Status Report

On

Environmental Audit of Thirumalai Chemicals Limited, Ranipet

Prepared by

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1. Background

Thirumalai Chemicals Limited (TCL) is one of the largest producers of Phthalic Anhydride, Malic Acid, and Fumaric Acid. It is a Zero Liquid Discharge (ZLD) plant. It is located in SIPCOT industrial estate, Ranipet, Tamil Nadu.

TCL requested IIT Madras to carry out an Environmental Audit and adequacy test to assess and certify the capability & capacity of upgraded ETP to achieve and maintain the ZLD status. Accordingly, the IIT Madras team comprising of Prof. Ligy Philip, Dr. J. Senthilnathan, Mr. R. Sarath Kumar, and Mr. D. Kumaran had visited TCL premises on 23rd July 2021 to overview the production processes, ETP, ZLD facilities, hazardous waste disposal, etc. and carried out the audit of the treatment systems. Based on the initial assessment, the IITM team had made a second visit to TCL premises on 9th October 2021 to evaluate the adequacy of the existing treatment system with 50% operating capacity.

2. Preamble

The wastewater generated from the plant is collected into two streams.

1. Process stream
2. Utility stream

TCL was operating the ZLD system by combining the wastewater streams and treating them in a large ETP, RO systems, MEE, and ATFD. In 2020, the company upgraded its ZLD system by incorporating three new RO systems, connected 3 High rated Solid contact Clarifiers (HRSCC), a large new MEE, and a larger ATFD. The process and utility streams are being treated separately and passed through newly added clarifiers and RO systems. The recovered permeate from RO systems is being recycled back for reuse. The rejects are evaporated in a four-stage MEE and a larger ATFD to separate salt. The team has collected flow data and composite samples from various treatment units of the upgraded ETP to evaluate and assess the performance of the upgraded ETP to treat the process and utility streams. The locations of composite samples collection are as follows:

- Process stream
- Utility stream
- Feed, permeate, and reject of all RO plants (RO VI, RO V, and RO VI).
- Inlet, condensate, and concentrate of MEE
- Sludge from Filter presses & slat from ATFD

A detailed study was conducted to assess the adequacy of the existing ETP and upgraded ZLD facilities and furnishing this report.

3. About the Industry and Activities

Thirumalai Chemicals Limited was established in 1973. In 1977, the firm set up its plant at Ranipet to manufacture Phthalic Anhydride. In 1995, TCL started manufacturing Malic acid and Fumaric acid. The ZLD system was established in 2006. The raw materials are O-Xylene and Maleic Anhydride for the production of phthalic anhydride and malic acid, respectively. Fumaric acid is recovered from the scrubber solution of the phthalic anhydride plant. Based on the information provided by the industry, the details of the manufacturing process of phthalic acid, fumaric acid, and malic acid are discussed in the proceeding sections.

3.1 Phthalic anhydride

Phthalic anhydride is manufactured by the reaction of o-xylene with air. The reaction is exothermic. The generated heat is utilized to produce steam (Fig 1). Phthalic anhydride is separated from impurities by de-sublimation. The off-gases are scrubbed with water in a wet scrubber. The waste products dissolved in water are termed as “scrubber solution.”

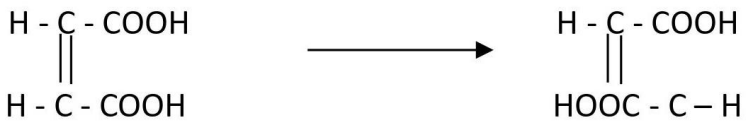
O-Xylene + oxygen --------> Phthalic anhydride

3.2 Fumaric acid

Fumaric acid is manufactured from scrubber solution of the Phthalic anhydride plant. The dissolved Maleic acid is isomerized to give Fumaric acid. The Fumaric acid gets precipitated, which is separated, dried, and bagged. The residual scrubber solution is pumped to the effluent treatment Plant.

Isomerization

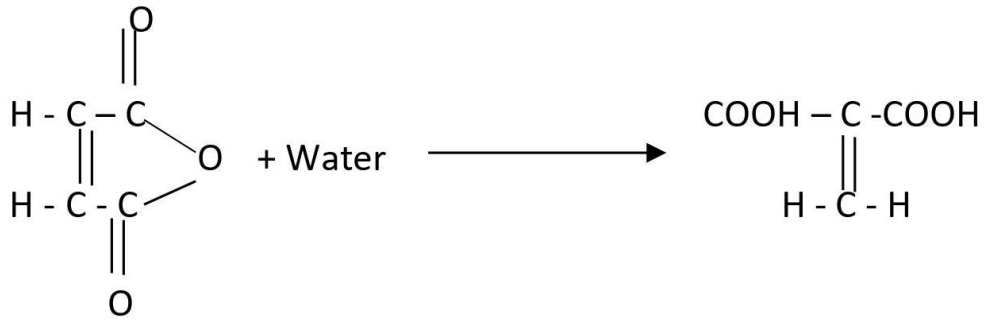
Maleic Acid ----------> Fumaric Acid



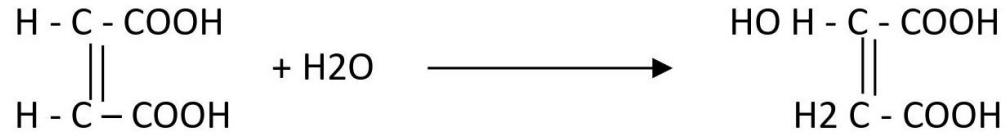
3.3 Malic acid

Maleic anhydride, dissolved in water (Maleic acid), is hydrated to produce Malic acid. The crude Malic acid is crystallized to separate from excess reactants. The excess reactants are recycled back. The crude Malic acid is re-crystallized to obtain pure Malic acid. The dried Malic acid is sieved to separate into granules and powder (Fig 2). The wastewater is sent to ETP.

