

**PERFORMANCE AND WASTEWATER QUALITY  
ASSESSMENT OF EFFLUENT TREATMENT PLANT OF  
ATTOCK REFINERY LIMITED, RAWALPINDI**



**By**

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A thesis submitted to Bahria University, Islamabad in partial fulfillment  
of the requirement for the degree of MS in Environmental Sciences

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**2019**

## **CERTIFICATE OF ORIGINALITY**

This is to certify that the intellectual contents of the thesis

### **PERFORMANCE AND WASTEWATER QUALITY ASSESSMENT OF EFFLUENT TREATMENT PLANT OF ATTOCK REFINERY LIMITED, RAWALPINDI**

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## **ABSTRACT**

The current study has been carried out to apprise the water footprint in terms of water consumption and effluent generation and to assess the performance efficiency of an effluent treatment plant (ETP) at Attock Refinery Limited. The samples were analyzed for wastewater quality parameters from raw and effluent (treated) stream, characterized their concentration load and compared with Punjab Environmental Quality Standards (PEQS) and International Finance Corporation (IFC), World Bank guidelines. Current treatment train mainly consists of API separators, DAF and activated sludge process. Grab samples were collected from DAF-inlet and final effluent outfall and tested for physico-chemical and heavy metals using instrumental methods and atomic absorption spectrometer. The parameters analyzed for the wastewater quality assessment were pH, Temperature, TSS, TDS, BOD<sub>5</sub>, COD, O&G, Phenols, TN, TP, Free Cyanide, As, Hg, Fe, V, Pb, Ni, Cr and Cu. The results indicated that the treatment plant was effective in reduction of some parameters like TDS, TSS, As and Fe while concentration for Phenols, O&G, BOD<sub>5</sub>, and COD were above the permissible limits of both EPA and IFC, World Bank. Hg, Cu and free cyanide were detected in one effluent sample each whereas V, Pb, Ni, and Cr were undetected throughout the sampling campaign. Efficacy or performance of treatment system was determined based on pollutant reduction to acceptable discharge limits while Pearson's coefficient determined the correlation among various parameters. The study concluded that some pollutant parameters are being discharged in the Soan water body very close or in excess to the prescribed limits and an optimization of the treatment system is required by installing advanced (tertiary) treatment units.

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## **ABBREVIATIONS**

PRE:	Petroleum Refinery Effluents
ETP:	Effluent Treatment Plant
NEP:	National Environmental Policy
PEPC:	Pakistan Environmental Protection Council
PEPA:	Punjab Environmental Protection Act
SMART:	Self-Monitoring & Reporting Rules
PEQS:	Punjab Environmental Quality Standards
IFC:	International Finance Corporation
API:	American Petroleum Institute
TSS:	Total Suspended Solids
TDS:	Total Dissolved Solids
TN:	Total Nitrogen
TP:	Total Phosphorus
mbpd:	Million barrels per day
MAF:	Million Acre Foot
GDP:	Gross Domestic Product
SDGs:	Sustainable Development Goals
PAHs:	Polycyclic Aromatic Hydrocarbons
PCBs:	Polychlorinated Biphenyls
DAF:	Dissolved Air Flotation
ASP:	Activated Sludge Process
GPM:	Gallons per Minute

RAS:	Return Activated Sludge
O&G:	Oil and Grease
BOD5:	Biochemical Oxygen Demand
COD:	Chemical Oxygen Demand
VSS	Volatile Suspended Solids
TPH	Total Petroleum Hydrocarbons
PEMEX	Petroleos Mexicanos

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## CHAPTER 1

### INTRODUCTION

#### 1.1 State of water

Water, air and soil are essentials of life and are precious resources of planet earth. In the past all living organisms including human beings, animals and plants enjoyed pure, clean water and pollution-free air, but industrial revolution during 19th century and its intensification, increasingly caused air, water and land pollution. Environmental pollution has already touched the heights that it threatens and jeopardizes the wellbeing of human beings and existence of lower life forms (Sadatipour et al., 2004).

The total amount of water present in the planet remains fixed but water changes its forms. Whenever water is used it is converted from useful to useless form often termed as “wastewater” or “used water”. Water stress is currently the greatest challenges of time driven by both natural and anthropogenic factors and faced in each hemispheres of the globe. A 1% increase in global water use per year has been observed since the 1980s (AQUASTAT, n.d.). This growth is contributed to a coadunation of population growth, progressive water consumption patterns and socioeconomic development. Global water demand will continue to increase at a similar rate until 2050, accounting for an escalation of 20 to 30% above the current levels of water use (Burek et al., 2016). Industrial and domestic sectors will have an extensive share in these increasing growth rates as per modeled projections (OECD, 2012; Burek et al., 2016). The 11th Five Year Plan, published by the Ministry of Planning and Commission, Pakistan, tallied the industrial sector to be using 3.5 million acre foot (MAF) of water, and an expected rise to 4.8 MAF is projected by 2025. This water requisition will not only put pressure on water resource but consumption in consequence will magnify the volume of wastewater produced and pollutant loads in natural ecosystems worldwide (11<sup>th</sup> Five Year Plan Govt. of Pakistan, 2013-18).

Rapid industrial expansion and population boom has heightened the pollution of water bodies staggeringly. The worldwide production and use of new & more hazardous chemical compounds have increased tremendously which find their way into

our ecosystem directly or as by-products and many of these compounds are non-biodegradable and some are even persistent to chemical and photolytic degradation.

Pollution of the water environment has numerous sources like sewage disposal, atmospheric fallout, agricultural & land runoff, and waste from industries. Industries are inducing approximately 300-400 million tons of waste in water bodies annually and in developing countries 80% of the sewage is discharged into water bodies directly without treatment. Agricultural runoff is causing eutrophication problems in coastal areas, lakes and rivers due to presence of nitrogen and phosphorous in high amount. Raw sewage and industrial wastewater are constantly being discharged into surface waters causing an impairment of water quality (Mustafa, 2013).

Water pollution not only upsets natural ecosystems by lessening its biodiversity but is also affecting social wellbeing. Number of people dying or getting ill due to water borne diseases increases with water pollution. Wastewater from industries can penetrate into the ground and pollute aquifers that are used as a source for drinking water. Bad water quality can also have serious repercussion on Gross Domestic Product (GDP) of the country by adversely impacting the economic activities. (UNEP, 2010). Untreated or ineffective treatment of wastewater causes serious threat to the environment because of its known harmful components. It contaminates water reservoirs, badly affects flora and fauna; affects land use and human wellbeing; disrupts economic activities such as farming, fishing, recreation and aesthetic values (Achaw and Danso-Boateng, 2013).

We should use environmental resources in such a way that it can fulfill our needs efficiently and effectively without compromising the needs of our future generation that is why most countries especially technologically developed countries have taken certain important actions to prevent environment pollution. Wastewater generation in modern times is increasing due to fast development and increased industrialization, therefore its treatment before ultimate dumping or reuse is now getting greater attention from all stakeholders and regulatory bodies (Mishra and Jhansi, 2013).

Freshwater is utilized for numerous local and industrial activities. It is discarded as waste after using it for economic or beneficial purpose. In various countries, these wastewaters are discharged after or before treatment into natural watercourses (Mishra

and Jhansi, 2013). Flowing rivers and streams have the capacity to go through self-purification. However, at certain heights of pollution, detoxification becomes difficult and takes longer period or becomes impossible. Treatment and management of wastewater is hence obligatory to correct these wastewater features in a way that the use or final disposal of the treated water can take place according to the rules set by the relevant legislative bodies (Njau and Mlay, 2003). In developing countries wastewaters are either not excellently treated or not treated at all before reuse or final disposal. Approximately, 80 per cent of all wastewater produced globally is discharged untreated into rivers, lakes or the oceans without adequate treatment (WWDR, 2017) mainly because conventional wastewater treatment systems involves energy intensive and mechanized treatment components that require heavy investment and demand high operating and maintenance costs (Mustafa, 2013).

On 25<sup>th</sup> September 2015, 17 Sustainable Development Goals or SDGs were included in the 2030 Agenda for sustainable development with a vision to conserve environment, end poverty and insure prosperity for all. A more ubiquitous and context specific SDG was included in the 2030 Agenda, entitled as SDG target 6.3, which emphasizes member countries to split in half the percentage of untreated wastewater and increase recycling and reuse by 2030. Many countries under this framework theme are also opting for the zero discharge policy to protect water environment/ecosystem.

In the industrial arena, five industries were noted to stand out in terms of their water use and in-effect wastewater generation. Out of these, petroleum refinery is one of the most water intensive sector (Eble and Feathers, 1992). Petroleum refinery wastewaters constitutes a considerable amount of toxic pollutants that needs to be removed at the source. These pollutants if left untreated will cause acute or chronic toxicity over time. Pollutants contained in refinery effluents responsible for the toxicity of the natural environment ranges from free hydrocarbons/oil & grease, sulphides, phenols, cyanide, ammonia, suspended & dissolved solids, organic chemicals and loads of heavy metals. However, the composition of wastewaters entailing these pollutants and their concentration load will vary in each refinery due to distinctive refinery configuration, the type of crude oil processed and the units in operation at any specific time (Wake et al., 2005).

Petroleum refining is a complex industrial process where crude oil is treated and refined into useful petroleum products like gasoline, asphalt base, diesel fuel, and kerosene, heating oil, and liquefied petroleum gas (Leffler, 1985). Petroleum derivatives are typically classified into three groups: light distillates (LPG, gasoline, and naphtha), middle distillates (kerosene, diesel), heavy distillates and residuum (heavy fuel oil, lubricating oils, wax, and asphalt). Fractional distillation and separation of crude oil lay the basis for this classification (Leffler, 1985). Great volume of water is used in refinery processes, especially for distillation, hydro-treating, desalting and cooling systems. Process wastewater arises from desalting crude oil, steam stripping operations; pump gland cooling, product fractionators reflux drum drains and boiler blow-down (Ravenswaay, 1995). Therefore, the generalized categorization of wastewaters from petroleum refining consist of cooling water, process oily water, storm and sanitary sewage water or non-process wastewater. Water used in processing operations accounts for a significant portion of the total wastewater.

Pollution from petroleum industries is causing a variety of adverse health impacts and is degrading environment quality on an increasing rate that is why management of petroleum industry's waste has been of much concern in recent years (Huang et al., 1999). The process-intensive petrochemical industry has difficult environmental administration challenges to keep water, land and atmosphere protected from refinery pollution. Petroleum refinery effluents (PRE) are wastes coming out of industries primarily engaged in refining crude oil and manufacturing fuels, lubricants and petrochemical intermediates (Harry, 1995). These are a chief source of aquatic environmental pollution (Wake et al., 2005). They are composed of oil and grease along with many other poisonous organic compounds and toxic heavy metals. The process of purifying crude oil uses great amounts of water. Consequently, large volumes of wastewater are produced (Coelho et al., 2006). Volume of effluent generated during processing is 0.4–1.6 times the amount of the crude oil processed (Coelho et al., 2006). According to an estimated yield of 84 million barrels per day (mbpd) of crude oil, a total of 33.6mbpd of effluent is produced globally (Doggett and Rascoe, 2009). World oil demand is projected to rise to 104-107mbpd over the next two decades, and oil fulfills 32% of the world's energy supply by 2030. Biofuels, including ethanol and biodiesel, are expected to account for 5.9mbpd by 2030, and the contributions from renewable energy sources like wind and solar power are estimated

to be 4–15% (Doggett and Rascoe, 2009; Marcilly, 2003). This calculation signifies that wastes specifically from the oil industry will constantly increase and will be discharged into water bodies unless otherwise policies are revised.

## **1.2 Policies, legislation and guidelines for pollutant discharge**

The enactment of comprehensive legislation on the environment, covering multiple areas of concern is a relatively new and ongoing phenomenon in Pakistan. Whereas, a basic policy and legislative framework for the protection of the environment in the country is now in place, detailed rules, regulations and guidelines required for the implementation of the policies and enforcement of legislations are still in various stages of formulation and discussion.

### **1.2.1 National environmental policy, 2005**

Pakistan Environmental Protection Council (PEPC) in its 10th meeting on 27<sup>th</sup> December, 2004 presided over by the Prime Minister of Pakistan presented the primal National Environmental Policy (NEP). After months of considerations, the policy was approved by Cabinet Division on 29<sup>th</sup> June, 2005. NEP is the primary policy of Government of Pakistan that addresses the environmental issues of the country. The broad goal of NEP is, “To protect, conserve and restore Pakistan’s environment in order to improve the quality of life of the citizens through sustainable development”. A set of sectoral and cross-sectoral guidelines were envisioned in the NEP to achieve its goal of sustainable development (NEP MOCC, 2005; Pakistan’s Waters at Risk WWF, 2007).

#### a) Sectoral Guidelines

Water and sanitation, air quality and noise, waste management, forestry, biodiversity and protected areas, climate change and ozone depletion, energy efficiency and renewable, agriculture and livestock, and multilateral environmental agreements.

#### b) Cross-Sectoral Guidelines

Poverty, population, gender, health, trade and environment, environment and local governance, and natural disaster management.



Six policy instruments laid the foundation to curtail environmental problems throughout the country:

- Integration of environment into development planning;
- Legislation and regulatory framework;
- Economic and market based instrument;
- Capacity development;
- Public awareness and education; and
- Public private civil society partnership.

### **1.2.2 National environmental legislation**

#### **a) Punjab environmental protection act, 1997 and amendments 2012**

Before the passage of 18th constitutional amendment by the parliament, Punjab Government had enforced The Punjab Environmental Protection Act, 1997 in the province which was originated and derived from the Pakistan Environmental Protection Act, 1997. After the legalization of 18th amendment Punjab provincial assembly passed an amendment in the act ‘The Punjab Environmental Protection (Amendment) Act 2012’. About 22 reforms were made in the original act (PEPA, 1997-2012).

The Act is quite comprehensive to provide for the protection, conservation, rehabilitation and improvement of the environment, for the prevention and control of pollution, and promotion of sustainable development in the province of Punjab. The Punjab Environmental Protection (Procedure) rules were issued by Government of Punjab Law and Parliamentary Affairs Department on 12th August, 2016.

