Studies on Zero Liquid Discharge (ZLD) plant in API Manufacturing Unit

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ABSTRACT
The concerns over the environmental impact of water pollution has increased, and also ground water resources are gradually being depleted. In the current situation, it is required to recycle the wastewater generated from industrial outlets. On other hand, environmental authorities are being directed to establish “Zero Liquid Discharge (ZLD) plants” in all industrial sectors. A study was conducted in a medium scale API (Active Pharmaceutical Ingredients) manufacturing industry where wastewater recycling through ZLD plant. The investigation shown that the plant was generated high quality water which was suitable to recycle plant premises and which resulted in reduction of water consumption to 40 KLD (Kilo Liter per Day). Total source of effluents generated in operations were categorized to HCS (High Concentration Streams) and LCS (Low Concentration Streams). HCS are treated in LCS effluent treatment unit and LCS in LCS effluent treatment unit. The HCS effluent treatment unit made of a Solvent stripper, MEE (Multiple Effective Evaporator) and ATFD (Agitated Thin Film Drier), and LCS effluent treatment unit made of a SBR (Sequential Batch Reactor) and MBR (Membrane Bio- Reactor). The other unit which is called as water recycling unit consisting RO (Reverse Osmosis) plant and P. RO (Polishing RO) 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 Solids) to 99.2, 100, 100 and 99.9 percent respectively.

Key words
ZLD, Re-cycle, API wastewater, MEE, Stripper, SBR, MBR, RO

1. INTRODUCTION
Industrialization needs to improve the country economy. Increase of industrial treated has raised water consumption, and which leads to depletion of water resource. In other hand, water pollution is a keeping mankind in worry [1]. People have long been trying to find cost effective and reliable ways to treat wastewater and recycle of wastewater has become an absolute necessity[2].

There is an increased awareness among the general public on environmental pollution aspects and consequently environmental regulations have become very stringent. Rapid advances made in the wastewater treatment technologies during the past one decade, particularly in the bulk drug sector. Now it is possible to reduce water consumption and wastewater generation considerably and even achieve the Zero discharge levels[3, 4, 5].

India in the forefront of manufacturing APIs in the world. The primary character of API/Bulk drug manufacturing industry is to produce substances that have therapeutic value of Human and animals. Pharmaceuticals are an impartant part in maintaining human health. But compounds in pharmaceuticals with therapeutic benefits for human at right dose can be pollutants in the environment[6, 7].

Active Pharmaceutical Ingredients (API) manufacturing is a complex blend of operations. In general, wastewater management is one of the critical areas and of major concern in this sector industry. There are number of streams with different characteristics which originate from various sections of the industry, requiring segregation and corresponding treatment [8, 9].

Major industrial establishments in the region have established in-house wastewater treatment facilities. Small and medium scale industries might need to send the wastewater to common treatment facilities or to be recycle within the premises through ZLD (Zero Liquid Discharge) plant. As per local and national regulations, it is mandatory to establish ZLD plant, and treated water should be recycled within the premises [10].

An assessment was made to evaluate the ZLD plant performance in a medium scale API manufacturing industry, where variety of effluents generated, treated through ZLD plant and recycled within the plant premises.

2. MATERIALS AND METHODS

2.1 Source of wastewater
The source of wastewater used in the pilot plant studies generated from various source of API manufacturing unit, which include process outlets, process equipment washings, process area floor washings, utilities wastewater (i.e., cooling tower blow downs, boiler blow downs and utilities washings), effluent treatment plant washings, etc.

2.2 Segregation of wastewater
Total effluents were broadly segregated to High Concentration Streams (HCS) and Low Concentration Streams (LCS), which was based on COD (Chemical Oxygen Demand) and TDS (Total Dissolved Solids). If a wastewater stream characteristics, i.e., COD >15000 mg/l and TDS >8000 mg/l, segregated to HCS. If both the above said parameters were within the below levels (i.e., COD <15000 mg/l and TDS <8000 mg/l), the wastewater streams falls under LCS. If anyone characteristics of wastewater crosses their limits to HCS (i.e., >15000 COD or >8000 TDS), those are also segregated as HCS.