Maleic anhydride + water ----------> Maleic acid



Maleic Acid + Water --------->. Malic Acid



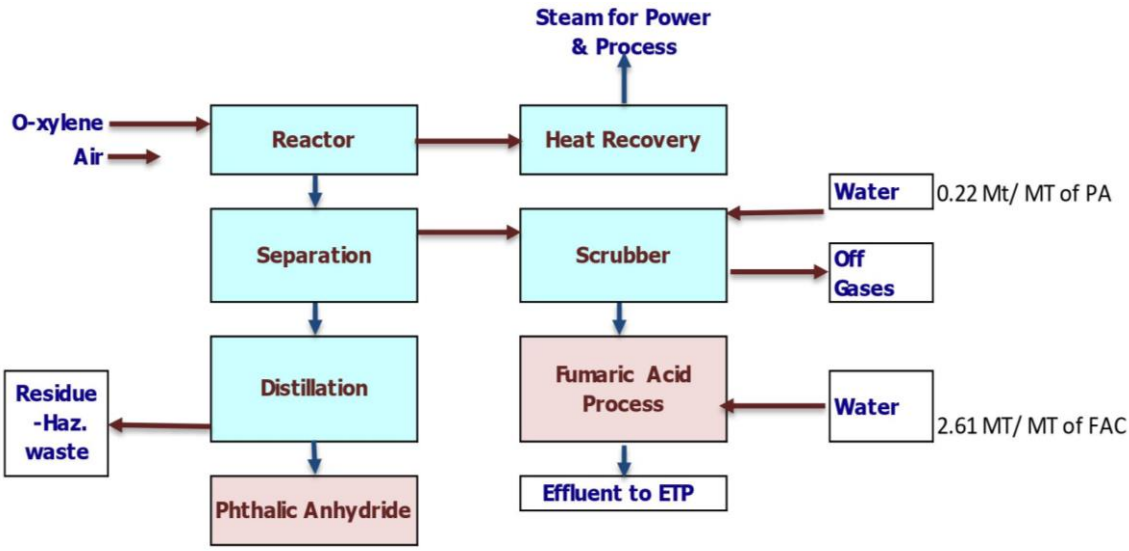


Figure 1: Manufacturing process of phthalic anhydride and fumaric acid

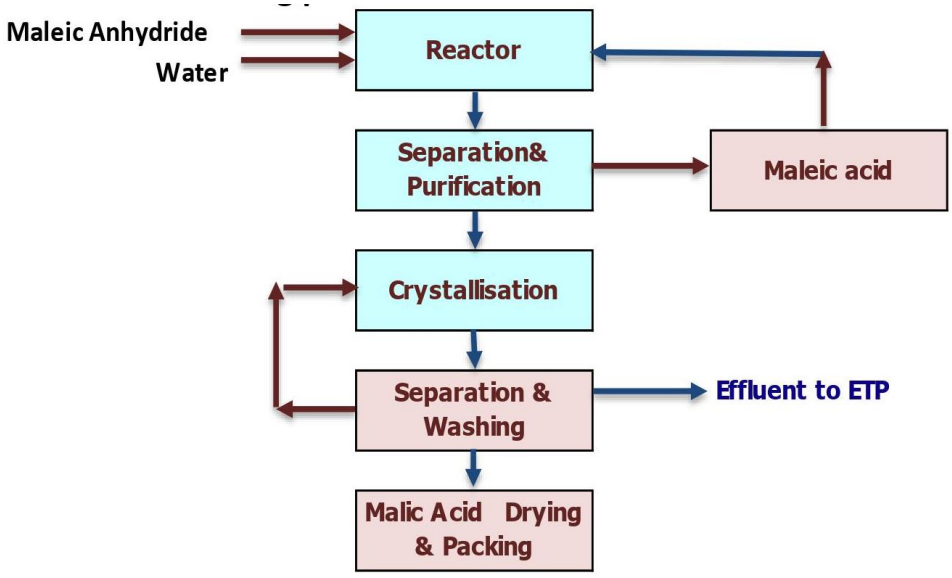


Figure 2: Manufacturing process of malic acid

The present upgraded ZLD facility consists of the following:

- Process stream treatment: Physico-chemical and biological treatment system.
- Utility stream treatment: Physico-chemical treatment.
- RO Systems
- MEE Plant followed by Agitated Thin Film Drier to separate solids.

The flow diagrams of the treatment scheme of process and utility streams, RO plants are given in **Figures 3 and 4**. The ZLD system was upgraded with the addition of three RO systems (IV, V, VI), a large MEE, and an ATFD.

- **Process Stream**

The biologically treated process stream is fed to RO-IV. The permeate is collected. The reject is treated with lime/ soda to reduce hardness and silica, clarified in HRSCC-1, and fed to RO-V. The permeate from RO-V is collected. The reject is collected in the feed tank of MEE.

- **Utility Stream**

The utility stream is treated with lime/soda to reduce hardness and silica, clarified in HRSCC-2, and fed to RO-VI. The permeate is collected. The reject is collected in the feed tank of MEE.

- **Treatment of RO rejects**

The mixed rejects of RO-V & RO-VI in the feed tank of MEE are treated with lime/ soda to reduce hardness and silica, clarified in HRSCC-3, and fed for evaporation in new MEE. The

condensate is collected. The concentrate from MEE is fed to ATFD (Agitated Thin Film Dryer). The salt is collected as hazardous waste, and the condensate is collected. The permeates thus collected from RO-IV, V, VI, and condensates from MEE & ATFD are reused as DM plant feed and cooling tower make-up.

4. Methodology

4.1. Sampling locations and analytical instruments

The composite sampling was carried out by collecting samples at every 2-hour time interval to evaluate the suitability of existing ETP and upgraded ZLD facilities for 24 hours.

Samples were collected from 26 different locations, namely,

- Process stream (8 locations)
- Utility stream & Upgraded ZLD facility (15 locations).
- Sludge and salt samples (3 locations)

For every 2 hours, the flow rate was recorded from flow meters fixed at different locations, and the details of locations are given in **Tables 1 and 2.** Similarly, the sampling locations of process and utility streams are shown in **Figures 3 and 4,** respectively. **Table 3** provides the details of the operation of various units of upgraded ZLD facilities on the sampling date. The process stream sludge, utility stream sludge, and ATFD salt were collected and analyzed for moisture content and various ions present in it. Composite 2-hour samples were made from the collected samples and analyzed for different parameters as per American Public Health Association (APHA, 2012) standard method (**Table 4**). The concentration of VOCs was quantified using Gas Chromatography with a flame ionization detector (GC-FID, Perkin Elmer, USA). The outcome of the analysis of various ETP and ZLD samples (composite samples) is presented in the succeeding sections.

4.2. Water balance, mass balance, and characteristics of effluent and treated water

The water balance & mass balance for different units of the process stream, utility streams, and MEE are shown in **Figures 4-8**. The summary of the water balance for the treatment units is given in **Table 5. Table 6** shows the physicochemical characteristics and organic contents of the collected composite samples. **Table 7** shows the volatile and dissolved solid content of the composite samples collected from ETP. **Table 8** provides the concentration of ions in the composite samples. **Table 9** shows the concentration of organic acids and volatile

compounds (VOCs) in the composite samples. The characteristics of salt and sludge samples are shown in **Table 10**.

5. Observations and Inferences regarding the Adequacy of the Treatment Systems

5.1. Process stream (ETP)

- The **total flow coming** to the equalization tank during the monitoring period – **179 m^3/day**

This stream undergoes the primary treatment, including flocculation, primary clarification, and neutralization. After primary treatment, the outflow was fed into the anaerobic filter, submerged aerobic fixed film reactor (SAFF). The clarified water was fed into the RO system after chlorination and tube settler.

- The **treated water outflow** from the ETP was observed as **176 m^3/day** with a loss of **1.67%. This difference is very insignificant. The loss might be due to the water lost through the sludge from the treatment system and the errors in the flow meters.**

The treated water from the ETP is fed into the ZLD system (RO IV) of the Utility stream. The Utility stream consists of RO IV and RO V systems. The Utility stream is fed into RO VI. The rejects from RO VI and the reject from RO V are fed into the MEE after flocculation and settling. The design and observed operating conditions are discussed below:

5.1.1. RO - IV

Design flow rate – 400 m^3/day

Design operating time – 20 h

- **Observed Inflow to RO-IV**

  Observed feed flow into RO-IV –180.7 m^3
- **Observed Outflow from RO-IV**

  Permeate flow –140.5 m^3

  Reject flow – 45 m^3
- **Observed operating time -9h 15 min** (Started at 10:15 am and stopped at 7:30 pm)

The RO-IV recovery was about 77.75%, and the remaining 24.9% rejected. RO-IV reject is blended with the water from the filter press and fed to HRSCC-1. The clarified reject was

sent to RO V. The volume of the holding tank before RO-IV feed is 224 kL. Permeate of RO-IV is used in DM plant.

5.1.2. RO –V

Design flow rate – 100 m^3/day

Design operating time: 23 h

- **Observed Inflow to RO-V**

  Observed feed flow into RO- V – 45.2 m^3

- **Observed outflow from RO-V**

  Permeate flow – 22.7 m^3

  Reject flow – 24.9 m^3

- **Observed operating time -10 h 5 min**

It was observed that RO-V was able to recover only about 49.78% of the feed flow. The recovered permeate goes to process reuse, and reject (24.9 m^3) goes to MEE along with RO VI reject (as shown in Fig 4). The recovered permeate of RO-V is used for the cooling tower.

5.2. Utility stream

5.2.1 RO-VI System (Utility stream)

Design flow rate – 200 m^3/day

Design operating time – 22 h

- **Observed Inflow to RO-VI**

  Observed feed flow into RO- VI – 100.5 m^3

- **Observed outflow from RO- VI**

  Permeate flow – 81.9 m^3

  Reject flow – 22.4 m^3

- **Observed operating time –** 10 h 40 min

The recovery of RO-VI was observed at about 81.49%. The recovered permeate goes to the cooling tower and reject to MEE.

5.3. Rejects management

5.3.1. MEE

Design flow rate – 150 m^3/day

Design operating time – 20 h

- **Observed inflow into MEE:**

  Flow into MEE – 56.3 m^3

- **Observed outflow from MEE**

  Condensate from MEE – 49.5 m^3

  Concentrate, which is going to ATFD from MEE -6.8 m^3

- **Observed operating time:** During the performance evaluation period, the MEE was operated for 8 h.

The MEE system can recover 87.92% of feed water, and the remaining 12.08% was further concentrated using ATFD, and salt is recovered. The recovered permeate is used for the cooling tower.

The storage tank size before MEE feed and ATFD feed is 28 kL and 2kL, respectively.

5.3.2. ATFD

Design flow rate – 42 m^3/day

Design operating time – 24 h

- **Observed inflow into ATFD: 6.8 m^3**

  Salt produced from ATFD – 1860 kg

The salt from the ATFD system was weighted and sent to the waste management site.

