WATER QUALITY VARIATIONS, ITS INFLUENCE ON DRINKING WATER TREATMENT AND REMEDIAL MEASURES - *A CASE STUDY OF PEECHI RESERVOIR, THRISSUR, KERALA*

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By

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DECLARATION

I hereby declare that the work presented in this thesis entitled "Water Quality Variation, its Influence on Drinking Water Treatment and Remedial Measures - A Case Study of Peechi reservoir, Thrissur, Kerala" is based solely on the original work done by me under the guidance of Dr. V. N. Sivasankara Pillai, Professor and Director, School of Environmental Studies, Cochin University of Science and Technology, and that no part of this thesis forms part of any other thesis or has been submitted previously for the award of any other degree.

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CERTIFICATE

This is to certify that the contents of this thesis entitled "Water Quality Variation, its Influence on Drinking Water Treatment and Remedial Measures - A Case Study of Peechi reservoir, Thrissur, Kerala" are based entirely on the work done by Mr. Peeter K. Varkey under my guidance in the School of Environmental Studies, Cochin University of Science and Technology, and that no part of this thesis forms part of any other thesis or has been submitted previously for the award of any other degree.

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PREFACE

The work presented in this dissertation was carried out during 1998 – 2001 in the Water Quality Laboratory of the School of Environmental Studies, and in the field laboratory set up in the Peechi Water Works premises. The Kerala Water Authority requested the School of Environmental Studies to carry out investigations on the mechanism of sporadic mobilization of iron and odour in the raw water drawn to the drinking water treatment plant. The currently used treatment process failed to remove iron completely. This led to problems in the filter and complaints of taste and colour due to iron in the finished water. The sporadic nature of the problem itself made the trouble shooting difficult.

The problem was looked in from three points of view.

1. Influence of environmental (climatic) conditions on the dynamics of the relevant basin of the reservoir.
2. Influence of the physical dynamics on the physico – chemical quality of water.
3. Identification of cost-effective treatment processes to suit the existing plant.

Since the problem emerged only during the post- monsoon to pre-monsoon months, a related problem was investigated, namely, influence of anions on the oxidation of Fe(II) in natural waters by air. This is presented in Part II of the dissertation.

Meanwhile, United Catalysts, Udyogmandal referred a problem faced by them in $Fe_2O_3.Cr_2O_3$ catalyst manufacture. In spite of best practices in the industry, the finished catalyst contained traces of Cr(VI) (which they called occluded), the blacklisted constituent in any waste material. Hence buyers always insist on the absence of Cr(VI). Our studies on the adsorption of Cr(VI) on Fe_2O_3/Cr_2O_3 revealed that Cr(VI) is reintroduced in the medium by the $Fe(OH)_3$ catalyzed oxidation of $Cr(OH)_3$ by dioxygen at $pH > 12$. It is for the first time that the oxidation of Cr(III) to Cr(VI) at ambient temperature by dioxygen is reported.

The content of the dissertation has been partly published/accepted for publication in the following forums

1. International Conference on Innovative Technologies for Rural Water Supply and Environmental Sanitation held at University of Roorkee from October 12-13, 2000.

   "Removal iron from groundwater – A comparative study of some selected methods"

2. National Seminar "Environmental Management & Pollution Abatement" held at Annamalai University on 2,3 March 2001.

   "Quality variations in Ghyben- Herzberg Lenses of Vypeen Islands, Kochi"

3. Paper communicated.

   "Water quality variations and management problems in a tropical reservoir". Lakes & Reservoirs Research and Management.

Chapter 1

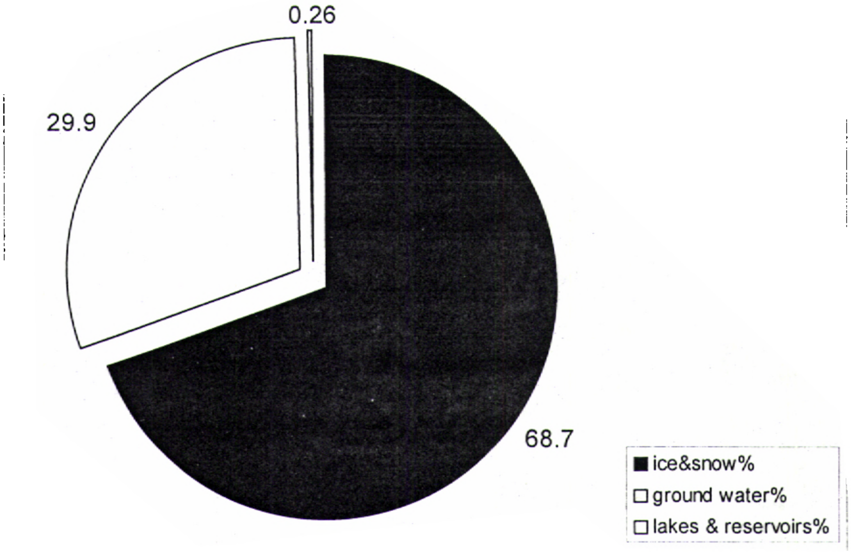
INTRODUCTION

1.1.1. Water Resources

Water resources occupy a special place among natural resources. Water is the basis of life on earth; it is the main component of the environment and essential constituent for human life. Water is also fundamental for sustaining a high quality of life, and for economic and social development. Just like other natural resources, water resources are limited at any location on earth at any time, and they should be used rationally for sustainable development.

The total amount of water in the hydrosphere consists of free water in liquid, solid or gaseous states in the atmosphere, on the earth's surface, and in the crust down to a depth of 20,000 meters. The earth's hydrosphere contains about 1,386 million cubic kilometers of water (Shiklomanov 2000). But not all this quantity is in usable form. Major portion of this (97.3%) is saline. The rest (2.7%) is fresh water. The greater portion of this fresh water stock (68.7%) is in the form of ice and permanent snow cover in the Arctic, Antarctic, and mountainous regions. Fresh groundwater comprises 29.9% of total freshwater resources. Only 0.25% of the total amount of freshwater on the earth is concentrated in lakes, reservoirs and river systems (Varma 1999, Shiklomanov 2000). Global freshwater distribution is given in Figure 1.1.1.

These estimates give a long term, average amount of water simultaneously contained in the water bodies, aquifers and the atmosphere



(Shiklomanov 2000)

Figure 1.1.1. Distribution of freshwater on earth.

For shorter time intervals the values of water storage in the hydrosphere vary during water exchange among the oceans, land and the atmosphere. The distribution of freshwater resources on earth is uneven. Renewable water resources include the yearly-replenished lakes, which play a major role in the process of water turnover on the earth. The annually renewed volume consists mainly of the regional runoff and the inflow of ground water in to the river network.

Data on earth's total river runoff, as a major component of the global hydrological cycle and basic characteristics of renewable freshwater resources are cited in many studies published since the turn of the past century in different countries of the world. (Nace 1967; Lvovitch 1974; Baumgartner and Reichel 1975; Korzoun 1974; Berner and Burner 1987). Estimates have also been regularly published in the proceedings of World Water Resources Institute. The data on renewable water resources and water availability by continents is given in Table 1.1.1.

The mean value of renewable global water resources is estimated at 42,750 km^3 per year and varies greatly in space and time (Shiklomanov 2000). The largest water resources of the world are located in Asia and South America (13,5000 and 2,400 km^3 per year respectively).

1.1.2. **Accessible Water Resources**

Since the greater portion of the total freshwater resources (68.7%) is in the form of ice and permanent snow cover in the Antarctic, Arctic and mountainous regions, they are inaccessible for human use. Groundwater comprises 29.9% of freshwater resources. The amount of freshwater

Table 1.1.1 Renewable water resources of the world and water availability by continents (Shiklomanov, 2000)

Continent	Area $10^6 km^2$	Water resources km^3/year				Potential water availability per km^2
		Average	Maximum	Minimum	C.V	
Europe	10.46	2,900	3,410	2,254	0.08	277
North America	24.3	7,890	8,917	6,895	0.06	324
Africa	30.1	4,050	5,082	3,075	0.10	134
Asia	43.5	13,510	15,008	11,800	0.06	311
South America	17.9	12,030	14,350	10,320	0.07	672
Australia & Oceania	8.95	2,400	2,880	1,891	0.1	269
The world	135	42,780	44,750	39,780	0.03	316

concentrated in lakes, reservoirs and river systems is the most accessible for human use. Surface water resources provide for more than 70% of the total water demand. Major surface water resources are the river systems.

Earth's water turnover depends on water storage and dynamics of storage. This storage dynamics is estimated by the period of full replenishment. The uneven distribution and differing climatic regimes influence the accessibility of water resources. Population growth and urbanization exert heavy demand on water resources. Surface as well as groundwater resources are under the threat of contamination. Accessible water resources also include the yearly renewable groundwater that is not drained by rivers. In certain regions of the world the groundwater resources are the main provider to water needs. In certain areas even though groundwater sources are available, their tapping is economically not feasible. Globally total water abundance is not the problem; the problem is water availability in the right place in the right time in the right form with right quality. Ambitious programmes for diversion of fresh water from areas of abundance (polar regions, high mountain ranges) to areas of scarcity are proposed. But the cost of such plans is exorbitant and prohibitive.

1.1.3. **Water Uses**

Water is a critical resource for sustainability and development of civilization. Water finds application in almost all spheres of life. In general, organized water uses can be generalized into municipal, industrial and agricultural water uses. The quantity and quality requirements depend on the intended use of water.

Global water use assessments have been made with different degrees of comprehensiveness and reliability in many countries of the world. Various studies on the quantity and pattern of water use were conducted at different periods in various countries. Most significant of these studies include (Lvovitch 1969, 1974; Holy 1971; Falkenmark and Lindth 1974; DeMare 1977; USGS 1980; Ambroggi 1980; Shiklomanov 2000). Several basic factors such as socio-economic development level, population, physiographic features and area of the territory determine the volume and structure of water use, its dynamics and future tendencies.

Municipal water uses are apportioned among housing estates, domestic and public services and enterprises. The volume of public water use depends on population, the level of services and the availability of resources. Climatic factors also play a crucial role in the nature and quantum of water use. Per capita use of water vary from country to country and from region to region. The pattern and quantity of water used is strongly influenced by economic condition of the population. There exists a disparity in the water use pattern of developing and developed countries. In developed countries per capita water use is in the range of 300 – 600 litres per day, where as in developing countries this comes to about 50-100 litres per day only (Shiklomanov 2000).

In industry water is used for cooling, transportation, as a solvent and as an ingredient of finished products. The principal use in industry is for thermal and atomic power generation. In addition to this, other industrial users include chemical and petrochemical, ferrous and non-ferrous metallurgy, and pulp and paper industry. As an offshoot of industrial development urbanization occurred. Thus industries indirectly influence water demand of other sectors like community water supply. Many industries use water in low quantities but with high quality. Electronic industry is a typical case in point.

Globally agriculture is the largest freshwater user. Water use by agriculture is determined by the development of irrigated land (Shiklomanov 2000). Quantity of water required for irrigation is determined by irrigated land area, values of specific water intake and returnable waters in percentage of water intake. These factors depend on general physiographic conditions, serviceable condition of irrigation systems, watering techniques and crop composition. Smallest values of water withdrawals for irrigation are observed in northern countries and regions. In northern Europe, withdrawal is 300 - 5,000 m^3/ha, while in southern and eastern European countries this amount to 7,000 – 11,000 m^3/ha (Shiklomanov 2000). The returnable waters equal approximately 20 – 30 percent of water intake. In the countries of Asia, Africa, Central and South America there is a great variation in climatic conditions, crop compositions and watering techniques. Therefore, the values of annual water withdrawal vary greatly, from 5,000-6,000 m^3/ha, and in individual regions of Africa to 20,000 or 25,000 m^3/ha (Shiklomanov and Markova 1987; Shiklomanov 1989, 1997; FAO 1995, 1999). In future, the quantity of water withdrawal will change considerably because of advanced irrigation systems, improved watering requirements and techniques. In agriculture, in addition to irrigation, water is spent on domestic needs of population, in cattle breeding and modernizing rural populated areas.

1.1.4. **Reservoirs**

The uneven distribution of water resources on the earth makes some regions water scarce while others water rich. This spatial and temporal variation in quantity necessitated the storage of water to meet the water demands. Reservoirs are storage structures for surface water sources. Hutchinson (1957) classified reservoirs as one of seventy six lake types based on basin origin, the key distinguishing feature being the presence of a man built dam located at the downstream end of the flooded river valley. The structural and operational characteristics play an important role in defining the characteristics of impounded water (Kennedy *et al.* 1985; Kennedy 1999a). The construction of large storage reservoirs leads to fundamental transformations in the temporal and spatial distribution of river runoff and increased the availability of water during low flow periods and dry years. Reservoirs were built from time immemorial. But they attained prominence in the second half of twentieth century. At present, the total volume of world reservoirs is about 6,000 km^3 and the total area of their water surface reaches 500,000 km^2 (Shiklomanov 2000).

The sizes of reservoirs vary widely. The size of the river, length and height of the dam and the discharge of the river determine the size of the reservoir. Based on the size of the dam, reservoirs are grouped into small reservoirs, medium reservoirs and large reservoirs. According to the International Committee on Large Dams (ICOLD) a dam is classified as large if it has a height of more than 15 m, or has a length of 500 m or more, or if the resulted reservoir has a storage volume of more than one million litres (BOR 1987; ICOLD 1998).

Reservoirs are the basis for large-scale water management systems. Reservoirs and their dams prevent or mitigate devastating floods and catastrophic droughts. They adjust natural runoff with its seasonal variations and climatic irregularities to meet the pattern of demand for irrigated agriculture, power generation, domestic and industrial water supply and navigation. Reservoirs provide recreation, attract tourism, promote aquaculture and fisheries, and can enhance environmental conditions (ICOLD 1998). Thus reservoirs and dams have become an integral part of our engineering infrastructure. Reservoirs are either single or multipurpose. On a global scale 48% of the reservoirs are multipurpose. A smaller portion (20%) is exclusively for power generation. The rest is for flood control and drinking water supply (Lecornue 1998). Usually reservoirs are constructed in mountainous, piedmont and sparsely developed regions with no flooding and vast areas of fertile lands suitable for agricultural use. Vast areas of land were brought under cultivation due to better irrigation facilities provided by reservoirs. Reservoirs helped a lot in developing agriculture and power generation in many countries. Reservoirs played a major role in the success of the "Green Revolution" in India.

Comparative studies of large reservoirs and natural lakes allowed identification of factors uniquely influencing the limnology of reservoirs (Thornton *et al.* 1980; Wetzel 1990). Large reservoirs have more expansive drainage basins, larger volumes and surface areas, greater depth, and shorter water residence times than natural lakes. Large drainage basins for reservoirs result in high aerial nutrient and sediment loading rates. High sediment loads decrease water clarity thus reducing potential phytoplankton production (Kennedy *et al.* 1982; Kimmel and Groeger 1984; Kimmel *et al.* 1990).

Even though reservoirs contribute greatly to the development of the region, they have many negative impacts on the environment. Alteration of water quality and ecology deserve mentioning in this regard. Studies indicated that reservoirs increased the occurrence of certain water borne diseases. The increased rate of occurrence of Schistosomiasis in the Nile delta region after the commissioning of Aswan High dam is a classical example of this phenomenon. The changed water quality of the reservoir and the resultant increase in the population of certain nematodes in the basin caused this interesting problem (Fahim 1981). In recent times old dams are dismantled for various reasons including dam safety. In United States of America more than 50 dams were decommissioned in the last decade (White and Moore 2000).

1.1.5. **National Scenario**

Globally India stands second in population and seventh in land area. Different climatic and geographical regions exist in the country. The availability of water differs from state to state. Since India has an agricultural economy, availability of water for agricultural purposes is crucial for Indian economy. India receives nearly 4,000 km^3 of water annually (IGIDR 1998). The amount of utilizable water available per person per year is 1250 m^3 and the average consumption is 680 m^3 per person per year (Varma 1999). Of this, agriculture consumes 84% of available water. Industry, thermal power and other sectors consume 12% and domestic sector consumes the remaining 4% of the available water.

Even though ancient Indians knew the concept of water storage and its conservation, large-scale storage projects were started during the British rule. Dam construction picked up in the country only after 1900. Dam construction attained its peak in the 1980s as is evident from Figure 1.1.2. At present, India has 4291 large dams counting the 695 currently under construction. This comes to around 9% of the global dam population (ICOLD 1998). In India reservoirs were constructed to meet the various demands of water during different seasons. The sector wise use of dams in India is given in Fig 1.1.3. Hydroelectric power generation, irrigation and drinking water supply are the three main objectives of these reservoirs. Major river systems in India are concentrated in the central and northern parts of the country. Most of the large river systems in India contain more than one reservoir. Many of these reservoirs are constructed in tectonically active areas especially in the Himalayan ranges.

In the southern part of the country the reservoirs are few in number. Kerala is noted for its waterfronts, inland waterways and streams. No major river system is present in the state. Of the 44 rivers of Kerala except Bharathapuzha, Periyar, Pamba and Chaliyar all others have watersheds less than 2000 km^2, and cannot be grouped as rivers (PWD 1974). They are better described as streams. With deforestation assuming large proportions in their watersheds, they have significant surface flow only during monsoon season. Many of these rivers dry up during non-monsoon period. In extreme cases

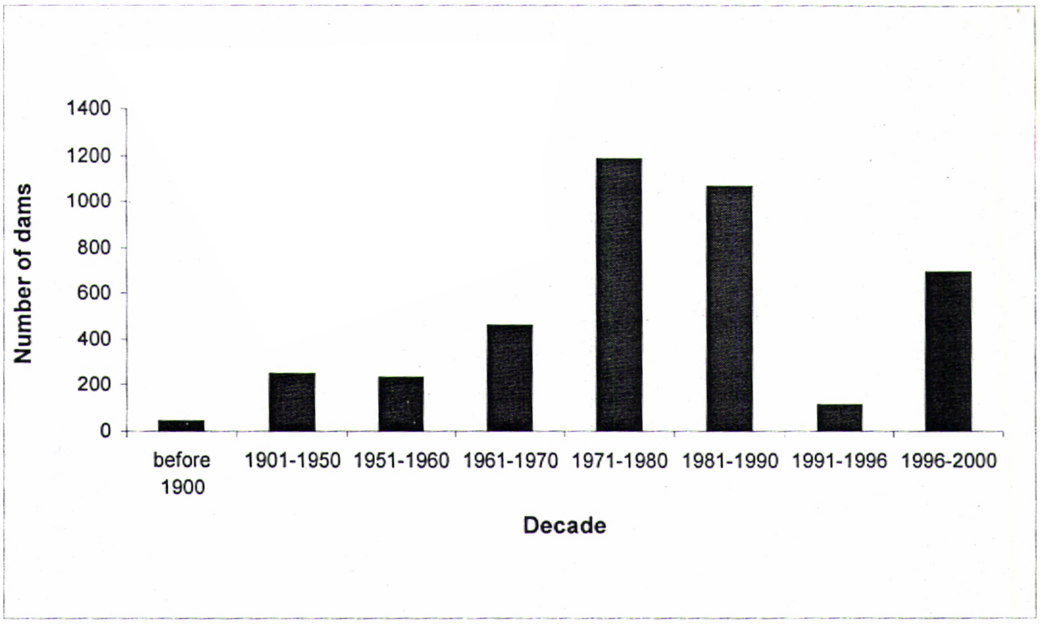


Figure 1.1.2. Dam commissioning in India by decades

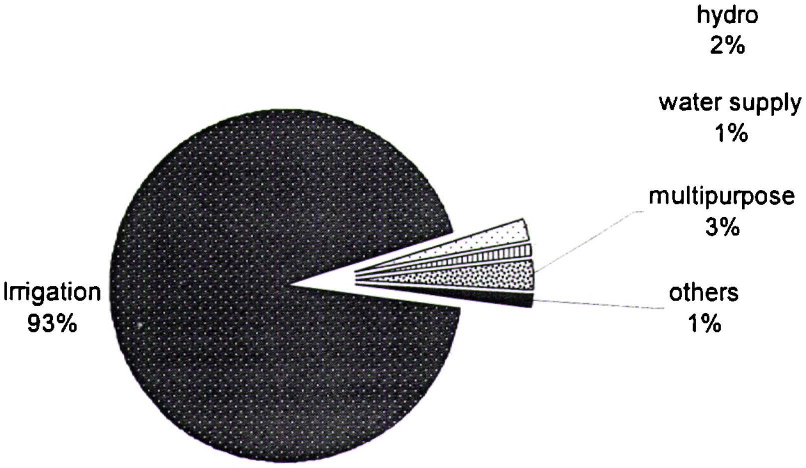


Figure 1.1.3. Sector wise use of dams in India.

people use these riverbeds for agricultural purposes. The monsoon rains extending from June to October replenish all the water bodies in the state. Naturally the reservoirs in Kerala have only small to moderate size. The most noted reservoir is Idukki reservoir with water spread area of 62 km^2, which is exclusively meant for hydroelectric power generation. Many small reservoirs were constructed in the rivers of Kerala. These include Peppara, Aruvikkara, Peechi, Malampuzha, Kuttiyadi, Chimmani, Mangalam, Neyyar and Edamalayar. Most of these reservoirs are multipurpose in character. Irrigation and power generation are the important intended uses of these structures. Many of the small reservoirs are used as drinking water sources for the adjoining villages and towns. Peechi in Thrissur district and Malampuzha in Palaghat district are two important irrigation-cum-drinking water supply reservoirs in the state. Water quality in these reservoirs shows sharp temporal variations leading to treatment problems. This problem is showing an increasing trend over the years.