#### **b) Punjab environmental quality standards, 2016**

PEQS were promulgated in 2016 under the Punjab Environmental Protection Act, 2012 by Punjab Environmental Protection Agency and approved by Punjab Environment Protection Council. PEQS are mainly adopted from NEQS after the enactment of Punjab Environmental Protection Act, 2012 as result of 18th amendment. The act specifies the imposition of a pollution charge in case of non-compliance with the PEQS (PEQS, 2016). The PEQS specified limits for liquid effluents discharge into surface waters and sewage treatment are presented in below Table 1.1:

Table 1.1. PEQS for municipal and liquid effluents (mg/l unless otherwise defined) (Qadir, 2003)

<b>Parameters</b>	<b>Into Inland Water</b>	<b>Into Sewage Treatment<sup>b</sup></b>
Temperature or temperature increase <sup>c</sup>	≤3°C	≤3°C
pH	6-9	6-9
Biochemical Oxygen Demand (BOD <sub>5</sub> ) at 20°C <sup>d</sup>	80	250
Chemical Oxygen Demand (COD) <sup>d</sup>	150	400
Total Suspended Solids (TSS)	200	400
Total Dissolved Solids (TDS)	3,500	3,500
Grease and oil	10	10
Phenolic compounds (as phenol)	0.1	0.3
Chloride (as Cl <sup>-</sup> )	1,000	1,000
Fluoride (as F)	10	10
Total cyanide (as CN <sup>-</sup> )	1.0	1.0
An-ionic detergents (as MBAS) <sup>e</sup>	20	20
Sulphate (SO <sub>4</sub> )	600	1000
Sulphide (S <sup>-</sup> )	1.0	1.0
Ammonia (NH <sub>3</sub> )	40	40
Pesticides <sup>f</sup>	0.15	0.15
Cadmium <sup>g</sup>	0.1	0.1
Chromium (trivalent & hexavalent) <sup>g</sup>	1.0	1.0
Copper <sup>g</sup>	1.0	1.0
Lead <sup>g</sup>	0.5	0.5
Mercury <sup>g</sup>	0.01	0.01
Selenium <sup>g</sup>	0.5	0.5
Nickel <sup>g</sup>	1.0	1.0
Silver <sup>g</sup>	1.0	1.0
Total Toxic metals	2.0	2.0
Zinc	5.0	5.0
Arsenic <sup>g</sup>	1.0	1.0
Barium <sup>g</sup>	1.5	1.5
Iron	8.0	8.0
Manganese	1.5	1.5
Boron <sup>g</sup>	6.0	6.0
Chlorine	1.0	1.0

Source: Qadar (2003)

## Notes

<sup>a</sup> All values are in mg/l, unless otherwise defined

<sup>b</sup> Applicable only when and where sewage treatment is operational and BOD<sub>5</sub>=80 mg/L is achieved by the sewage treatment system

<sup>c</sup> The effluent should not result in temperature increase of more than 3°C at the edge of zone where initial mixing and dilution take place in the receiving body. In case zone is defined, use 100 meters from the point of discharge

<sup>d</sup> Assuming minimum dilution 1:10 on discharge, lower ratio would attract progressively stringent standards to be determined by the Federal Environmental Protection Agency. By 1:10 dilution means, for example that for each one cubic meter of treated effluent, the recipient water body should have 10 cubic meter of water for dilution of this effluent

<sup>e</sup> Modified Benzene Alkyl Sulphate; assuming surfactant as biodegradable

<sup>f</sup> Pesticides include herbicide, fungicides and insecticides

<sup>g</sup> Subject to the total toxic metals discharge should not exceed level of total toxic metals

### c) Self-monitoring and reporting rules, 2001

A more simplified and realistic monitoring procedure was devised for the enforcement of environmental quality standards, labeled as the “Self-Monitoring and Reporting Rules, 2001”. As per the rules set by this system, industries have to monitor effluents and emissions in compliance with the NEQS/PEQS and report it to respective provincial EPAs. The system classifies industries into three categories A, B and C based on pollution levels and corresponding to a particularized reporting frequency for listed priority parameters. Petroleum refinery lies under Category A for effluent discharges and are bound to report effluent flow, temperature, pH, TSS, COD, BOD<sub>5</sub>, Oil and Grease, and phenolic compounds on a monthly basis. SMART tool has worked out to ensure industrial NEQS/PEQS compliance and maintaining an environmental pollution directory on a regional scale by constructing database and baselines (NEQS SMART Rules, 2001).

### 1.2.3 International guidelines and framework

#### a) 2030 sustainable development agenda

The discharge of untreated wastewater in waterways creates environmental, health and climate related hazards. To raise cognizance of this global issue, “wastewater” was focused as the subject manuscript for UN-World Water Day, 2017. The leitmotif was already sealed as target 6 of the 17 Sustainable Development Goals, asserting states to halve the volume of untreated wastewater and significantly increase recycling and reuse potential. To frame the efficacy of the SDGs, inter-agency Expert Group formulated an indicator tool to quantify progress towards each goal and targets. Indicator tools are implemented at global level, however, member countries were also

compelled to form their own national level indicators. Indicators proposed to endorse achievements within target 6.3, exercised on a global scale are; a) proportion of wastewater safely treated, b) fraction of water bodies with good ambient quality. A smooth transition to a circular economy particularly for developing countries can be achieved through progressions in wastewater management (IWA Wastewater Report, 2018).

b) EHS guidelines for petroleum refining – World Bank Group

The International Finance Corporation (IFC) is a directive of the World Bank Group originally founded with the principal vision to increment prosperity for all. As part of its sustainability framework floated in 2012, IFC encourages sound environmental and social practices for its borrowers through enactment of a sustainability policy to promote a positive development impact. IFC under its “performance standards initiative” has put in motion several technical reference documents known as the Environment, Health and Safety Guidelines (EHS Guidelines) construing general and industry specific impacts and mitigations and performance level indicators adapted by an evolutionary process of consultation among high-tech countries with more stringent laws and regulations. The document contains pollutant limit concentrations for effluents emitted by the petroleum refining sector and are listed in below Table 1.2:

Table 1.2. World Bank liquid effluent levels for petroleum refining facilities<sup>a</sup>(IFC, 2017)

<b>Parameters</b>	<b>Guidline Value</b>
pH	6-9
Biochemical Oxygen Demand (BOD <sub>5</sub> )	30 <sup>b</sup>
Chemical Oxygen Demand (COD)	125 <sup>c</sup>
Total Suspended Solids (TSS)	30
Grease and oil	10
Phenol	0.2
Cyanide (Total)	1.0
Free	0.1
Benzene	0.05 <sup>e</sup>
Benzo(a)pyrene	0.05
Sulfides	0.2
Chromium (total)	0.5

<b>Parameters</b>	<b>Guidline Value</b>
Chromium (hexavalent)	0.05
Copper	0.5
Lead	0.1
Mercury	0.003 <sup>d</sup>
Nickel	0.5
Total Nitrogen	10 <sup>f</sup>
Total Phosphorus	2.0
Arsenic	0.1
Vanadium	1.0
Iron	3
Temperature increase	<3°C <sup>g</sup>

#### Notes

<sup>a</sup> Assumes an integrated petroleum refining facility

<sup>b</sup> Guideline value from EC JRC, BREF (2015) Table 3.16; National legislations may have lower values such as China: 20 mg/L.

<sup>c</sup> Guideline value from EC JRC, BREF (2015); National legislations may have lower values such as China: 120 mg/L.

<sup>d</sup> EC JRC, BREF (2015) Table 3.16.

<sup>e</sup> Guideline value from EC JRC, BREF (2015).

<sup>f</sup> The effluent concentration of nitrogen (total) may be up to 40 mg/l in processes that include Hydrogenation.

<sup>g</sup> At the edge of a scientifically established mixing zone, which takes into account ambient water quality, receiving water use, potential receptors, and assimilative capacity.

### 1.3 Literature review

Ashfaq et al (2010) executed a performance evaluation study for an effluent treatment plant of a petroleum refinery located in India. The crux of the case study was to get the idea of refinery processes, the kind of waste generated and impurities received at the effluent treatment plant, the treatment units operational at ETP and their design parameters and the removal efficiency achieved by carrying out wastewater sample analysis at the influent and effluent stream. The results obtained as independent monitors were analyzed and compared with local regulatory norms. Samples collected over a month period at intervals were analyzed for pH, temperature, TSS, Oil and grease, BOD, and COD. The pollutant parameters showed considerable reduction at the effluent stream at an average of 96% for BOD, 90% COD, 70.5% TSS, and 95.5% for Oil and Grease, thereby depicting that the ETP is operating quite efficiently and the values are within permissible limits laid by local regulatory agencies.

Abubakar (2014) performed a fairly similar performance evaluation study of a wastewater treatment process at Kaduna Refinery and Petrochemical Company (KRPC), located in Kaduna State, Nigeria. The core of his research was to assess the quality of predisposal treatment and the impacts that the final effluent might have on River Romi, a major tributary of River Rigasa in their study area. The temporal extent of his research was quite extensive, encompassing a six month sampling period based on dry and wet seasons (January, February and March) and (June, July and August). Three wastewater sampling points were selected as; A (effluent before treatment), B (effluent after treatment) and C (effluent at the discharge point) and their mean values were subjected to a Paired Student t-test to figure out the statistical significance of various pairs designed by the researcher. The values for discharged effluent stream were compared for compliance with standards set by Federal Environment Protection Agency (FEPA), United Nation Environment Program (UNEP) and World Health Organization (WHO). Raw effluent data for sampling points A and B was acquired from the refinery's safety and control unit, however, the researcher collected his own effluent samples by Grab method at the discharge point C to analyze physico-chemical parameters and validate the efficacy of treatment system by correlating researcher's data with data provided by KRPC and UNEP standards. The study deduced that treatment at KRPC was effective for the entire research period, especially during wet season but moderately during dry seasons, but this alone cannot single out KRPC as the principle polluter of environment in the region.

Al Zarooni and Elshorbagy (2006) carried out a sponsored research work aiming to understand the major refining processes at Al Ruwais refinery, UAE as a trail to track down the percentage contribution of wastewater streams originating from different refining units and analyzing concentrations of some general and component specific parameters such as BOD, COD, TPH, Kjeldahl nitrogen, Sulfate, Naphthalene as Polyaromatic hydrocarbons (PAHs), Polychlorinated biphenyl compounds (PCBs), and phenolic compounds. Researcher's objectives were to quantify effluent stream received at the treatment system and analyze the concentrations of selected parameters by collecting effluent samples from identified sampling ports. Samples were obtained from five sampling points; CPI In, CPI out, Caustic, Cooling Water, and Mixing Pit on monthly basis from a period of June 2002 to June 2003 to ascertain removal efficiency (%), dilution factor and finally the treatment efficacy and compliance by comparing

values of discharged effluent with UAE industrial wastewater standards. Although parameters were significantly reduced by dilution and their concentrations were within permissible limits, researchers accentuated the load variations of some effluent streams and recommended the installation of dissolved air floatation to cater unexpected shock loads.

Al Suhaili and Abed (2008) published their research and drew attention to the local environmental problems caused by oil refinery effluents. The objective designed for their thesis was to gauge the performance of an effluent treatment plant responsible for effluent management at Dora Refinery, Baghdad situated on the bank of Tigris River. Researchers identified six sampling points in the treatment plant and collected grab samples over a period of six months with an average of two samples per month. These sampling points aided them to diagnose pollutant load variations and reduction efficiency at each stage alone by plotting graphs of designed vs. actual performance conditions and compliance status by analyzing values of final effluent with Iraqi discharge limits. Study pointed high removal efficiencies for TSS, Oil, COD, BOD, Sulfide and Phenol at 95%, 88%, 86%, 81%, 85% and 97% respectively, whereas reduction rate of NH<sub>3</sub>, SO<sub>4</sub> and PO<sub>4</sub> were not very efficient.

Aljuboury et al (2017) published a narrative review of various researches conducted by research scholars exclusively incorporating the treatment of petroleum refinery wastewater by conventional and more advanced technologies. Before citing these treatment techniques, the reviewer quoted the pollutant concentrations for refinery wastewater reported by a total of 13 different scholars and draw conclusion to a fact that effluent composition in each refinery varies based on crude quality, operating conditions, environmental factors, and origin of wastewater pollutants. Later on based on literature review the treatment phase was narrowed down to two stages, firstly, pre-treatment or physical stage to reduce oil and suspended material content, secondly, a more advanced stage to degrade pollutants to an acceptable discharge limit. Furthermore, the reviewer formulated tables for both conventional and advanced physicochemical and biological treatment applications entailing the method applied to treat the type of wastewater, the pollutants removed, and the maximum removal efficiency achieved by the applied processes.

Santo et al (2015) carried out a diagnostic study for evaluating the effectiveness of main units of a wastewater treatment plant operational at a Portuguese petroleum refinery. Porto oil refinery (Galp Energia) processes both sweet and crude oil and the resultant wastewater produced contains high concentrations of oil, mercaptans, cyanides, ammoniacl nitrogen, phenols and many micro pollutants that requires adequate treatment to meet more tighter discharge laws before ultimately dumping the wastewater in inland waters. The Porto WWTP has a designed capacity to receive 450m<sup>3</sup>/h of wastewaters. The sampling period designed by the researchers for weighing the removal efficiencies of pollutants viz. TSS, VSS, TPH, O&G, Sulphides, Phenols, COD, BOD<sub>5</sub>, TN and Chlorides extended over five sampling campaigns at six sampling points. These sampling campaigns were distinguished as Campaign A, B & C (dry season) and Campaign D and E (wet season). The treatment techniques employed at the refinery constituted four steps: pre-treatment (API & PPIs), physicochemical treatment (coagulation & floatation), biological treatment (ASP) and advanced treatment (chlorination, mechanical aeration & filtration). After analyzing the physicochemical characteristic of refinery wastewater at different units the researchers in their concluding remarks stipulated the overall treatment process to be effective with an average removal efficiencies of 96.7% for TSS, 99.1% for O&G, 99% for Sulfides, 99.1% for TPH, 87.3% for COD, 90.5% for BOD<sub>5</sub>, 94.6% for Phenols, 68% for TN, and 62.8% for Chlorides.

Perez (2015) performed a comprehensive research project and drafted a dissertation pertaining analysis and improvement proposal of a Mexican refinery wastewater treatment plant. A full scale gap analysis of the wastewater treatment plant at Refinery 1, operated by PEMEX was executed to evaluate the discharge limits of refinery effluents against Mexican standards and identify in-depth operational weaknesses in the wastewater treatment trains. The research methodology adopted was based on interviews, physical inspection of the plant to collect process data, and statistical analysis of the effluent data (2014-mar 2015) collected from refinery's certified laboratory. Student t-pair test supported in quantifying the removal performance by determining statistical relationship between certain pollutant parameters in the influent and effluent streams. Although, the treatment was computed as an acceptable count, the researcher recommended that an intense maintenance and



reintegration program would be required to meet more stringent laws in subsequent times.

#### **1.4 Objectives of study**

- 1) To perform independent bulk parameter analysis including physico-chemical and heavy metals to validate and assess the quality (concentration load) of wastewater influent and effluent stream of Effluent/wastewater Treatment Plant at Attock Refinery Limited.
- 2) To determine the current performance effectiveness of Effluent/wastewater Treatment Plant.

## CHAPTER 2

### METHODS AND METHODOLOGY

#### 2.1 Site selection

The undertaken study is initiated to ascertain the compliance efficiency of an Effluent Treatment Plant operational at Attock Refinery Limited, Rawalpindi by conducting independent wastewater quality assessment of raw and discharged effluent streams and comparing values with Punjab Environmental Quality Standards for Municipal and Liquid Industrial Effluents and more stringent liquid effluent levels specified for petroleum refineries by IFC, World Bank. The treated wastewater is currently being discharged in River Soan, a principal feeding tributary of Simly dam. Soan watercourse has become severely contaminated over the course of time due to drainage of effluents and industrial waste from Rawalpindi city. The intended study area is located at 33°33'04.60" N and 73°04'33.26" E in the midst of a densely populated area and is presented in Figure 2.1.

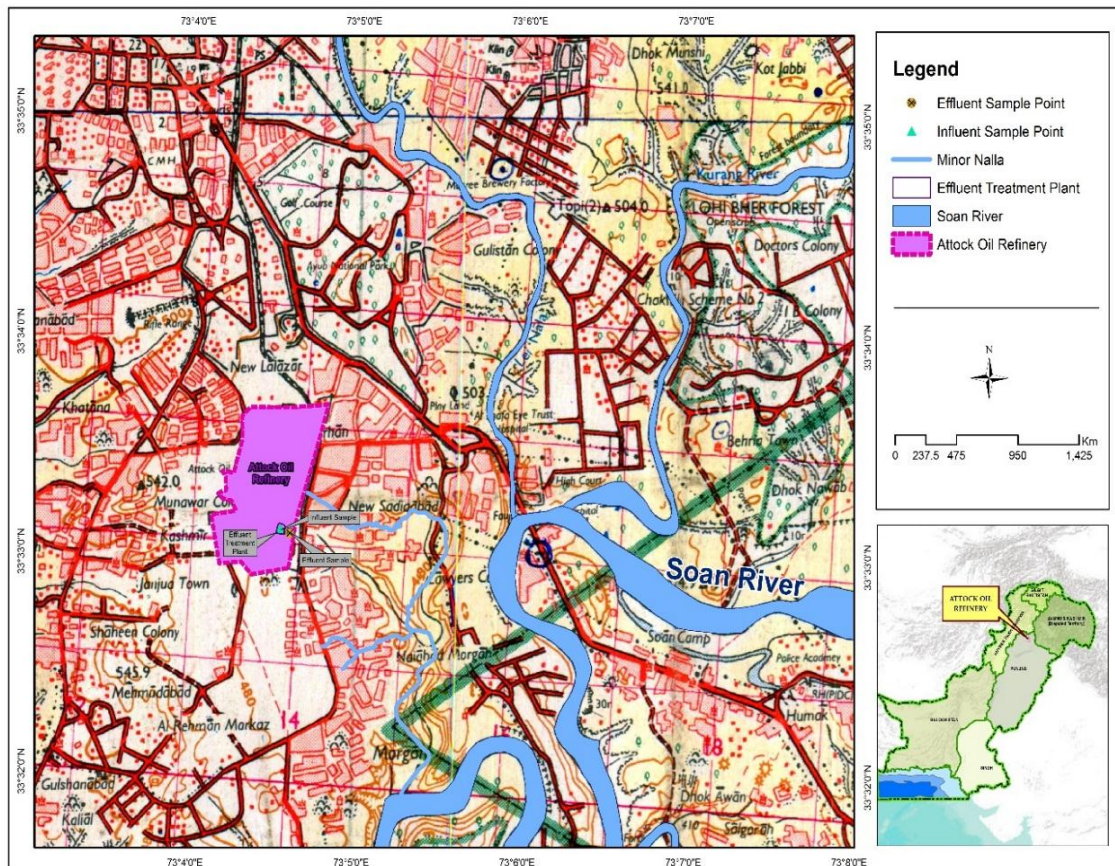


Figure 2.1. Location map of Attock Oil Refinery

## **2.2 Sample collection and storage**

Visits were made to the refinery to collect baseline process and operational data of ETP and identify sampling points that would generate most reliable and representative data. Sampling schedule extended over a period of three months (Dec-2018 to Feb-2019) with an average of two samples per week. The sampling range encompassed all possible fluctuations that might occur during ETP operation. Wastewater samples were collected from DAF inlet (Raw influent) and final effluent exiting the facility in 1.5L plastic bottles using Grab method.