2.3 Characterization of wastewater
Wastewater characterized by approved methods (i.e., pH by pH Electrode, COD by HACH COD track, BOD by HACH BOD track, TSS by Gravimatory, Millipore, and TDS by Gravimatory, watt man). Characteristics of wastewater in various stages has been characterized and tabulated in table 1.
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Table 1: Characteristics of wastewater.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameter</th>
<th>Unit</th>
<th>HTDS Effluents from Process/Stripper</th>
<th>LTDS Effluents from Process &amp; Utilities</th>
<th>Stripper Outlet/MEE Feed</th>
<th>MEE Condensate</th>
<th>ATFD Feed/MEE Concentrate</th>
<th>ATFD Condensate</th>
<th>SBR Outlet/MBR Feed</th>
<th>MBR Outlet/RO Feed</th>
<th>RO Permeate</th>
<th>Polishing RO Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td></td>
<td>7.75</td>
<td>7.91</td>
<td>6.58</td>
<td>8.52</td>
<td>5.92</td>
<td>8.13</td>
<td>7.96</td>
<td>6.68</td>
<td>6.91</td>
<td>6.84</td>
</tr>
<tr>
<td>2</td>
<td>COD</td>
<td>mg/l</td>
<td>54105</td>
<td>7712</td>
<td>33148</td>
<td>8951</td>
<td>83216</td>
<td>11520.7</td>
<td>2318</td>
<td>658</td>
<td>71</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>BOD</td>
<td>mg/l</td>
<td>15846</td>
<td>3103</td>
<td>10206</td>
<td>3128</td>
<td>---</td>
<td>2751</td>
<td>652</td>
<td>128</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>TSS</td>
<td>mg/l</td>
<td>114</td>
<td>1862</td>
<td>263</td>
<td>24</td>
<td>---</td>
<td>127</td>
<td>364</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>5</td>
<td>TDS</td>
<td>mg/l</td>
<td>42202</td>
<td>7703</td>
<td>43814</td>
<td>1981</td>
<td>140683</td>
<td>1510</td>
<td>3372</td>
<td>3235</td>
<td>324</td>
<td>32</td>
</tr>
</tbody>
</table>

2.4 Structure of ZLD plant

As shown in figure 1, in API manufacturing site, ZLD plant consists three units, such as: (i) HCS treatment unit (ii) LCS treatment unit and (iii) Effluents recycling unit. The HCS treatment unit consists a solvent stripper, followed by a MEE (Multiple Effective Evaporator) and an ATFD (Agitated Thin Film Drier). The LCS unit comprises a wastewater equalization system, followed by a biological system Sequential Batch Reactor (SBR) and a Membrane Bioreactor (MBR). The third unit wasa wastewater recycling unit where semipermeable (Reverse Osmosis) membranes used to filter the wastewater to recyle.

2.5 Wastewater flow and treatment in experimental ZLD

Effluents generated from various sources has been collected in HCS and LCS collection tanks. Wastewater collected in HCS collection tanks were fed to Solvent stripper, where mixedsolvents werestripped and collected in top distillate collection tank. Stripper processed effluent collected from stripper column bottom fed to MEE, where maximum liquid extracted and condensate collected to condensate collection tank. The concentrate collected form MEEled to ATFD, and condensate generated during ATFD operations were collected to condensate collection tank and salts generated wasdisposed to TSDF (Transport Storage Disposal Facility). The condensates from condensate collection tanks were transferred to Low concentration wastewater collection tanks for further treatment.
Effluents collected in Low concentration streams collection tanks were fed to Equalization cum neutralization system where all effluents were equalized to unified and neutralized to required pH (6.5 to 8.5). After neutralization and equalization process, effluents fed to SBR which is a fill and draw activated sludge process and where microbial cells reduces the Organic load. SBR processed wastewater was passed through Decant tank followed by Lamella clarifier to remove settleable solids. The overflow of Lamella clarifier was fed to MBR system which removes suspended solids to zero in permeate. The tanks and setters bottom drains were collected in sludge collection tank and which was fed to sludge decanting system. The sludge generated during this process was disposed to TSDF.