1.1.6. **Water Quality Variations in Reservoirs**

Reservoirs and dams redistribute water from water surplus areas to water deficit areas. There are more than 46,000 major dams in the world (Kinney and Schoch 1996). The distribution and concentration of reservoirs vary from country to country. For many countries especially in the tropics reservoirs control the water regime and dictate the water budget of the country.

Water quality in reservoirs is different from that in stream/ river systems. Reservoirs are formed by impounding the water of streams/rivers.

Dams allow the storage and release of water and their operations have important secondary effects on water quality. Principal among these are influences on thermal budgets, thermal structure, mixing regime, and material budgets. The influence of outlet depth on thermal budgets for reservoirs is well documented (Kennedy *et al.* 1985; Kennedy and Walker 1990; Ford 1990). In general, the release of cool bottom waters through the near bottom outlets result in heat storage, while surface release result in dissipation of heat by removing warm surface water (Martin and Arneson 1978). These differences can lead to marked variations in thermal structure throughout an annual thermal cycle. The change from near surface to near bottom release would result in pronounced warming of the water column and a deepening of the seasonal thermocline. Conversely, near surface release would lead to the establishment of a seasonal thermocline similar to that for natural lakes of similar size and located in the same climatic region. These have important implications on trophic responses, since the depth of the thermocline will influence the depth of the mixed layer and the ratio of the mixed layer depth to the depth of the photic zone, both of which influence phytoplankton response.

The depth of withdrawal also influences the material budgets (Wright 1967; Kennedy and Walker 1990). Lakes and reservoirs function as settling basins for particulate material and because their bottom waters are influenced by interaction with underlying sediments (e.g., nutrient release during periods of anoxia), release of bottom water can reduce material detention times.

Hydraulic retention times strongly influence limnological processes in lakes and reservoirs (Straskraba *et al.* 1993). According to US EPA studies natural lakes have higher geometric mean values of hydraulic residence time than reservoirs (Thornton *et al.* 1980).

The location of the dam, distant from the point of inflow provides a physical setting conducive to the establishment of longitudinal gradients in water quality (Thornton *et al.* 1980; Kennedy *et al.* 1982). Reservoirs with large surface area and limited circulation exhibit lateral or regional differences in water quality conditions. Loss of suspended solids and particulate organic matter by sedimentation leads to increasing water clarity with increasing distance from inflows. For stratified reservoirs, cool inflows sink below surface waters at the point at which buoyant forces exceed advective forces and progress through the water column as an interflowing or under flowing density current (Kennedy *et al.*1985).

The impoundment also affects the characteristics of the adjoining land in the upstream and downstream sections of the river. These obstructions of flow cause physical, morphological and biological changes in the aquatic and land environments. River/stream is a very dynamic ecosystem, the more significant elements being water, sediment, banks, land and biota. The system elements are interactive and supportive. The following morphological and ecological changes do occur consequent to completion of a dam.

1.1.7. **Aging of Reservoirs**

Reservoirs are manmade structures and they are built to regulate flow regime and derive energy. Reservoirs are designed with an estimated life span. But in majority of cases heavy silting and related problems shorten the estimated life of the reservoir (Murthy 1974). Physicochemical as well as biological quality of water varies as the reservoir gets aged. The aging of reservoirs also affects its water holding capacity.

Water level changes in the reservoir affects the upstream and downstream regions differently. In the upper side of the reservoirs inundation occurs. In this region the flow becomes stagnant or becomes very slow. In most cases forestlands gets inundated and loss of biodiversity results. When the water regime changes from lotic to lentic the species pattern changes. Many aquatic organisms, which thrive in flowing water, perish or were restricted in number and habitat. The down stream stretch of the river dries up or the quantity of flowing water is minimum. The flow velocity and flow pattern change considerably. This changed velocity and reduced discharge have considerable impact on the aquatic communities in the downstream. The reduced flow in the downstream side facilitates anthropogenic activities like sand mining. Excessive sand mining alter structure of the riverbed and pose threat to riverine structures. In certain instances heavy encroachment of the channel banks have resulted. These activities cause accelerated erosion and disappearance of riverine flora and fauna.

Reservoirs having extensive shallow areas (i.e., depth of 3 meters or less) support extensive growth of rooted aquatic plants (macrophytes). Macrophytes contribute greatly to raw water quality problems. These aquatic plants contribute significant quantities of dissolved and particulate organic matter to the sediments and water column. Macrophytic photosynthesis contributes to elevated raw water pH. Rooted aquatic plants produce phenolic compounds that add to problems of taste and odour (Cooke and Kennedy

2001). Organic molecules from macrophytes are important disinfection bye products (DBP) precursors (Palmstrom et al. 1988).

In the case of certain anadromous fish species like salmon, which migrates from the sea to rivers for spawning, reservoirs pose great threat (USACE 2002). The construction of dams hinders navigation and transportation through water body.

The appearance of significant levels of DBPs, as well as problems of taste, odour, and toxic algae in finished drinking water are strongly related to ecological characteristics and the uses of watershed, to the timing, sources, and amount of total organic carbon (TOC), silt and plant nutrients such as phosphorous and nitrogen transported to the reservoir, and to the physical, chemical, and biological characteristics and responses of the reservoir to these materials (Karner *et.al.* 2001). Watershed linkages and the resulting water quality responses of the reservoir are part of the eutrophication process in the reservoir. The watersheds particularly influence reservoirs because they normally have a larger ratio of drainage area to surface area than do natural lakes. Reservoir with large drainage area receives large volumes of water and high loading of material. The water quality of tributaries is directly linked to the land use in the watershed (Cook and Kennedy 2001). Forests and vegetated land such as pastures and agricultural fields are more retentive of silt and plant nutrients, although they can be major sources of organic matter. The impact of nutrient enriched streams on reservoirs is better understood in terms of nutrient concentrations (Cook and Kennedy 2001). Agricultural and urban drainage areas have higher peak discharge and flow volumes than non disturbed areas. These accounts for enhanced erosion and nutrient loss, and therefore degrade stream quality. Local conditions, climate, landform and soil erodability and chemistry, as well as the percent of land area farmed or urbanized influence runoff quality and quantity (Yurista et.al. 2001). When rolling land is farmed without terraces erosion and runoff will be higher and suspended matter concentration increases sharply. Sandy and gravel laden soils have higher infiltration capacities and lower potential for erosion and nutrient loss than silt and loam soils or peat soils (Cook and Kennedy 2001).

Reservoir design and operation affect reservoir water quality. Kennedy (1999a) identified three primary reservoir designs. Tributary reservoirs are located on higher gradient streams and have low to moderate basin volumes. Mainstream reservoirs developed on large rivers, have moderate to large capacities and surface areas. Run-of-the river reservoirs are constructed on downstream reaches of rivers. Tributary reservoirs are deep and thermally stratified, whereas run-of-the river reservoirs are shallow and easily mixed. In these shallow reservoirs bottom sediments are important nutrient sources for algae but deep reservoirs have oxygen free bottom waters, which are rich in dissolved iron (Cook and Kennedy 2001).

Fate of tributary inflows, and reservoir design and operation have significant effects on raw water quality. Of particular importance are the effects of upstream reservoirs, longitudinal, physical, chemical and biological gradients, and operational decisions that affect depth, timing and volumes of water releases (Cook and Kennedy 2001).

Kennedy (1999b) found that if the operation of an upstream reservoir is regulated to increase its average annual volume and water residence time, phosphorous loading in the downstream reservoir would be minimum. Longer water residence time will also increase silt retention in the upstream reservoir. Significant gradients of water quality will be established down the length of the reservoir, depending upon reservoir design, tributary flow, and temperature (Thornton *et al.* 1980; Kennedy *et al.* 1985). This gradient has great impact on raw water quality depending upon location and depth of the treatment plant's intakes. The upper portions of the reservoir, termed the riverine zones, will have high flows and may have high nutrient concentrations, excessive levels of turbidity and low algal production. As momentum is lost due to increasing reservoir width and depth, inflowing tributary water assumes characteristic density and continues downstream as density current. If the water in the density current is loaded with organics from stream or watershed production, these may be carried onto the plant, depending on the intake depth.

There is a transition zone below the riverine area that remains nutrient rich but is clearer and has high algal productivity. This zone is a source of algal cells for the downstream reaches of the reservoir below the transition zone.

The last zone of the reservoir is the lacustrine zone. This zone extends to the dam, is broader and clear, may support significant algal biomass, and where depth permits, will exhibit thermal stratification. Size, depth, basin design and hydrology will influence the horizontal and vertical distribution and exchange of nutrients.

The amount of water withdrawn and the depth from which it is withdrawn can have an important effect on raw water quality. The elevation of water intake structures in a stratified reservoir will determine the quality of water taken to the treatment plant. For treatment plants with intakes at multiple depths, selecting an intake depth based on knowledge of vertical differences in water quality conditions in the reservoir will improve source water quality. Withdrawal of deep anoxic water will produce impaired source water, particularly if it is influenced by an underflow of cold tributary water or has become rich in dissolved iron. A potentially greater effect of withdrawal of cold hypolimnitic water is the vertical expansion of the reservoirs' warm, surface layer and the resultant decreased resistance to wind mixing through a decrease in the temperature difference between the epilimnion and hypolimnion. This means that warm summer winds could partially or completely mix the reservoir, leading to the introduction of nutrient rich hypolimnitic water to the surface. An intense algal bloom is likely to follow, possibly producing taste, odour, and algal toxins (Kennedy, 2001). Knowing the location of intake structures relative to tributary inflows or the location of macrophyte beds provide valuable management information.

In reservoirs with weak summer stratification, deep-water withdrawal or discharge increases the probability of mixing nutrient rich deep water to the surface by increasing the thermal instability of the water column. If mixing of this type occurs an algal bloom will result. Reduction in tributary loading of nutrients, silt and organic matter is required in order to improve raw drinking water quality (Kennedy 2001). Many watersheds already had extensive human modifications. These changes produced increased runoff to streams, decreased tributary and reservoir water quality (Carpenter *et al.* 1998) and increased costs and difficulties in meeting finished drinking water standards.

A comprehensive watershed and reservoir assessment programme consists of five parts.

1. Watershed delineation and contaminant sources inventory
2. Estimation of seasonal and annual loading of water and contaminants
3. Analysis of current reservoir condition
4. Projection of future reservoir conditions and
5. Establishment of a reservoir protection and rehabilitation plan.

In this study only the current reservoir conditions are analyzed. Based on this future condition of the reservoir and its influence on drinking water treatment is projected. Based on these an appropriate reservoir management plan should be implemented to conserve the reservoir and protect the water quality of the reservoir.

Basic watershed information is needed to identify and assess the actual and potential causes of poor reservoir water quality. These include topography, geology, soil type, vegetation, and demographic features. Two types of information are required to describe the reservoir, its physical characteristics and water quality condition. Basic information on the reservoir's morphometry, hydrologic and engineering characteristics help to define the physical influences on water quality. Tributary storage reservoirs are located on lower-order rivers in the upland areas of the drainage basins and thus, often reside in steeply sloping and dendritic basins with long, complex shorelines. Such reservoirs are relatively deep and strongly stratified. Inflows are lower in suspended sediment concentrations and exhibit great seasonal or short-term variability (Kennedy 2001). A measure of water quality and biological attributes determine the reservoir's response to loads from the watershed. Mean depth provides valuable information about the physico-chemical and biological processes in a reservoir. This taken together with information describing the inflow and outflow of water estimates the reservoir volume. Mean depth calculation also allows estimation of water residence time and flushing rate.

The sediment acts as a trap for various agricultural and industrial chemicals, which enter the aquatic environment through leaching and wash off. In the sediments these chemicals undergo various transformations through the action of biological agents and microorganisms. These transformations give rise to smaller biologically assimilable organic compounds (BAO) and affect the water quality. In many regions of the world intensive agricultural practices in the catchment area of reservoirs cause high influx of solids in to the reservoir. The runoff from the agricultural fields contains traces of pesticides and other agrochemicals, which affect the water quality in the reservoir. This non point source of pollution is difficult to control and cause problems in drinking water treatment.

In reservoir management, procedures are developed to regulate the flow of silt, nutrients and other pollutants and thereby improve the raw water quality. These procedures are grouped as those that reducing algal biomass, those reducing the macrophyte biomass, and those providing multiple water quality benefits.

1.1.8. Physical Processes in Lakes and Reservoirs

The global occurrence of lakes corresponds broadly to basin runoff. Within the equatorial region (~10^0 S to ~10^0 N latitude), approximately 1.5% of the earth's surface is covered by lakes. Here precipitation generally exceeds evaporation, surface runoff is maximized and lakes are hydrologically open. The largest surface coverage by lakes occurred in mid latitudes zones (~25^0 to ~60^0 north and south latitude)(Hostetler 1995). In these regions climatic factors critically affect the physical processes and energy budget of the water body. The various physical processes include interaction of water body with atmosphere, change in volume, transport and mixing. Thermal response of the reservoir and the heat budget of the water body critically influence the water quality in a reservoir.

1.1.9. Heat budget of lakes and reservoirs

All stagnant water bodies exhibit regular variation in water temperature that corresponds to seasonal cycles of prevailing climate (Hostetler 1995). The primary control of the seasonal cycle of water temperature at latitude is the seasonal cycle of insolation received at that latitude. Diurnal variations of water temperature results from the day-night variation in solar insolation and local weather conditions such as gusty wind or cloud cover.

The heating of a water body is governed by the partitioning of energy at the surface of a lentic water body (Hostetler 1995). If negligible heat transfer occurs between the water column and the underlying sediments, and if the lake is unfrozen, the surface energy balance (SEB) is given by the equation

$$Dq_s./dt == (1-\alpha_{SW})\ \Phi sw + (1-\alpha_{lW})\ \Phi_{lW} . \Phi_{lU} - q_{le} - q_h, \qquad (1.1)$$

Where dq_s/dt is the change in lake heat storage in the surface layer (W/m^2). α_{SW} is short–wave albedo (reflectivity) of lake surface (dimensionless); Φsw is global short-wave (direct + diffuse) radiation (W/m^2); Φ_{lU} is long wave radiation from lake surface (W/m^2); q_{le} is latent heat flux, positive if directed away from lake (W/m^2); and q_h is sensible heat flux, positive if directed away from lake (W/m^2).

Lake temperature is a measure of the heat stored in the lake. Roughly 40% of the net solar radiation passes through the surface layer and is absorbed at depth in accordance with Beer's law of light transmission in water (Hostetler 1995).

In the case of most lakes and reservoirs the SEB and subsurface absorption of solar radiation adequately account for the heating processes occurring. But in certain cases other sources and sinks of heat are important components of the annual heat budget. In some lake basins large volumes of warm or cold inflow (outflow) advect heat into (out of) lakes and influences the heat regime of the water body. In shallow lakes heat is transferred between the water and underlying sediment by conduction. The sediments generally act as sink to heat during spring and summer warming, and a source of heat during fall and winter (Hutchinson 1957; Dutton and Bryson 1962; Hughes 1967).

Thermal stratification and lake mixing are affected by non-climatic factors such as basin morphometry (surface area and depth), the geostrophic Coriolis force that arises from the rotation of the earth, and physical and chemical properties of lake water (Hutchinson 1957; Straskraba 1980; Wetzel 1983; Kirk 1988; Imboden and Wuest 1995). Shallow lakes and reservoirs often do not exhibit persistent temperature stratification because full-depth solar heating and wind driven mixing effectively suppress it. Stratification and vertical-temperature contrasts in shallow lakes follow the diurnal patterns of solar radiation and winds.

Lakes are complicated and diverse physical systems. The case of reservoirs is analogues. The difference lies in their age as well as the geological setting, which gave rise to their origin. The variety of size and shape results in different boundary effects. The large variability in topography and external forcing is responsible for the wide variety in physical appearance of lakes. Size increases the sensitivity to meteorological or climatic gradients. Mixing in lakes and reservoirs is highly variable in both time and space. This variability is due to climate and weather. Because of its influence on density, the chemical composition of lake water represents another key variable in lacustrine environment. The availability of competing, scavenging phases, like detrital particles, phytoplankton and authigenic precipitates contributes to the complexity and dynamics of mixing and transport phenomena in lakes and reservoirs.

The density stratification is of significance in determining the pattern of mixing in lakes and reservoirs. Although the horizontal extension of a lake is much larger than its vertical extension, mixing is usually faster horizontally than vertically. Stratification slows down vertical mixing and enhances horizontal mixing. Limnologists used the temporal evolution of thermally induced stratification for the classification of lakes (Hutchinson 1957).

External forces drive all mixing and transport phenomena in the aquatic environment, with the exception of molecular diffusion. The mixing patterns are the result of both external forces and internal properties of the system such as morphometry and stability of the water column. In density stratified lakes small-scale turbulence is essential for energy and mass transfer. Due to large diversity in the characteristic properties of lakes and reservoirs different mixing phenomena occur in them (Imboden and Wuest 1995). Relevant mixing processes depend on external forcing such as river inflow and outflow, turbidity currents, underwater springs, wind, surface heat flux and geothermal heat flux. Lake morphometry like boundary mixing and differential heating/cooling/mixing also contribute to the mixing regime in lakes and reservoirs.

Wind stress, surface buoyancy flux and river inflows create turbulent mixing in the surface layer of a lake or reservoir. The sharp density interface commonly found at the end of the stratification period results from positive buoyancy flux produced by surface cooling and subsequent convection in the mixed layer. Density gradients are caused by differential heating and cooling, or by varying concentrations of dissolved substances.

Experimental results indicate that mixing in the bottom boundary layer is important for the whole water body. Imboden and Joller (1984) concluded that mixing is more intense near the boundary than in the interior of the strata. Microstructure measurements show a strong increase in turbulence toward sediment (Wuest et al 1994). The contribution to the overall diapycnal fluxes in the hypolimnion of processes occurring at the bottom boundary is significant in small to medium sized water bodies. The contribution made by bottom - boundary mixing to overall mixing in all density stratified natural water bodies is significant (Garret 1990).

At lake surfaces wind is the main driving force for the currents that are responsible for the velocity shear and thus for isopycnal diffusion. In the density stratified hypolimnion currents are also driven by intrusion, i.e. by isopycnal pressure forces resulting from horizontal density – density gradients between adjacent water columns and from lateral water input. Intrusions can have several origins including plunging rivers, subsurface springs, the subsurface withdrawal of water, differential mixing at the sediment surface and topographical features, such as sills and narrows, differential deepening of the pycnocline due to spatial heterogeneity of the surface, wind stress and large scale exchange between basins with different mixing characteristics. In epilimnion intrusions also result from differential cooling and heating, especially in the shallow parts of the water body.

The annual stratification of a lake or reservoir is the most prominent feature occurring on a time scale of weeks and months. Surface waters show inherent seasonal changes in both isotopic composition of the influx and the atmospheric moisture in the hydrological balance, in the relationship between inflows and evaporation rates, as well as in the mixing regime in the lakes. In most cases the parameters that govern isotopic composition undergo seasonal changes that affect the enrichment of the heavy isotopic species in the water body. A lake's isotopic composition is largely influenced by the size of the lake. For a shallow reservoir the water at any time will show a steady state of isotopic composition.

1.1.10. Biogeochemical Processes in Lakes

The exchange of chemical substances between the atmosphere and surface water bodies influences the abiotic and biotic conditions, and the level of contamination in them. Natural substances like carbon dioxide, oxygen, hydrogen sulfide and methane migrate between air and water in pristine conditions. There is often appreciable cycling of chemicals between air and water with magnitude and direction of net movement changing with seasons.

Most of the elements present in water and sediments are involved to some degree in redox cycling of constituents in lakes (Hamilton-Taylor and Davison 1995). Sholkovitz (1985) emphasized the relation between redox reactions and mobility of elements. The predominant mechanisms driving the redox cycling of elements in lakes and reservoirs are plankton synthesis in surface waters and the bacterial degradation of organic matter in subsurface waters and sediments. Organic matter degradation proceeds through a series of redox reactions involving dioxygen (intrusive and interstitial), nitrogen, and sulfate as electron acceptors. These redox reactions are responsible for regulating the redox potential of the local environment. These processes in a variety of ways affect elements. They may be adsorbed or assimilated by plankton in surface waters and released back into solution at depth, possibly in a different redox state. The actions of chemoautotrophic bacteria, which obtain energy from the oxidation of reduced inorganic species, can also have a significant effect on element behaviour in lakes and reservoirs.

The redox driven cycling of elements additionally occurs through more obscure pathways. Chemical association (sorption/co precipitation) between elements and redox sensitive carrier phases are important in cycling of elements (Kawashima *et al.* 1988).

In aquatic ecosystems iron plays a central role in numerous chemical and biological processes. In cells iron exists in more than one oxidation state. Iron acts as an important cofactor in the electron transport chain and in redox enzymes (Emmenegger *et al.* 2001). Iron has been shown to be a widespread limiting factor for the growth of phytoplankton in high nitrate, low chlorophyll oceanic regions (Coale *et al.* 1996). Redox cycling of iron in the environment influences acid mine drainage and catalysis of oxidation reactions in natural water (King and Farlow 2000). Iron cycle is capable of markedly influencing the concentration of humic substances, which sometimes increases in the anoxic waters of a seasonally stratified lake/reservoir due to release from dissolving iron oxides (Davison 1993).

In anoxic sediment:

$$4Fe(OH)_3\,\text{sediment} + 4e^- \rightarrow 4Fe^{2+} + 12(OH)^-$$

$$CH_2O + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

$$4Fe(OH)_{3\,\text{sediment}} + CH_2O + H_2O \rightarrow 4Fe^{2+}_{\text{solution}} + CO_2 + 8(OH)^- + 3H_2O \tag{1.2}$$

$(SO_4)^{2-} + 8(OH)^- + 8e^- \rightarrow S^{2-} + 4H_2O$

(1.3)

$Fe^{2+}_{solution} + 2HCO_3^- \rightarrow Fe\ (HCO_3)_{2\ Solution}$

(1.4)

$Fe\ (HCO_3)_2 + Humic/Fulvic\ COO^- \rightarrow Fe\ (humate/fulvate)_{solution} + 2HCO_3^-$

(1.5)

This redox process coupled with complexation of iron makes it mobile in the sediment environment.