Sample bottles were initially rinsed with distilled water and were later flushed with source wastewater. After collection the sample bottles were sealed and given an identification number, preserved at 4°C in ice boxes and were transported to the laboratory for analysis. Sampling period was consistent throughout and utmost care was taken to prevent any contamination of the samples by using protocols listed in standard methods for the examination of water and wastewater. Only pH and temperature were analyzed in-situ immediately after sample collection using digital meter (Hanna-HI991001). The meter was calibrated using buffer solutions prior to analysis. The meter probe was first cleaned to prevent any contamination and readings were recorded by dipping the probe in wastewater samples.

## **2.3 Analysis of parameters**

### **2.3.1 Total suspended solids**

For TSS analysis a pre-weighed filter paper and aluminum dish was utilized and marked with the sample volume to be used. The filter paper was placed on the filter support using tweezers. Wastewater sample was mixed well and a 5ml pipette was used to collect and distribute the sample on the filter paper. Sample was then allowed to rinse through the filter paper using DI water leaving behind residues on the filter. Filter paper was then dried in an oven at 103-105°C for one hour. Filter paper after cooling was placed on a weighing scale and readings were noted. To calculate the final readings in mg/l the following formula was used:

$$\text{TSS} = (\text{final weight} - \text{original weight}) \times 1,000 / \text{Sample volume}$$

### 2.3.2 Total dissolved solids

TDS were analyzed using preheated and pre-weighed porcelain dish. Sample was then filtered in a beaker through Whattman paper. 10ml filtered sample was then transferred to the porcelain dish and was heated at 108°C allowing the sample to evaporate. After drying the dish was allowed to cool at room temperature. Dish with residues was finally placed on a weighing scale to record values. To calculate final readings, the formula used was:

$$\text{TDS} = [\text{final weight(dish+residue)} - \text{original weight}] \times 1,000 / \text{sample}$$

### 2.3.3 BOD5

BOD5 is a bioassay procedure measuring the amount of oxygen consumed by bacteria to degrade organic matter. The procedure was performed by preparing dilution water for BOD with reagents and adding specified volume of sample in 300ml BOD bottle based on dilution factor. Initial DO concentration of the dilution water was recorded. BOD bottles were sealed and left for incubation for 5 days at 20°C in dark. After incubation, DO concentration in BOD bottles was again measured to know the difference and final calculations were made using formula:

$$\text{BOD} = (A-B) \times 300 / \text{Sample volume}$$

### 2.3.4 COD

COD analysis was performed as a close reflux titration. Procedure adopted was adding 50ml sample followed by strong oxidizing agent (potassium dichromate) and sulfuric acid reagent in a flask. The flask was mixed well and was refluxed for about 2 hours to allow complete oxidation of organic and inorganic matter. Sample was later titrated with ferroin indicator and the color change to reddish brown was noted as the end point reading. Formula used for calculation was:

$$\text{COD} = (A - B) \times \text{Normality} \times 8000 / \text{Sample volume}$$

A = titrant used by sample

B = titrant used by blank

### 2.3.5 O&G

Solvent extraction method is applied to measure O&G content in wastewater samples. Samples were initially acidified with HCL. Later n-hexane was added to the

acidified sample, mixed thoroughly and was placed in a separatory funnel allowing to settle layer of n-hexane and wastewater. After three repetitive extractions, wastewater was drained leaving behind oil and n-hexane solution in the separatory funnel. Oil and n-hexane were then collected in a pre-weighed flask and were finally subjected to rotary evaporator at 70°C. After complete evaporation of n-hexane the flask was allowed to cool and weighed again to calculation the difference.

$$\text{O\&G} = (A-B) \times 1000 / \text{Sample volume}$$

A = weight of flask and residue

B = weight of flask

### **2.3.6 Phenols**

Analysis was performed by adjusting the pH of sample and adding 2ml buffer solution to the working sample. Later 2ml aminoantipyrine solution was mixed followed by 2ml of potassium ferricyanide and the sample was left for 15 minutes. After 15 minutes, the absorbance at 510nm was measured by uv-spectroscopy.

### **2.3.7 Total nitrogen**

TN is the sum of organic and reduced nitrogen. For organic content analysis was performed by adding 50ml of sample in a Kjeldahl flask and adding sulphuric acid, allowing the mixture to evaporate and the solution to turn pale yellow. 30ml distilled water was added and the solution was turned alkaline by adding sodium hydroxide. Flask was then connected to a distillation apparatus with tip of the condenser dipped in boric acid in the receiving flask. 30ml of the sample was steam distilled in the receiving flask. The sample was then titrated with 0.01 N sulphuric acid until the color appeared pink and the end point was recorded.

For nitrate-nitrite measurements, 25ml of sample is mixed with 75ml ammonium chloride and poured in a reduction column. First 25ml is rejected and later volume is collected in a flask. Color reagents are added to the sample and left for 10 minutes to allow color development. Finally, the absorbance at 543nm is measured in UV-spectrum.

### **2.3.8 Heavy metals**

The concentration load of heavy metals viz, chromium, copper, iron, nickel, lead, vanadium and phosphorus in all influent and effluent samples were analyzed by

Inductively coupled plasma atomic emission spectroscopy (ICP-OES) while arsenic and mercury concentrations were measured through Hydride generation atomic absorption spectrometry (HG AAS) available at Central Analytical Facility Division.

## **2.4 Statistical Analysis**

Lastly, Pearson's coefficient correlation ( $r$ ) statistical analysis was performed using EXCEL worksheet to summarize data and illustrate the interdependence of wastewater quality parameters. The dependencies were visualized as matrices and a heat-map demonstrating strong, moderate, and weak correlations.

## **2.5 Refinery background**

Attock Refinery Limited (ARL) is considered as the forerunner in crude oil refining in Pakistan. The set-up was established in 1922, however, through the process of continual improvement, ARL has kept itself abreast with the latest technological advancements and state of the art facilities to meet the modern-day challenges in refining process.

Operations at ARL began in 1922 with the discovery of crude oil at Khaur, Punjab. The setup was established to meet the refining needs of the indigenous discovery. Later, based on additional development in drilling processes and discovery of crude oil in neighboring areas of Khaur, the refining capacity of ARL was enhanced to 5,500 Barrels Per Day (BPD) through installation of distillation, wax purification and heavy crude treatment units. Another major expansion of ARL took place between the period of 1980 to 2000 in which 02 additional distillation units of 20,000 and 5,000 BPD each capacity were installed along with additional 10,000 BPD capacity Heavy Crude Unit and Catalytic Reformer and a 7.5 MW Powerhouse for local power generation. Current refining capacity of ARL stands at 53,400 BPD (ARL Sustainability Report, 2018).

Following major refining operations are taking place at ARL, whereas a brief about each refining process is descriptively given as under that produce usable fuel fractions along with process/oily water residue/wastewater that is ultimately routed via drains to a state of the art installed Effluent/Wastewater Treatment Plant. Table 2.1. at the end of these processes will help to fathom the approximate volume of wastewater generated against each operation per barrel of feedstock and the possible pollutants

contained within, however, exact figures may vary from refinery to refinery depending on factors such as: capacity, nature of crude, technology, operating and environmental conditions.

- Atmospheric Distillation
- Vacuum Distillation
- Reforming
- Hydrodesulphurization and Gas Sweetening

### **2.5.1 Refinery processes description - ARL**

#### a) Atmospheric distillation

The atmospheric distillation unit is employed for treatment/separation of light sweet crude distillates with crude of API > 30. Sweet crude refining process involves separating the crude oil into different fractions by virtue of their boiling points. The process consists of operations such as heating, fractionation, cooling, condensing of crude oil into fractionated components. The oil is heated to about 400 – 500 °C in dedicated heaters and is then entered into a vertical distillation column that operates at atmospheric pressure. Feedstock is separated using distillation trays that vary from 30 to 50 in number depending upon the capacity of the unit. Heavier fractions are separated from bottom whereas light fractions are removed from top of the column.

The pre-process of atmospheric distillation involves desalting process, a technique adopted to remove salts, metals, suspended solids and water from the crude. The general products of column include bitumen, furnace oil, diesel, kerosene and naphtha often termed as “Straight-run liquids”. Similarly, other low-boiling point mixtures in equilibrium with heavier components are also removed using separate stripping tower. Steam is used to strip the light-end components from the heavier components (BREFs EIPPCB, 2015). A simplified diagram of atmospheric distillation column with process inputs and outputs including process wastewater is given in Figure 2.2:

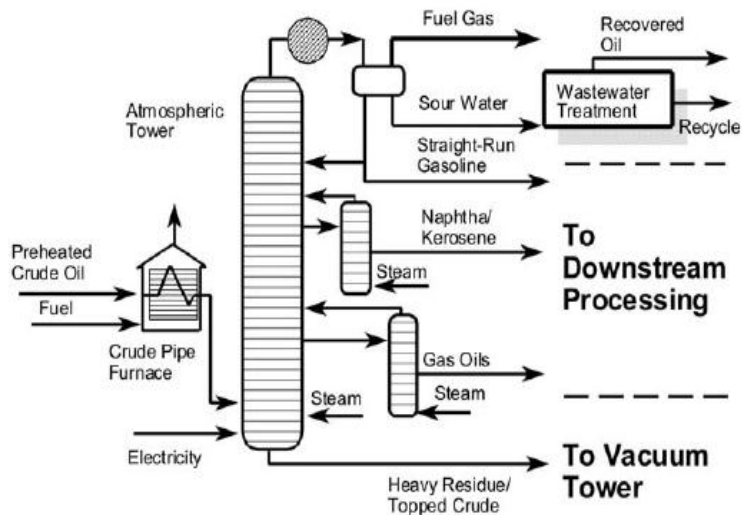


Figure 2.2. Typical atmospheric distillation (HP 1993a, EPA 1995a, ANL 1981).

b) Vacuum distillation

The vacuum distillation unit is employed for treatment/separation of heavy crude distillates with crude of API < 30. The heavier fractions from atmospheric unit are pre-heated to 400 °C and enter the base of vacuum column at a pressure between 40 and 100 mbar. The induced vacuum inside the column is through steam ejectors, vacuum pumps and low-pressure condensers. Superheated steam is used to reduce the partial pressure of the hydrocarbons in the distillation column. The flashing vapor in the column is interacted with oil to wash out any entrained liquid in vapors. In the lower section of the vacuum tower, gas oil and heavy furnace oil are condensed whereas in the upper section, light components are collected.

Good quality vacuum gas oil from the lower section of vacuum column is used as feedstock for hydrocracker unit where the carbon content is critical for better performance. The process of vacuum distillation also utilizes desalter for the removal of sour water and salts from the crude (BREFs EIPPCB, 2015). A simplified diagram of vacuum distillation column with process inputs and outputs entailing process wastewater is given in Figure 2.3:



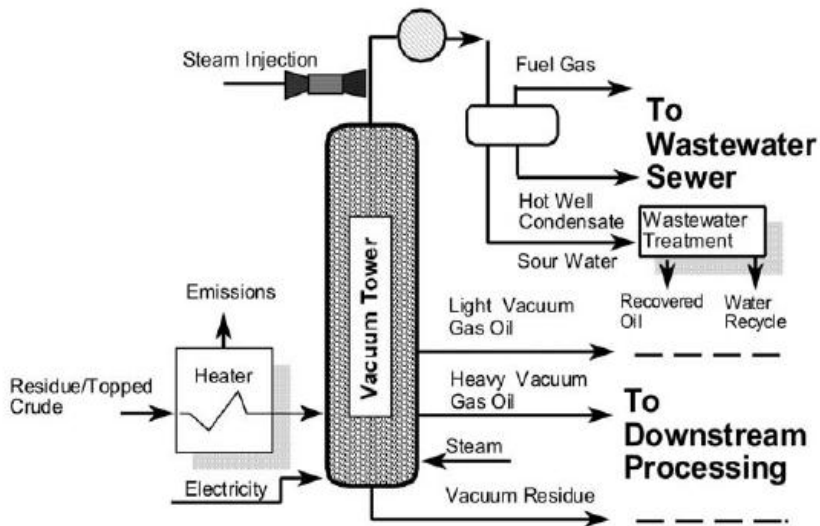


Figure 2.3. Typical vacuum distillation (HP 1993a, EPA 1995a, ANL 1981).

c) Reforming

The naphtha that is separated in the atmospheric distillation unit is a relatively unconditioned gasoline blend due to its low octane number. The purpose of reforming is to enhance the octane number of the naphtha blend thus improving the combustion characteristics and reducing fuel knocking. Octane numbers are generally very low for naturally occurring n-paraffins, slightly better for naphthenes and isoparaffins and are highest for aromatics (BREFs EIPPCB, 2015). Four type of reactions occur during the reforming process.

- Dehydrogenation of Naphthenes to Aromatics
- Dehydrocyclisation of Paraffins to Aromatics
- Isomerisation
- Hydrocracking

Naphtha blends fed to the reformers are first hydro-treated to remove sulphur and other impurities using Platinum, bimetallic or multi-metallic catalysts depending on refinery configuration.

d) Hydrodesulphurization and gas sweetening

Hydrodesulphurization is a process to remove sulphur from refined fuels like diesel, gasoline, natural gas, jet fuel and kerosene thus leading to lower SO<sub>x</sub> emissions during combustion in vehicles and making the fuels more environmentally friendly.

The process takes place in a reactor at high temperatures in the presence of cobalt, molybdenum and nickel catalyst.

The liquid is fed into the reactor from bottom of the column along with hydrogen rich gas after pre-heating. This gas liquid mixture at high temperature reacts in the presence of catalyst where desulphurization occurs. The gas from the reactor exits into a separator vessel which is then fed to an amine contactor for the removal of H<sub>2</sub>S whereas the hydrogen gas is recycled back to the reactor. The liquid from the gas separator vessel enters a stripper where desulphurized liquid is removed from the bottom and the gas enters gas processing facility for the removal of H<sub>2</sub>S from gas containing methane, ethane, butane and other heavier fractions (BREFs EIPPCB, 2015).

H<sub>2</sub>S removed from hydrogen and other hydrocarbon gases can be converted to elemental sulphur through Claus Process.

Table 2.1. Process and Sources of Process Wastewater (EPA, 1995a, Meyers, 2004)

<b>Process</b>	<b>Largest Sources of Process Wastewater</b>
Desalting	Hot salty process water (hydrogen sulfide, ammonia, phenol, suspended solids, dissolved solids). Water flow = 2.1 gal/bbl of oil
Distillation (atmospheric & vaccum)	Oily sour water (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, phenol). Water flow = 26.0 gal/bbl of oil
Reforming (isomerization)	Process wastewater (levels of oil, suspended solids, hydrogen sulfide, chloride salts). Water flow = 6.0 gal/bbl of oil
Sulfure removal/gas treatment	Little or no wastewater (hydrogen sulfide, ammonia)
Deasphalting	Steam stripping wastewater (oils)

**Note:**

These estimates are approximate while the exact figures for ARL for the amount of water utilized & wastewater flow in each operation per barrel of feedstock were unavailable.

