INTRODUCTION

Water is renewable natural resource of earth and is essential for all living organisms for their existence and metabolic processes in the world. Water is not only the most important essential constituent of all animals, plant and other organisms but also the pivotal for the survivability of mankind in the biosphere.\(^1\)

Water is an excellent solvent for many materials and is described as an universal solvent. It is the basic transport medium for nutrients and waste products in life processes. It also has the capacity to absorb heat without substantial rise in temperature. Because of this property there are no sudden changes in temperature, especially in large water bodies. This protects aquatic organisms from instantaneous shock and also moderates the earth’s climate.

About three-fourth of the earth’s surface is covered by water. The earth’s water resource called hydrosphere, consists of the oceans, ice and snow in the polar and other regions, mountain glaciers, lakes, streams, rivers, swamps, water in surface soil and in underground strata.

Chemically water is a compound consisting of two atoms of hydrogen and one atom of oxygen (H\(_2\)O). Though it can exist in all the three forms- solid (ice at 0 °C), liquid (water at normal temperatures) and gas (water vapor at 100 °C), most water on the earth is found in the liquid form. Water in its liquid state is made up of groups of molecules associated together by linkage between the two hydrogen atoms of one water molecule and the oxygen atom of an adjacent water molecule. This is known as hydrogen bonding. It is an unique bonding that imparts special properties to water making it an essential component of life.

Section I : Groundwater

Distribution of water in the hydrosphere is shown in Table -1.1. It shows that the majority of water is stored in oceans and there is very little freshwater available (only 2.4%). Most of this freshwater is stored in ice caps and glaciers.\(^2\)
Table 1.1: Distribution of water in the hydrosphere\textsuperscript{2}.

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Quantity (km\textsuperscript{3})</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plants and animals</td>
<td>700</td>
<td>0.000049</td>
</tr>
<tr>
<td>Rivers</td>
<td>1700</td>
<td>0.001</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>13000</td>
<td>0.009</td>
</tr>
<tr>
<td>Soil</td>
<td>65000</td>
<td>0.0046</td>
</tr>
<tr>
<td>Lakes, reservoirs, wetlands</td>
<td>125000</td>
<td>0.008</td>
</tr>
<tr>
<td>Groundwater</td>
<td>7000000</td>
<td>0.498</td>
</tr>
<tr>
<td>Ice and glacier</td>
<td>26000000</td>
<td>1.8529</td>
</tr>
<tr>
<td>Oceans</td>
<td>1370000000</td>
<td>97.633</td>
</tr>
</tbody>
</table>

The rate of transfer between different water reservoirs depends on the residence time, which are the time periods that a volume of water spends in each reservoir. For example, atmospheric water cycles every 9 days, meaning, water that evaporates from the earth’s surface returns as precipitation in 9 days. Table -1.2 shows the global residence time of water\textsuperscript{3}:

Table 1.2: Global residence time of water\textsuperscript{3}.

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Residence time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>9 days</td>
</tr>
<tr>
<td>Oceans</td>
<td>2500 years</td>
</tr>
<tr>
<td>Glaciers and ice caps</td>
<td>9700 years</td>
</tr>
<tr>
<td>Freshwater lakes</td>
<td>17 years</td>
</tr>
<tr>
<td>Rivers</td>
<td>16 years</td>
</tr>
<tr>
<td>Soil</td>
<td>1 year</td>
</tr>
<tr>
<td>Groundwater</td>
<td>1400 years</td>
</tr>
</tbody>
</table>
The hydrological cycle or water cycle maintains the water budget. The total volume of water in the global water cycle is estimated to be about 1400 million cubic km.

India has the reacheast water resources in Asia having about 14% of Asia's renewable freshwater resource. It receives an average annual rainfall of 1150 mm of which 73.9% is received through the south west monsoon during June-September. However; the rainfall distribution varies widely across the land, both spatially and temporally. The average annual precipitation including snowfall, as per estimate of Central Water Commission is of the order of 4000 billion cubic meters (b.cu.m).

As per the estimates of the Central Groundwater Board, the total replenishable groundwater potential is about 432 b.cu.m. Agriculture consumes about 95.7% of the total groundwater resource while the domestic sector and industrial uses about 3.1 & 1.3% respectively. The average annual utilizable water resource for India is shown in Table -1.3.

**Table 1.3 : Average annual utilizable water resource for India.**

<table>
<thead>
<tr>
<th>Type of water</th>
<th>Quantity (in b.cu.m)</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface water</td>
<td>690</td>
<td>61.49</td>
</tr>
<tr>
<td>Groundwater</td>
<td>432</td>
<td>38.50</td>
</tr>
</tbody>
</table>

Against these, the total amount of water used in India is about 605 b.cu.m. The demand for water in India is mainly for irrigation which accounts for 501 b.cu.m, domestic usage accounts for 30 b.cu.m., industries and power generation accounts for 20 b.cu.m, and other usage accounts for 34 b.cu.m. The current stage of utilization of surface water and groundwater is about 70% and 30% respectively.

In addition to drinking and personal hygiene, water is needed for agricultural production, industrial and manufacturing process, hydroelectric power generation, waste assimilation, recreation and
wildlife etc. when a resource is used for so many diverse purposes, it is important that it be developed and used rationally and efficiently. Water is absolutely fundamental to life. It is difficult even to imagine a form of life that might exist without water.

Water is never found pure in nature. Rainwater is the nearest approach to chemically pure water, but it contains small amounts of organic matter and dissolved gases, principally O₂ and CO₂ taken from the air. The composition of the ground over which and through, which it flows after falling to the earth will determine the additional impurities that it absorbs. The earth's surface contains large amounts of mineral salts such as the carbonates and sulphates of lime and magnesia, which are dissolved by water.

Groundwater is a water located beneath the ground surface in soil pore spaces and in the fractures of lithologic formations. Groundwater is stored in, and moves slowly through, moderately to highly permeable rocks called aquifers. The word aquifer comes from the two Latin words, *aqua*, or water, and *ferre*, to bear or carry. Aquifers literally carry water underground. An aquifer may be a layer of gravel or sand, a layer of sandstone or cavernous limestone, a rubbly top or base of lava flows, or even a large body of massive rock, such as fractured granite, that has sizable cracks and fissures.

The depth at which soil pore spaces or fractures and voids in rock become completely saturated with water is called the water table. Groundwater is recharged from, and eventually flows to, the surface naturally; natural discharge often occurs at springs and seeps, and can form oases or wetlands.

Some water underlies the earth's surface almost everywhere, beneath hills, mountains, plains, and deserts. It is not always accessible, or fresh enough for use without treatment, and it's sometimes difficult to locate or to measure and describe. This water may occur close to the land surface, as in a wetland, or it may lay many hundreds of feet below the surface, as in some arid regions. Water at very shallow depths might be just a few hours old; at moderate depth, it may be hundreds of years old; and at great depth or
after having flowed long distances from places of entry, water may be several thousands of years old. In terms of storage at any one instant in time, groundwater is the largest single supply of fresh water available for use by humans.

Groundwater has been known to humans for thousands of years. Many ancient chronicles show that humans have long known that much water is contained underground, but it is only within recent decades that scientists and engineers have learned to estimate how much groundwater is stored underground and have begun to document its vast potential for use.

When rain falls or snow melts, some of the water evaporates, some is transpired by plants, some flows overland and collects in streams, and some infiltrates into the pores or cracks of the soil and rocks. The first water that enters the soil replaces water that has been evaporated or used by plants during a preceding dry period. Between the land surface and the aquifer water is a zone that hydrologists call the unsaturated zone. Some water is held in the unsaturated zone by molecular attraction, and it will not flow toward or enter a well. After the water requirements for plant and soil are satisfied, any excess water will infiltrate to the water table, the top of the zone below which the openings in soil and rocks are saturated. Below the water table, all the openings in the soil or rocks are full of water that moves through the aquifer to streams, springs, or wells from which water is being withdrawn. Natural refilling of aquifers at depth is a slow process because groundwater moves slowly through the unsaturated zone and

the aquifer. (Fig.1.1)
**Fig. 1.1: Water table**

A well dug, bored or drilled into saturated rocks will fill with water approximately to the level of the water table. If water is pumped from a well, gravity will force water to move from the saturated rocks into the well to replace the pumped water.10

Fig. 1.2-1.4 shows how water level decline and groundwater contamination occur compare to the natural condition.

**Fig. 1.2 : Natural condition**

**Fig. 1.3 : Water-level declines**
Thus, groundwater is the part of the hydrological cycle which begins with the river water evaporating from the oceans and other water bodies forming clouds, which on cooling release water as rain fall.

Groundwater is brought to the surface by drilling into saturated rocks which are just below the water table whose pores and cracks are completely filled with water, and pumping the water out. It is generally of good quality and apart from disinfection it usually needs no treatment prior to distribution. It has low development and distribution costs in comparison to the costs in developing water from surface sources such as rivers, lakes, streams, ponds etc.