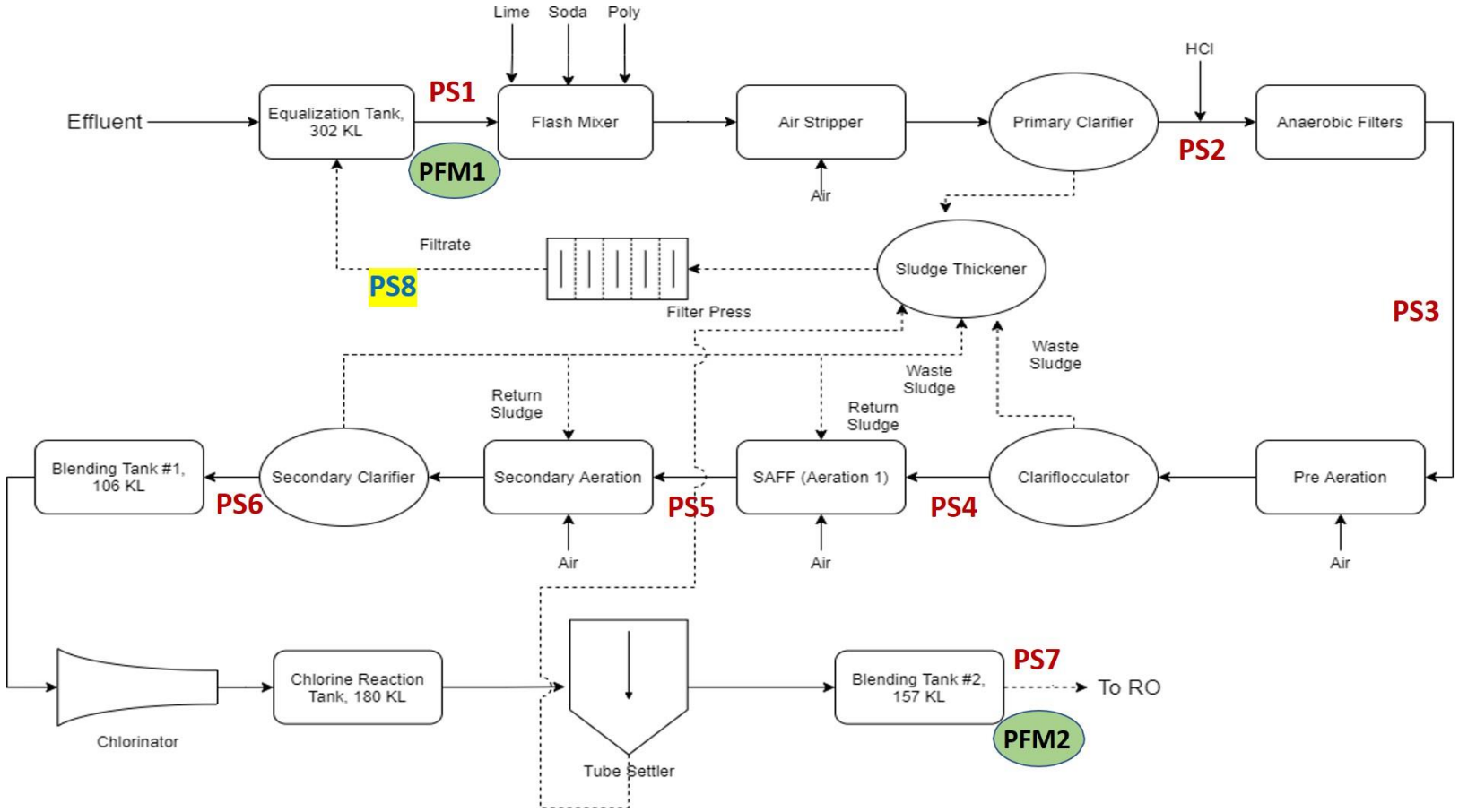


Figure 3: Flow diagram showing the treatment scheme of process stream (Old ETP)

