



Wastewater Treatment By Zero Liquid Discharge Process (ZLD)

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Abstract : A ZLD treatment system utilizes advanced technological water treatment processes are environmentally friendly and highly reliable. For difficult to-treat wastewaters or for situations where scarcity of water demands water recovery (recycle/reuse) Zero Liquid Discharge (ZLD) technologies help you achieve environmental compliance, reduce your carbon which eliminates liquid waste by converting it into disposable dry solids and Recover around 95% of your liquid waste for reuse. ZLD treatment process can be adopted as advanced waste water treatment constituents to by-products that are more readily biodegradable and reducing overall toxicity, pH, COD, TDS, SS, BOD parameters. Zero Liquid Discharge (ZLD) system is to minimize the volume of liquid waste that requires treatment, while also producing a clean stream suitable for use elsewhere in the plant processes. ZLD capable to reduce the all types of waste water and make it reusable and recyclable further for different applications. As per study results shows that the 99 % TDS, 100 % of both COD and BOD, 98 % of SS and TSS reduced (Removed) make it Zero liquid discharge. ZLD plant generated high quality water which suitable to recycle in plant premises and which resulted in reduction of water consumption.

Keywords: ZLD, UF, RO, UASB, MEE Pharmaceutical Waste Water Treatment.

INTRODUCTION

A ZLD wastewater treatment system investment can help your facility conserve water that is important to your process while protecting the resources that are valuable to your local community. A Zero Liquid Discharge treatment system utilizes advanced technological water treatment processes to limit liquid waste at the end of your industrial process to as the name suggests zero which environmentally friendly and highly reliable. For getting the strict environmental discharge guidelines and provide effective treatment with the lowest possible life-cycle cost ZLD is the solution. ZLD system based on standalone thermal/evaporative processes, membrane processes or a combination of the two namely hybrid systems resulting in added value, ease of operation and reduced operating costs. More and more, industries are prohibited from discharging any liquid waste originating from their facilities Zero Liquid Discharge treatment system can help you.

ZLD treatment system should be capable to

1. Various types of waste contamination and flow.
2. Can be helps to chemical volumes adjustments.
3. This treatment process recover around 95% of your liquid waste for reuse.
4. System can be treat and retrieve valuable byproducts from your waste.
5. System can be produce a dry solid cake for disposal

Application Of Treated Waste Water

1. In cooling towers for large scale industry
2. Can be used in the gardening purpose for watering plants and lawns.
3. Boiler feed water. (particularly for generating steam for MEE)
4. In water scrubber as scrubbing media .

5. For preparing lime slurry for ETP.

5. Different industrial washing operations.

LITERATURE REVIEWS

After ZLD treatment process total effluent generation from the industry is segregated into high COD/TDS and low COD/TDS concentration streams. Stripper followed by Multiple Effect Evaporator is treated high concentrated wastewater stream from manufacturing process. WTP reject is sent to MEE and condensate water from MEE is sent to ETP along with other low COD/TDS waste streams i.e. cooling, washing and boiler and ETP followed by RO, permeate from RO is reused for cooling and reject is sent to MEE. So there is no discharge of treated effluent from the industry and unit maintains Zero Liquid Discharge.[2]. Water which is evaporated in MEE recovered and recycled while the brine is continually concentrated to a higher solids concentration and the levels of COD and total suspended solids are to be reduced to acceptable values given by the Pollution Control Board and pH to neutral. [3]. ZLD is a process that is beneficial to industrial, municipal organizations and the environment because no effluent, or discharge, is left over. In 2013 Veolia water treatment ZLD systems employ the most advanced wastewater treatment technologies to purify and recycle all the wastewater produced within the plant. Effluent Segregation, Effective Treatment, Complete Reuse, Transformation of COD into Incinerable Organics and TDS Into Dry Salts for Disposal in Secured Landfill by the Zero Liquid Discharge Based Treatment System. [5] By the application of powdered activated carbon and by reverse osmosis almost 50 % TOC removal was taking place during the coagulation-lime softening step including the use of powdered activated carbon. Remaining value of TOC was removed by the reverse osmosis

