

**BEFORE THE NATIONAL GREEN TRIBUNAL  
SOUTHERN ZONE, CHENNAI  
Original Application No. 131 of 2020 (SZ)**

**IN THE MATTER OF:**

M. Jayachandran,  
Ranipet District and Anr.

... Applicant(s)

With

The Ministry of Environment,  
Forest & Climate Change and Ors.

...Respondent(s)

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(Dr. R. Sridhar)  
Scientist D  
Integrated Regional Office (IRO)  
MoEFCC, Chennai

**Place: Chennai**  
**Date: 13-12-2021**

**OBSERVATIONS OF THE JOINT COMMITTEE (APPOINTED IN OA NO. 131 OF 2020) ON THE ALLEGATIONS MENTIONED BY THE APPLICANT IN THEIR REPLY DATED 05-11-2021.**

**1. Background**

The Hon'ble NGT, in Original Application No. 131 of 2020 (SZ) in the matter of M. Jayachandran, Ranipet District and Anr. Vs The Ministry of Environment, Forest & Climate Change and Ors, vide its order dated 08-11-2021 directed to Joint Committee to ascertain as to whether the allegations mentioned by the applicant in O.A. No.131/2020 in their reply are genuine or not.

The allegation mentioned by the applicant in O.A. No.131/2020 in their reply 05.11.2021 pertains to releasing of untreated effluents by the 8<sup>th</sup> Respondent, M/s Thirumalai Chemicals Ltd, SIPCOT, Ranipet on 24-10-2021 and 29-10-2021 at the time of raining/rainy season through rain water channel in indiscriminate way.

The applicant further complained that the 8<sup>th</sup> Respondent had failed to comply with the Joint Committee's recommendations related to (i) Conducting adequacy test from IIT Madras and obtaining certification that the unit has achieved 100% ZLD capacity after commissioning of upgraded ETP and (ii) Preparation of DPR through IIT, Madras for the remediation of the land where the untreated effluent was discharged within the industry site and execution of the task of remediation of contaminated site, under the supervision of TNPCB.

**2. Joint Committee's visit**

In order to ascertain the allegations of the applicant and review the compliance status of the recommendations that are 'Partially Complied' or the 'Compliance is under progress', the Joint Committee had briefing meeting at the office of RDO, Ranipet and carried out a site visit at 8<sup>th</sup> Respondent Unit on 01-12-2021. The following committee members attended the site visit and reviewed the compliance status:

1.	Dr. R. Rajkumar Scientist 'D' CPCB, Regional Directorate, Chennai
2.	Smt. R. Poonkodi RDO, Ranipet
3.	Er. Muthaiya SE,WRD, Pennaiyar Basin Circle, Tiruvannamalai
4.	Shri G. Ravichandran DEE, TNPCB, Vellore
5.	Dr. R. Sridhar Scientist 'D', Integrated Regional Office (IRO), MoEF&CC, Chennai

### 3. Joint Committee's observation

Committee's observation on the allegations mentioned by the applicant related to releasing of untreated effluents by the 8<sup>th</sup> Respondent Unit and compliance status of recommendations given in the following table:

No.	Issues	Joint Committee's observation
1	The allegation mentioned by the applicant in O.A. No.131/2020 in their reply 05.11.2021 pertains to releasing of untreated effluents by the 8 <sup>th</sup> Respondent, M/s Thirumalai Chemicals Ltd, SIPCOT, Ranipet on 24-10-2021 and 29-10-2021 at the time of raining/rainy season through rain water channel in indiscriminate way	<p>The Committee noted that the water samples collected on 24-10-2021 (by Ranipet DSP office) and further on 25-10-2021 and 11-11-2021 (by TNPCB) were analysed and the test reports produced for Committee's information. The reports are enclosed at <b>Annexure-I</b>. The test reports were discussed by the Committee.</p> <p>From the analysis of water sample collected on 24-10-2021, 25-10-2021 and 11-11-2021 it was observed that that the effluent of the industry was mixed with the rain water.</p> <p>The Committee has gone furthest in this analysis. During the site inspection held on 1-12-2021, the Committee also collected water samples from the stagnated water</p>

	<p>inside the premises of the industry and got analyzed through the external and third-party laboratory (M/s Glens Laboratory, EPA approved). The analysis results are given in the following Table No.1. As per this analysis, the stagnated water samples collected inside the premises were showing the characteristic of the effluent generating from industry.</p> <ul style="list-style-type: none"> <li>• TDS is ranging from 2500 to 19984 mg/l, total hardness ranging from 210 to 1050 mg/l, Total Alkalinity ranging from 521 to 2654 mg/l, Chloride ranging from 517 to 7634 mg/l indicates the untreated effluent characteristics of inorganic stream.</li> <li>• Maleic Acid presence 16.81 mg/l is observed at one location in the stagnated water collected near ATFD and Phthalic Acid ranges from 8.93 to 296.32 which indicates the effluent characteristics of process effluent.</li> </ul> <p>This might be due to the fact that untreated effluent was discharged on the land inside the industry premises.</p> <p>Also, the samples which are collected at the location (treated effluent storage tank), near the storm water drain, was analyzed and it was observed that sample is showing the characteristics of untreated effluent. This further confirms that untreated effluent is stored in the industry premises without following proper</p>
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		<p>effluent management in the industry premises.</p> <p>The above observation clearly indicates the gross violation of industry in spite of having ZLD system for effluent management.</p>
2	<p>The unit was directed by TNPCB to restrict the production of 50 % of its consented quantity so as to achieve zero liquid discharge consistently till the commencement &amp; effective functioning of newly constructed Zero Liquid Discharge (ZLD) components.</p>	<p>The unit has provided ZLD system and adequacy of the same is also carried out by IIT, Chennai.</p> <p>The 8<sup>th</sup> Respondent unit has obtained CTO from TNPCB vide letter dated 29-11-2021 which is valid up to 31<sup>st</sup> March 2022.</p>
3	<p>Conducting adequacy test from IIT Madras and obtaining certification that the unit has achieved 100% ZLD capacity after commissioning of upgraded ETP.</p>	<p>Complied.</p> <p>The 8<sup>th</sup> Respondent Unit has obtained report from the IIT Madras which carried out the audit of the treatment systems to access the capacity for 100% ZLD capacity.</p> <p>The IIT report has recommended the following:</p> <ol style="list-style-type: none"> <li>1) The existing ZLD facility in M/s TCL is adequate to treat 600 KLD of wastewater, provided the plant is operated and maintained properly.</li> <li>2) 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</li> </ol>

		<p>activity of biomass in the system may be assessed.</p> <p>3) The water mass balance of the system was satisfactory, within a permissible error limit</p> <p>4) 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.</p> <p>5) The plant may avoid unnecessary storage facilities</p> <p>Copy of the report of the IIT Madras titled “Status report on Environmental Audit of Thirumalai Chemicals Ltd, Ranipet” is enclosed at <b>Annexure-II.</b></p>
4	<p>Preparation of DPR through IIT, Madras for the remediation of the land where the untreated effluent was discharged within the industry site and execution of the task of remediation of contaminated site, under the supervision of TNPCB</p>	<p>Complied.</p> <p>The DPR has been prepared by IIT Madras for remediation of the land where the untreated effluent was discharged within the industry site (<b>Annexure-III</b>).</p> <p>The Report was submitted to TNPC Board on 20.09.2021. As suggested by the TNPCB vide letter dated 23-9-2021, the 8<sup>th</sup> Respondent Unit has submitted the action plan with time schedule for execution of the work by the unit to the TNPCB. The contaminated site is being developed a green park with trees, shrubs and grass.</p>

**Table No.1: Analysis results of the samples collected by the Joint Committee**

<b>Parameters</b>	<b>Stagnated Sample near ATFD</b>	<b>Stagnated Sample near ETP (at storm water discharge point)</b>	<b>Stagnated Sample (inside premises near ATM)</b>	<b>Treated Effluent Storage tank</b>
pH	7.81	9.82	8.33	8.33
Conductivity	27800	10240	3810	15940
TDS	19984	7445	2500	11300
Colour	Yellow	Yellow	Yellow	Yellow
Odour	Disagreeable	Agreeable	Agreeable	Disagreeable
Turbidity	34	16.4	7.8	151.2
Total Hardness	1050	210	672	189
Total Alkalinity	2267	2654	521	4516
Chloride as Cl	7634	1320	517	2303
BOD	2123	79	87	3556
COD	9225	353	369	14350
Sulphate as SO <sub>4</sub>	1372.9	214	528	359.5
Nitrate as NO <sub>3</sub>	100.5	249	BDL (DL:1.0)	230
Sodium as Na	9080	3365	895	4900
Potassium	210	53	66	28
Total Suspended Solids	231	60	21.5	136
Fluoride as F	0.62	0.62	0.18	0.55
Hexavalent Chromium	0.148	BDL (DL:0.01)	BLD (DL:0.01)	0.03
T. Chromium as Cr	0.2	0.018	BLQ (LOQ:0.005)	0.042
Maleic Acid	16.81	BLQ (LOQ:1.0)	BLQ (LOQ:1.0)	BLQ (LOQ:1.0)
Fumaric Acid	BLQ (LOQ:1.0)	BLQ (LOQ:1.0)	BLQ (LOQ:1.0)	BLQ (LOQ:1.0)
Phthalic Acid	296.32	50.39	8.93	326.34

**Water samples collected by th Joint Committee on 1-12-2021 within the industry site**



#### **4. Directions issued by TNPCB:**

The Committee noted that the TNPCB, vide letter dated 20-11-2021 (**Annexure-IV**), has issued certain directions to the 8<sup>th</sup> Respondent Unit for the above violations which are extracted below:

- (i) The unit shall restrict the number of water discharge points connected with outlet drains to drain the excess rain water in and around the above unit.
- (ii) The unit shall install online continuous monitoring systems in consultation with JCEE (M), VLR in the discharge points for the parameters such as TDS, TSS, PH, BOD, COD and other relevant parameters along with surveillance camera and it shall be connected with WQW of TNPCB and CPCB web portal for continuous monitoring.
- (iii) The unit shall reuse the entire treated trade effluents (RO permeate and MEE Condensate) in their process continuously and to ensure 100% ZLD.
- (iv) The unit shall not discharge any treated /untreated effluent outside the premises and shall not be stagnated /ponding of water under any circumstances.

#### **5. Conclusion/Suggestions:**

- The unit has complied with the earlier directions issued by TNPCB.
- As directed by the Hon'ble Tribunal to verify the allegation made by the applicant, the Joint Committee observed that water samples collected by the TNPCB & Joint Committee from the industry site, shows the effluent characteristics, which might be due to the fact that effluent was discharged on the land inside the industry premises by violating the consent condition in spite of having ZLD system. The unit has to comply with the above directions issued by the TNPCB vide letter dt 20-11-2021.

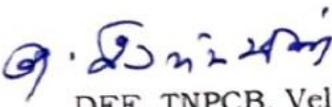
In view of the above, it is prayed by the Joint Committee that the TNPCB shall take necessary action on the repeated violations by the 8<sup>th</sup> Respondent Unit and periodically review the Unit to comply with the directions issued. The operation of the unit shall not attract repeated complaints.

**By considering the above facts and observation of the Joint Committee, the Hon'ble Tribunal may pass appropriate Order (s)/Direction (s) as deemed fit.**

  
RDO, Ranipet



R. Rajkumar  
Scientist 'D'  
CPCB  
Regional Directorate, Chennai

  
DEE, TNPCB, Vellore.



Scientist 'D',  
Integrated Regional Office,  
MoEF&CC, Chennai

  
SE, WRD, Palaniyar Ilasa Circle,  
Tiruvannamalai



**Tamilnadu Pollution Control Board**  
Advanced Environmental Laboratory – Vellore  
[ email - delvlr2011@gmail.com ]

Annexure-I

From

P. Sakthivel M.Sc., M.Phil.,  
Assistant Director  
Advanced Environmental Laboratory  
Tamil Nadu Pollution Control Board  
Opposite to Auxilium College  
Gandhi nagar , Katpadi  
Vellore - 632 006

To

The District Environmental Engineer  
Tamil nadu Pollution Control Board  
Vellore

Letter No : TNPCB / AEL / VLR / ROA / 015908/1 / 2022 - 22 / 02 . 11 . 2021  
&2

Sir,

Sub : Analysis of water / trade effluent samples - Report of analysis -  
Furnished - regarding

- Ref : 1) Board Lr. no : 02 / Labs / DDL / P1 / 2003 / 03.01.03  
2) T.O. Ackn. No : 015908/1&2 dated 26 . 10 . 2021  
3) T.O. Invoice No : 015908/1&2 dated 02 . 11 . 2021

Please find enclosed herewith the report of analysis along with the  
invoice / bill ( in duplicate ) for the samples received at this laboratory as per the  
references cited above .

A) Sample code numbers from	<u>VLR - 156</u>	to	<u>VLR - 157</u>
B) Number of samples received	<u>Two</u>		
C) Date of receipt of the sample	<u>26 . 10 . 2021</u>		

It is further informed that the duplicate copy of the enclosed bill is to be certified  
( as per reference one cited above ) & returned back to this laboratory for further  
action at our end.

The receipt of the report of analysis and the invoice is to be acknowledged.

Rs 14500

  
Assistant Director  
Advanced Environmental Laboratory  
TNPCB , Vellore  
02/11/21

Enclosed :

- 1) Report of analysis of Two samples ( in duplicate )  
2) Invoice / bill of Two samples ( in duplicate )

ROA of : M/s



## Tamilnadu Pollution Control Board

Advanced Environmental Laboratory – Vellore

[ email - delivr2011@gmail.com ]

Report No : W / 015908/1 / AEL / VLR / 2021 - 22 / 02.11.2021  
&2

- 1 Sample sent by : DEE , TNPCB , Vellore
- 2 Sample collected by : Ranipet DSP office
- 3 Date & time of collection : 24.10.2021 @ 19.00 Hrs Hrs
- 4 Date & time of sample receipt : 26.10.2021 @ 15.40 Hrs Hrs
- 5 Details of samples received : Two numbers of Water sample
- 6 Point of collection & sample nature :

a	VLR - 156	Sample taken at 7.00PM on 24.10.2021	Water sample
b	VLR - 157	Sample taken at 8.00PM on 24.10.2021	Water sample

### REPORT OF ANALYSIS

Sl No	Parameter	code no :	VLR - 156	VLR - 157
			746	747
1	pH	number	5.2	6
2	TSS	mg /L	80	246
3	TDS	mg /L	2574	1490
4	Chloride	mg /L	775	450
5	Sulphate	mg /L	112	125
6	BOD	mg /L	130	95
7	COD	mg /L	999	692
8	Sulphides	mg /L	24	28
9	Fluoride	mg /L	<1.0*	<1.0*
10	Total Chromium	mg /L	<0.01*	<0.01*
11	Hexavalent Chromium	mg /L	<0.01*	<0.01*
12	Phenolic Compounds	mg /L	0.32	0.23
13	Phosphate	mg /L	<0.15*	<0.15*
14	Lead	mg /L	<0.015*	<0.015*

Note \* Below detectable limit

\*\* Value could not be ascertained

Rs 14500

DCSO

Assistant Director  
Advanced Environmental Laboratory  
TNPCB , Vellore

Note :

- 1) The samples were collected and sealed by the officials of the Ranipet DSP office and handed over to the O/o the DEE , TNPCB , Vellore at 13.45 Hrs on 26.10.2021 by the revenue officials of Ranipet.
- 2) The samples were received after 24 Hrs from the time of collection. Samples were analysed at the request of the JCEE , ( M ) , TNPCB , Vellore.

ROA of: M/s



## Tamilnadu Pollution Control Board

Advanced Environmental Laboratory - Vellore

[ email - delvir2011@gmail.com ]

Report No : W / 015908/1 / AEL / VLR / 2021 - 22 / 02.11.2021  
&2

- 1 Sample sent by : DEE , TNPCB , Vellore
- 2 Sample collected by : Ranipet DSP office
- 3 Date & time of collection : 24.10.2021 @ 19.00 Hrs Hrs
- 4 Date & time of sample receipt : 26.10.2021 @ 15.40 Hrs Hrs
- 5 Details of samples received : Two numbers of Water sample
- 6 Point of collection & sample nature :

a	VLR - 156	Sample taken at 7.00PM on 24.10.2021	Water sample
b	VLR - 157	Sample taken at 8.00PM on 24.10.2021	Water sample

### REPORT OF ANALYSIS

Sl No	Parameter	code no :	VLR - 156	VLR - 157
			746	747
1	pH	number	5.2	6
2	TSS	mg / L	80	246
3	TDS	mg / L	2574	1490
4	Chloride	mg / L	775	450
5	Sulphate	mg / L	112	125
6	BOD	mg / L	130	95
7	COD	mg / L	999	692
8	Sulphides	mg / L	24	28
9	Fluoride	mg / L	<1.0*	<1.0*
10	Total Chromium	mg / L	<0.01*	<0.01*
11	Hexavalent Chromium	mg / L	<0.01*	<0.01*
12	Phenolic Compounds	mg / L	0.32	0.23
13	Phosphate	mg / L	<0.15*	<0.15*
14	Lead	mg / L	<0.015*	<0.015*

\* Note \* Below detectable limit

\*\* Value could not be ascertained

Rs 14500

DCSO

  
Assistant Director  
Advanced Environmental Laboratory  
TNPCB , Vellore

Note :

- 1) The samples were collected and sealed by the officials of the Ranipet DSP office and handed over to the O/o the DEE , TNPCB , Vellore at 13.45 Hrs on 26.10.2021 by the revenue officials of Ranipet.
- 2) The samples were received after 24 Hrs from the time of collection. Samples were analysed at the request of the JCEE , ( M ) , TNPCB , Vellore.



# Tamilnadu Pollution Control Board

Advanced Environmental Laboratory – Vellore

[ email - delvr2011@gmail.com ]

## INVOICE

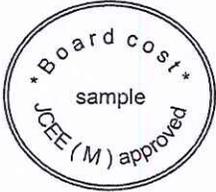
No 015908/1&2 Date 02 . 11 . 2021

To The District Environmental Engineer  
Tamil nadu Pollution Control Board Vellore

- Ref :
- 1) Board Lr. no : 02 / Labs / DDL / P1 / 2003 / 03.01.03
  - 2) BP. Ms. No : 6 dated 31 . 03 . 09
  - 3) T.O. Ackn. No : 015908/1&2 dated 26 . 10 . 2021
  - 4) T.O. Report No : 015908/1&2 dated 02 . 11 . 2021

Sl. No.	Sample code number of		Charges for the sample			Total ( Rs )
	DEE	Lab	collection	preparation	analysis	
1	VLR - 156	746	960	880	5670	7510
2	VLR - 157	747	440	880	5670	6990
Total charges						14500

Rupees Fourteen thousand Five hundred only



*[Signature]*  
02/11/21  
Checked by

*[Signature]*  
24/11/21  
Assistant Director  
Advanced Environmental Laboratory  
TNPCC, Vellore  
*[Signature]*  
02/11/21

*Certificate by the DEE*

### Certified that the

- 1) analytical charges claimed in the invoice is as per reference two above
- 2) analytical charges claimed in the invoice above ( as per reference : two ) has been collected fully from the industry from which the sample was collected vide this office

C R No \_\_\_\_\_ date \_\_\_\_\_

- 3) analytical charges claimed in the invoice above may be treated as board cost and has been accounted in the register of acceptance maintained for the year.

SI No \_\_\_\_\_ Page No \_\_\_\_\_



# Tamilnadu Pollution Control Board

Advanced Environmental Laboratory – Vellore

[ email - delv1r2011@gmail.com ]

## INVOICE

No 015908/1&2

Date 02 . 11 . 2021

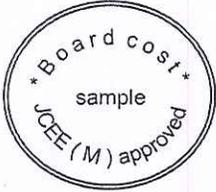
To The District Environmental Engineer  
Tamil nadu Pollution Control Board

Vellore

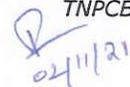
- Ref :
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Sl. No.	Sample code number of		Charges for the sample			Total ( Rs )
	DEE	Lab	collection	preparation	analysis	
1	VLR - 156	746	960	880	5670	7510
2	VLR - 157	747	440	880	5670	6990
Total charges						<b>14500</b>

Rupees Fourteen thousand Five hundred only



  
02/11/21  
Checked by

  
2x/21  
Assistant Director  
Advanced Environmental Laboratory  
TNPCB, Vellore  
  
02/11/21

*Certificate by the DEE*

### Certified that the

- 1) analytical charges claimed in the invoice is as per reference two above
- 2) analytical charges claimed in the invoice above ( as per reference : two ) has been collected fully from the industry from which the sample was collected vide this office

C R No \_\_\_\_\_ date \_\_\_\_\_

- 3) analytical charges claimed in the invoice above may be treated as board cost and has been accounted in the register of acceptance maintained for the year.

