

CHARACTERIZATION & IDENTIFICATION OF WASTE STREAM FROM BISACODYL PRODUCT TO ACHIEVE ZERO LIQUID DISCHARGE IN PHARMACEUTICAL INDUSTRY

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ABSTRACT: Zero liquid discharge (ZLD) refers to a treatment process in which the plant discharges no liquid effluent into surface waters, in effect completely eliminating the environmental pollution associated with treatment. Apart from this benefit, a ZLD process also makes effective use of wastewater treatment, recycling, and reuse, thereby contributing to water conservation through reduced intake of fresh water. The pharmaceutical industry can be divided into two major segments — Bulk drug and formulations. Bulk drugs are the active pharmaceutical ingredients (APIs) with medicinal properties, which are used to manufacture formulations. The Indian pharmaceutical industry manufactures more than 1000 bulk drugs belonging to various therapeutic segments. Formulations are the end—products of the medicine manufacturing process, and can take the form of tablets, capsules, injectable or syrups. ZLD technologies are mostly applied to API manufacturing industries. Looking to the present situation of Ankleshwar cluster and same cluster is identify as CPA (Critically polluted area) by CPCB/MOEFCC and due to that, there shall be no any effluent permissions are allowed in the cluster due to direction imposed under section 18 (1) b of water act 1974. This retards the growth of industries which have potential to expand. Keeping this restriction in view, If alternative of CETP is explored, a situation may come up in favour to the industry which will not only comply the prevailing imposition of restriction under 18(1) b of the Water Act 1974 but also will allow industrial unit to grow with sustainable development. In this regards, a case study of Pharmaceutical products converted into ZLD by using advance technology.

Key word: Zero liquid discharge, Critically polluted area, Multi Effect Evaporator, RO, stripper

I. INTRODUCTION

The Ankleshwar industrial estate is Asia's largest industrial estate and comprises of approximately 3,000 individual units, half of them chemical units that manufacture chemicals like dyes, paints and fertilisers, Pesticides and Pharmaceutical industries.

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ZLD technologies are mostly applied to API manufacturing industries. The production of special niche API brings with it the problem of specific type of pollutant in the effluent. The effluent parameters vary with the niche of product and hence there is no single solution common for all. Pollution control boards are being very strict on the API industry for effluent release outside the premises and are being pushed to adopt ZLD regime. Active Pharmaceutical Ingredients from waste water streams are the emerging contaminants in the aquatic environment, because of their adverse effect on aquatic life and humans. The waste from API industries contains high COD, high TSS, other harmful chemicals and high amount of salt along with various nascent chemicals such as bromine, chlorine etc. The chemicals present in the effluent is dependent on the product being processed at the manufacturing facility and hence a tailor made solution is required for making each API manufacturing facility ZLD.

Based on above scenario we have identified characteristic of product namely Bisacodyl to implement zero liquid discharge in the pharmaceutical industry. We have studied overall process for this product and implemented technologies to achieve zero liquid discharge for particular product in pharmaceutical industry. The main aim of zero liquid discharge is to recovery of reusable water/other materials from waste water and minimization/no discharge of polluting substances into the environment / natural bodies.

1.1 Concept of Zero Liquid Discharge in Pharmaceutical Industry

ZLD can be defined as the combination of the techniques or facilities and systems which will help the water loop of the industry to become close one for absolute recycling of permeate and converting solute (dissolved organic and in-organic compounds/salts) into residue in the solid form by adopting.

Methods like concentration and thermal evaporation. ZLD will be recognized and certified based on two broad parameters that is, water consumption versus waste water re-used or recycled (permeate) and corresponding solids recovered (percent total dissolved / suspended solids in effluents). Or in general word we can also define that ZLD means industrial plant excluding discharge of waste water.



Figure 1: Concept of ZLD

1.2 Major Sources and Characteristics of Effluent

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II. METHODOLOGY

2.1 Different Methods to Achieve ZLD:

ZLD can be achieved in pharmaceutical industry by the conventional primary, secondary and tertiary effluent treatment modified by the combinations of facilities such as:

- Solvent Stripper
- Multi Effect Evaporator
- Spray Dryer
- Agitated thin film dryer(ATFD)
- RO (Reverse Osmosis)
- Co-processing
- Incineration

We can either select any one or combination of techniques given above depends upon the feasibility of reuse of treated waste water or recovered waste, as well as type of the industry.