When groundwater is extracted, for instance, pumped out for well water extraction, the water surface in and near the drill hole or well will be lower than the original groundwater table. The distance between the well and the point where no significant influence on water level is observed is called the “zone of influence” of the well; the zone of lowered water level is referred to as the “drawdown,” which is located in a “cone of depression.”

The one-dimensional flow of water in a saturated zone or aquifer is described by Darcy’s law: $q = KhA/L$
Where,
\[ q = \text{Flow rate (volume per unit time)} \]
\[ K = \text{Hydraulic conductivity of the flow medium (distance/unit time)} \]
\[ h = \text{Hydraulic head or potential causing flow (distance)} \]
\[ A = \text{Cross-sectional area of flow (distance}^2) \]
\[ L = \text{Length of the flow path (distance)} \]

This equation is valid for most conditions of one-dimensional flow, whether vertical (as in downward infiltration), horizontal, or upward. Groundwater is discharged into surface waters (lakes, streams and wetlands) at the land-water interface. Groundwater is therefore a major (perhaps, the major) contributor to the base flow for most surface waters\(^8\).

It has been reported that 77% of urban population and only 31% of rural population in India has access to potable water supply\(^13\). The groundwater is an important source of water for agricultural (about 45% of our country’s agriculture demand is met), domestic (about 88% of rural areas in our country) and industrial purposes\(^1\).

Groundwater is also ecologically important. Groundwater sustains rivers, wetlands and lakes, as well as subterranean ecosystems\(^9\).

Although it is more difficult to pollute groundwater than surface water because the soil can either stop reaching groundwater or help to reduce its concentration, many of our activities affect it adversely\(^12\).

Growing urbanization, rapid industrialization without proper plan, excess use of chemical fertilizers, insecticides, pesticides in agriculture field has deteriorated the quality of groundwater. Further, with the increase in agriculture command and industrial and population growth, groundwater withdrawal is steadily increasing at alarming rate\(^14\).

Groundwater is an important source but unfortunately prone to contamination by materials deleterious to human health. In many areas of the world, the contamination is so heavy that the water is unfit even for agricultural use. The danger of groundwater pollution or contamination also exists in densely populated areas\(^8\). Scientists also
predict that in the next few decades more contaminated aquifers will be discovered, new contaminations will be identified and more contaminated groundwater will be discharged into wetlands, streams and lakes\textsuperscript{15}.

A vast majority of groundwater quality problems are caused by contamination, over-exploitation, or combination of the two\textsuperscript{16}. Table -1.4 shows a list of the potential groundwater contamination sources\textsuperscript{17}.

**Table 1.4 : Potential groundwater contamination sources\textsuperscript{17}.

<table>
<thead>
<tr>
<th>Place of origin</th>
<th>Potential groundwater contamination source</th>
</tr>
</thead>
<tbody>
<tr>
<td>At or near the land surface</td>
<td>Municipal</td>
</tr>
<tr>
<td>air pollution</td>
<td>air pollution</td>
</tr>
<tr>
<td>municipal waste</td>
<td>chemicals: storage &amp; spills</td>
</tr>
<tr>
<td>land spreading</td>
<td>fuels: storage &amp; spills</td>
</tr>
<tr>
<td>salt for de-icing streets</td>
<td>mine tailing piles</td>
</tr>
<tr>
<td>streets &amp; parking lots</td>
<td>pesticides</td>
</tr>
<tr>
<td></td>
<td>motor oil</td>
</tr>
<tr>
<td>Below the land surface</td>
<td>Landfills</td>
</tr>
<tr>
<td>leaky sewer lines</td>
<td>underground storage tanks</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Groundwater contamination occurs when man-made products such as gasoline, oil, road salts and chemicals get into the groundwater and cause it to become unsafe and unfit for human use. Some of the major sources of these products, called contaminants, are storage tanks, septic systems, hazardous waste sites, landfills, and the widespread use of road salts, fertilizers, pesticides and other chemicals.

Septic systems can be another serious contamination source. Septic systems are used by homes, offices or other buildings that are not connected to a city sewer system. Septic systems are designed to slowly drain away human waste underground at a slow, harmless rate. An improperly designed, located, constructed, or maintained septic system can leak bacteria, viruses, household chemicals, and other contaminants into the groundwater causing serious problems.

Landfills are another major source of contamination. Landfills are the places that our garbage is taken to be buried. Landfills are supposed to have a protective bottom layer to prevent contaminants from getting into the water. However, if there is no layer or it is cracked, contaminants from the landfill (car battery acid, paint, household cleaners, etc.) can make their way down into the groundwater.

Pollutants that contaminate groundwater may be some of the same pollutants that contaminate surface water. Compounds from the surface can move through the soil and end up in the groundwater. For example, pesticides and fertilizers can find their way into groundwater supplies over time18. Nowadays, the groundwater potential and its quality level in major cities and urban areas is getting deteriorated due to population explosion, urbanization, industrialization, and also the failure of monsoon and improper management of rain water1. It is a general belief that groundwater is purer and safer than surface water due to earth mantel covering. But contrary to that presence of more than 200 chemical constituents in groundwater has been documented which includes about 175 organic and more than 50 inorganic and radio nucleotides13.
The use of fertilizers, pesticides and insecticides in rural areas, lime, bleaching powder, septic tanks, refuse dumps, etc in urban areas are main source of soil and underground water pollution.19

Water quality studies are regarded as one of the thrust areas in the water recourses sector, as investigated in the National Water Policies 1987 and 2002 that “both surface and ground water should be regularly monitored, and a phased program should be undertaken for improvements in water quality”20.

It is very difficult to distinguish the origin of many water quality problems. Once the groundwater is contaminated, it may remain in an unusual or even in hazardous condition for decades or even for centuries.13

The chemistry of groundwater is an important factor determining its use for domestic, irrigation or industrial purpose. The quality of groundwater is controlled by several factors, including climate, soil characteristics, groundwater through the rock types, topography of the area, saline water intrusion in the coastal areas, human activities etc.21

Gujarat has a hydrogeology representative of almost all aquifer types and depositional and formation eras. The Western Saurashtra is part of the Deccan Basaltic terrain with flat to medium slopes except for some places such as Junagadh to the South and Chotila in the North. Kutch is characterized by complex geology of Limestone, Clay, Sandstone and alluvial stretches. The central Alluvial plains of Gujarat consist of North-South ranging aquifers which are vast deposits of rivers flowing from the Aravallis. The South parts of the state possess areas of hilly terrain known as the Dangs. The North-Eastern region of the State comprises of the Aravalli mountain range whose aquifers are of hard rock Crystalline nature. The Sabarmati, Mahi, Narmada and the Tapi are the major rivers which flow across the Alluvial terrain. The hydrology of the State shows high variation with a humid environment in South Gujarat to highly arid climate of Kutch22. Groundwater quality problem in Gujarat is shown in Table -1.516.
Table 1.5 : Groundwater quality problem in Gujarat\textsuperscript{16}.

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Districts affected in parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity</td>
<td>Banaskantha, Junagarh, Bharauch, Surat, Mehsana, Ahmedabad, surendranagar, Kheda, Jamnagar</td>
</tr>
<tr>
<td>Fluoride</td>
<td>Kutch, Surendranagar, Racket, Ahmedabad, Mehsana, Banaskantha, Sabarkantha</td>
</tr>
</tbody>
</table>

Not only groundwater, India’s overall environment is becoming fragile and environmental pollution is one of the undesirable side effects of industrialization, urbanization, population growth and unconscious attitude towards the environment. At present, environmental protection is the main need of the society. Though industrialization and development in agriculture are necessary to meet the basic requirement of people, at the same time it is necessary to preserve the environment. In India, too, the environmental pollution has become a cause of concern at various level\textsuperscript{23}.

In recent years, manufacturing processes being practiced in pharmaceutical and other chemical industries have resulted in introduction of newer organic chemicals in their effluents, which are having complex structure or toxicity towards biological agents. Thus these are capable of causing serious threat to environment if allowed in sewers or surface water bodies\textsuperscript{24}.

Reported work of groundwater survey :

Groundwater pollution is a global issue. The study of assessment of ground water quality has been done at various places in India as well as in abroad with different aims and objectives.

Amita R. Oka et al.\textsuperscript{25} studied over anaerobic hydrocarbon degradation in historically contaminated groundwater and found that the site is enriched for anaerobic hydrocarbon biodegradation and provides strong evidence in support of natural attenuation. Guey-Shin Shyu et al.\textsuperscript{26} applied factor analysis combined with kriging and
information entropy theory for mapping and evaluating the stability of groundwater quality variation in Taiwan. Stephen E. Silliman et al.\textsuperscript{27} studied issues of sustainability of coastal groundwater resources: Benin, West Africa.

Michio Murakami et al.\textsuperscript{28} studied groundwater pollution by perfluorinated surfactants in Tokyo and found that wastewater and surface runoff contributed to 54–86\% and 16–46\% of perfluorocarboxylates (PFCAs), respectively in groundwater. Yu Umezawa et al.\textsuperscript{29} researched for the sources of nitrate and ammonium contamination in groundwater under developing Asian mega cities. A. Van Geen et al.\textsuperscript{30} worked on comparison of arsenic concentrations in simultaneously-collected groundwater and aquifer particles from Bangladesh, India, Vietnam and Nepal. Bradley D. Cey et al.\textsuperscript{31} studied the impact of artificial recharge on dissolved noble gases in groundwater in California.