Sl No \_\_\_\_\_ Page No \_\_\_\_\_

DEE office round seal

DEE signature



**Tamilnadu Pollution Control Board**  
Advanced Environmental Laboratory - Vellore  
[ email - aelvlr@tnpcb.gov.in ]

Report No : W / 015923/1- / AEL / VLR / 2021 - 22 / 30.11.2021  
5

- 1 Sample sent by : DEE , TNPCB , Vellore
- 2 Sample collected by : G. Kesavamoorthy AEE
- 3 Date & time of collection : 11.11.2021 @ 11.30 Hrs
- 4 Date & time of sample receipt : 11.11.2021 @ 16.50 Hrs
- 5 Details of samples received : Five numbers of Water sample
- 6 Point of collection & sample nature :

a	VLR - 244 - 2	Outlet of rain water runoff from TCL outside the compound wall of the unit premises	Water sample
b	VLR - 245	Rainwater runoff drains 1 located inside the unit premises	Water sample
c	VLR - 246	Rainwater runoff drains 2 located inside the unit premises	Water sample
d	VLR - 247	Stagnation water inside the unit premises of M/s. TCL near ATM compound wall	Water sample
e	VLR - 248	Rainwater roof run off collected at the unit premises of TCL(During raining)	Water sample

### REPORT OF ANALYSIS

Sl No	Parameter	code no :	VLR - 244 - 2	VLR - 245	VLR - 246	VLR - 247	VLR - 248
			829	830	831	832	833
1	pH	number	5.2	7.6	5.3	7	6.2
2	TSS	mg/L	14	80	12	118	10
3	TDS	mg/L	1140	1280	1210	1190	360
4	Chloride	mg/L	480	535	400	350	85
5	Sulphate	mg/L	117	167	159	146	31
6	BOD	mg/L	105	6	3	24	2
7	COD	mg/L	640	56	48	254	16
8	Sulphides	mg/L	4	4	<2.0*	48	<2.0*
9	Fluoride	mg/L	<1.0*	<1.0*	<1.0*	<1.0*	<1.0*
10	Total Chromium	mg/L	<0.01*	<0.01*	<0.01*	<0.01*	<0.01*
11	Hexavalent Chromium	mg/L	<0.01*	<0.01*	<0.01*	<0.01*	<0.01*
12	Phenolic Compounds	mg/L	<0.0005*	<0.0005*	<0.0005*	<0.0005*	<0.0005*

\* Below detectable limit

\*\* Value could not be ascertained



**Tamilnadu Pollution Control Board**  
 Advanced Environmental Laboratory – Vellore  
 [ email - delvlr2011@gmail.com ]

Report No : W / 015903/1 / AEL / VLR / 2021 - 22 / 22.11.2021

- 1 Sample sent by : DEE , TNPCB , Vellore  
 2 Sample collected by : G. Kesavamoorthy AEE  
 3 Date & time of collection : 25 . 10 . 2021 @ 9.30 Hrs  
 4 Date & time of sample receipt : 25 . 10 . 2021 @ 16.50 Hrs  
 5 Details of samples received : One number of Water sample  
 6 Point of collection & sample nature :

a	VLR - 155	Stagnation water inside the unit premises of M/s. TCL near SBI ATM	Water sample
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**REPORT OF ANALYSIS**

Sl No	Parameter	code no :	VLR - 155
			736
1	pH	number	7.3
2	TSS	mg / L	16
3	TDS	mg / L	1554
4	Chloride	mg / L	625
5	Sulphate	mg / L	230
6	BOD	mg / L	14
7	COD	mg / L	138
8	Sulphides	mg / L	<2.0*
9	Fluoride	mg / L	<1.0*
10	Total Chromium	mg / L	<0.01*
11	Hexavalent Chromium	mg / L	<0.01*
12	Phenolic Compounds	mg / L	<0.0005*

Note \* Below detectable limit

\*\* Value could not be ascertained

Rs 6360

*Handwritten signature*  
 22/11/21  
 DCSO

*Handwritten signature*  
 22/11/21  
 Assistant Director  
 Advanced Environmental Laboratory  
 TNPCB , Vellore

**Status Report**      **Annexure-II**  
**On**  
**Environmental Audit of Thirumalai Chemicals**  
**Limited, Ranipet**



Prepared by  
**Prof. Ligy Philip and the team**



Environmental and Water Resource Engineering Division  
Department of Civil Engineering  
Indian Institute of Technology Madras  
Chennai 600 036

**October 2021**

## 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 23<sup>rd</sup> 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 9<sup>th</sup> 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

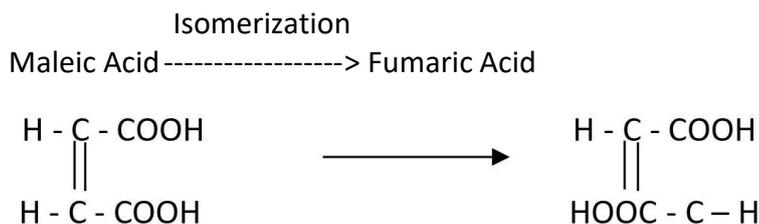
Phthalic anhydride is manufactured by the reaction of o-xylene with air. The reaction is exothermic. The generated heat is utilized to produce steam (Fig 1). Phthalic anhydride is separated from impurities by de-sublimation. The off-gases are scrubbed with water in a wet scrubber. The waste products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



### 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.

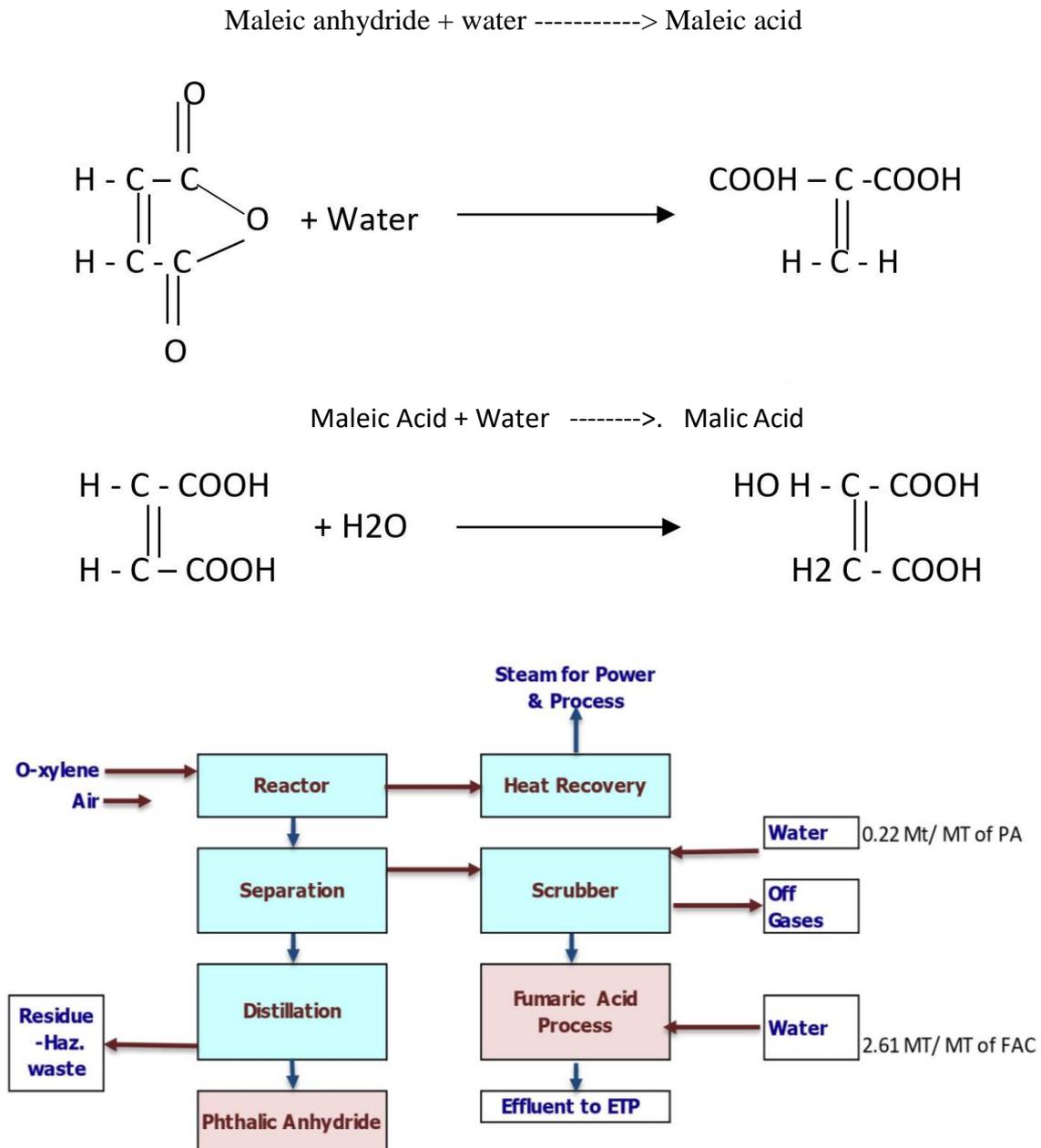
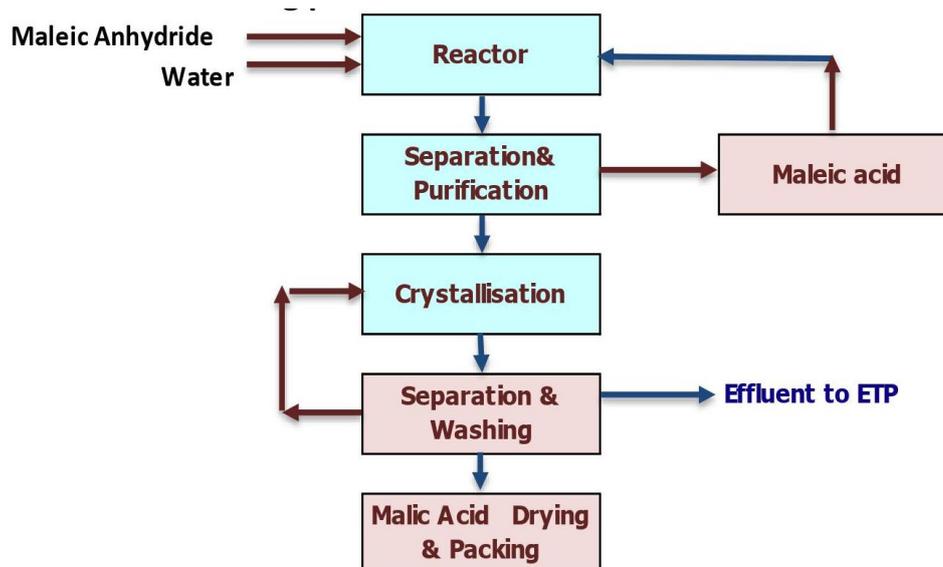


Figure 1: Manufacturing process of phthalic anhydride and fumaric acid



**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<sup>3</sup>/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<sup>3</sup>/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<sup>3</sup>/day

Design operating time – 20 h

- **Observed Inflow to RO-IV**

Observed feed flow into RO-IV – 180.7 m<sup>3</sup>

- **Observed Outflow from RO-IV**

Permeate flow – 140.5 m<sup>3</sup>

Reject flow – 45 m<sup>3</sup>

- **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<sup>3</sup>/day

Design operating time: 23 h

- **Observed Inflow to RO-V**

Observed feed flow into RO- V – 45.2 m<sup>3</sup>

- **Observed outflow from RO-V**

Permeate flow – 22.7 m<sup>3</sup>

Reject flow – 24.9 m<sup>3</sup>

- **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<sup>3</sup>) 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<sup>3</sup>/day

Design operating time – 22 h

- **Observed Inflow to RO-VI**

Observed feed flow into RO- VI – 100.5 m<sup>3</sup>

- **Observed outflow from RO- VI**

Permeate flow – 81.9 m<sup>3</sup>

Reject flow – 22.4 m<sup>3</sup>

- **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<sup>3</sup>/day

Design operating time – 20 h

- **Observed inflow into MEE:**

Flow into MEE – 56.3 m<sup>3</sup>

- **Observed outflow from MEE**

Condensate from MEE – 49.5 m<sup>3</sup>

Concentrate, which is going to ATFD from MEE -6.8 m<sup>3</sup>

- **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<sup>3</sup>/day

Design operating time – 24 h

- **Observed inflow into ATFD: 6.8 m<sup>3</sup>**

**Salt produced from ATFD – 1860 kg**

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



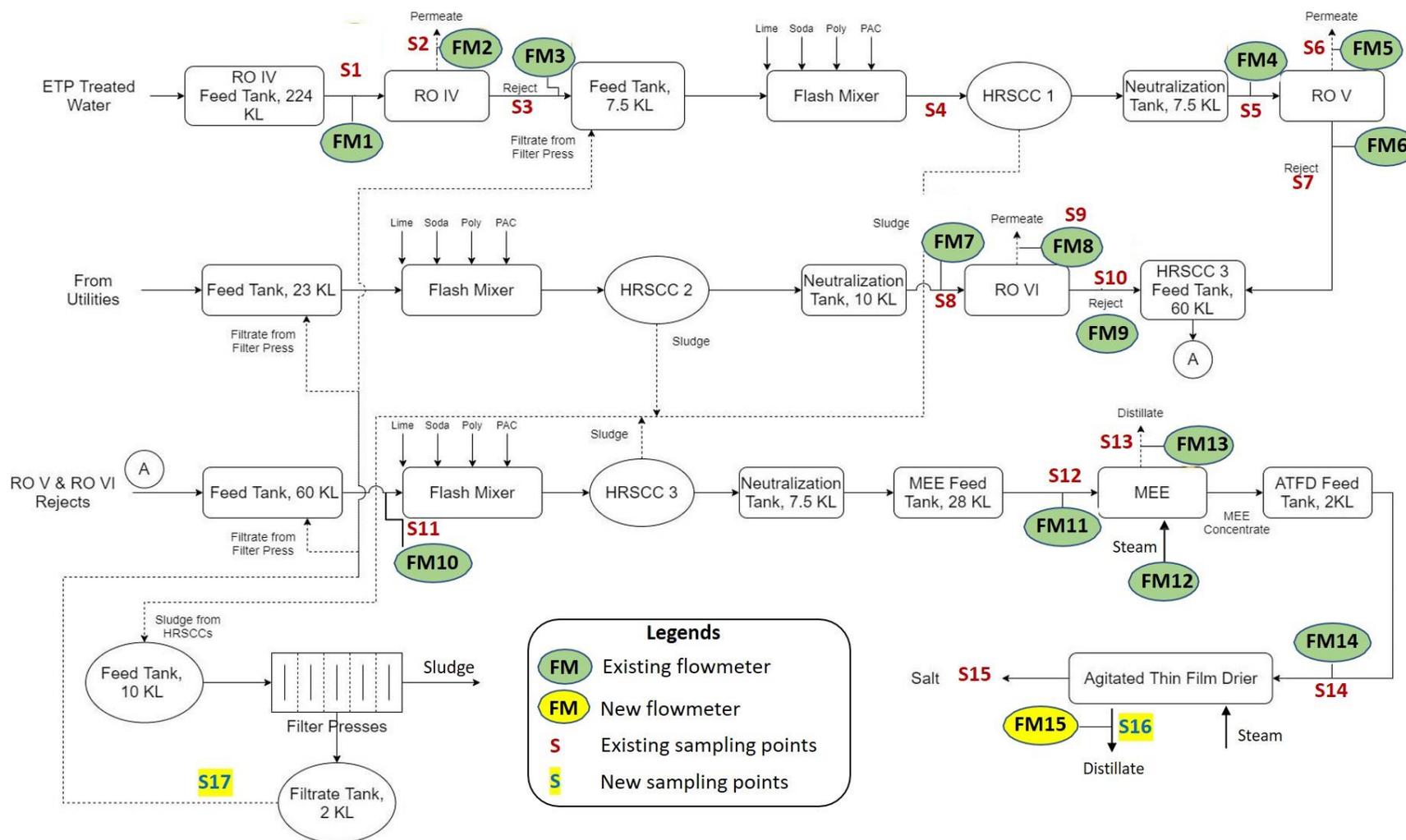


Figure 4: Flow diagram showing the treatment scheme of Utility stream

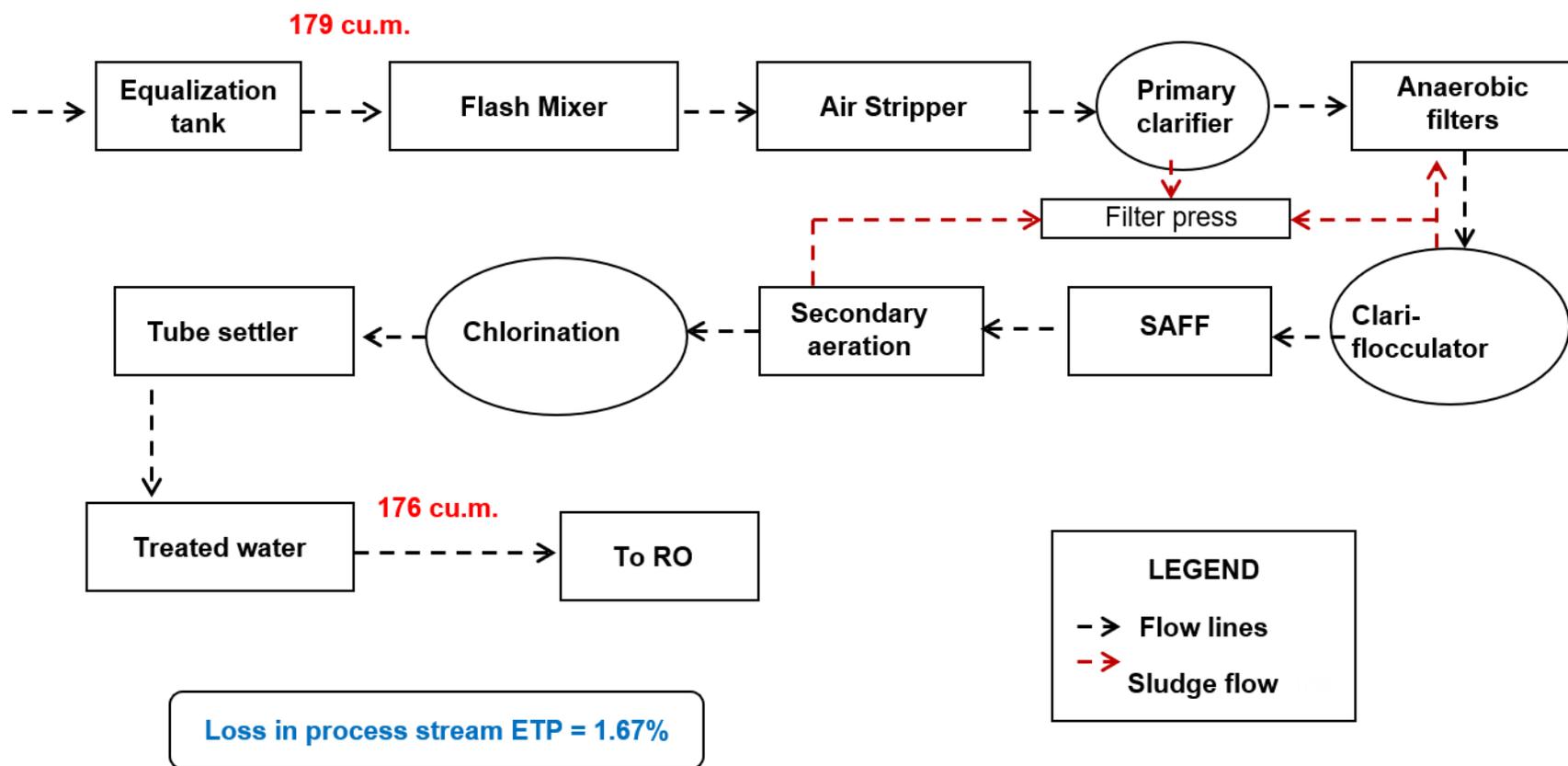


Figure 5: Water mass balance of Process Stream (Water Mass Balance Matching)

