hydrochloric /

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sulphuric acid, Sodium formate, Sodium bicarbonate, Formic acid, Oxalic acid. These chemicals are specifically used to: Increase / decrease alkalinity / acidity alter the electrostatic properties of leather; act as buffers; fix / strip specialty chemicals / tannins. As the leather absorbs no more than 20% of the chemicals applied, many of these chemicals are discharged into the wastewater streams (Reddy and Ghaffour 2007). The characteristics of raw wastewater from various processes and membranes used were listed in Table 1 & 2.

Two pilot RO unit with a capacity to treat $8 \text{ m}^3/\text{h}$ each has been set up to treat secondary treated tannery effluent. The unit had all necessary inputs for regular operation of the system, complete with all monitoring units and trained operators. Tanks required for the unit except intermediate collection tanks were constructed in RCC M 25.

Pilot RO system complete with pre-treatment units

Two pilot RO unit with a capacity to treat $8 \text{ m}^3/\text{h}$ each has been set up to treat secondary treated tannery effluent. The unit had all necessary inputs for regular operation of the system, complete with all monitoring units and trained operators. Tanks required for the unit except intermediate collection tanks were constructed in RCC M 25. The flow chart of the system was as follows:

RESULTS AND DISCUSSION

In order to ascertain the impact of the various effluent streams on the pollution levels, different effluent streams from the tannery was collected and checked. Samples were collected from tanneries of different production processes, viz., raw to semi-finished, raw to finished and wet blue/EI to finished. All samples were collected as composite sample to ensure the representativeness. Wherever improbable or non-linear values were obtained, the analysis were repeated till consecutive

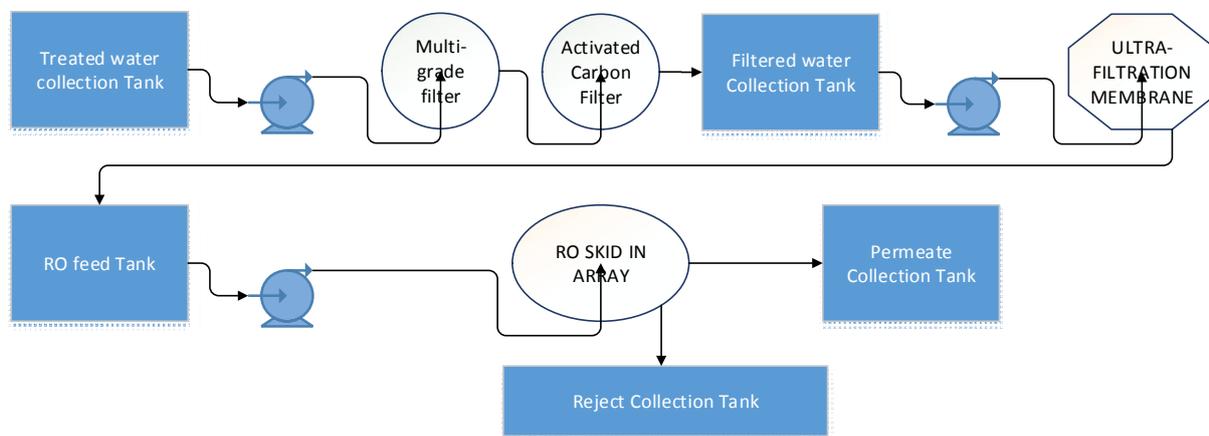
Table 1. The comparative specifications of the different membranes used in the study

Specification	1 Aromatic polyamide composite	2 Composite polyamide	3 Polyamide thin-film composite	4 multilayer composite
1) Size (inches)	8"	8"	8"	8"
2) pH range	2 – 11	2 – 11	2 – 11	4 – 11
3) Operational flux $\text{l/m}^2/\text{h}$	10-19	11-18	10-16	12-19
4) Op. pressure max, bar	82 Bar (1200 PSI)	82 Bar (1200 PSI)	55 bar (800 PSI)	82 Bar (1200 PSI)
5) Feed SDI max	5	5	5	5
6) Feed turbidity	1	1	1	1

Table 2. Characteristics of treated effluent from tanning industries

Parameter	Minimum	Maximum	Required limit for RO
pH	6.6	7.9	6.0 – 6.9
TSS (mg/L)	34	115	should be Nil
TDS (mg/L)	10000	20000	--
S^{2-} (mg/L)	0	1.2	< 0.1
COD (mg/L)	160	465	50
BOD (mg/L)	10	45	2
Chloride (mg/L)	5500	14000	--
Total Hardness (mg/L)	650	1700	1000