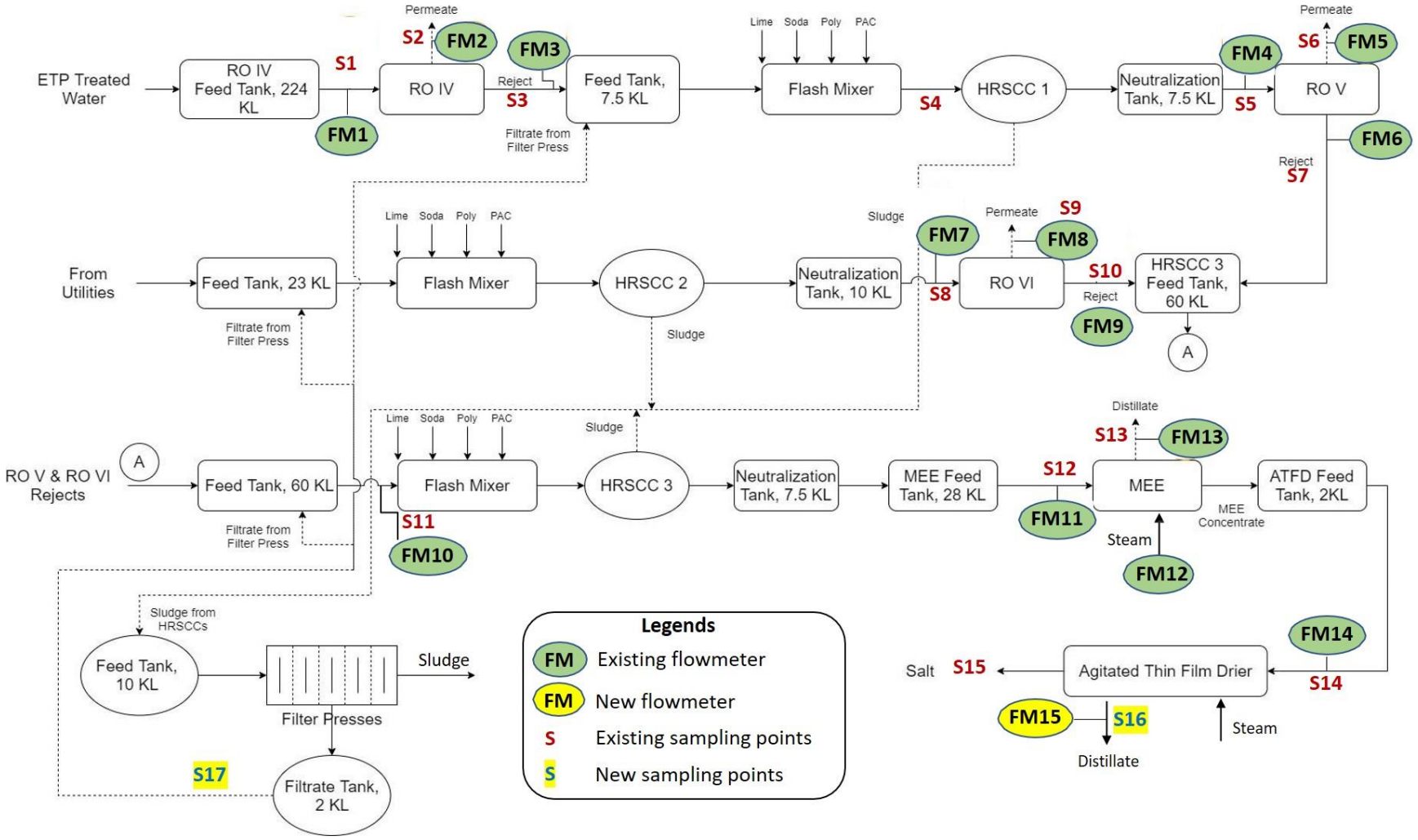


Figure 4: Flow diagram showing the treatment scheme of Utility stream

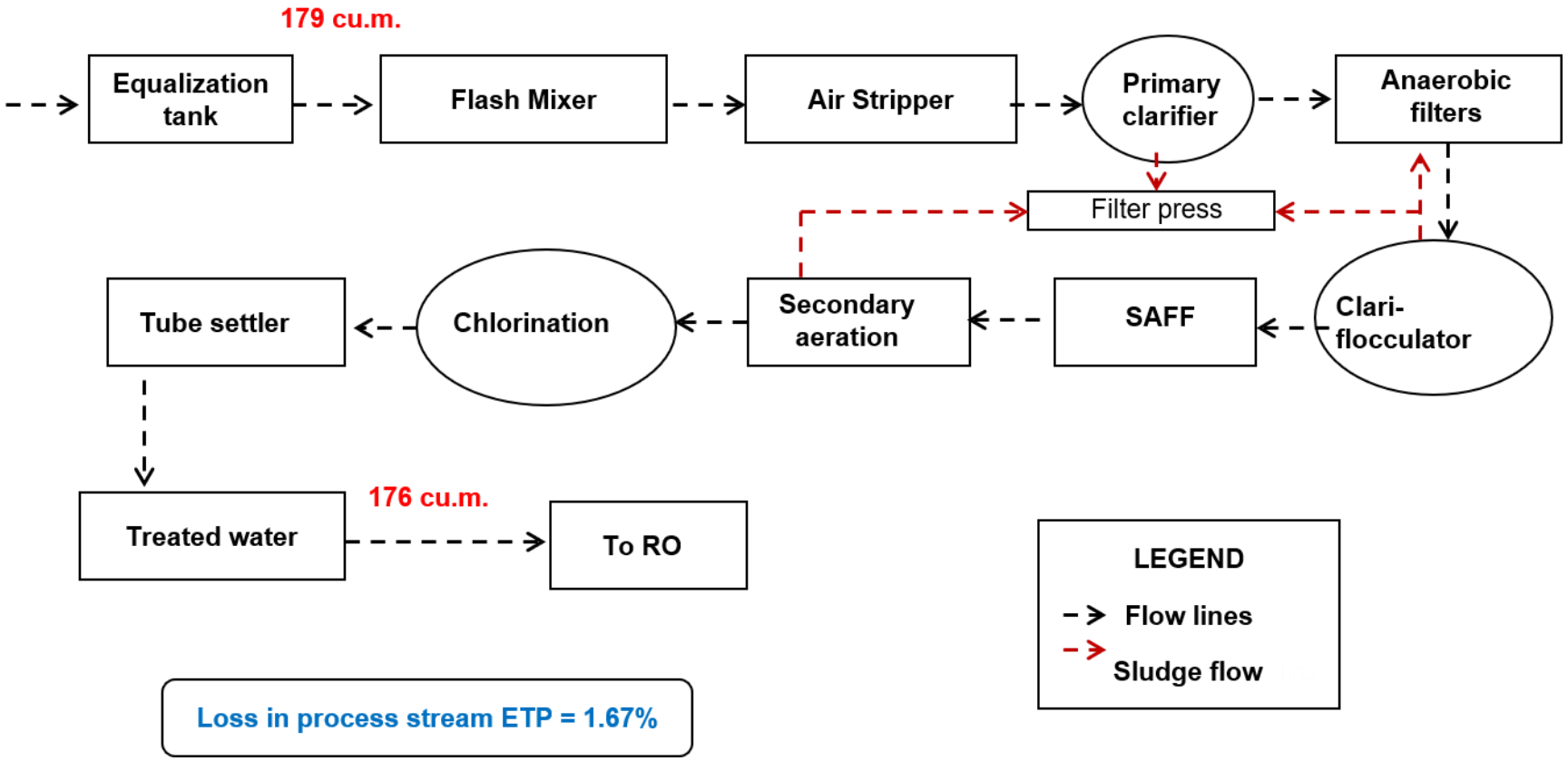


Figure 5: Water mass balance of Process Stream (Water Mass Balance Matching)

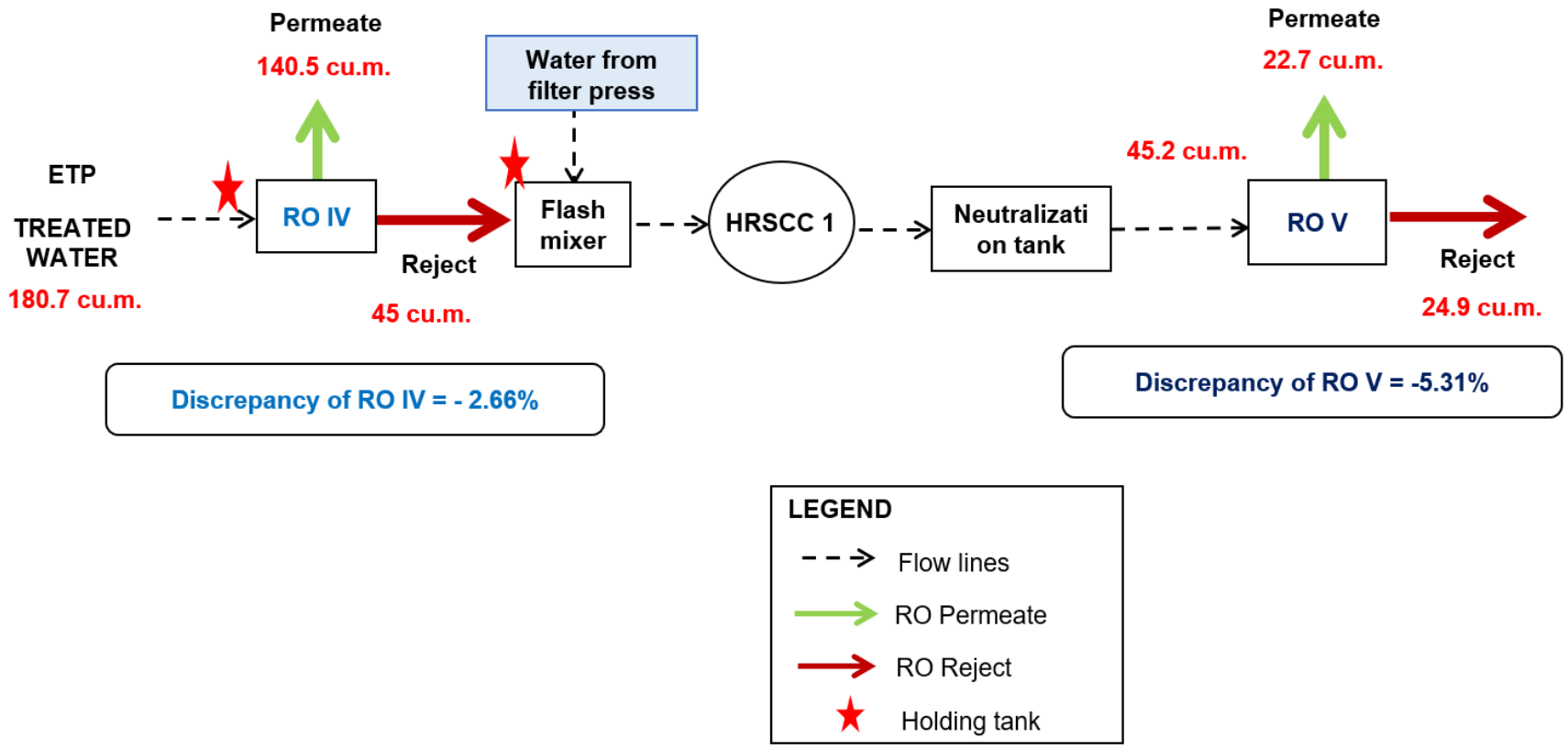


Figure 6: Water Mass Balance of Utility Stream of ETP – RO IV and RO V

(Size of the storage tank before RO-IV and flash mixer of HRSCC1 is 224kL and 7.5kL)