Humic substances are known for their metal complexing ability and hence metal mobility in these water bodies is increased. pH variations and increased concentrations of metabolites also influence metal mobility in reservoirs. pH can vary temporally and vertically by more than three units in productive, poorly buffered water bodies due to the effects of photosynthesis and respiration (Talling 1976).

Eutrophic layer

$$nHCO_3^- + nH_2O \xrightarrow{hv} nCH_2O + 1.5n\ O_2 + 4n\ H^+ \qquad (1.6)$$

Alkalinity decreases and acidity increases, net effect is decrease in alkalinity.

Subsurface layer

$$nCH_2O + 4n\ H^+ + 1.5n\ O_2 \rightarrow nHCO_3^- + nH_2O + energy \qquad (1.7)$$

Here acidity is consumed, alkalinity is increased and the net effect is an increase in alkalinity.

Direct photochemical oxidation and reduction of elements may occur in lakes. These photochemical transformations are more pronounced in estuarine and oceanic waters.

1.1.11. **Iron and Manganese**

High productivity of biomass in eutrophic lakes and the subsequent consumption of oxygen for its mineralization result in anoxic conditions, which may occur seasonally in part of the water column and in the sediments. The occurrence of anoxic conditions cause a significant cycling especially of iron and manganese at the oxic-anoxic interface, due to changes in solubility related to the changes in oxidation state (Egeberg et al. 1988; Landing and Westerlund 1988). The redox behaviour of iron and manganese in lakes has been well studied and comprehensively reviewed (Balisteri *et al* 1992, Davison 1993). Other current reviews have addressed the role of iron (Davison and De Vitre 1992) and manganese (De Vitre and Davison 1993) particles in freshwaters. Stumm and Sulzberger (1992) have considered current knowledge and understanding of the mechanisms of redox transformations of iron.

In well-oxygenated waters the stable forms of iron and manganese are their higher oxidation states [Fe (III) and Mn (III/IV)], which are completely hydrolyzed species (hydrated oxides) present as colloidal particles or agglomerated. Where oxygen is absent, the lower redox states are favoured. These divalent ions are very soluble in the pH range 4 – 8. Iron and manganese are mainly present in well-mixed, fully oxygenated lake water as particles at typical concentrations of 0.4 – 2.0 µmole/L. In seasonally or permanently stratified lakes and reservoirs, where the bottom waters become anoxic, Fe (II) can accumulate to high concentrations sometimes approaching 100 μmole/L (Hamilton- Taylor and Davison 1995). The reduced metal ions are supplied by reductive dissolution of oxide present in surface sediments and in particles sinking through water column. The relative dominance of these two-supply terms change with season.

1.1.12. **Case study of Peechi Reservoir**

This study was targeted (i) to identify the conditions under which iron and odour are mobilized, and (ii) evolve an efficient treatment modification in the existing conventional drinking water treatment plant, which draws water from the lower/ middle stratum of the water column in the dam. This necessitated characterization of the stratification process in the reservoir. Hence this part of the work is divided into

(i) Brief study of reservoir dynamics with reference to the trough (basin) near the dam, from where raw water is drawn for treatment.

(ii) Treatment modification during the period of iron mobilization.

Since odour producing volatile materials are removed during aeration this aspect was not considered in this study. Various treatment options to remove iron, which is the constituent causing nuisance in the treatment plant operation and water quality, was covered in this study.

Chapter 2

PHYSICO-CHEMICAL STRATIFICATION OF THE TARGET BASIN OF PEECHI RESERVOIR

Abstract

This chapter gives a brief description of the materials and methods used in the study of physicochemical stratification of the target basin of Peechi Reservoir. Salient climatic and physiographic features affecting reservoir processes are presented. The sampling, preservation and analytical procedures of chemical parameters are also given.

Seasonal variations in water quality observed in an annual cycle are presented. Features of thermal stratification and thermal processes, which lead to thermal stratification, are briefly described. Since the basin has a relatively small shallow area, density currents are not observed. Concomitant with the thermal stratification there is a chemical stratification and details of chemical stratification are given. In the oxycline oxygen dependent species show a decline and anoxic products build up. These are correlated with seasonal variations.

A. MATERIALS & METHODS

1.2.1. Peechi Reservoir - a brief description

The Peechi Irrigation Project, commissioned in 1957 is one of the major irrigation projects in Kerala. The project utilizes water of Manali River, one of the major tributaries of Karuvannur River.

Peechi reservoir is situated in Thrissur district of the state. The geographical location of the reservoir is $10^0$26'North and $76^0$24'East (Figure1.2.1). Even though it was conceived as an irrigation reservoir, during the course of time it became the only source of drinking water for one million people of Thrissur Corporation and adjoining gramapanchayaths (villages). Kerala Water Authority operates a 50.5 MLD treatment plant drawing raw water from the reservoir. Hence this reservoir plays a crucial role in the socio-economic development of the district.

The Manali River rises in the Vaniampara hills of the Western Ghats. The river flows 48 km before it joins the Kurumali River at Palakkadavu, near Arattupuzha. These two tributaries together form Karuvannur River, which drains in to the Laccadives Sea through the backwaters. The terrain in the upper reaches of the Manali river consists of six valleys namely, Plachivakom, Puthumada, Olakara, Thalikuzhi and Pulakkal. Of these Thalikuzhi valley and Pulakkal valley join at about 6 km upstream of Peechi dam (KERI 1983).

1.2.2.**The catchment**

The catchment area of Manali River comprises of a number of hills, adjoining one another. These hills are extension of the Sholayar hill range, which is part of Western Ghats. A major portion of the catchment area is forestland with abundant growth of trees and plants. The forest type is moist deciduous and is notified as reserve forest for forest conservation measures. The thick vegetation and consequent stable soil cover restrict both erosion of soil and weathering of rock, which are the major sources of sediment load coming into the reservoir. Part of the catchment area consists of agricultural

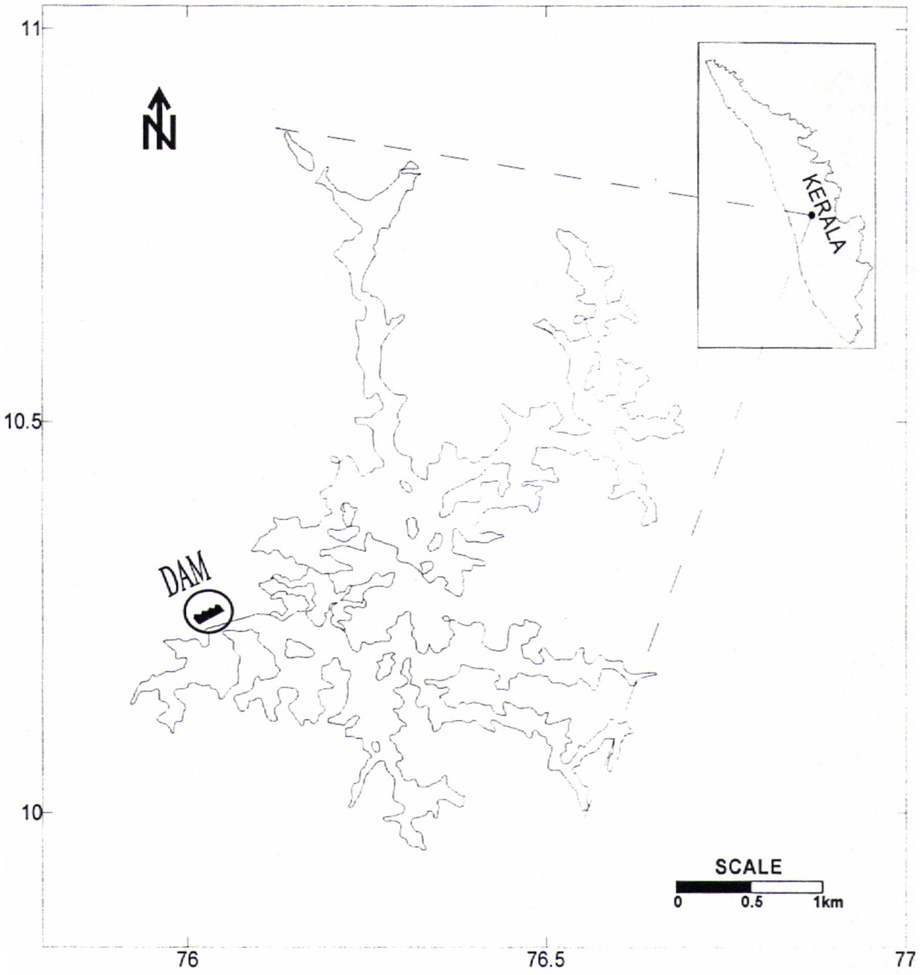


Fig. 1.2.1 Location map of Peechi Reservoir

lands. The catchment area of the reservoir is 107.09 km^2. The water-spread area of the reservoir is 12.95km^2. The presence of many islands of different sizes is unique to the reservoir. These islands effectively divide the reservoir into many small basins (KERI 1983).

The reservoir is formed by erecting a rubble masonry dam across Manali River. The estimated annual runoff to the reservoir is 209.5 Mm^3 and the maximum storage capacity of the reservoir is 113.27 Mm^3 The silting rate of the reservoir is 0.87 Mm^3/year (KERI 1983). This is high when compared to other reservoirs in India (Murthy 1975; KERI 1983). The length of the dam is 213.36m. Top level of the dam is at an elevation of +80.70 m. The full reservoir level is at +79.25 m.

Two main canals are constructed to deliver water for irrigation purposes. These canal systems draw water during post monsoon period. The basic features of the discharge of dam outlets are given in Table 1.2.1. (KERI 1983). Withdrawal for 50 MLD water treatment plant of KWA is continuous.

The high siltation rate in the reservoir reduces its holding capacity. The accumulation of silt also affects the quality of water and influences the aquatic processes. The reservoir has a labyrinthine shape. This uneven pattern of the reservoir bed divides the reservoir into many basins with different depths. During summer season, when water level recedes the submerged mounts become exposed. The maximum depth of the reservoir is in the basin adjacent to the dam. The mean depth of the reservoir is 8 m and the maximum depth is 34 m. Since the water withdrawal for irrigation is seasonal and varied, it affects the residence time calculation.

Table1.2.1. Basic features of the discharge outlets of Peechi Reservoir.

(KERI 1983)

Sl.No.	Reservoir outlet	Sill level (m)	Diameter of outlet (m)	Discharge (m^3/s)
1	Right bank	+ 56.39	1.22	7.08
2	Left bank	+67.06	0.91	3.54
3	KWA Treatment Plant	+53.34	0.61	0.58

The basin adjoining the dam is considered for this study since its water quality is significant from the treatment point of view. This basin is the deepest one and all the outlets of the reservoir are located in this basin. The sediment carried by the runoff settles in the upstream basins. The lotic and transient sections of the basins have appreciable shallow regions. In the target basin (basin adjacent to the dam) there is a channel, which extends to the dam wall. This channel ensures availability of water to the treatment plant even at the lowest reservoir level. The high siltation rate probably makes the channel a source of fresh unconsolidated silt.

Raw water is drawn for the drinking water treatment plant from the stretch adjoining the dam. This stretch acts as a basin of approximate capacity of 17,00,000 m^3 at full reservoir level (KERI 1983). This basin is charged by

(a) runoff from its local catchment area and

(b) from the main stretch which extends to the northeast and southeast directions.

In the absence of major hydraulic disturbances the basin adjoining the dam has its unique identity with regard to heat flux and stratification.

A section of the target basin is shown in Figure 1.2.2.

1.2.3. Sampling and analysis

The study was carried out in two ways

(a) stratification studies in the water column in the target basin and

(b) water quality variations in the intake of Peechi water treatment plant.

Occurrence and pattern of stratification is influenced by meteorological parameters like temperature, wind speed, wind direction, humidity,

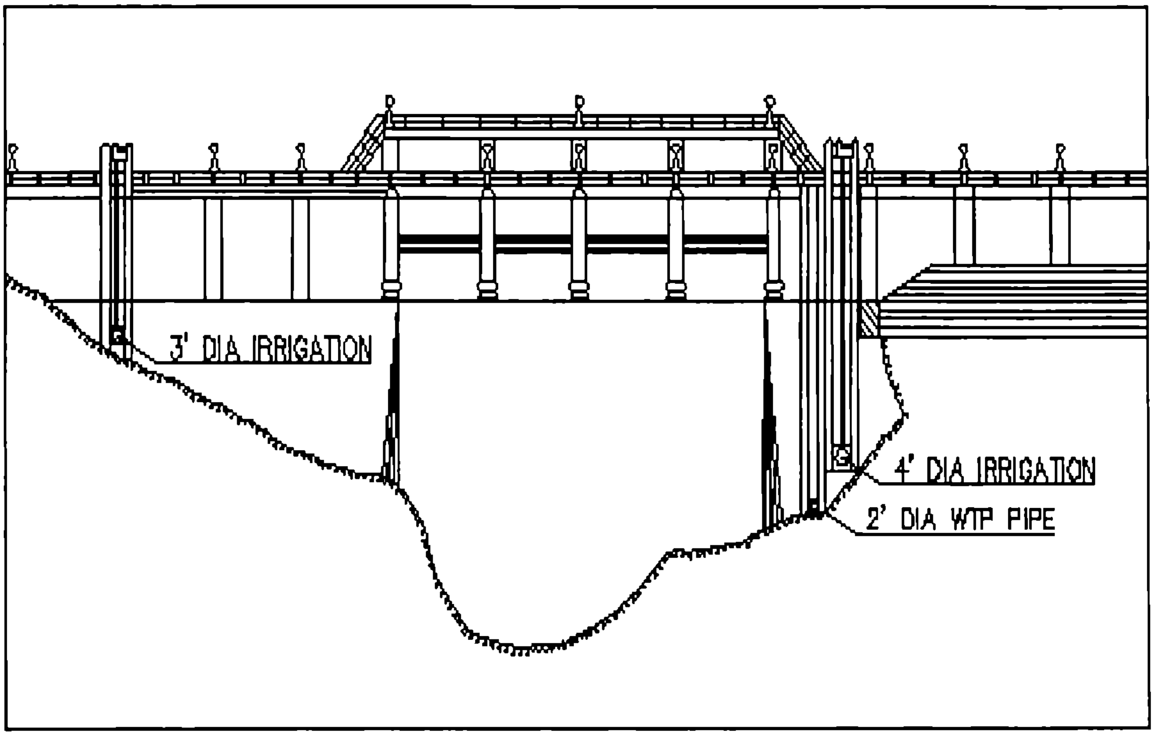


Figure 1.2.2. Schematic view of the study basin, Peechi Reservoir

precipitation, solar radiation flux and evaporation. Hence the relevant meteorological parameters were acquired. All the relevant meteorological parameters except evaporation rate data were collected through the automatic weather station maintained by Kerala Forest Research Institute Peechi. Data for the years 1998-2000 were collected. Evaporation data for the study period (1998-2000) was collected from Kerala Engineering Research Institute, Peechi. These include daily data for solar radiation, humidity, maximum and minimum temperatures, and rainfall. Since meteorological data collected were from the immediate vicinity of the target basin, they were used without any further correction.

Evaporation measurements were done by KERI using evaporating pans. Evaporating pans are circular basins with a diameter of 1.2 m and a height of 0.25 m. They were exposed on a wooden platform so that air may freely circulate around the pan.

Stratification studies were carried out during the post monsoon period when the water level in the reservoir was low. For stratification studies depth profiling of various water quality parameters were selected. The task proved to be particularly elusive, since even mild variations in meteorological conditions could affect the intensity and occurrence of stratification.

The following physico-chemical parameters were measured for stratification studies.

i) Temperature

ii) Dissolved oxygen.

iii) Total Iron

iv) Sulfide

v) Phosphorous

vi) Nitrate

vii) Turbidity

1.2.4. **Instruments**

The instruments and equipments used in the study are described below.

1.2.4a. ***Water sampler***

Water samples were collected using constant volume Krammer water sampler. The sampler has a cylindrical body made up of transparent plexi glass. The sampler volume is 1 L. A gravity messenger was used to activate the lid at desired depth. Provision is provided to siphon the water to container without trapping air.

1.2.4b. ***Thermometer***

For temperature measurements digital thermometer was used. The measurement accuracy of the thermometer is ± 0.1^{0}C.

1.2.4c. ***pH meter***

pH measurements were done using Systronics digital pH meter (model 335). The meter was calibrated before each measurement using standard buffer solutions.

1.2.4d. ***Turbidity meter***

For turbidity measurements Systronics make digital nephelo-turbidity meter was used. The instrument was calibrated as per manufacturer's directions using standard formazin suspensions of known turbidity.

1.2.4e. *Conductivity meter*

Conductivity measurements were carried out using calibrated Century make digital conductivity meter (model CC601-P). The measurement unit was μScm^{-1}

1.2.4f. *Hach DREL 2010 Advanced Water Quality Laboratory*

Field measurements of chemical parameters were done using Hach DREL - 2010 Advanced Water Quality Laboratory. This field water quality laboratory consists of data logging DR 2010 VIS spectrophotometer, a CO150conductivity meter (Hach) and pH meter.

1.2.4g. *UV-VIS spectrophotometer*

For $SUVA_{254}$ measurement Varian UV-VIS spectrophotometer (Model Carey 50) was used.

1.2.5. **Analytical Procedures**

All chemicals used were of analytical grade unless otherwise specified. For analyses using Hach Advanced water quality laboratory, special reagents were used, which were supplied by the manufacturer.

1.2.5a. *Dissolved oxygen.*

Dissolved oxygen was measured using Winkler method (APHA 1998). Water samples were collected in BOD bottles of 60 mL volume. Dissolved oxygen was fixed at the sampling site itself. Fixed samples were kept in iceboxes and transported to the laboratory and analysis was conducted within four hours of sampling.

1.2.5b. ***Iron***

Iron was measured spectrophotometrically using Hach Advanced Water Quality Laboratory. The proprietary reagent FerroVer Iron reagent (Cat No 21507 – 69) was used for colour development. This reagent is 1,10 phenanthroline based and buffered. The measurement wavelength is 510 nm. The range of measurement was 0- 3.0 mg/L. the Estimated Detection Limit for the method is 0.02 mg/L.

1.2.5c. ***Nitrate***

Nitrate concentration in the water samples was measured spectrophotometrically. Measurement was done using Hach DR 2010 data logging spectrophotometer. The proprietary reagent Nitra Ver 5 Nitrate reagent (Cat No 14034 – 99) was used for the analysis. The measurement wavelength is 500nm. The range of measurement for the method is 0.0-30.0 mg/L.

1.2.5d. ***Phosphate***

Phosphate concentration in water samples was measured spectrophotometrically. Measurement was done using Hach DR 2010 data logging spectrophotometer. The proprietary reagent Phos Ver Phosphate reagent (Cat No 14034 – 99) was used for the analysis. The measurement wavelength is 890nm. The range of measurement for the method is 0.0-2.5 mg/L. The Estimated Detectable Limit is 0.01 mg/L.

1.2.5e. ***Sulfide***

Sulfide concentration in water samples was measured spectrophotometrically. Measurement was done using Hach DR 2010 data logging spectrophotometer. Proprietary reagents (Cat No 1816 – 42 & 1817 - 42) were used for the analysis. The principal ingredient was N, N – dimethyl p-phenyldiamine oxalate. The measurement wavelength is 665nm. The range of measurement for the method is 0.0-0.6 mg/L. The Estimated Detectable Limit is 0.01 mg/L.

1.2.6. **Sampling and preservation**

Sampling was done according to USEPA guidelines (EPA 1983). Sampling of water from the intake of the treatment plant was done using a hand held surface water sampler. Samples were collected in clean rinsed 5L white polyethylene cans from the raw water channel of the water treatment plant. The sampling depth in the channel is 0.2 m. pH of the water samples was measured online using a pre calibrated digital pH meter.

For total iron determination samples were filtered through 0.45-µm filters. This was followed by the addition of 0.2 mL con. HNO_3 as preservative. Analysis was done within 24 hours.

Water quality parameters relevant to drinking water and treatment process were analyzed. The parameters selected included pH, turbidity, electrical conductivity, total alkalinity, total hardness, calcium hardness, magnesium hardness, total iron, specific UV-absorbance at 254 nm and chloride.

1.2.7. **Water quality variations at the intake of Peechi Water Treatment Plant**

The water quality variations affect the efficiency of the drinking water treatment plant. The variations were studied by regular sampling and analysis of various physicochemical parameters of water quality. The study period extended from November 1998 to June 2000. Samples were collected on a fortnightly basis. No sampling was carried out during the monsoon season since the reservoir undergoes total mixing due to large and steady influx. No mobilization of iron was noticed during this period. So the study was confined to post monsoon period (November – May), which also corresponded to low water level in the reservoir.

B: RESULTS AND DISCUSSION

1.2.8. Introduction

The water quality in a reservoir on a long term basis is influenced by:

1. Geomorphology as a barrier to horizontal and vertical currents
2. Dissolved and suspended material budget of the reservoir
3 Water balance, which is influenced by overflow, temperature, seepage and evaporation.

Hence these aspects are presented separately

1.2.9. Geomorphology

Geomorphology of a water body influences the physicochemical processes in the water body. Since the physical processes directly influence the material and energy exchange processes in the reservoir, this leads to water quality variations. The morphological parameters like shape, volume and depth of the reservoir strongly influence and control the various mixing processes and material cycling in the reservoir. From the site map of Peechi reservoir it is evident that the shoreline of the reservoir is labyrinthine. Due to this labyrinthine shape wind influence is minimal. The wind velocity is also low. Hence the formation of strong surface waves is negligible. The absence of strong surface winds rules out surface mixing. The presence of shoreline vegetation and scattered islets further prevent strong winds.

