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ENVIRONMENTAL WASTE MANAGEMENT: A CASE STUDY OF REFINERY

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ABSTRACT

The monitoring and performance evaluation studies were carried out for an effluent treatment plant of a refinery located in the western region of India. The samples from the inlet and outlet locations of ETP were collected at regular intervals and were analyzed for different parameters. The pH, oil & grease, BOD, COD, suspended solids were found to be reduced significantly, where as the pH of the raw as well as the treated effluent remain almost the same. The generated data presented the evidence that the plant is working with the norms specified by the pollution control board and hence meeting the discharge standard line.

INTRODUCTION

An oil refinery or petroleum refinery is an industrial process plant where crude oil is processed and refined into more useful petroleum products, such as gasoline, diesel fuel, asphalt base, heating oil, kerosene, and liquefied petroleum gas.[Gary et al., 1984, Leffler, 1985] The first oil refineries in the world were built by Ignacy Lukasiewicz near Jaslo, Austrian Empire (now in Poland) from 1854 to 1856,(Frank, 2005) but they were initially small as there was no real demand for refined fuel. Petroleum products are usually grouped into three categories: light distillates (LPG, gasoline, naphtha), middle distillates (kerosene, diesel), heavy distillates and residuum (heavy fuel oil, lubricating oils, wax, asphalt). This classification is based on the way crude oil is distilled and separated into fractions (called distillates and residuum) as in the above drawing (Leffler, 1985). Waste waters from petroleum refining consist of cooling water, process water, storm water, and sanitary sewage water. A large portion of water used in petroleum refining is used for cooling which is recycled over and over. It typically does not come into direct contact with process oil streams and therefore contains less contaminant than process wastewater. However, it may contain some oil contamination due to leaks in the process equipment. Water used in processing operations accounts for a significant portion of the total wastewater. Process wastewater arises from desalting crude oil, steam stripping operations; pump gland cooling, product fractionators reflux drum drains and boiler blowdown (Ravenswaay, 1995). Petroleum waste management has been of much concern in recent years since pollution from petroleum industries may lead to a variety of impacts, risks, and liabilities environmental systems. (Huang *et al.*1999). The process-intensive petrochemical industry has demanding environmental management challenges to protect water, soil and atmosphere of the refinery pollution. Oils either used in food processing or those resulted from petrochemical and petroleum

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refining industries considered as serious types of hazardous pollutants find their way into aquatic environments where, they completely damage the ecology of the beach areas in addition to their high toxicity on aquatic organisms (Mendiola, *et al*. 1998). Microorganisms for treatment and bioremediation purposes affords a very efficient tool for purifying contaminated effluents and natural water (Gloges, *et al*. 1995). Physicochemical parameters were determined in order to characterize the industrial effluent. These parameters included temperature, pH, total dissolved solids (TDS), total suspended solid (TSS), total solid (TS), Biochemical oxygen demand (BOD_3), chemical oxygen demand (COD). Characterization of the industrial effluent was carried out before and after the treatment to determine the efficiency of the treatment. To clean up petroleum contaminated sites, many remediation activities were undertaken in the past decades. However, the costs for cleaning up waste on site were enormous (Cohen and Mercer, 1993; Wang and McTernan, 2002). The water used and wastewater generation in the oil refineries in the country are noted to be greatly influenced by the type of cooling system and recirculation cooling water system adopted. Refineries having once through cooling system due to an enormous amount of water used because easy availability of sea water, a huge amount of valuable hydrocarbon is lost along with the wastewater. Pollutants in the wastewater depend on the amounts of steam, process water and cooling water used in a refinery. Wastewater collection and treating systems consist of API separators, dissolved air flotation (DAF) units and of further treatment (such as an activated sludge biotreater) are required to make such water suitable for reuse or for disposal (Beychok, 1967). The refinery under consideration is situated in western India and is one of the largest & energy efficient one. Its facilities include five Atmospheric Crude Distillation Units (ADU). The major secondary units include CRU, FCCU and the first Hydrocracking unit of the country. The total effluent so generated from these processing, amounting to 5000 m^3/d approximately is received and after treatment it is disposed to river body. In view of the above, monitoring and performance evaluation studies were carried out for an effluent treatment plant of a refinery.