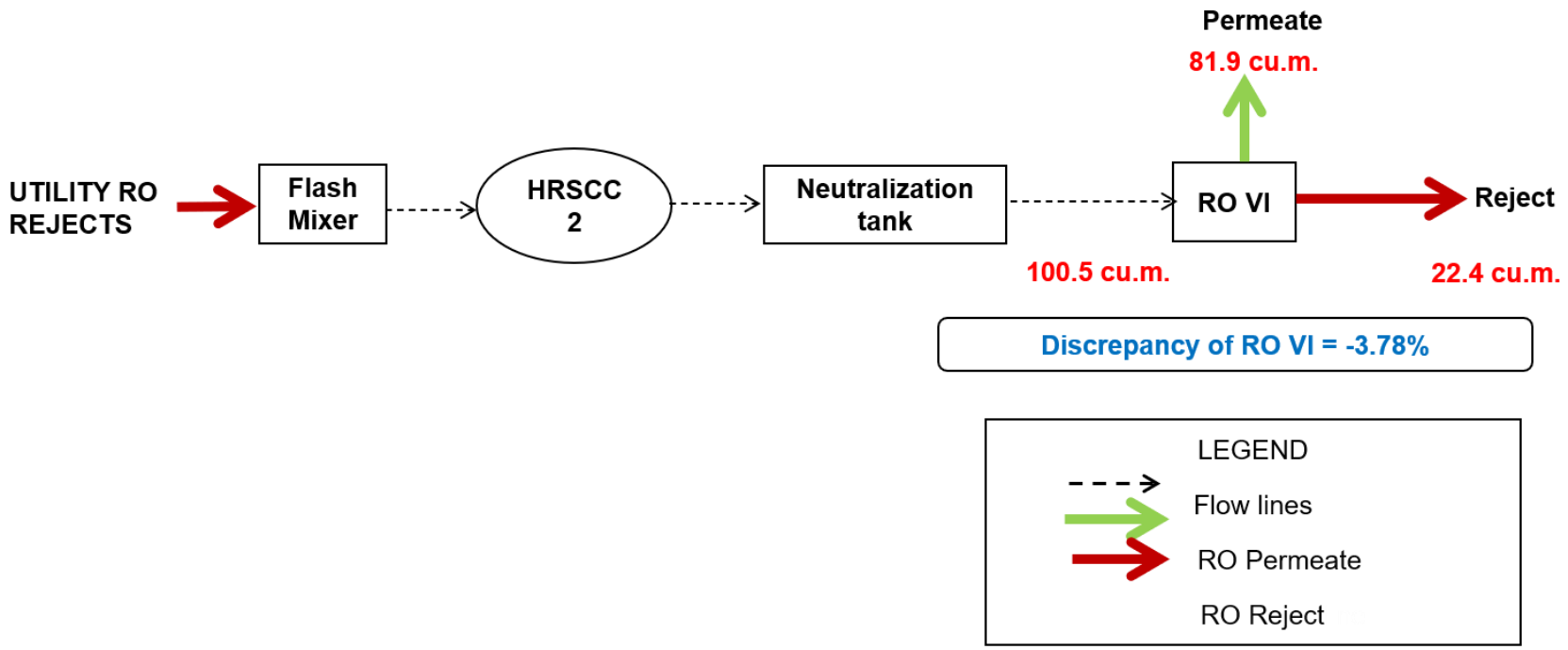


Figure 7: Water Mass Balance of Utility RO Stream – RO VI System

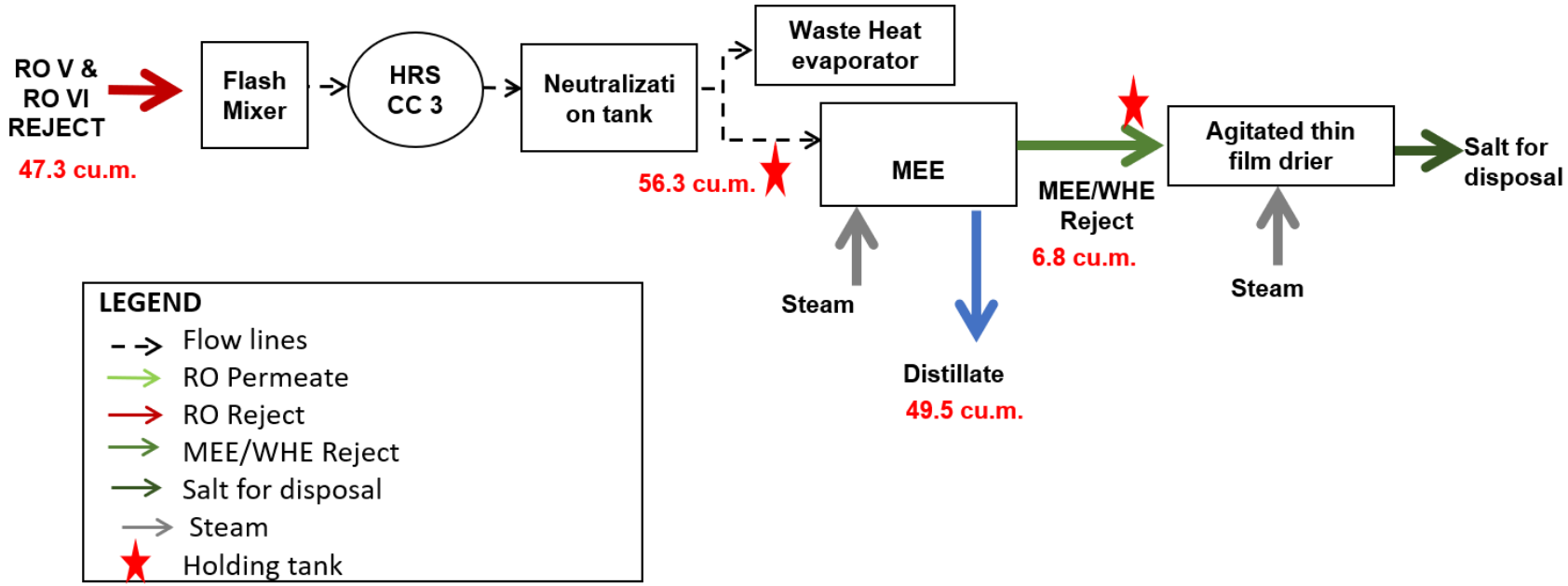


Figure 8: Water mass balance of RO V and RO VI rejects and MEE system (Water balance matching)

(Sizes of storage tank before MEE – 28 kL and storage tank before ATFD – 2 kL)

Table 1: Sampling locations of process streams

Sl. No	Sample ID	Sampling location	Type of sampling
1	PS1	Equalized Waste water feed to ETP	Composite
2	PS2	Feed To Anaerobic Filter	Composite
3	PS3	Outlet from Anaerobic Filter	Composite
4	PS4	Feed to Aeration stage # 1	Composite
5	PS5	Feed to Aeration stage # 2	Composite
6	PS6	Outlet of Aeration stage # 2	Composite
7	PS7	Final Outlet of ETP	Composite
8	PS8	Filtrate from PS filter press	Grab

Table 2: Sampling locations of utility stream

Sl. No	Sample ID	Sampling location	Type of sampling
1	S1	ETP treated Water	Composite
2	S2	RO IV Permeate	Composite
3	S3	RO IV Reject	Composite
4	S4	HRSCC #1 Inlet	Composite
5	S5	RO V Feed	Composite
6	S6	RO V Permeate	Composite
7	S7	RO V Reject	Composite
8	S8	RO VI Feed	Composite
9	S9	RO VI Permeate	Composite
10	S10	RO VI Reject	Composite
11	S11	Flash Mixer # 3 Inlet	Composite
12	S12	MEE Feed	Composite
13	S13	MEE Distillate	Composite
14	S14	ATFD Feed	Composite
15	S15	ATFD salt	Composite
16	S16	ATFD distillate	Composite
17	S17	Filtrate from US filter press	Grab

Table 3: Operational Schedule and Time of Operation of ETP

Sl. No	Treatment Units	Operational schedule for 50% capacity	Time of operation observed on 09-10-2021	Remarks
1	RO IV	10 h	9 h 15 min	● Started at 10:15 am and stopped at 7:30 pm
2	RO V	10 h	10 h 5min	● Started at 10 am ● Stopped for 40 min (2:45 pm to 3:25 pm) due to power fluctuations ● Stopped at 8:35 pm
3	RO VI	10 h	10 h 40 min	● Started at 10 am and stopped at 8:40 pm
4	MEE	10 h	8 h	● Started at 10 am and stopped at 6 pm
5	ATFD	6 h	3 h 15 min	● Started at 4 pm and stopped at 7:15 pm

Table 4: Instruments/methods used for the analysis of various pollutants

Sl. No	Parameters	Instruments/Method used
1	pH, EC, Turbidity	Hach Digital meter
2	TS, TSS, TDS, VSS, FSS, VDS and FDS	Gravimetric method
3	COD	Closed reflux method
4	TOC	TOC analyzer
5	Alkalinity	Titration method
6	Chlorides, Sulphates, Nitrates	Titration method
7	Sodium, Potassium, Calcium, Magnesium	Ion chromatography
8	Malic acid, oxalic acid, maleic acid, fumaric acid	High-performance liquid chromatography (HPLC)
9	Phthalic anhydride	
10	Diethyl phthalate	
11	VOCs – Acetonitrile, Isopropyl alcohol, o-xylene, ethanol	GC-FID