For the purpose of discussion the reservoir can be envisaged as a number of basins, which are interconnected. When there is no inflow of water from contributing streams (November to May) these basins can be considered as independent water bodies. During this period, the horizontal flow of water from other basins to the first basin (adjacent to the dam) occurs. Hence the water quality variations observed in the first basin is more important from the treatment point of view.

The basin targeted for this study has a triangular cross section and is of maximum depth. The inflow to the first basin enters from the far end passing through other basins. The particles carried over by these inflows settle in the distant shallow basins. So the carry over of materials from other basins to this basin is negligible.

1.2. 10. **Water and water borne material balance of the reservoir**

Peechi reservoir is in a state of transition from oligotrophic to mesotrophic in character. The euphotic zone depth and phosphate concentration clearly establish this fact (Wetzel 2001). The geochemical nature of formations (granite with interspersed charnakite) supports the low mineral composition (KERI 1983). Since the catchment area consists of reserve forest with agricultural land along its outer edge, they contribute to the nutrient budget of the reservoir. But the overall nutrient concentration is low.

1.2.11. Water balance – influence of temperature, overflow, seepage and evaporation

For any reservoir,

Inflow = outflow + seepage + evaporation

$Q_{inflow} = Q_{outflow} + Q_{seepage} + Q_{evaporation}$

The residence time of water influences the material exchange processes and energy budget of the water body. Residence time influences the nutrient status of the reservoir. The residence time of water in the Peechi reservoir is estimated as twenty-two months.

Peechi reservoir stands over bedrock of more or less intact granite gneiss located below a few meters of overburden consisting of soil and laterite. No detectable seepage is observed on the exposed edges of the reservoir or down the dam site. Hence it is reasonable to assume that seepage from the reservoir is negligible. The reservoir is fed only through precipitation and subsequent surface runoff. The inflow to the reservoir is confined mainly to the monsoon period and the rainfall pattern affects the water level in the reservoir. The temporal variation in the water level during a typical year and the corresponding rainfall are shown in Figures 1.2.3. and 1.2.4.

Major outputs from the reservoir are the seasonal discharge for irrigation and the continuous supply to the drinking water treatment plants. The crop management in the irrigated areas are so planned that demand for irrigation water is limited to the period from November to March. The only continuous withdrawal is for KWA water treatment plant (50 MLD). This coupled with evaporation and seepage accounts for the fall in water level. The

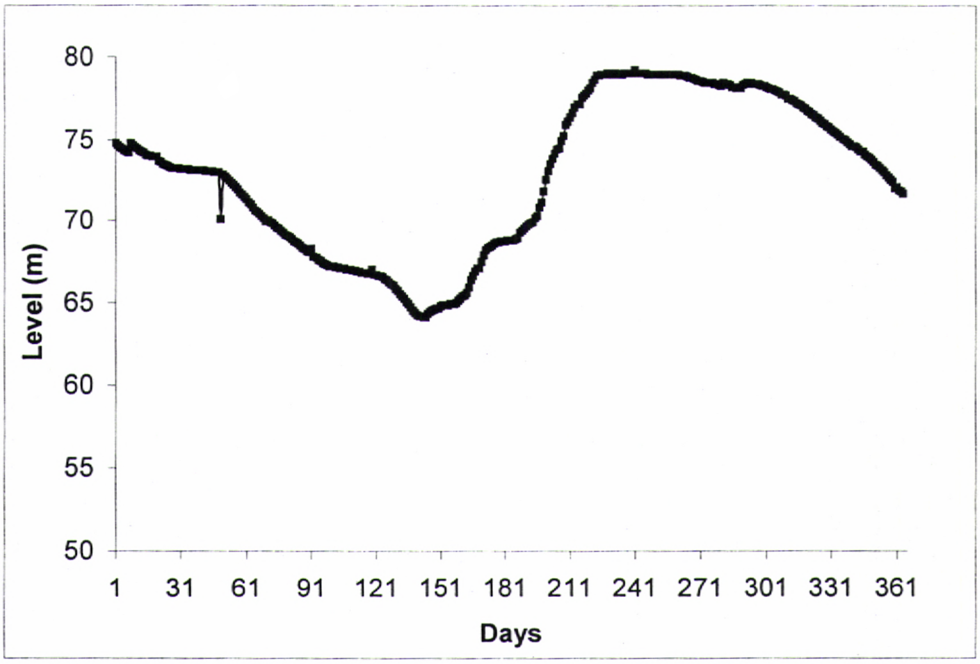


Figure 1.2.3. Temporal variation in water level for a typical year (1999)

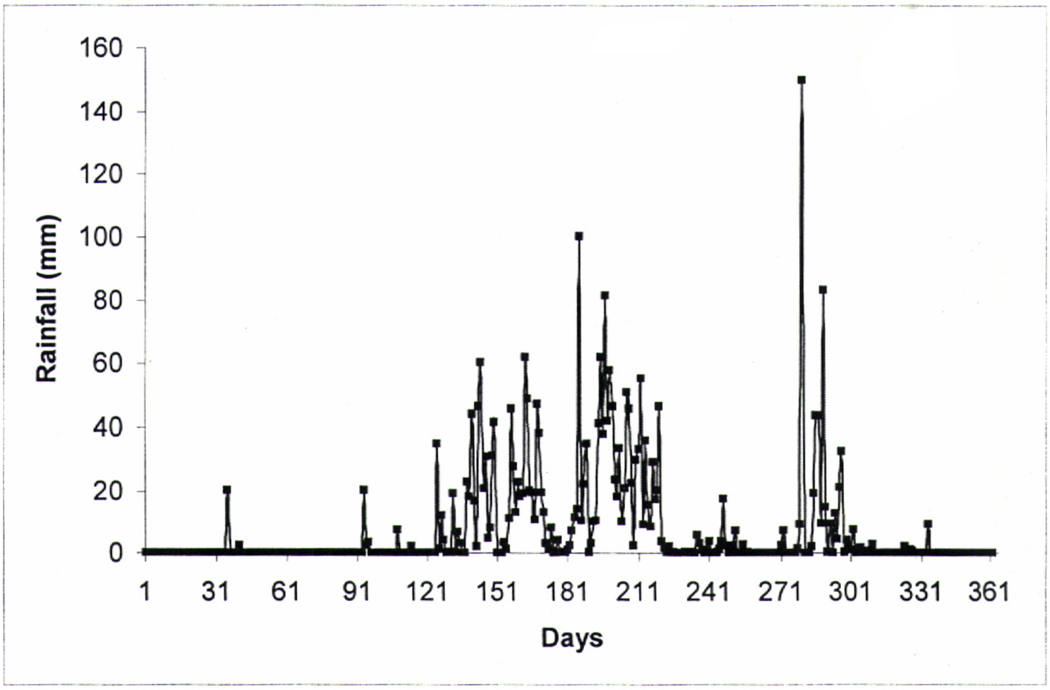


Figure 1.2.4. Temporal variation in rainfall for a typical year (1999)

geological setting excludes any significant seepage from the reservoir. Accounting for the discharge, the daily evaporation rate for a typical year is shown in Figure 1.2.5. The level of water in the reservoir falls rapidly when the irrigation canal is open (10.62 m^3/sec). Left bank canal is at an elevation of 67 m and it can be operated only during the months of July to November. During the remaining months withdrawal for irrigation water can be discharged only through the right bank canal, which is at an elevation of 53.3 m. The right bank canal discharges at a rate of 7.08 m^3 /sec. A total daily discharge of 0.97 Mm^3, which is 1.1% of the estimated reservoir capacity, resulted when all the three discharge outlets of the reservoir are operational. But this situation occurs only for a few days in a year. During the problem period (November to May) the water level in the reservoir is below the left bank canal outlet level Since the water level falls off rapidly and the safety level for the priority water supply has to be retained, irrigation supply is curtailed when the level reaches a critical level. This leads to a conflict of interest between the priority water supply and the originally intended use for irrigation.

Rate of evaporation from a reservoir (mass/unit time) depends on the concentration of dissolved constituents, surface films, wave generation, temperature and wind. As revealed by analysis dissolved constituents in the surface water are low. Visual inspection and analysis of surface water did not show the presence of petroleum films or floating iron oxide. The wind pattern shows that it is weak during the period, November – May. The ambient temperature and humidity variations are shown in Figure 1.2.6. and

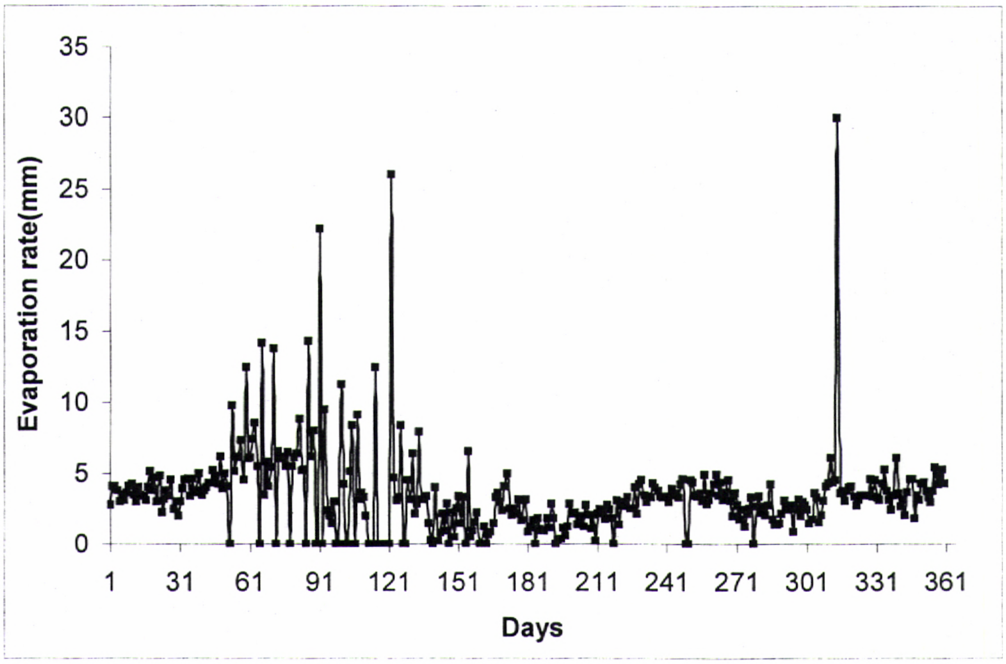


Figure 1.2.5. Evaporation pattern for a typical year (1999)

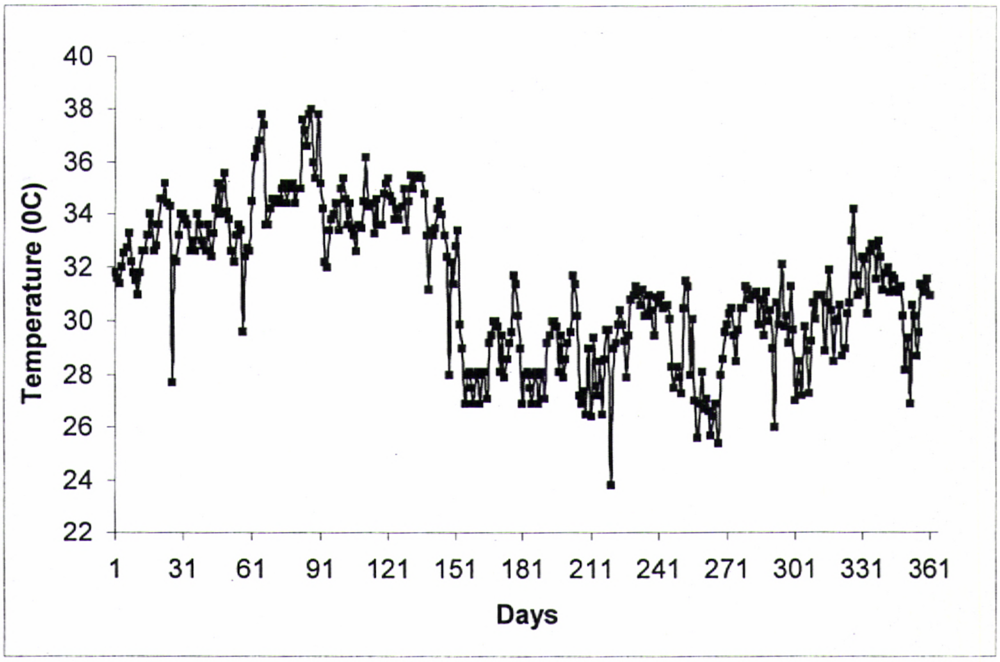


Figure 1.2.6. Variations in daily maximum temperature for a typical year (1999)

Figure 1.2.7. Evaporation rate for the corresponding period is already given in Figure 1.2.5.

1.2.12. **General comments on annual cycle of water quality**

Essential water quality parameters relevant to drinking water were measured periodically to cover all seasons. The results are presented in Table1.2.2. Corresponding sampling dates are given in Table 1.2.3. In all cases pH is within agreeable range for surface raw water. During rainy season alkalinity shows a lower value from the average. This may be due to dilution of reservoir water by fresh rainwater. However the raw water collected from the water treatment plant intake shows a higher alkalinity, magnitude of the value reaching high at times of stratification. This can be explained in terms of the mobilization of calcium and magnesium phosphate in the sediment and their confinement in the hypolimnion (Stumm and Morgan 1996). The dissolution of calcium carbonate from the sediment is ruled out since the calcium alkalinity concentrations are far below the saturation values (Stumm and Morgan 1996). Calcium concentrations also show correspondingly higher values.

High turbidity values (>5NTU) are showed during times of intense rain, particulates larger than 2μm settle during their passage through the stretch of the reservoir. The low persistent turbidity observed during non-rainy period is mainly due to the particles derived from the sediment circulating in the hypolimnion. All other chemical parameters are well within the prescribed limit for drinking water. Seasonal variations of water quality parameters relevant to drinking water treatment are shown in Figures 1.2.8 to 1.2.12.

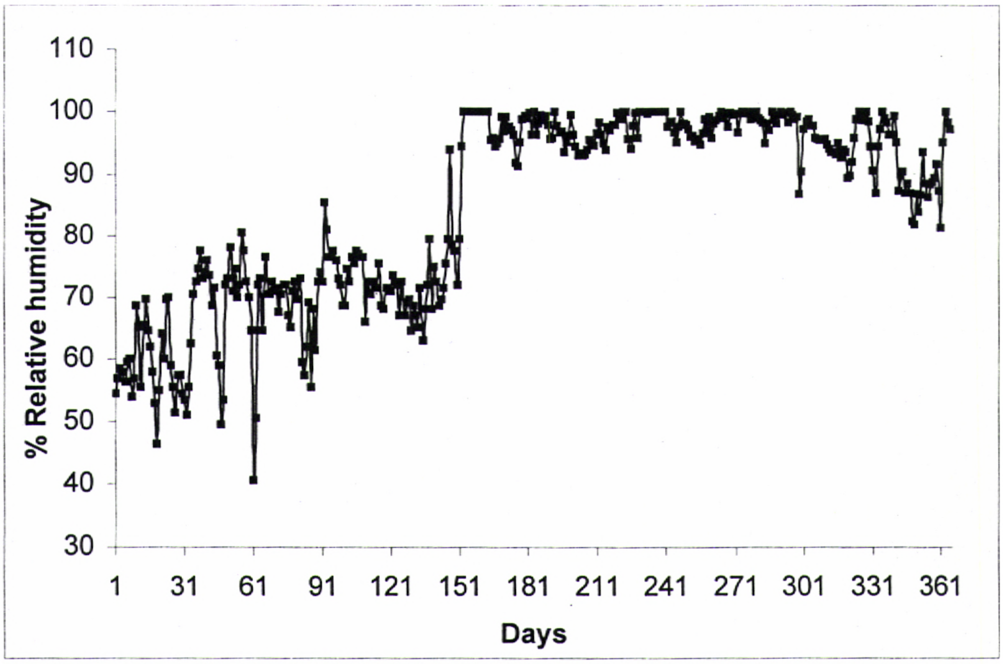


Figure 1.2.7. Variation in ambient humidity for a typical year (1999)

Table 1.2.2. Water Quality of Peechi Reservoir water, 1999-2000

Sl. No.	pH	Turbidity NTU	EC(*) µS	TDS(**) mg/L	Total hardness mg/L as $CaCO_3$	Ca hardness mg/L as $CaCO_3$	Mg hardness mg/L as $CaCO_3$	Total iron mg/L	Alkalinity mg/L as $CaCO_3$	Chloride mg/L
1	6.9	0	49	6	16.2	2.8	2.3	1	9.8	9.9
2	8.1	3	71	34	20.9	3.7	2.8	0.48	39	3.2
3	7	3	47	88	13.9	2.8	1.6	0.15	19.5	5
4	6.8	2	51	20	20	7	1.5	0.12	26	3
5	7.1	5	42	24	18	5	1	0.2	28	4
6	7.2	4	42	51	13.9	2.8	1.6	0.15	19.5	5
7	6.9	6	52	34	18	4.1	1.3	0.2	18	4
8	6.6	3	61	40	26	7.3	0.9	0.48	18	5
9	7.1	5	47	43	22	3.5	1	0.27	25	4
10	6.8	5	49	51	12	3	1	0.23	14	6
11	6.9	3	47	48	13.9	1.9	2.3	0.34	19.5	5
12	6.5	2	49	42	15.3	2.2	2.4	0.41	3	3
13	6.6	2	48	46	15.3	2.8	2	0.61	19.5	4
14	6.6	2.5	44	51	18	3.4	2.1	0.54	21	6
15	6.8	2	55	84	22.4	5.1	2.3	1.8	BDL	7.2
16	6.9	3	36	80	9	3	0.9	0.55	16	6
17	6.4	1	62	52	23.7	6.1	2	2.03	35	7.6
18	7.2	2	42	76	12	3.2	1	0.19	18	5.8
19	7.1	4	75	28	22.4	4.9	2.5	0.31	38	6.3
20	7.1	2	46	40	16	3	2.1	0.88	24	7.9
21	7.6	6	53	34	9.5	2.2	1	0.04	40	4.2

Continued..

Sl. No.	pH	Turbidity NTU	EC* µS	TDS** mg/L	Total hardness mg/L as $CaCO_3$	Ca hardness mg/L as $CaCO_3$	Mg hardness mg/L as $CaCO_3$	Total iron mg/L	Alkalinity mg/L as $CaCO_3$	Chloride mg/L
22	7.5	3	51	40	12	4	0.8	0.62	20	5.3
23	7	8	78	56	18	3.6	1.9	0.04	22	3
24	7.4	8	84	44	10	2.2	1	0.09	14	3
25	7.3	10	91	48	12	3.6	1.2	0.06	18	3
26	7.2	13	90	51	15	4	2	0.02	19	3
27	7.6	10	81	45	18	4.8	1.6	0.05	22	3
28	7.4	3	96	55	20	4	2.1	0.03	19	4
29	7.1	6	59	60	22	5.2	3.5	0.02	26	3
30	6.9	9	76	55	20	3.6	2.8	0.02	30	2
31	6.8	10	48	26	16	4.1	2.5	0.09	14	5.6
32	6.6	4	53	40	18	3.3	2.4	1.3	17	6.6
33	7.3	6	38	20	10	3.1	0.5	0.39	14	7
34	7	3	35	20	8	2.4	0.5	0.28	26	9
35	7.1	12	31	20	8	2.4	0.5	0.04	12	7.3
36	6.6	4	62	43	18	3.3	2.4	0.62	17	8.3
37	7.2	7	44	30	14	3.2	1.4	0.73	20	7.2
38	7.1	3	63	40	26	4	3.8	0.11	20	9
39	7	3	77	40	16	4	1.5	0.27	20	12
40	7	4	40	20	14	2.4	1.6	0.11	14	8
41	7.1	2	42	80	13	3.6	1	0.19	18	10

Table 1.2.3. Sampling dates

Sample No	Sampling date	Sample No.	Sampling date
1	06-01-1999	21	22-05-1999
2	11-01-1999	22	30-05-1999
3	16-01-1999	23	11-06-1999
4	22-01-1999	24	17-06-1999
5	29-01-1999	25	26-06-1999
6	06-02-1999	26	02-07-1999
7	13-02-1999	27	18-07-1999
8	20-02-1999	28	29-07-1999
9	27-02-1999	29	04-08-1999
10	06-03-1999	30	20-08-1999
11	13-03-1999	31	02-09-1999
12	23-03-1999	32	17-09-1999
13	27-03-1999	33	04-10-1999
14	04-04-1999	34	19-10-1999
15	10-04-1999	35	28-10-1999
16	17-04-1999	36	06-11-1999
17	24-03-1999	37	22-11-1999
18	01-05-1999	38	03-12-1999
19	08-05-1999	39	17-12-1999
20	15-05-1999	40	28-12-1999
		41	05-01-2000

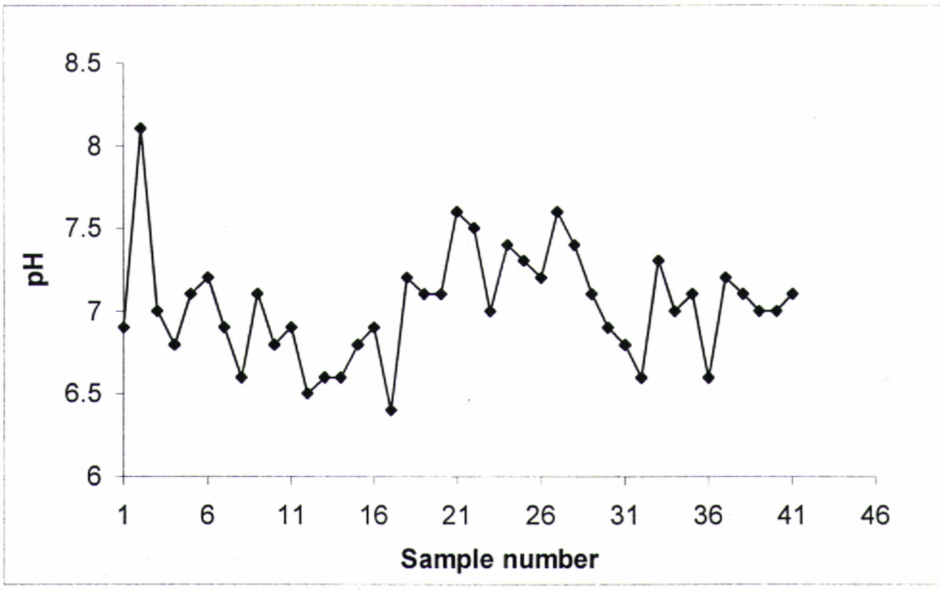


Figure 1.2.8a. Seasonal variation in pH of reservoir water

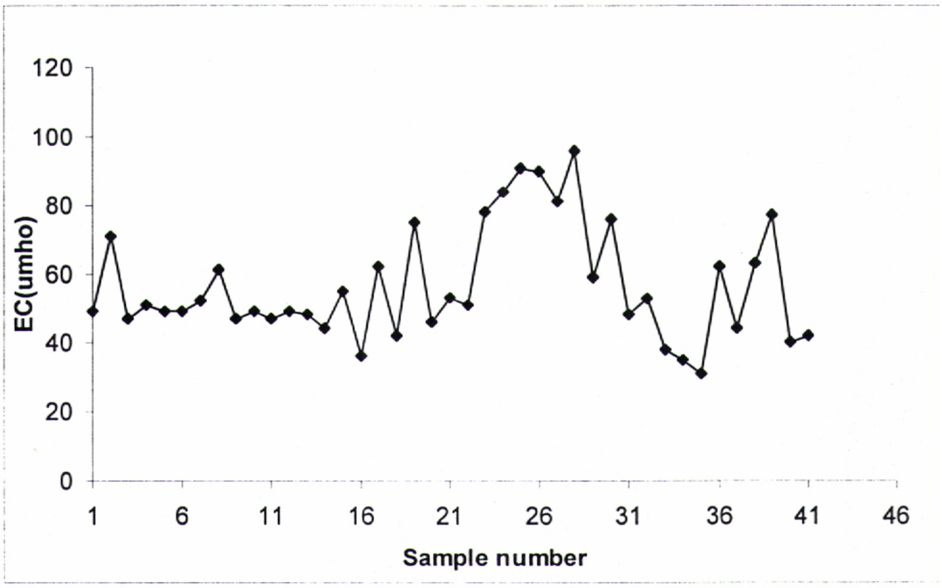


Figure 1.2.8b. Seasonal variation in electrical conductivity of reservoir Water

(Sampling dates corresponding to sample number are given in Table 1.2.3.)