Quality of Indian groundwater resources in the last several decades has altered considerably due to various natural and manmade polluting sources. Investigation for various objectives and targets\textsuperscript{32-57} throughout the world, describe the gravity of the situation. Nawlakhe et al.\textsuperscript{58} study observes nitrate, fluoride, TDS and hardness as problem parameters in order to determine groundwater quality in Shivpuri district of Madhya Pradesh. Mohapatra et al.\textsuperscript{59} reported increased concentration of organochlorine insecticides in rural areas of Indo-Gangatic plains in July-November half of the year. Ozha et al.\textsuperscript{60} detected excess of nitrates in Churu and Barmar districts of Rajsthan. Landfill used for dumping refuses and municipal waste contribute effectively to groundwater pollution is reported by Jeevanrao and Shantaram’s\textsuperscript{61} study in Hyderabad city. It concludes that pollution in well waters decreases as we move further from the landfills. Subbarao and Subbarao\textsuperscript{62} study has found that the septic tank density of a residential colony largely affects the groundwater salinity of that area. Hegde et al.\textsuperscript{63} have found an abnormally high concentration of sodium in a well near leather washing point in Hubly city. Ganguli et al.\textsuperscript{64} measured total mercury (Hg\textsubscript{T}) and monomethylmercury (MMHg)
concentrations in coastal groundwater and seawater over a range of tidal conditions near Malibu Lagoon, California, and used Rn-derived estimates of submarine groundwater discharge to assess the flux of mercury species to nearshore seawater. A. Biswas et al. studied for arsenic and manganese in drinking water wells. V. S. Raval and G.M. Malek have studied the seasonal variation in groundwater in and around Surat.

The Central Pollution Control Board (CPCB) reports that the groundwater analysis of samples from bore wells in Ratlam indicate high TDS (200-13000 mg/l), total hardness, bacteriological contamination, heavy metals and pesticides. At Chembur (Mumbai) bacteriological contamination was detected. At Howrah (West Bengal) contaminations with pesticides and bacteria is reported. TDS and ionic species concentrations were very high. Presence of lead and cadmium at Patanchero (Andhra Pradesh) and high TDS at Manali (Chennai) was reported. In Delhi electrical conductivity (EC) ranged between 720-6310 mmho/cm and TDS from 446-4509 mg/l.

Monitoring of water quality is fundamental for understanding the water resources as it gives an insight into the consequences of its management due to the increasing public interest in water as a resource and in increasing the awareness of the need to protect water quality.

The quality of groundwater available in an area is as important as the quantity of resources. Hence there is always a need for and concern over protection and management of groundwater quality.

The investigation in groundwater resources in any region is primarily concerned with its utility for irrigation. Another interesting purpose of studying groundwaters would be to consider the distribution of various salts from geochemical viewpoint. Quality of irrigation water is an important factor of crop production. In India, the irrigated area is extent of about 61 million hectares of the total irrigated area, 41.1 % is irrigated by canals, 26 % by wells, 7.7 % by tube wells, 16.7 % by tanks and 8.5 % by other sources. In Gujarat total irrigated area is
about 2.155 million hectares of which only 21.3 % area is covered by canals and about 65.3 % area is irrigated by wells or tube wells.

Section II : CETP

During the past 30 years the industrial sector in India has quadrupled in size simultaneously, the major waste generators in India including the petrochemical, pharmaceutical, pesticide, paint, dye, petroleum, fertilizer, asbestos, caustic soda, inorganic chemicals and general engineering industries. The bulk of industrial pollution in India is caused by the small and medium scale industrial (SMIs) sector. Though the quantity of industrial waste generated by individual SMIs may not be large, it aggregates to be a large percentage of the total since almost 3 million SMIs are widely scattered throughout the country. SMIs account for over 40% of the total industrial output in the country and generate over 44% of hazardous wastes alone as compared to 13% generated by the large scale industry.

An industrial estate is a composition of several different types of industries located in one area, each producing effluent of varying wastewater characteristics. For treatment of such waste waters, application of conventional biological treatment like activated sludge process and other chemical methods like wet air oxidation, wastewater incineration, and advance oxidation process (AOPs) are available but not economical and technically feasible for the small scale industries.

Government of India floated the idea of Common Effluent Treatment Plant (CETP) to overcome these problems. The Ministry has undertaken a Centrally Sponsored Scheme for enabling the Small Scale Industries (SSI) to set-up CETPs in the country for installation of pollution control equipment for treatment of effluents.

CETP offer an alternative to the practice of having individual effluent treatment systems and makes better overall use of the resources of an industrial estate. In a CETP, the effluents from the different industries are treated using one universal treatment system. CETP eliminate duplicity of treatment systems among the industries on
the industrial estate and hence results in a reduction in the total capital required for construction of the industrial estate\textsuperscript{71}.

**Reported work of CETP:**

Several studies have been done to evaluate CETP performance\textsuperscript{73-75}. K. L. Rao\textsuperscript{75} studied the role of CETP at Jeedimelta industrial estate in Andhra Pradesh and S. Rajamani et al.\textsuperscript{76} studied CETP for a group of 14 tanneries in Bangalore and considered CETP as appropriate and viable in technical, environmental, social and commercial angle. Based on preceding data design of CETP was finalized. It was decided that the CETP will receive effluent from each industry after it is neutralized.

Agencies such as World Health Organization (WHO) and National Cancer Institute (NCI), USA have found that 60 to 90\% of human cancer cases are due to toxic chemicals present in the environment. They are released through wastewater discharged from petroleum products such as coaltar, aromatic amino and nitro compounds, pesticides, herbicides and soil sterilent\textsuperscript{77}.

Waleed Manasreh and Atef S. Alzaydien\textsuperscript{78} studied the analysis of treated wastewater produced from Al-Lajoun wastewater treatment plant, Jordan to assess the treated wastewater quality in term of major anionic composition, heavy metal content, organic pollutants, and physico parameters such as pH, EC and Temperature.

A study on CETP, Sachin industrial area was done by D. J. Naik\textsuperscript{73}. Anju Singh\textsuperscript{79} studied the performance evaluation of CETP treating textile wastewaters in India. Vikas Singh\textsuperscript{80} studied performance evaluation and capacity assessment of a CETP for metal plating industries. Pathe et al.\textsuperscript{81} evaluated performance of an existing CETP serving a cluster of small scale tanneries and suggested measures and modifications for improving the performance. Whether a CETP is a solution or a problem in itself was discussed by Maheshvari and Dubey\textsuperscript{82}. Eswaramoorthi et al.\textsuperscript{83} have studied performance of a CETP at Manickapurampudur, Tirupur, which is handling dying effluent from over 900 small scale dying units, and found that the treated effluent,
except for TDS is in compliance with the effluent discharge norms of state pollution control board. Pophali et al.\textsuperscript{84} have studied the influence of hydraulic shock loads and total dissolved solids (TDS) on the performance of three large-scale CETPs of Rajasthan (two at Pali and one at Balotra) treating textile effluents. Vinod Tare et al.\textsuperscript{85} compared cost and quality of treatment of tannery wastewater by two CETPs both serving tannery clusters in Uttar Pradesh. Central Pollution Control Board (CPCB) studied performance of 78 CETPs operating throughout the country during 2002-2005 and published a report\textsuperscript{16} – “Performance Status of Common Effluent Treatment Plants in India”.

Performance status of 78 CETPs studied by CPCB during 2002-2005 shown in Table -1.6\textsuperscript{16}, while status of CETP in Gujarat as on March 2010\textsuperscript{86} is shown in Table -1.7.

Table 1.6: Performance status of CETPs studied by CPCB during 2002-2005\textsuperscript{16}.

