Journal of Hazardous Materials 189 (2011) 273–277

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Treatment of refractory organics from membrane rejects using ozonation

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ARTICLE INFO

Article history:
Received 3 December 2010
Received in revised form 11 February 2011
Accepted 11 February 2011
Available online 17 February 2011

Keywords:
Ozonation
Tannery effluent
Refractory organics
Reverse osmosis
Nano filtration

ABSTRACT

The reject water or retentate generated from membrane application for recovery of water from tannery wastewater treatment contains certain refractory organics. These refractory organics are present in substantial quantity in the condensate of reject water also. Hence the treatment of rejects using conventional methods is rather difficult. In this paper, an attempt has been made to treat the reject water from the reverse osmosis (RO) and nano filtration (NF) operation on tannery wastewater using ozonation treatment technique. Ozonation studies on RO and NF rejects indicate that ozone dose of 80 and 100 mg/min for 60 and 70 min contact time achieves 59 and 78% chemical oxygen demand (COD) reduction, respectively. The mass balance in ozone indicates the ozone consumption for RO and NF rejects varies from 2.4 to 3.4 and 2.8 to 4.5 g/g of COD removed respectively. The results suggest that ozonation of RO and NF rejects would significantly reduce the refractory organic pollutant loading into the environment from wastewater reuse facility.

1. Introduction

Wastewaters generated in many industrial processes contain organic compounds which are not amenable to conventional biological oxidation. This has led to the development of several alternative oxidation processes ranging from wet oxidation, ozonation, and UV irradiation to electrochemical treatment [1,2].

Treatment of effluents generated from the leather processing industries poses a major challenge in achieving the desired effluent discharge standards in India. Due to fresh water scarcity for the tanning processes, it has been realized that the industrial effluent should not only be treated to the extent to meet the prescribed discharge standards but also be treated to recycle and reuse in the manufacturing processes. The treatment of tannery effluent involves both conventional treatment methods and advanced processes. Conventional treatment methods include primary, secondary and tertiary treatment. Primary treatment consists of screen and grit removal, oil and grease removal, equalization basin and primary settling [3] and/or chemical precipitation [4] followed by secondary treatment which is normally biological treatment and consists either or combination of unit operations such as anaerobic and aerobic treatment [5–9]. Tertiary treatment normally includes media filtration followed by carbon adsorption and sometimes physico-chemical treatment [10]. Advance treatment processes for tannery effluent treatment include advance oxidation processes such as Fenton, H_2O_2/UV, electrochemical oxidation, and electro-Fenton oxidation and membrane bio-reactors and membrane separation processes [2,10–17].

Amongst the advanced treatment processes, the membrane separation processes are mostly implemented on full scale to ensure complete removal of organic matter and dissolved solids, thereby making the treated effluent (permeate) suitable for recycling and reuse [18].

The increasing use of membrane technologies for recovery of water from wastewater treatment has led to generation of concentrated wastewater referred to as 'reject' or 'retentate'. This reject water, though small in quantity (10–15% of the feed), contains high concentration of the dissolved solids and certain recalcitrant compounds. These organic compounds are difficult to treat using conventional methods and referred to as 'refractory' or 'recalcitrant organics. Management of rejects in tannery industry is of significant importance in the backdrop that the regulatory bodies in southern part of India have enforced implementation of "zero effluent discharge" based treatment technologies in all tanneries.

The membrane reject water is further evaporated in multiple effect evaporators to recover the condensate water and further concentrate the pollutants in rejects. However, the analysis of condensate water, as will be described later in this paper indicates presence of some organic compounds in it, which are not readily biodegradable and further contribute to organic loading, as the condensate water is reused in the process. Therefore, it is considered important to remove refractory organics from the rejects using advanced oxidation process prior to application of thermal methods. Accordingly, this paper presents the treatment of refractory organics in 'reject water' using ozonation. It is pertinent