MATERIALS AND METHODS

The sample was collected with utmost care to ensure that no contamination occurs at the time of collection of prior to examination. The sample were collected from the inlet and outlet of effluent treatment plant and brought to the laboratory for the analysis of different environmental parameters. The samples were analyzed using the standard methods for the examination of water and wastewater. [Clisceral. et al 1998]

Description of Effluent Treatment Plant

The Effluent Treatment Plant (ETP) had been constructed in 1997 for 5000 m3/d capacity. Presently 3850 m^3/d effluent is received. The waste generates includes formation water from HP, MP, LP (High, Medium and Low pressure) separators, in CSU (Crude stabilization Units) other processes drains, crude tank bottom drains floor wash, cooling tower blow down, floor washing and filters backwashing. After proper treatment at ETP and meeting Pollution Control Board (PCB) norms, the wastewater was disposed off into river body. The treatment is mainly for reduction of free and emulsified oil, total suspended solids (TSS), bio-chemical oxygen demand (BOD5) and chemical oxygen demand (COD).

Table1. Summarization of different kinds of wastes generated by petroleum refineries: (WB, 1996)

Pollution	Approximate quantities
Cooling systems	3.5-5 m3 of wastewater generated per ton of crude.
Polluted wastewater	BOD : 150-250 mg/L, COD : 300-600 mg/L, Phenol : 20-200 mg/L, Oil : 100-300 mg/L (desalter water), Oil 5000 mg/L in tank bottom, Benzene 1-100 mg/L, Heavy metals 0.1- 100 mg/L.
Solid waste and sludge	3 to 5 kg per ton of crude (80 % should be considered as hazardous waste because of the heavy metals and toxic organic presence).
VOC emissions	0.5 to 6 kg/ton of crude.
Other Emissions	BTX (Benzene, Toluene and Xylene) 0.75 to 6 g/ton of crude Sulfur oxides 0.2-0.6 kg/ton of crude, Nitrogen oxides 0.006-0.5 kg/ton of crude.

Note: All the figures depend on the process configuration but a general guide is provided.

WASTEWATER GENERATION

Hydraulic Flows to ETP

The existing Effluent Treatment Plant receives the following flow rates from different sources;

Formation Waters

- From CSU@ 170m3/h (4080m^3/d)
- From Metering Station@ 10m3/h (240m^3/d)
- Total Formation Water Flow rates 180 m^3/h (4320 m^3/d)
- Blow down for Cooling towers (CTBD) is [960m^3/d].

WASTEWATER TREATMENT UNIT OPERATION AND PROCESSES

The comprehensive treatment scheme is shown and further different units for ETP are shown in Fig1. Each treatment unit operation and process is described in Table 3.

1. BULK OIL REMOVAL

Raw Effluent Wash Sump

The formation water from various process sources is received in raw effluent wash sump. It acts as bulk oil removal facility. A constant level is being maintained in the tank. Oil collecting trough is provided with V notches along the circumference of the sump, for the collection of floating oil. The effluent from the bottom of the tank is taken to Raw Effluent Transfer Sump under gravity.

Raw Effluent Transfer Sump (RETS)

It is an open RCC (Reinforced Concrete Cement) sump with 2 compartments (1 working + 1 standby) each having a liquid storage capacity of 185m^3. It is provided with a common pumping chamber. These pumps discharge the effluent either to the Equalization Tank or to the Raw Effluent Wash Tank.

Raw Effluent Wash Tank (REWT) : It is a Carbon steel tank which also acts as a bulk oil removal facility with constant level. The effluent is taken from the bottom of the tank to the equalization tank by gravity.

Equalization Tank : The purpose of Equalization tank is to maintain constant flow and hydraulic load. The effluent from raw effluent transfer sump or raw effluent wash tank is received in the equalization tank.