<table>
<thead>
<tr>
<th>State</th>
<th>Number of CETPs studied by CPCB</th>
<th>CETPs complying pH, BOD, COD, TSS and TDS standards</th>
<th>CETPs complying pH, BOD, COD and TSS but not complying TDS standard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number</td>
<td>Name</td>
<td>Number</td>
</tr>
<tr>
<td>Andhra Pradesh</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Delhi</td>
<td>10</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Gujrat</td>
<td>15</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Haryana</td>
<td>1</td>
<td>1*</td>
<td>0</td>
</tr>
<tr>
<td>Karnataka</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Maharashtra</td>
<td>9</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Madhya Pradesh</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Punjab</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Rajasthan</td>
<td>5</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Tamilnadu</td>
<td>29</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Uttar Pradesh</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>78</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>Sr. No.</td>
<td>Management’s Name and Location</td>
<td>No. of Members</td>
<td>Capacity in MLD</td>
</tr>
<tr>
<td>------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>---------------</td>
<td>----------------</td>
</tr>
<tr>
<td>1.</td>
<td>The Green Environment Services Co-op. Society Ltd. 244-251, Phase II, GIDC Vatva Ahmedabad</td>
<td>671</td>
<td>16</td>
</tr>
<tr>
<td>2.</td>
<td>Odhav Enviro Project Ltd., 25, GIDC Odhav, Ahmedabad</td>
<td>54</td>
<td>1.6</td>
</tr>
<tr>
<td>3.</td>
<td>Gujarat Vepari Maha Mandal Sahkari Udhyogik Vasahat Ltd., 181, GVMMS Industrial Estate, Odhav, Ahmedabad</td>
<td>372</td>
<td>1.00</td>
</tr>
<tr>
<td>4.</td>
<td>Odhav Green Enviro Project Association, 394, GIDC Odhav, Ahmedabad</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>5.</td>
<td>Naroda Enviro Projects Ltd., 512-515, Phase I, GIDC Naroda, Ahmedabad</td>
<td>180</td>
<td>3.5</td>
</tr>
<tr>
<td>6.</td>
<td>Narol Dyestuff Enviro Society, 1083 Near Vishal Textile Mill, B/h Narol-Court, Narol, Ahmedabad</td>
<td>27</td>
<td>0.10</td>
</tr>
<tr>
<td>7.</td>
<td>Sanand Eco Projects Ltd. (Incineration system), Ajanta Industrial Estate, Iyara – Sanand Dist. Ahmedabad</td>
<td>49</td>
<td>0.20</td>
</tr>
<tr>
<td>10.</td>
<td>Pollution Advisory Committee, NIA [Nandesari Industries Association] 153/A, GIDC Nandesari District Vadodara</td>
<td>177</td>
<td>5.5</td>
</tr>
<tr>
<td>11.</td>
<td>Enviro Infrastructure Co. Ltd. ECP Canal road, Umraya, Ta. Padra District Vadodara</td>
<td>89</td>
<td>2.25</td>
</tr>
<tr>
<td>No.</td>
<td>Name of the Company</td>
<td>Address</td>
<td>Area (in Sq.m)</td>
</tr>
<tr>
<td>-----</td>
<td>---------------------</td>
<td>---------</td>
<td>----------------</td>
</tr>
<tr>
<td>12</td>
<td>Enviro Technology Ltd., 2413/2414, GIDC Estate, Ankleshwar, District Bharuch</td>
<td>268</td>
<td>1.80</td>
</tr>
<tr>
<td>13</td>
<td>Bharuch Eco-Aqua Infrastructure Ltd., (BEAIL), Ankleshwar</td>
<td>1051</td>
<td>60</td>
</tr>
<tr>
<td>14</td>
<td>Panoli Enviro Technology Ltd. 619, GIDC Estate, Panoli, District Bharuch</td>
<td>119</td>
<td>1</td>
</tr>
<tr>
<td>15</td>
<td>Globe Enviro Care Ltd. [chemical units], PP 1, Off road no. 2, B/h Kay Tex Mills, GIDC Estate, Sachin – Surat</td>
<td>50</td>
<td>0.5</td>
</tr>
<tr>
<td>16</td>
<td>Sachin Enviro Infra Ltd., [process houses] P/2, GIDC Sachin Dist. Surat</td>
<td>71</td>
<td>50</td>
</tr>
<tr>
<td>17</td>
<td>Palsana Enviro Protection Ltd., Kadodara-Surat</td>
<td>102</td>
<td>100</td>
</tr>
<tr>
<td>18</td>
<td>Vapi Waste &amp; Effluent Management Co. Ltd., 4807, Phase IV, GIDC Vapi, District Valsad</td>
<td>786</td>
<td>70</td>
</tr>
<tr>
<td>19</td>
<td>Tata motors Ltd, Vendor Park Sanand, Dist-Ahmedabad.</td>
<td>42</td>
<td>2</td>
</tr>
<tr>
<td>20</td>
<td>Veraval Industries Association 5/6, GIDC Veraval, District Junagadh</td>
<td>68</td>
<td>5</td>
</tr>
<tr>
<td>21</td>
<td>Jetpur Dyeing &amp; Printing Association Kankiya Plot, Jetpur, District Rajkot</td>
<td>1174</td>
<td>11</td>
</tr>
<tr>
<td>22</td>
<td>Shri Dhareshwar GIDC Vistar Association, Nr. Dhareshwar Temple, National Highway, Navagadh, Rajkot</td>
<td>26</td>
<td>0.1</td>
</tr>
<tr>
<td>23</td>
<td>Jay Kay Enviro-Technologies Pvt. Ltd., Kalipat, Bhavnagar road, Rajkot</td>
<td>130</td>
<td>0.035</td>
</tr>
<tr>
<td>24</td>
<td>Rajkot Electroplating Association, Rajkot Shapar (Veraval), Ta: Kotadasangani Dist. Rajkot</td>
<td>21</td>
<td>0.01</td>
</tr>
<tr>
<td>25</td>
<td>Kalol GIDC Industries Association 65/66, GIDC Estate Kalol, District Gandhinagar</td>
<td>39</td>
<td>0.4</td>
</tr>
<tr>
<td>26</td>
<td>Zydus Infrastructure Pvt.Ltd, Changodar, District Ahmedabad</td>
<td>12</td>
<td>0.75</td>
</tr>
<tr>
<td>No.</td>
<td>Name of the Establishment</td>
<td>District</td>
<td>Passenger Capacity</td>
</tr>
<tr>
<td>-----</td>
<td>---------------------------------------------------------------</td>
<td>----------</td>
<td>--------------------</td>
</tr>
<tr>
<td>27.</td>
<td>Pandesara Green Co-op. Society Ltd., GIDC – Surat</td>
<td>Surat</td>
<td>122</td>
</tr>
<tr>
<td>30.</td>
<td>Jamnagar Electroplaters Association, Jamnagar</td>
<td>Surat</td>
<td>87</td>
</tr>
<tr>
<td>31.</td>
<td>CETP for Washing Ghat, Derdi Road, Jetpur Dist. Rajkot</td>
<td>Rajkot</td>
<td>100</td>
</tr>
<tr>
<td>32.</td>
<td>ATPA Swarnim Gujarat Enviro Pvt Limited Pirana Sewage Farm Area, Village Gysapur, Ahmedabad</td>
<td>Surat</td>
<td>89</td>
</tr>
<tr>
<td>34.</td>
<td>CETP for Washing Ghat, Village Bhat Gam Ta: Bhesan, Dist. Junagadh</td>
<td>Surat</td>
<td>150</td>
</tr>
</tbody>
</table>

Thus Gujarat is having 28 CETPs in operation, among one is at Vapi.

Treatment of the industrial wastewater is complicated by the presence of a wide variety of both inorganic and synthetic organic pollutants, many of which are not readily susceptible to biodegradation. Solvents, oils, plastics, metallic wastes, suspended solids, phenols and various chemical derivatives of manufacturing processes are apt to be difficult to identify and impossible to remove without more advanced technology than we know now. An old saying “The solution to pollution is dilution” has some meaning\(^87\).

Chemical treatment of industrial waste may be used in addition to and to some extent in place of biological treatment. The aims are somewhat different since biological treatment is mainly a way of oxidizing organic matter or a way of converting into a settable form. Chemical treatment also provide oxidation through chlorine, ozone tec, but it is used only for oxidizing compounds like cyanides since it is expensive
and liable to lead to the production of undesirable chlorinated organics. It is mainly used for pH correction and improving the removal of solids. The commonest chemicals in use are lime, calcium hydroxide, aluminum sulfate, alum, potash, charcoal etc.\textsuperscript{88}

The methods of treatment used for altering the characteristics of liquid water fall into the following classification\textsuperscript{89-92}:

1. Preliminary treatment
2. Primary treatment
3. Secondary treatment

**1. Preliminary treatment:**

It includes those processes which do not significantly reduce the pollution strength of a waste but which do serve to protect or prepare the waste for subsequent treatment by altering the waste characteristics. Coarse screening, grit removal and preaeration are common preliminary treatment process.

**2. Primary treatment:**

Primary treatments include those processes which reduces the floating and suspended solids (SS) present in the waste by mechanical means or by the action of gravity. Fine screens and sedimentation tanks are commonly used in primary treatment processes. It will generally remove 98-99% settleable solids, 60-80% SS and 30-50% of Oxygen Demand (OD) from the waste.

It uses the force of gravity to separate the raw wastewater into a water component and a concentrated solids or sludge component. The water component will still contain significant amount of dissolved and colloidal pollutants unaffected by primary treatment. The water component can be discharged or given further treatment to remove these residual pollutants. The sludge component however can not be discharged to water course and must be given further treatment to prevent the creation of a nuisance.
3. Secondary treatment:

Secondary treatment depends on biological processes to further reduce the suspended and dissolved solids which are reasoning in the liquid effluent after primary treatment. Lagoons, conventional treatment, Trickling filter and activated sludge processes are typical secondary treatments. In general, the influent to secondary treatment has received primary treatment may and may not have received preliminary treatment. If a waste has received both primary and secondary treatment, it is considered to have received complete treatment.