### **2.5.2 Wastewater treatment techniques at ARL**

Petroleum refinery is among the major water intensive industries functioning in Pakistan. A significant proportion of the total fresh/raw water in petroleum refinery is consumed in process operations, ultimately responsible for the generation of process wastewater or oily wastewater, as it often comes in contact with the hydrocarbons and

is exceedingly contaminated. A reasonable understanding of the aforementioned process operations at ARL will guide in apprehending the sources of oily wastewater and the possible pollutants that are treated at the Effluent/Wastewater Treatment System installed at ARL.

As the process is highly water dependent, ARL has ensured a continuous supply of fresh water through a total of 16 installed shallow (11) and deep (5) wells at Shahpur, Sohan and ARL owned land at Morgah. Apportionment of water abstracted by ARL from different aquifers for the year 2018 is presented in below Table 2.2:

Table 2.2. Water Withdrawal in Mega Liter (ARL Sustainability Report, 2018)

<b>Source</b>	<b>Water Withdrawn</b>
Shahpur Shallow Well	312 MegaLitre
Tube Wells	781 MegaLitre
Soan / Hummak	18 MegaLitre
<b>Total</b>	<b>1111 MegaLitre</b>

ARL installed its first ever Effluent Treatment Plant (ETP) back in 1996 and technological expansions / up-gradations in the refining process subsequently led to the commissioning of ETP phase II project in 2014 to bear flow rate, enhance recycling potential and meet compliance status of the discharged wastewater with Punjab Environmental Quality Standards. Presently, the Effluent Treatment Plant at ARL is designed to handle 200 GPM (US) of oily/process wastewater by an engineered network of wastewater collection and treatment system (ARL Sustainability Report, 2018). A schematic flow scheme of the Effluent Treatment Plant is given below in Figure 2.4:

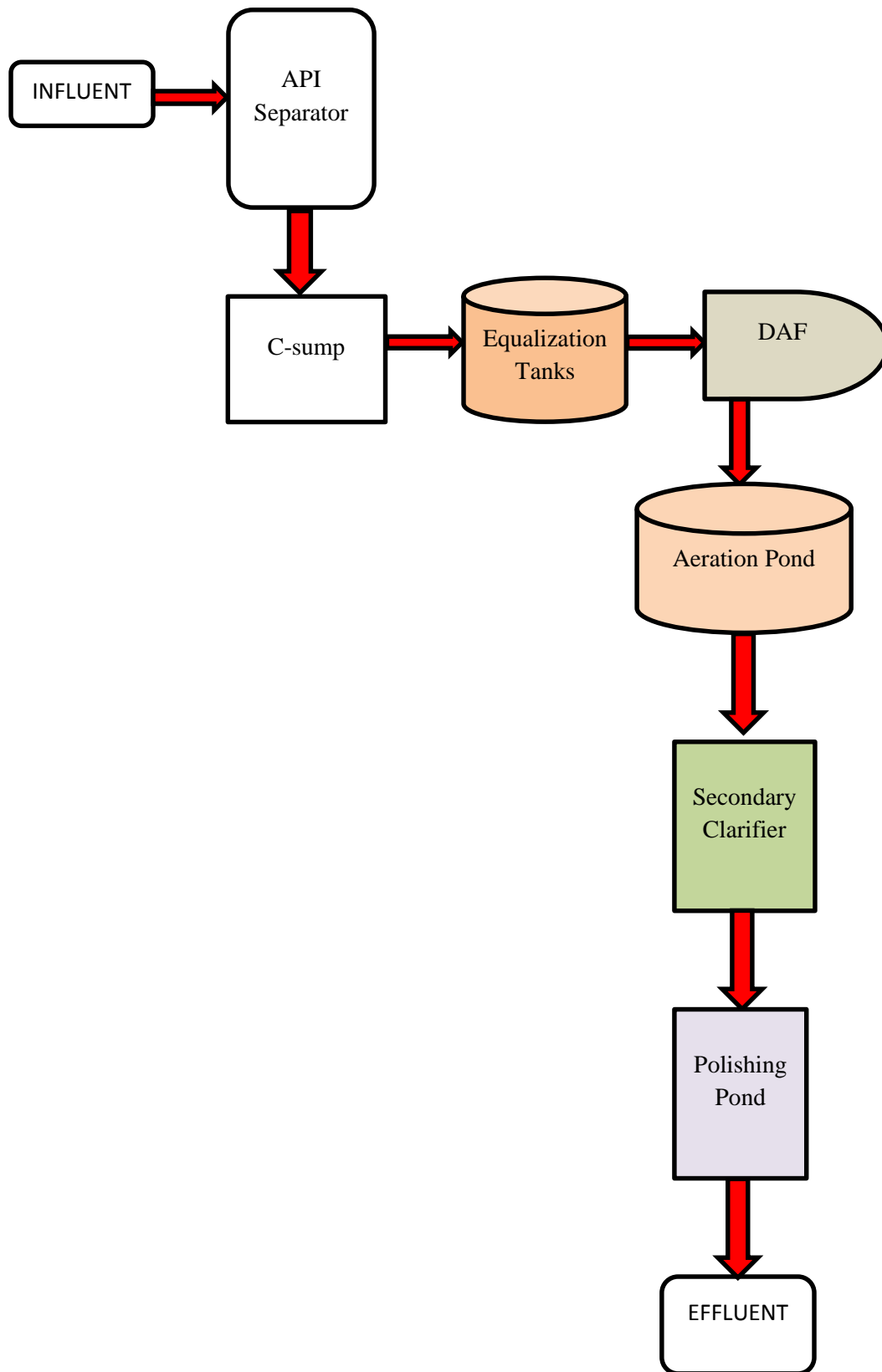


Figure 2.4. ETP flow diagram at ARL

The contaminant load in oily wastewater received at the ETP in ARL is treated via a primary and secondary treatment system before discharging the surplus volume in River Soan. A portion of the treated wastewater is reused in cooling operations and in fire utility systems. Approximately, 182.26 Megalitres of wastewater was discharged in the year 2018 and 78.4 Megalitres were recycled from the Effluent Treatment Plant and reused in various operations (ARL Sustainability Report, 2018). Flow meters/checks are installed at both receiving and discharge ends to control and quantify wastewater flows in m<sup>3</sup>/hr. Primary treatment is the first screening stage in any wastewater treatment plant and removes material that floats or settle by gravity by means of API separators paired with sumps, flow equalization tanks and dissolved air flotation unit (pre-DAF/DAF). The partially treated wastewater then undergoes biological treatment in the aeration tank or secondary treatment phase before finally rerouting the treated wastewater to “C-sump A-side” for reuse or discharging the super-fluent outside refinery premises. A brief concerning each treatment phase/unit and an all-inclusive technical details of ETP are provided in Table 2.3.

a) API – Oil/Water separator

The API oil/water separator, as the name implies was designed and constructed by the American Petroleum Institute and Rex Chain Belt Company to effectively isolate and extract bulking quantities of free oil droplets and suspended matter from refineries wastewater. Despite technological achievements, API separators are still the most preferred option of primary wastewater treatment prior to introducing wastewater stream to more advanced treatment processes, including DAF and biological processes. The basic design principle of API is separation by gravity, whereby the differences in specific gravities of oil, suspended solids and wastewater tends to form three separate layers; drifting heavier suspended solids at the bottom, free oil floats on top and a middle layer of water further subjected to downstream treatment processes.

Currently, five API separators are installed at ARL with varying volume handling capacities, however, for an ideal performance the flow distribution at the API inlet must be kept constant to support retention time so that most of the free oil floats to the surface. The design parameters of API limits its capacity to separate free oil droplets of size smaller than 150 microns. Oil particles of 150 micron in size and larger are continually skimmed off from the surface while lesser particles and particles in

emulsion will eventually exit the API outlet. Other design limitations and factors affecting efficiency include:

- Excessive sludge volume buildup
- Water temperature  $>5^{\circ}\text{C}$
- Oils having high density and escalated levels of dissolved hydrocarbons.

Wastewater exiting the outlets of separators is initially received in “B-side C- sump” at parallel to the ETP. This wastewater contains insoluble dispersed oil, emulsified oil, soluble organic and inorganic substances and settleable and suspended solids. The purpose of this sump is to prevent any flow and load variations at ETP by regulating flow and reserving large volumes of wastewater approaching from process area. The wastewater from “B-side C- sump” is pumped to two flow equalization tanks “TK-94” and “TK-95” to sustain a uniform homogenized load in the wastewater mixture. This flow is then further routed to the dissolved air floatation unit for treatment.

b) Dissolved air flotation – DAF

DAF is an effective process used for the treatment of industrial wastewater and efficiently removes suspended solids, fats, oil, grease and other pollutants from wastewater. In DAF system, wastewater feed is mixed with a stream of recirculated clarified “white water” saturated with dissolved air in a pressure vessel commonly known as the air drum. The wastewater prior to entering the floatation tank is usually dosed with a coagulant and/or flocculants to transform the particles into bigger sizeable clusters. Coagulants used in the process are dependent upon the temperature of water and concentration of pollutants in water. During the treatment, pollutants are removed by dissolving air in wastewater under pressure and then air is released in floatation tank at atmospheric pressure through a control valve. When streams of whitewater and wastewater merge with each other, very minute air bubbles stick to the contaminants. These bubbles and solid particles of waste adhere and rise to the top of the surface of tank and make a floating layer which is continuously removed by skimming devices. (Tetteh, E, and Rathilal, S, 2018) studied the operating factors of DAF for the removal of oil refinery wastewater pollutants and concluded that the system performed best with over 80% efficiency at air water ratio of 5-15%, air saturator pressure of 300-500 kPa, rising rate of 15minutes, dosage of 10mg/l and at optimum pH of 5. The clarified

wastewater from DAF then enters the biological aeration tank or the secondary treatment phase for further treatment.

c) Biological treatment (activated sludge process) – Secondary Treatment Phase

A conventional activated sludge process is operational at ARL as part of the secondary (biological) treatment to receive wastewater flow from the dissolved air flotation tank. First developed around 1912-1914, this process has a large variety in design. The basic components of AS are three, namely;

- An aeration tank with aerators serving as a bio reactor;
- The sedimentation tank (secondary clarifier) separating AS solids and treated wastewater,
- Lastly, a return activated sludge (RAS) system that is used to transfer settled AS from the clarifier back to the aeration tank influent.

The pure oxygen which is also known as the atmospheric air is introduced via mechanical aerators to a mixture containing primary treated wastewater which is combined with microorganisms to trigger and develop a biological floc. The mixture of biological mass and wastewater is commonly known as Mixed Liquor. The concentrations of dry solids in mixed liquor (MLSS) ideally ranges from 3-6 g/L. The feeding mechanism of microorganisms in the aeration tank causes the breakdown and reduction of biodegradable matter in the influent stream. Different boundary conditions control removal efficiency e.g. the hydraulic residence time (HRT) in the aeration tank, which is defined by aeration tank volume divided by the flow rate. Some other factors include; Influent load, oxygen supply and temperature.

Mixed liquor is discharged at the effluent of the tank and the supernatant can undergo further treatment before discharge or is run off to be discharged to a receiving water body. To the head of the aeration tank also known as RAS, the settled AS is returned in order to re-seed the new feed entering the tank. Biological growth often leads to excess sludge that eventually accumulates beyond the desired MLSS concentration in the aeration tank. This amount of Waste Activated Sludge is then removed from the clarifier to keep a balanced ratio between biomass and food supplied, this also helps in keeping the F: M ratio in a defined range. “WAS” prior to disposal is treated by digestion, either under anaerobic or aerobic conditions in isolated storage tanks. The treated water then enters a polishing pond acting as an accumulation basin

and the super-fluent is finally discharged outside the refinery premises or is pumped to “A-side C-sump” for reuse options.

Table 2.3. Details of Treatment Plant Units at Refinery

<b>Unit</b>	<b>Number</b>	<b>Area/Size</b>	<b>Effective Volume Handling</b>
API Separators	5	-	284812 US-Gallons
C-sump	1	-	598975 US-Gallons
Equalization Tanks	2	-	48026 US-Gallons
Pre-DAF	1	-	1437 US-Gallons
DAF	1	-	6932 US-Gallons
Aeration Pond	1	42.65ft L x 37.73ft W x 12.87ft D	138228 US-Gallons
Clarifier	2	9.84ft L x 32.81ft W x 12.87ft D	26340 US-Gallons
Polishing Pond	1	-	19751 US-Gallons



## CHAPTER 3

### RESULTS AND DISCUSSION

#### 3.1 Characterization of raw (influent) refinery wastewater

Continual monitoring of wastewater flow rates at a treatment facility is vital as it can affect the basic hydraulic characteristic and operational parameters of the treatment units. Industrial flow rates are typically constant, however, striking variations are noticeable during shut down, clean-up or operational failures, exposing the system to severe shock loadings. Designed to handle 200 US-GPM of flow rate, the average wastewater flow rate monitored at the ETP during the sampling campaign was 31.27 m<sup>3</sup>/h or 138 US-GPM, thus within the design limits. Variations in flow rate over time is also illustrated in the Figure 3.1.

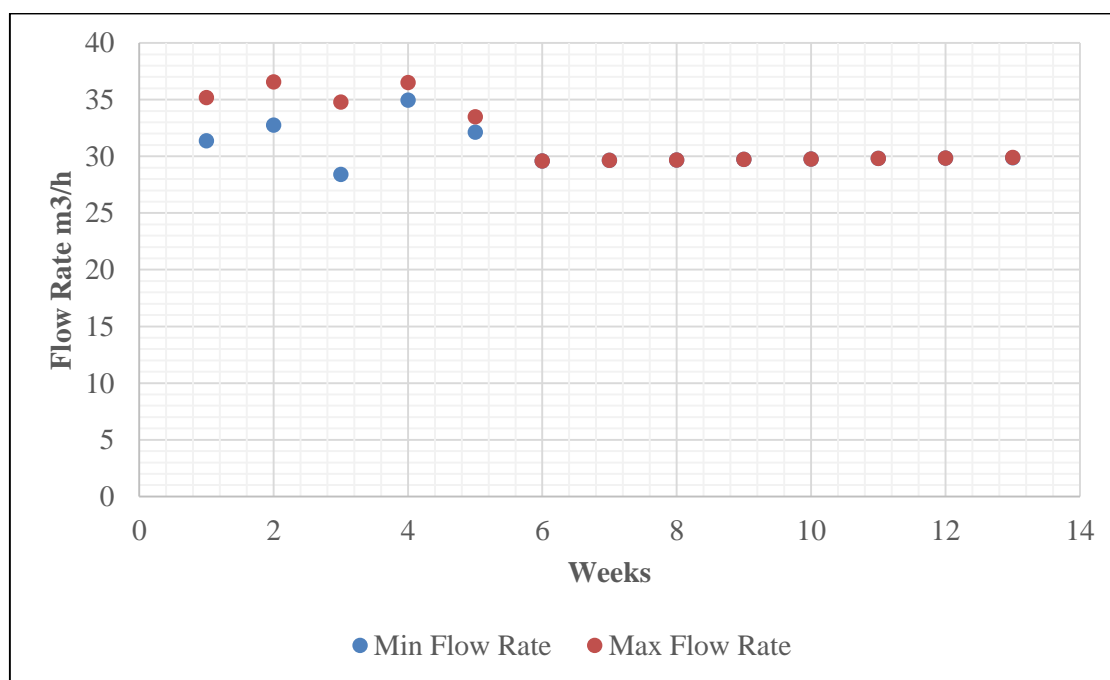


Figure 3.1. Flow rate in m<sup>3</sup>/h over time.