Table 2. Wastewater generation sources and type of impurities

Sources	Pollutants	Processing unit
Crude Oil Storage tank & Crude Stabilization Unit	Turbidity, Suspended and Dissolved Solids, Oil & Grease, Chlorides, Phenolic compound etc.	Drained off to inlet of ETP
Cooling tower	Heavy metals (Fe, Zn, Ld, Cu) Filter feed sump and	Drained off to inlet of treated through filters
Filter backwashing	Suspended solids, turbidity and heavy metals	Drained off to Raw Effluent Transfer Sump
Floor washing	Miscellaneous impurities	Drained off to inlet of ETP

Table 3. Technical details of treatment plant at refinery

Unit	Number	Area/Size	Effective volume m^3	Flow (m^3/hr)
Raw effluent wash sump	1	13m ϕ x 3.2m LD+1.0m free board	424	-
Raw effluent transfer sump	1	11.75m x 5m x 3.15m LD	185	-
Raw effluent wash tank	1	16m ϕ x 10 m LD	2010	-
Equalization tank	1	14m ϕ x 10.25m (total height)	1578	-
Dissolved air flotation tank	2	4.2m x 4.2 m x 3m LD	53	105
Equalization/ neutralization Tank	1	3m x 3m x 2m LD	18	210
Bio tower	1	21m ϕ x 14m (total height)	4850	60– 525
Intermediate clarifier	1	25m ϕ x 2m SWD	982	525
Aeration tank	1	31m x 31m x 3.5mLD	-	210
Final clarifier	1	16m ϕ x 3m SWD	603	210
Pressure sand filters	3	3.4 m ϕ x 1.9m total height	18	250
Granular activated carbon filters	3 (2+1)	3.5m ϕ x 2.8m height	27	250

It is provided with floating oil skimmer, having four funnels separated at an angle of 90° by each other. The flow from the equalization tank is routed under gravity to Tilted Plate Interceptor (TPI), for primary oil separation.

Primary Oil Separation : The free oil is removed in tilted plate interceptor (provided with a static mixture) which is arranged for on line dosing of 20% caustic solution to maintain the pH. This enables the formation of complexes of sulphide as Na_2S for sulphide precipitation. Each channel of TPI consists of three bays. The free oil with particle size greater than 50 micron is removed. The separator unit is provided with live steam separating arrangement to keep the separated oil in flowing condition. The oil removed at TPI is taken to wet slop oil sump by gravity. The settled sludge at the bottom of the TPI is removed intermittently by gravity to oil and chemical sludge sump.

Secondary Oil Separation : The secondary oils are separated by coagulation followed by flocculation process. In this scheme the solution of coagulant (NaOH and $FeCl_3$) is mixed thoroughly with in the wastewater, by means of a flash mixer.

Flash Mixture : The effluent from TPI (containing traces of free oil and bulk of emulsified oil and sulphides) is routed under gravity to flash mixing tank (provided with an agitator). In this tank the effluent is mixed with caustic solution to maintain the pH range around 10.5, along with the addition of $FeCl_3$ solution, which reacts with Na_2S to form precipitates of FeS, Sulphur and $Fe(OH)_3$. Deoiling polyelectrolyte (DOPE) solution is dosed at the outlet of flash mixing tank to enhance the agglomeration of emulsified oil. The effluent from flash mixing tank is taken to the flocculation tank.

Dissolved Air Flotation Tank : The flocculated effluent overflows to the tilted plate flotation tank (TPF). The emulsified oil particles along with precipitate of FeS, Sulphur and $Fe(OH)_3$ rise to the top of the flotation tank (due to the action of air bubbles), which are skimmed off by skimmer. This top scum is taken by gravity either to wet slope oil sump or chemical and oily sludge sump.

Neutralization Tank : NaOH solution is used to increase the pH while dilute H_2SO_4 is used to decrease it. It is an RCC tank and provided with pH adjustment arrangement mixer. Dilute H_2SO_4 is dosed to bring down the pH of the effluent around 7.0. The neutralized effluent is taken to bio-tower feed sump under gravity.

2. BIOLOGICAL TREATMENT

The main objective of biological treatment is to remove/reduce the concentration of colloidal and dissolved organic matter in the effluent (expressed as BOD and COD).The complete biological treatment of effluent is achieved in two stages. The first stage consists of a bio-tower and its intermediate clarifier. The second stage is an activated sludge system comprising of aeration tank, final clarifier and bio-sludge re-cycle arrangement.