It can be designed to provide overall plant removals of 90-95% of the suspended solids and oxygen demand present in the raw waste.

Secondary treatments are required where the standards of permissible pollution established for the receiving stream would be exceeded by the discharge of waste receiving only primary treatment.

After primary treatment the neutralized effluent enters into a primary settling tank and then to an aeration tank. The effluent from aeration tank is settled in a secondary settling tank. A part of sludge is recirculated to the aeration tank and the excess sludge is sent to sludge drying beds.

4. Tertiary treatment:

It has been evident that the industrial waste include many contaminants that are resistant to, or even totally unaffected by conventional water and waste treatment processes. Such contaminants called refractory substances include both organic and inorganic materials and require advanced waste treatment or tertiary treatment processes for their removal. Adsorption, electrodialysis, extraction foaming and iron exchange are typical treatment processes being evaluated for separation of refractories from water and wastes.

Disposal of waste water:

The untreated waste water from any industry is not fit for direct disposal into any waste course or on land for irrigation. It does not
specify the tolerance limits of specified standards of disposal. It requires considerable treatment before being discharged from the CETP.

The Gujarat Pollution Control Board (GPCB) in as general guidelines for discharge of industrial treated effluent:
1. Into inland surface water.
2. Into public sewers.
3. Onland for irrigation
4. For marine disposal.

To protect the water resources from being polluted by domestic and industrial activities, several national and international criteria and guidelines have been established for water quality standard by several agencies like United States Environmental Protection Agency (USEPA), World Health Organization (WHO) etc. To achieve these standards, industries have been forced to change their working culture from one in which effluent discharge and disposal of water were not issues to one involving a high priority on waste minimization through reduction of the volume and toxicity of the discharge adoption of alternative processing methods, and recycling and reuse of water, chemicals and colourants\textsuperscript{93}.

Vapi is located around 28 km south of the district headquarter city of Valsad. It is surrounded by Union Territories of Daman on the West and by Dadra and Nagar Haveli on the East. The industrial township of Vapi holds its place of importance on the “industrial” map and it is one of the largest industrial zone in Asia in terms of small-scale industries, dominated by chemical industry plants.

Vapi Industrial Estate, a declared chemical zone, developed by Gujarat Industrial Development Corporation (GIDC), in about 25 year since inception became one of the largest cluster of SSI and medium scale units, majority being in the SSI sector and over 60% engaged in chemical related activities. Vapi Estate has distinct advantages of geographic location with road and rail links to Mumbai on one side and Surat-Vadodara-Ahmedabad on the other. It has abundant water
supply and has close proximity to Arabian Sea which is only 4 km downstream. Thus it was considered an ideal spot for high water consuming industries and easy disposal avenue, which attracted chemical and paper conversion, units and soon it became a major producer of dyes intermediates, drum intermediates and packaging paper among other products.

Along with high production, the issue of environmental pollution began to emerge as a major challenge and Vapi Waste and Effluent Management Co. Ltd (VWEMCL) was assigned the task of preparing and implementing a Comprehensive Environment Management Program (CEMP) for Vapi estate. On 17\textsuperscript{th} January 1997 the CETP was commissioned. The CETP of Vapi is one of the largest of its kind in India, with an area of 77 acres and treatment capacity of 55,000 m\textsuperscript{3}/d. Total 786 small, big industries are member of CETP. Once the CETP was commissioned and stabilized gradually every unit, polluting or non polluting, commercial or residential unit is obliged to discharge its wastewater into common underground piping\textsuperscript{94}. CETP is having primary and secondary stages of treatment. Tertiary treatment was started from February 2008, but it was on partial bases, hence its efficiency checking was worthless.

However, Vapi also has the dubious distinction of being on the list of the 10 worst polluted places in the world\textsuperscript{95}. Hence it will be useful to find out the performance evaluation of the CETP in this Vapi industrial area.

**Groundwater and Wastewater quality parameters:**

The physical and chemical quality of water is important on the potability of water and its fitness for domestic purposes largely depends on the chemical quality\textsuperscript{96}.

It is important to remember that while measuring any of the parameter, one is making a determination at a given time. The measurement and analysis, therefore, hold good only for the period of a particular state.
One of the key elements in the design of a water quality monitoring programme is selection of the properties, elements, and compounds (indicators) to be measured\textsuperscript{97}.

Groundwater quality may be characterized by literally thousands of indicators. Selection of indicators for monitoring programmes should be based on their relevance to important water-quality issues, such as human health protection, the monitoring objectives outlined above, and the existence of appropriate analytical methodologies\textsuperscript{98}.

Based on these criteria, groundwater samples were analyzed for seventeen physico-chemical parameters like pH, Colour, Electrical Conductivity (EC), Total Hardness (TH), Calcium (Ca), Magnesium (Mg), Total Alkalinity (TA), Total Dissolved Solids (TDS), Silica, Chloride, Sulphate, Fluoride, Sodium, Chemical Oxygen Demand (COD) and metals like Copper (Cu), Lead (Pb) and Manganese (Mn), while CETP samples were analyzed for parameters like pH, Colour, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Phenol, Chloride and metals like Copper (Cu), Lead (Pb) and Manganese (Mn).

**pH:**

pH is a measurement of acid-base equilibrium achieved by various dissolved compounds\textsuperscript{99}.

The pH of water is an important parameter to assess its quality as drinking water. Low pH, viz., below 6.5 corrodes metal pipes, resulting in the release of toxic metal compounds\textsuperscript{19}. However, pH alone does not provide a full picture of the characteristics or limitations with the water supply\textsuperscript{100}.

In so far, as pH affects the various processes in water treatment that contribute to removal of virus, bacteria, and other harmful organisms, it could be claimed that pH has an indirect effect on health. The pH of most natural waters ranges from 6.5 to 8.5. Deviation from the neutral pH 7.0 is largely the result of interaction between acids and bases. Industrial and community wastes, acid rain, bedrock type, and biological process of photosynthesis and respiration influence the pH.
level. The lower pH value tends to make water corrosive and higher pH results in the taste complaint and can have negative impact on skin and eyes\textsuperscript{101,102}. pH value of 7 is considered to be the best and most ideal\textsuperscript{103}.

**Colour:**

Colour in water may result from the presence of natural metallic ions (iron and manganese), humus and peat materials, plankton, weeds, and industrial wastes\textsuperscript{99}.

Ideally drinking water should be free from colour. The presence of colour may be due to presence of coloured organic matter, metals such as iron and manganese\textsuperscript{104}.

Colour due to organic acids may not be harmful as such but highly coloured waters are objected on aesthetic grounds\textsuperscript{105}.

**Electrical Conductivity (EC):**

Conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. This ability depends on presence of ions, their total concentration, mobility, valence, and relative concentration and on the temperature of measurement. Solution of most inorganic acids, bases and slats are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly\textsuperscript{99}.

The physical measurement made in a laboratory determination of conductivity is usually the resistance measured in ohms or megohms. The resistance of a conductor is inversely propositional to its cross-sectional area and directly proportional to its length\textsuperscript{106}. Pure water is a poor conductor of electricity.

Some researchers identified that the water quality can be predicted with sufficient accuracy just by measurement of EC alone\textsuperscript{107}. Waters with conductivity range between 750 to 2250 micromho/cm are successfully used for irrigation with satisfactory crop growth, along with good management and favorable drainage conditions\textsuperscript{108}. However, water with low conductivity need not be always suitable for irrigation,
since the presence of significant concentration of specific ions such as sodium, magnesium, chloride, bicarbonates and carbonates do produce toxicity and bring crop hazards\textsuperscript{109}.

**Total Hardness (TH):**

Originally, water hardness was considered as a measure of the capacity of water to precipitate soap. Soap is precipitate chiefly by the calcium and magnesium ions present\textsuperscript{99}.

The term “hardness” is one of the oldest terms used to describe characteristics of water. Hippocrates (450-354 BC) used the hard and soft terms in a discourse on water quality\textsuperscript{110}.

Hardness in principle is the total of calcium and magnesium salts present in water expressed in terms of calcium carbonate\textsuperscript{67}. Most natural water supplies contain at least some hardness due to dissolved calcium and magnesium salts\textsuperscript{111}.

The hardness of water varies considerably from place to place. In general, surface water are softer than groundwater. The hardness of water reflects the nature of geological formations with which it has been in contact\textsuperscript{106}.

The principal hardness causing ions are calcium and magnesium, the ions strontium, iron, barium and manganese also contribute\textsuperscript{112}. The two main industrial sources of hardness are the inorganic chemical and the mining industries\textsuperscript{103}. In areas with very hard water, household pipes can be chocked with deposited scale\textsuperscript{113}.

Hardness of water may be temporary or permanent. Temporary hardness is mainly due to the presence of calcium, magnesium and bicarbonates. Permanent hardness is due to the presence of sulphates and chlorides of calcium and magnesium\textsuperscript{114-116}.

**Calcium:**

Calcium normally occurs in combination with carbonate ions\textsuperscript{67}.