(RO) outlet was around 0.2 mg/L. By the treatment of coagulation-flocculation turbidity removal was around 60 % and which was increased to 80 % after the pH adjustment taking place at the outlet of the clarifier. Studied by the Laine et al. 2000 using multimedia filter was reducing the turbidity to values below 1 NTU and further reduction was taking place at the ultrafiltration stage the water had values below 0.1 NTU. [6]RO has a tight pore structure (Membrane used less than 0.001 micron) that effectively removes up to 99% of the dissolved salts (ions), particles, colloids, organics, bacteria and pathogens from the feed water. With the treatment by ZLD-system can produce a clean stream from industrial wastewater and suitable for reuse in the plant and a concentrate stream that can be disposed or further reduced to a solid. In ZLD system 40-50% water rejected during the RO process but this ration can be reduced up to 20-25% by means of recycling the rejected water again and again to achieves its goal of 70-75% efficiency. [7].Designed for overall recovery of > 87.5% as condensate the MVR Evaporator to be used . In the ZLD system main use of MVR-Evaporators was designed to handle 15% of the R.O reject and the auxiliary Evaporator is designed to handle 2% of the regenerate liquor from Softener and Decolorate Resin filters. Part of liquid remains which can evaporated in MEE with crystallization of salt. [8] In zero liquid discharge system the overall loads reduction was 99.2 percent in TDS, 99.9 percent in COD and 100 percent in both the TSS and BOD. By the various experimental analysis relieving that the designed ZLD unit can be used effectively to treat and recycle API manufacturing unit effluents, which helps to meet statutory requirements and reduce concerns on ground water depletion. By the experimental studied MEE (Multiple Effective Evaporator), ATFD (Agitated Thin Film Drier) and LCS effluent treatment unit made of a SBR (Sequential Batch Reactor) and MBR (Membrane Bio-Reactor) with other unit which is called as water recycling unit consisting RO (Reverse Osmosis) plant the pilot plant of ZLD shown a huge reduction in TDS (Total Dissolved Solids), TSS (Total Suspended Solids), BOD (Biological Oxygen Demand) and TSS (Total Suspended Solid) to 99.2, 100, 100 and 99.9 percent respectively .[9]

Basic ZLD system

ZLD treatment technologies that will make up a facility's treatment system will vary greatly depending on volume of dissolved material present in the waste and the system's required flow rate and what specific contaminants are present. ZLD System Consisting Three-Step Process

1.Pretreatment and conditioning

In the ZLD system pretreatment used to remove simple things from the wastewater stream that can be filtered or precipitated out, conditioning the water and reducing the suspended solids and materials that would otherwise scale and/or foul following treatment steps. ZLD treatment block consists of some type of clarifier or a reactor to precipitate out metals, hardness, and silica. Liquid that is then filter-pressed into a solid, resulting in a solution much lower in suspended solids and without the ability to scale up concentration treatment.

2.Phase-one concentration

Phase-one concentration is usually done with membranes like reverse osmosis (RO), brine concentrators or electrodialysis. This stream and concentrate it down to a high salinity and pull out up to 60–80% of the water.

3.Evaporation/Crystallization

The next step is generating a solid which is done through thermal processes or evaporation where you evaporate all the water off, collect and reuse it. Remaining waste then goes from an evaporator to a crystallizer which continues to boil off all

the water until all the impurities in the water crystallize and are filtered out as a solid.

These steps are implemented in your specific ZLD system will vary depending on your facility's individual needs. Wastewater treatability study done to be sure the contaminants present in your wastewater stream are dealt with accordingly. Specific contaminants, volume of those contaminants and required system flow rate will all affect what technologies make up your ZLD system. In ZLD system if your plant runs consistently at a lower flow rate usually looking at a lower capital cost for your and If your plant generally runs a greater flow in a shorter amount of time your capital cost is usually higher for equipment.