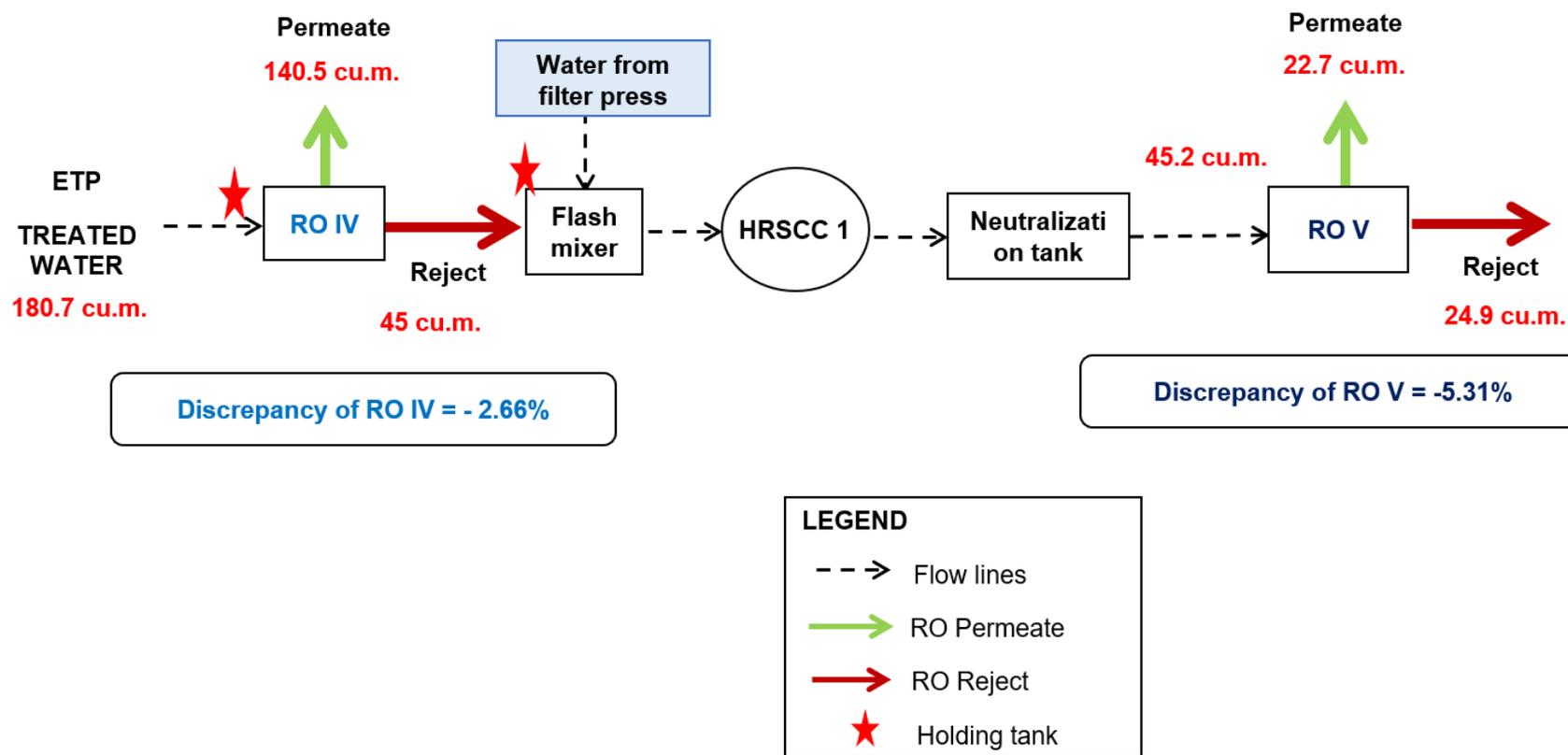


Figure 6: Water Mass Balance of Utility Stream of ETP – RO IV and RO V

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

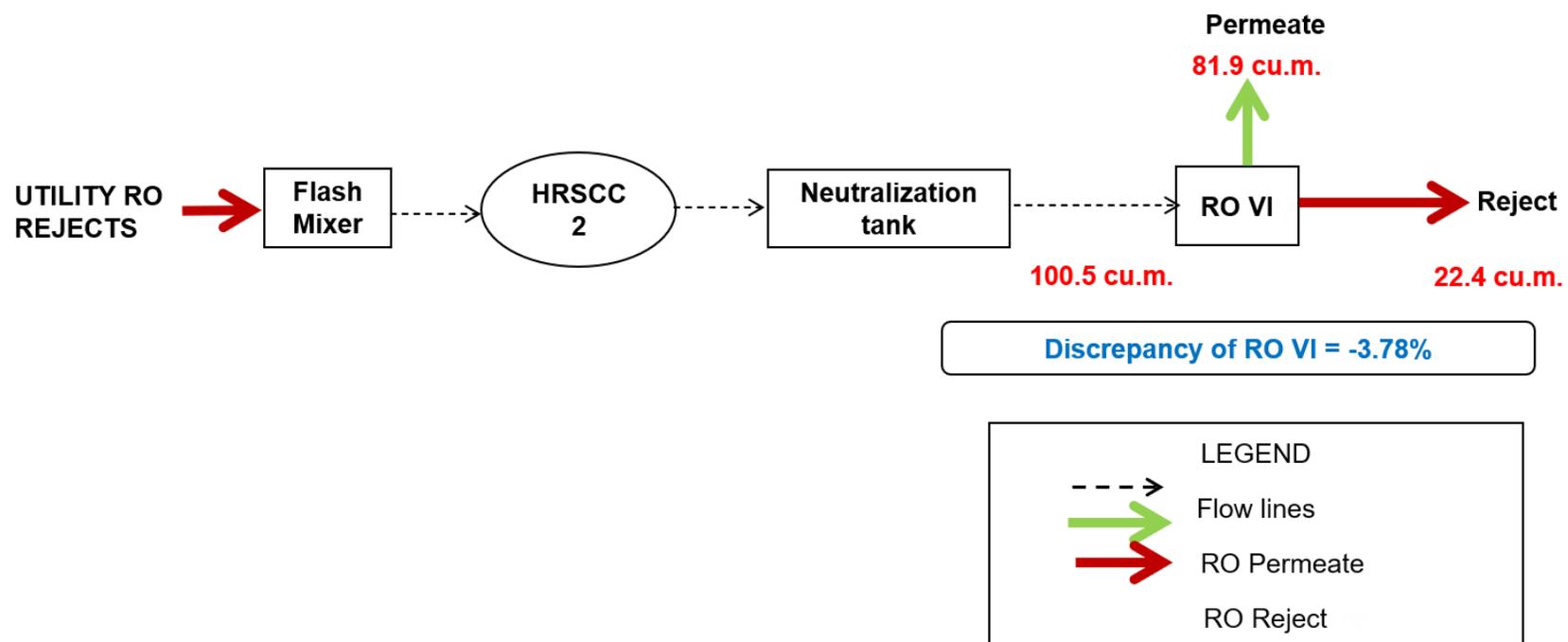
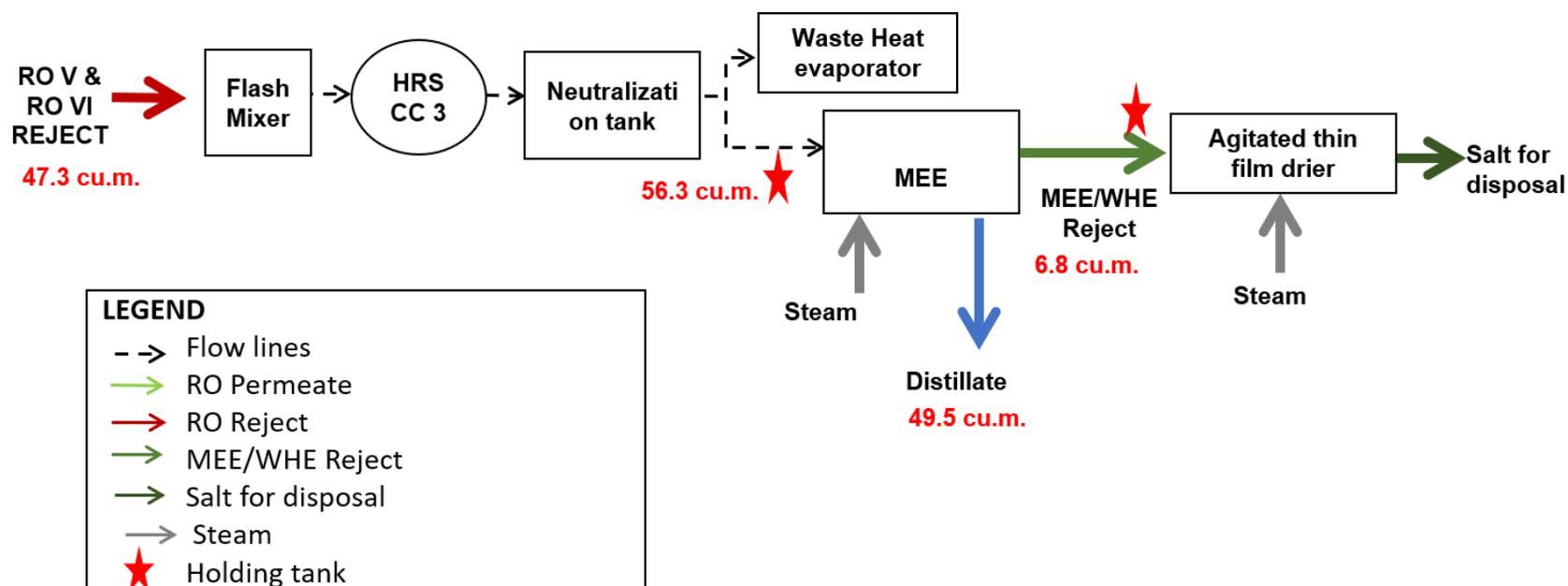


Figure 7: Water Mass Balance of Utility RO Stream – RO VI System



**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	<ul style="list-style-type: none"> <li>Started at 10:15 am and stopped at 7:30 pm</li> </ul>
2	RO V	10 h	10 h 5min	<ul style="list-style-type: none"> <li>Started at 10 am</li> <li>Stopped for 40 min (2:45 pm to 3:25 pm) due to power fluctuations</li> <li>Stopped at 8:35 pm</li> </ul>
3	RO VI	10 h	10 h 40 min	<ul style="list-style-type: none"> <li>Started at 10 am and stopped at 8:40 pm</li> </ul>
4	MEE	10 h	8 h	<ul style="list-style-type: none"> <li>Started at 10 am and stopped at 6 pm</li> </ul>
5	ATFD	6 h	3 h 15 min	<ul style="list-style-type: none"> <li>Started at 4 pm and stopped at 7:15 pm</li> </ul>

**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 <sup>3</sup> )	Observed outflow from the unit (m <sup>3</sup> )	Discrepancy	Remarks
1	<b>Process effluent stream – ETP</b> (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 <sup>3</sup> 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 <sup>3</sup> and 2m <sup>3</sup> 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)
<b>Process stream</b>									
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
<b>Utilities Stream</b>									
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 <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	Total alkalinity (mg/L)	Na <sup>+</sup> (mg/L)	K <sup>+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	Ca <sup>2+</sup> (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)
<b>Process stream</b>											
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
<b>Utilities stream</b>											
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  $2.87\pm 0.15\%$ ,  $1.59\pm 0.02\%$ , and  $1.65\pm 0.01\%$ , 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
<b>1</b>	<b>Process Stream (Old ETP)</b>		
a	<i>Effluent to be treated at Process stream</i>		
	Inflow into Equalization tank (Old ETP)	179	m <sup>3</sup>
	Average total dissolved solids concentration	16550	mg/L
	Mass into the process stream	2962.5	kg
<b>2</b>	<b>Utility stream</b>		
a	<i>Feed to RO VI</i>		
	Inflow into RO VI	180.7	m <sup>3</sup>
	Average total dissolved solids concentration	6880	mg/L
	Mass into RO VI	1243.2	kg
<b>3</b>	<b>Chemical consumption</b>		
a	Lime	800	kg
b	Soda	1200	kg
c	Poly electrolyte	12.5	kg
d	PAC	1.5	kg
e	Mg(OH) <sub>2</sub>	0	kg
f	HCl	740	kg
	<i>Total chemical consumed</i>	2754	kg
	<b>Total mass into the system</b>	<b>6959.7</b>	<b>Kg</b>

**Table 12: Mass outflow from the system**

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

**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 <sup>3</sup> )	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	<i>from weighing slip data</i>		1860	1860.00	

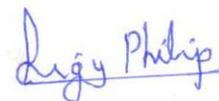
## 8. Summary

- 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.

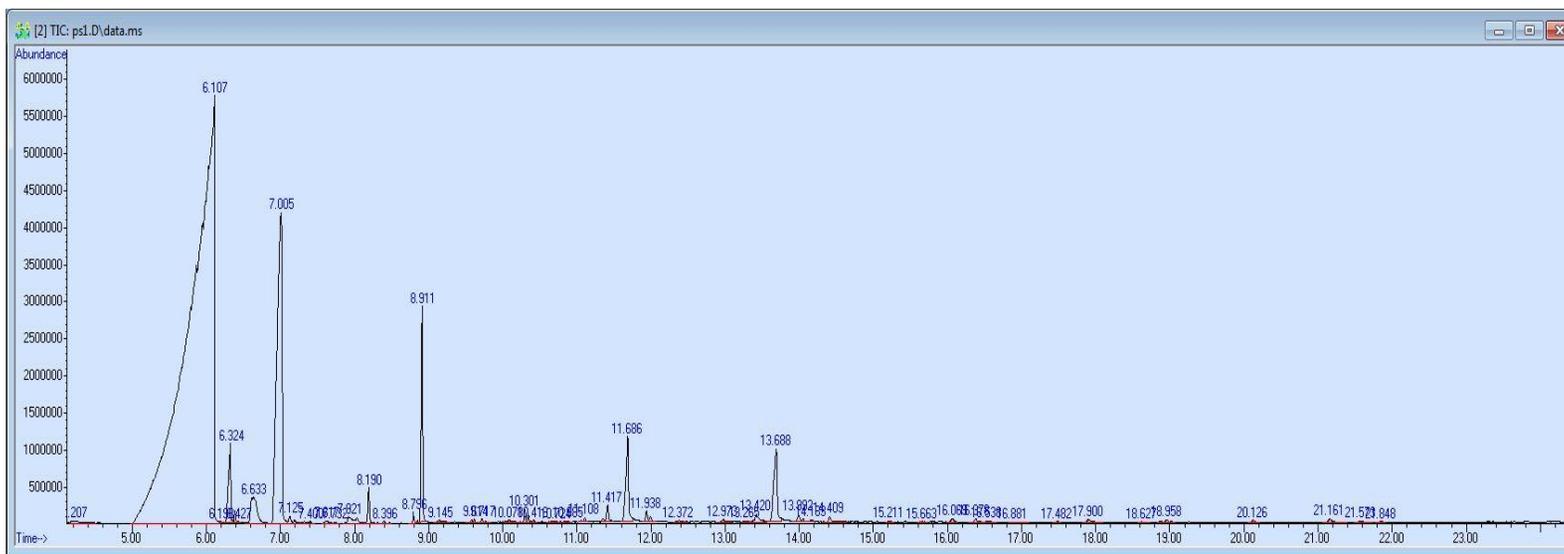
## 9. Recommendations

- **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.**



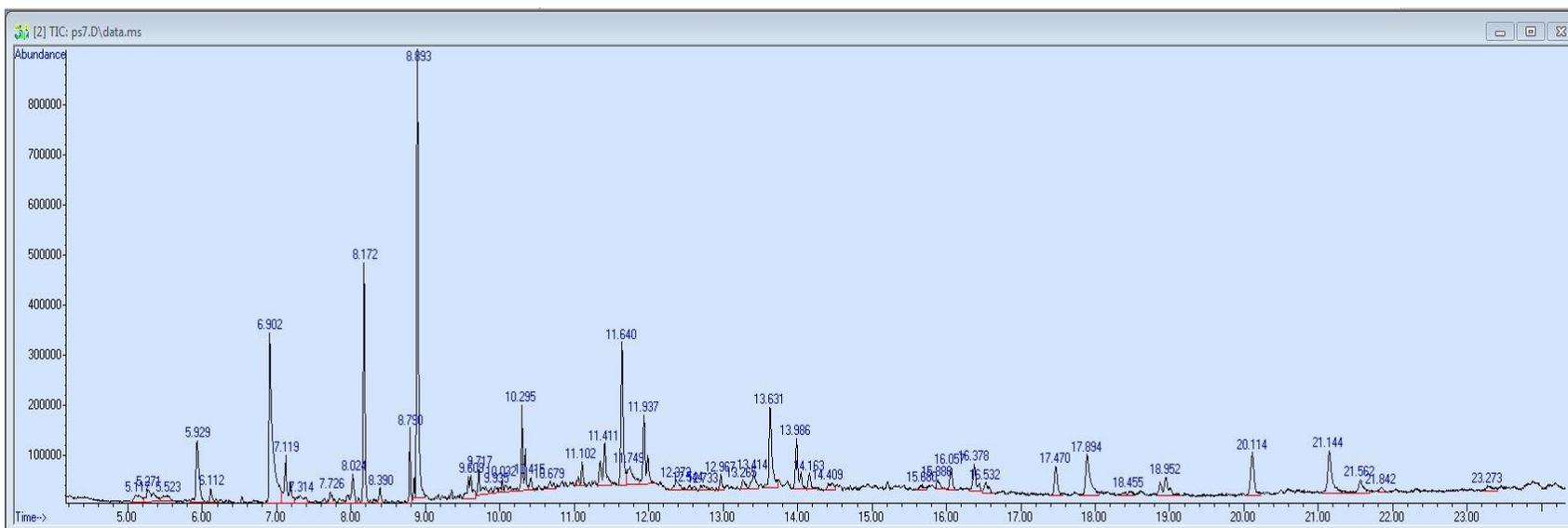
(Ligy Philip)

## Annexure-1



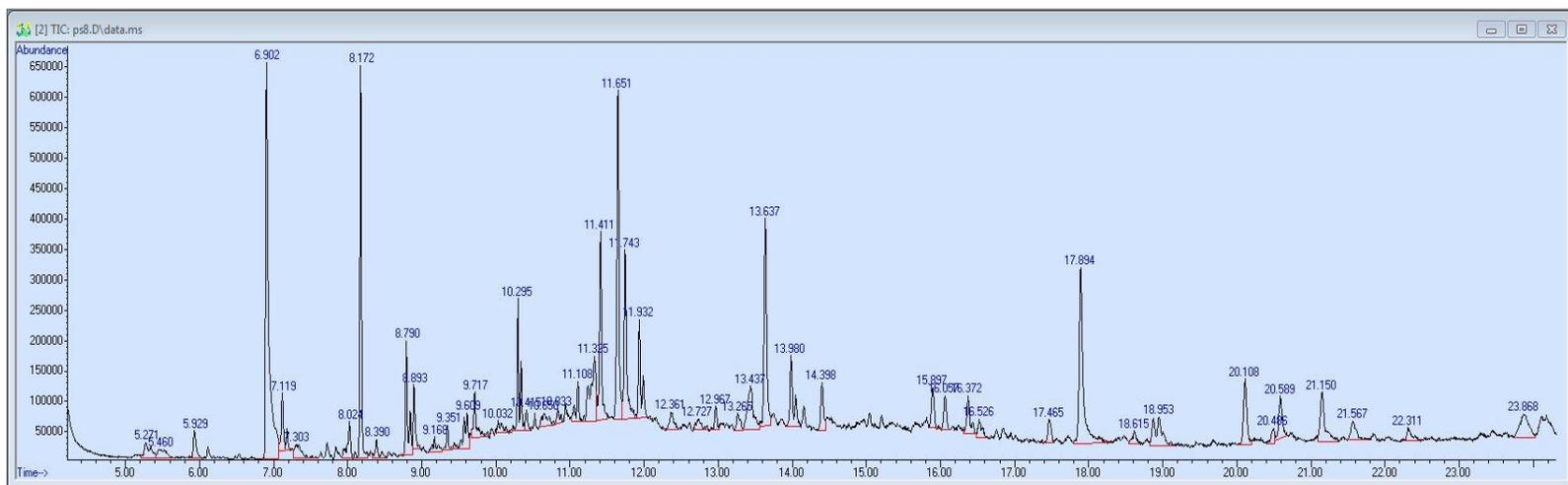
**Fig 1: GC/MS total ion chromatograph for Equalized Waste water feed to ETP (PS1)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
PS1	1-1	5.681	42.6	Benzoic acid
	1-2	6.313	86.7	2- methyl benzoic acid
	1-3	6.639	67	Phthalic anhydride
	1-4	6.948	74.2	1(3H)-Isobenzofuranone
	1-5	8.184	56.4	2,4 Di-tert-butylphenol
	1-6	8.831	5.33	Oxalic acid
	1-7	8.893	70.9	Diethyl phthalate/Phthalic acid
	1-8	11.68	89.3	N-Hexa deconic acid
	1-9	13.648	76.6	Octo deconic acid