The flow chart of the pilot unit used for the studies was as follows:



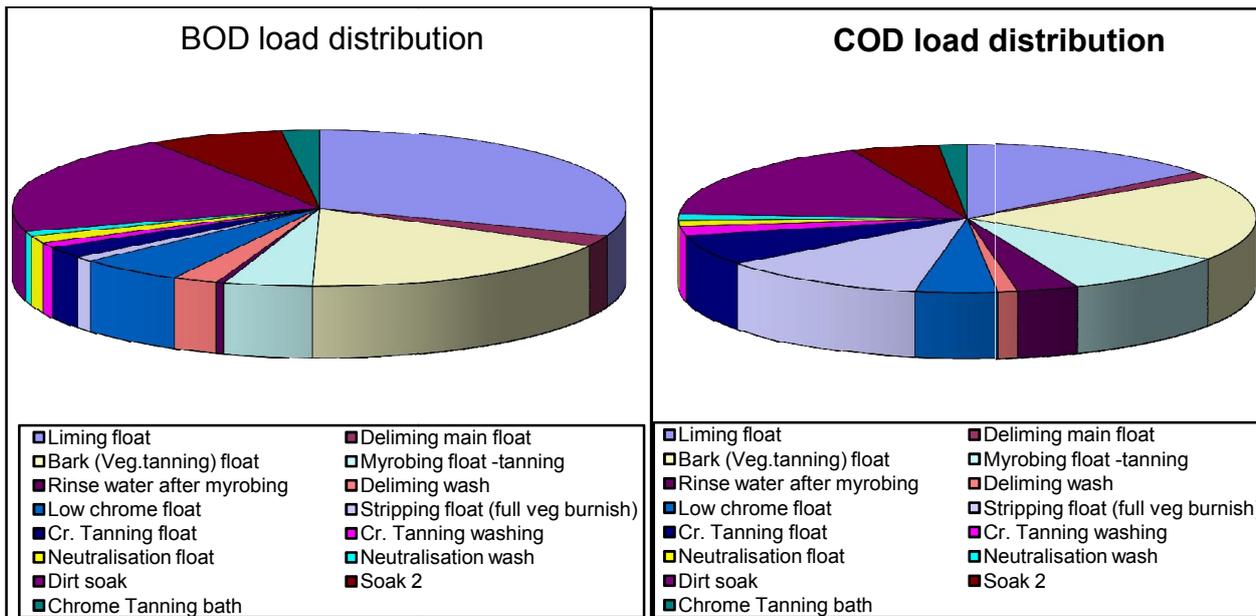


Fig. 1. Distribution of BOD & COD load in tannery effluent

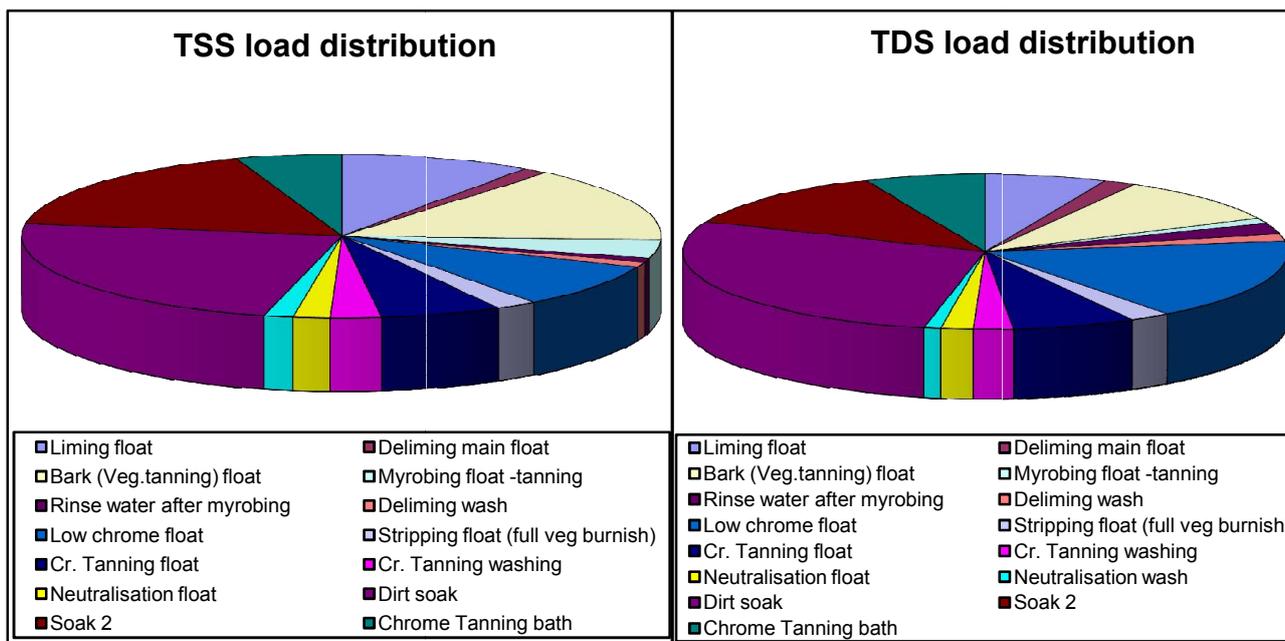


Fig. 2. Distribution of total suspended solids and dissolved solids from tannery effluent

results match. The contribution of pollution load has been worked out based on the analysis. As can be seen (Fig.1), the Liming float accounts for 31% of the BOD load, followed by the vegetable tanning float forming another 17% of the BOD load. While the veg. tanning float results in 19% of the COD load, thus forming the maximum COD contributor, the COD load from liming is about 14% (indicating readily degradable nature of the effluent), with stripping float (veg) accounting for about 12% of the COD load. As can be expected, dirt soak gives maximum TDS load of 28%, the chrome float gives the TDS load of about 17%. The soak-2 stream also account for about 12% of the TDS load. The soak streams accounts for high suspended solids too with dirt soak contributing around

24%. Other contributors of suspended solids are veg tanning float and liming floats (15% & 10% respectively). Whereas the dye fat liquor gives 14% of the BOD load, the 2 dye basic and dye float forming 11% each of the BOD load. While the veg. re-tanning float results in 15% of the COD load, thus forming the maximum COD contributor, the COD load from dye float and cr-re tanning streams account for 12% and 13% COD respectively. The dye float gives maximum TDS load of 14%, the veg retanning float gives around 11% TDS load (Fig.2).

The veg retanning float accounts for about 21% TSS load and streams such as dye fat liquor (12%), dye float (11%) and fat liquor (14) too contribute to the TSS load. Since overall