Five Common Problems with ZLD

Zero liquid discharge (ZLD) for wastewater treatment and effluent reduction whether it's to comply with local discharge regulations or recycle and reuse as much water as possible in your process more information is becoming available. Due to scope of ZLD systems being used and the difference in treatment depending on your industry and individual process.

1. RO Membrane Fouling

RO is an integral part of the ZLD process but when pretreatment isn't removing harmful solids properly prior to entering the RO phase it extremely likely you will see some level of fouling in your RO membranes. Accumulation of deposits in your filtration membranes as a result of contaminants Calcium , Magnesium , Silica, Metal oxides ,Bacteria and other colloidal and suspended solids is called as Fouling.

Options that avoid RO fouling

1.Ultrafiltration (UF). UF technology for your ZLD system is effective in reducing RO membrane fouling by allowing more control when it comes to membrane pore size, turbulence and polarization control, and backwash capabilities.

2.The evaluation and treatability study of your wastewater stream is helpful in designating the correct technology for your system and can't be stressed enough.

3.Due to certain chemicals used in the process that can hinder the effects of certain coagulants when being processed for ZLD.

4.Some effective chemical treatment can include softening, precipitation, coagulation, and adsorption, among others.

5.Some of chemical pretreatment used in collaboration with ZLD systems can be tricky and important to implement a treatability study to ensure your water treatment engineers understand exactly what contaminants are entering your wastewater stream.

2. System Scaling

Due to heat related treatment scaling occurs in the RO membranes and when small particles that get through pretreatment and filtration form deposits but scaling forms much harder deposits than what you see with fouling. Scaling reduced water permeability, greater energy usage and damaged membranes and equipment.

Alkalinity (pH) can play a major role on scaling As the value of pH increases many scale-forming compounds decrease in solubility, precipitating out in higher rates when the water is heated.

Amount of the scale-causing contaminants present in the water -

The amount of these scale-causing contaminates becomes greater than their natural saturation point due to evaporation and scale is likely to occur regardless off the alkalinity or temperature.

Treatments to prevent these issues might include

1.PH control**2.Chemical scale inhibitors 3.Degasifiers.****3.Problematic balance of TSS/TDS**

With an incorrect ratio of total suspended solids (TSS) to total dissolved solids (TDS) by adding heat can quickly and easily result in corrosion of piping and fouling and/or scaling. The solids remaining concentrate after evaporation of water and as the remaining solid properly removed in blowdown or prevented in the first place by properly pretreating the wastewater these solids and hardness begin to build up on heat transfers and other internal piping. The ration of TSS to TDS vary depending on your system by ensuring level of TSS and TSD to the proper concentrations will ensure a smoother and more efficient process.

4.Corrosion

In the some processes of the ZLD process such as crystallization and dewatering it is important to be aware of the cause and effects of corrosion. As the higher salt concentrates in the remaining liquor or brine which can cause a breakdown in the piping or other mechanical parts of the system. Due to the scale buildup can also cause corrosion and the loss of heat transfer. Hence much of the contamination that can cause corrosion in the thermal parts of the ZLD process need to be addressed based on the individual system. Level of heat , the chemical balance, concentrations and pressure can all contribute to this complex calculation.

5.Chemical feed

In the ZLD system chemical feed be the another level of complexity to an already complicated process. Lot of chemical treatments for cooling water include certain dispersants to prevent fouling and scaling and benefits these chemicals offer the cooling tower water treatment process make it more difficult to effectively use coagulants when they need to be removed via clarification or filtration.

Unit operations or processes used in ZLD system

1.Membrane Bio Reactor (MBR) - Biological secondary treatment for reduction of organic load.

Advantages - Secondary clarifier not required.

Treated water quality is better than conventional ASP, MBBR and SBR.

Post treatment of sand filtration not required.