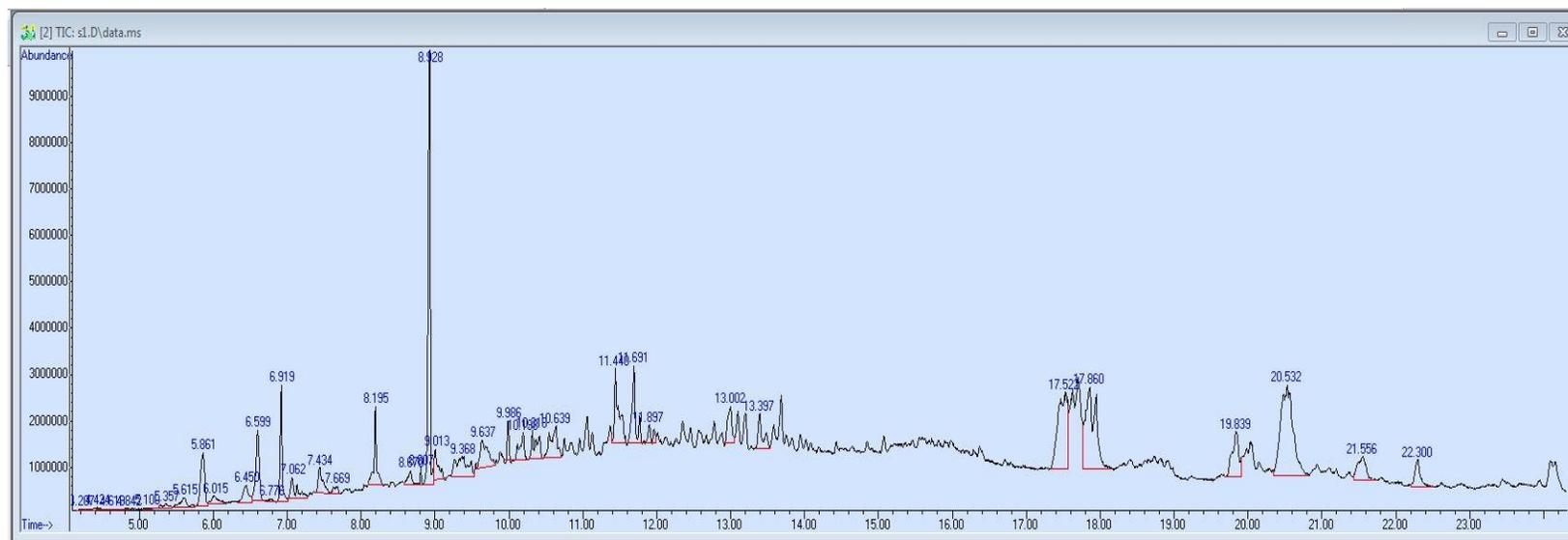
**Fig 2: GC/MS total ion chromatogram for Final Outlet of ETP (PS7)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
PS7	2-1	5.958	60.1	1,3 bis ((1,1) di methyl ethyl) benzene
	2-2	6.948	58.7	1 Isobenzo furanone
	2-3	8.195	30.2	2,4 Di-tert-butylphenol
	2-4	8.79	8.23	Difluoro acetic acid
	2-5	8.91	59.7	Diethyl phthalate/Phthalic acid
	2-6	10.312	3.78	Oleic acid
	2-7	11.651	52.7	N-Hexa deconic acid
	2-8	13.65	48.9	Octo deconic acid



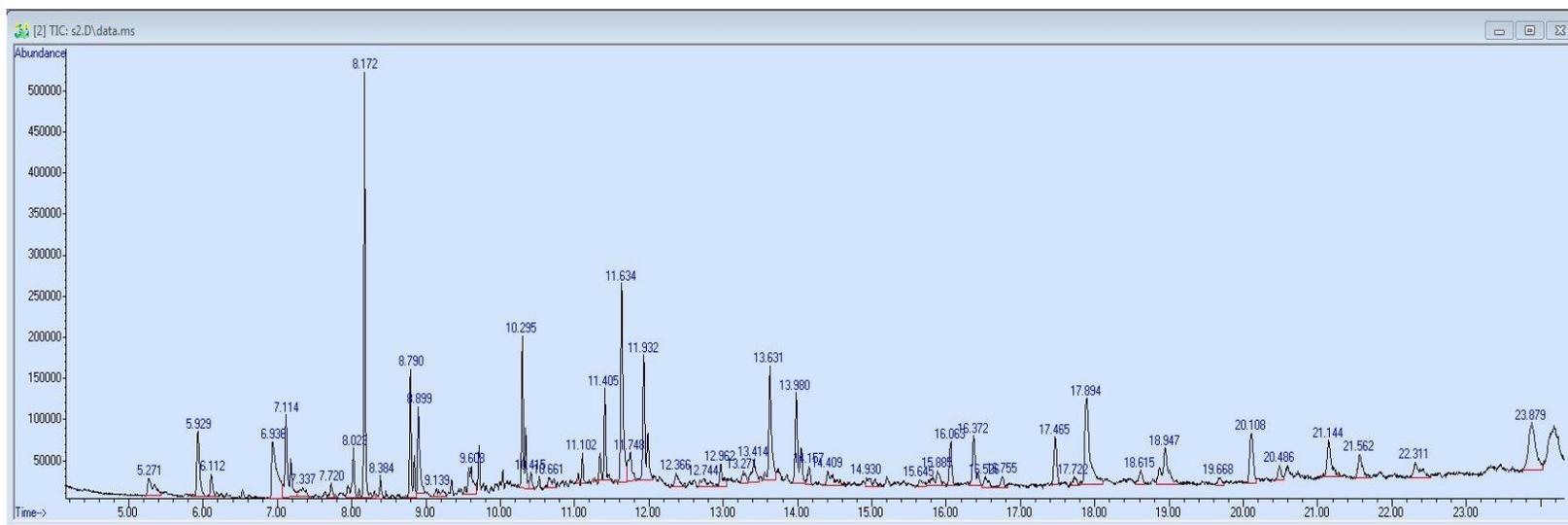
**Fig 3: GC/MS total ion chromatograph for Filtrate from PS filter press (PS8)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
PS8	3-1	5.94	54.8	1,3 bis ((1,1) di methyl ethyl) benzene
	3-2	6.91	74.3	2- methyl benzoic acid
	3-3	7.102	13.3	Melonic acid
	3-4	8.167	60.3	2,4 Di-tert-butylphenol
	3-5	8.79	.543	1 hexa decanol
	3-6	8.91	29	Diethyl phthalate
	3-7	11.68	89.3	N-Hexa deconic acid
	3-8	11.96	6.51	Oleic acid
	3-9	13.63	63.9	Octo deconic acid
	3-10	13.992	6.4	2-hexa deconol



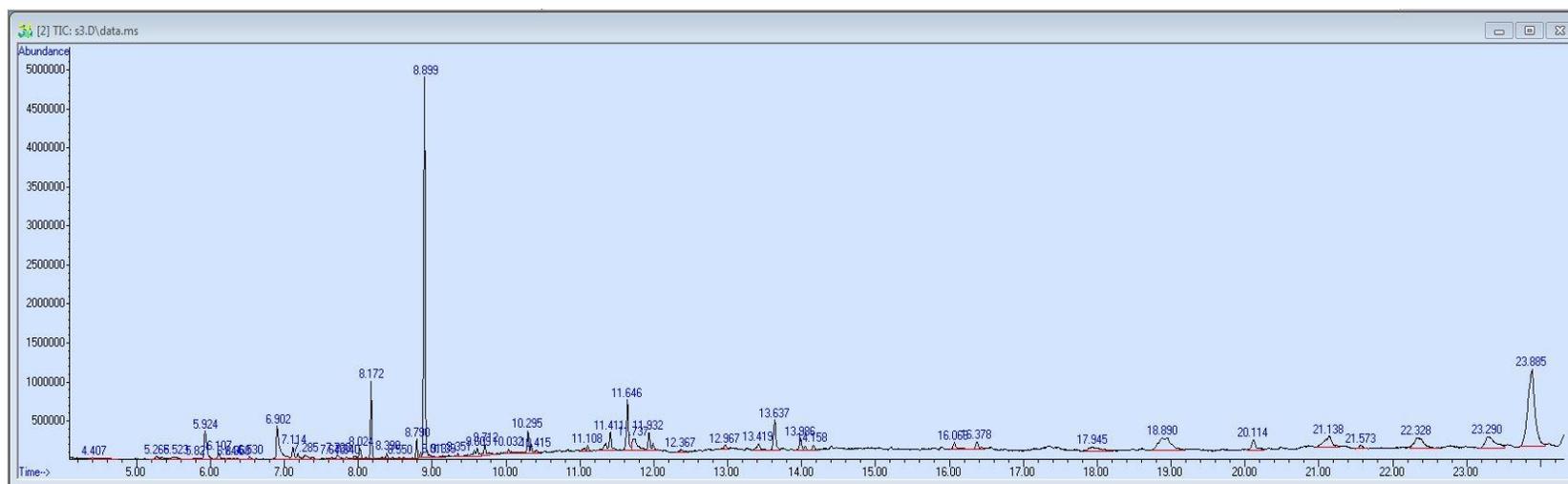
**Fig 4: GC/MS total ion chromatograph for ETP treated water (S1)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S1	4-1	5.94	51.6	1,3 bis ((1,1) di methyl ethyl) benzene
	4-2	6.936	26.1	1 Iso benzofuranone
	4-3	8.195	34.1	2,4 Di-tert-butylphenol
	4-4	8.933	55.5	Diethyl phthalate/Phthalic acid
	4-5	11.6	1.73	N-hexa deconic acid
	4-6	13.397	8.51	Octa deconic acid



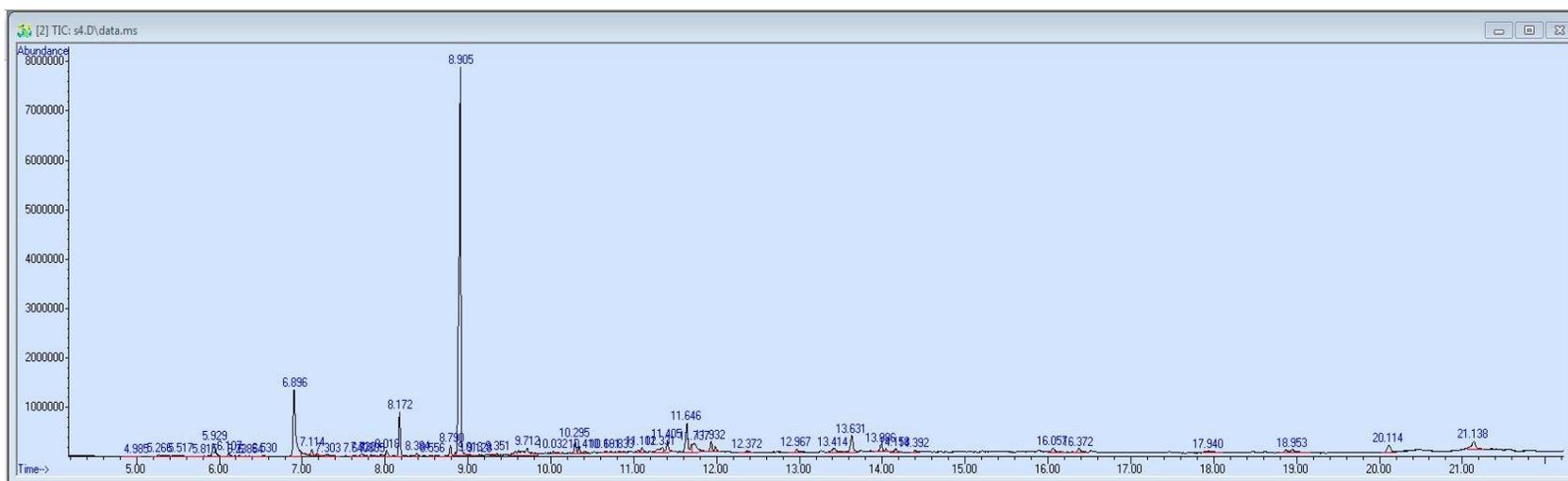
**Fig 5: GC/MS total ion chromatograph for RO IV permeate (S2)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S2	5-1	5.331	2.71	Dichloro acetic acid
	5-2	5.935	62	1,3 bis ((1,1) di methyl ethyl) benzene
	5-3	6.604	10.1	Oxalic acid
	5-4	6.931	64.5	1 Iso benzo furanone
	3-5	8.035	8.06	Nonadecane
	5-6	8.161	57.4	2, 4 di tert butyl phenol
	5-7	8.882	48.7	Diethyl phthalate/Phthalic acid
	5-8	10.28	5.28	1 octa decene
	5-9	11.4	2.1	Parponic acid
	5-10	11.657	42.6	2-hexa deconic acid
	5-11	13.649	54.9	Octa deconic acid
	5-12	14.003	21.6	Fumaric acid



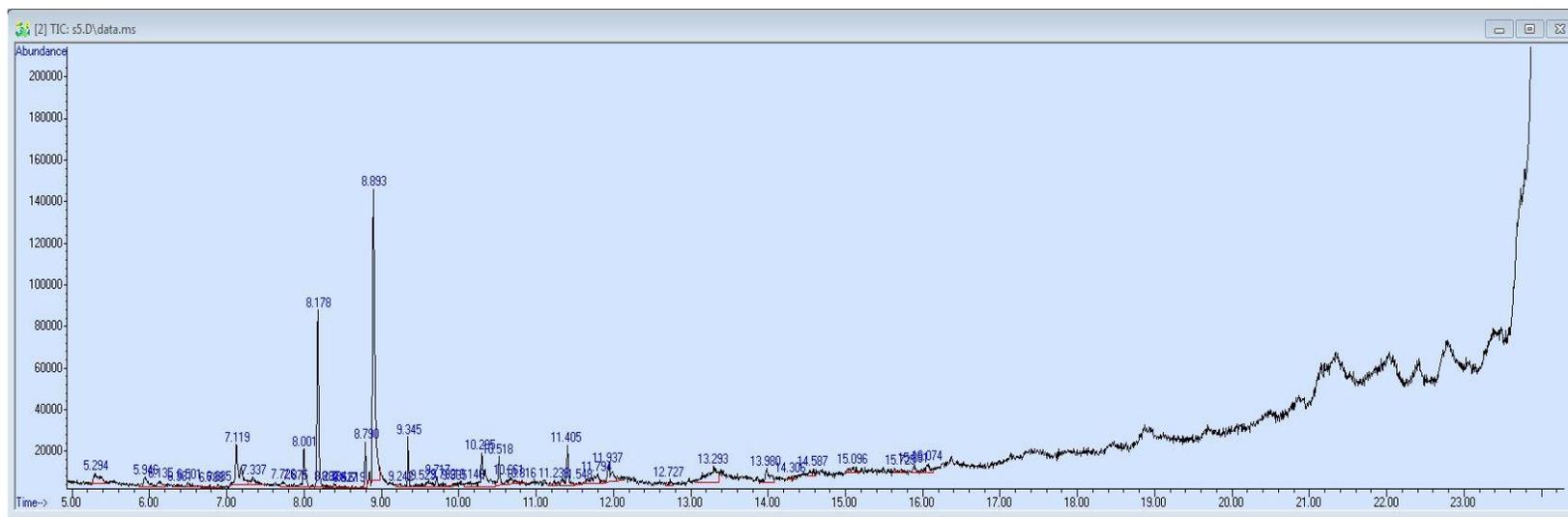
**Fig 6: GC/MS total ion chromatograph for RO IV reject (S3)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S3	6-1	5.924	74.5	1,3 bis ((1,1) di methyl ethyl) benzene
	6-2	6.908	74.3	1 Iso benzo furanone
	6-3	8.167	62.6	2, 4 di tert butyl phenol
	6-4	8.876	79.5	Diethyl phthalate/Phthalic acid
	6-5	11.646	69.3	N-hexa deconic acid
	6-6	11.943	7.7	Oleic acid
	6-7	13.64	50.3	Octa deconic acid
	6-8	14.07	2.7	Fumaric acid



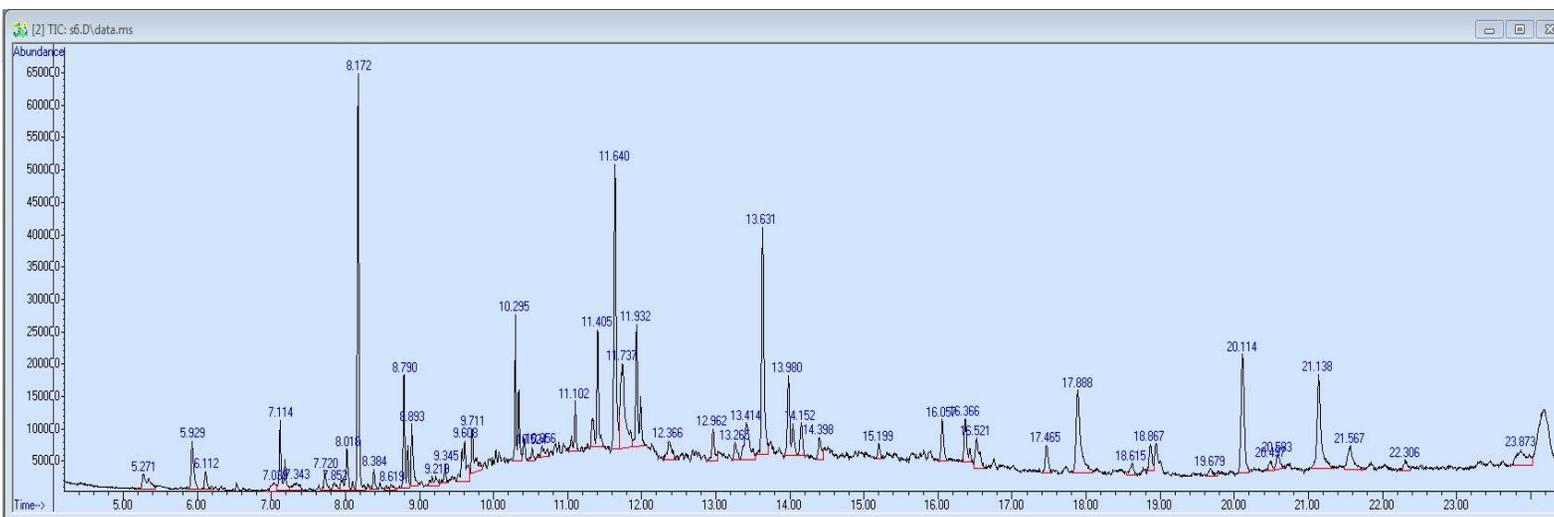
**Fig 7: GC/MS total ion chromatograph for HRSCC #1 Inlet (S4)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S4	7-1	5.592	74.9	1,3 bis ((1,1) di methyl ethyl) benzene
	7-2	6.896	73.6	1 Iso benzo furanone
	7-3	8.172	60.8	2, 4 di tert butyl phenol
	7-4	8.905	70	Diethyl phthalate/Phthalic acid
	7-5	11.657	22.7	N-hexa deconic acid
	7-6	13.625	54.9	Octa deconic acid
	7-7	14.026	21.6	Fumaric acid



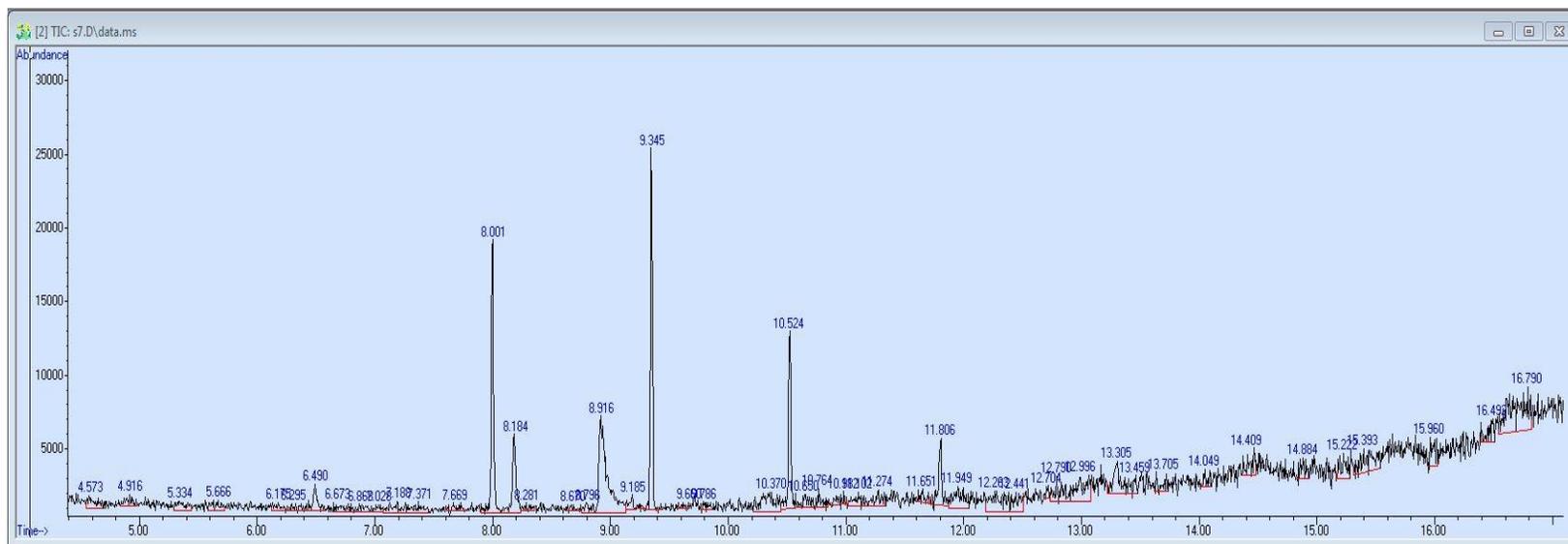
**Fig 8: GC/MS total ion chromatograph for RO V feed (S5)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S5	8-1	7.142	1.92	Malenoic acid
	8-2	8.167	57.1	2, 4 di tert butyl phenol
	8-3	8.825	8.42	Oxalic acid
	8-4	8.899	62.7	Diethyl phthalate/Phthalic acid
	8-5	11.811	2.6	Phthalic acid