effluent could not meet the COD standards, sectional effluent streams were subjected to biological treatability studies. The effluent streams were treated in a pre-stabilized activated sludge pilot plant with retention time from 2 h to 182 hours with aeration fit enough to maintain a residual DO of 2.5 mg/l - 3.0 mg/l. It is very clear that the re-tanning liquor has the lowest bio-degradability. Hence it would be useful to segregate this stream from the rest of the effluents and treat it separately. Since the TDS load of this stream too is higher, it may not be a bad idea to segregate this stream and directly mix it with the RO reject for onward evaporation. The efficiency of multi-grade filter in removing suspended solids and turbidity was checked with all three types of treated effluent after softening with lime-soda treatment. The results obtained during about 120 days of operation are discussed. Since treated tannery effluent is likely to have more suspended solids than normal UF feed water, impact of inlet turbidity on the yield of the UF in terms of operating flux rates of the UF were tested by varying the turbidity levels and observing the flux at inlet turbidity levels of 1.0 NTU to 80 NTU. In order to obtain a treated effluent with around 1 NTU turbidity for the trial, the treated effluent was first filtered through a nano-filtration (NF) unit and was collected in a separate tank to be used in the trial. Figure 3 shows, almost all membranes tested performed in the

same fashion against the increasing SDI levels in the influent and the performances were in line with their claimed efficiencies. As can be seen from the Chart, Hydranautics membrane performs well at moderate SDI levels (5-10 range, observed as most common levels), though Tricep maintains a steady flux at higher SDI levels after the initial sharp drop.