Calcium and magnesium are common constituents of natural water, and important contributor to the hardness of water. The natural source of Ca and Mg are the rocks from which it is leached. Calcium
and magnesium are important parameters for irrigation water, and in some situations they help to offset the effects of sodium\textsuperscript{20}.

**Magnesium:**

Magnesium is absolutely essential for chlorophyll bearing algae and plants\textsuperscript{67}.

**Total Alkalinity (TA):**

Alkalinity of water is its acid-neutralizing capacity. It is the sum of all titrable bases\textsuperscript{99}.

Alkalinity is an important parameter involved in corrosion control. It must be known in order to calculate the Langelier Saturation Index\textsuperscript{117}. Alkalinity is the presence of different ions of carbonate, bicarbonate, hydroxyl and free CO\textsubscript{2}. Alkalinity due to naturally accruing compounds like calcium carbonate is safe for consumption\textsuperscript{118}.

**Total Dissolved Solids (TDS):**

A large number of solids are found dissolved in natural waters, the common ones are carbonates, bicarbonates, chlorides, sulphates, phosphates and nitrates of calcium, magnesium, sodium, potassium, iron, magnesium etc. In other words, TDS is simply the sum of the cations and anions concentration expressed in mg/l\textsuperscript{106}.

A high content of dissolve solids elevates the density of water, influences osmo regulation of freshwater organisms, reduces solubility of gases (like oxygen) and reduces utility of water for drinking, irrigation and industrial purposes\textsuperscript{106}.

**Silica:**

Silicon ranks next to oxygen in abundance in the earth’s crust. It appears as the oxide (silica) in quartz and sand and is combined with metals in the form of many complex silicate minerals, particularly igneous rocks. Degradation of silica containing rocks results in the presence of silica in natural waters as suspended particles, in a colloidal or polymeric state, and as silisic acids or silicate ions. The
silica (SiO$_2$) content of natural water most commonly is in the 1-30 mg/l range, although concentration as high as 100 mg/l are not unusual and concentrations exceeding 1000 mg/l are found in some brackish waters and brines$^{99}$.

**Chloride:**

Chloride, in the form of chloride ion, is one of the major inorganic anions in water and wastewater. In potable water, the salty taste produced by chloride concentrations is variable and dependent on the chemical composition of water. Some waters containing 250 mg/l may have a detectable salty taste if the cation is sodium. On the other hand, the typical salty taste may be absent in waters containing as much as 1000 mg/l when predominant cations are calcium and magnesium$^{99}$.

The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common article of diet and passes unchanged through the digestive system. Along the sea coast, chloride may be present in higher concentration because of leakage of salt water into the sewage system. It also may increased by industrial processes$^{99}$.

Limits of maximum concentration of chloride have been set on basis of taste preferences. However, large amounts of chloride when Ca and Mg are also present, lead to increase in water’s corrosiveness and may adversely affect the water quality by acquiring harmful elements. Main source of chloride is the discharge of sewage. It is harmless up to 1500 mg/l$^{119}$.

High chloride content in water bodies harms metallic pipes and structure as well as agricultural crops$^{120,121}$. The high chloride ion concentration has adverse effect on irrigated soil porosity, moisture percentage and soil permeability and also leads to accumulation of high chloride content in soil$^{107}$. 
**Sulphate:**

Sulfate ($\text{SO}_4^{2-}$) is widely distributed in nature and may be present in natural waters in concentrations ranging from a few to several thousand milligrams per liter\(^9\). Sulphate is one of the major anion present in natural water\(^1\). It is of importance in public water supplies because of its cathartic effect upon humans when present in excessive amounts. It is one of the least toxic anions. However, catharisis, dehydration and gastrointestinal irritation observed at higher concentration. Waters with 300-400 mg/l sulphate have a bitter taste and those with 1000 mg/l or more of sulphate may cause intestinal disorder\(^1\).

Sulphate is poorly absorbed from the human intestine, it slowly penetrates the cellular membranes of mammals and is rapidly eliminated through kidneys\(^2\). Water containing appreciable amount of sulphate forms hard scale in boilers and heat exchangers. Sulphate also causes odour or corrosion of sewer in anaerobic conditions because it gets converted to hydrogen sulfide\(^1\). Considerable amount of sulphate are added to the hydrological cycle from precipitation. This comes from dried sea spray as cyclic salt, continental dust, oxidation of $\text{H}_2\text{S}$ that enters the atmosphere from coastal marshes, volcanic emanations and air pollution\(^3\). Further addition of $\text{SO}_4$ to groundwater takes place from the breakdown of organic substances in the soil\(^4\). Leachable sulfates present in fertilizers and other human influences\(^5,6\).

**Fluoride:**

Fluoride is the most electronegative element and most abundant element in the earth’s crust. It occurs as fluorspar ($\text{CaF}_2$) or cryolite. The concentration of fluoride in natural water mainly depends on solubility of the fluoride bearing rocks with which water is in contact. Concentration of fluoride in sea water is 0.8-1.4 ppm\(^7\).

Accurate determination of fluoride has increased in importance with the growth of practice of fluoridation of water supplies as a public
health measures\textsuperscript{99}. Table – 1.8 shows concentration of fluoride in drinking water and its effects on human health:

**Table 1.8 : Effects of Fluoride on human health.**

<table>
<thead>
<tr>
<th>Fluoride concentration (mg/l)</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>Limited growth and fertility</td>
</tr>
<tr>
<td>&lt; 0.5</td>
<td>Dental caries</td>
</tr>
<tr>
<td>0.5-1.5</td>
<td>Promotes dental health, prevents tooth decay</td>
</tr>
<tr>
<td>1.5-4.0</td>
<td>Dental fluorosis (mottling and pitting of teeth)</td>
</tr>
<tr>
<td>4.0-10.0</td>
<td>Dental Fluorosis, skeletal Fluorosis (pain in neck bones and back)</td>
</tr>
<tr>
<td>&gt; 10.0</td>
<td>Crippling Fluorosis</td>
</tr>
</tbody>
</table>


Fluoride is more common in groundwater than in surface water. The main sources of fluoride in groundwater are different fluoride bearing rocks\textsuperscript{106}. In India, the presence of fluorides in groundwater was initially detected through the mottling of teeth and deformation of bone structures\textsuperscript{128}.

Fluoride is considered as one of the minor constituents of natural waters, but it is an important parameter in ascertaining the stability of water for potable purposes. Fluoride contamination in groundwater has now become a major geo-environment issue in many parts of the world due to its toxic effects even if consumed in trace quantities. India is among 23 nations around the globe, where health problems occur due to the consumption of fluoride contaminated water. In India, high fluoride occurrence in top aquifer system has reached an endemic level in 15 out of 32 states where fluoride concentration form 5 to 15 mg/l have been reported and the worst affected ones are Andhra Pradesh, Tamilnadu, Karnataka, Gujarat, Rajasthan, Punjab, Haryana, Bihar and Kerala\textsuperscript{129-132}. 
Fluoride is more common in groundwater than surface water. The main sources of fluoride in groundwater are the fluorine bearing minerals in igneous and metamorphic rocks.

**Chemical Oxygen Demand (COD):**

The Chemical Oxygen Demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. COD is widely used as a means of measuring pollution strength of domestic and industrial effluents.

The dichromate reflux method is preferred over procedures using other oxidants because of superior oxidizing ability, applicability to a wide variety of samples, and ease of manipulation.

Oxidation of most organic compounds is 95 to 100 % of the theoretical value. Pyridine and related compounds resist oxidation and volatile organic compounds are oxidized only to the extent that they remain in contact with the oxidant. Ammonia, present either in the waste or liberated from nitrogen containing organic matter, is not oxidized in the absence of significant concentration of free chloride ions.

During the determination of COD, organic matter is converted to carbon dioxide and water regardless of the biological assimilability of the substance.

COD is a measure of organic matter which estimates the carbonaceous factors of organic matter. Oxygen is the most vital factor for living beings to maintain the metabolic process and reproduction.

**Heavy metals:**

Metals with specific gravity greater than 5 or often more are termed as heavy metals. The term simply used to denote metals that are toxic. The effect of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Some metals are essential, others may adversely affect water consumers, wastewater treatment systems and receiving body.
Metals differ from other toxic substances in way that they are neither created nor destroyed by humans\textsuperscript{133,134}.

Copper is of physiological importance as a supplement to iron for hemoglobin regeneration and is essential constituent of tissue cells, but the body requirements is met by food intake since the amount of copper usually available in the drinking water is inadequate\textsuperscript{135}.

Heavy metals in wastewater come from industries and municipal sewage, and they are one of the main causes of water and soil pollution. Accumulation of these metals in wastewater depends on many local factors such as type of industries in region, people’s way of life and awareness of the impacts done to the environment by careless disposal of wastes. Therefore the presence of heavy metals in wastewater is not only of great environmental concern but also strongly reduces microbial activity, as a result adversely affecting biological wastewater treatment processes. Moreover the toxicity of heavy metals in wastewater was shown to be dependent on factors like metal species, concentration, pH, wastewater pollution load and solubility of the metal ions. Wastewater is known to be a major source of pollution with heavy metals\textsuperscript{136}. The principal concerns about the heavy metals are their persistency in environment as they do not generally degrade, volatilize or decay by photolysis\textsuperscript{137}. Heavy metals tend to be extracted in primary treatment and separate out in primary sludge.