2.2 Treatment Option for Wastewater

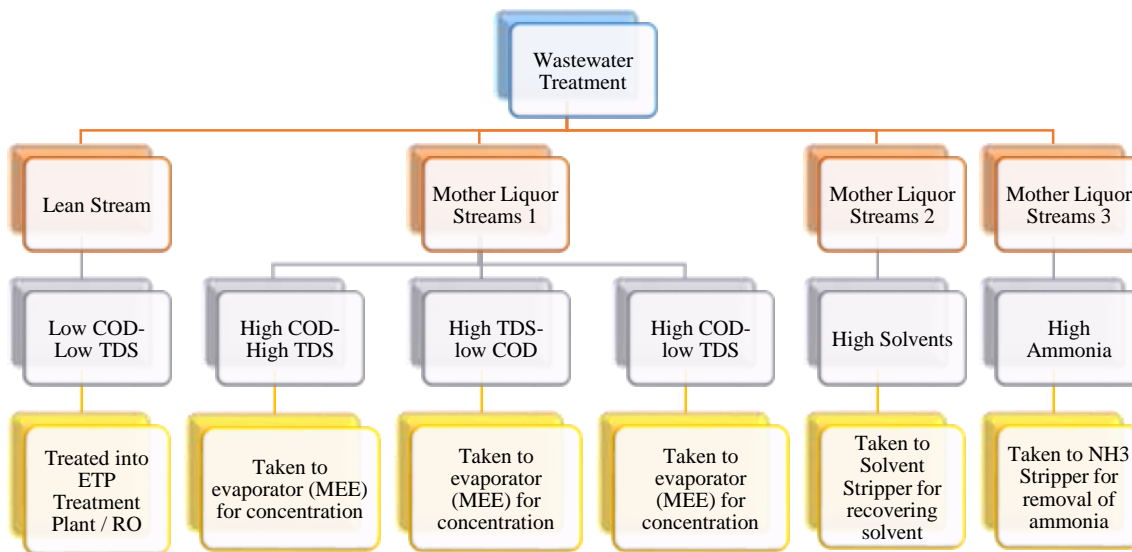


Figure 2: Treatment Option for Wastewater

A typical treatment of segregated streams is as follows:

- Low COD—Low TDS streams: Taken to Effluent Treatment Plant (ETP) for primary, secondary biological treatment (ASP/MBR/SBR) and then to tertiary treatment of sand filtration/UF and RO.
- ML—1: Mother Liquor Stream: (High COD—High TDS, High TDS-low COD, High COD-low TDS): Taken to evaporator (MEE) for concentration of the stream. Distillate from MEE is routed to ETP, if not of recyclable quality.
- ML-2: Mother Liquor Stream (with solvents): Taken to Solvent Stripper for recovering solvent

- ML-3: Mother Liquor Stream (high NH₃): Taken to NH₃ Stripper for removal of ammonia. Or it is treated with high grade (>95% lime) and Magnesium Ammonium Phosphate is isolated and sent to cement industry.
- It is observed that while effluent with high NH₃-N content owing to inorganic ammonia may be treated as above but the effluent containing NH₃-N owing to organic content may require incinerations or its segregation for further purification.
- RO permeate is recycled back in process, cooling tower, boiler make up Water.
- RO rejects are concentrated in MEE, dried by crystallizer / ATFD and mixed salt sent to TSDF.
- Sludge from ETP is dewatered and sent to TSDF.