The membranes were tested against various COD levels (Fig.4) in influent from the lowest levels to around 600 mg/l. Though the tests were planned with a COD range starting from 150 mg/l, this could not be done as the lowest COD obtained from pre-treatments and UF was only 180 mg/l. It was possible to obtain lower COD through a tighter UF/nano-filtration, but the same would have resulted in incorrect observations and hence was not attempted. In order to get the recovery at a certain COD value, average value of 120 hours of continuous operation was taken without any chemical cleaning in between, though forward flush/ rinsing with permeate was carried out every day. In order to get influent of uniform COD values, the feed was collected in large storage tank before the trial. It was noted that there was no much change in the COD (i.e., <2%) in the beginning and end of the trial indicating the COD to be stable. The effluent used for the first three membranes and the second round was brought in the same range of ± 5 mg/l to

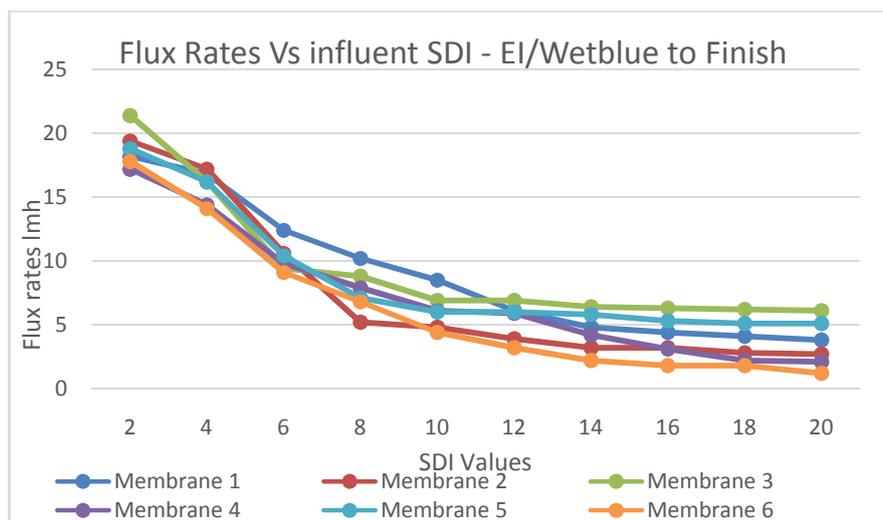


Fig.3. Membrane efficiency against flux rate on RO unit

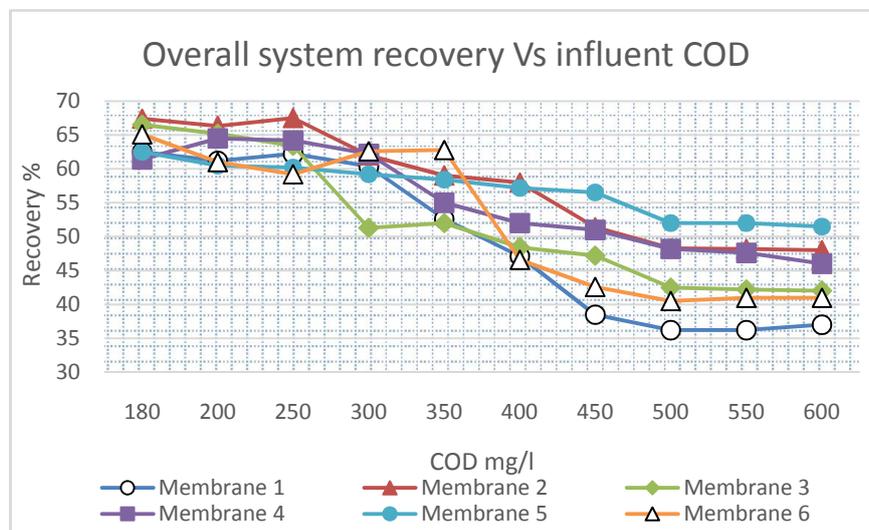


Fig 4. Efficiency at various COD levels for different RO membranes

ensure meaningful comparison. The results clearly indicated that the fears regarding the fouling of membranes due to COD was completely unwarranted. Though even the lowest level of COD fed to the membrane (180 mg/l) was far higher than the original levels sought by the membrane manufacturers (<50 mg/l), no significant reduction in recovery was noted. Barring the individual variations in different membranes, almost of them operated without much problem till the COD was around 350 mg/l (Fig.4).

Conclusion

The tests using multi-grade filter, activated carbon filter and ultra-filters using commercial unit of plant scale revealed that the performances were, i) the MGF was quite effective with removal of suspended solids with 80 to 83 % and turbidity removal of 93%. Verification of power consumption by various membranes were done in an attempt to determine which membrane configuration is ideal for field installations. The spiral wound membranes had shown an average power consumption of 1.435 kWh/m³ for desalination of raw to finish effluent and overall energy consumption of the entire section including pre-filters and UF/RO was 2.52 kWh/m³. For better functioning it would be better to have a system with physico-chemical treatment biological treatment, softening, pre-filtrations and ultra-filters with two stage spiral RO reject management system will be a better choice.

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