Sodium:

Sodium is present in most natural waters. The levels may vary from less than 1 mg/l to more than 500 mg/l. The ratio of sodium to total cations is important in agriculture and human pathology. Soil permeability can be harmed by a high sodium ratio\textsuperscript{99}.

It is the dominant cation in most mineralized groundwater with the exception of gypsiferous and many Ca-HCO\textsubscript{3} waters\textsuperscript{138}. In humid environment sodium is flushed from the soil and unsaturated zones, whereas in the arid climates the concentration of sodium in groundwater is due to the precipitation of calcite. Sodium is generally present in fresh waters and sodium ions, in concentrated solutions,
however, complex ions and sodium ion pairs, such as Na$_2$CO$_3$, Na$_2$SO$_4$ are present$^{139,126}$. With the increased use of sodium compounds in different industries like pigment, colour and paper mill the effluents of these units increases the sodium content in surface and groundwater$^{140}$. The sodium concentration more than 50 mg/l make the water unsuitable for domestic use$^{14}$. Kelley pointed out the importance of considering the concentration of sodium ions in assessing the suitability of water for irrigation. According to him, excess of sodium ions in irrigation water reacts with soil to reduce its permeability as a result of clogging of particles$^{107}$.

**Total Suspended Solids (TSS):**

These solids denote the suspended impurities present in the water. In most of the cases, they are of organic in nature and pose severe problems in water pollution$^{106}$.

**Phenol:**

Phenols, defined as hydroxyl derivatives of benzene and its condensed nuclei, may occur in domestic and industrial wastewaters, natural waters, and potable water supplies$^{99}$.

Phenol is potential or known human carcinogen and is considerable health concern even at low concentration. Hence the treatment of wastewater containing phenol is a necessary.

**Biochemical Oxygen Demand (BOD):**

The measurement of BOD is used to determine the relative oxygen requirements of wastewaters, effluents and polluted waters. BOD gives an idea about the extent of pollution. It should be noted that BOD is an indicator and not a pollutant.

The test measures the oxygen utilized during a specified incubation period for biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron$^{99}$. 
BOD is defined as the amount of oxygen required by bacteria in decomposing organic material in a sample under aerobic condition at 27 °C over a period of 3 days\textsuperscript{141}.
\[ C_6H_{12}O_6 + 6O_2 \xrightarrow{\text{Microbes}} CO_2 \uparrow + H_2O + \text{new microbes} \quad \text{...(1.1)} \]

Thus the test involves measurement of O\textsubscript{2} consumed by bacteria while stabilizing organic matter under aerobic condition\textsuperscript{106}.

Information concerning BOD of waste is an important consideration in the design of treatment facilities. It is a factor in the choice of treatment method and is used to determine the size of certain units, particularly trickling filters and activated sludge units. It can be used to evaluate the efficiency of various units, once the treatment plants are placed in operation\textsuperscript{127}.

The BOD\textsubscript{3} test is a very important parameter for the determination of pollution stage of wastewater, in order to evaluate the efficiency of wastewater treatment system, industrial waste and any type of water pollution\textsuperscript{78}.

**Quality analysis of groundwater:**

The investigation of groundwater resources in any region is primarily concerned with its utility for irrigation. Another interesting purpose of studying groundwater would be to consider to distribution of various salts from geochemical view point\textsuperscript{8}.

The present study also involves some different aspect related to quality of groundwater and its suitability for drinking, domestic purpose. Hence the study is divided into following aspects:

1.1 Classification of irrigation water
1.2 Rating of water quality
1.3 Interrelationship between the different characteristics of groundwater.
1.4 Water Quality Index.
1.1 Classification of irrigation water:

Water quality plays an important role in irrigated agriculture. Many problems arise during inefficient management of water for agriculture use. The concentration and composition of dissolved constituents in water determine its quality for irrigation use. Quality of water is an important consideration in any appraisal of salinity or alkali conditions in an irrigated area. Under good soil and water management practices, good quality water has the ability to cause maximum yield.

The suitability of groundwater for irrigation depends upon its mineral constituents. The salts present in the water, besides affecting the growth of the plants directly also affect the soil structure, permeability and aeration, which indirectly affect the plant growth. The sodium hazard of irrigation water can be well understood by knowing SAR. High sodium in water leads to the development of alkali soil, which has unfavorable structure and restricts aeration.

Sodium is the most important element, which influences the soil quality and plant growth either by affecting the permeability of soil by clogging or replacing other cations. The extent of replacement of other cation by sodium is denoted by SAR.

Sodium Absorption Ratio (SAR) is defined by following equation:

\[ \text{SAR} = \frac{\text{Na}^+}{\sqrt{(\text{Ca}^{+2} + \text{Mg}^{+2})/2}} \]

Salinity is also one of the main factors for judging the quality of groundwater for irrigation purpose. Classification of water for irrigation use based on SAR and EC is shown in Table – 1.9 and Table – 1.10 respectively.

Table 1.9: Classification of water based on SAR.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sodium hazard</th>
<th>Class</th>
<th>SAR</th>
<th>Category of water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Low</td>
<td>S₁</td>
<td>&lt; 10</td>
<td>Excellent</td>
</tr>
<tr>
<td>2</td>
<td>Medium</td>
<td>S₂</td>
<td>10 to 18</td>
<td>Good</td>
</tr>
<tr>
<td>3</td>
<td>High</td>
<td>S₃</td>
<td>18 to 26</td>
<td>Fair</td>
</tr>
<tr>
<td>4</td>
<td>Very high</td>
<td>S₄</td>
<td>&gt; 26</td>
<td>Poor</td>
</tr>
</tbody>
</table>
Table 1.10: Classification of water based on EC\textsuperscript{142}.

<table>
<thead>
<tr>
<th>No.</th>
<th>Salinity</th>
<th>Class</th>
<th>EC (mmhos/cm)</th>
<th>Category of water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Low</td>
<td>C\textsubscript{1}</td>
<td>&lt; 0.25</td>
<td>Excellent</td>
</tr>
<tr>
<td>2</td>
<td>Medium</td>
<td>C\textsubscript{2}</td>
<td>0.25 – 0.750</td>
<td>Good</td>
</tr>
<tr>
<td>3</td>
<td>High</td>
<td>C\textsubscript{3}</td>
<td>0.750 – 2.250</td>
<td>Fair</td>
</tr>
<tr>
<td>4</td>
<td>Very high</td>
<td>C\textsubscript{4}</td>
<td>&gt; 2.250</td>
<td>Poor</td>
</tr>
</tbody>
</table>

EC and SAR are responsible for salinity and sodium hazard respectively. Therefore, U.S. Salinity Laboratory proposed a classification\textsuperscript{142,144} with reference to SAR as an index for sodium hazard S and electrical conductivity (EC) as an index of salinity hazard C. This classification categorizes for water into 16 classes as shown in Table – 1.11:

Table 1.11: Classification of water based on EC and SAR\textsuperscript{142,144}.

<table>
<thead>
<tr>
<th>Class</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1S1</td>
<td>Low salinity low sodium hazard water</td>
</tr>
<tr>
<td>C1S2</td>
<td>Low salinity low sodium hazard water</td>
</tr>
<tr>
<td>C1S3</td>
<td>Low salinity low sodium hazard water</td>
</tr>
<tr>
<td>C1S4</td>
<td>Low salinity low sodium hazard water</td>
</tr>
<tr>
<td>C2S1</td>
<td>Medium salinity low sodium hazard water</td>
</tr>
<tr>
<td>C2S2</td>
<td>Medium salinity medium sodium hazard water</td>
</tr>
<tr>
<td>C2S3</td>
<td>Medium salinity high sodium hazard water</td>
</tr>
<tr>
<td>C2S4</td>
<td>Medium salinity very high sodium hazard water</td>
</tr>
<tr>
<td>C3S1</td>
<td>High salinity low sodium hazard water</td>
</tr>
<tr>
<td>C3S2</td>
<td>High salinity medium sodium hazard water</td>
</tr>
<tr>
<td>C3S3</td>
<td>High salinity high sodium hazard water</td>
</tr>
<tr>
<td>C3S4</td>
<td>High salinity very high sodium hazard water</td>
</tr>
<tr>
<td>C4S1</td>
<td>Very high salinity low sodium hazard water</td>
</tr>
<tr>
<td>C4S2</td>
<td>Very high salinity medium sodium hazard water</td>
</tr>
<tr>
<td>C4S3</td>
<td>Very high salinity high sodium hazard water</td>
</tr>
<tr>
<td>C4S4</td>
<td>Very high salinity very high sodium hazard water</td>
</tr>
</tbody>
</table>
1.2 Rating of water quality:

Various parameters like Total hardness, chloride, TDS are used for mapping of groundwater quality. Classification of water based on Total hardness\textsuperscript{68,145}, chloride\textsuperscript{62} and TDS\textsuperscript{146} is shown in Table – 1.12, Table – 1.13 and Table – 1.14 respectively.