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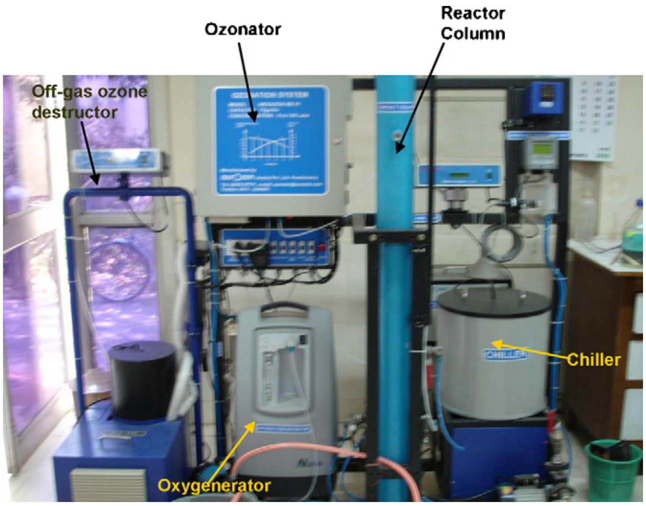
doi:10.1016/j.jhazmat.2011.02.030



Picture 1. Various components of pilot scale ozonator.

to mention here that removal of refractory organics from RO and NF rejects from tannery effluent treatment has not been investigated earlier.

2. Treatment of refractory organics

Ozone (O_3) is a powerful oxidant and has been extensively used in various industries at various levels to remove the organic and inorganic content present in the wastewater. Ozonation is one of the best treatment processes since there is no sludge generation and it is effective for both color removal and organic reduction through a single step [19]. Kurniawan et al. [20] studied ozonation in combination with granular activated carbon for degradation of recalcitrant organics in leachate and stated that the combination of ozone–GAC adsorption using ozone-modified GAC had the highest removal performance for COD when compared to ozonation alone. Aparicio et al. [21] have reported treatment of recalcitrant wastewater from resin manufacturing using a combination of ozonation and biological process. They concluded that an ozone dose around 13 mg/l/min and contact time between 45 and 60 min followed by biological treatment can be applied to recalcitrant wastewater from a resin-producing factory. Hagman et al. [22] presented an evaluation of potential methods of advanced oxidation processes for treatment of refractory organics in landfill leachate. They concluded that the most biodegradable organic material was produced after oxidation with only ozone and ozonation at pH 9. However, a combination of biological pretreatment, chemical oxidation with O_3/H_2O_2 and a subsequent biological process resulted in the most efficient oxidation method for the leachate. Westerhoff et al. [23] stated that UV irradiation in the presence of titanium dioxide (UV/TiO_2) can remove a high percentage of organic matter from RO retentates.

3. Materials and methods

Experiments were carried out on reverse osmosis (RO) and nano filtration (NF) rejects from a tannery industry using a commercially available pilot scale ozonator (Megazone MZ01® Aurozon India) as shown in Picture 1. The major components of ozonator are oxygen concentrator, ozone generator, mixing pump, mixing column, high concentration ozone analyzer, residual ozone analyzer, off gas ozone analyzer, ozone destructor, chiller and ambient ozone leak detector. The capacity of ozone generation is 15 g/h at a concentration of 7% w/w in oxygen. Ozone is produced at high voltage of 2500 V and 50 kHz frequency from more than 90% pure oxygen at minimum flow rate of 2 l/min. The mixing column has a capacity of 25 l and the reactor is operated in semi-batch mode wherein a minimum of 10 l effluent sample is used and ozone is applied continuously for a known time period. Reject water from a tannery industry in Southern part of India having primary, secondary, tertiary and pretreatments to RO and NF process were collected and analysed according to procedures described in the standard methods [24]. Studies on RO and NF rejects using ozonator were carried out to optimize the ozone dose and contact time in order to achieve maximum reduction in chemical oxygen demand (COD). All the experiments were carried out as single run for a batch of 10 l sample with ozone flow rate of 2 l/min, specific ozone dose and contact time to avoid errors and obtain accurate ozone mass balance. All the experiments were conducted at room temperature and at the original pH of the effluent. Initially the ozone dose was kept constant and the contact time was varied and then based on the COD reductions, ozone dose was varied keeping the contact time constant. A trade-off was obtained for reduction in COD for RO and NF rejects after conducting a number of runs. The ozone consumption as g O_3/g COD removal was obtained based on the mass balance for each run.