Bio-Tower : The bio-tower is a vertical RCC tank packed with random type plastic (Polypropylene) media. The purpose is removal of high concentration of BOD, phenolic compounds and other toxic materials. The neutralized effluent from pH adjustment tank is received in the bio-tower feed sump, from where it is pumped to the bio-tower. The combined effluent under pumping is uniformly distributed from the top of the tower by a hydraulic distributor with flow distribution arms. The effluent passes over the plastic media and the dissolved organics are oxidized by the micro-organisms present as a bio-film on the surface of the plastic media. The nutrients (DAP and Urea) in the form of solution are added for efficient growth of biomass. The air requirement is supplied by forced draft air blowers/ fans fitted (04) directly to the base of the tower below the media. The biomass slime is sloughed off regularly along with the effluent. The treated effluent from the media is collected in central collection channel and taken to intermediate clarifier to remove sloughed biomass by gravity.

Intermediate clarifier : The effluent is fed to the clarifier from the bottom. It is RCC construction, provided with rotating scraper with scum skimmer at the top. The clarified effluent overflows through V- notch weirs in to circumferential launder and taken to splitter box. The biomass settled at the clarifier bottom along with the scum skimmed at the top, is removed intermittently to bio tower sludge sump, by gravity.

Aeration Tank : The purpose of this unit is to remove the biodegradable matter from wastewater. In this unit the waste is oxidized by the bacteria in the presence of O_2. The oxygen is supply with help of aerators. This is an RCC tank divided in two compartments of equal capacity each being provided with fixed type aerators. The effluent undergoes aeration

under extended aeration mode of the activated sludge process. The biomass developed in this tank acts on the bio-degradable organics and oxidize them to simpler products (CO_2 and H_2O) to obtain energy for cell multiplication, growth and maintenance. The soluble BOD is converted into solid biomass i.e. mixed liquor volatile suspended solids-MLVSS. The air required for the biomass is supplied by the surface aerators. Nutrients required for the biomass (Urea and DAP solutions) are added at the inlet of the aeration tank. The aerated effluent with MLSS is taken to the final clarifier by gravity.

Final clarifier : The MLSS settled in this unit is removed by the central driven rotating scraper mechanism with scum skimmer at the top. The clarified effluent overflows through V-notch weirs into circumferential launder and taken to the filter feed sump. The biosludge removed from the clarifier bottom and the scum skimmed from the top are removed to aerated biosludge sump.

3. POLISHING TREATMENT

The effluent after two stages biological treatment needs polishing for reduction of chemical oxygen demand (COD) and total suspended solids (TSS). Further, clean stream with respect to all parameters except TSS needs treatment for reduction of TSS. Hence, both the streams are mixed and the combined stream undergoes the tertiary treatment, comprising pressure sand filters and granular activated carbon (GAC) filters.

Pressure sand filters and Granular Activated Carbon Filters : Pressure sand filters are used for removal of turbidity and color. The filter media is sand with gravel support layer. Each filter is backwashed with treated water from backwash pumps as per schedule. The dirty backwash water is discharged to OWS (oily water sewer) and taken back to raw effluent transfer sump (RETS) for treatment, along with the raw effluent. The filtered effluent is taken to activated carbon filters which are used for the removal of remaining COD and extract of heavy metals. Final polishing in terms of COD removal is achieved at these filters. The filtered effluent is led to the treated effluent tank. The backwashing of these filters are done utilizing the backwash pump and air scour blowers.

Wet slop oil sump : The wet slop oil sump is divided into two compartments of equal capacity with a common pumping chamber. Live steam sparging arrangement is provided for heating the oil. The wet slop oil is pumped to slop oil tanks. The separated water is drained from the bottom and then relatively dry oil free from water is pumped to intermediate crude storage tank.

4. SLUDGE COLLECTION AND DISPOSAL

Different units for sludge handling system are shown

Sludge Thickener

Oil chemical sludge
: 70 m^3/d
Oily and chemical sludge quantity : 1350 kg/d
Size of the thickener :
8.75 m ϕ x
3 m SWD

The oily and chemical sludge, the bio-tower sludge and excess sludge from extended aeration system are received at this thickener. It is provided with picket and fence type sludge scraping mechanism. The supernatant is returned back to raw effluent transfer sump through Oily Water Sewer (OWS). The thickened sludge is taken from the bottom of the thickened sludge sump for its dewatering.