Table 3.1 illustrates the features and physicochemical characteristics of raw (influent) wastewater stream collected at DAF-inlet. Data formulated aided in the identification of wastewater constituents and their concentration ranges. The pH and Temperature of the Influent samples ranged from 7.06 to 8.3 and 4°C to 24°C respectively. TSS in influent ranges from 264 to 646 while TDS is found in concentration between 1588 and 3770. BOD<sub>5</sub> values varies at a minimum 60 and 138 maximum while values for COD concentration ranges between 270 and 916

respectively. O&G and phenolic contents were found in concentration ranging from 48 to 518.3 and 0.12 to 0.39. Results for Total nitrogen (TN) and Total phosphorus (TP) indicated concentration ranges of 2.5 to 28 and 0.12 to 0.76 respectively. Free cyanide was undetected in most influent samples except for three with concentration ranging from 0.01 to 0.02 thus its presence in wastewater stream cannot be overlooked. Moreover, influent stream was also found contaminated with heavy metals viz. arsenic and iron with varied concentrations ranging from 0.00464 to 0.00794 and 0.04 to 1.42 while mercury, vanadium, lead, nickel, copper and chromium were undetected in all influent samples.

Table 3.1. Analysis of physicochemical and heavy metal concentrations in influent samples

Samples	pH	Temp Increase	Concentration (mg/l)																
			TSS	TDS	BOD5	COD	O&G	Phenol	TN	TP	As	Hg	V	Fe	Pb	Ni	Cu	Free Cyanide	Cr
Sample-1	8.30	4	646	2149	132	660	134	0.39	5.7	0.12	0.00505	ND	ND	0.34	ND	ND	ND	ND	ND
Sample-2	7.76	4	553	3130	138	270	96	0.33	2.6	0.29	0.00526	ND	ND	0.08	ND	ND	ND	ND	ND
Sample-3	7.22	6	319	2198	84	410	356	0.38	ND	0.49	0.00794	ND	ND	0.19	ND	ND	ND	ND	ND
Sample-4	7.19	7	446	2471	96	480	258	0.12	14	0.33	0.00464	ND	ND	0.5	ND	ND	ND	0.02	ND
Sample-5	7.17	19	357	3030	90	447	272	0.27	28	0.49	0.00655	ND	ND	0.35	ND	ND	ND	ND	ND
Sample-6	7.64	20	384	1925	126	460	48	0.24	2.5	0.76	0.00651	ND	ND	0.14	ND	ND	ND	ND	ND
Sample-7	8.29	24	472	3770	134	662	86	ND	9.9	0.39	0.00775	ND	ND	1.42	ND	ND	ND	ND	ND
Sample-8	7.06	21	418	1588	114	556	126	0.25	15.2	0.5	0.00587	ND	ND	0.44	ND	ND	ND	ND	ND
Sample-9	8.01	21	317	3270	96	390	518.3	ND	6.9	0.29	0.0062	ND	ND	0.29	ND	ND	ND	ND	ND
Sample-10	7.91	20	625	2960	66	916	145	ND	11.6	0.41	0.00751	ND	ND	0.04	ND	ND	ND	ND	ND
Sample-11	7.71	20	616	3070	60	608	138.4	ND	4.1	0.6	0.00788	ND	ND	0.62	ND	ND	ND	0.02	ND
Sample-12	7.14	23	264	2791	102	518	91.5	0.34	2.7	0.29	0.00633	ND	ND	0.31	ND	ND	ND	0.01	ND
Minimum	7.06	4	264	1588	60	270	48	0.12	2.5	0.12	0.00464	0	0	0.04	0	0	0	0.01	0
Maximum	8.3	24	646	3770	138	916	518.3	0.39	28	0.76	0.00794	0	0	1.42	0	0	0	0.02	0
EPA limits	6-9	≤3°C	200	3500	80	150	10	0.1	-	-	1.0	0.01	-	8	0.5	1.0	1.0	1.0	1.0
IFC limits	6-9	≤3°C	30	-	30	125	10	0.2	10	2.0	0.1	0.003	1.0	3	0.1	0.5	0.5	0.1	0.5
DL	0.01	°C	1	0.5	0.1	10	5	0.1	0.01	0.03	0.0008	0.0008	0.02	0.02	0.04	0.01	0.03	0.01	0.02

\*ND=Not Detected; DL=Detection Limit

### **3.2 Characterization of the final effluent**

The aforementioned principal pollutant parameters were investigated as performance benchmark for the Effluent Treatment Plant at ARL. Table 3.2. Illustrates the experimental results representing the physicochemical features and concentrations of pollutants in the final effluent stream samples. The effluent eventually gets fused downstream in Soan River, therefore the concentration of pollutants in comparison with EPA & IFC, World Bank discharge standards and the potential impacts are discussed in the subsequent sections.

Table 3.2. Analysis of physicochemical and heavy metal concentrations in effluent samples

Samples	pH	Temp Increase	Concentration (mg/l)																
			TSS	TDS	BOD5	COD	O&G	Phenol	TN	TP	As	Hg	V	Fe	Pb	Ni	Cu	Free Cyanide	Cr
Sample-1	8.03	1	54	2090	96	240	26	1.56	7.1	2.87	0.00621	ND	ND	0.22	ND	ND	0.03	0.06	ND
Sample-2	7.99	1	15	1490	108	180	22	0.46	4.6	0.84	ND	ND	ND	0.18	ND	ND	ND	ND	ND
Sample-3	8.06	1	17	1871	24	40	ND	0.86	7	1.94	0.00566	ND	ND	0.44	ND	ND	ND	ND	ND
Sample-4	7.76	1	8	1877	54	108	ND	0.58	23	0.35	0.00212	ND	ND	0.06	ND	ND	ND	ND	ND
Sample-5	7.76	1	29	3360	42	84	174	1.3	6	1.41	0.00436	ND	ND	0.31	ND	ND	ND	ND	ND
Sample-6	7.75	1	67	2120	96	192	ND	1.51	1.2	1.93	0.00491	0.00193	ND	0.27	ND	ND	ND	ND	ND
Sample-7	7.79	1	50	3170	108	216	42	ND	9	0.48	0.00529	ND	ND	0.02	ND	ND	ND	ND	ND
Sample-8	7.75	1	14	1684	84	140	ND	0.26	0.06	0.39	0.00232	ND	ND	0.05	ND	ND	ND	ND	ND
Sample-9	7.64	1	31	2670	102	170	ND	ND	5.4	0.12	0.00569	ND	ND	ND	ND	ND	ND	ND	ND
Sample-10	8.12	1	69	2550	84	140.5	ND	ND	9.7	0.17	0.00653	ND	ND	0.02	ND	ND	ND	ND	ND
Sample-11	7.89	1	21	2810	78	133	ND	ND	10.3	0.11	0.00347	ND	ND	0.12	ND	ND	ND	ND	ND
Sample-12	7.41	1	53	1730	86	120	37.8	ND	8.05	0.08	0.00468	ND	ND	0.02	ND	ND	ND	ND	ND
Minimum	7.41	1	8	1490	24	40	22	0.26	0.06	0.08	0.00212	0.00193	ND	0.02	ND	ND	0.03	0.06	ND
Maximum	8.12	1	69	3360	108	240	174	1.56	23	2.87	0.00653	0.00193	ND	0.44	ND	ND	0.03	0.06	ND
EPA limits	6-9	≤3°C	200	3500	80	150	10	0.1	-	-	1	0.01	-	8	0.5	1	1	1	1
IFC limits	6-9	≤3°C	30	-	30	125	10	0.2	10	2	0.1	0.003	1	3	0.1	0.5	0.5	0.1	0.5
DL	0.01	°C	1	0.5	0.1	10	5	0.1	0.01	0.03	0.0008	0.0008	0.02	0.02	0.04	0.01	0.03	0.01	0.02

\*ND=Not Detected; DL=Detection Limit

### 3.2.1 Variation of pH and Temperature

In the present study, pH values for all twelve samples of the final effluent were slightly alkaline but within the discharge limits regulated by EPA and IFC, World Bank. The average effluent pH throughout the experimental period was 7.8. The maximum and minimum pH values observed were 8.12 and 7.41 respectively and values are organized in Table 3.2.

pH in common terms is defined as to what extent the water is acidic or basic and is a critical quality parameter of both natural/surface waters and wastewaters. pH in natural waters plays a pivotal role in the availability and solubility of many chemical constituents, thus its impacts are far reaching. Many heavy metals are soluble at low pH, therefore their solubility in-effect determines the toxicity of these metals. At high pH values the toxicity of ammonia surges (Walakira and Okot Okumu, 2011). The optimum pH value discharge limits set by EPA and IFC, World Bank falls between 6-9. Surges in pH even for a short span can alter microbial growth therefore treatment plants must monitor and balance the pH of process influent and effluent for better performance. (Ghanizadeh and Sarrafpour, 2001) in their findings revealed that COD removal percentage increases from 87% to 96% while the amount of SS in effluent decreased substantially when pH values were in the range 5.7 to 9.0. Data analysis indicated that pH values in nine effluent samples were slightly above the values recorded at influent stream. The trend has been supported by literatures where a positive relationship was found between increase in nitrate concentration and increase in pH values at the effluent in an aerobic process (Colmenarejo et al., 2006). (Villaverde et al., 1997) reported reduction in CO<sub>2</sub> by stripping in aeration process, contributing to the slight increase of pH in effluent. Graphical representation of the data with acceptable pH range for the study period is presented as Figure 3.2.

EPA and IFC, World Bank sets the limit for industrial effluent temperatures at  $\leq 3^{\circ}\text{C}$ . In the current study, varying temperature extremes were recorded in the influent samples, whereas temperature records of the final effluent in all samples were rounded at  $1^{\circ}\text{C}$ .

Temperature is another vital parameter as it greatly influences biological growth and activity by promoting or hindering chemical reactions and reaction rates. Higher temperatures of water tends to dissolve lesser oxygen, thereby lowering dissolved

oxygen concentration and an increase in biochemical reactions would further deplete its concentration thus putting the survival of aquatic life at risk.. Water is used in various refinery operations including desalination, steam stripping and heat exchangers etc. elevating its temperature up to 20°C and more. The significant drop in water temperature in the final effluent can be contributed to lower air temperatures during winter months (Dec, Jan & Feb). Figure 3.3 represents the acceptable range and temperature records of influent and effluent samples.

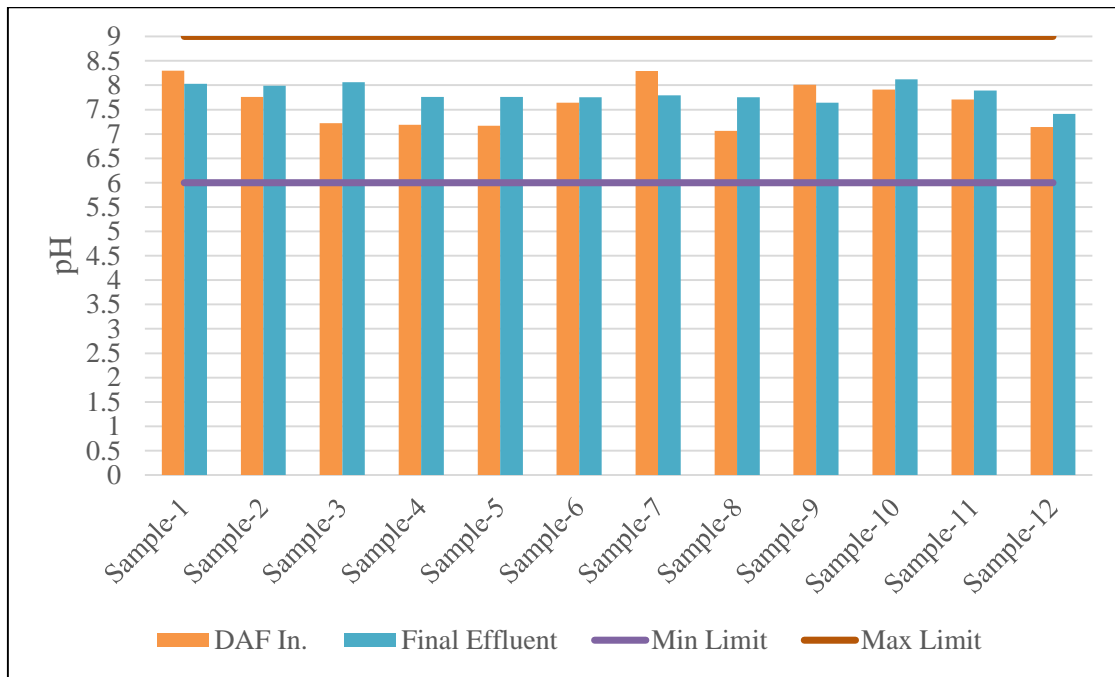


Figure 3.2. Variation of pH in influent and effluent samples

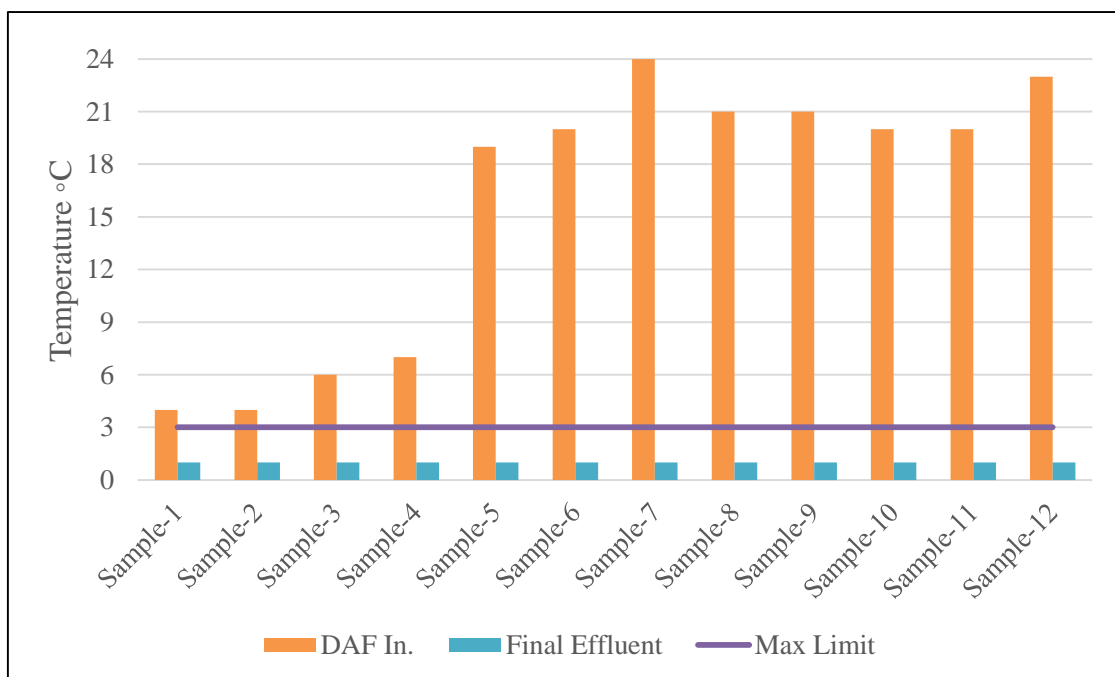


Figure 3.3. Variation of temperature in influent and effluent samples

### 3.2.2 Variation of TSS and TDS

Table 3.2 shows that the minimum value of TSS recorded was 8mg/l while maximum concentration was reported to be 69mg/l with an average of 35.6 mg/l for all effluent samples. The effluent discharge limits for TSS set by EPA is 200mg/l, while IFC, World Bank exercises a more stringent standard of 30mg/l. Diverse concentrations were found in influent samples due to fluctuations in flow rates, and these were reduced to acceptable limits in all effluent samples with an average removal efficiency of 90%. In comparison with the IFC, World Bank guidelines, six effluent samples (Sample-1, 6, 7,9,10 & 12) were recorded out of range.

TSS doesn't float on water layer but are rather in suspension and constitute an extensive range of organic and inorganic matter/particles that are held in suspension due to turbulence. TSS is regarded as an important performance indicator in the wastewater treatment system and any deterioration of the treatment units can lead to high concentrations of TSS released in the receiving water body which can alter its physical, biological and chemical properties. The interrelationship between these are such that alterations in physical alone can trigger a corresponding effect on the latter properties. (Bilotta and Brazier, 2008) summarized the physical, biological and chemical alterations as; temperature changes, reduced light infiltration, release of heavy metal contaminants and affecting aquatic biota by critically depleting dissolved oxygen levels. (Owens et al., 2005) reported that TSS concentration levels as low as 8mg/l would cause 3-13% reduction in primary productivity in periphyton and macrophytes. Figure 3.4 presents TSS values for influent and effluent samples and compliance benchmark achieved against EPA and IFC, World Bank standards.