4. Results and discussion

As mentioned in introduction, the reject water from RO and NF are evaporated in multiple effect evaporators and the condensate water reused in the tanning process. This condensate water contains certain organics and thereby contributes to COD loading. The characteristics of RO and NF rejects and their condensate with respect to pH, COD and total dissolved solids (TDS) are presented in Table 1. In the present study, COD concentrations in RO and NF rejects were 226 and 178 mg/l respectively and the condensate water of RO and NF had COD concentrations 110 (48%) and 96 mg/l (54%) respectively. It has been shown earlier [2] through GC-MS investigation that secondary clarifier effluent in tannery units contains several organic compounds viz., phenol, naphthalene, benzoyloxy benzoic acid, 1-mwthoxy-4-(2-phenyl-ethenyl)-benzen, dibutyl phthalate, 2,4-dioctyl phenol, 1,2-benzene dicarboxylic acid, di-iso-octyl ester and 17-α-ethyneyl-17-β-hydroxy-5-β-ester-3-one. Several of these compounds are recalcitrant and steroid compounds are endocrine disrupting compounds also. The identified compounds would make for a part of the measured COD in the reject sample. This also means that if the rejects water is treated for removal of refractory organics, a substantial amount of organic loading can be prevented from reentering into tannery process, or into environment if discharged onto land or into water bodies otherwise.

4.1. Ozonation of RO rejects

Initially, ozonation studies were carried out at ozone concentration of 100 mg/l and varying contact time between 10 and 80 min at an interval of 10 min. The amount of ozone consumed by the wastewater to degrade organics was determined by subtracting the amount of ozone dissolved in water and the amount of ozone detected in off gas analyzer. The performance of ozonation studies at various contact times and 100 mg/l ozone concentrations is presented in Fig. 1. COD reduction increases with increase in contact time upto 60 min, thereafter slight reduction in COD removal was observed. Maximum reduction was observed at 60 min contact time and COD decreases from 226 to 114 mg/l amounting to 50% reduction. Further studies were conducted by varying ozone concentrations between 40 and 120 mg/l at an interval of 20 and keeping contact time fixed at 60 min. The performance of ozonation studies at various ozone concentrations and 60 min are presented in

Table 1
Characteristics of membrane rejects and condensates water.

Parameters[a]	Reject		Condensate[b]	
	RO	NF	RO	NF
pH	7.5 ± 0.2	7.8 ± 0.2	8.2 ± 0.2	8.4 ± 0.2
COD	226	178	110	96
TDS	23,080	20,230	–	–

[a] All values except pH, are in mg/l.
[b] 200 ml of reject was distilled till 150 ml condensate was obtained.

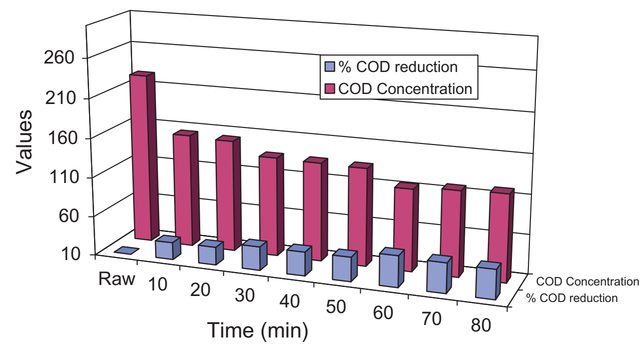


Fig. 1. COD reduction with time at constant ozone dose, 200 mg/min (conc. ~ 100 mg/l).

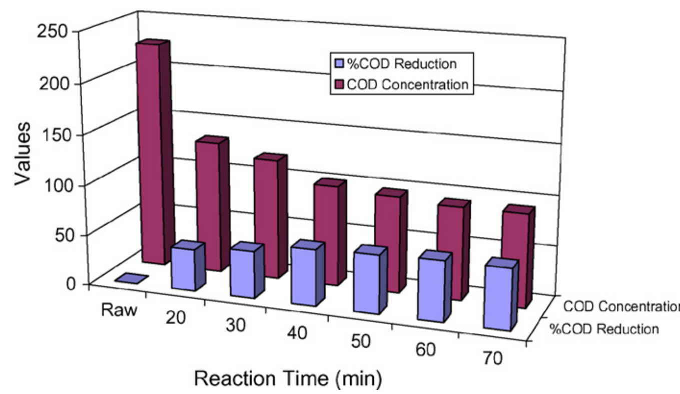


Fig. 3. COD reduction with time at constant ozone dose 80 mg/min (O_3 conc. 40 mg/l).