Dewatering Centrifuge

No. of centrifuge	:	06
Sludge flow (Max)	:	60 m^3/d
Capacity of centrifuge	:	10 m^3/h
Size of centrifuge	:	6m x 4m

The thickened sludge having a consistency of 3-5 % solids (dry weight) is dewatered in the centrifuge. A dry cake with solid content of 30% (by weight) is achieved at the outlet of the centrifuge with the dewatering polyelectrolyte dosing. The concentrate from centrifuge is recycled back to raw effluent transfer sump and the sludge cake is collected in a trolley, which can be directly connected to a truck. The dewatered cake is stored in lagoons, which is disposed off as per the guidelines of GPCB.

SOLID WASTE MANAGEMENT

The refinery unavoidably generates enormous quantity of tank bottom oily sludge as well as oil contaminated soil waste which constitutes a major challenge for hazardous waste management as well as environment management. Oil sludge is removed from the crude oil tanks while cleansing as well as is generated in ETP during various stages of treatment uses specialized bacteria known as Oilzapper which, transforms harmful substances to non-toxic components. One of the technologies is "Bioremediation" of crude oil/oily sludge which is an eco-friendly and cost effective technique. Biotechnology approach is for disposal of oily sludge/oil contaminated soil and wastewater effluent sludge.

Figures 7 to12 of bioremediation sites shows the bioremediation process at different time intervals.

Sludge analysis of TPH (Total petroleum hydrocarbon)

Quantity of Oily Sludge Bioremediated : 200 tones
Total time utilized for bioremediation : 5 months

TPH content of the oily sludge

Before bioremediation : 44.65%
After bioremediation : 0.67%
Biodegradation of oil : 98.5%

Table 4. Sludge characteristics before and after bioremediation process

Obser-vations	Sample depth	HCn content %	Moisture content %	Total inorganic content %
Initial	Surface	11.4	24.27	63.90
	Below 50 cm	2.93	27.83	69.24
Final	Surface	7.48	22.73	69.79
	Below 50 cm	1.22	27.90	70.80

RESULTS AND DISCUSSION

The results of treatment efficiency for the major pollutants in the treated and untreated waste water of the refinery are discussed below:

pH

Its value is an indication of the presence of acidic or basic chemicals in the wastewater and the extent of toxicity caused by them. As it can be seen from Fig. 2, pH is more or less invariable; however pH in the influent is slightly lower than the effluent stream. The maximum pH in the two streams is found to be 8.19 and 8.48 respectively. The minimum values for the same being 8.0 and 8.35 with an average of 8.08 and 8.41 respectively. This is due to the use of caustic solution (NaOH) in flash mixing tank. As per guidelines, the standard value ranges are from 6.5-8.5. Almost all the values are within the permissible limits.