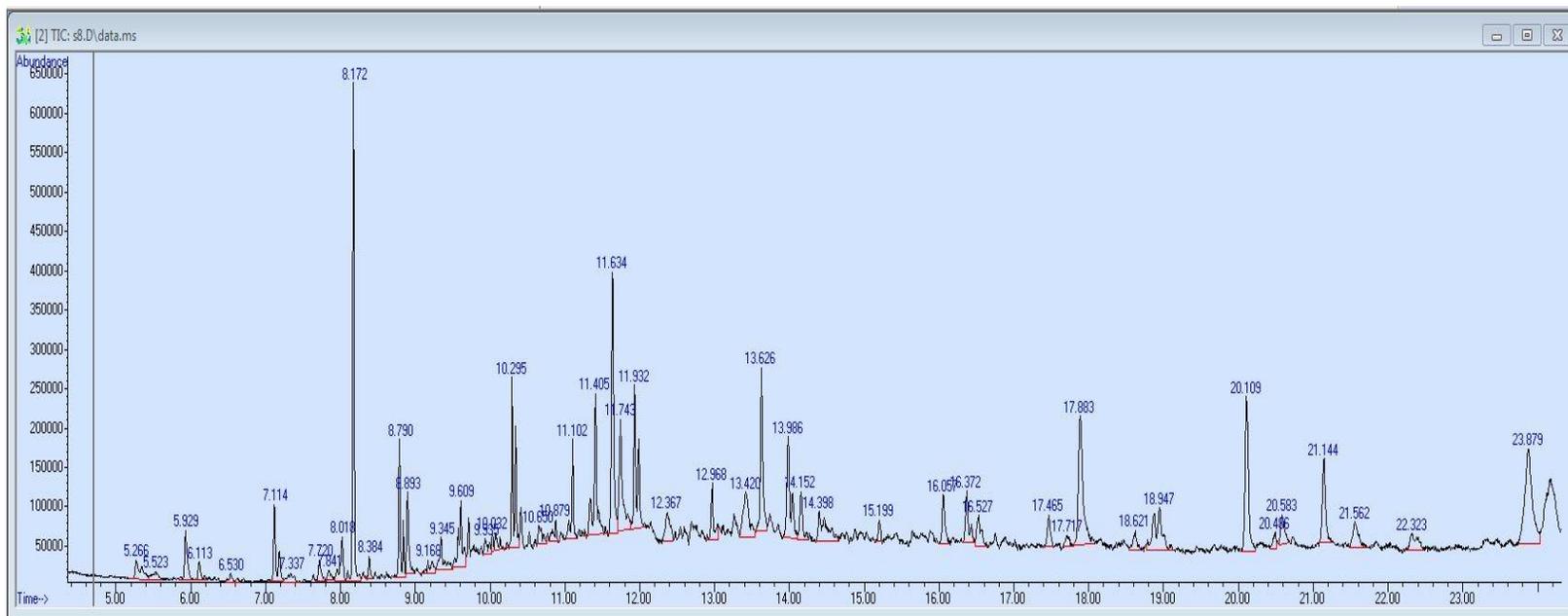
**Fig 9: GC/MS total ion chromatograph for RO V permeate (S6)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S6	9-1	5.952	57.4	1,3 bis ((1,1) di methyl ethyl) benzene
	9-2	6.559	2.61	Oxalic acid
	9-3	7.131	5.85	1 Tetradecene
	9-4	8.184	54	2, 4 di tert butyl phenol
	9-5	8.144	18.5	Nonadecene
	9-6	8.899	48.6	Diethyl phthalate/Phthalic acid
	9-7	10.312	7.6	1 octa decene
	9-8	11.68	1.75	2-Hexadecanol
	9-9	11.79	4.88	Oleaic acid
	9-10	13.648	70.9	Octa deconic acid
	9-11	14.014	4.63	2-Hexadecanol
	9-12	14.089	0.99	Fumaric acid



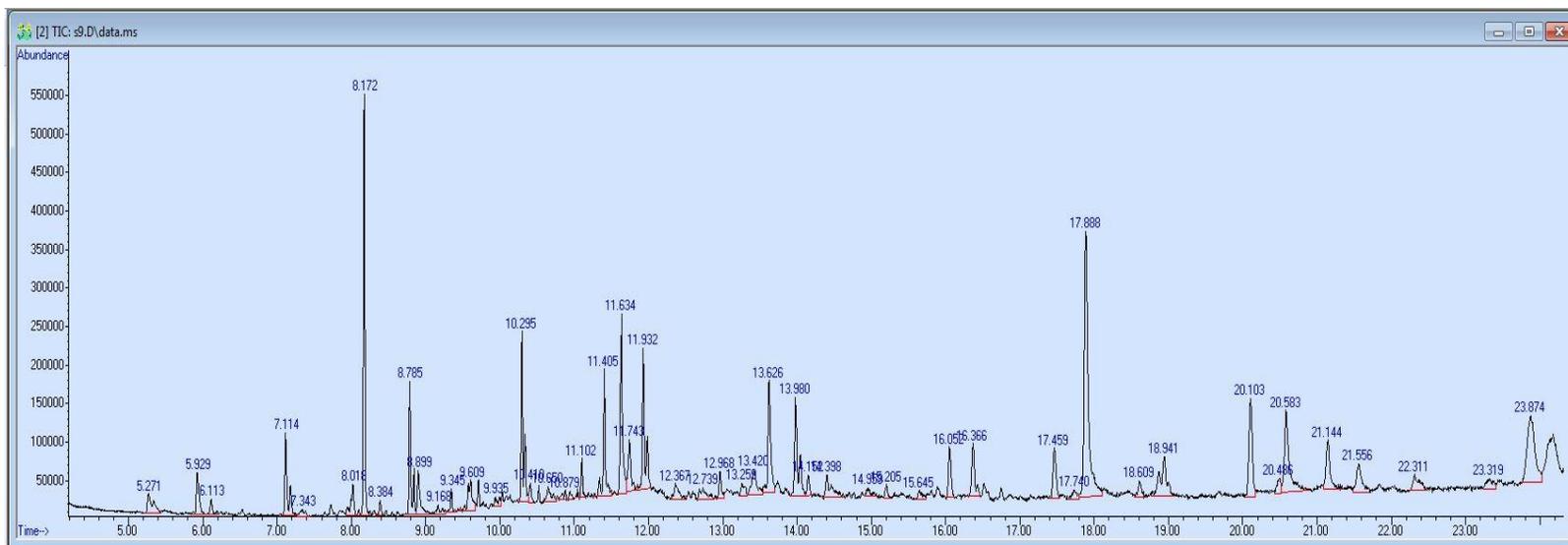
**Fig 10: GC/MS total ion chromatograph for RO V reject (S7)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S7	10-1	8.172	2.87	2, 4 di tert butyl phenol
	10-2	8.91	35.9	Diethyl phthalate/Phthalic acid
	10-4	9.43	93.9	2,4 Dihydroxy benzoic acid
	10-3	11.789	1.75	Phthalic acid



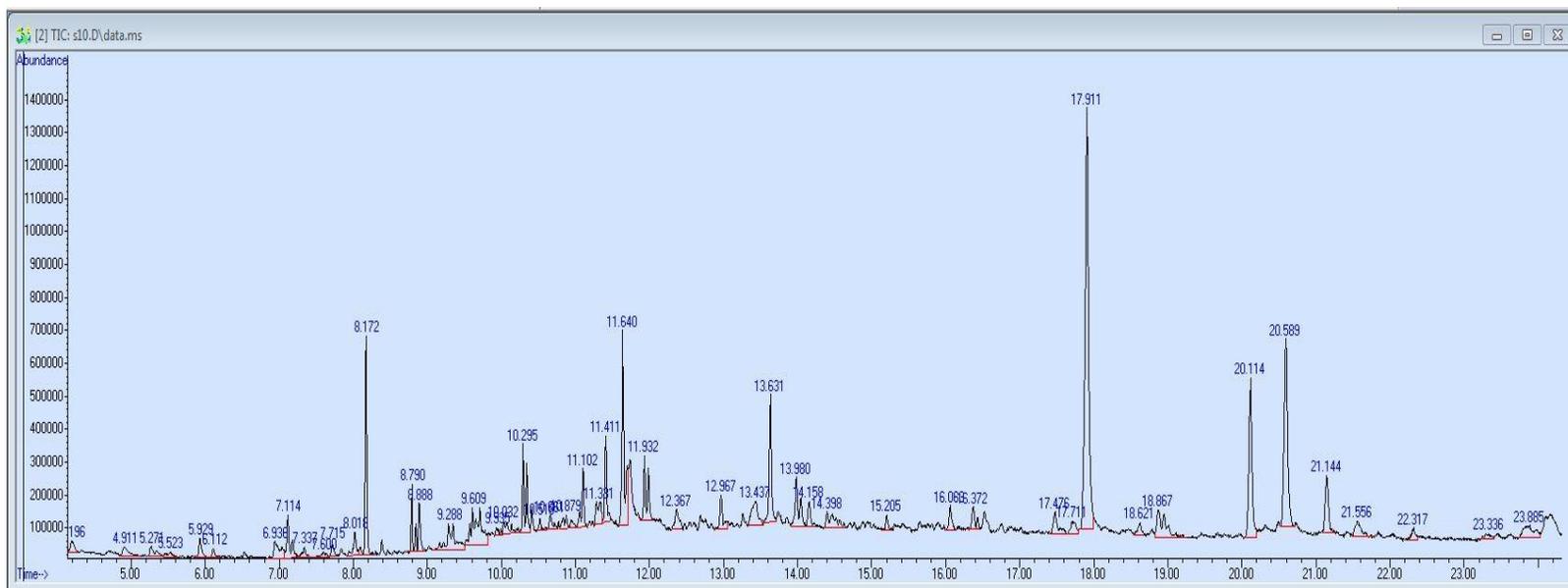
**Fig 11: GC/MS total ion chromatograph for RO VI feed (S8)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S8	11-1	5.929	46	1,3 bis ((1,1) di methyl ethyl) benzene
	11-2	7.131	9	1 Tetradecene
	11-3	8.178	56.64	2, 4 di tert butyl phenol
	11-4	8.773	3.6	Trichloro acetic acid
	11-5	8.893	34.7	Diethyl phthalate/Phthalic acid
	11-6	10.29	5.07	1-Hexadecanol
	11-7	11.63	69.1	N-Hexadecanic acid



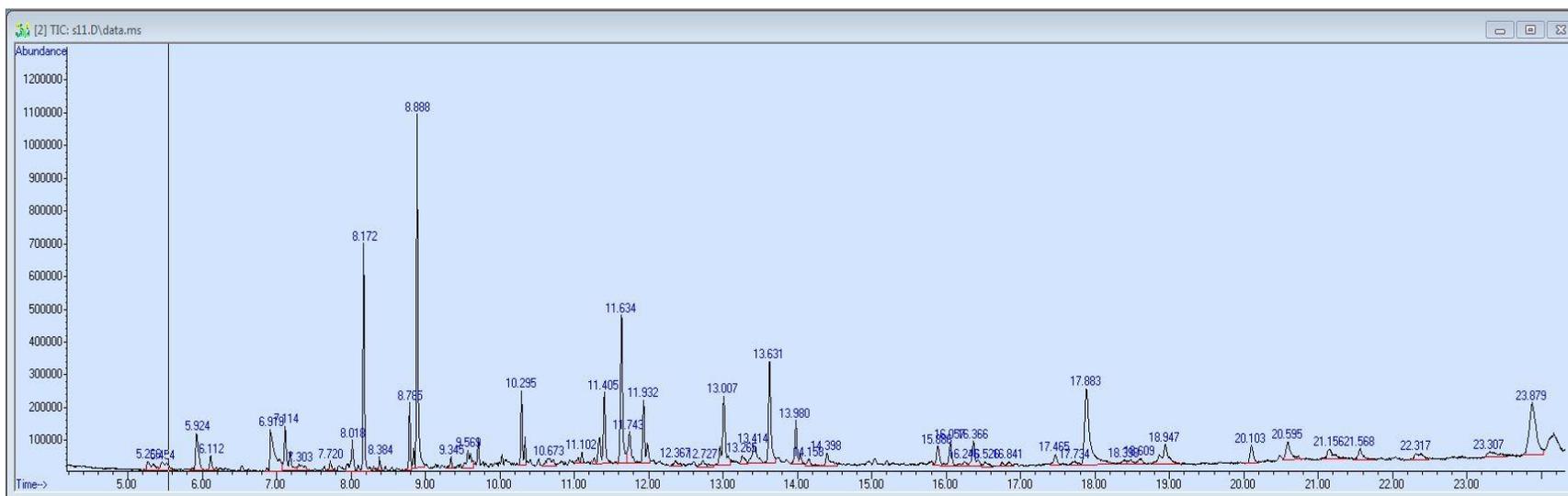
**Fig 12: GC/MS total ion chromatograph for RO VI permeate (S9)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S9	12-1	5.929	65	1,3 bis ((1,1) di methyl ethyl) benzene
	12-2	7.134	6.46	1 Tetradecene
	12-3	8.178	56.64	2, 4 di tert butyl phenol
	12-4	8.89	72.4	Diethyl phthalate/Phthalic acid
	12-5	13.648	70.9	Octa decanoic acid
	12-6	13.98	9.44	2-Hexadecanol



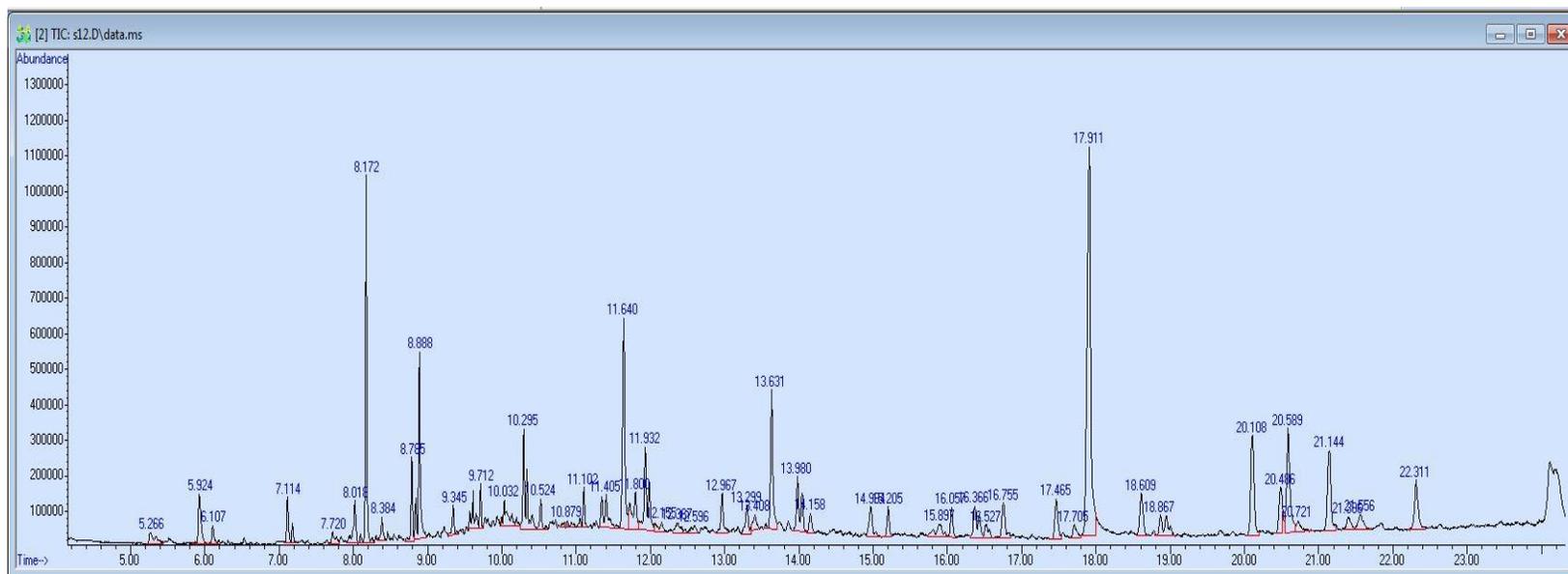
**Fig 13: GC/MS total ion chromatograph for RO VI reject (S10)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S10	13-1	5.929	65.3	1,3 bis ((1,1) di methyl ethyl) benzene
	13-2	7.131	6.14	1 Tetradecene
	13-3	8.178	60.9	2, 4 di tert butyl phenol
	13-4	8.88	56.5	Diethyl phthalate/Phthalic acid
	13-5	11.64	41.9	n-Hexadeconic acid
	13-6	13.648	48.1	Octa deconic acid
	13-7	17.877	79.5	Hexadecanoic acid
	13-8	20.11	40.1	4,4-(p-phenylene) diphenol



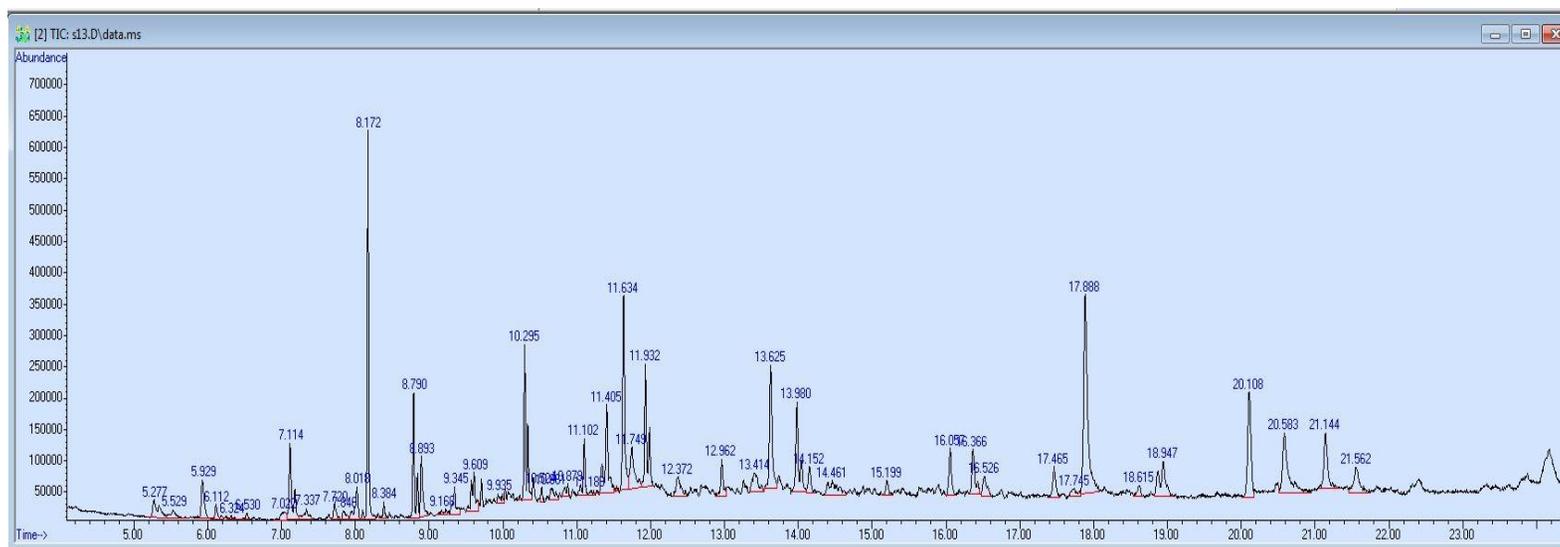
**Fig 14: GC/MS total ion chromatograph for Flash mixer #3 inlet (S11)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S11	14-1	5.929	67.1	1,3 bis ((1,1) di methyl ethyl) benzene
	14-2	7.114	6.03	1 Tetradecene
	14-3	8.195	49.7	2, 4 di tert butyl phenol
	14-4	8.882	76.2	Diethyl phthalate/Phthalic acid
	14-5	11.64	77.3	n-Hexadeconic acid
	14-6	13.608	53.4	Octa deconic acid
	14-7	17.877	82.8	Hexadecanoic acid