TDS values in effluent samples for the research period varied between 1490mg/l and 3360mg/l with an average of 2285mg/l and are within the permissible limits. EPA defined effluent discharge limits for TDS is 3500mg/l while IFC, World Bank has not defined standards for TDS discharge.

TDS is the summation of all inorganic and organic substances in a liquid in dissolved form existing either as ionized, molecular or in a colloidal sol suspension and is yet another an important water quality parameter. In common terms, the hardness of water is defined by its TDS values. Higher TDS concentrations (500 – 30,000ppm) will cause the water to taste brackish thereby affecting its palatability. Higher fluctuations in



TDS values tends to affect wildlife and aquatic biota more as compared to humans. (Bernstein, 1961) raised major concerns on how high osmotic conditions and specific ion exertion will cause acute or chronic toxicity in plant tissues. Re-use of wastewater in industrial applications is also dependent on its TDS concentrations, as excessive salts will cause scaling and corrosion and will shorten the service life of process units. Figure 3.5 presents TDS values for influent and effluent samples and compliance benchmark achieved against EPA standards.

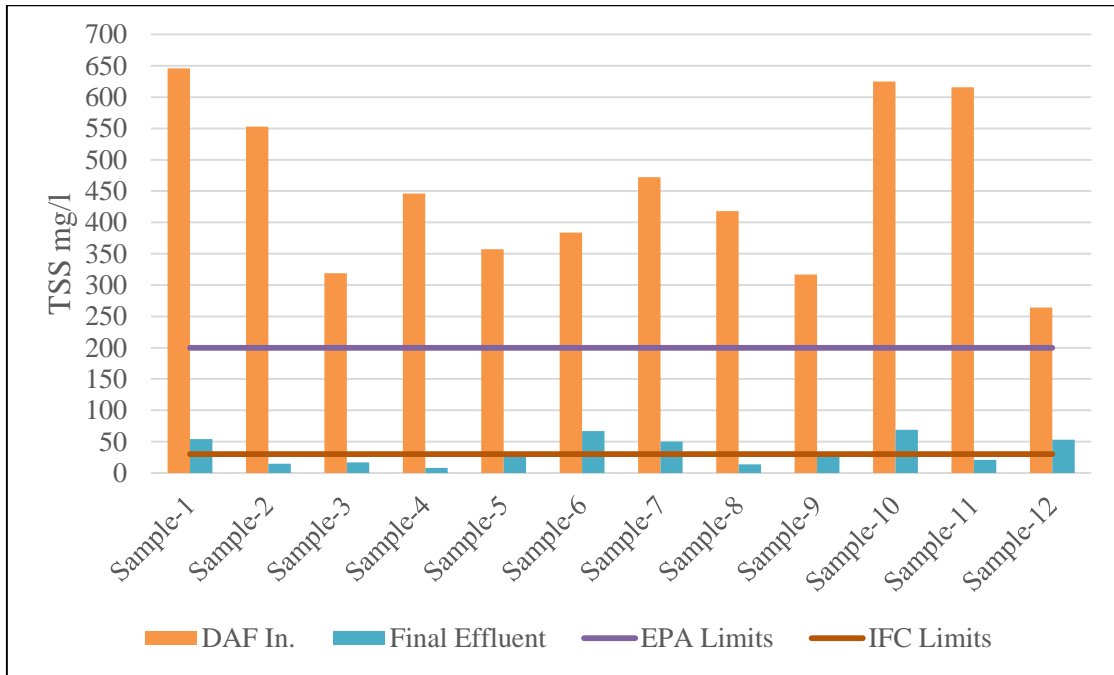


Figure 3.4. Variation of TSS in influent and effluent samples

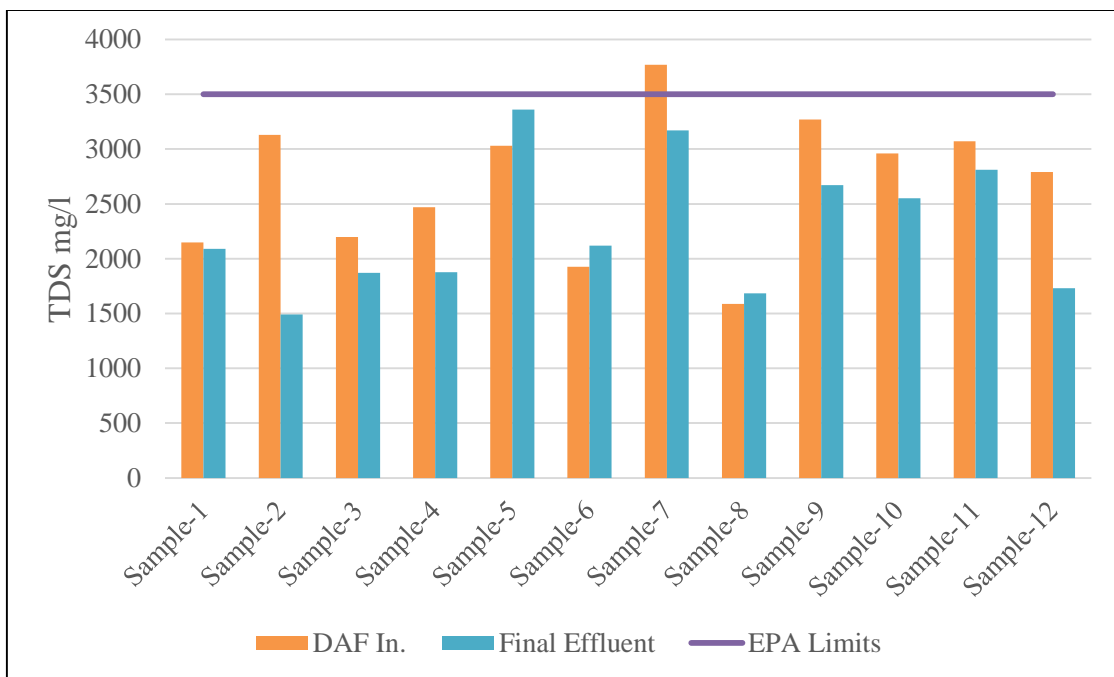


Figure 3.5. Variation of TDS in influent and effluent samples

### 3.2.3 Variation of phenols

In the undertaken study, Phenols detected in seven effluent samples were found in concentrations between 0.26mg/l and 1.56mg/l with an average of 0.93mg/l, while its concentration was undetected in five effluent samples. Detected values of phenols in all seven samples were exceeding the permissible limits laid by both EPA and IFC, World Bank. Industrial effluent discharge limit for phenols ruled by EPA is 0.1mg/l while IFC, World Bank has adopted 0.2mg/l as discharge standards for phenol and its compounds.

Phenols in organic chemistry are defined as the hydroxy derivatives of benzene and are considered among the class of most hazardous organic compounds due to its known toxicity and persistency and are registered by US EPA in the list of priority pollutants. Phenols naturally exist in our ecosystem but their concentrations are exacerbated when phenols and their derivatives are released as waste products of industrial activities. The hydroxy radical in phenols often gets surrogated with chlorine atoms, gets nitrated, methylated or alkylated aggravating the toxic action of these eco toxins. (Michalowicz and Duda, 2006) has termed the fate of phenols as hepatotoxic, hematotoxic, and provoking carcinogenesis and mutagenesis in humans and other life forms. Effluent discharges of petroleum refinery constitute phenolic compounds and are responsible for the contamination of receiving water bodies. (Delfino and Dube, 1976; Kadi and Benrachedi, 2018) has reported phenol detection in groundwater due to leaching and mobility through soil. (Kobayashi et al., 1979) reported bio concentration factor of 0.28 for phenols in goldfish and 1.3 for golden orfe. Due to these rising concerns, effluent discharges in water bodies must be regularly investigated for their phenolic concentrations. Phenolic concentration in the detected effluent stream exhibited a slight increase as compared to influent samples. The results could stem from one time spot (grab) sampling or fluctuations in changing flow over time. Extensive literature was reviewed to understand the fate of phenol compounds in wastewater treatment system. (Hansen and Lassen, 2008) studied the fate and behavior of phenolic compounds in nordic environment and concluded a similar trend of increase in concentration at some effluent stream due to degradation of several poly structured phenolic compounds into mono-units.

(Short et al., 1974) studied the trend of phenolic wastewater in US petroleum refineries and their research was reviewed and approved by the Office of Research and Development, US EPA. In one of the petroleum refinery investigated by the authors, same trend was observed in influent and effluent samples during their second week sampling. The refinery had the same treatment system as in the current study. Slightly increased effluent concentration as compared to influent was reported similar to the current research. The authors termed this trend as “upset” of the system and attributed this upset to increased sulfur compounds in the system or its derivatives. Although this upset was not continuous over time. Phenols or phenolic is a direct bonding of hydroxyl group (-OH) to aromatic hydrocarbons. Based on the number of phenol units, they can be classified as polyphenols. Mercapto-phenols are compounds analogous to phenols except the oxygen atom in the hydroxyl group (-OH) bonded to the aromatic ring is replaced by a sulfur atom. The trend in the current research can be attributed to a cause incurred by sulfur or its derivatives, thereby resulting in slight increase in effluent samples. Authors further stated that changes in phenolic concentrations will upset biological systems easily and at times biological systems will upset with no obvious cause. Figure 3.6 presents Phenol values for influent and effluent samples and compliance benchmark achieved against EPA and IFC, World Bank standards.

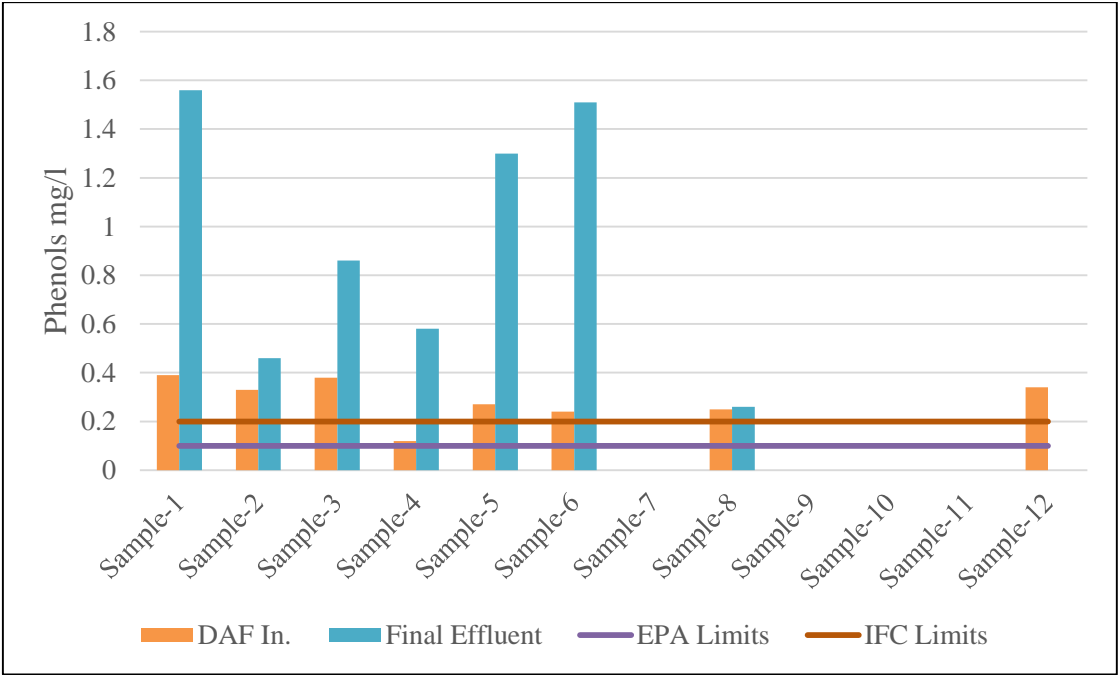


Figure 3.6. Variation of phenols in influent and effluent samples

### 3.2.4 Variation of oil and grease

In the current study, O&G concentrations in seven effluent samples were undetected (LOD=5mg/l) while other five samples exhibited values exceeding the permissible limits with minimum and maximum values reported at 22mg/l and 174mg/l respectively. O&G analyses has become a common performance index in wastewater treatment system and both EPA and IFC, World Bank has defined the maximum discharge limit of 10mg/l for industrial effluents

Oily wastewater stream in refineries is generated in consequence of process operations utilizing water in desalting units, using as a stripping medium in distillation and from tank bottoms and contains oil in phases either as free, dissolved or emulsified oil. O&G content of refinery wastewater contains a wide range of related organic compounds and several other toxic compounds including petroleum hydrocarbons, polycyclic and polyaromatic hydrocarbons with variable concentrations based on nature of crude oil processed. (Pawlak et al., 2008) interpreted the experimental results of TPH and O&G in petroleum contaminated soils and defined that TPH fraction accounted for O&G with ratios ranging between 12% - 50%. Higher concentrations of O&G discharged in receiving water bodies have deleterious impacts on the ecosystem. They are generally known for their floating properties forming layers on top of aqueous medium, inhibiting light penetration and altering concentrations of dissolved oxygen. Constituents in O&G can even persist in environment for longer periods and PAH in particular have been reported to travel up food chains due to their lipid-based solubility in lower life forms. (Pawlak et al., 2008) reported excessive amounts and load fluctuations over flow rate as factors to disturb aerobic process and reducing treatment/removal efficiency. Figure 3.7 presents O&G values for influent and effluent samples and compliance benchmark achieved against EPA and IFC, World Bank standards.

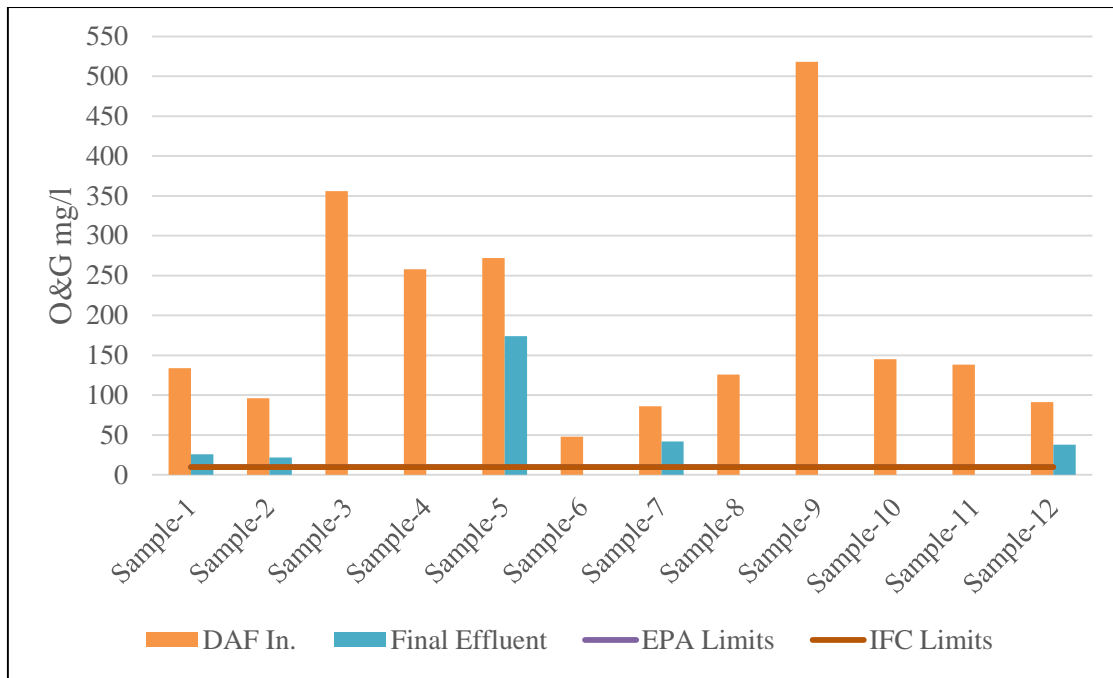


Figure 3.7. Variation of O&G in influent and effluent samples

### 3.2.5 Variation of total nitrogen (TN) and total phosphorus (TP)

In the present study, the minimum, maximum and average TN concentrations were recorded at 0.06mg/l, 23mg/l and 7.6mg/l respectively. TN concentrations in two effluent samples were reported out of range. IFC, World Bank exercises strict discharge limits of 10mg/l for Total nitrogen (TN) in industrial effluents while EPA has defined standards for NH<sub>3</sub> at 40mg/l whereas discharge limits for TN are unavailable.