Temperature

Temperature plays a vital role in the life and death

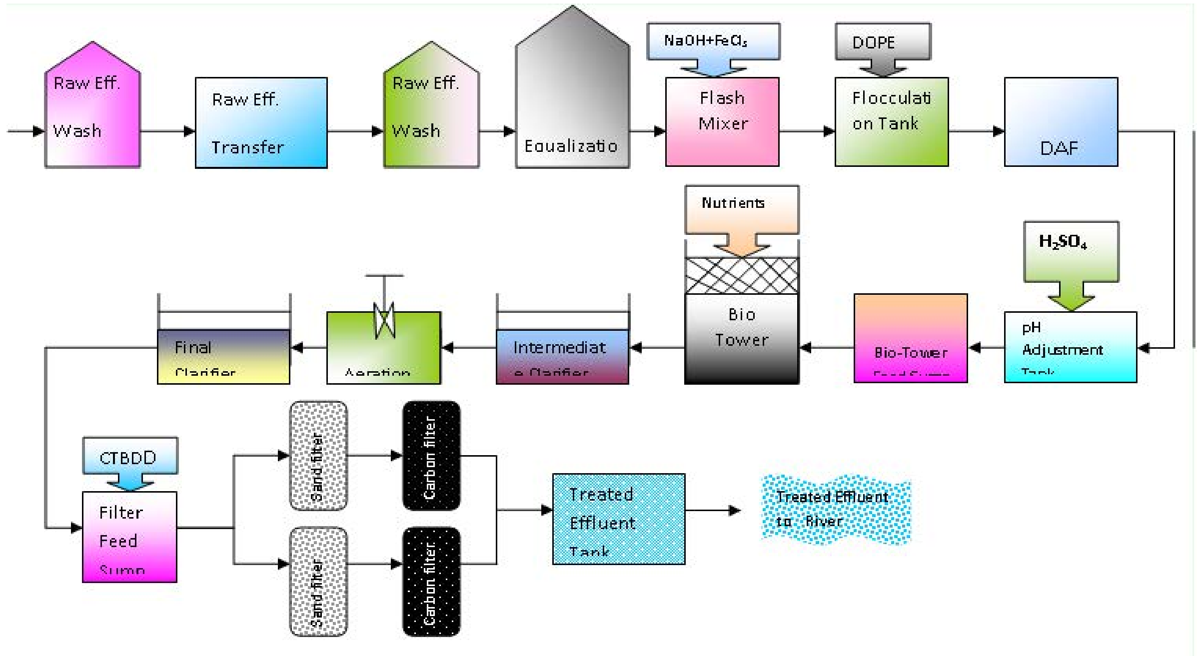

Fig. 1 Schematic diagram for treatment of ETP at refinery

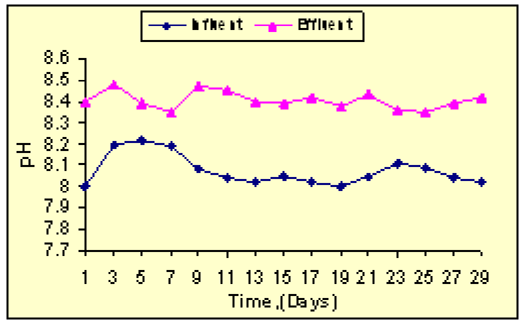

Fig 2. Variation of pH with time

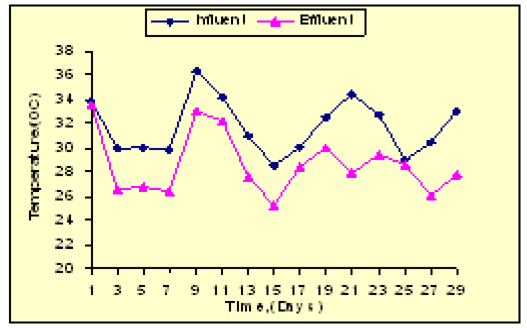

Fig 3. Variation of temperature with time with time

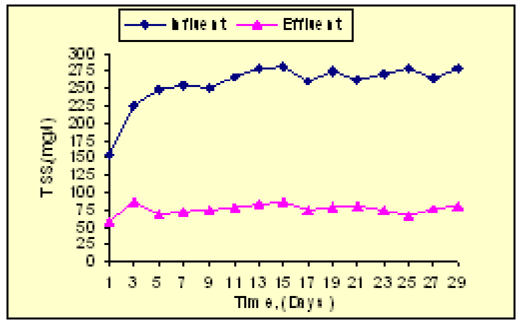

Fig 4. Variation of TSS with time

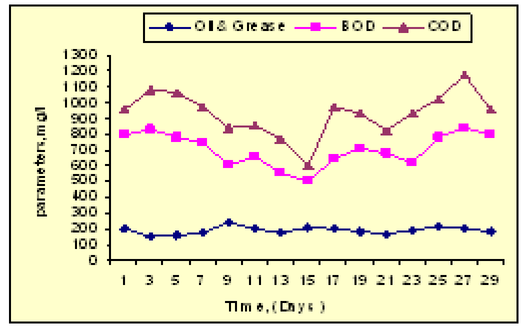

Fig 5. Variation of different parameters in influent

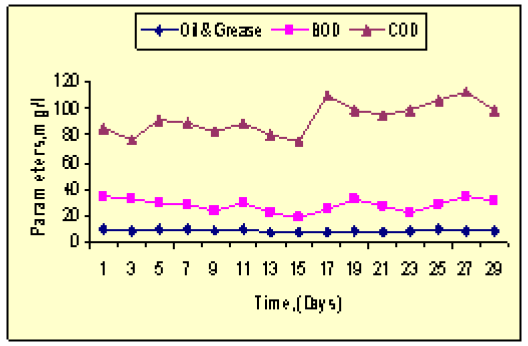

Fig. 6 Variation of different parameter in effluent

of bacteria. It has been observed that the rate of reaction for microorganisms increases with increasing temperature, for which the standard value is 40°C. It is evident from Fig 3, temperature range varied from 28.5 to 36.4°C in the influent whereas in the effluent it ranges from 25.2 -33.6°C.