Disadvantages - Capital cost is more than other aerobic biological technologies (ASP, SBR, MBBR).

Membrane replacement after five years.

Applications - Oil Refineries , Fertilizer Industry , Textile Industry , CETPs .

2.Solvent recovery – Air Stripper - Used for recovering solvents/ammonia recovery by providing air

Advantages - Economical when solvents with low solubility in water are present in wastewater and Conventional proven method for removal of solvents.

Disadvantages - Applicable only when large quantity of solvent with low solubility in water is present in wastewater. Difficult to capture solvent when in low concentration.

Applications - Recovery of useful solvents, ammonia in pharmaceutical industry , Pesticide Industry , Chemical Industry.

3.Solvent Recovery – Steam Stripper - Solvents can be reused or are saleable.

Advantages - Useful even less quantity of solvent present in wastewater.

Disadvantages - Scaling occurs in column which is to be cleaned periodically.

Applications - Pesticide Industry , Chemical Industry.

4.Ultra-Filtration (UF) - Used for removal of colloidal matter and bacteria and viruses and Used as pre-treatment to RO.

Advantages - Removes suspended, colloidal particles, bacteria, viruses.

Best pre-treatment for RO.

Most effective treatment for removal of salinity (TDS) with more than 99% salt rejection.

Disadvantages - Replacement of membranes after 5 years required.

Very high capital cost.

Applications - Pre-treatment to RO in all ZLD plants

5.Reverse Osmosis (RO) - Used for removal of salinity (TDS) and residual organics by passing wastewater through semi-permeable membrane by applying high pressure.

Advantages - Clean technology and no handling of chemicals like acid/alkali like ion exchange technology and Permeate water is free of ions and can be used in industrial processes.

Disadvantages - High energy consumption due to high pressure pumps.

Membrane replacement required after application of 3 years.

Cleaning of membrane frequently due to membrane fouling
Reject Water

Applications - Pre-treatment to RO in all ZLD plants.

6.Multiple Effect Evaporator (MEE)- Used to evaporate wastewater to separate water and salt by using heat of steam in sequence of vessels.

Advantages - Proven method for recovery of water from saline water and separation of salt.

Disadvantages - Very high operating cost due to steam requirement.

Applications - Pharmaceutical Industry, Textile Industry, Pesticide Industry, Dyes and Dye Intermediates, Steel Industry, Fertilizer Industry.

7.Mechanical Vacuum Compressor (MVR) - Water vapor generated in the evaporator is compressed to higher pressure which acts as heat source for evaporation.

Advantages-Eliminates thermal energy requirement.

Useful when steam not available. Low operating cost.

Disadvantages - Suitable only for liquid with narrow boiling point rise (BPR).

Suitable when ready steam is not available in the industry.

Applications - Textile Industry .

8.Crystallizer - Used to dry high TDS water or products using heat.

Advantages - Used for recovery of salts like Sodium Sulphate, Sodium Chloride, Sodium Thiosulphate, Zinc Sulphate etc.

Simple Evaporation method of single effect evaporation.

Good heat conductivity so can be applied for highly viscous fluids.

Disadvantages - Scaling and corrosion of unit is a problem.

Requires frequent cleaning.

Applications - Application in salt recovery in Dye and Dye Intermediates , All industrial sectors.

9. Agitated Thin Film Dryer (ATFD) - Used to dry high TDS water or products using fast revolving rotor in a heating jacket.

Advantages - Gentle evaporation and high evaporation rate.

Continuous cleaning of heating surface.

Disadvantages - Scaling and corrosion of unit is a problem.

Requires very high energy.

Applications - Textile Industry, Pharmaceutical Industry for final drying before disposal Pharmaceutical Industry.

10.Incinerator-Used for burning the concentrated effluent by thermal energy

Advantages - Useful method for very high strength (High COD) effluent which is difficult to biodegrade. No further treatment is required.

Disadvantages - Operational cost is high. Capital cost is high. Viable for only small quantities of effluent.