Total nitrogen is accounted as the sum total of organic nitrogen, ammonia, nitrite and nitrate and forms an integral part of the biogeochemical cycle acting as an essential bio stimulant in life forms. On the other hand, the over enrichment has induced nutrient imbalances in the system, cultivating toxic algal blooms, intensifying frequencies of hypoxic and anoxic events in ecosystem and causing biodiversity loss. Moreover, many toxicological and infectious diseases in humans and wildlife have been attributed to the nutrient enrichment of certain forms of nitrogen. A constituent of concern released in refinery effluents is ammonia-nitrogen and its concentrations as low as 1mg/l have been classified as toxic to the environment. Data analysis revealed that effluent values in first four samples were higher in contrast to influent values followed by a decreasing trend in later samples except for the last two samples where a repetitive behavior of slightly higher effluent values were observed. (Santo et al., 2015) attributed this reverse trend to the addition of feed in ASP process to nurture bacteria

and sustain C/N/P ratio, resulting in a net increase of nitrogen in system life later on. (Shen et al., 2012) reported higher TN values in effluent as organic nitrogen emission in the system due to bacterial death. (Adonadaga, 2014) reported this trend in his research as shock loads by ammonia or reduced nitrification due to inhibition by other chemicals. (Figuerola and Erijman, 2010) interpreted higher TN values in effluent stream corresponding to increased phenolic concentrations. Figure 3.8 presents TN values for influent and effluent samples and compliance benchmark achieved against IFC, World Bank standards.

The minimum, maximum and average TP concentrations reported were 0.08mg/l, 2.87mg/l and 0.8mg/l respectively. TP in discharged industrial effluents must be monitored for compliance with regulatory standards. IFC, World Bank has adopted 2mg/l for TP discharge in receiving waters while EPA has not devised limits for TP. Total Phosphorus concentration in sample-1 was out of range and in non-compliance with the IFC limits while all other samples were within the regulatory limits.

Total Phosphorus is also regarded as an essential nutrient for plants, animal and human growth and its absorption in fair concentrations are adequate for survival, while hyper mineralization of TP tends to create ecological imbalances proving detrimental to the ecosystem. Few Decades back cultural eutrophication started intensifying as more and more anthropogenic TP was released in natural environment speeding the proliferation of many unwanted algal blooms, creating deoxygenated environment and causing premature aging and mutations. (Gazulla et al., 2017) indicated the presence of phosphorus in refineries in antifouling additives and crude oil processed, making its way in refinery wastewater. A reverse trend of higher TP concentration in seven effluent samples were observed and this behavior is normal for wastewater treatment system's life cycle and can be understood by looking into the fate of phosphorus during the treatment system. In a biological removal system such as ASP, organisms accumulating phosphorus settles with sludge and must be wasted during sludge removal as "excess sludge". Increased sludge life can contribute more problems to the system. Phosphorus that does not settle with the sludge is released in effluent either as dissolved form or with TSS. A small amount of TSS could contribute to increased total phosphorus content in final effluent if sludge life and removal of "surplus sludge" is not kept into consideration. Another factor of consideration is the secondary release of phosphorus. This secondary phosphorus is attributed to the microorganism's cell which

rather does not store the nutrient as intracellular energy. Figure 3.9 presents TP values for influent and effluent samples and compliance benchmark achieved against IFC, World Bank standards.

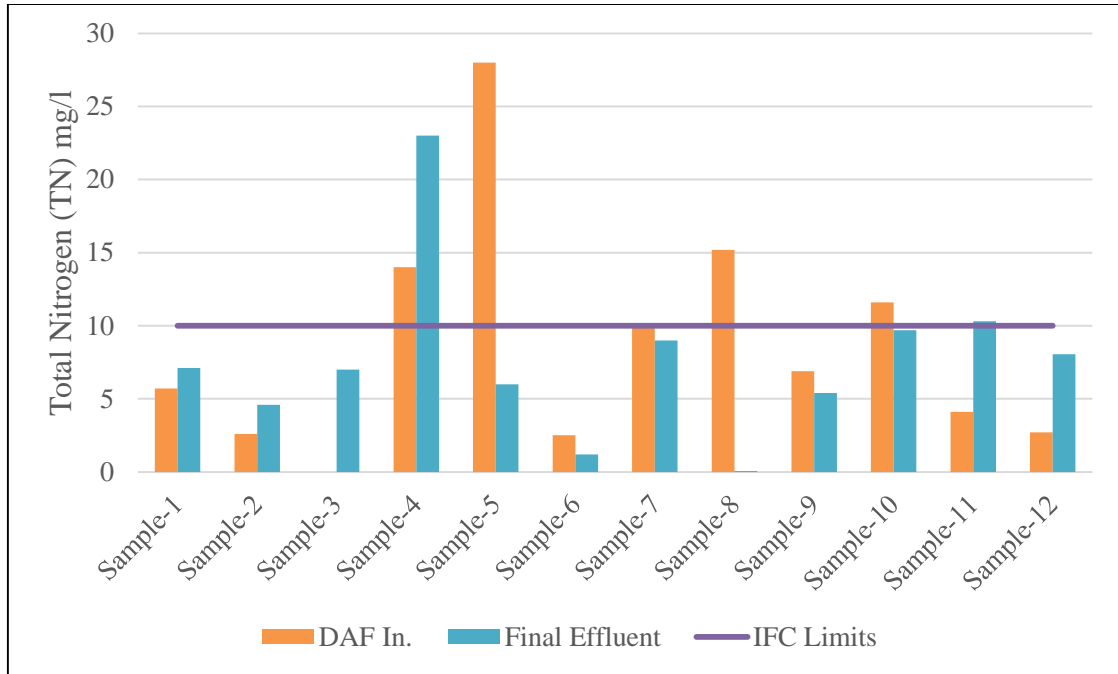


Figure 3.8. Variation of TN in influent and effluent samples

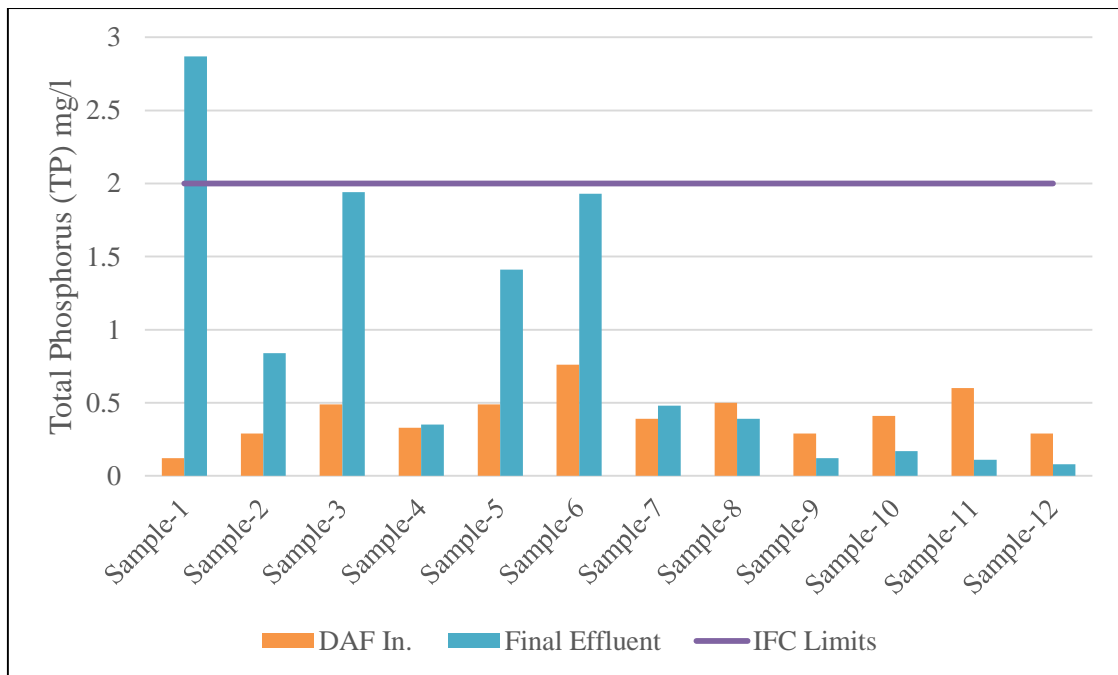


Figure 3.9. Variation of TP in influent and effluent samples

### 3.2.6 Variation of BOD5 and COD

In the present research, the minimum, maximum and average BOD5 concentrations reported were 24mg/l, 108mg/l and 80mg/l respectively. BOD5 is a

widely used quality index parameter in wastewater treatment and EPA prescribed limit for industrial effluent discharge is 80mg/l while IFC, World Bank has enacted a stricter limit of 30mg/l. In four detected effluent samples, BOD5 values were within the permissible limits of EPA while concentrations were slightly above or higher in other samples. In comparison with IFC, World Bank standards, except for Sample-3, reported values of all other samples were out of range.

Biochemical Oxygen Demand or BOD5 is a substitutive term for the extent of organic pollution of water/wastewater and further elaborated as a bioassay procedure quantifying the amount of oxygen desired by aerobic organisms to breakdown putrescible organic matter. The oxygen consumed is expressed as milligrams per litre of sample during 5-days of incubation at 20°C. The self-cleansing ability of water is steered by microorganism consuming oxygen at steady states to breakdown pollutants, though aggressive discharge of organic pollutants in receiving inland waters by increased industrial activities means an overconsumption of dissolved oxygen levels, thus creating anaerobic conditions and threatening the existence of higher life forms. (Wen et al., 2017) projected changes in water patterns due to climate change and overexploitation/pumping of water resources as agents swelling up impacts of organic pollutants on an entire ecosystem. (Ukpong et al., 2014) in his research on water quality analysis of groundwater samples (dug wells & boreholes) reported higher BOD values than the acceptable standard of 2-4mg/l set by WHO, indicating higher organic pollution. (Pal et al., 2014) indicated sludge bulking, foaming and rising solids as common operating problems impairing the removal efficiency and performance of Activated sludge process. Figure 3.10 presents BOD5 values for influent and effluent samples and compliance benchmark achieved against EPA and IFC, World Bank standards.

In the present study, minimum, maximum and average COD concentrations reported were 40mg/l, 240mg/l and 146mg/l respectively. EPA permissible limit for COD in industrial effluents is 150mg/l whereas IFC, World Bank defined limit is 125mg/l. COD reported concentrations in five effluent samples were not within the prescribed limits of EPA while in comparison with IFC, World Bank standards, eight effluent samples were out of range.

Chemical Oxygen Demand (COD) much like BOD is an indication of the extent of pollutant load in water/wastewater measured as oxygen equivalent of the amount of



organic matter oxidized by a strong oxidizing agent as potassium dichromate and is preferred over BOD due to its short test run and its ability to oxidize matter that are not quantifiable in a BOD test. COD analysis is performed in correlation with BOD to assess the quality of wastewater being discharged in receiving water bodies. Figure 3.11 presents COD values for influent and effluent samples and compliance benchmark achieved against EPA and IFC, World Bank standards.

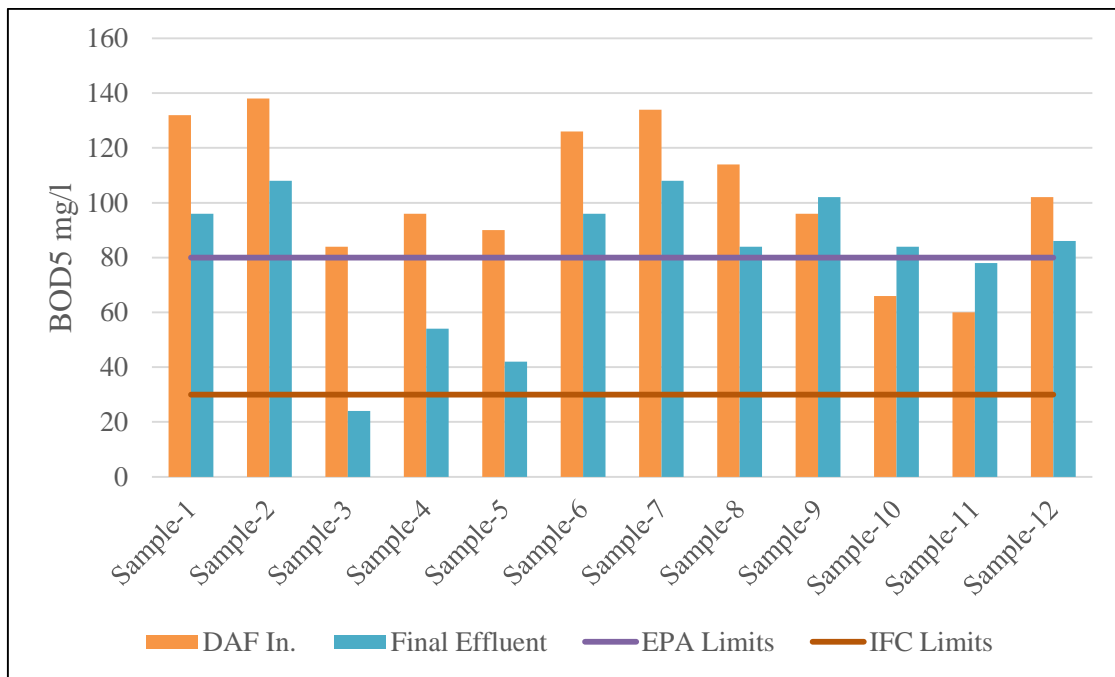


Figure 3.10. Variation of BOD5 in influent and effluent samples

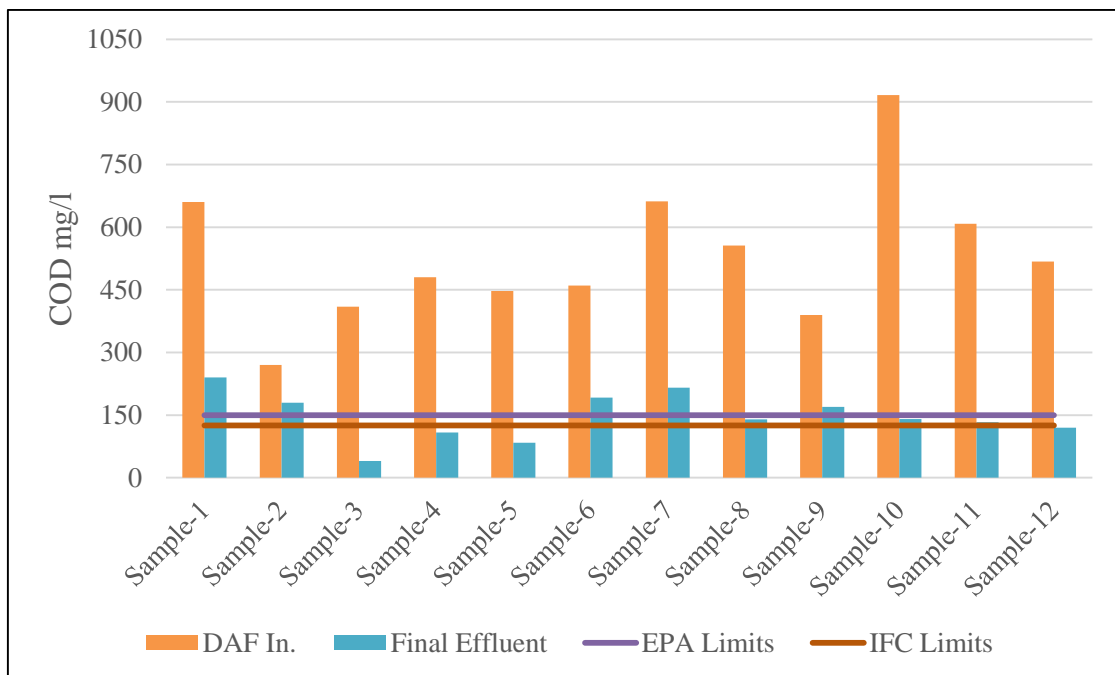


Figure 3.11. Variation of COD in influent and effluent samples

### **3.2.7 Variation of free cyanide**

In the present study, free cyanide was detected in just three influent samples and as for the final effluent, free cyanide was undetected in all samples except for Sample-1 with concentration of 0.06mg/l. EPA defined limit for free cyanide in industrial effluents is 1mg/l while IFC, World Bank has enforced 0.1mg/l discharge standard.