Fig. 2. COD reductions at ozone concentrations 40, 80 and 120 mg/l were maximum and reduces from 226 to 92 mg/l (59.3%). Whereas, COD removals were slightly less at concentrations 60 and 100 mg/l. All the experiments were repeated twice and COD values represent the average of three sets. Since the maximum COD reduction was obtained at 40 mg/l concentration, further studies were carried out keeping ozone dose constant and varying contact time between 20 and 70 min and the results are shown in Fig. 3. The performance of ozonation studies at 40 mg/l reveals increase in COD removal with increase in contact time. The maximum removal was observed at 60 min and COD was reduced from 226 to 92 mg/l (59.3%). Thus ozone dose of 80 mg/min at ozone concentration 40 mg/l and a contact time of 60 min offer maximum COD reduction from RO rejects. The ozone mass balance for RO rejects for maximum COD reduction is presented in Table 2. The mass of ozone supplied was 4800 mg and the dissolved ozone concentration was 2.75 mg. The concentration of unreacted ozone was 13 mg/l and the mass of unreacted ozone was 1560 mg. The ozone consumption is obtained by subtracting the mass of dissolved and off gas ozone from the total mass of ozone supplied. Ozone consumption for all runs at various concentrations and contact times varies between 2.4 and 3.4 g/g of COD removed. The treated effluent obtained after optimizing the contact time and ozone dose considerably reduces the organic loading through condensate reuse in tannery processing.

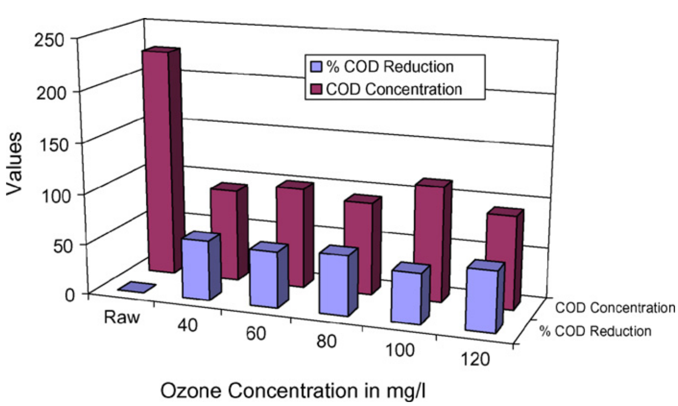


Fig. 2. COD reduction at various ozone doses at constant time (60 min) (ozone dose: 80, 120, 160, 220, 240 mg/min).

4.2. Ozonation of NF rejects

Studies were also carried out on NF rejects using ozone at various doses and contact time. Initially ozone concentration was fixed at 40 mg/l and contact time was varied between 30 and 60 min at an interval of 10 min. The performance of ozonation studies at 40 mg/l ozone concentration under variable contact time is presented in Fig. 4. It was observed that maximum COD reduction occurs at 40 min contact time and COD reduces from 173 to 80 mg/l (54%). Further increase in contact time did not increase COD reduction. The COD reduction at 30 min was 49%, which was slightly less than that of 40 min contact time, therefore further ozonation studies on NF rejects were carried out keeping 30 min contact time and varying ozone concentration between 40 and 80 mg/l. The performance of ozonation studies at 30 min contact time is presented in Fig. 5. It was observed that COD reduces from 173 to 60 and

Table 2
Ozone mass balance for RO rejects at concentration 40 mg/l and 60 min contact time.