The permeate collected from MBR system fed to RO system which filters the wastewater through semipermeable membrane. The permeate generated from RO system fed to Polishing RO, where wastewater polished to portable water quality. Polished water was recycled to Utilities for use and rejects generated in the process was sent to MEE for treatment.

Effluent flow quantity was followed as per system design. The entire system and individual units performance was investigated with the help of physical, chemical and biological parameters in various intervals (i.e., end of the day 1, 2, 3, 4, 5… and 30). Values were considered after stabilizing the system.

3. RESULTS AND DISCUSSION

3.1 Effluent Characteristics and Hydraulic Loads

Characteristics of effluents in various stages of pilot plant operations are presented in table 1. Loads of raw effluents fed to the system was within the designed specifications. Hydraulic loads fed to the various system were presented in figure 1. For ease of discussion, henceforth, loads of all parameters, viz., COD, BOD, TDS and TSS are presented in terms of kilograms per day (KPD) based on average volumes of fed to individual systems.

3.2 Performance of HCS treatment unit

As shown in fig.1 and 2, a huge reduction in loads were achieved in HCS treatment system. 890 KPD of COD reduced in stripper alone out of 2184.8 KPD, also in MEE system, it was 966.2 KPD out of 1294.8. As shown in fig. 2, a significant quantity of TDS was reduced in MEE (i.e., 1629.6 KPD, out of 1705.1 KPD). The BOD also reduced in the quantity of244 and 281.2 KPD (out of 640.4 KPD) in Stripper and MEE respectively. However there is an increase of TSS in stripper outlet. It was due to formation of precipitates during initial heating process of effluents [11].

3.3 Performance of LCS treatment unit

The LCS system consists SBR and MBR, where biological operations are made possible to oxidize Organic matter and remaining organic matter removed through MBR respectively. As sown in fig. 1 and 2, there was a reduction of 168.7 KPD of BOD in SBR, where it was 33.7 KPD in MBR. The total BOD quantity reduced to 8.2 KPD from 210.6 KPD in LCS treatment system. SBR is an activated sludge process for treatment of wastewater where separate tanks are not required for aeration and sedimentation. This type of systems are typically suitable for small scale processes [12]. In the present investigation, TSS quantity was reduced to “ZERO” after LCS treatment unit, where 78 and 23.4 KPD of TSS reduced in SBR and MBR systems correspondingly. Pharmaceutical wastewater treatment with a pilot-scale plant was studied by a membrane bioreactor (MBR) process in southern Taiwan, the investigation reported that there is no suspended solids in outlet of MBR [13, 14]. However, there was no much significant reduction in TDS as LCS treatments unit was not designed for reduction of TDS loads. Although in the present investigation, the designed LCS treatment unit made comfort to effluent recycle unit. In similar, a laboratory study conducted with MBR system in China with wool mill wastewater shown excellent effluent quality which was useful for recycle [15]. An investigation made with MBR post treatment of secondary wastewater contains 80% textile and 20% of municipal wastewater to recycle treated wastewater in industrial premises after RO polishing of MBR outlets [16].

3.4 Performance of Effluents recycling unit

The quantity of TDS present in LCS treatment unit outlet was reduced to 1.3 KPD after polishing RO treatment with quality of 32 ppm (fig. 1 and table. 1). The total quantity of TDS fed to the primary RO system was 207.8 KPD and it was reduced to 15.0 KPD in permeate. As revealed in table 1, the recycle water generated after polishing RO contained COD of 35 ppm and TDS of 32 ppm, and other parameters (BOD and TSS) were “ZERO ppm” in quality. The effluent recycling unit was in key role of making effluents to portable quality. However the pressure driven RO system cannot be used to feed raw water as it was designed for tertiary treatment of effluents to generate recycle water [17, 18, 19].

4. CONCLUSION

The system designed for recycle of effluents has shown marvel outcome in generation of high quality permeate. The overall loads reduction was 99.2 percent in TDS, 99.9 percent in COD and 100 percent in both the TSS and BOD (figure 3). The studies 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.
REFERENCE