2.3 ZLD Treatment Options for Pharmaceutical Industry:

Option No. I

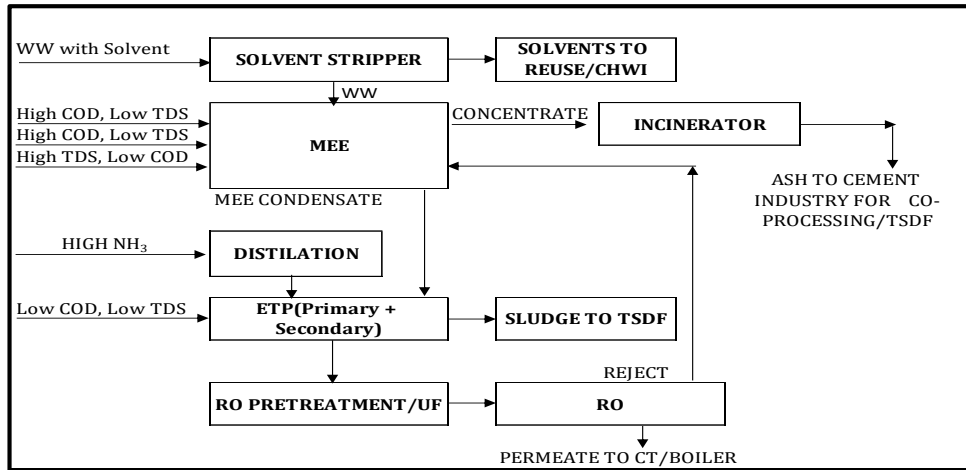


Figure 3: ZLD Treatment Option-1 for Pharmaceutical Industry

Option No. II

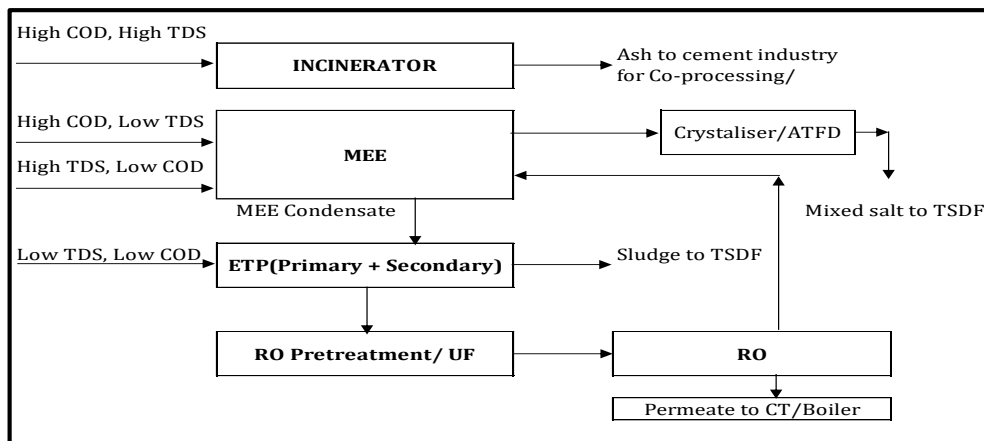


Figure 4: ZLD Treatment Option-2 for Pharmaceutical Industry

Option No. III

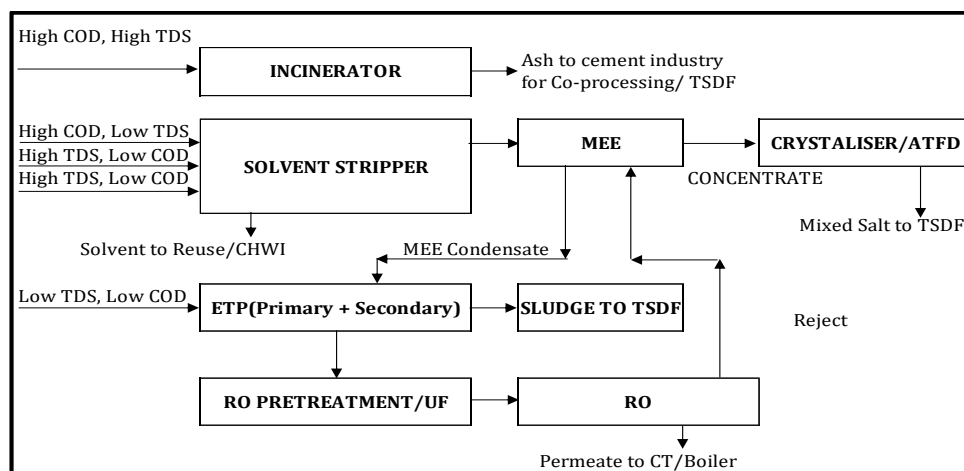


Figure 5: ZLD Treatment Option-1 for Pharmaceutical Industry

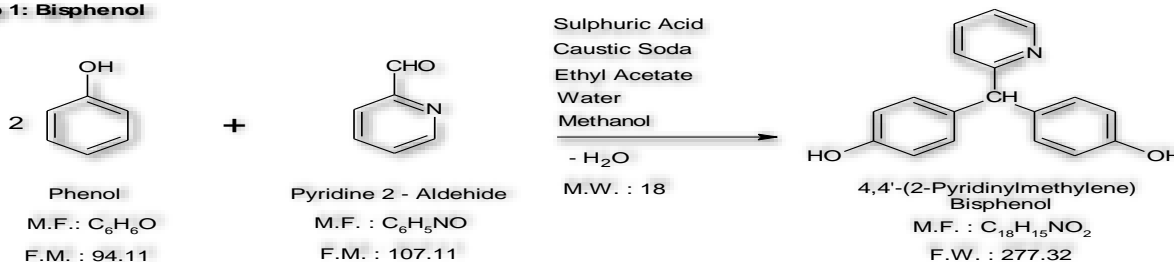
2.4 To Achieve Zero Liquid Discharge for Bisacodyl Product in Pharmaceutical Industry

The brief manufacturing process of Bisacodyl is mentioned below.