Free cyanide is defined as the sum of hydrogen cyanide (HCN) and its salts and is the most toxic form of cyanide such that a single teaspoon of 2% solution is sufficient to kill a person. The exposure pathway is through ingestion, inhalation and absorption and its concentration even in low doses can cause seizures, permanent paralysis, nervous lesions, and liver and kidney damage. The anthropogenic entrance of free cyanide in waterways is through industrial effluents. Due to extreme poisoning, its presence must not be ignored and effective monitoring should be imposed.

### **3.2.8 Variation of heavy metals**

Both influent and effluent wastewaters were analyzed for heavy metals including; arsenic, mercury, vanadium, iron, lead, nickel, copper, and chromium. Throughout the sampling campaign chromium, nickel, lead, and vanadium were undetected in all influent and effluent samples while mercury and copper were detected in one effluent sample each with concentrations of 0.00193mg/l (Sample-6) and 0.03mg/l (Sample-1).

The minimum, maximum and average As concentrations in the present study were 0.00212mg/l, 0.00653mg/l and 0.00465mg/l respectively. EPA permissible limit for arsenic discharge in industrial effluents is 1mg/l while IFC, World Bank exercises 0.1mg/l as a discharge standard. . All values were within the permissible limits set out by both EPA & IFC, World Bank.

Arsenic toxicity of water bodies is among the major environmental concerns of modern world (Mandal et al., 2017). Short and long term exposure to arsenic have been reported to cause neuropathological disorders, endothelial cell dysfunction, inflammation, oxidation and angiogenesis. Neurochemical alterations were reported in animals and lower life forms. Other detrimental effects of arsenic identified were higher risks of cancer (Panagiotaras and Nikolopoulos, 2015). (Barwick and Maher, 2003) studied the bio transference and bio magnification factor of arsenic and

concluded positive relation through three successive trophic levels within four food web chains. (Hayase et al., 2010) studied the bio magnification profile of arsenic in deep sea ecosystem of Japan and reported significant positive transference of lipid-soluble arsenic in pelagic organisms. Figure 3.12 presents Arsenic values for influent and effluent samples and compliance benchmark achieved against EPA and IFC, World Bank standards.

In the present study, the minimum, maximum and average values for Iron were reported to be 0.02mg/l, 0.44 mg/l and 0.2 mg/l respectively. EPA has defined a permissible limit of 8mg/l for iron in industrial effluent discharge while IFC, World Bank regulates 3mg/l as a discharge standard. All effluent concentrations were within the prescribed limits of EPA & IFC, World Bank.

Iron is an essential element that drives many basic physiological features of the body but an overload of iron can cause severe poisoning and in extreme cases hypovolemic shock or even death due to liver failure. (Xing and Liu, 2011) studied the effects of iron on the ecology and physiology of aquatic plants and reported that iron toxicity greatly influenced the entire species composition and even their morphology and anatomy. (Grazuleviciene et al., 2009) investigated the long term exposure of iron in drinking water supplies and reported an escalated risk of delivering low birth weight (LBW) newborns. Figure 3.13 presents Iron values for influent and effluent samples and compliance benchmark achieved against EPA and IFC, World Bank standards.

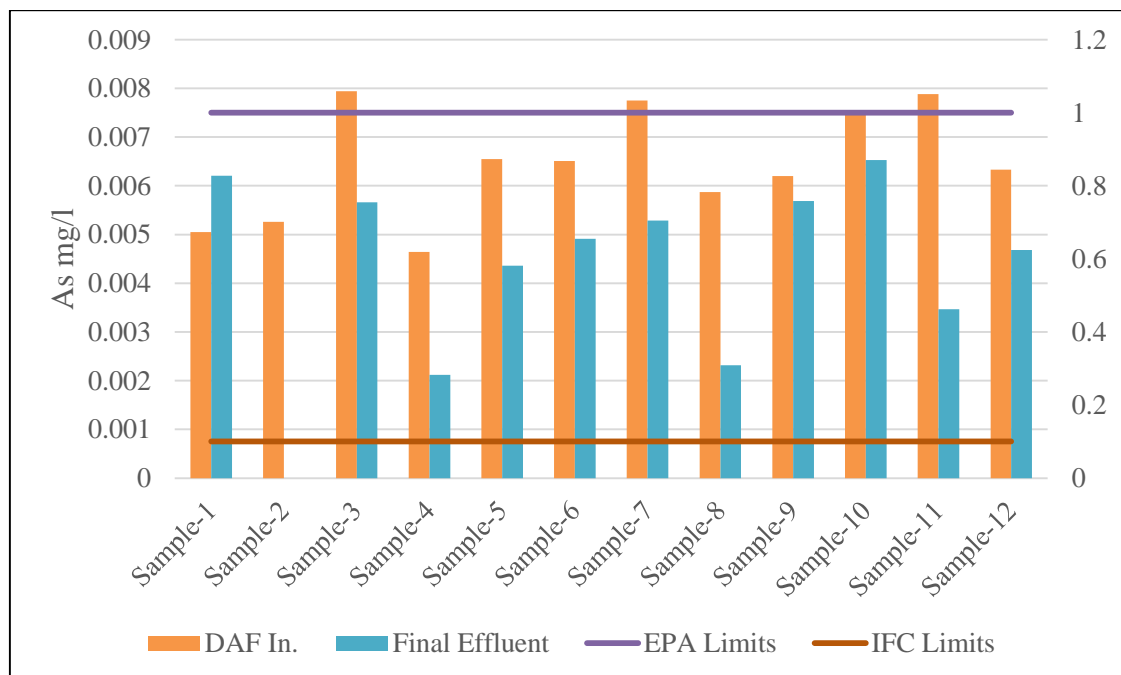


Figure 3.12. Variation of Arsenic in influent and effluent samples

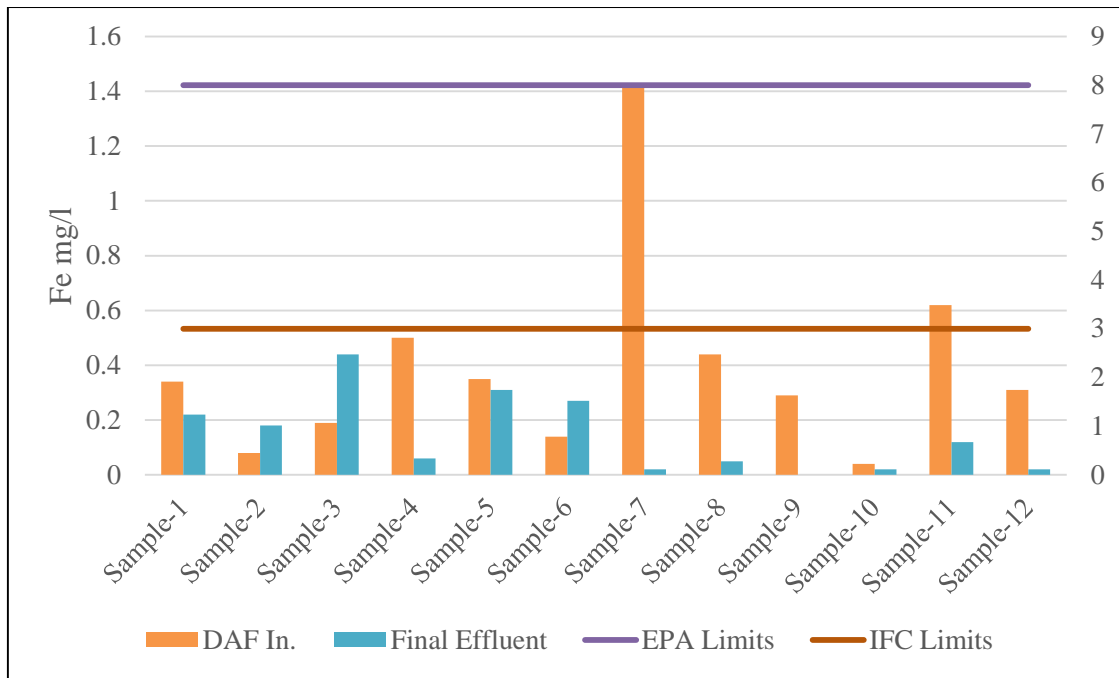


Figure 3.13. Variation of Iron in influent and effluent samples

### 3.3 Statistical correlation matrix

This statistical technique defines the linear relationship among variables and the matrix is portrayed as a mirror image of variables with direct increasing, inverse or uncorrelated relationship. An increase or decrease in the value of a parameter with an equivalent increase or decrease in other parameter exhibits a positive correlation while an inverse relation among values displays a negative correlation. The coefficient ( $r$ ) value ranges between +1 and -1 with strong interdependencies appearing in the range of +0.8 to 1.0 and -0.8 to -1.0, weak ranging between +0.0 to 0.5 and -0.0 to -0.5, and moderate stretching from +0.5 to 0.8 and -0.5 to -0.8. Table 3.3 shows correlation among tested effluent wastewater quality parameters.

Table 3.3. Heat-map correlation matrix

Variables	pH	Temp	TSS	TDS	BOD5	COD	O&G	Phenol	TN	TP	As	Hg	Fe	Cu	CN-
pH	1														
Temp	0.00	1													
TSS	-0.01	0	1												
TDS	-0.01	0	0.24	1											
BOD5	-0.15	0	0.42	-0.04	1										
COD	0.04	0	0.48	0.05	0.89	1									
O&G	-0.19	0	0.01	0.54	-0.29	-0.19	1								
Phenol	0.23	0	0.13	-0.07	-0.28	0.08	0.33	1							
TN	0.03	0	-0.23	0.06	-0.31	-0.23	-0.09	-0.19	1						
TP	0.41	0	0.20	-0.11	-0.20	0.17	0.18	0.91	-0.28	1					
As	0.09	0	0.69	0.45	-0.07	0.08	0.03	0.12	-0.09	0.28	1				
Hg	-0.12	0	0.45	-0.08	0.19	0.25	-0.16	0.49	-0.35	0.35	0.10	1			
Fe	0.41	0	-0.14	-0.06	-0.59	-0.36	0.29	0.76	-0.25	0.79	0.07	0.28	1		
Cu	0.32	0	0.26	-0.10	0.19	0.52	0.01	0.52	-0.03	0.67	0.31	-0.09	0.1	1	
CN-	0.32	0	0.26	-0.10	0.19	0.52	0.01	0.52	-0.03	0.67	0.31	-0.09	0.1	1	1

The output data with heat-map overlay image demonstrates strong positive correlation among COD-BOD5 ( $r=0.89$ ) and TP-Phenols ( $r=0.91$ ), moderate positive interrelationship among parameters; As-TSS, O&G-TDS, Cu-COD, CN<sup>-</sup>-COD, Fe-Phenols, Cu-Phenols, CN<sup>-</sup>-Phenols, Fe-TP, Cu-TP, CN<sup>-</sup>-TP. While weak or slightly weak correlation was observed between variables; Phenols-pH, TP-pH, Fe-pH, Cu-pH, CN<sup>-</sup>-pH, TDS-TSS, BOD5-TSS, COD-TSS, Hg-TSS, Cu-TSS, CN<sup>-</sup>-TSS, As-TDS, Phenols-O&G, Hg-Phenols, As-TP, Hg-TP, Cu-As, CN<sup>-</sup>-As, Fe-Hg, Cu-Fe, CN<sup>-</sup>-Fe.

Moderate negative correlation was observed among Fe-BOD5 whereas slightly weak or weak (negative) correlation among all other variables were reported.

## CONCLUSIONS

This study assisted in evaluating the effectiveness of ARL's wastewater treatment units by analyzing the concentration load of various conventional and toxic/priority pollutants (primary objective) and comparing values for compliance with permissible limits of EPA and IFC, World Bank standards.

Results showed that the minimum and maximum concentrations in influent and effluent samples for pH ranged from 7.06 to 8.3 and 7.41 to 8.12, temperature ranged from 4 to 24°C and 1°C, TDS ranged from 1588mg/l to 3770mg/l and 1490mg/l to 3360mg/l and although TDS removal percentages were low but their values in all tested samples were within the prescribed limits of EPA & IFC, World Bank. Minimum and maximum concentrations in influent and effluent samples for TSS ranged from 264mg/l to 646mg/l and 8mg/l to 69mg/l. The parameter exhibited conformity with our national standards but comparable to strict IFC laws, 50% of the samples were exceeding discharge limits.

The minimum and maximum concentrations in influent and effluent samples for BOD5 ranged from 60mg/l to 138mg/l and 24mg/l to 108mg/l with 66% of the samples beyond our national discharge limits while 91% of the samples were exceeding IFC international standards. Minimum and maximum concentration in influent and effluent samples for COD ranged from 270mg/l to 916mg/l and 40mg/l to 240mg/l. 58% of the total samples were in complete compliance with EPA while in comparison with IFC, World Bank only 33% of the total samples showed compliance.

The values for minimum and maximum concentrations in influent and effluent samples for phenols ranged between 0.12mg/l to 0.39mg/l and 0.26mg/l to 1.56mg/l. Its concentration in 58% of the samples were exceeding the limits of EPA & IFC, World Bank. Minimum and maximum values for O&G in influent and effluent samples were in range from 48mg/l to 518.3mg/l and 22mg/l to 174mg/l. The removal performance was satisfactory as concentrations of 58% of the effluent samples were reduced below the detection limit whereas five effluent samples showed exceeding values.

Minimum and maximum concentrations in influent and effluent samples for TN ranged between 2.5mg/l to 28mg/l and 0.06mg/l to 23mg/l while for TP 0.12mg/l to

0.76mg/l and 0.08mg/l to 2.87mg/l. Even though the removal performance presented a reverse trend, 83% of TN and 92% of TP in effluent samples were in conformity with legislative guidelines.

Most heavy metals were undetected in both influent and effluent streams except for Arsenic and Iron. The minimum and maximum concentrations for Arsenic in influent and effluent samples ranged from 0.00464mg/l to 0.00794mg/l and 0.00212mg/l to 0.00653mg/l and for iron 0.04mg/l to 1.42mg/l and 0.02mg/l to 0.44mg/l, thus within the permissible limits of EPA and IFC, World Bank.

Taking into account the antecedent analysis, the study concluded by justifying research objectives that overall ETP units performed effectively/satisfactory in reducing the concentrations of some pollutants while others were not degraded down to acceptable limits, having far-reaching impacts on Soan water body. A reasonable explanation of low removal performance for certain parameters in some samples could be the competitive inhibition kinetics where some pollutants compete and are more effectively bonded to adsorption/removal sites. Urbanization and industrial proliferation has turned Soan River into a mass of poisoned water, endangering its aquatic life and the inhabitants around it and strict measures are required to ensure safe effluent discharge from industrial sector.

## RECCOMENDATIONS

- 1) Treatment train must be audited and troubleshooting of the underperformed units must be executed to cater increasing flow rates. Alternative advanced treatment technologies such as O3/UV/TiO2 process with over 90% removal performance can be introduced to enhance efficiency.
- 2) Neural networking models can be employed to further optimize the performance efficiency of wastewater treatment train to meet increasingly stringent laws for conserving and protecting the environment.
- 3) Implementing advanced zero discharge systems like forward osmosis, membrane distillation, electro dialysis, Nano filters to achieve 99% resource recovery and complying with SDG 6 for wastewater management, hence pumping less fresh water and discharging little or no waste in receiving water bodies. ARL has already decided in its medium term plan to design and install tertiary treatment plant to reuse the effluent.
- 4) Lethal and sub-lethal toxicity studies can be carried out near the outfall and at the far downstream end to investigate the effects on environment.



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# ANNEXURE

(A)

## Photographic Evidence





# PERFORMANCE AND WASTEWATER QUALITY ASSESSMENT OF EFFLUENT TREATMENT PLANT OF ATTOCK REFINERY LIMITED, RAWALPINDI

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