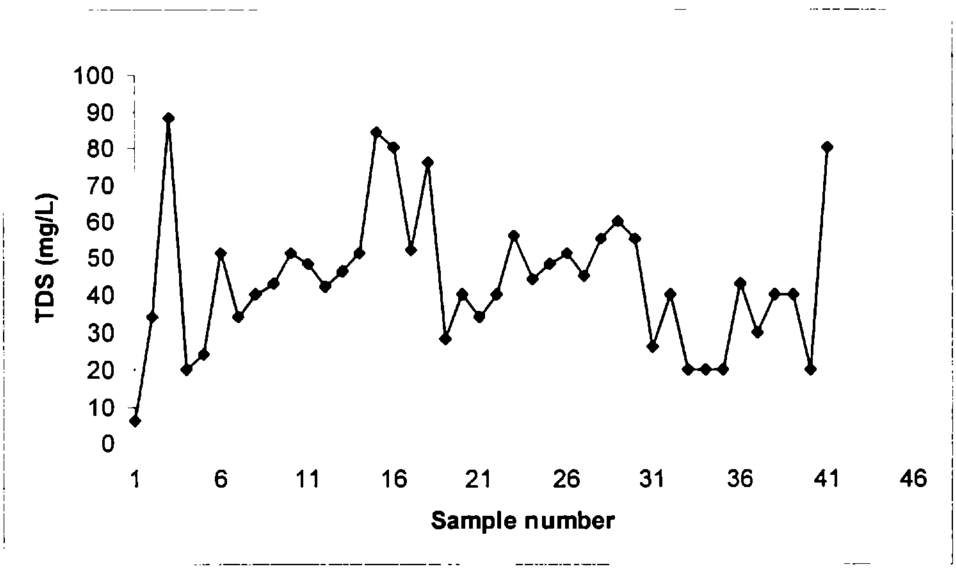


Figure 1.2.9a. Seasonal variation in TDS of reservoir water

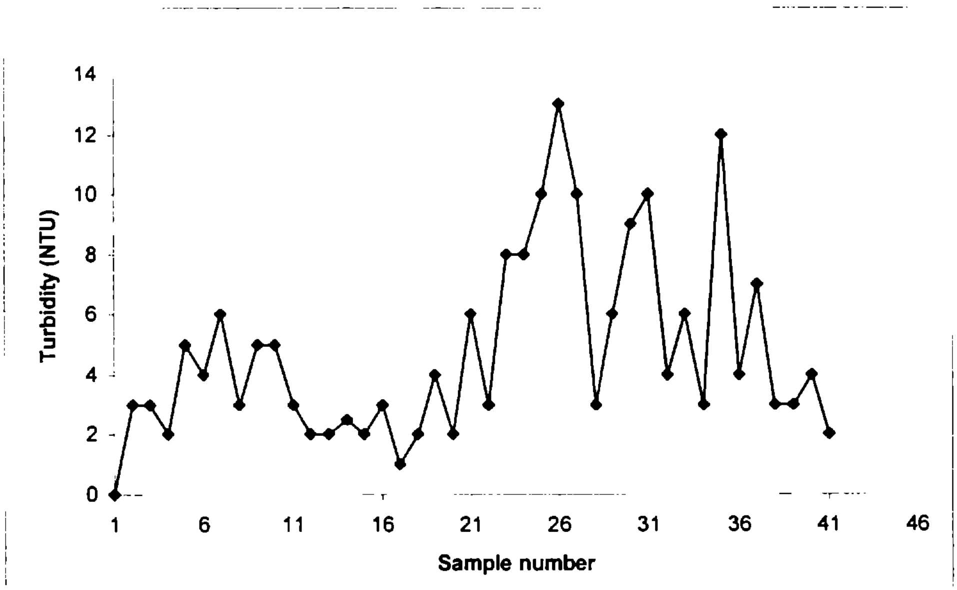


Figure 1.2.9b. Seasonal variation in turbidity of reservoir water

(Sampling dates corresponding to sample number are given in Table 1.2.3.)

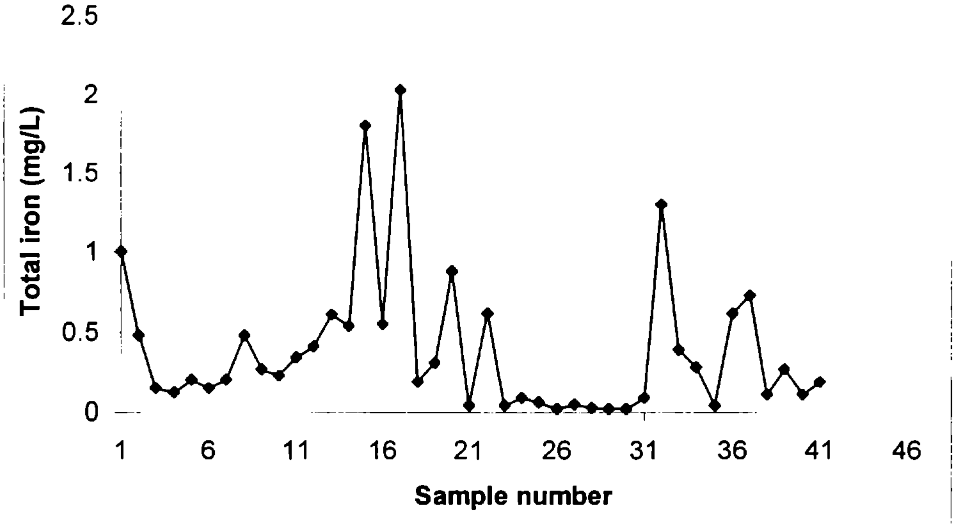


Figure 1.2.10a. Seasonal variation in total iron of reservoir water

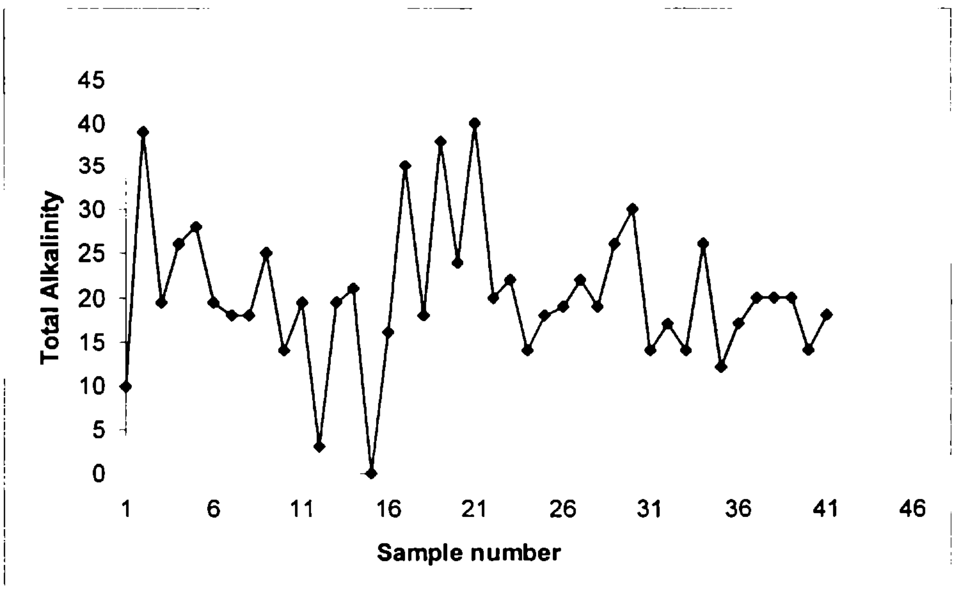


Figure 1.2.10b. Seasonal variation in total alkalinity of reservoir water

(Sampling dates corresponding to sample number are given in Table 1.2.3.)

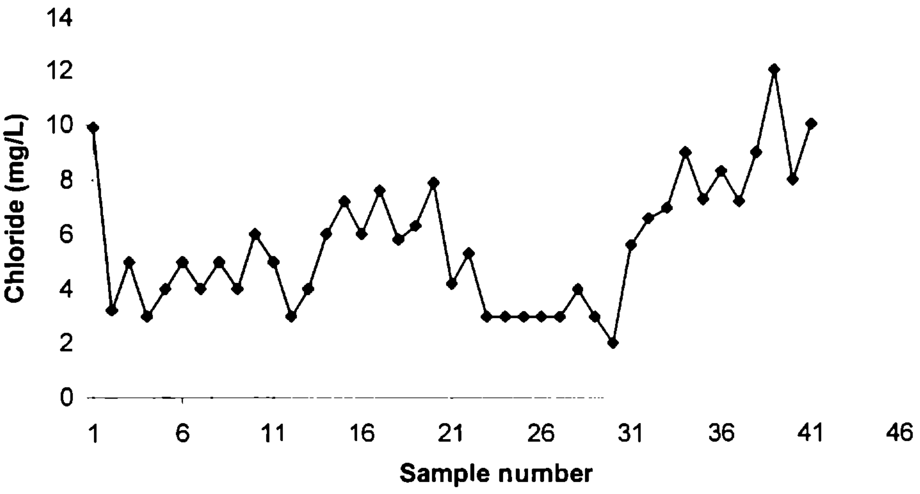


Figure 1.2.11a. Seasonal variation of chloride of reservoir water

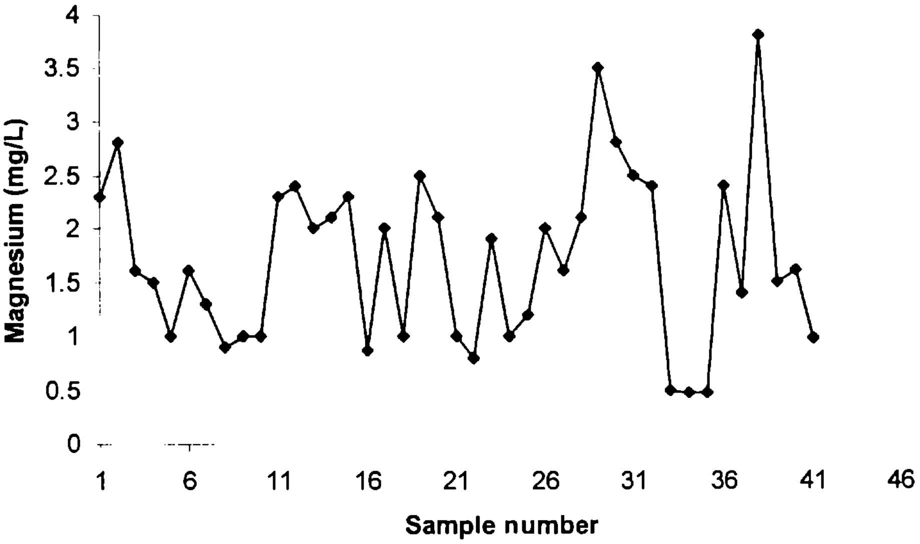


Figure 1.2.11b. Seasonal variation of magnesium of reservoir water
(Sampling dates corresponding to sample number are given in Table 1.2.3.)

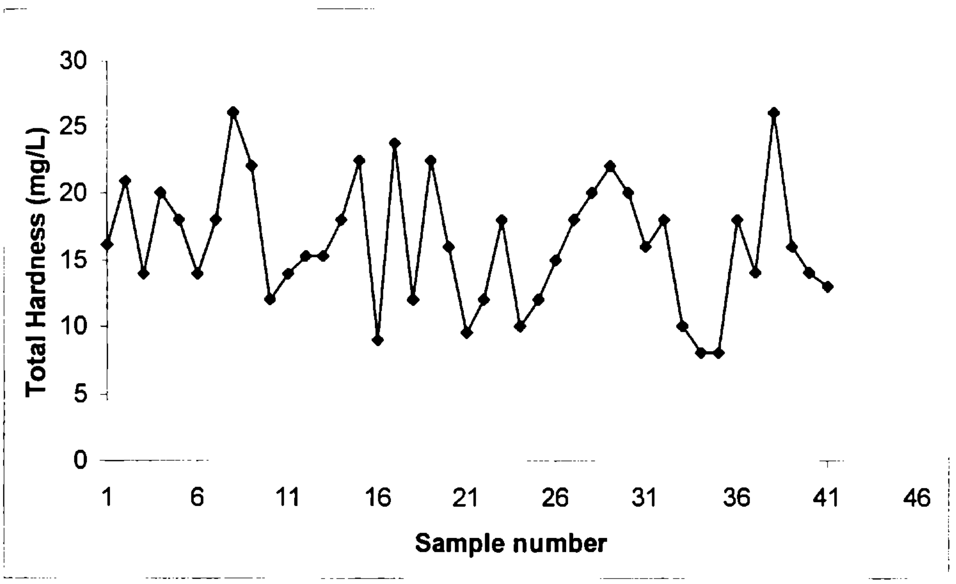


Figure 1.2.12a. Seasonal variation of total hardness of reservoir water

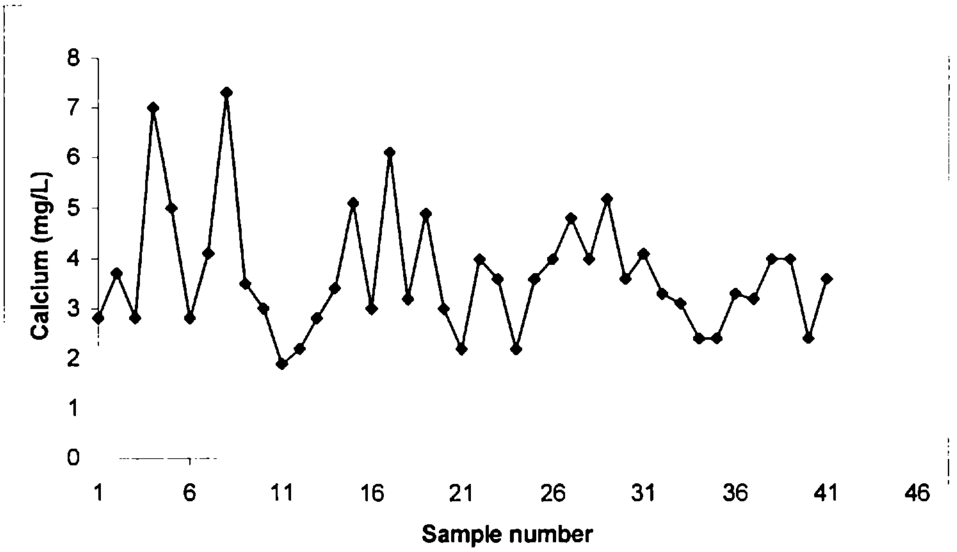


Figure 1.2.12b. Seasonal variation of calcium of reservoir water

(Sampling dates corresponding to sample number are given in Table 1.2.3.)

1.2.13. **Stratification**

Stratification studies were carried out in the reservoir during pre-monsoon period when the problem existed at the treatment plant and water level in the reservoir was below 67 m.

Sampling was done at a point 25 m away from the dam. The euphotic zone depth was measured using Secchi disc (Wetzel 1983). The average value of euphotic zone depth was found to be 1.75 m.

1.2.14. **Temperature**

Ambient temperature at the time of measurement was 32.6^0C. Temperature measurements were done at various depths. Temperature variations in the water column are shown in Figure1.2.13. Temperature decreased with increasing depth. At 0.1 m depth the temperature was 31.8^0C. Temperature dropped to 26.9^0C at 15 m depth. Thermocline occurs at 7 m. Hence it is expected that corresponding pycnal and chemical stratification can be possible.

Warm climate follows the monsoon. The solar radiation received at 10° N latitude is about 895 cal cm^{-2} d^{-1} during the month of April (Thompson 1999). The average day temperature is fairly high whereas night temperature reaches a minimum during this time. Solar radiation is received for maximum period during this season. This high rate of solar insolation warms up the euphotic zone. The subsurface water is stagnant and does not receive enough solar radiation. This leads to a cooling below the euphotic layer. Since turbulence is minimum, density stratification occurs. This type of temperature transition is fairly sharp with lakes and reservoirs in the temperate region.

With considerable shallow regions a density current is often established in reservoirs due to heat loss (Wells and Sherman 2001). In Peechi reservoir there is no identifiable shallow regions due to the steep slope at the basin edges. Hence any disturbance to a density current is ruled out. The radiation processes (in and out) in the reservoir is schematically represented in Figure 1.2.14.