Step 1: Bisphenol

In a clean & dry glass flask, charge phenol followed by ethyl acetate and cooled to 10°C. Add sulphuric acid in such a way that mass temperature should not exceed than 25 °C. After completion of addition, maintain mixture temperature of 15°C for 3 hrs. Now add mixture of pyridine 2- aldehyde and ethyl acetate then maintain the temperature of reaction mixture below 20 °C for 15 hrs with stirring. Then allow it to cool down temperature to achieve temperature of 15°C & at that temperature add water, stir it for 15 minutes. By Maintaining temperature of 15°C adjust the pH using the caustic solution. Filter the product and wash with little amount of Methanol. Dry the Product. Check dry weight and melting point.

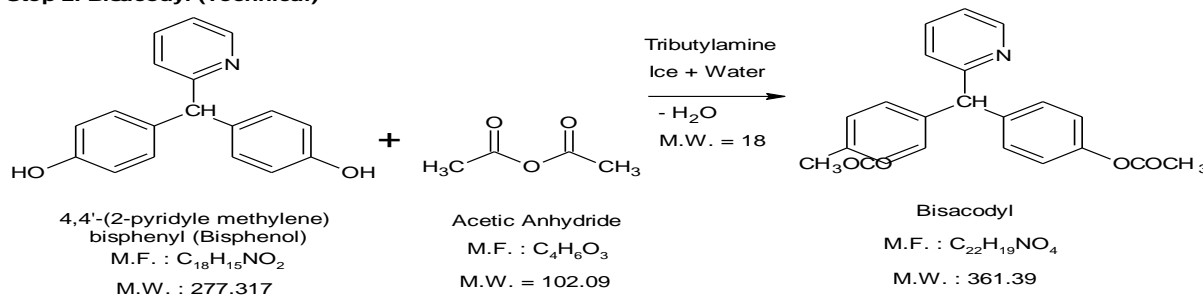
Step 1: Bisphenol



Step 2: Bisacodyl (Technical)

In to a clean and dry glass flask, charge Bisphenol and acetic anhydride. Chill the mixture to 0 °C. Add drop wise Tributylamine in such a way that temperature of reaction mixture should not exceed 10 °C. Maintain 5-10 °c temperature for 3 hrs. Now allow it to cool down till attain room temperature and maintain it for 10 hrs. Quench reaction mixture in ice + water and stir it for 3 hrs. Filter the product wash with water till neutral pH. Filter the slurry, unload, dry and weigh.

Step 2: Bisacodyl (Technical)



Step 3: Bisacodyl (Pure)

In a clear flask, charge Methanol and add wet technical Bisacodyl. Heat it to reflux and make clear solution. Add some Activated carbon and reflux for 1/2 hr. Filter. Distilled out 50% of Methanol charged. Chill the reaction mixture to 5 °c and maintain it for 1 hr. Filter the pure product, wash with chilled Methanol. Dry the product at 65-70 °c.

Step 3: Bisacodyl (Pure)

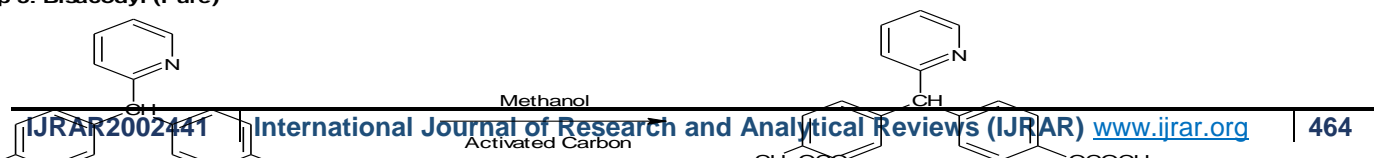


Table 1: Material Balance for Bisacodyl Product

Sr No.	Raw Material (Input)	Quantity (kg/Batch)	Output	Quantity(kg/Batch)
1	Sulphuric Acid	106.000	Product	50.000
2	Caustic Soda Lye	90.000	Ethyl Acetate recovery	70.550
3	Pyridine 2-Aldehyde	14.800	Methanol recovery	30.250
4	Ethyl Acetate	72.000	Tributyl Amine recovery	5.300
5	Phenol	26.050	Spent Carbon	2.250
6	Acetic Anhydride	14.100	Waste Water	1296.860
7	Tributyl Amine	5.400	Solid Waste	0.500
8	Methanol	35.000	Evaporation Loss	9.650
9	Activated Carbon	2.000		
10	Water	600.000		
11	Ice	500.000		
	Total	1465.350		1465.360