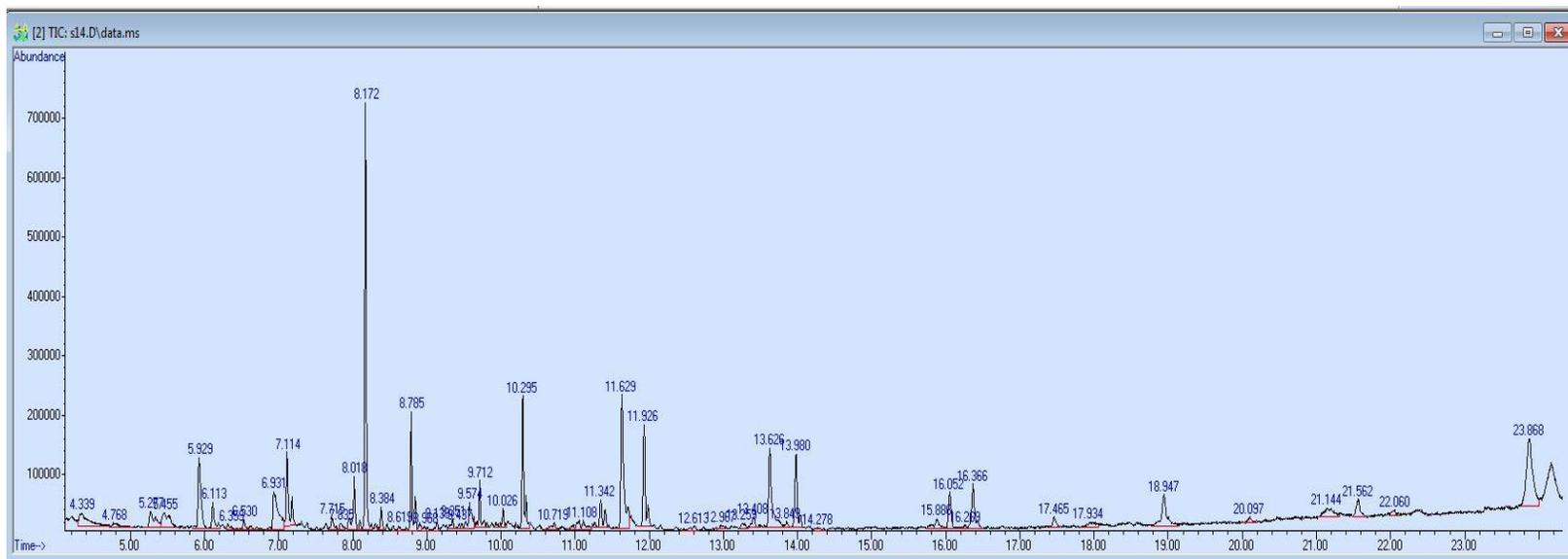
**Fig 15: GC/MS total ion chromatograph for MEE feed (S12)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S12	15-1	5.924	59.6	1,3 bis ((1,1) di methyl ethyl) benzene
	15-2	7.114	5.45	1 Tetradecene
	15-3	8.184	56.7	2, 4 di tert butyl phenol
	15-4	8.889	69.9	Diethyl phthalate/Phthalic acid
	15-5	10.29	5.65	1-Hexadeconol
	15-6	11.64	75.4	n-Hexadeconic acid
	15-7	13.62	71.9	Octa decanoic acid
	15-8	17.877	85.3	Hexadecanoic acid



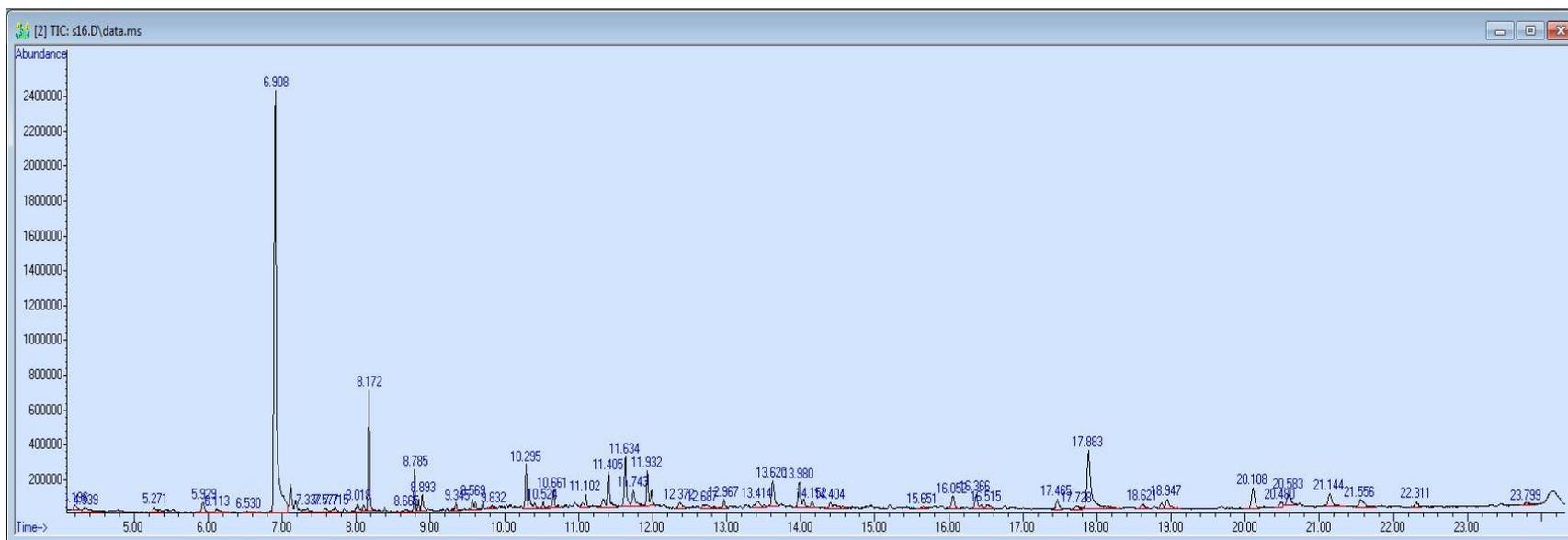
**Fig 16: GC/MS total ion chromatograph for MEE Condensate (S13)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S13	16-1	5.924	68.3	1,3 bis ((1,1) di methyl ethyl) benzene
	16-2	7.114	5.45	1 Tetradecene
	16-3	8.172	60.4	2, 4 di tert butyl phenol
	16-4	8.893	40.5	Diethyl phthalate/Phthalic acid
	15-5	11.64	68	n-Hexadeconic acid
	15-7	13.62	25.8	Octa decanoic acid
	15-8	17.877	79.4	Hexadecanoic acid



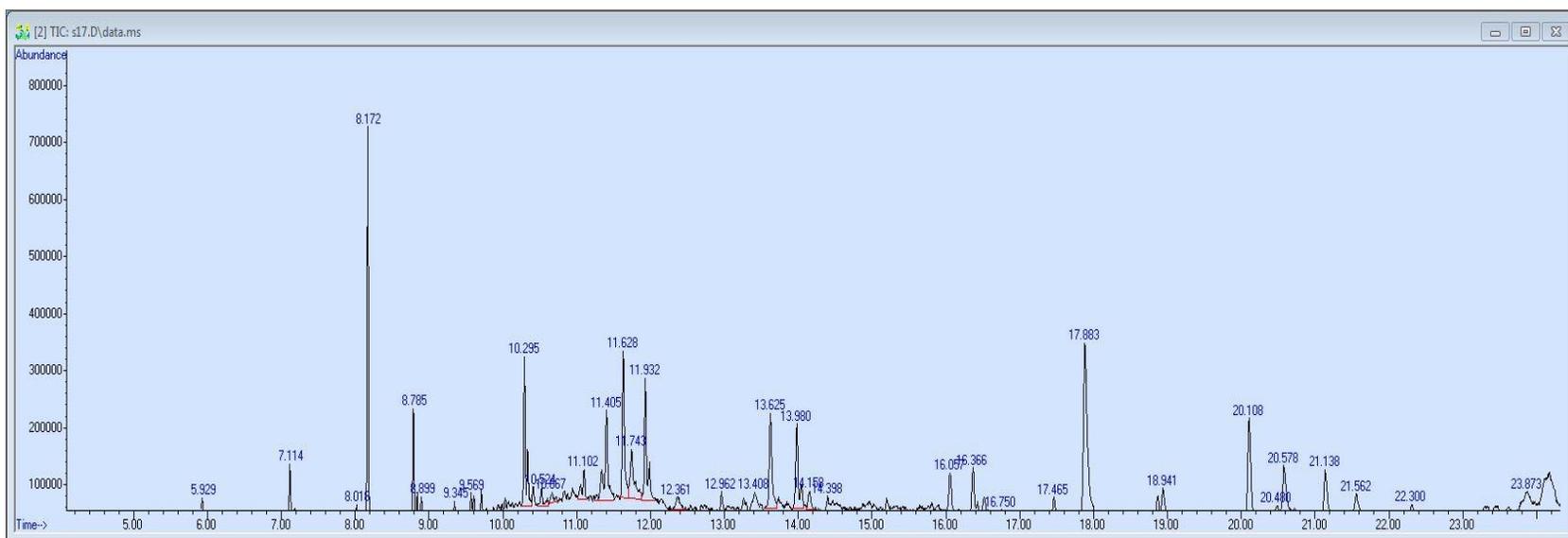
**Fig 17: GC/MS total ion chromatograph for MEE reject (S14)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S14	17-1	5.924	63.9	1,3 bis ((1,1) di methyl ethyl) benzene
	17-2	7.114	6.2	1 Tetradecene
	17-3	8.172	53.4	2, 4 di tert butyl phenol
	17-4	11.64	81.4	n-Hexadeconic acid



**Fig 18: GC/MS total ion chromatograph for ATFD Distillate (S16)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S16	18-1	5.924	46.7	1,3 bis ((1,1) di methyl ethyl) benzene
	18-2	6.9	73.6	1 3H isobenzofuranone
	18-3	8.172	55.4	2, 4 di tert butyl phenol
	18-4	8.889	35.1	Diethyl phthalate/Phthalic acid
	18-5	11.64	29.7	n-Hexadeconic acid
	18-6	17.877	80.6	Hexadeconic acid



**Fig 19: GC/MS total ion chromatograph for Filtrate from US filter press (S17)**

Sample no	Peak no	RT (min)	Probability (%)	Compound
S17	19-1	5.924	66.6	1,3 bis ((1,1) di methyl ethyl) benzene
	19-2	7.114	6.86	1 Tetradecene
	19-3	8.172	6.86	2, 4 di tert butyl phenol
	19-4	10.3	9.39	2-Hexadecenol
	19-5	11.64	34.7	n-Hexadeconic acid
	19-6	17.877	80.1	Hexadeconic acid

## Annexure-2

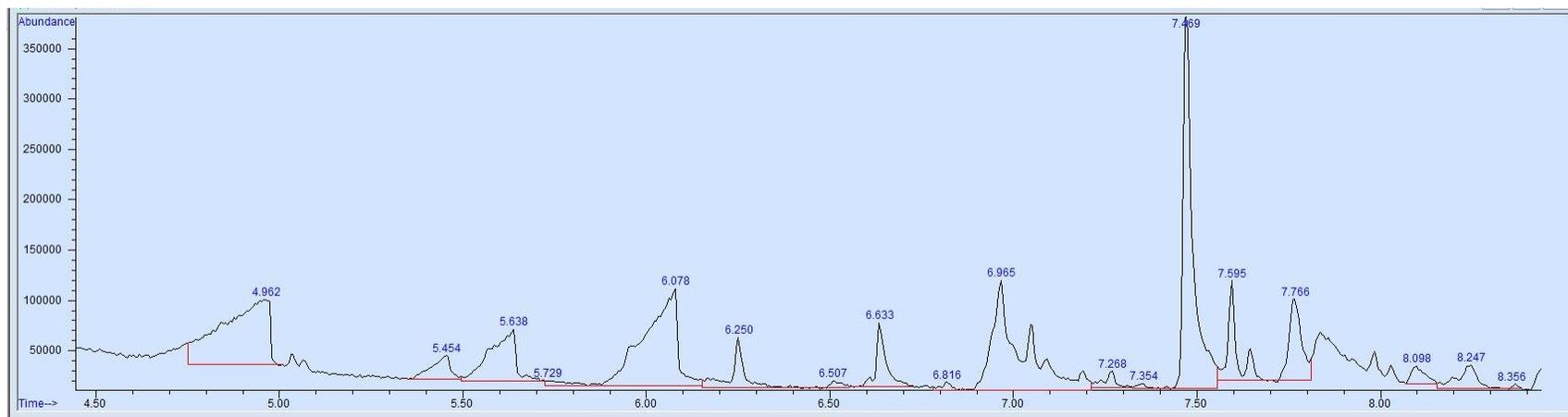


Fig 1. GC-MS chromatogram of o-xylene in PS1

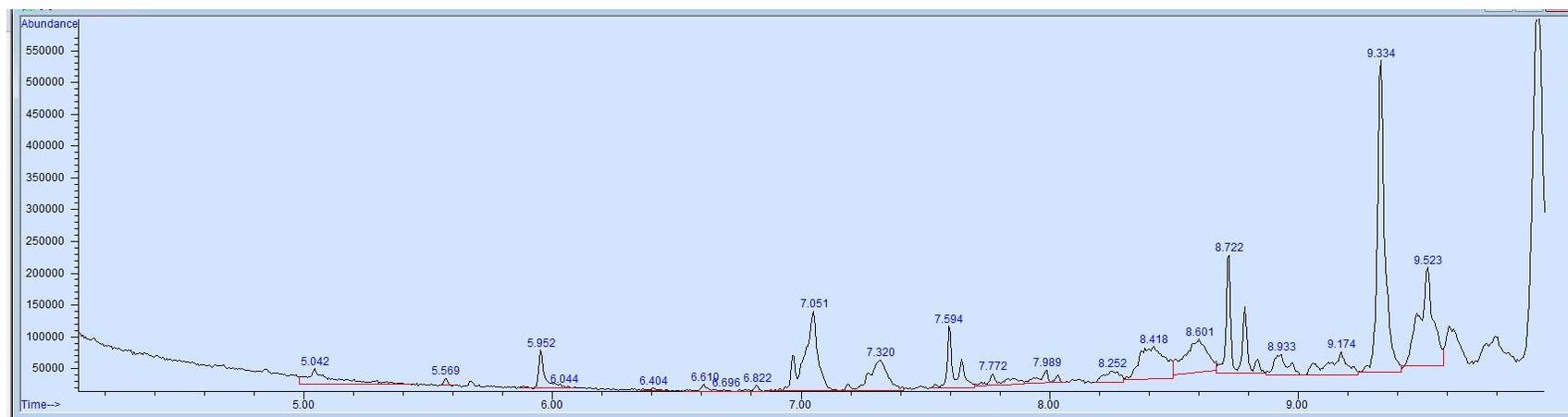


Fig 2. GC-MS chromatogram of o-xylene in PS7

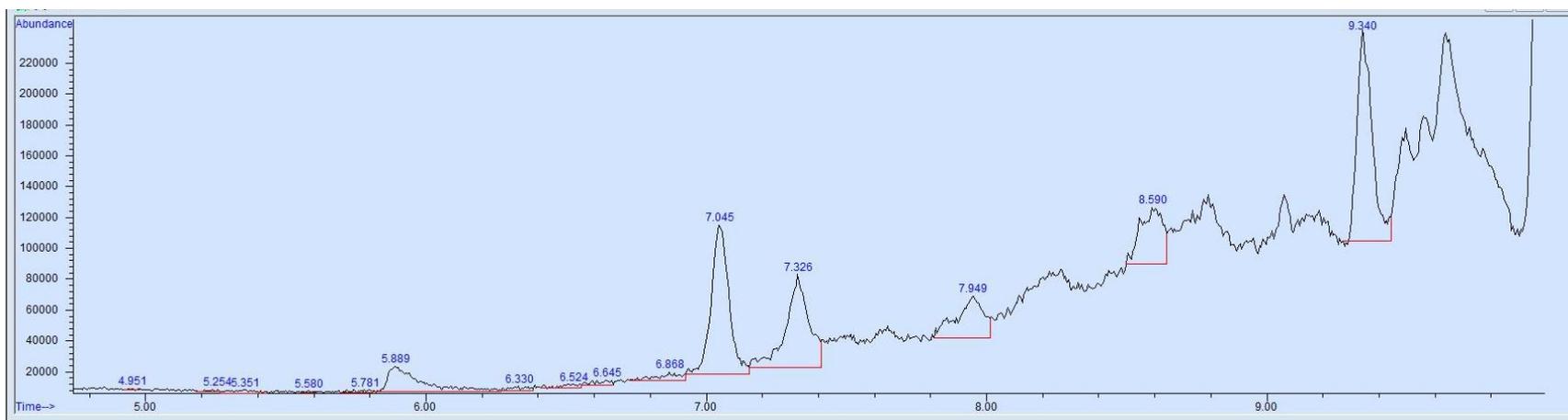


Fig 3. GC-MS chromatogram of o-xylene in S1

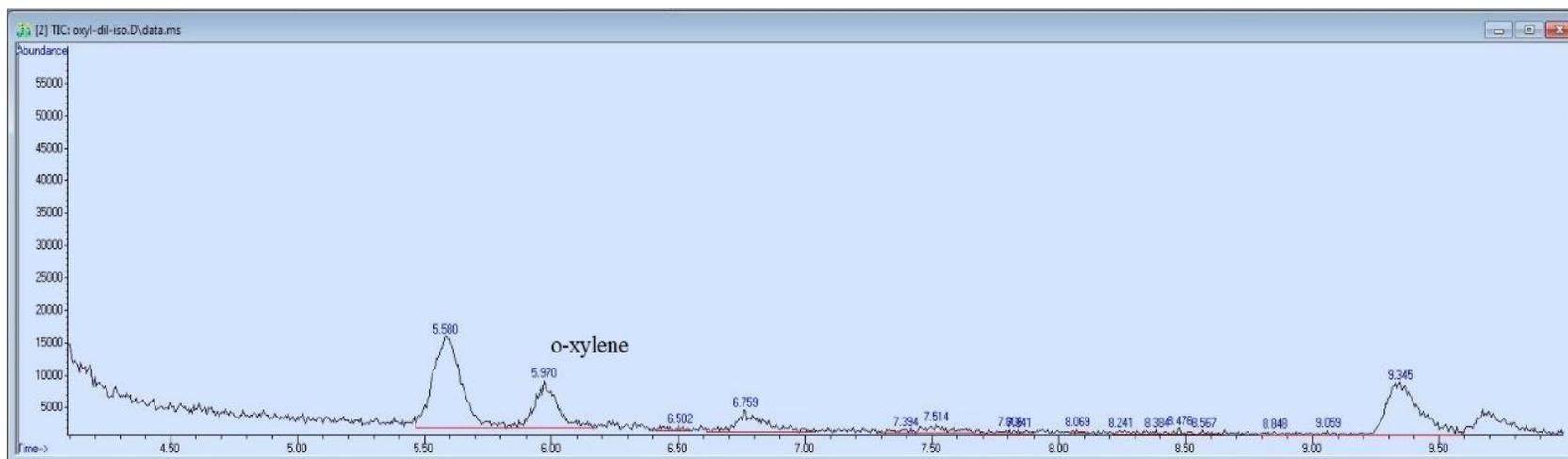


Fig 4. GC-MS chromatogram of o-xylene (RT-5.9min)

### Annexure – 3

#### Photographs taken during first visit on 23.7.2021



**Fig.1: IITM team during the visit at M/s:Thirumalai Chemicals Pvt. Ltd.**



**Fig.2: Inspection of operation in ETP, M/s:Thirumalai Chemicals Pvt Ltd**



**Fig.3: Inspection of operation in old ETP, M/s:Thirumalai Chemicals Pvt Ltd**

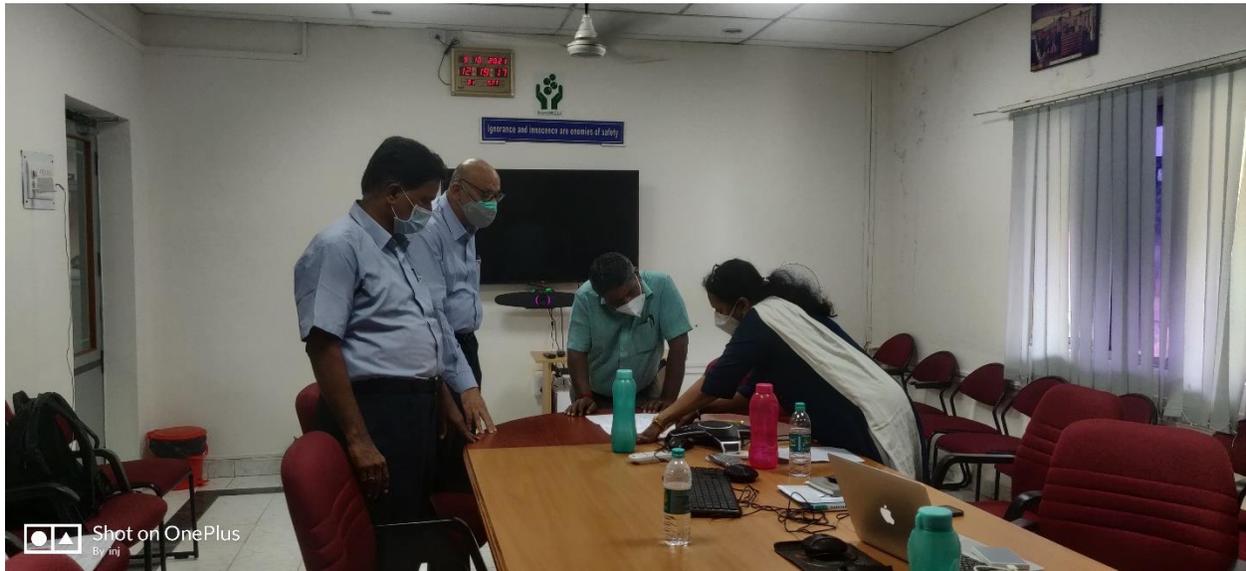


**Fig.4: Photograph of old ETP, M/s:Thirumalai Chemicals Pvt. Ltd. Ranipet**



**Fig.5: Composite Sample collection at RO plants in new ETP**

**Photographs taken during second visit on 9.10.2021**



**Fig.6: Discussion with TNPCB Official Mr.Rajan, Joint Chief Environmental Engineer, Vellore**



**Fig.7: Checking of water level in feed tanks of process and utilities stream in ETP**



**Fig.8: Sample Collection in utility stream during second visit**



**Fig.9: Sample Collection in RO plants (utilities stream) during second visit**

Annexure-III

**ASSESSMENT OF CONTAMINATION  
LEVEL AT THE YARD AREA OF  
THIRUMALAI CHEMICALS LIMITED,  
RANIPET**

*Prepared by*

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**Professor**

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**Chennai-600036**



**SEPTEMBER 2021**

## **Team Members Involved**

- 1. Mr. R. Manthiram Karthik**
- 2. Mr. R. Sarath Kumar**
- 3. Mr. A. Vishnu Vardhan**
- 4. Mr. D. Kumaran**
- 5. Mr. Sumit Kumar**
- 6. Mr. Mohammed Iqbal Thayyil**
- 7. Mr. Insamam ul Huq**

# **ASSESSMENT OF CONTAMINATION LEVEL AT THE YARD AREA OF THIRUMALAI CHEMICALS LIMITED, RANIPET**

## **1. Background**

Thirumalai Chemicals Limited (TCL), Ranipet manufactures phthalic anhydride, malic acid, and fumaric acid. TCL approached IIT Madras to prepare a Project Proposal for Remediation of Contaminated site within the premises of M/S Thirumalai Chemicals Ltd (TCL), Ranipet. After a site visit and discussion with TCL officials, IIT Madras agreed to take up the work. The objective and scope of the work are defined on mutual agreement.