Total Suspended Solids (TSS)

Its determination is used to control the biological solids in the activated sludge process and is a means to measure the effectiveness of the treatment units. The standard value for the discharge of TSS in the wastewater prescribed by the pollution control board is 100 mg/L. The results from the analysis and the graphical representation in Fig. 4, shows that the values obtained are within the permissible limits for the disposal onto the water bodies. The maximum and the minimum values at the inlet are 282 mg/L and 154 mg/L respectively and in the final treated effluent they are 86mg/L and 58mg/L respectively. The average TSS in the two streams is 257.1and 75.7mg/L respectively. A significant reduction is seen in TSS removal with an average reduction of 70.5%.

Biochemical Oxygen Demand (BOD)

This test gives a measure of the amount of biologically oxidizable organic matter present in wastewater. Fig. 5 & 6 shows the variation of influent and effluent values of BOD during the entire duration of monitoring. Inlet BOD varies from 500-840 mg/L whereas it ranges from 18 - 41 mg/L in the final treated effluent. The average BOD, at the two sampling points is 703.8mg/L and 28.5mg/L respectively. BOD is reduced to an average of about 96% in the final treated effluent. Results obtained from the analysis and graphical representation shows that the values obtained are more or less around the permissible limit i.e. 30mg/L as per CPCB, for the disposal of wastewater onto the water bodies.

SITE PHOTOGRAPHS FOR BIOREMEDIATION PROCESS AT REFINERY

Fig. 7 At Zero time

Fig. 8 Application of Oilzapper

Fig. 9 After four months

Fig.10 After six months

Fig. 11 Site after process completion.

Chemical Oxygen Demand (COD)

This test is helpful in indicating toxic conditions and the presence of biologically resistant organic substances. Fig. 5&6 shows the variation of influent and effluent values of COD during the entire duration of monitoring. It has been observed that the average value of COD in the samples collected from ETP inlet is 930.6mg/L whereas it is 92.8mg/l in the final treated effluent. The maximum and minimum COD in the influent are 1176 and 600mg/l respectively whereas they are 112 and 76 mg/L in the treated effluent. The average COD reduction is found to be 90%.

Oil and Grease

The oil and grease range varied from 110-220 mg/L. This is due to crude oil fractionation, reforming & catalytic cracking in oil manufacturing processing. As per permissible limits the standard value 10 mg/L. Fig. 5 and 6 shows the variation of oil and grease depicting a maximum of 240mg/L, a minimum of 162mg/L and an average of 190.7mg/l in the influent stream whereas in the effluent oil and grease varies from 7.0-9.8mg/L with an average of 8.6mg/L. From the results an average reduction of 95.5% is observed.

CONCLUSION

Based on the results and observations obtained during the study following conclusions have been achieved :

- On an average 3850m^3/ day of wastewater is received by the ETP and after treatment disposed to river.
- Influent to the treatment plant consists of loads with an average value of pH 8.1, temperature 31.7, BOD 703.9 mg/L, COD 930.6 mg/L, TSS 257.1 mg/L and oil & grease 190.7mg/L.
- After treatment, the pollutant load in the wastewater is reduced to an average value of 8.4 for pH, 28.7 for temperature, 8.8 mg/L for BOD, 184.3mg/L for COD, 75.7 mg/L for TSS and 8.6 mg/L for oil & grease.
- The plant is quite efficient in treating the wastewater of the refinery and obtaining an average reduction of 96% in BOD, 90% in COD, 70.5% in TSS and 95.5% in oil & grease.
- The total petroleum hydrocarbon (TPH) in oily sludge is normally reduced more than 80% during bioremediation.
- All the parameters are within the permissible limits and disposal parameters are successfully meeting the prescribed discharge norms stipulated by the regulatory authorities.

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