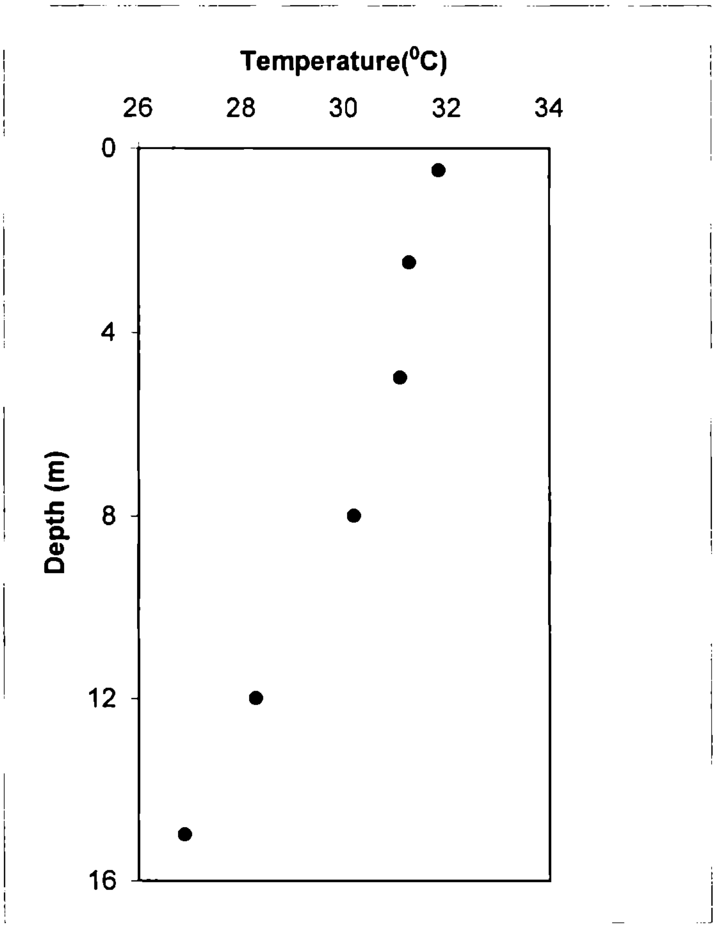
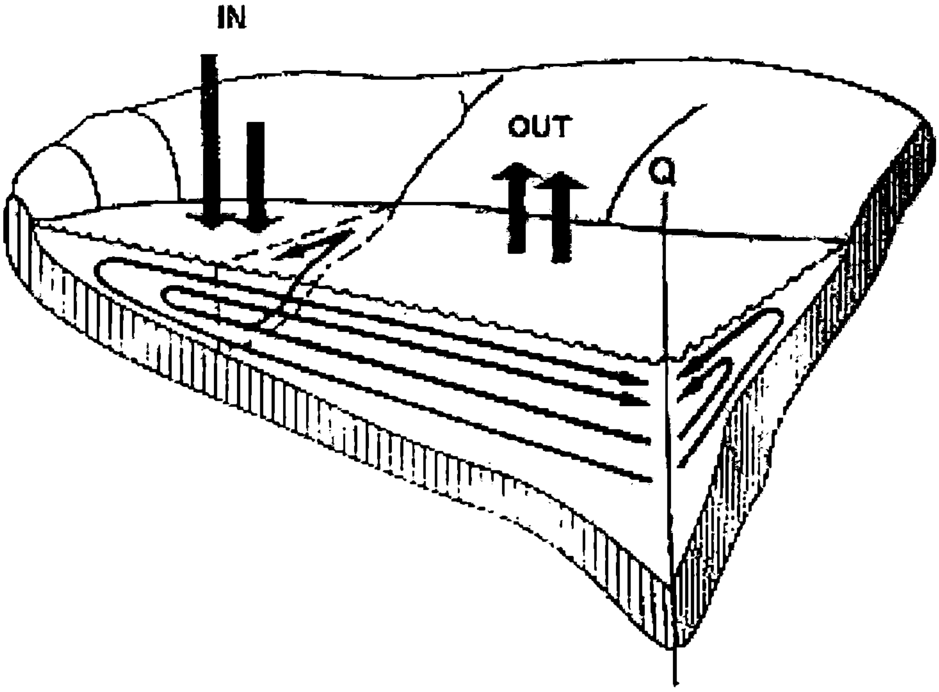


Figure 1.2.13. Depth profile of temperature in the study basin



(Wells and Sherman 2001)

Figure 1.2.14. Radiation process in and out of reservoir

1.2.15. **Turbidity**

Turbidity variations in the water column are shown in Figure 1.2.15. Turbidity varies from 3.8 NTU at 0.1 m to 15.3 NTU at 15 m. Turbidity increases with depth, but around 5 m depth turbidity shows a decrease and then sudden increase. The drop in turbidity at 5 m is probably due to the settling of particulate matter. Corresponding to the continuous increase in turbidity, there is a steady decrease in dissolved oxygen concentration. This pattern of turbidity variations can be explained as follows. The iron(II) mobilized from sediment is soluble. It moves up in the water column by diffusion. As it gets mixed with increased DO, it is oxidized to iron (III). Fe (III) so formed hydrolyses at the pH condition existing in water (pH-6.9-7.8) forming dense ferric hydroxide, which settles down. The colloidal as well as particulate iron hydroxide contributes to the increase in turbidity observed at the section B of the turbidity-depth profile. The process is schematically represented in Figure 1.2.16.

1.2.16. **Dissolved oxygen**

Surface water analysis did not show any significant presence of algae at the site. Hence the only significant source of dissolved oxygen is partition at the water surface. Oxygen enters the water body through diffusion from atmosphere and this process is temperature dependent. The diffusion coefficient of O_2 is about 2.05×10^{-1} cm^2/s in air and 10^{-5} cm^2/s in water (Lerman 1979). Hence the diffusion transport in the vertical direction in the water column is slow.

Depth – wise, dissolved oxygen concentration is shown in Figure1.2.17. The concentration varies from 4.8 mg/L at the surface to zero at 8 m. A value of 4.8 mg/L at the surface at 31.6^0C corresponds to a saturation level of 65.7 % in water with a chloride concentration range of 0-1000 mg/L (APHA 1998).

Dissolved oxygen concentration decreases with depth. After 8 m the water column becomes depleted of oxygen. Oxygen from the atmosphere diffuses to the water column. Diffused oxygen moves vertically as well as

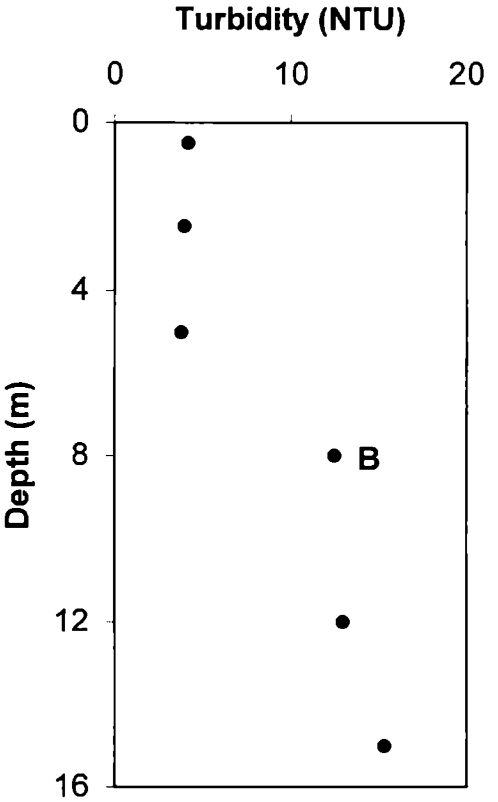
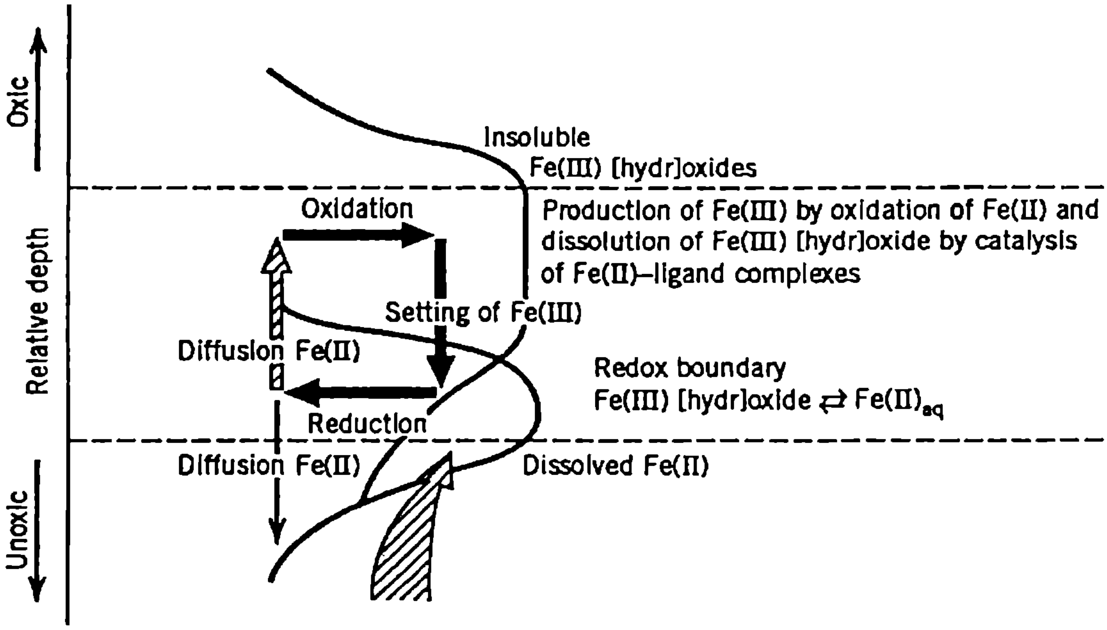


Figure 1.2.15. Depth profile of turbidity in the study basin



(Stumm and Morgan 1997)

Figure 1.2.16. Redox processes of iron in a water column

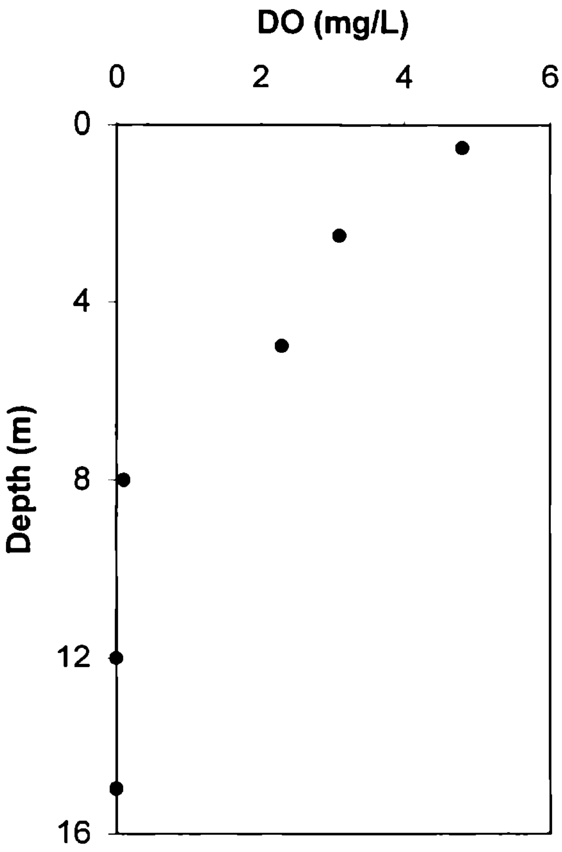


Figure 1.2.17. Depth profile of Dissolved Oxygen in the study basin

horizontally. Wind action generates different kinds of surface waves, though weak, these facilitate the surface dissolution of oxygen. In the case of Peechi reservoir wind influence is negligible and only weak surface winds are prevalent. During monsoon period wind velocity is appreciable. During this period the wind velocity is above 3 ms^{-1} Only when the wind velocity exceeds 3 ms^{-1} Langmuir circulation develops (Imboden and Wuest 1995). Hence during the period of stratification the vertical diffusion of dissolved oxygen is greater than horizontal diffusion. As DO diffuse down the column it oxidizes the reduced species present in the water column.

During stratification events build up of mobilized constituents from the underlying sediment occurs at the stratum. As these constituents move upwards, the increasing concentration of dissolved oxygen on the way oxidizes easily oxidisable constituents. The presence of natural organic matter and hydrogen sulfide also affects the downward distribution of oxygen.

1.2.17. Specific absorbance at 254 nm ($SUVA_{254}$)

It has been established that there is a good correlation between $SUVA_{254}$ and dissolved organic carbon (DOC) (Patterson and Bishop 1996; Vuorio *et. al.* 1998; Abbt-Braun and Frimmel 1999). Hence it is reasonable to assume that in the absence of specific organic pollutants $SUVA_{254}$ represents DOC derived from NOM. Specific UV absorbance at 254 nm ($SUVA_{254}$) is an indicator of natural organic matter (NOM) in a water body. For routine monitoring of the water body this is recommended as a convenient parameter (APHA 2000; Exall and vanLoon 2000).

Biomass production occurs mainly in the euphotic zone where light penetration is high. Part of this biomass sinks and part of it is used up by the organisms. Natural organic matter is also derived from leaching of plant residues from the water shed. All these contribute to the value of $SUVA_{254}$. The depth wise variation of $SUVA_{254}$ is given in Figure 1.2.18. $SUVA_{254}$ corrected for turbidity increases with depth. Absorbance varies from 0.051 at the surface to 0.162 at 15 m depth. It shows a sharp increase at around 7 m.

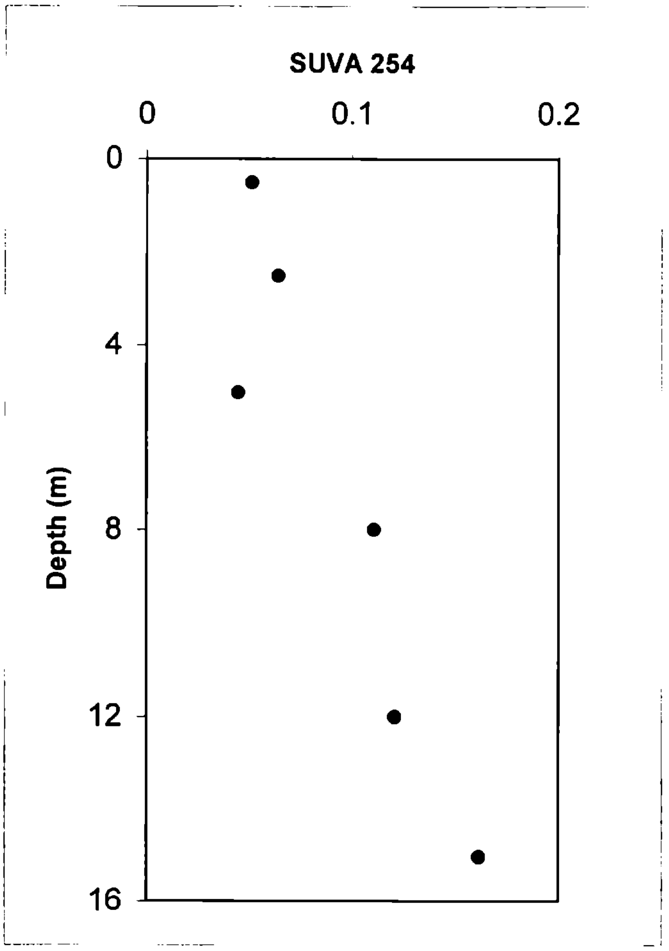


Figure 1.2.18. Depth profile of $SUVA_{254}$ in the study basin

The gradual increase corresponds to a slow diffusion from the sediment layer. This also matches with iron, which is also mobilized from the sediment layer,

1.2.18. Iron

Iron concentration in the reservoir shows variations in the water column. The depth profile of iron is given in Figure I.2.19. Iron concentration varies from 0.05 mg/L at the surface to 5.0 mg/L in the lowest sampled depth i.e. at 15 m. It has been reported that the occurrence of anoxic conditions causes a significant cycling especially of iron and manganese at the oxic–anoxic interface, due to changes in solubility related to the changes in the oxidation state (Davison et al. 1982; Yagi 1986; De Vetre *et al.* 1988; Egeberg *et al.* 1988; Landing and Westerlund 1988). The classic work of Mortimer (1941) on Esthwaite Water provided the basic features of iron cycling in a seasonally anoxic lake as well as an interpretation of those observations in terms of the redox condition of the lake and fluxes across the sediment-water interface. During summer, when water column in the reservoir is stratified, the hypolimnion of the water body becomes anoxic and upward mobilization of mineral constituents occurs. When the water column is anoxic, Fe_2O_3 reduction occurs in the strongly reducing sediment stratum (Stumm and Morgan 1996).

$$Fe_2O_{3(s)} + 3\ H^+ + 2e^- \rightarrow 2\ Fe^{2+} + 3\ OH^-$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$$

$$Fe(OH)_{3(amorphous,s)} + e^- \rightarrow Fe^{2+} + 3OH^-$$

$$Fe(OH)_{3(amorphous,\ s)} + 2H^+ + HCO_3^- \rightarrow FeCO_3 + 3H_2O$$

Reduced Fe (II) diffuses to the sediment-water interface where it is gradually oxidized to Fe^{3+} and hydrolyzed to insoluble Fe $(OH)_3$. As a result there is no build up of dissolved iron in the water column.

When stratification develops, biological processes consume oxygen and the bottom waters become anoxic. Reductive dissolution of iron oxide continues to occur in the sediments. Fe (II) diffuses in to the anoxic bottom water and is oxidized at the oxycline forming a peak in particulate iron hydroxide in the water column. Below the oxycline, where the water is

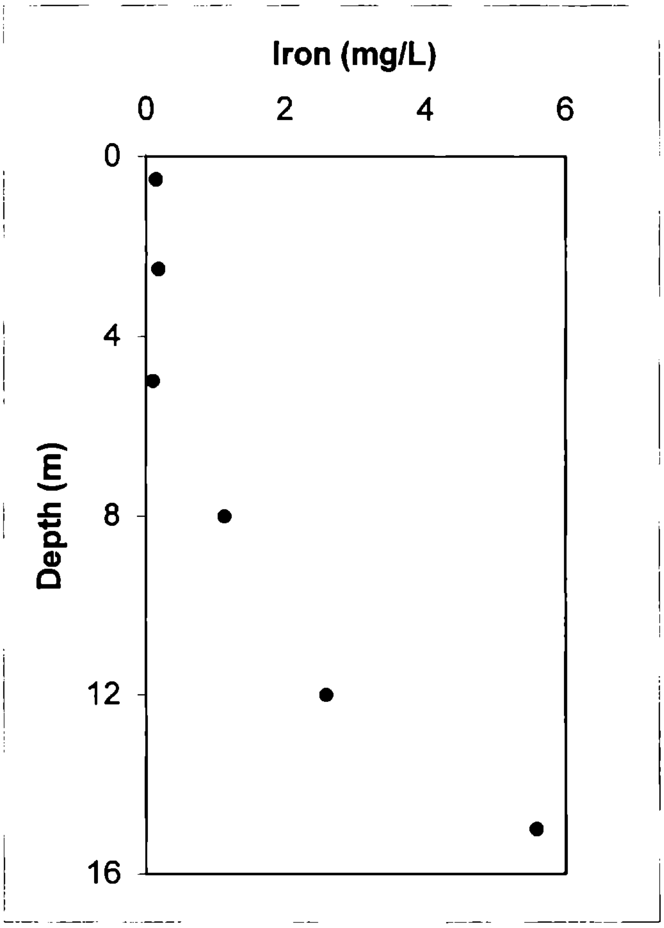


Figure 1.2.19. Depth profile of Iron in the study basin

strongly reducing, dissolved Fe (II) is stabilized and its concentration increases with time. pε of the hypolimnion is lowered far below what is required to remove essentially all of the oxygen. After virtually all of the O_2 is gone, the pε can go sufficiently low for the sequential reduction of nitrate, ferric and sulfate (Stumm and Morgan 1985, Pankow 1991).

$\frac{1}{2} O_{2(g)} + H^+ + e^- \rightarrow \frac{1}{2} H_2O$ $p\varepsilon^0 = +13.75$

$\frac{1}{2} NO_3^- + H^+ + e^- \rightarrow \frac{1}{2} NO_2^- + \frac{1}{2} H_2O$ $p\varepsilon^0 = +7.15$

$1/6 NO_2^- + 4/3\, H^+ + e^- \rightarrow 1/6\, NH_4^+\ 1/3\, H_2O$ $p\varepsilon^0 = +5.82$

$FeOOH_{(s)} + HCO_3^-(10^{-3}) + e^- \rightarrow FeCO_{3(s)} + 2H_20$ $p\varepsilon^0 = -0.8$

$1/6\, SO_4^{2-} + 4/3\, H^+ + e^- \rightarrow 1/6\, S_{(s)} + 2/3\, H_2O$ $p\varepsilon^0 = -3.30$

$1/8\, SO_4^{2-} + 5/4\, H^+ + e^- \rightarrow 1/8\, H_2S_{(g)} + \frac{1}{2} H_2O$ $p\varepsilon^0 = -3.50$

This colloidal iron (III) hydroxide particles agglomerate into larger particles and settles to the bottom. Thus the concentration of iron increases towards the bottom layers. Other mineral constituents like phosphate bind with iron species and become immobile.

1.2.19. **Sulfide**

dai [illegible] Scan ?

The presence of sulfide in an environment is closely related to the redox condition of the environment. Under oxidizing conditions sulfur exists exclusively as sulfate. But under reducing condition it can be converted to S^0 or S^{2-} In Peechi reservoir, during stratification, sulfide concentration varies from 0.0 mg/L to 0.075 mg/L at 15.0 m depth. At a sampling depth of 0.5 m the concentration of sulfide is below detectable level (BDL). On further going down the concentration increases. The depth wise variation of sulfide concentration is shown in Figure 1.2.20. Sulfur undergoes cyclic transformations. In deoxygenated hypolimnitic conditions the simultaneous presence of iron (II) and sulfide is possible because these are the preferred oxidation states at low redox potentials. Measurements have shown that iron (II) and sulfide can coexist in solution at values in excess of the theoretical solubility product, and the possibility of organic complexation and the formation of kinetically inert metastable states have been suggested (Hutchinson 1957; Hem 1960). The reduction of sulfate in biosynthesis is

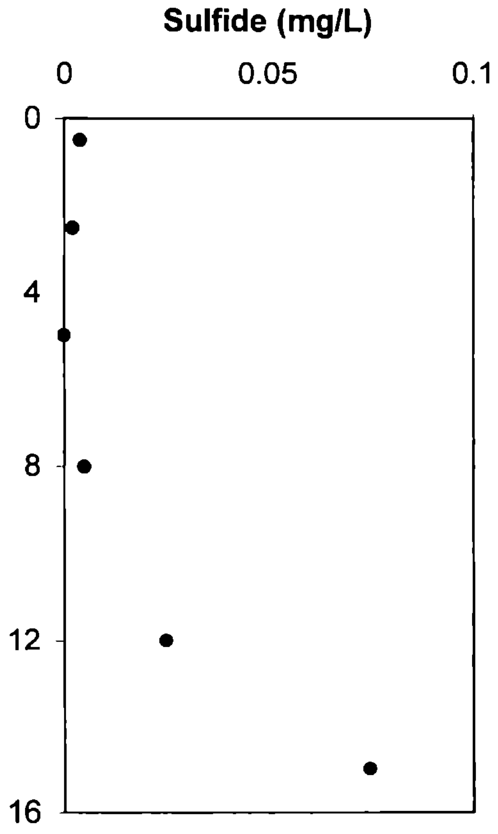


Figure 1.2.20. Depth profile of sulfide in the study basin

termed *assimilatory sulfate reduction* and can take place in aerobic and anaerobic environments. Under reducing conditions (pЄ < -2) various microorganisms mediate the reduction of SO_4^{2-} by natural organic matter. Metal sulfides, especially amorphous ferrous sulfide may be formed which gradually crystallizes to FeS. Sulfate reducing bacteria *Desulfovibrio desulfuricans* prefers a pH between 6 and 8 but can function between pH 4.2 and 9.9 (Baas Becking et al. 1960; Karamenko 1969; Zehnder 1988). At the anoxic boundary in the reservoir redox cycling of sulfur compounds occur (Davison and Heany 1978; Davison et.al. 1982; Jacob and Emerson 1982; Stumm and Morgan 1996; Langmuir 1997).