## **2. Objective**

Preparation of Detailed Project Report for Remediation of Contaminated **site within the premises of M/S TCL., Ranipet**

## **3. Scope**

- Identifying the concentration and the extent of pollution of Contaminated site within the premises of M/S Thirumalai Chemicals Ltd., Ranipet. Based on the discussion with the officials of TCL and the information provided regarding the raw materials and products, the signature compounds for analyses were finalized as pH, TDS, EC, chloride, sulfate, chromium, COD, Phthalic anhydride (Dicarboxylic Anhydrides), Fumaric Acid, Malic Acid, and O-xylene.
- Reporting the concentration of the pollutants
- Suggesting appropriate methodology for the remediation of the site.
- Estimating approximate time and duration of remediation activity.

## **4. Assessment of Contamination Level**

The study focussed on the assessment of contamination level at the yard area of TCL, Ranipet. IIT Madras team led by Prof. Ligy Philip visited the site on 10<sup>th</sup> April 2021 and had a detailed discussion with the officials of the industry. On 30<sup>th</sup> June 2021, the team made the second visit to the contaminated site. The entire site area (approx. area 14680 m<sup>2</sup>) was examined for the formation of grids (to collect representative samples) after fixing the boundaries (Fig 1). The contaminated site was then divided into 11 grids so that the samples collected would be representative of the entire area (Fig 2 & 3). After marking the exact sampling points, bore drilling was carried out at the mid-point of each grid up to the hard rock strata (Fig 4 & 5). The soil samples were collected at different depths. Besides, water

samples were collected from auger point 3 and point 8. The details of the sampling points are provided in **Table 1**. The nature of soil type with depth was also recorded as in Table 2.

**Table 1. Details about the sampling points**

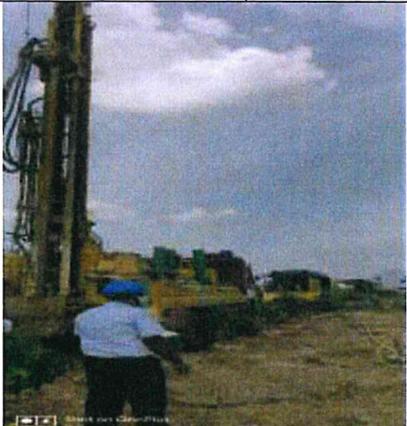
S.No.	Sampling Location details	GPS coordinates	Observed nature of the soil	Remarks
1.	<b>Location 1</b> Near Ponnai road	N12°57'19.4" E079°18'54.3"	0 cm- Muram* (top soil) 0.5 m- Quartzite* (white coloured) 1.8 m- Black coloured soil (contaminated soil) 2.1 m- Hard rock (powder)	Hard rock/Rough stone reached at 2.1 m approx.
				
2.	<b>Location 2</b> Near Security room	N12°57'19.2" E079°18'52.7"	0 cm-Muram* 0.5 m- Filled up soil/ weathered rock* 0.9 m- filled up soil 1.8 m- Black colored soil (contaminated soil) 2.7 m- Hard rock	Hard rock reached at 2.7 m approx.
				

3.	<b>Location 3</b> Near reed bed	N12°57'20" E79°18'54"	0 cm- Muram 3.9 m- Hard rock slurry (water was found)	Hard rock reached at 3.9 m approx. A water sample was also collected using a sampler after 15 mins.
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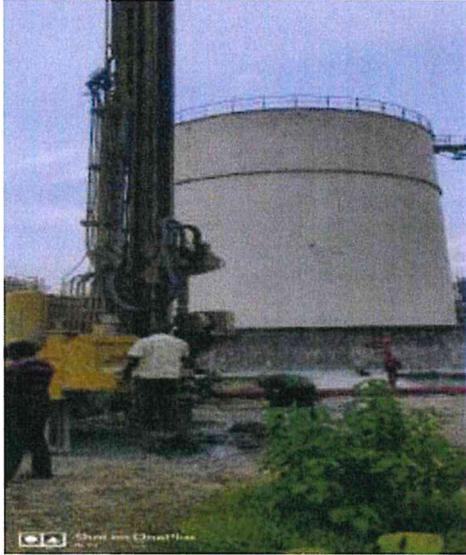


4.	<b>Location 4</b> Light tower entrance area	N12°57'19.8" E79°18'51.9"	0 cm- Muram 0.9 m- filled up soil 2.1 m- Hard rock	Hard rock reached at 2.1 m approx.
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5.	<b>Location 5</b> Near reed bed	N12°57'20.8" E79°18'52.4"	0 cm-Muram 0.9 m- filled up soil 1.8 m- Black colored soil (contaminated soil) 2.7 m- Hard rock	Hard rock reached at 2.7 m approx.
				
6.	<b>Location 6</b> Front of o-xylene tanks	N12°57'19.3" E79°18'50.7"	0 cm-Muram 0.9 m- Black colored soil (contaminated soil) 1.8 m- Hard rock	Hard rock reached at 1.8 m approx.
				
7.	<b>Location 7</b>	N12°57'21.2" E79°18'51.3"	0 cm-Muram 0.9 m- Black colored soil (contaminated soil) 2.4 m- Hard rock	Hard rock reached at 2.4 m approx.
				

8.	<p><b>Location 8</b> Front of o-xylene storage Near yard shed</p>	<p>N12°57'19.5" E79°18'50"</p>	<p>0 cm- Muram soil* 0.9 m- Muram soil* 1.8 m- Black colored soil 3 m- Black colored soil (contaminated soil) 3.6 m- Hard rock slurry (water was found)</p>	<p>Hard rock reached at 3.6 m approx. A water sample was also collected using a sampler after 15 mins.</p>
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9.	<p><b>Location 9</b> Front of o-xylene storage Near yard shed</p>	<p>N12°57'20.3" E79°18'50.2"</p>	<p>0 cm- Muram soil 0.9 m- Muram soil 1.8 m- Black colored soil (contaminated soil) 3.6 m- Hard rock</p>	<p>Hard rock reached at 3.6 m approx.</p>
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10.	<b>Location 10</b> Near TN warehouse	N12°57'21.6" E79°18'50.4"	0 cm- Muram soil 0.9 m- Black colored soil (contaminated soil) 2.1 m- Hard rock	Hard rock reached at 2.1 m approx.
				
11.	<b>Location 11</b> Near TN warehouse	N12°57'21.1" E79°18'50.4"	0 cm- Muram soil 0.9 m- Black colored soil (contaminated soil) 2.1 m- Black soil & rock powder 3.0 m- Hard rock	Hard rock reached at 3 m approx.
				

**Note:** \* denotes soil sample collected using a manual auger.



Fig 1. Grids made at the contaminated site of Thirumalai Chemicals for sample collection

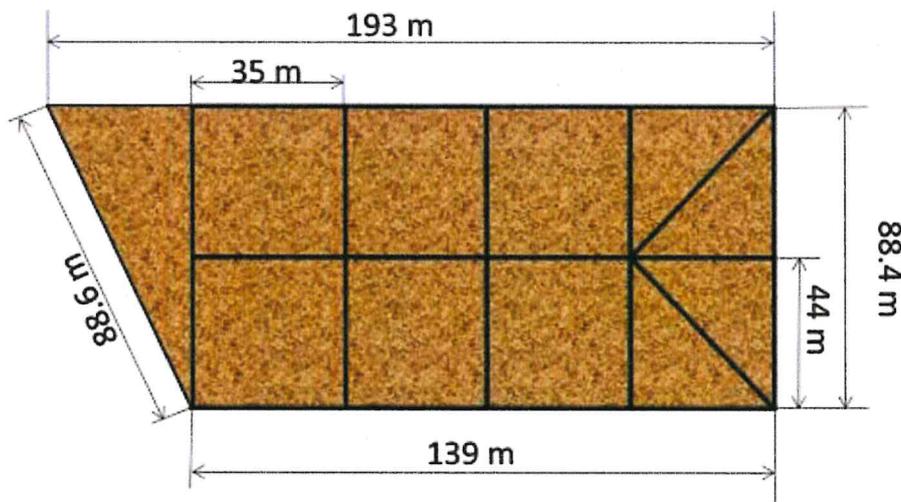


Fig 2. Schematic representation of the contaminated site with the grids made for sampling



Fig 3. Google earth image of the contaminated site with sampling points



Fig 4. Google earth image of the contaminated site with marked sampling points at each grid

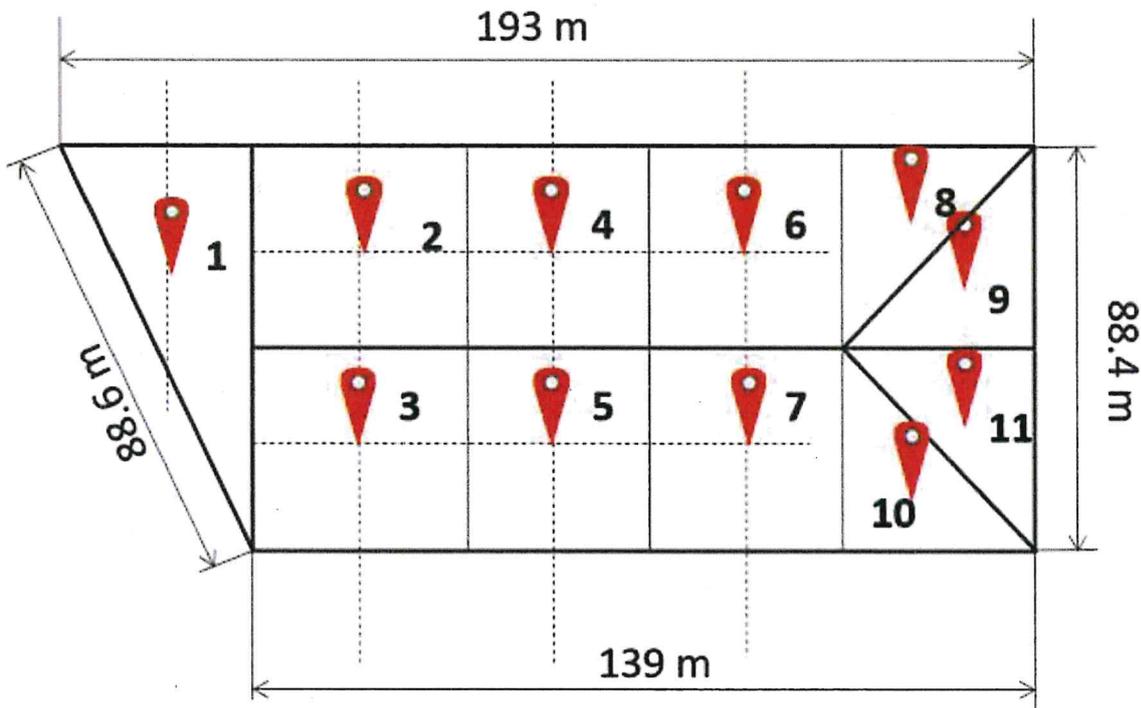


Fig 5. Schematic representation of the site with 11 sampling points marked at each grid

**Table 2. List of sampling points and their ID notions**

<b>Borehole ID</b>	<b>Sample ID</b>	<b>Depth (m)</b>	<b>Observed nature of the soil</b>
1	1.1	0	Muram
	1.2	0.5	Quartzite (white colour)
	1.3	1.8	black colored contaminated soil
	1.4	2.1	Hard rock
2	2.1	0	Muram/Filled up soil
	2.2	0.9	Weathered rock
	2.3	1.8	black colored contaminated soil
	2.4	2.7	Hard rock
3	3.1	0	Muram
	3.2	3.9	Hard rock slurry + water
4	4.1	0	Muram
	4.2	0.9	filled up soil/quartzite
	4.3	2.1	hard rock
5	5.1	0	muram
	5.2	0.9	filled up soil/quartzite
	5.3	1.8	black colored contaminated soil
	5.4	2.7	hard rock
6	6.1	0	muram
	6.2	0.9	black colored contaminated soil
	6.3	1.8	hard rock
7	7.1	0	muram
	7.2	0.9	black colored contaminated soil
	7.3	1.8	hard rock
8	8.1	0	muram
	8.2	0.9	Muram
	8.3	1.8	black colored contaminated soil
	8.4	3	black colored contaminated soil
	8.5	3.6	hard rock
9	9.1	0	muram
	9.2	0.9	muram
	9.3	1.8	black colored contaminated soil
	9.4	3.6	hard rock
10	10.1	0	muram
	10.2	0.9	black colored contaminated soil
	10.3	2.1	hard rock
11	11.1	0	muram
	11.2	0.9	black colored contaminated soil
	11.3	2.1	rock powder
	11.4	3	hard rock

## **5. Analytical methods**

### **5.1 Moisture content**

Initially, the dry crucible was weighed in a weighing balance up to four-digit accuracy. A known weight of soil sample (10 g) was added to the crucible and kept in the oven at  $105\pm 5^{\circ}\text{C}$  for 24 h. Then, the crucible was cooled to room temperature using a desiccator. The weight of the crucible with the sample was measured for the concurrent values.

### **5.2 Physicochemical parameters**

Soil samples were mixed with reagent grade water in a 1:1 ratio. The flasks were covered and continuously stirred for 5 min. The soil suspension was allowed to settle for about one h or centrifuge off the aqueous phase for the analysis (Method 9045D, US EPA). The collected supernatant was analyzed for pH, EC, anions, COD, TDS as per Standard Methods (APHA, 2012). TDS was measured by the gravimetric method after filtering the sample using a 0.45-micron nylon membrane filter.

### **5.3 Chromium**

#### **5.3.1 Total chromium**

The fresh samples (0.5 g) were extracted with 12 mL of  $\text{HNO}_3$ :  $\text{HCl}$  (3:1) using a microwave digester and diluted sufficiently with reagent grade water (Method 3052, US EPA). The diluted samples were filtered and analyzed for heavy metals using ICP-OES.

#### **5.3.2 Hexavalent chromium ( $\text{Cr}^{6+}$ )**

The fresh samples (2.5 g) were digested with 10 mL of digestion solution (2:3 ratio of  $\text{NaOH}$ :  $\text{Na}_2\text{CO}_3$ ), 0.1 g of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and 1 mL of phosphate buffer using a hot plate at  $90^{\circ}\text{C}$  for one h. After digestion, the samples were allowed to cool, filtered, and diluted sufficiently with reagent grade water after adjusting pH to 7.2 to 7.5. An aliquot of a sample (0.5 mL) was mixed with 0.2 mL of diphenyl carbazide (DPC) and 0.2 mL of 5 N  $\text{H}_2\text{SO}_4$ . The concentration of  $\text{Cr}^{6+}$  was determined using UV Spectrophotometer at 540 nm.

### **5.4 Organic acids**

Into a 50-mL beaker, 10 g of fresh soil sample was weighed, then 20 mL of 1 N  $\text{H}_2\text{SO}_4$  was added. This mixture was thoroughly blended and allowed to stand for 20 min. The resulting slurry was vacuum filtered using a Buchner funnel which held a GFD filter. While the soil cake was still moist, it was washed with 15 mL of water which first was used to rinse the

extraction beaker. After a second 10-mL water wash, the combined filtrate volume was adjusted to 50 mL with water. A 3-mL aliquot of extract solution was filtered using a 5-mL syringe fitted with a membrane filter (Dietz and Singley, 1994).

Organic acids were separated by reversed-phase high-performance liquid chromatography (HPLC, Dionex, USA) using an Hypersil gold column at 30°C, using isocratic elution with 4 mM H<sub>2</sub>SO<sub>4</sub> as carrier solution at a flow rate of 0.5 mL/min. Organic acids were detected at 232 nm. Standard acids were prepared as individual stock solutions and then combined to give diluted reference standards.

### **5.5 Volatile organic compounds**

The extraction of VOCs from soil samples (10 g) was carried out with 10 mL of methanol, and the supernatant was collected in a glass vial after centrifugation at 4000 rpm for 15 min. The extraction was repeated twice with 10 mL of methanol at each step. The combined supernatant was made up to 30 mL with methanol. The sample was filtered using a 0.22-micron syringe filter and analyzed for VOCs using gas chromatography with a flame ionization detector (GC-FID, Perkin Elmer, USA).

To estimate VOCs content, 5 µl of the sample was injected into the GC-FID system. The optimum conditions: Carrier gas used was nitrogen; the initial oven temperature was 90°C (hold for 5 min) which was increased to 200°C and held for 10 min. Injection temperature was 250°C with column of 30m and 530mm diameter.

### **5.6 Quality assurance and quality control**

The physicochemical parameters were carried out independently by two candidates in duplicates, and the average values were reported. For organic acids and VOCs, a known quantity of pollutants was spiked to the soil samples and extracted per the protocol mentioned in sections 2.4 and 2.5. The recovery of pollutants was observed to be more than 80%.

## **6. Results and inferences**

The physicochemical parameters (pH, EC, moisture content, COD, TOC, TDS, chlorides, and sulfates) for all the soil samples mentioned above are given in **Table 3**. The concentration of heavy metal (total chromium and hexavalent chromium), organic acids, and VOCs of the soil samples are shown in **Table 4**. The characteristics of water samples collected from the auger holes 3 and 8 are shown in **Table 5**.