<table>
<thead>
<tr>
<th>Total Hardness (mg/l)</th>
<th>Water quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-75</td>
<td>Soft</td>
</tr>
<tr>
<td>75-150</td>
<td>Moderate hard</td>
</tr>
<tr>
<td>150-300</td>
<td>Hard</td>
</tr>
<tr>
<td>&gt; 300</td>
<td>Very hard</td>
</tr>
</tbody>
</table>

**Table 1.12 : Sawyer and McCarthy’s classification of water based on TH\textsuperscript{68,145}.**

<table>
<thead>
<tr>
<th>Chloride (mg/l)</th>
<th>Water quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 100</td>
<td>Safe</td>
</tr>
<tr>
<td>100-150</td>
<td>Tolerable</td>
</tr>
<tr>
<td>150-200</td>
<td>Tolerable to some extent</td>
</tr>
<tr>
<td>200-250</td>
<td>Intolerable</td>
</tr>
<tr>
<td>&gt; 250</td>
<td>Health hazard</td>
</tr>
</tbody>
</table>

**Table 1.13 : Classification of water based on Chloride\textsuperscript{62}.**

<table>
<thead>
<tr>
<th>TDS (mg/l)</th>
<th>Water quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Up to 500</td>
<td>Desirable for drinking</td>
</tr>
<tr>
<td>500 – 1000</td>
<td>Permissible for drinking</td>
</tr>
<tr>
<td>Up to 3000</td>
<td>Useful for irrigation</td>
</tr>
<tr>
<td>Above 3000</td>
<td>Unfit for drinking and irrigation</td>
</tr>
</tbody>
</table>

**Table 1.14 : Classification of water based on TDS\textsuperscript{146}.**

1.3 Interrelationship between the different characteristics:

A number of techniques and methods have been developed to interpret the chemical data. Zaporozec summarized the various modes of data representation and discussed their possible uses\textsuperscript{147}. The task of monitoring the quality of water is facilitated if one can find some correlation among these numerous parameters. When such correlation
do exists, then by measuring a few important parameters one can easily calculate the remaining parameters and the quality of water can be easily and quickly assessed.\textsuperscript{107}

**Correlation** is the mutual relationship between two variables. Direct correlation exists when increase or decrease in the value of one parameter is associated with a corresponding increase or decrease in the value of the other. The correlation is positive when increase in one parameter causes the increase in other parameter. And it is negative when the increase in one parameter causes decrease in the other parameter. The correlation coefficient \((r)\) has a value between +1 and -1. The correlation between the parameters is characterized as strong, when it is in the range of +0.8 to 1.0 and -0.8 to -1.0, moderate in the range of 0.5-0.8 and -0.5 to -0.8, weak when in the range of 0.0 to 0.5 and -0.0 to -0.5.\textsuperscript{148} Correlation coefficient is zero means that there is no linear relationship between the variables.\textsuperscript{149}

It was concluded that correlation study and correlation coefficient values can help in selecting treatment to minimize contaminants in water.\textsuperscript{150}

**Regression analysis** helps to find out how the change in one variable corresponds to changes in the other variable. The statistical regression analysis has been found to be a highly useful tool for correlating different parameters.\textsuperscript{151-154} A systematic study of correlation and regression coefficients of the water quality parameters not only helps to assess overall water quality but also to quantify relative concentration of various pollutants in water and provide necessary cues for implementation of rapid water management programmes.\textsuperscript{155}

The regression equation is \(y = ax + b\), where \(x\) and \(y\) are the independent and the dependent variables respectively and ‘\(a\)’ and ‘\(b\)’ are constants called regression coefficients. The constant ‘\(a\)’ tells us about the quantitative changes in \(y\) for each unit of change in \(x\). If ‘\(a\)’ is positive, then the value of \(y\) increases with increase in \(x\). If ‘\(a\)’ is negative then the value of \(y\) decreases with increase in the value of \(x\). If ‘\(a\)’ is zero then the value of \(y\) does not change with change in \(x\) values. The value of \(y\) is equal to the constant ‘\(b\)’ when \(x\) is equal to
zero. ‘b’ is also called the y intercept and its value may be positive or negative.7

1.4 Water Quality Index (WQI):

Water Quality Index (WQI) is one of the most effective tools to communicate information on the quality of water to the concerned citizens and policy makers. It, thus, becomes as important parameter for the assessment and management of groundwater. WQI is defined as a rating reflecting the composite influence of different water quality parameters. WQI is calculated from the point of view of the suitability of groundwater for human consumption.

The WQI, which was developed in the nearly 1970s, can be used to monitor water quality changes in a particular water supply over time, or it can be used to compare a water supply’s quality with other water supplies in the region or from around the world. The results can also be used to determine if a particular stretch of water is considered as “healthy”.121

In this present study, WQI created by Canadian Council of Minister of the Environment (CCME) was used. The advantages of an index include its ability to represent measurements of a variety of variables in a single number, its ability to combine various measurements in a variety of different measurement units in a single metric and its effectiveness as a communication tool. When the same objectives and variables are used, the index can be used to convey relative differences in water quality between sites over time. The sampling protocol requires at least four parameters, sampled at least four times. No maximum number of parameters or samples has been set. The type and number of parameters and samples used for the WQI calculation is left to the specialist’s discretion. It is flexible with respect to the type and number of water quality parameters to be tested, the period of application and type of water body. These decisions are left to the users.161

An environmental index is similar to stock market index. It is not intended to replace a detailed analysis of environmental monitoring
data, nor should be used as the only tool for management of water bodies. What it can do is provide a broad overview of environmental performance. Disadvantages of using an index include the loss of information on single variables, the sensitivity of the results to the formulation of the index, and the loss of information on interactions between variables. Table -1.15 shows CWQI rating system

<table>
<thead>
<tr>
<th>WQI</th>
<th>Rating</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>95-100</td>
<td>Excellent</td>
<td>Water quality is protected with a virtual absence of threat or impairment; conditions very close to natural or pristine levels. These index values can only be obtained if all measurements are within objectives virtually all of the time</td>
</tr>
<tr>
<td>80-94</td>
<td>Good</td>
<td>Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels.</td>
</tr>
<tr>
<td>65-79</td>
<td>Fair</td>
<td>Water quality is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable levels.</td>
</tr>
<tr>
<td>45-64</td>
<td>Marginal</td>
<td>Water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels.</td>
</tr>
<tr>
<td>0-44</td>
<td>Poor</td>
<td>Water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels.</td>
</tr>
</tbody>
</table>

The main objectives of present study are as under:

OBJECTIVES :
[1] To evaluate the quality of groundwater of Valsad District.
[5] To evaluate Water Quality Index (WQI) to identify overall water quality of Valsad District.
[7] To find out the performance evaluation of the CETP in Vapi GIDC.
REFERENCES


6. IWRS, Theme paper on five decades of water resources development in India, Indian Water Resources Society publication (1998)


17. http://www.uwsp.edu


49. T. Mkandawire, Quality of groundwater from shallow wells of selected villages in Blantyre district, Malawi, Physics and Chemistry of the Earth, Parts A/B/C, 33(8-13), 807-811 (2008)


70. B. M. Prasad, An overview of CETPs in India, CPCB, Delhi (2000)

71. http://www.bvsde.paho.or

72. http://envfor.nic.in


82. M. Maheshvari and S. Dubey, Common Effluent Treatment Plant -A solution or a problem itself, Toxic Link (a non profit environmental organization) (2000)


95. http://www.time.com
100. M. Buragohain, B. Bhuyan and H.P.Sharma, Distribution of water quality parameters in Dhemaji district, Assam, *J. of Envi. Sci. and Engg.*, **52(3)**, 241-244 (2010)
102. Statement of basis purpose for the national secondary drinking water regulations, Washington DC, US Environmental Protection Agency (1977)
108. USSLS, Diagnosis and Improvement of Saline and Alkali soils, United States Salinity Laboratory Staff, Oxford & IBH Publishing Co. Ltd, New Delhi, 166 (1968)
111. D. E. Fulvio and L. Olori, Hardness of drinking water and public health, Pergamon publication, New York, 95 (1965)
112. Quality criteria for water, Washington, DC, Environmental Protection Agency (1976)


122. A. Senning, Sulfer in organic and inorganic chemistry, Marcel Dekker Inc., 2, New York, 160 (1972)


133. C. D. Klaassen, Casarett and Doul’s Toxicology, the basic science of poisons, 5th International edition, McGraw Hill, Health profession division, USA, 691-721 (1996)


147. A. Zaporozec, groundwater, 10, 32-43 (1972)
149. http://www.stats.gla.ac.uk


157. S. Naik and K. M. Purohit, Indian J. of Environ. and Ecoplan., 5(2), 397-402 (2001)