$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$

$1/8\ SO_4^{2-} + 5/4\ H^+ + e^- \rightarrow 1/8\ H_2S_{(g)} + \frac{1}{2} H_2O$ $\qquad p\varepsilon^0 = -3.50$

1.2.20. **Nitrate**

Nitrate shows increasing trend in the water column as depth increases. Nitrate concentration in the water column varies from 0.1mg/L at the topmost sampling depth (0.1 m) to 0.7 mg/L in the lowermost sampling point (15 m). The variation of nitrate concentration with respect to depth of the water column is given in Figure 1.2.21. The trend indicates that nitrate reduction is not efficient in the anoxic layer.

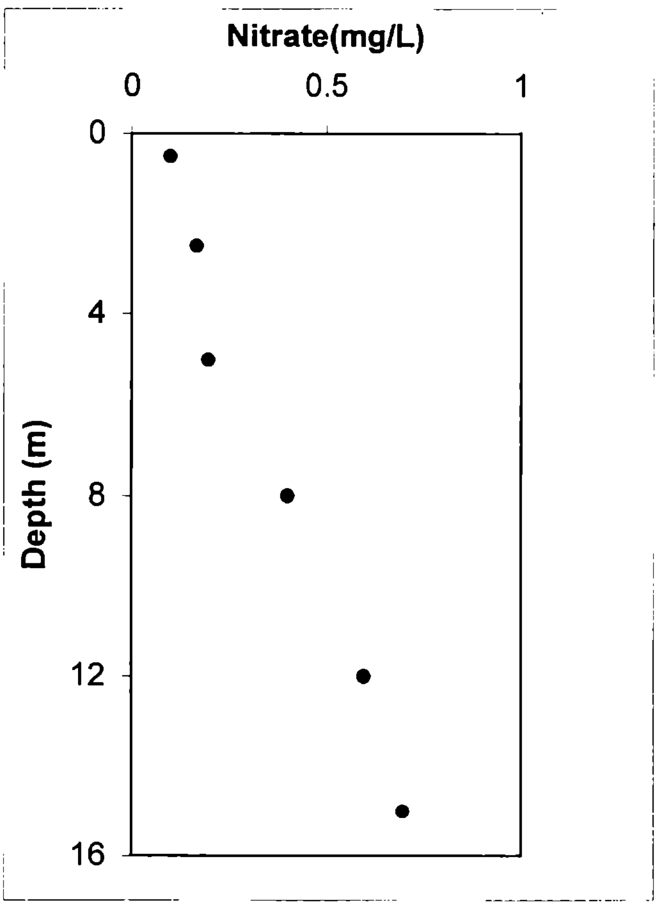


Figure 1.2.21. Depth profile of nitrate in the study basin

Chapter 3

A STUDY OF SELECTED OPTIONS FOR THE REMOVAL OF IRON FROM RAW WATER AT PEECHI WATER TREATMENT PLANT

Abstract

An understanding of the existing operational aspects of drinking water treatment plant is necessary to implement any modification of the treatment process to remove the periodic problem of iron. Incomplete oxidation of Fe(II) in raw water leaves a residue of dissolved iron (II) in finished water. The transient character of iron (II) in presence of dissolved oxygen and its slow oxidation and subsequent hydrolysis leaves a fine mat of $Fe(OH)_3$ *on the filters. This mat increases the hydraulic resistance of the filter, increases the head loss rapidly and necessitates frequent backwashing. This in turn reduces the throughput and quality of finished water.*

It is evident that rapid oxidation of Fe(II) (compared to its oxidation by dioxygen) can alleviate the problem. Hence oxidants, which can be applied without any significant modification in the existing treatment trail, were investigated. The oxidant tried is permanganate. The settling characteristics of the corresponding flocs under the operating conditions were studied using a settling column with in-line detection of turbidity by photoelectric method. These studies reveal that potassium permanganate alone can effect rapid oxidation of iron (II). Precipitation of a suspension of ferric hydroxide and manganese dioxide (formed from permanganate) is very rapid and can ideally

be done in the conventional clarifier. Excess permanganate can be destroyed by split stream treatment, or using a green sand filter.

1.3.1. **Introduction**

Water resources vary widely in their quality. Geological factors, climate and biological and chemical processes taking place in water influence the quality of raw surface water. These quality variations critically affect their intended uses. Hence surface water resources are categorized into various classes according their quality that will meet the standards set for their best-designated use. The classification is given in Table 1.3.1.

1.3.2. **Raw water quality**

The Peechi reservoir is a class C category surface water resource (KSPCB 1997). Hence the water is suitable for drinking purpose with conventional treatment followed by disinfection. The reservoir is replenished through the annual precipitation cycle. No other inflows are contributing to the water budget of the reservoir. Peechi reservoir water is chemically soft. The ranges of various water quality parameters measured at different times are already given in Table 1.3.2. The main sources of non-point pollution are agricultural practices and the traffic residue left in National Highway 47 running through the north-east side of the catchment area. The soil in the catchment area of the reservoir is principally laterite type and hence iron mobilization is possible. The iron so mobilized will be in the oxidized form and hence would be deposited in the sediment.

Table 1.3.1. Classification of surface water according to best-designated use

(KSPCB 1997)

Sl. No	**Parameter**	**A**	**B**	**C**	**D**	**E**
1	Dissolved Oxygen (DO) mg/L, minimum	6	5	4	4	
2	B.O.D (3 days at 27^0C) mg/L, maximum	2	3	3		
3	Total coliform organism MPN/100 mL, maximum	50	500	5000		
4	pH	6.5-8.5	6.5-8.5	6-9	6.5-8.5	6-8.5
5	Free ammonia (as N) mg/L, maximum				1.2	
6	Electrical conductivity micromhos/cm, maximum					2250
7	Sodium absorption ratio					26
8	Boron, mg/L, maximum					2

Table 1.3.2. Typical water quality of Peechi Reservoir

Parameter	**Unit**	**Minimum**	**Maxim um**	**Mean***	**Standard Deviation**
pH		6.4	8.1	7.0	0.33
Turbidity	NTU	1.0	13	4.8	3.1
Total dissolved solids	mg/L	6.0	88	44	18.7
Electrical conductivity	μScm^{-1}	31	96	56.7	16.6
Total hardness	mg/L as $CaCO_3$	26	8	16	4.7
Calcium hardness	mg/L as $CaCO_3$	1.9	7.3	3.7	1.2
Magnesium hardness	mg/L as $CaCO_3$	0.4	3.8	1.7	0.8
Iron	mg/L	0.02	2.03	0.39	0.5
Alkalinity	mg/L as $CaCO_3$	3	40	20.8	7.7
Chloride	mg/L	2	12	5.6	2.3

1.3.3. **Treatment target**

The temporal quality of raw water and the quality standard prescribed for the designated use determine the extent of treatment required. Quality of drinking water directly affects human health, and the production and distribution of good quality drinking water assumes top priority. The technologies available for drinking water treatment are varied. The technological capability and economic condition of the community influence the selection of the treatment technology. The treatment options vary according to source water quality, size of the population benefited from the source, availability of land, availability of trained manpower, and cost of installation, operation and maintenance (Schulz and Okun 1984). The treatment technologies widely used in developed and developing countries differ much. Many water resources are of high quality such that they do not need any treatment except disinfection. When lakes and reservoirs are used as drinking water sources the main threat is from non point sources of pollution. The unscientific agricultural practices and deforestation in the reservoir basins accelerate the problem of soil erosion and consequent leaching of chemicals (Beaulec and Reckhow. 1982; Straskraba *et al.* 1995; Kennedy 1999b; Heathwaite *et.al.* 2000). In developing countries of the tropics soil erosion is a major problem for most of the reservoirs. Soil erosion brings nutrients and residues of agricultural chemicals as suspended solids, which settle down and reduce the holding capacity of the reservoir. Many surface water resources, which are drinking water sources, need conventional treatment with disinfection (Schulz and Okun 1984, Stewart et. al. 2002). Raw water sources are chosen in such a way that minimum pretreatment is required. General design criteria are established for the implementation of water supply projects that reflect the prevailing social, economic and technical conditions encountered (Schulz and Okun 1984). A schematic diagram of Peechi Water Treatment Plant is given in Figure 1.3.1 and flow chart of the treatment operations is given in Figure 1.3.2. This conventional treatment is intended only to remove stable, suspended inorganic and organic constituents in the raw water. These suspended materials will act as a substrate for microbial growth and reduce the disinfection efficiency.

Seasonal quality variations of raw water necessitate treatment modifications. During summer months, when water level in the reservoir becomes low, quality of raw water for WTP deteriorates. During this period iron and organic matter mobilize in the reservoir. When irrigation outlets are opened this mobilization intensifies. Irrigation outlets are situated at higher elevation than the water treatment plant intake point. The draft caused by irrigation withdrawal disturbs the bottom layer of the water column in the basin. The water drawn by the treatment plant contains iron (II) that gets oxidized when contacted with air. During this problem period smell of hydrogen sulfide is detected in the plant. Turbidity gradually increases and a red mat builds up on the filter bed. The tiled walls of the filter beds became coloured due to the deposition of iron. Filtration rate decreases sharply. The number of backwashing required increases. This seriously affects the throughput of the treatment plant. Around 20% of the treated water is taken up for backwashing of the filter beds.

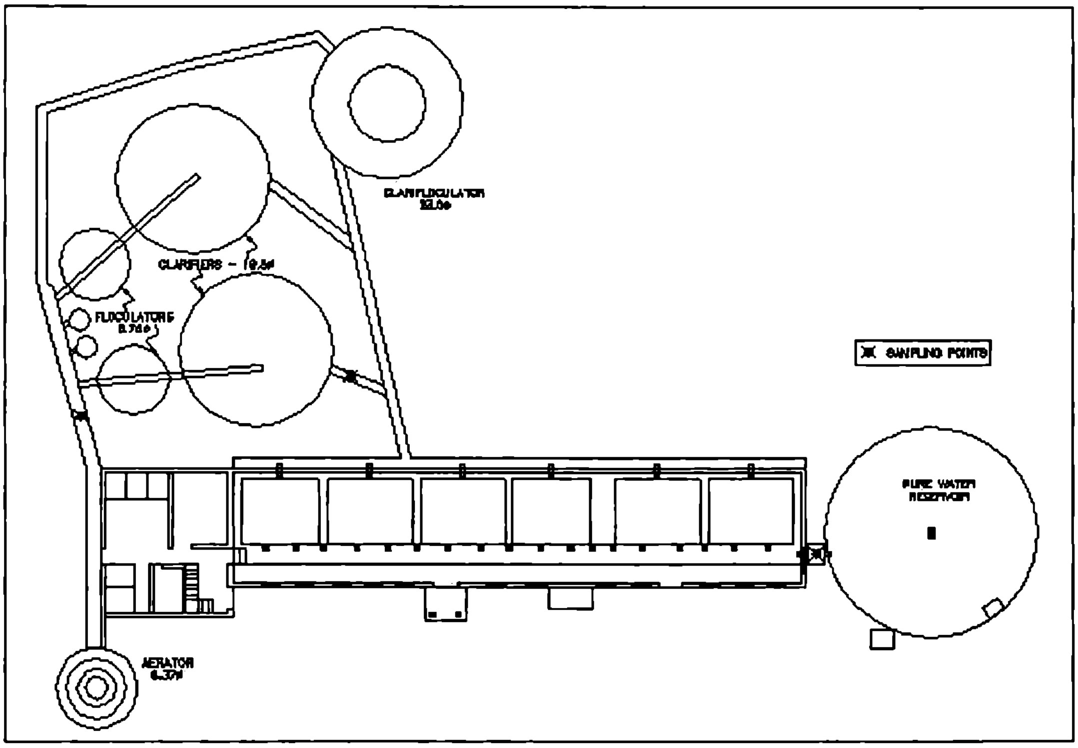


Figure 1.3.1. Schematic diagram Water Treatment Plant, Peechi

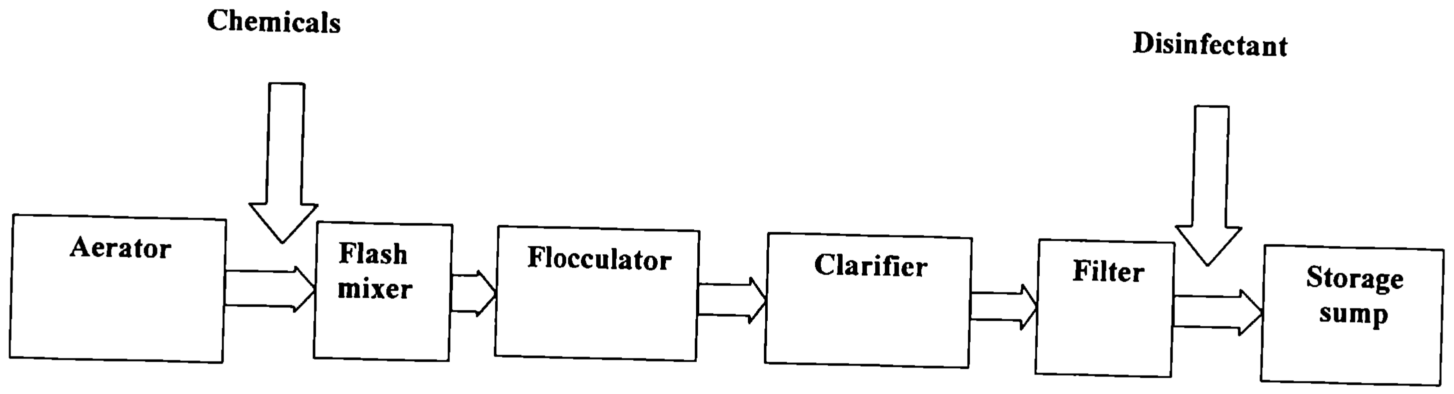


Figure 1.3.2 Treatment trail in Peechi Drinking Water Treatment Plant

The treatment scheme adopted in the treatment plant is not suitable for surface water sources, which contain heavy loads of algae or heavy metals. The principal constituents that require treatment are turbidity, iron and microorganisms. Turbidity levels vary widely. In summer season turbidity is low and within allowable limit (< 5 NTU). But during the monsoon period turbidity reaches high levels (> 80 NTU). In order to bring this high turbidity to within the acceptable levels treatment is needed. Likewise the microbial pollution of water is high during monsoon due to heavy runoff and leaching from the nearby land area (personal communication-KWA).

1.3.4. Drinking water treatment process

Aeration

Aeration is the first operation in the treatment trail. Drinking water treatment plants which use river water as their raw water can avoid aeration. When lake water and other stagnant water bodies are used as raw water sources aeration is mandatory. Aeration flushes out dissolved gases, introduces oxygen and induces oxidation of easily oxidisable substances. Odour producing components are removed through aeration. Aeration converts soluble form of iron into insoluble forms and facilitates its removal in the subsequent stages.

Chemical dosing and flash mixing

Alum and lime are the treatment chemicals used in the Peechi drinking water treatment plant. Alum is used as a flocculent in the existing treatment trail. It is dispersed as saturated solution. Alum reduces alkalinity. Lime slurry is added to correct the pH.

$$Al_2(SO_4)_3 + 6\ H_2O \rightarrow 2\ Al(OH)_3 + 3\ H_2SO_4 \qquad (1.3.1)$$

$$3\ Ca(HCO_3^-)_2 + 3\ H_2SO_4 \rightarrow 3\ CaSO_4 + 6\ H_2O + 6\ CO_2 \qquad (1.3.2.)$$

The dosed stream passes through a flash mixer to ensure efficient mixing and it remains in the flash mixer for one minute.

Flocculation and sedimentation

As a prerequisite to disinfection, aerated raw water is subjected to turbidity removal. This is achieved by flocculating fine suspended solids with alum. Aluminium hydroxide formed scavenges suspended solids and floc formation occurs. These flocs settle easily.

$$\begin{aligned} &Al_2(SO_4)_3 + 6\ HCO_3^- + 3\ H_2O \rightarrow \\ &\qquad 2\ Al(OH)_3 + 3\ SO_4^{2-} + 6\ H^+ + 6\ CO_2 \quad (1.3.3) \end{aligned}$$

Flocculation-clarification has two operational stages: orthokinetic flocculation and sedimentation. Orthokinetic flocculation requires controlled velocity in the medium. The force exerted by velocity should be less than the shear force and at the same time collision among particles should lead to agglomeration. The upward velocity of water in the clarifier is less than the settling velocity of particles, and a good proportion of particles settle under these conditions.

The nominal design parameters of the flash mixer, flocculator and sedimentation tank are given in Table 1.3.3.

Flocculation is the aggregation of particles under gentle and continuous agitation, during which suspended particles in water coalesces in to larger masses, which are denser, and granular so that they may be removed by sedimentation and filtration. The rate at which flocculation proceeds depend

Table1.3.3. Nominal design parameters of flash mixer, flocculator & clarifier

(CPHEEO 1984)

Sl.No.	Operational Unit	Detention time	Velocity (m/s)
1	Flash Mixer	20 – 40 seconds	2 – 4
2	Flocculator	30 minutes	0.3 – 0.4
3	Clarifier	120 minutes	0.15 – 0.25

on physical and chemical parameters such as charges on particles and exchange capacity, particle size and concentration, pH, water temperature, time of flocculation, size of mixing basin and nature of mixing device. Slow mixing is meant to bring the particles to collide and to aggregate. The time provided for flocculation is also a critical factor along with the intensity of agitation. The intensity of mixing is dependent upon the temporal mean velocity gradient G. The desirable values of G in a flocculator vary from 20 to 70 $sec^{-1.}$ The value of GT for aluminium coagulants varies from 2 to 6×10^5 (CPHEEO 1984).

In ortho kinetic flocculation the maintenance of uniform velocity is critical for better coagulation. In water treatment plants flocculation basins are designed for a retention time of 20 to 30 minutes. At low temperatures the rate of flocculation is slow necessitating longer detention periods. The water is drawn from a fixed level and hence temperature variations are minimum. The varying turbidity and suspended matter concentration necessitate control of flocculent/ coagulant dosage.

The clarifier (sedimentation tank) follows the flocculator. This unit is used to separate settleable suspended solids from water. The factors that influence sedimentation include size, shape and weight of the particle, viscosity and temperature of the water, surface overflow and surface area, velocity of flow, inlet and outlet arrangements, detention time and effective depth of the basin. Clarifiers are designed either as separate basin or in concentric fashion. Concentric design requires less space and construction costs. The water from flocculator enters to the clarifier with a flow velocity of

0.25 – 0.45 m/S. This low velocity helps to avoid breakup of flocs. The detention time in clarifiers is between 2 to 2.5 hours for coagulated waters. About 80% of the particles settle in the clarifier within the detention time. Settled sludge is mechanically scraped continuously to a central sump and withdrawn periodically.

1.3.5. **Effect of iron mobilization on clarification**

Iron is mobilized as soluble iron (II) in the anaerobic sediment of a stratified water body. Iron present as Fe_2O_3 is solubilized as follows

$$Fe_2O_3 + H_2O + (CH_2O)_x \xrightarrow{\text{microbes}} Fe^{2+} + CO_2 + H^+ \qquad (1.3.3.)$$

$$2\,Fe(OH)_3 + CH_2O \rightarrow 2\,Fe(OH)_2 + CO_2 \qquad (1.3.4)$$

$$Fe_2O_3 + 3\,H_2O + CH_2O \rightarrow 2\,Fe(OH)_2 + CO_2$$

$$Fe(OH)_2 + CO_2 \rightarrow Fe(HCO_3)OH_{(aq)}$$

$$SO_4^{2-} + 4\,CH_2O \rightarrow H_2S + CO_2 + 3\,H_2O + 2\,H^+ \qquad (1.3.5)$$

The sediment in the Peechi reservoir does not contain any significant amount of manganese. Fe(II) and S^{2-} species are soluble under these pH and redox conditions and diffuse out from the pores of the sediment and remain stable in the anoxic hypolimnion. Upon releasing in to open treatment trail, volatile H_2S escapes and Fe(II) is oxidized to insoluble species. The oxidation process is slow and incomplete within the detention time of the flocculator and clarifier.

Filtration

Clarified water enters the filtration unit. Filtration is a physical, chemical and biological process for separating suspended impurities from water by passage through porous media. Various types of filters are used in water treatment plants. Rapid gravity filters are the most common in use. The feed to the filters distributed to get maximum efficiency of operation. Standard rate of filtration through a rapid sand filter is 80 to 100 Lpm/m^2. Design features of rapid sand filters in Peechi Plant are given in Table 1.3.4.

Disinfection

In the case of drinking water microbiological quality is of paramount importance. All the surface water sources are prone to microbial contamination from various sources. Hence disinfection is a must for drinking water treatment. The most commonly used disinfectant is chlorine. Chlorine is used either as liquid chlorine or in the form of bleaching powder. In Peechi drinking water treatment plant liquid chlorine is used as disinfectant. The disinfected water is collected in a sump and this provides sufficient contact time for chlorine.

1.3.6. **Finished water quality during non-problematic period**

During most of the period the treatment scheme followed in the treatment plant gives satisfactory results. The treatment provides potable water, which satisfies all the regulatory criteria. The turbidity of the treated water comes down to below 5 NTU and total iron levels were below 0.3mg/L. The microbial quality of the water is also satisfactory.

1.3.7. **Finished water quality during problem period**

During non - rainy months (November to May) especially when the irrigation outlet is open, iron mobilization is intense. The aeration provided become insufficient to oxidize soluble iron (II) to iron (III) and to induce its

Table 1.3.4. Design features of rapid sand filter in Peechi Treatment Plant.