Table 5: Summary of Water mass balance of the treatment units

S.No	Treatment unit/process	Observed operating time	Observed inflow into the unit (m^3)	Observed outflow from the unit (m^3)	Discrepancy	Remarks
1	**Process effluent stream – ETP** (Includes primary treatment, anaerobic filter, SAFF, chlorination and tube settler)	24h	179	176	1.67 %	-
2	RO-IV	9h 15min	180.7	185.5 *(140.5 (P) + 45(R))*	-2.66%	The storage tank of 224 m^3 is available in the RO-IV feed
3	RO-V	10h 5min	45.2	47.6 *(22.7 (P) + 24.9(R))*	-5.31%	Reject from RO-IV and water from filter press were fed into RO-V after HRSCC1
4	RO-VI	10h 40min	100.5	104.3 *(81.9(P) + 22.4(R))*	-1.23%	-
5	MEE	8h	56.3	56.3 *(49.5(D) + 6.8(R))*	0.0%	The storage tanks of 28 m^3 and 2m^3 is available in the MEE feed and MEE reject, respectively

Note: P – Permeate, R – Reject, and D - Distillate

Table 6: Physical parameters and organics of the composite samples collected from ETP

Sl.No	Sample ID	pH	EC (mS/cm)	Turbidity (NTU)	TS (mg/L)	TSS (mg/L)	TDS (mg/L)	COD (mg/L)	TOC (mg/L)
	Process stream								
1	Equalized Wastewater feed to ETP	5.10 ±0.14	26.50 ± 0.14	Coloured sample	22200 ± 480.83	2865 ± 1590.99	16550 ± 113.14	16631.50 ± 12.02	6347.50 ± 51.62
2	Feed To Anaerobic Filter	7.11 ±0.01	28.65 ± 0.07	Coloured sample	29865 ± 7.07	2530 ± 127.28	26060 ± 5685.14	16970.00 ± 14.14	5886.00 ± 8.49
3	Outlet from Anaerobic Filter	8.20 ±0.02	24.30 ± 0.08	Coloured sample	26460 ± 84.85	1350 ± 113.14	22175 ± 2213.24	10300.00 ± 28.28	3945.65 ± 9.40
4	Feed to Aeration stage # 1	8.26 ±0.01	11.91 ± 0.02	Coloured sample	22525 ± 252.5	2531 ± 141.42	18835 ± 1520.28	11245.00 ± 49.50	4229.00 ± 8.49
5	Feed to Aeration stage # 2	8.20 ±0.01	11.64 ± 0.10	Coloured sample	14530 ± 169.71	4650 ± 622.25	10055 ± 1435.43	2942.00 ± 19.80	968.76 ± 8.83
6	Outlet of Aeration stage # 2	8.43 ±0.01	11.34 ± 0.21	Coloured sample	15215 ± 148.49	832 ± 115.6	9720 ± 424.26	2534.00 ± 31.11	958.00 ± 1.41
7	Final Outlet of ETP	8.55 ±0.07	12.74 ± 0.03	Coloured sample	13060 ± 1315.22	1055 ± 106.07	9560 ± 1117.23	2438.00 ± 36.77	994.60 ± 3.68
8	Filtrate from PS filter press	8.30 ±0.10	17.13 ± 0.30	Coloured sample	14885 ± 1548.56	705 ± 7.07	13135 ± 473.76	8119.00 ± 12.73	2613.00 ± 33.94
	Utilities Stream								
9	ETP treated water	7.90 ±0.12	10.93 ± 0.03	Coloured sample	9155 ± 1279.86	560 ± 28.28	6880 ± 1951.62	2090.00 ± 14.14	719.78 ± 10.22

10	RO IV permeate	7.20 ±0.11	0.84 ± 0.01	4.22 ± 0.103	1470 ± 480.83	150 ± 70.71	650 ± 14.14	25.20 ± 2.83	17.88 ± 1.45
11	RO IV reject	7.95 ±0.01	28.85 ± 0.21	Coloured sample	30400 ± 56.57	2060 ± 169.71	18970 ± 3931.51	6240.00 ± 45.25	2844.06 ± 48.00
12	HRSCC #1 Inlet	7.91 ±0.05	28 ± 0.12	Coloured sample	22310 ± 10125.77	1955 ± 7.07	20157 ± 2182.13	5963.00 ± 15.56	2333.56 ± 33.15
13	RO V feed	7.74 ±0.04	24.10 ± 0.14	Coloured sample	23525 ± 417.19	1015 ± 134.35	17620 ± 84.85	4825.00 ± 21.21	1828.00 ± 49.50
14	RO V permeate	7.03 ±0.01	1.31 ± 0.01	9.50 ± 0.287	1245 ± 233.35	190 ± 169.71	850 ± 70.71	55.00 ± 4.24	25.81 ± 3.29
15	RO V reject	7.66 ±0.12	45.70 ± 0.14	Coloured sample	45700 ± 636.40	2030 ± 169.71	35055 ± 1039.45	9264.00 ± 33.94	3616.65 ± 41.51
16	RO VI feed	7.93 ±0.01	19.95 ± 0.21	Coloured sample	15650 ± 141.42	595 ± 106.07	11610 ± 381.84	504.80 ± 11.03	164.44 ± 0.62
17	RO VI permeate	7.75 ±0.04	1.15 ± 0.01	Coloured sample	1470 ± 480.83	160 ± 42.43	675 ± 148.49	12.63 ± 1.37	3.94 ± 0.85
18	RO VI reject	7.86 ±0.02	78.15 ± 0.07	Coloured sample	72040 ± 28.28	2730 ± 155.56	52105 ± 417.19	2345.00 ± 35.36	739.43 ± 38.11
19	Flash mixer #3 inlet	7.74 ±0.01	36.75 ± 0.07	Coloured sample	36570 ± 183.85	2280 ± 367.70	26555 ± 190.92	5654.50 ± 13.44	2333.55 ± 2.76
20	MEE feed	7.70 ±0.10	49.75 ± 0.07	Coloured sample	44055 ± 261.63	1525 ± 289.91	31530 ± 579.83	3484.00 ± 28.28	1368.35 ± 7.28
21	MEE Condensate	9.20 ±0.11	0.59 ± 0.01	8.58 ± 0.133	1835 ± 403.05	280 ± 155.56	315 ± 120.21	61.60 ± 0.01	25.34 ± 3.11
22	MEE reject	8.35	265 ± 1.41	13.36 ±	277150 ±	11690 ±	196395 ±	35360.00 ±	11732.50 ±

		±0.01		0.023	1767.77	2291.03	3019.35	0.00	62.93
23	ATFD Distillate	8.68 ±0.04	1.45 ± 0.01	Coloured sample	1660 ± 650.54	195 ± 7.07	1115 ± 544.47	444.80 ± 0.00	129.38 ± 1.61
24	Filtrate from US filter press	12.16 ±0.01	33.65 ± 0.07	Coloured sample	29144 ± 316.78	1380 ± 127.28	21740 ± 212.13	3184.00 ± 0.00	1250.50 ± 4.24

*Number of samples analyzed for average ± SD (N=4)

Table 7: Volatile and dissolved solids of the composite samples collected from the Old ETP

Sl.No	Sample ID	TS (mg/L)	TSS (mg/L)	VSS (mg/L)	FSS (mg/L)	TDS (mg/L)	VDS (mg/L)	FDS (mg/L)
1	Equalized Waste water feed to ETP	22200 ± 480.83	2865 ± 1590.99	1587± 130.78	803± 20.451	16550 ± 113.14	11650 ±141.42	4900 ±28.28
2	Feed To Anaerobic Filter	29865 ± 7.07	2530 ± 127.28	1578± 82.325	843± 45.44	26060 ± 5685.14	13980 ±2531.44	12080 ±3153.7
3	Outlet from Anaerobic Filter	26460 ± 84.85	1350 ± 113.14	521± 16.32	729± 36.73	22175 ± 2213.24	15710 ±1895.05	6465 ±318.2
4	Feed to Aeration stage # 1	22525 ± 252.5	2531 ± 141.42	500± 36.99	2259± 203.26	18835 ± 1520.28	13430 ±890.95	5405 ±629.33
5	Feed to Aeration stage # 2	14530 ± 169.71	4650 ± 622.25	431± 13.89	3098± 156.32	10055 ± 1435.43	4980 ±919.24	5075 ±516.19
6	Outlet of Aeration stage # 2	15215 ± 148.49	832 ± 115.6	465± 12.57	270± 17.86	9720 ± 424.26	4495 ±21.21	5225 ±445.48
7	Final Outlet of ETP	13060 ± 1315.22	1055 ± 106.07	794± 187.36	230± 86.36	9560 ± 1117.23	4540 ±268.7	5020 ±848.53

*Number of samples analyzed for average ± SD (N=4)