2.5 Details of Effluent Treatment Scheme

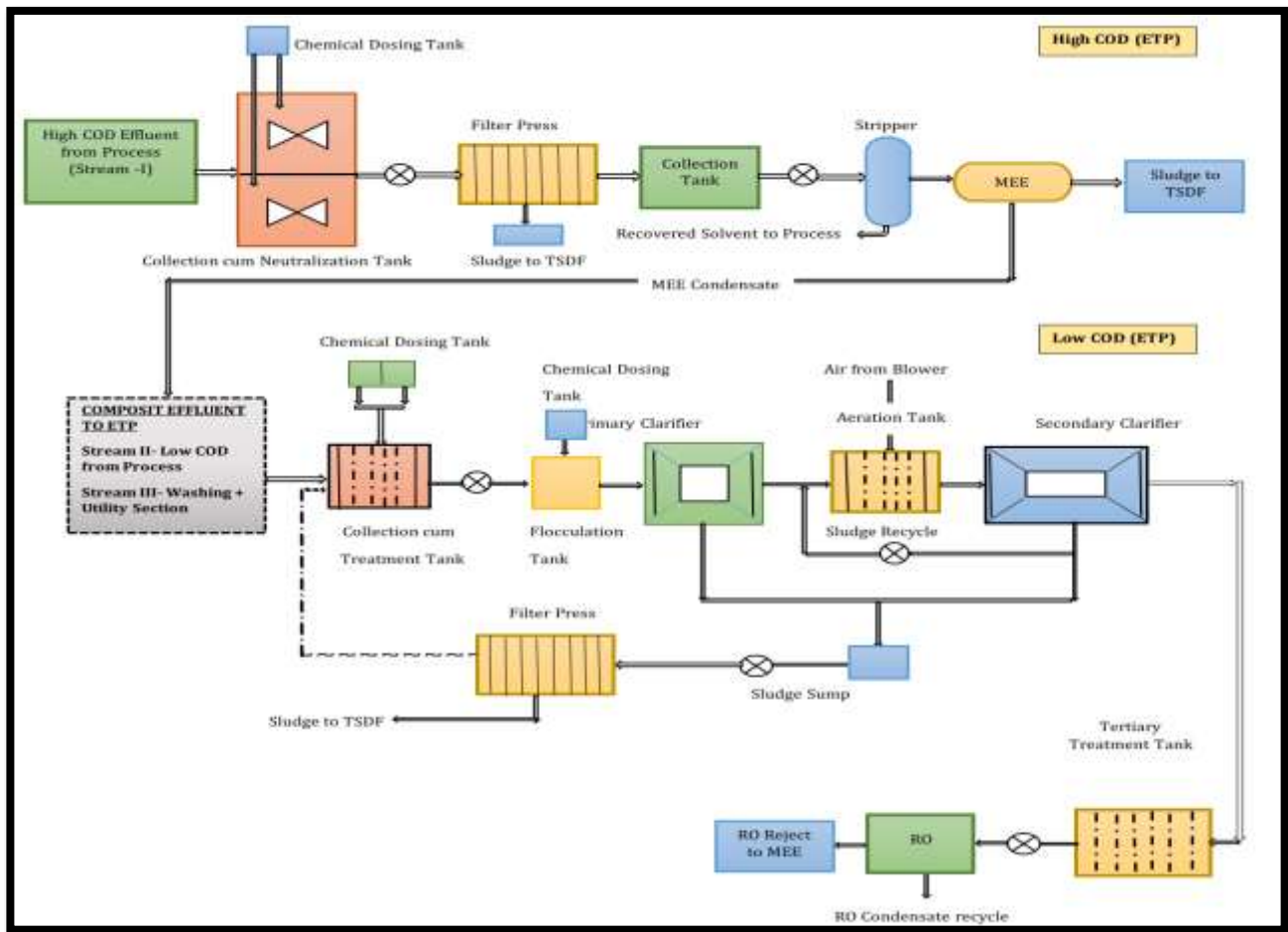


Figure 6: ETP Flow diagram

2.5.1 Treatment for High COD Stream:

The effluent treatment plant is designed on basis of worst-case scenario. The worst-case scenario is arrived considering both the products are manufactured at the same time at full production capacity. High COD effluent stream is treated separately in ETP-I [i.e. Primary treatment] followed by MEE plant. The effluent from process plant is collected in collection tank. Effluent is then pumped to equalization cum neutralization tank where pH is neutralized and compressed air is used for agitation. After neutralization effluent is passed from stripped to strip out the solvent and then subjected to in-house MEE. After MEE treatment salt is separated and MEE condensate is send for primary and secondary treatment and after treatment the effluent is send to RO for further treatment. RO permeate is used in Boiler/Cooling process and RO reject is send to MEE for further treatment. By this, they can achieve zero liquid discharge.

2.5.2 Treatment for Low COD Stream:

The effluent from Boiler Blow Down, Cooling Tower Blow Down, and Washing and MEE Condensate are collected and effluent is then pumped to equalization cum neutralization tank and compressed air is used for agitation. Then it is transferred to coagulation tank/Flocculation tank where suspended solids are settled, and the sludge is taken into membrane filter to separate the solid. Dried sludge is stored in a sludge storage tank. Clear water from settling tank is taken into aeration tanks. In this tanks, extended type aeration system is adopted. Biological treatment is given to the effluent. Overflow is taken into secondary settling tank for excess sludge settling, biomass is recirculated in aeration tank if required or sent to membrane filter press. Overflow from secondary settling tank is passed through activated carbon filter + Sand filter and then taken into collection tank. After adequate treatment, treated water is subjected to RO and after treatment RO permeate is used in Boiler/Cooling process and RO reject is send to MEE for further treatment. By this, they can achieve zero liquid discharge.

2.6 Sample Analysis of Wastewater





Figure 7: Sample Analysis of wastewater

III. RESULTS AND DISCUSSION

The result of parameters of Effluent before and after treatment are as below:

Table 2: Characteristics of Wastewater Before & After Treatment High COD [Effluent from Process]

Sr. No.	Parameters	Unit	Before Treatment	After Primary Treatment	After Stripper Treatment	MEE condensate mixed with ETP II
1.	pH	--	3.0-5.5	5.5-7.5	5.5-7.5	5.5-7.5
2.	T.S.S.	mg/l	4500-5500	1000-1265	800-1000	800-1000
3.	C.O.D.	mg/l	25000-32000	22500-30000	6300-8000	1300-1550
4.	T.D.S.	mg/l	35000-40000	36500-41000	36500-41000	800-1000

Table 3: Characteristics of Wastewater Before & After Treatment:-Low COD [Effluent from Washing +Utilities + MEE Condensate]

Sr. No	Parameters	Unit	Before Treatment	After Primary Treatment	After Secondary Treatment	After Tertiary Treatment treated	After RO Treatment [Characteristics of RO Permeate recycle Water]	After RO Treatment [RO Reject Send to MEE]
1.	pH	--	5.5-7.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5
2.	T.S.S	mg/l	800-1000	200-250	100-150	80-100	80-100	80-100
3.	C.O.D.	mg/l	3000-4000	2800-3800	640-860	620-840	200-250	300-350
4.	T.D.S.	mg/l	4000-4500	4200-4700	4500-5000	4500-5000	100-400	4000-5000

The waste water generation from manufacturing of Bisacodyl product is reused after conventional treatment in the plant to achieve zero liquid discharge. The treated water will be reused in utilities within plant premises by using advance treatment technology. Segregation of stream (i.e. high COD & low COD) to achieve Maximum COD reduction with primary, secondary and tertiary treatment plant along with MEE+RO and maximum water shall be reused.

The treatment for High COD effluent is quite economically viable for above mention product. Considering the value of the products and other parameters, it reveals that even after advance treatment, it is profitable to manufacture Bisacodyl with selection of alternative to conventional ETP/CMEE.

IV. CONCLUSION:

Segregation of effluent from source cause better result of Effluent Treatment Plant. Separate treatment for segregated stream (i.e. High COD & Low COD Stream) gives better reduction in COD. Solvent recovery should be increased up to 97 % by using or installation of solvent stripper and due to that fresh solvent consumption should be minimized. Generated effluent after stripper will be send to In-House MEE and RO to recover the treated water to minimize fresh water consumption. By adopting advance treatment methodology as explained above "Zero Liquid Discharge" in present scenario is quite possible to achieve sustainable development.

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