Applications - Dye and Dye Intermediates , Pesticide Industry

Material And Methodology

Different treatment Processes used in ZLD

1.Primary Treatment

In ZLD process Primary Treatment Section the process effluent will be collected in existing aeration tank. After aeration system is pumped to the new ETP site to the oil/ Solvent Separator to remove any floating oil/solvent separation. Finally it is collected in the collection tanks wherein it will be mixed to ensure uniformity in the quality and to even out any flow variations. Neutralization of the Process effluent will be with either lime or HCL in neutralization tank, depending on the pH. Then effluent will be further coagulated with Ferrous Sulphate and then flash mixed with polyelectrolyte to ensure proper flocculation with a Polyelectrolyte. Finally the effluent will be clarified in a Primary Clarifier and will be collected in UASB feed sump for further anaerobic treatment.

2.Secondary Treatment

Primarily treated effluent from the UASB Feed sump will be pumped to the UASB reactor wherein an anaerobic culture of microorganisms will degrade the effluent in the absence of free oxygen and reduce a major part of the organic load (COD/BOD). Biodegradation of effluent in Anaerobic process and biodegraded effluent will be then taken to a pre-aeration tank to remove the septicity and gas entrapped which will also render the suspended solids to settle for which a solids settling clarifier is provided. Clarification of effluent is done to separate the solids and clarified effluent will be fed to the aerobic biodegradation treatment from where the effluent with biomass will be clarified of biomass in a secondary clarifier. The need of BOD concentration is low at the feed to RO system a well-designed aerobic system in extended aeration mode will be installed to ensure maximum removal of organic matter.

3.Tertiary Treatment

In the tertiary treatment process the clarified effluent from the secondary clarifier will be disinfected by sodium hypochlorite and further treated through a Pressure Sand Filter and an Activated Carbon absorber. For additional treatment and a tertiary clarifier may be required to remove the silica content in the effluent before feeding to RO. After disinfection treated effluent and anticipated additional treatment to remove silica will then be fed to Ultrafiltration (UF) system for removing colloidal matter and improving the silt density index (SDI) before feeding to Reverse Osmosis and permeate generated from RO will be recycled and reused in the process plant for suitable activity while the Reject generated from RO will be evaporated in MEE to separate the salt which will be landfilled at the authorized Secured Landfill site.

4.Reverse Osmosis Systems

Single stage Reverse Osmosis systems complete with all peripherals will be sufficient for maximum recovery of reusable permeate. Permeable liquid will be recycled and reused depending upon the quality of permeate and suitability of reuse in the process. RO Systems rejects will be evaporated in the Multi Effect Evaporator and the salt separated will be sent for Secured Landfill. The Condensate will be treated in the ETP.

5.Multi Effect Evaporator

MEE will be provided to treat RO Rejects basically consisting of the dissolved solids and the condensate will require further treatment and will therefore be treated in the ETP. MEE will be followed by agitated thin film dryer (ATFD) to ensure

conversion of the slurry to almost dry solids. Separated salts will be disposed of secured landfill.

ZLD Treatment Options (Sector wise)

1. Distillery

1.Bio-methanation followed by R.O/MEE followed by incineration (slop fired).

2.Bio-methanation followed by R.O/MEE followed by drying (spray/rotary).

3.Concentration through MEE followed by coprocessing in cement/thermal power plant.

4.Bio-methanation and RO followed by MEE followed by bio-composting. (As per new protocol)

2.Tannery

Primary treatment + secondary treatment+ pre- treatment for RO + Reverse Osmosis +, MEE (recovery of permeate, crystallized salt, reuse of the recovered condensate).

3.Pulp & Paper

Primary treatment + Degasification + RO (2 stage) + NF and UF + Evaporator Concentrator/Crystallizer.