Table 8: Concentration of ions in the composite samples collected from ETP

Sl.No	Sample ID	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	Total alkalinity (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)
1	Equalized Wastewater feed to ETP	1737.05 ± 70.19	68.36 ± 1.56	9008.45 ± 0.92	1600±10	2933.19 ± 23.91	9.99 ± 1.22	382.24 ± 26.46	260.80 ± 1.13
2	Final Outlet of ETP	1985.20 ± 10.12	9.56 ± 0.94	495.35 ± 1.63	2000±20	1211.53 ± 1.65	11.72 ± 0.54	60.51 ± 0.34	60.40 ± 0.57
3	ETP treated water	2282.98 ± 140.37	124.29 ± 1.25	406.13 ± 2.79	750±0.0	1288.66 ± 8.40	14.10 ± 0.68	52.49 ± 1.1	43.66 ± 12.25
4	RO IV permeate	326.73 ± 5.85	116.99 ± 10.32	19.91 ± 0.83	50±0.0	108.86 ± 0.81	58.29 ± 0.33	1.64 ± 0.37	58.72 ± 1.81
5	RO IV reject	3970.40 ± 1403.75	163.20 ± 8.13	1006.35 ± 2.61	2350±50	2516.00 ± 4.81	29.64 ± 3.91	201.08 ± 3.75	109.18 ± 5.91
6	HRSCC #1 Inlet	4963.00 ± 1403.75	22.16 ± 3.75	938.28 ± 0.46	2300±100	3025.25 ± 1.06	68.83 ± 0.11	233.43 ± 0.14	95.80 ± 0.28
7	RO V feed	3970.40 ± 0.00	120.31 ± 10.00	715.47 ± 2.02	950±50	2387.80 ± 14.99	28.89 ± 0.45	31.61 ± 3.75	47.80 ± 5.94
8	RO V permeate	736.18 ± 11.70	13.53 ± 0.31	14.46 ± 0.06	30±0.0	380.00 ± 11.03	13.65 ± 1.20	2.26 ± 0.38	10.36 ± 2.32
9	RO V reject	9926.00 ± 0.00	166.29 ± 6.25	1246.83 ± 2.50	1050±50	5666.40 ± 8.34	52.86 ± 0.25	47.99 ± 0.86	121.00 ± 1.41
10	RO VI feed	3970.40 ± 0.00	18.18 ± 0.63	108.32 ± 0.25	288±12.5	2379.30 ± 2.97	27.35 ± 1.48	43.5 ± 7.49	43.66 ± 12.25

11	RO VI permeate	165.43 ± 0.00	24.59 ± 0.31	8.17 ± 0.07	25±5	101.95 ± 9.12	30.05 ± 1.63	4.75 ± 0.37	2.37 ± 0.89
12	RO VI reject	24815.00 ± 0.00	3219.68 ± 50.02	467.18 ± 0.88	900±50	15517.94 ± 12.11	228.55 ± 4.18	42.97 ± 15	51.96 ± 0.06
13	Flash mixer #3 inlet	6948.20 ± 0.00	40.73 ± 1.25	916.64 ± 2.21	1550±50	4382.40 ± 56.43	44.16 ± 0.59	93.6 ± 16.08	96.10 ± 12.59
14	MEE feed	11911.20 ± 0.00	16.85 ± 1.25	731.04 ± 1.50	750±0.0	7662.44 ± 401.98	385.80 ± 3.46	15.26 ± 0	44.94 ± 0.08
15	MEE Condensate	37.22 ± 17.55	3.59 ± 0.00	16.03 ± 1.10	150±0.0	28.86 ± 0.58	1.96 ± 0.16	1.22 ± 0	0.00 ± 0.00
16	MEE reject	115141.60 ± 1403.75	237.92 ± 7.50	8301.63 ± 0.10	3900±100	67546.47 ± 2811.82	147.40 ± 1.19	174.11 ± 27.32	283.30 ± 30.69
17	ATFD Distillate	41.36 ± 1.450	53.99 ± 1.25	240.23 ± 1.51	65±5	104.06 ± 1.78	17.33 ± 1.63	1.91 ± 0.01	0.92 ± 0.11
18	Filtrate from US filter press	3970.40 ± 16.4	20.39 ± 1.88	925.25 ± 1.63	1550±0.0	2372.75 ± 13.79	26.11 ± 1.17	366.13 ± 0.1	17.10 ± 0.14

*Number of samples analyzed for average ± SD (N=4)

Table 9: Concentration of organic acids and volatile organic compounds (VOCs) in the composite samples collected from ETP

Sl.No	Sample ID	DEP (mg/L)	Oxalic acid (mg/L)	Malic acid (mg/L)	Maleic acid (mg/L)	Fumaric acid (mg/L)	Phthalic acid (mg/L)	Ethanol (mg/L)	Acetonitrile (mg/L)	Iso-propyl alcohol (mg/L)	o-Xylene (mg/L)
Process stream											
1	Equalized Wastewater feed to ETP	50.14	2.86	80.52	179.90	244.54	1101.98	BDL	BDL	BDL	BDL
2	Final ETP Outlet	2.23	0.87	23.38	54.59	19.05	581.31	BDL	BDL	BDL	BDL
3	Filtrate from PS filter press	5.39	BDL	BDL	BDL	BDL	104.94	BDL	BDL	BDL	BDL
Utilities stream											
4	ETP treated water	BDL	1.11	16.23	22.36	7.79	338.01	BDL	BDL	BDL	BDL
5	RO IV permeate	4.10	BDL	BDL	BDL	BDL	2.37	BDL	BDL	BDL	BDL
6	RO IV reject	BDL	BDL	30.84	11.01	BDL	699.88	BDL	BDL	BDL	BDL
7	HRSCC #1 Inlet	5.55	BDL	10.39	BDL	BDL	789.35	BDL	BDL	BDL	BDL
8	RO V feed	0.90	BDL	8.12	BDL	BDL	684.84	BDL	BDL	BDL	BDL
9	RO V permeate	0.18	BDL	BDL	BDL	BDL	34.43	BDL	BDL	BDL	BDL
10	RO V reject	BDL	BDL	12.85	BDL	BDL	443.88	BDL	BDL	BDL	BDL
11	RO VI feed	BDL	BDL	BDL	BDL	BDL	18.07	BDL	BDL	BDL	BDL
12	RO VI permeate	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13	RO VI reject	BDL	BDL	BDL	BDL	BDL	17.05	BDL	BDL	BDL	BDL
14	Flash mixer #3	BDL	BDL	BDL	BDL	BDL	340.84	BDL	BDL	BDL	BDL
15	MEE feed	BDL	BDL	BDL	BDL	BDL	130.83	BDL	BDL	BDL	BDL
16	MEE Condensate	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
17	MEE reject	0.27	BDL	BDL	BDL	BDL	1837.78	BDL	BDL	BDL	BDL
18	ATFD distillate	BDL	BDL	BDL	BDL	BDL	50.84	BDL	BDL	BDL	BDL
19	Filtrate from US filter press	BDL	BDL	1.56	BDL	BDL	683.53	BDL	BDL	BDL	BDL

BDL: Below detectable limit

Table 10: Characteristics of salt and sludge samples collected from ETP

SI.No	Parameters	Process Stream (PS) sludge	Utility stream (US) sludge	ATFD Salt extract
1	Moisture content (%)	16.26 ± 1.05	13.55 ± 0.02	1.71 ± 0.05
2	pH in water	7.81 ± 0.12	9.28 ± 0.14	10.61 ± 0.01
3	Volatile solids (%)	2.87 ± 0.15	1.59 ± 0.02	1.65 ± 0.01
4	Fixed solids (%)	97.13 ± 0.15	98.41 ± 0.02	98.35 ± 0.01
5	TDS (mg/g)	11.35 ± 0.49	40.95 ± 0.38	641.23 ± 4.22
6	COD (mg/g)	1.640 ± 0.01	1.79 ± 0.02	126.80 ± 6.04
7	TOC (mg/g)	0.768 ± 0.01	1.026 ± 0.01	37.34 ± 0.06
8	Chloride (mg/g)	0.62 ± 0.17	12.9 ± 0.26	468.38 ± 4.39
9	Sulphate (mg/g)	0.47 ± 0.01	3.28 ± 0.02	14.48 ± 0.20
10	Nitrate (mg/g)	0.89 ± 0.01	0.92 ± 0.01	70.84 ± 0.06
11	Total alkalinity (mg/g)	2.50 ± 0.01	17.5 ± 0.00	2.51 ± 0.00
12	Sodium (mg/g)	0.29 ± 0.01	8.08 ± 0.03	380.5 ± 1.92
13	Potassium (mg/g)	0.01 ± 0.00	0.12 ± 0.00	4.27 ± 0.03
14	Magnesium (mg/g)	0.14 ± 0.09	0.20 ± 0.02	1.02 ± 0.00
15	Calcium (mg/g)	0.76 ± 0.15	0.05 ± 0.00	2.99 ± 0.01

6. Inferences from Sample analyses

- The TDS concentration of the process stream was observed as 16550 mg/L. The concentration of chloride and nitrate ions in the process stream was 1737.05 and 9008.45 mg/L, respectively.
- The COD of the treated water from ETP is above 2000 mg/L. There was almost a 98.23% reduction of COD value from the MEE inlet stream to MEE condensate. The COD value of permeate of RO IV, RO-V, and VI is observed as 25.2±2.83mg/L 55±4.24 mg/L and 12.63±1.37 mg/L, respectively.
- The moisture content of process stream (PS) sludge, Utility stream (US) sludge, and ATFD salt was observed as 16.26±1.05%, 13.55±0.02%, and 1.71±0.05%, respectively. It was found to be rich in chloride and sodium ions, as given in **Table 10**.