Description	Values
Sample volume, *V*1	10 l
Time, *T*1	60 min
Flow rate of ozone, *F*1	2 lpm
Concentration of ozone, *C*1	40 mg/l
Ozone dose, $D = F1 \times C1$	80 mg/min
Total ozone passed, $D1 = D \times T1$	4800 mg
Dissolved ozone at that time, *E*	0.275 mg/l
Dissolved ozone for that sample, $E1 = E \times V1$	2.75 mg
Off gas ozone concentration, *C*2	13 mg/l
Unreacted off gas ozone, $U1 = C2 \times F1 \times T1$	1560 mg
Total of unreacted and reacted ozone, $F1 = E1 + U1$	1562.75 mg
Total ozone consumed, $A1 = (D1 - F1)$	3477.25 mg
Ozone consumed per litre, $B1 = A1/V1$	347.725 mg/l
COD removed (initial – final)	136 mg/l
Ozone consumption g/g of COD removed	2.6 g O_3/g of COD

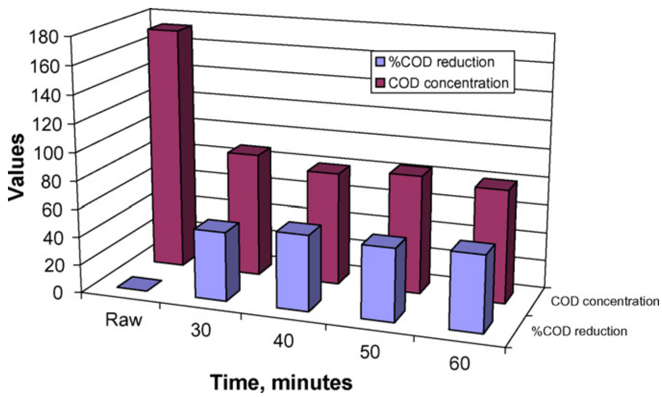


Fig. 4. COD reduction with time at constant ozone dose 80 mg/min (ozone concentration 40 mg/l).

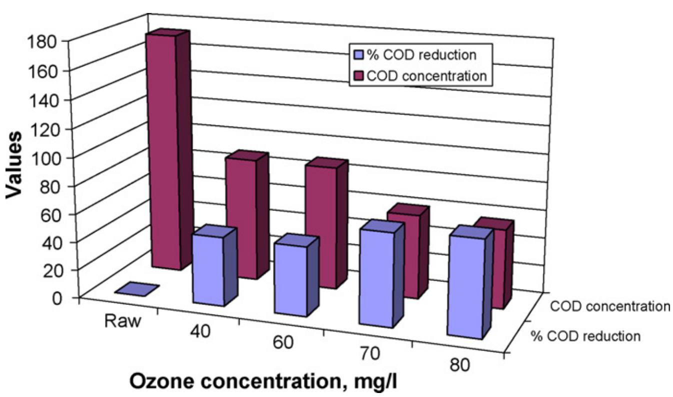


Fig. 5. COD reduction at various ozone doses and constant time (30 min) (Ozone doses 80, 120, 140 and 160 mg/min).

56 mg/l at ozone concentrations 70 and 80 mg/l, respectively. In order to further optimize the COD reduction, studies were carried out at ozone concentrations 50 mg/l and varying contact time between 30 and 80 min. Fig. 6 shows the results of ozonation studies at 50 mg/l ozone concentration under various contact times. The COD reduction improved with increase in contact time and a maximum reduction of 78% occurs at 70 min. Ozonation studies on NF rejects under different ozone concentrations and contact time indicate that maximum reduction is obtained at 50 mg/l ozone concentration and 70 min contact time and COD reduces from 173 to 38 mg/l (78%). The ozone mass balance for NF rejects for maximum COD reduction is presented in Table 3. Ozone consumption for all runs at various concentrations and contact time varies between 2.8 and 4.5 g/g of COD removed. Generally a requirement of 3:1

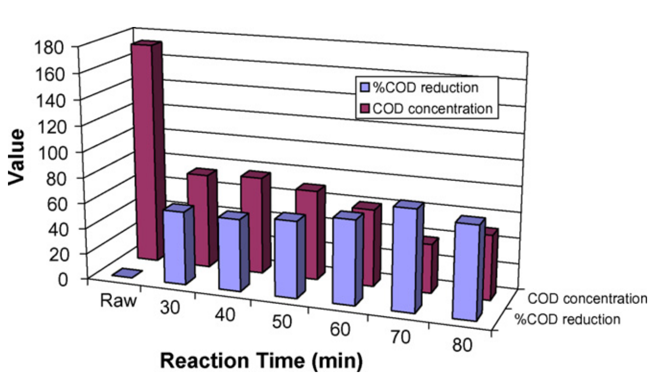


Fig. 6. COD reduction with time at constant ozone dose 100 mg/min (ozone concetration 50 mg/l).