4.Sugar - Treatment options

For the sugar industry restricting effluent generation to 100 Liters/ton cane crushed and consumption of water to be restricted to 100 liters / ton initially and further to 50 Liters/ton cane crushed. Recycle of excess condensate to process or ancillary units. Water management/audit to reduce spray pond/cooling tower blow downs and excess condensate and the irrigation protocol for disposal into land applications

5.Pharmaceuticals

Primary treatment for Low TDS Effluent treatment system + Secondary treatment + Tertiary chemical treatment to reduce TDS (Pressure sand filter, Activated Carbon filter and filter press for dewatering of sludge) + RO system (permeate is utilized as cooling tower makeup water) + Multi effect evaporator/incinerators. Primary treatment for High TDS Effluent treatment system + stripper to remove VOC + 3 stages Multi Effect Evaporator (forced circulation) Agitator Thin Film Drier (ATFD)+(MEE condensate is being taken along with Low TDS effluent for further treatment)+MEE/incineration.

6.Textiles

1.Ozonation + bio-oxidation + sand filtration + activated carbon adsorption + micro filtration + reverse osmosis (3 stage) + multiple effect evaporator

2.Chemical precipitation + bio-oxidation + chemical precipitation + sand filtration + Activated carbon adsorption + micron filtration + reverse osmosis (3 stages) + multiple effect evaporator

3.Chemical precipitation + bio-oxidation + sand filtration + dual media filtration + micron filtration + reverse osmosis (3 stages) + multiple effect evaporators.

7.Refinerries

Primary treatment, secondary treatment and tertiary treatment. Reverse Osmosis mainly used for the tertiary treatment and permeate is utilized and rejects are discharged into cooling tower.

8.Fertilizer

Chemical treatment+ Reverse Osmosis (Rejects as filler material and permeate in the process)

9.Dye & Dye intermediates

Chemical Treatment + MEE

CONCLUSION

ZLD treatment process can adopted as advanced waste water treatment constituents to by-products that are more readily biodegradable and reducing overall toxicity , pH , COD , TDS , SS , BOD parameters effectively than the convectional processes. ZLD is very effective method in the removal of

many hazardous organic pollutants from wastewaters. ZLD for pharmaceutical industrial waste water treatment which consists of Pretreatment, Anaerobic treatment (UASB), Secondary Aeration System, Filtration System and Sludge Dewatering System has different process units like Screening, Coagulation, Filtration, UASB, UF, RO, MEE etc.

FUTURE SCOPE AND BENEFITS

- ZLD can be adopted to treatment of waste water.
- ZLD can be used as an additional treatment to treat waste water.
- ZLD process can make waste water for reusable.
- This treatment process can treat any type of industrial waste water so have wide scope to treat different types of industrial waste water .
- ZLD capable to make recyclable any type of waste water can avoid the shortage of waste water and Recover around 95% of your liquid waste for reuse. BENEFITS

1. Water Conservation

2.ZLD systems employ the most advanced wastewater treatment technologies to purify and recycle virtually all of the wastewater produced.

3.Reduces the wastewater discharge i.e. reduces water pollution

4.Preferred option for industry where disposal of effluent is major bottleneck

5.Prevents exploitation of hydraulic capacity of disposal system

6.Separation of salts / residual solvents improve efficiency of ETP and CETP

7.Separated solids valuable by-product which helps in reducing the payback period

8.Mixed solvent separated in stripper can be reused or used as Co-processing

9.Ease in getting environmental permissions

10.More focus on production/ business rather than tracking after regulatory authorities

11.Reduction in water demand from the Industry frees up water for Agriculture and Domestic demands.

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Nomenclature

ATFD - Agitated Thin Film Drier BOD - Biological Oxygen Demand LCS - Low concentrated Sludge MBR - Membrane Bio-Reactor

MEE - Multiple Effective Evaporator NTU - Nephelometric Turbidity Units SBR - Sequential Batch Reactor) TDS - Total Dissolved Solids),

TSS - Total Suspended Solids), TSS - Total Suspended Solid TOC – Total Organic Carbon ZLD - Zero liquid discharge