- The volatile solid content in the salt/sludge samples –PS sludge, US sludge, and ATFD salt was found to be 2.87±0.15%, 1.59±0.02%, and 1.65±0.01%, respectively.

- Organic acids in the process stream (PS1) – oxalic acid, malic acid, maleic acid, fumaric acid, and phthalic acid was 2.86mg/L, 80.52mg/L, 179.9mg/L, 244.54mg/L, and 1101.98mg/L, respectively. The concentration of diethyl phthalate (DEP) in the process stream was observed as 50.14mg/L. The presence of DEP in the samples was witnessed in GCMS scan analysis (Annexure-1).

- The VOCs such as o-xylene, ethanol, acetonitrile, and isopropyl alcohol were not detected in the samples using GC-FID. However, the traces of o-xylene were evidenced in samples such as Equalized wastewater feed to ETP (PS1), Final Outlet of ETP (PS7), and ETP treated water (S1) (Annexure-2).

7. Mass Balance

Table 11: Mass inflow into the system

S.No.	Parameters		Value	Unit
1	**Process Stream (Old ETP)**			
	a	***Effluent to be treated at Process stream***		
		Inflow into Equalization tank (Old ETP)	179	m^3
		Average total dissolved solids concentration	16550	mg/L
		Mass into the process stream	2962.5	kg
2	**Utility stream**			
	a	***Feed to RO VI***		
		Inflow into RO VI	180.7	m^3
		Average total dissolved solids concentration	6880	mg/L
		Mass into RO VI	1243.2	kg
3	**Chemical consumption**			
	a	Lime	800	kg
	b	Soda	1200	kg
	c	Poly electrolyte	12.5	kg
	d	PAC	1.5	kg
	e	$Mg(OH)_2$	0	kg
	f	HCl	740	kg
		Total chemical consumed	2754	kg
	Total mass into the system		**6959.7**	**Kg**

Table 12: Mass outflow from the system

S.No.	Parameters		Value	Unit
1	**Utility stream**			
	a	***RO IV Permeate***		
		Permeate water flow from RO IV	140.5	m^3
		Average total dissolved solids concentration	650	mg/L
		Mass out of RO IV	91.33	kg
	b	***RO V Permeate***		
		Permeate water flow from RO V	22.7	m^3
		Average total dissolved solids concentration	400	mg/L
		Mass out of RO V	9.08	kg
	c	***RO VI Permeate***		
		Permeate water flow from RO VI	81.9	m^3
		Average total dissolved solids concentration	675	mg/L
		Mass out of RO VI	55.28	kg
	d	***MEE Distillate***		
		Flow out of MEE as distillate	49.5	m^3
		Average total dissolved solids concentration	315	mg/L
		Mass out of MEE as distillate	15.59	kg
2	**Sludge/Salt produced**			
	a	Sludge produced in Process stream	2200	kg
	b	Sludge produced in Utility stream	2140	kg
	c	ATFD salt	1860	kg
	Total mass-produced out from the system		**6371.28**	**kg**

A discrepancy in the mass balance is 8.45%. The recovery of RO IV, V, and VI was found to be 77.75%, 49.78%, and 81.49%, respectively. In all the RO systems, outflow from the units (permeate and reject) is slightly higher than the feed flow rate. This variation in the flow might have led to the discrepancy in the mass balance**. In all RO systems, the feed volume was less than the reject plus permeate. It may be due to the error in the flow meters or may be due to the pumping of stored clean water.**

Table 13: Mass balance in each treatment units

Si.No	Treatment unit	Stream	Flow (m^3)	TDS (mg/L)	Mass (kg)	Mass in and out of each unit (kg)	Discrepancy (%)
1	RO-IV	Feed	180.7	6880	1243.22	1243.22	23.99
		Permeate	140.5	650	91.33	944.98	
		Reject	45	18970	853.65		
2	RO-V	Feed	45.2	17620	796.42	796.42	-10.74
		Permeate	22.7	400	9.08	881.95	
		Reject	24.9	35055	872.87		
3	RO-VI	Feed	100.5	11610	1166.81	1166.81	-4.77
		Permeate	81.9	675	55.28	1222.43	
		Reject	22.4	52105	1167.15		
4	MEE	Feed	56.3	31530	1775.14	1775.14	23.89
		Permeate	49.5	315	15.59	1351.08	
		Reject	6.8	196395	1335.49		
5	ATFD	Feed	6.8	196395	1335.49	1335.49	-39.28
		Salt	*from weighing slip data*		1860	1860.00	

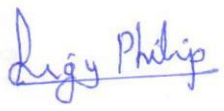
8. Summary

- The TDS concentration of the process stream was 16550 mg/L. The concentrations of chloride and nitrate ions in the process stream were 1737.05 and 9008.45 mg/L, respectively.
- *The Effluent Treatment Plant for the Process Stream was able to achieve 85.3% of COD reduction & 84.3 % of TOC reduction during the observation period.*
- Organic acids in the process stream (PS1) – The concentrations of organic acids like oxalic acid, malic acid, maleic acid, fumaric acid, and phthalic acid in the process stream were 2.86mg/L, 80.52mg/L, 179.9mg/L, 244.54mg/L, and 1101.98mg/L, respectively.
- The removal efficiencies of the organic acids varied between 47.2 to 95.5% in the ETP. Especially, Malic acid (70.96%) and phthalic acid (47.24%) showed less removal.
- The VOCs such as o-xylene, ethanol, acetonitrile, and isopropyl alcohol were not detected in the samples using GC-FID. However, traces of o-xylene were observed in a few samples in GC-MS analysis.

- The concentration of diethyl phthalate (DEP) in the process stream was observed as 50.14mg/L. The removal of DEP in ETP was observed as 95.5%.
- The moisture content of Utility stream (US) sludge, process stream (PS) sludge, and ATFD salt was observed as 16.26±1.05%, 13.55±0.02%, and 1.71±0.05%, respectively. It was found to be rich in chloride and nitrate ions.
- The volatile solid content in the salt/sludge samples – US sludge, PS sludge, and ATFD salt was found to be 2.87±0.15%, 1.59±0.02%, and 1.65±0.01%, respectively
- There was almost a 98.23% reduction of COD from the MEE inlet stream to MEE condensate. It may be due to the escape of organic acids from the system.
- The COD value of permeate of RO IV, RO-V, and RO-VI is observed as 25.2±2.83mg/L 55±4.24 mg/L and 12.63±1.37 mg/L, respectively.
- **There was a discrepancy of 8.45% in the salt mass balance.**
- The recovery of RO IV, V, and VI was found to be 77.75%, 49.78%, and 81.49%, respectively.
- In all the RO systems, outflow from the units (permeate and reject) is more than the feed flow rate. This variation in the flow would have led to a discrepancy in the mass balance**.**

9. Recommendations

- **The existing ZLD facility in M/S TCL is adequate to treat 600 KLD of wastewater, provided the plant is operated and maintained properly.**
- **The performance of the ETP can be improved significantly by optimizing the reactor sizes and properly operating them. The COD value of the treated water from ETP is above 2000 mg/L. Also, the activity of biomass in the system may be assessed.**
- **The water mass balance of the system was satisfactory, within a permissible error limit**
- **There was an 8% discrepancy in the solid mass balance. It may be due to the variation in the quality of wastewater and intermittent storage.**
- **The plant may avoid unnecessary storage facilities.**



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