Table 3. Physicochemical parameters of soil samples at different depths

Sample point	Sample ID	pH in water	EC in water ( $\mu\text{S}/\text{cm}$ )	Moisture content (%)	TDS ( $\mu\text{g}/\text{g}$ )	Chlorides ( $\mu\text{g}/\text{g}$ )	Sulphates ( $\mu\text{g}/\text{g}$ )	COD ( $\mu\text{g}/\text{g}$ )	TOC ( $\mu\text{g}/\text{g}$ )
1	1.1	7.05 $\pm$ 0.02	1284.50 $\pm$ 4.24	7.16 $\pm$ 0.22	890 $\pm$ 15.6	63.54 $\pm$ 14.52	507.96 $\pm$ 30.94	146.0 $\pm$ 2.8	58.24 $\pm$ 0.74
	1.2	8.03 $\pm$ 0.02	1595.00 $\pm$ 1.41	4.77 $\pm$ 0.36	1040 $\pm$ 5.5	176.01 $\pm$ 14.5	622.53 $\pm$ 15.72	112.0 $\pm$ 28.3	38.58 $\pm$ 0.86
	1.3	7.72 $\pm$ 0.02	1106.20 $\pm$ 0.00	2.93 $\pm$ 0.90	760 $\pm$ 7.3	176.28 $\pm$ 28.81	168.73 $\pm$ 4.06	62.0 $\pm$ 28.3	27.25 $\pm$ 1.14
	1.4	7.37 $\pm$ 0.00	855.50 $\pm$ 0.00	3.11 $\pm$ 1.26	540 $\pm$ 5.5	125.76 $\pm$ 39.56	59.52 $\pm$ 21.26	40.0 $\pm$ 0.8	13.61 $\pm$ 0.99
2	2.1	6.67 $\pm$ 0.02	6998.50 $\pm$ 20.51	5.72 $\pm$ 0.22	4860 $\pm$ 25.8	2044.84 $\pm$ 92.4	521.72 $\pm$ 5.40	82.0 $\pm$ 28.3	24.58 $\pm$ 0.36
	2.2	7.55 $\pm$ 0.06	2199.00 $\pm$ 12.73	4.97 $\pm$ 0.52	1500 $\pm$ 4.7	453.85 $\pm$ 95.39	111.80 $\pm$ 26.50	32.0 $\pm$ 8.5	9.63 $\pm$ 0.52
	2.3	7.19 $\pm$ 0.01	2316.50 $\pm$ 7.07	6.71 $\pm$ 0.17	1640 $\pm$ 6.3	353.35 $\pm$ 30.46	545.04 $\pm$ 7.28	26.0 $\pm$ 19.8	7.49 $\pm$ 0.27
3	2.4	7.94 $\pm$ 0.04	1487.50 $\pm$ 3.54	1.27 $\pm$ 0.64	960 $\pm$ 7.1	113.26 $\pm$ 21.89	565.99 $\pm$ 12.36	20.4 $\pm$ 2.0	6.74 $\pm$ 0.05
	3.1	7.40 $\pm$ 0.01	3095.10 $\pm$ 23.33	9.20 $\pm$ 0.39	2050 $\pm$ 7.9	593.17 $\pm$ 44.74	650.33 $\pm$ 13.28	39.6 $\pm$ 4.8	11.54 $\pm$ 0.09
	3.2	7.79 $\pm$ 0.01	3245.00 $\pm$ 0.50	11.73 $\pm$ 0.9	2200 $\pm$ 16.0	977.76 $\pm$ 89.38	62.36 $\pm$ 10.76	58.0 $\pm$ 4.2	20.80 $\pm$ 0.02
4	4.1	7.40 $\pm$ 0.01	1314.10 $\pm$ 3.54	8.30 $\pm$ 0.94	770 $\pm$ 24.2	214.56 $\pm$ 14.66	62.28 $\pm$ 10.94	58.6 $\pm$ 7.6	17.28 $\pm$ 0.46
	4.2	7.51 $\pm$ 0.01	1345.00 $\pm$ 3.54	7.40 $\pm$ 1.21	640 $\pm$ 23.4	176.81 $\pm$ 2.63	335.03 $\pm$ 32.44	24.2 $\pm$ 5.4	7.40 $\pm$ 0.08
	4.3	7.82 $\pm$ 0.00	894.50 $\pm$ 2.12	1.24 $\pm$ 0.76	610 $\pm$ 21.2	126.56 $\pm$ 37.60	157.56 $\pm$ 17.82	40.5 $\pm$ 10.6	13.88 $\pm$ 0.45
5	5.1	7.56 $\pm$ 0.02	7895.50 $\pm$ 0.71	6.39 $\pm$ 0.39	3660 $\pm$ 27.1	1414.72 $\pm$ 56.7	948.94 $\pm$ 22.26	96.0 $\pm$ 0.5	35.70 $\pm$ 0.76
	5.2	7.64 $\pm$ 0.02	4157.10 $\pm$ 1.41	8.98 $\pm$ 1.45	2150 $\pm$ 18.7	605.93 $\pm$ 26.70	623.74 $\pm$ 13.06	88.0 $\pm$ 8.5	27.64 $\pm$ 1.15
	5.3	7.40 $\pm$ 0.01	7572.00 $\pm$ 10.9	12.39 $\pm$ 0.2	4940 $\pm$ 6.3	1401.43 $\pm$ 32.7	1093.24 $\pm$ 52.2	124.0 $\pm$ 11.3	44.52 $\pm$ 0.52
6	5.4	7.86 $\pm$ 0.01	2404.00 $\pm$ 8.49	5.95 $\pm$ 0.80	1470 $\pm$ 28.3	416.63 $\pm$ 11.66	105.55 $\pm$ 27.43	102.4 $\pm$ 7.9	35.12 $\pm$ 1.10
	6.1	7.50 $\pm$ 0.01	4315.60 $\pm$ 10.45	4.78 $\pm$ 1.12	2980 $\pm$ 2.4	618.16 $\pm$ 80.09	1142.65 $\pm$ 31.1	75.0 $\pm$ 4.2	26.70 $\pm$ 0.15
	6.2	7.34 $\pm$ 0.01	4295.10 $\pm$ 14.14	6.36 $\pm$ 0.66	3040 $\pm$ 20.4	1125.98 $\pm$ 84.6	774.90 $\pm$ 18.6	68.0 $\pm$ 11.3	22.02 $\pm$ 0.78
7	6.3	7.48 $\pm$ 0.01	3356.50 $\pm$ 12.02	5.05 $\pm$ 1.04	2009 $\pm$ 12.4	593.17 $\pm$ 44.74	484.64 $\pm$ 18.75	44.6 $\pm$ 6.2	17.82 $\pm$ 0.09
	7.1	8.13 $\pm$ 0.00	3952.00 $\pm$ 0.00	7.90 $\pm$ 1.49	2650 $\pm$ 7.9	1189.26 $\pm$ 93.4	715.76 $\pm$ 40.19	76.0 $\pm$ 0.9	26.52 $\pm$ 0.08
	7.2	7.67 $\pm$ 0.02	4423.10 $\pm$ 14.14	10.98 $\pm$ 0.7	2640 $\pm$ 5.9	643.15 $\pm$ 95.43	715.82 $\pm$ 58.06	62.4 $\pm$ 12.2	26.56 $\pm$ 0.65
	7.3	7.05 $\pm$ 0.03	4211.00 $\pm$ 14.14	5.79 $\pm$ 0.24	2160 $\pm$ 5.9	618.16 $\pm$ 80.09	1057.70 $\pm$ 22.7	56.0 $\pm$ 5.7	22.10 $\pm$ 0.24

8	8.1	6.34 ± 0.01	5095.40 ± 0.00	12.95 ± 0.9	3450 ± 11.8	996.77 ± 71.17	973.20 ± 60.5	72.0 ± 1.4	21.42 ± 0.12
	8.2	7.32 ± 0.01	4105.60 ± 14.14	6.49 ± 0.01	2800 ± 9.1	718.66 ± 82.03	722.06 ± 76.35	120.0 ± 11.3	51.32 ± 0.03
	8.3	4.27 ± 0.04	4431.40 ± 14.14	9.28 ± 0.02	2940 ± 27.3	599.68 ± 17.86	968.61 ± 39.64	34.0 ± 7.1	14.20 ± 1.40
	8.4	4.53 ± 0.02	3455.20 ± 0.00	10.57 ± 0.1	1681 ± 21.6	239.55 ± 50.	754.40 ± 21.19	62.0 ± 2.8	21.46 ± 0.17
	8.5	5.57 ± 0.00	2809.50 ± 21.21	11.90 ± 0.9	1560 ± 12.6	365.84 ± 48.13	603.90 ± 52.03	108.0 ± 7.1	39.04 ± 0.19
9	9.1	7.00 ± 0.01	9345.60 ± 21.21	7.18 ± 0.33	6380 ± 7.1	2411.49 ± 53.3	923.18 ± 49.33	80.4 ± 5.1	27.34 ± 0.42
	9.2	7.13 ± 0.02	5315.10 ± 14.14	8.21 ± 0.45	3640 ± 13.4	886.66 ± 26.66	817.29 ± 59.04	114.0 ± 7.1	40.98 ± 0.98
	9.3	7.27 ± 0.02	2167.00 ± 2.83	7.13 ± 0.48	1070 ± 5.7	365.58 ± 83.85	359.21 ± 33.26	38.8 ± 4.0	13.19 ± 0.28
	9.4	6.98 ± 0.01	1427.50 ± 0.00	4.80 ± 0.39	1000 ± 17.8	218.50 ± 20.24	472.81 ± 15.78	68.0 ± 5.7	22.55 ± 0.45
	10.1	7.40 ± 0.02	7776.70 ± 0.00	9.99 ± 0.26	5360 ± 13.9	1856 ± 25.96	1175.48 ± 37.2	56.4 ± 2.3	17.18 ± 0.27
10	10.2	6.69 ± 0.01	5349.50 ± 9.90	11.24 ± 0.3	3720 ± 23.6	1073.33 ± 1.89	1590.87 ± 53.8	48.0 ± 2.8	16.99 ± 0.28
	10.3	6.77 ± 0.01	1196.40 ± 2.12	1.88 ± 0.43	680 ± 16.5	328.10 ± 30.82	3.81 ± 0.44	14.0 ± 5.7	4.87 ± 0.40
	11.1	6.31 ± 0.01	4854.20 ± 14.14	7.51 ± 0.74	3390 ± 3.1	921.79 ± 4.14	920.92 ± 17.02	32.0 ± 5.7	12.63 ± 0.34
11	11.2	6.63 ± 0.00	2615.10 ± 0.00	5.34 ± 0.19	1620 ± 22.0	580.67 ± 27.07	471.81 ± 9.22	24.4 ± 0.8	7.58 ± 0.11
	11.3	6.87 ± 0.02	1215.80 ± 4.24	4.54 ± 0.46	710 ± 8.6	302.83 ± 31.21	191.33 ± 21.9	29.6 ± 2.3	9.49 ± 0.36
	11.4	6.93 ± 0.01	1940.50 ± 2.12	6.39 ± 0.43	1050 ± 18.1	567.91 ± 45.12	32.38 ± 2.27	12.0 ± 0.24	4.12 ± 0.29





**Table 5. Characteristics of water samples collected at auger holes - 3 and 8**

Si.No	Parameters	Auger Hole 3	Auger hole 8
1	pH	7.12 ± 0.02	7.50 ± 0.01
2	EC (µS/cm)	24319 ± 26.87	12800 ± 14.14
3	TDS (mg/L)	14810 ± 669.77	8432.5 ± 457.65
4	Chlorides (mg/L)	9396.44 ± 71.64	3731.10 ± 95.77
5	Sulphates (mg/L)	116.88 ± 5.47	485.13 ± 16.17
6	COD (mg/L)	427 ± 5.66	216 ± 7.07
7	TOC (mg/L)	111.2 ± 14.6	61.99 ± 16.48
8	Total Chromium (µg/L)	BDL	BDL
9	Cr6+ (µg/L)	BDL	BDL
10	Phthalic anhydride (µg/L)	BDL	BDL
11	Oxalic acid (µg/L)	811.90 ± 34.56	BDL
12	Maleic acid (µg/L)	BDL	BDL
13	Fumaric acid (µg/L)	BDL	BDL
14	Acetonitrile (µg/L)	BDL	BDL
15	Isopropyl alcohol (µg/L)	BDL	BDL
16	o-Xylene (µg/L)	BDL	BDL

## **Summary and Recommendations:**

### **Preamble:**

**Thirumalai Chemicals Ltd. (TCL) is an Organic chemical manufacturing company. Based on the information provided by the industry, they use Ortho Xylene and Maleic anhydride as raw materials and manufacture Phthalic anhydride, Malic acid, and Fumaric acid. According to the information provided by TCL, they are not using any solvents in the manufacturing process, and no other intermediates are generated during the process.**

### **Summary:**

**The analyses results showed that the organic content of the soil is not significant. Very low concentrations of oxalic acid are found in a few locations. Traces of hexavalent chromium and relatively high concentrations of total chromium (max 13.0 µg/g) are found in the topsoil. Total chromium and hexavalent chromium are primarily absent or at very low levels below the topsoil. The TDS of the two water samples is high. Some of the soil samples possess high TDS. The water samples show high COD and chlorides.**

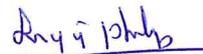
- **The raw materials, by-products, and products of Thirumalai Chemicals Ltd. are organic in nature. All of them are highly biodegradable. Hence, the pollutants might have degraded due to biological activity. It is evident from the low COD values of the soil samples. The method of analysis ensures the leaching potential under normal conditions.**
- **Though Thirumalai Chemicals Ltd. is not using chromium in any form in their plant, the chromium found in the topsoil layer, while collecting the soil samples from the contaminated site, we observed a clear color difference between the topsoil and the soil about 1 m deep.**
- **Though oxalic acid, an organic substance, is neither made nor used by Thirumalai Chemicals Ltd, traces of oxalic acid was found in some soil samples and the water samples.**



**Dr. Ligy Philip**

Professor  
Environmental & Water Resources Engg.,  
Department of Civil Engineering  
Indian Institute of Technology Madras  
Chennai - 600 036, India

- It might have entered from other contaminated sites through rainwater or subsurface flow from other industries in the industrial estate that could have used oxalic acid or chromium.
- To remediate the traces of organics present in the soil, it is advised to inject bacteria through the boreholes. It will enhance the bacterial concentration and accelerate the degradation. To remediate chromium contamination, bioremediation is recommended by employing chromium-reducing bacteria and an appropriate carbon source.
- The TDS concentrations of the soil and water are very high. Natural remediation by rainwater will flush out the TDS. The groundwater contamination potential is low as the hard-rock strata exist about 3 m below the contaminated area. Since the soil depth is not high, planting trees and shrubs in the area is the best solution. Thirumalai Chemicals Ltd. has already started the work in January 2021. 502 tree saplings that were planted have grown to 5 feet plus now. It will bring the soil to its original condition in the course of time.
- The water samples collected from the site showed relatively high COD and very high TDS. COD might be coming through the irrigation water and leaching of the natural manure (chicken droppings) employed for the tree plantations. Thirumalai Chemicals Ltd. shall ensure control on the usage of the natural manure (chicken droppings) properly. Thirumalai Chemicals Ltd. shall control the amount of water used for irrigation and ensure the quality of the water used for watering the plants.
- It is recommended to develop the contaminated site as a green park with trees, shrubs, and grass. Thirumalai Chemicals Ltd. has started developing the site by turning it into a green zone in the last six months.



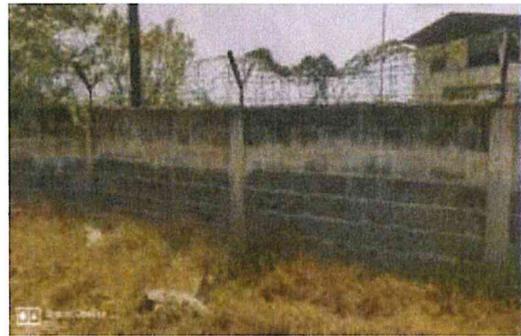
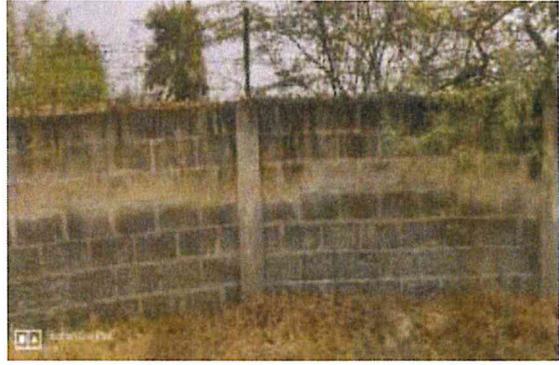
(Ligy Philip)  
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## Annexure 1

Photographs were taken during the site visit, sample collection, and meeting with industry officials





# TAMIL NADU POLLUTION CONTROL BOARD

## Annexure-IV

Proc. No.: T5/ TNPCB/F.0892/VLR/RL/W/2020, Dated: 20.11.2021

**SUB:** TNPCB – Industries – **M/s. Thirumalai Chemicals Limited**, S.F. No. 287, SIPCOT Industrial Complex, Navlock Village, Walajah Taluk, Ranipet District – Certain directions under Section 33(A) of the Water (Prevention and Control of Pollution) act, 1974 as Amended - Issued – Regarding.

- REF:** 1. Proceedings No.T5/TNPCB/F.0892VLR/RL/VLRW&A/2019 Dated: 03/07/2019.  
2. Proc. No.: T5/ TNPCB/F.0892/VLR/RL/W&A/2020, Dated: 09.12.2020.  
3. Proc. No.: T5/ TNPCB/F.0892/VLR/RL/W&A/2020, Dated: 21.10.2021.  
4. A complaint dt. 9.11.2021 enclosing the public complaint received from Novlock & Puliyan kannu villagers, Ranipet, Ranipet District  
5. Inspection of the unit by JCEE(M) on 25.10.2021  
6. Lr.JCEE(M)/TNPCB/VLR/F.004/RL/Complaint/2021 DT:9.11.2021.

\*\*\*\*\*

Whereas the consent was renewed to the unit of M/s. Thirumalai Chemicals Limited, S.F. No. 287, SIPCOT Industrial Complex, Navlock Village, Walajah Taluk, Ranipet District valid up to 31.03.2020 vide reference first cited subject to comply with certain conditions.

Whereas, based on the complaints against the unit regarding discharge of untreated trade effluent outside the premises, directions under section 33A of the Water (Prevention & Control of Pollution) Act, 1974 as amended has been issued to the unit vide reference second to comply with following among others:

- **The unit shall restrict the production to 50 % of its consented quantity so as to achieve zero liquid discharge consistently till the commencement & effective functioning of newly constructed ZLD components.**

and again direction under section 33A of the Water (Prevention & Control of Pollution) Act, 1974 as amended was issued vide reference third cited to the unit to comply with the following:

**The unit shall restrict the production quantity 50% of consented quantity as said in the Board's proc. Dt. 09.12.2020 until submit the certification from IIT, Madras that the unit has achieved 100 % ZLD capacity.**

Whereas JCEE (M), TNPCB, Vellore has inspected the unit on 25.10.2021 and during inspection it was found that the rain water stagnated inside the unit behind the SBI ATM point which is located at south east corner of the unit. Hence, JCEE(M) instructed the unit vide letter Dt. 26.10.2021 to empty the stagnated water and sent back the same to their ETP for further treatment and disposal through ZLD system provided by the unit so as to avoid further ground water contamination if any and also instructed to fill up this area by earth and utilize the above area for some other purposes such as landscaping, parking etc., since this location is sloping downwards. Further it was also instructed the unit not to stagnate the rain water within the premises in future under any circumstances and it shall be collected and disposed through rainwater harvesting system which has been provided in the unit premises itself.

Whereas a complaint petition dt. 9.11.2021 enclosing the public complaint received from Novlock & Puliyan kannu villagers, Ranipet, Ranipet District regarding the discharge of chemical polluted water along with rain water through the drains from the unit of M/s. Thirumalai Chemicals Limited , S.F.No.287, Navlock Village, SIPCOT Industrial Complex, Ranipet, Ranipet District. Further, it was reported in the complaint letter that the complainant visited the drains on 25.10.2021 along with RDO, Ranipet, collected the water samples from the water bodies which are the collection points of drains and sent the same to AEL, TNPCB, Vellore.

Whereas, the JCEE(M), Vellore inspected the unit on 9.11.2021 and based on the observations, the JCEE (M), Vellore has recommended for the issue of certain direction to the unit vide letter dated:9.11.2021.

Therefore, in exercise of the powers conferred under Section 33 A of Water (P&CP) Act 1974 as amended in 1988, Board issues the following directions to the unit of **M/s. Thirumalai Chemicals Limited**, S.F. No. 287, SIPCOT Industrial Complex, Navlock Village, Walajah Taluk, Ranipet District **to comply with the following conditions within 3 months time :**

- 1) The unit shall restrict the number of discharge points connected with Outlet drains to drain the excess rain water in and around the above unit.
- 2) The unit shall install online continuous monitoring systems in consultation with JCEE(M), VLR in the discharge points for the parameters such as TDS, TSS, pH, BOD, COD and other relevant parameters along with surveillance camera and it shall be connected with WQW of TNPCB and CPCB web portal for continuous monitoring.
- 3) The unit shall reuse the entire treated trade effluent (RO Permeate and MEE Condensate) in their process continuously and to ensure 100 % ZLD.



## TAMIL NADU POLLUTION CONTROL BOARD

- 4) The unit shall not discharge any treated/untreated effluent outside the premises and shall not be stagnated/ ponding of water under any circumstances.

Failure to comply with the above said directions, will lead to issue of further directions for closure and stoppage of power supply to your unit under section 33 A of Water (P&CP) Act 1974 as amended in 1988.

The receipt of the proceeding shall be acknowledged.

*[Signature]*  
23/11/21  
For Chairman

To

*[Signature]*  
The Managing Director,  
**M/s. Thirumalai Chemicals Limited,**  
No.25A, SIPCOT Industrial Complex,  
Navlock Village, Walajah Taluk,  
Ranipet – 632 403.

*[Signature]*  
23/11

Copy to

1. The Joint Chief Environmental Engineer (M),  
Tamil Nadu Pollution Control Board,  
Vellore Region – **Requested to identify the discharge points in which the online monitors TDS, TSS, p<sup>H</sup>, BOD, COD to be provided and instruct the same to unit and also Requested for further follow-up and report to Board.**
2. The District Environmental Engineer,  
Tamil Nadu Pollution Control Board,  
Vellore.
3. Technical file.