Table 3
Ozone mass balance for NF rejects at concentration 50 mg/l and 70 min contact time.

Description	Values
Sample volume, $V1$	10 l
Time, $T1$	70 min
Flow rate of ozone, $F1$	2 lpm
Conc. of ozone, $C1$	50 mg/l
Ozone dose, $D = F1 \times C1$	100 mg/min
Total ozone passed, $D1 = D \times T1$	7000 mg
Dissolved ozone at that time, E	0.232 mg/l
Dissolved ozone for that sample, $E1 = E \times V1$	2.32 mg
Off gas ozone concentration, $C2$	9 mg/l
Unreacted off gas ozone, $U1 = C2 \times F1 \times T1$	1260 mg
Total of unreacted and reacted ozone, $F1 = E1 + U1$	1262.32 mg
Total ozone consumed, $A1 = (D1 - F1)$	5373.68 mg
Total ozone consumed per litre of sample, $B1 = A1/V1$	537.368 mg/l
COD removed (initial – final)	135 mg/l
Ozone consumption g/g of COD removed	4.0 g O_3/g of COD

(O_3: COD) is reported to be applicable in ozonation of wastewater sample [25]. The treated effluent obtained after optimizing the contact time and ozone dose considerably reduces the organic loading through condensate reuse in tannery processing.

4.3. Energy consumption in ozonation of rejects

In order to assess the applicability of ozonation method for membrane rejects vis-à-vis the treatment cost, energy consumption studies were also carried out. For this purpose, energy consumption in terms of voltage and current towards O_3 generation were observed during the experiments. The average voltage and current were 232 V and 3.8 A. The power factor was maintained at 0.9. Then power required was calculated as follows:

$$P = V \times I \times \cos\phi$$

where, P = power required in watts, V = voltage, I = current, $\cos\phi$ = power factor (0.9). The estimated power consumption was approximately 0.8 kW/h. If 60 min contact time is considered for 60 and 78% removal of refractory organics from RO and NF rejects, respectively; then the power consumption for 10 l of sample is 0.80 kW. The power consumption under these conditions for 1 m^3 of rejects water works out to be 80 kW/h. The energy cost in Indian rupee (INR), though varies from place to place, but approximately is in the range of 5.0–8.0 INR/kW h. The energy cost for 1 m^3 rejects water considering the cost of 6 INR/kW h for removing refractory organics would be 480 INR/m^3. This can be linked to reduction in COD load as well. Considering the concentrations of COD removed from RO and NF rejects using O_3 as 135 g/m^3, the cost for reduction in COD load would be 3.5 INR/g of COD. However, these costs are case specific and should not be considered as guidelines. These refractory organics can be removed to a great extent by using ozonation treatment method.

5. Conclusions

The RO and NF rejects of tannery industry contain several refractory organics. These refractory organics can be removed to a great extent by using ozonation treatment method. The present research demonstrated that an ozone dose between 80 and 100 mg/min with a contact time of 60 min affords 60–80% COD reduction. The O_3 consumption for COD removal from RO rejects using O_3 varied from 2.4 to 3.4 g/g of COD; whereas it is in the range 2.8–4.5 g/g of COD for NF rejects. An assessment of energy cost for removal of refractory organics using O_3 indicates energy cost to vary from 400 to 640 INR/m^3. Ozonation treatment of membrane rejects significantly reduce the refractory organic pollutant loading into the environment from wastewater reuse facilities.

Acknowledgements

Authors are thankful to Council of Scientific and Industrial Research (CSIR) for sponsoring the research under eleventh five year plan for "zero emission initiative". Authors are also thankful to Director NEERI for giving this opprtunity to work in this project. The co-operation rendered by M/s E.K.M. Tannery is gratefully acknowledged.

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