(CPHEEO 1984)

Sl.No.	Characteristic	Range
1	Rate of filtration	4 – 21 m/hour
2	Size of bed	40-400 m^2
3	Depth of bed	30 – 45 cm of gravel
		60 – 70 cm of sand
4	Effective sand size	0.55 mm or larger
	Uniformity coefficient	1.5 and lower
5	Grain size distribution of sand in the filter	Stratified with smallest or lightest grains at the top and coarsest at the bottom

precipitation as $Fe(OH)_3$ Delayed formation of iron (III) hydroxide chokes the filter beds and stains the walls of the filter units. As the concentration of solids increases the frequency of backwashing will rise. This will affect the throughput of the treatment plant.

The problem of iron mobilization in the raw water is sporadic. The intensity and duration of the problem varies widely. To investigate the problem in detail online monitoring was done. The options for treatment modification also have to be in tune with the existing treatment plant. The major constraint in the study of raw water quality variation and dependent treatment study was that replication under identical conditions could not be done. Even during a span of hours water quality showed variations with respect to the target constituent, namely soluble iron. Hence typical results are given, and statistical validation could not be done.

1.3.8. Influence of water quality on treatment process

The surface layer of the reservoir water during non-monsoon period is of almost the same composition as observed for river water except for turbidity. Typical values are shown in Table1.3.2. Since the topsoil in the watershed area is derived from charnakite and weathered laterite, ionic content is very low (CESS 1974). However during periods of turbulence iron content is observed to be higher than normal. Similar phenomenon has been observed by other workers (De Vitre et al. 1988). However, low concentrations of insoluble ferric hydroxide does not cause problem in the treatment process. During alum coagulation iron is removed to acceptable levels in treated drinking water In oxic environment and at pH observed at reservoir water, iron is converted to ferric hydroxide, which if carried to the plant is easily removed by clarification and filtration.

During the problem period chemical constituents which are significant from the treatment point of view, are drawn into the treatment plant show a higher than normal values. These constituents include H^+/ OH^-, HCO_3^-, organics, Fe^{2+} etc. A higher pH is expected since the sediment process is anaerobic (Talling 1976; Davison and Seed 1983; Sigg et al. 1991). The following reaction schemes support the variations in pH. The mobilization of constituents from sediment leads to an increase in the concentration of mineral constituents such as phosphate, nitrate, and sulfide

$$FePO_4.2H_2O \rightarrow Fe^{3+} + PO_4^{3-} + 2H_2O$$

$$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$$

$$SO_4^{2-} + 9H^+ + \rightarrow HS^- + 4H_2O$$

The $SUVA_{254}$, which is characteristic of natural organic compound, increases. Strong complexation of metals in solution by humic substances is well documented (Stevenson and Fitch 1986; McKnight, *et al.* 1983; Cabaniss and Shuman 1988; Buffle 1988). This can be argued to be due to mobilization of natural organic matter, which is normally adsorbed or bound to ferric oxide. Dissolution of ferric oxide as iron (II) by microbial activities leads to the increase in iron, phosphate and organic matter.

All natural waters contain dissolved organic compounds (Gjessing 1976; Drever 1997). Dissolved organic carbon concentration in the lake or reservoir varies with the biological productivity of the lakes (Thurman 1985). Most of the dissolved organic carbon in natural waters is in the form of humic and fulvic acids, with fulvic acid predominating in surface waters (Drever 1997). The exact structure of individual compounds has not been elucidated (Hayes et al. 1989). A representative molecular structure of fulvic acid is given in figure 1.3.3. Humic substances are polymeric organic acids of variable composition; acidity (typically 10-20 mequiv/g of C) is contributed by carboxyl and phenolic functional groups. They have molecular weights in the range of several hundred to several million (Schnitzer and Khan 1972; Gjessing 1976). Terrigenous humic substances are derived in large part from degradation of higher plant material and retain a high degree of aromaticity from their biogenic precursors. Metal complexation by humic substances is attributed to chelation by proximate acidic functional groups (Aiken et al. 1985). The structural complexity of humic substances is reflected in their acid-base and metal complexation chemistry and in their adsorption behavior. The physico chemical nature of humate-metal interactions has kinetic as well as thermodynamic implications (Cacheris and Choppin 1987; Lavigne *et al.* 1987). Complexation of trace metals by humic acids may affect the aquatic biota in two ways. One is the reduction of toxicity of certain trace metals. In other case the availability of certain metals like iron is increased.

The redox state of reservoir systems is governed by biologically mediated reactions that involve diagenesis of organic matter. The various microorganisms utilize a thermodynamically predictable sequence of oxidants. The transformation of organic matter into bicarbonate and methane is the final step in the sequence (Froelich et al. 1979).

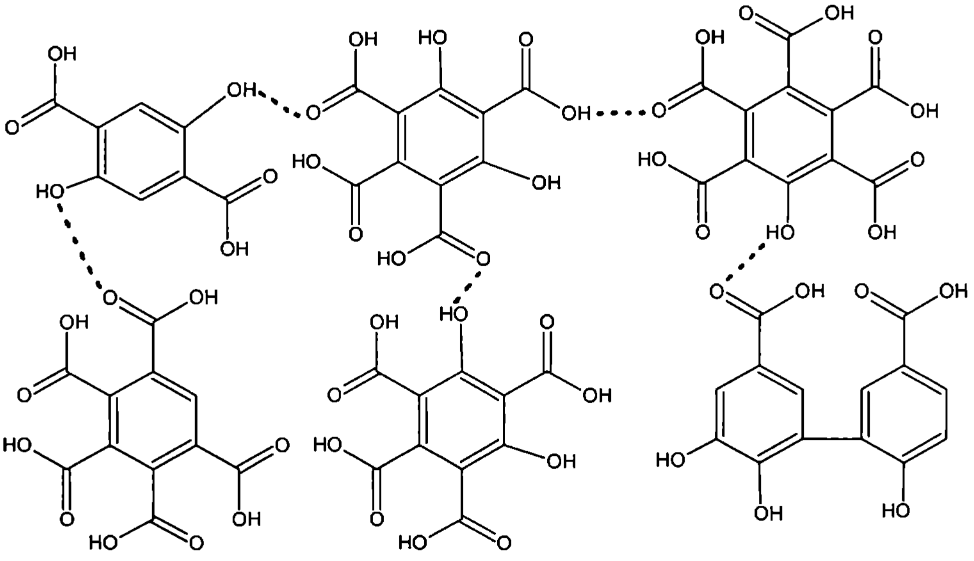


Figure 1.3.3. Representative structure of NOM

$FeOOH_{(s)} + HCO_3^-(10^{-3}) + e^- \rightarrow FeCO_{3(s)} + 2H_20$ $p\varepsilon^0 = -0.8$

$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$

$HCO_3^- + 9H^+ + 8e^- \rightarrow CH_{4(aq)} + 3H_2O$

Since the bicarbonate is taken up in the reaction the alkalinity decreases, if this reaction dominates.

Oxidation of iron by DO in natural water is a slow process (Davison and Seed 1983). When Fe(II) is present in raw water at every stage of treatment process oxidation and conversion to ferric oxide is incomplete and iron is carried through. A considerable portion of iron is retained in the filter units forming a mat. This increases the resistance to flow, making a rapid head loss. This in turn necessitates frequent backwash. This affects the throughput of treated water as evident from Table 1.3.5.

It is observed that iron concentration at the intake is higher than average on most of the days. However it exceeds the permissible values for about 20 days in a year. Development of high concentrations of dissolved ferrous iron is a typical feature of meromictic soft water lakes in forested areas (Kjensmo 1967). The stabilities caused by chemical gradients in such lakes are low (Hongve 1980, 1997). Redox dependent seasonal cycling of iron between water and sediment is one of their dominant character (Hongve 1997). Limited mixing increases the dissolved oxygen concentration at depth of the reservoir. Presence of natural polymeric compounds such as humic and fulvic acids enhance the coagulation and trace metal binding. This is due to the presence of negative surface charge on them (Tipping and Cooke 1982; Laxen 1985:

Table 1.3.5 Backwashing details of WTP, Peechi.

Sl No	**Time of operation**	**Water requirement for backwash/day**	**% of total throughput**	**Frequency of backwashing**
1	Normal period	1.2MLD	3.3	Once in 24 hour
2	Iron mobilization	2.0MLD	5.5	Once in 6 hours

Liang and Morgan 1990). The increasing dissolved oxygen concentration enhances oxidation of iron (II) to iron (III) and subsequent hydrolysis of iron (III) to iron (III) hydroxide, which is in the process of settling, at the intake point. Colloidal ferric hydroxide undergoes perikinetic agglomeration in stagnant zones and orthokinetic agglomeration at adequate turbulence. Agglomerated ferric hydroxide is in the process of settling. Consequently a higher concentration of ferric hydroxide, and turbidity due to $Fe(OH)_3$ can be expected at some depth. If there is no turbulence and a steady stratification circulation exists, anoxically utilized material is limited to the bottom. Under these circumstances a higher iron concentration can be found in raw water.

The problem is further aggravated when a draft is established at the bottom layer towards the intake. This is caused by releasing water from irrigation outlet. It is also found that concentration of iron and intensity of odour are very high in the irrigation outlet during this period. This observation indicates that the origin of the problem has a sound correlation to natural processes and made turbulence. It remains as a minor nuisance during normal stratification. Enhanced withdrawal from the irrigation canal aggravates the problem.

1.3.9.**Column studies**

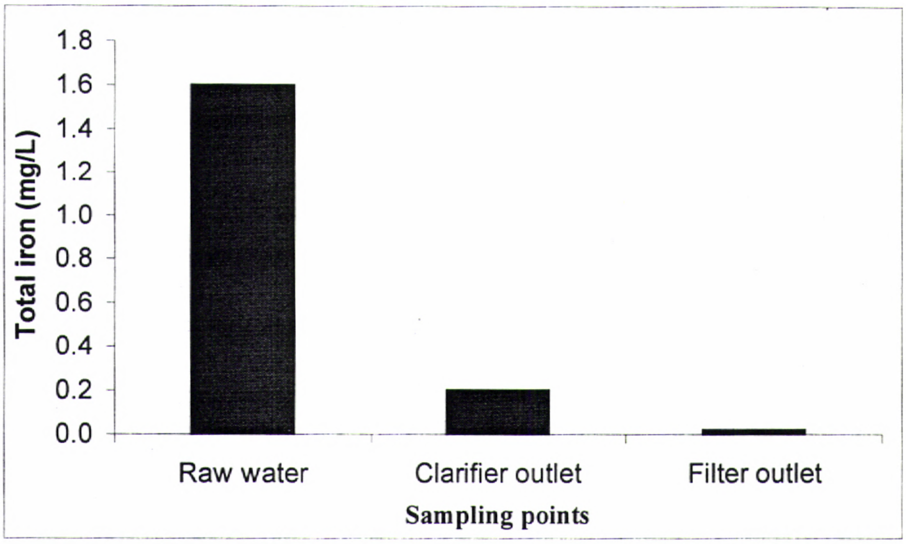
Materials and methods

Raw water quality variations affect the treatment efficiency of the drinking water treatment plant. Jar test experiments were conducted to identify the pattern of settling. As a preliminary step jar test experiments were carried out using auxiliary oxidants along with usual treatment chemicals viz. alum and lime. During problem period the treatment was not able to take care of the high concentration of iron present in the intake water of the treatment plant. The problem was also traced by analyzing samples from different treatment stages.

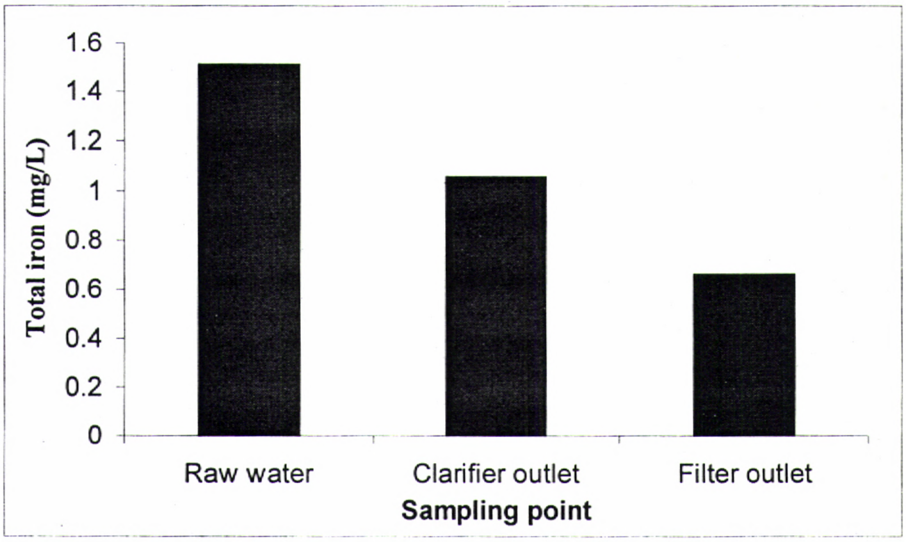
Samples were collected from aeration tray, flocculator, clarifier and filter outlet. By analyzing the concentration of indicator parameters in these points efficiency of each operational stage of treatment trail were evaluated. These experiments were carried out during the normal operational period, when no constituent mobilization occurs and during the problem period, when iron and odour producing compounds were mobilized. Typical results are given in Figures 1.3.4 and 1.3.5. To optimize the efficiency of the treatment plant especially during the period of mobilization of iron and foul odour operational modifications were applied. These modifications were tried under simulated plant conditions. The floc settling characteristics under the modified operating conditions of the plant were ascertained using a specially designed column set up.

The efficiency of the modifications was evaluated by analyzing iron and turbidity as indicative parameters. These parameters were selected because they directly affect the efficiency and are easy to monitor.

During the problem period concentration of dissolved iron and organic matter (as measured as $SUVA_{254}$) are high. Chlorination of natural water containing DOC is known to give trihalomethanes (THM) and halo acetic acids (HAA), which are known carcinogens (Zhou and Xie 2002; Roberts *et. al.* 2002; Xie and Zhou 2002; Hart, 2002). They are also implicated as

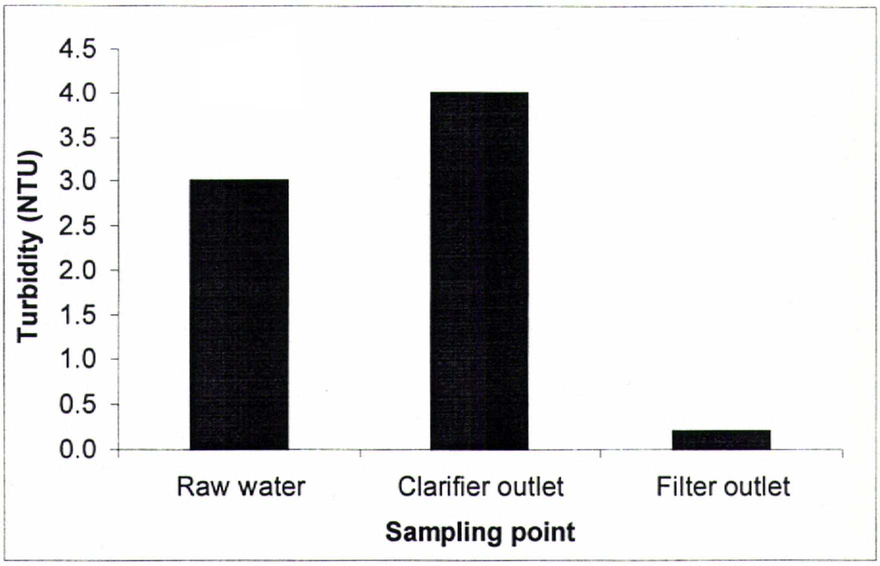


(a) Non problem period

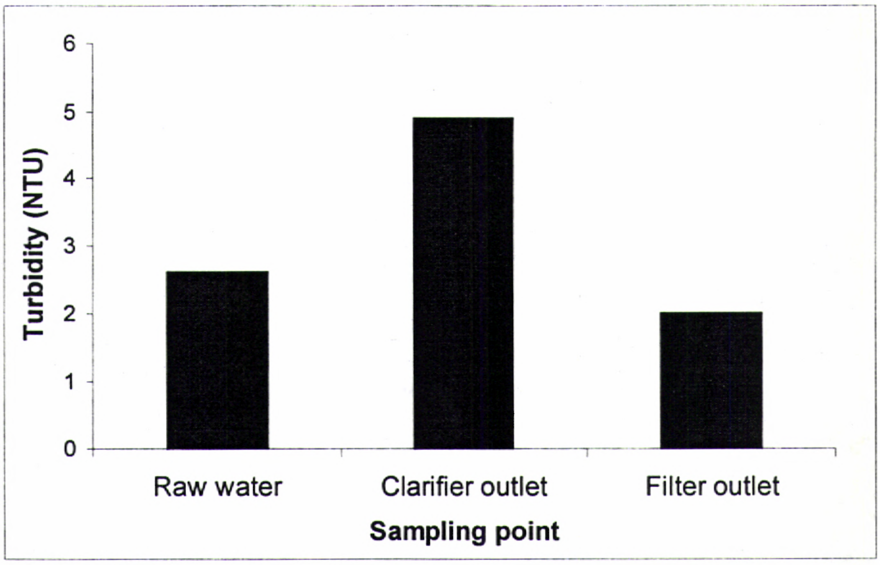


(b) Problem period

Figure 1.3.4. Concentration of iron at different treatment stages



(a) Non-problem period



(b) Problem period

Figure 1.3.5. Turbidity of water at different treatment stages

causative of still birth, hence water containing THM is not even recommended for use in personal showers since THM is known to be absorbed through skin (Hart, 2002). Hence from the current state of knowledge it is not advisable to treat problematic raw water with any potential chlorine source. The only option that can be implemented in the existing plant without any structural modification is rapid oxidation with a reagent, which leaves a non-toxic residue. Now the selection falls on potassium permanganate, which has been tried and implemented for the treatment of many problematic waters.

Oxidation with permanganate

Iron is oxidized rapidly by permanganate in acid, neutral and alkaline media.

In acid media

$$5\ Fe^{2+} + MnO^{4-} + 8\ H^{+} \rightarrow Mn^{2+} + 4\ H_2O + 5\ Fe^{3+}\ (1.3.6)$$

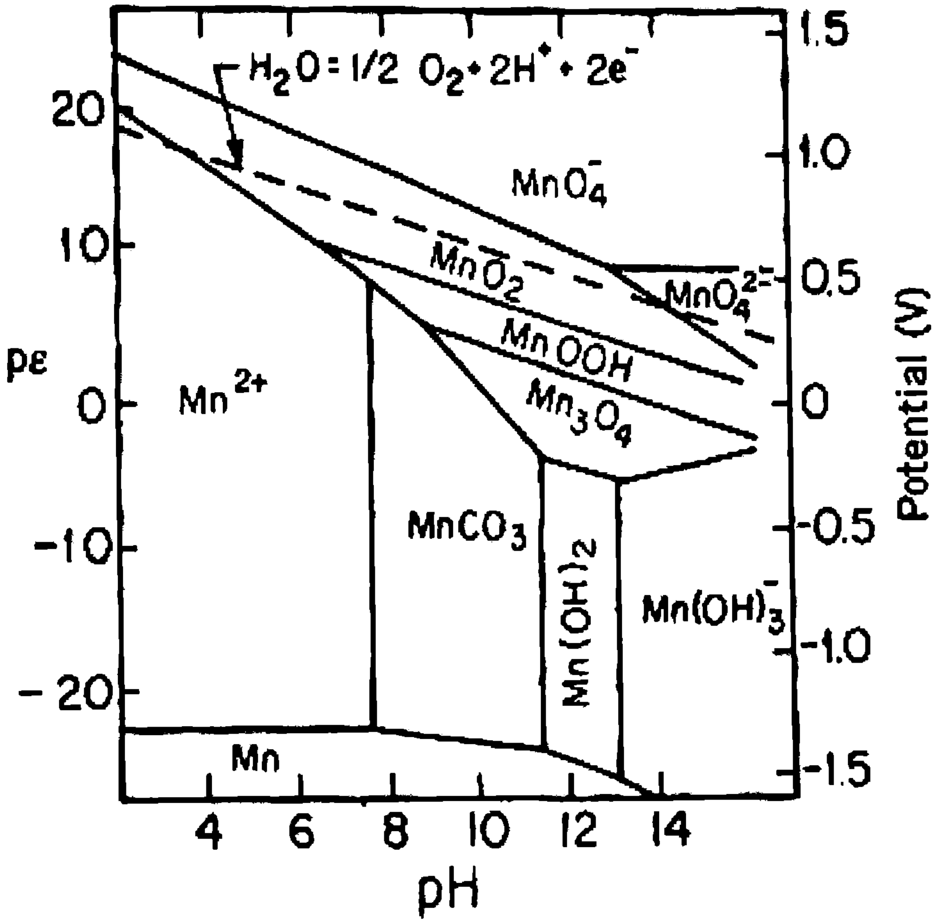
In acid medium Mn^{2+} is soluble. However in neutral and alkaline medium

$$MnO_4^{-} + 3\ Fe^{3+} + 4\ H^{+} \rightarrow MnO_2 + 3\ Fe^{3+} + 2\ H_2O(1.3.7)$$

The pH dependant speciation diagram of Mn is shown in Figure 1.3.6. This means that acid is consumed hence an increase in pH. This means that MnO_2 formed by the treatment is virtually insoluble. Moreover MnO_2 is denser than $Fe(OH)_3$ and settles down very fast. The semi empirical jar test results are shown in Table.1.3.6. Precipitated MnO_2 is known to be an excellent scavenger (by adsorption of DOC). This is an added advantage.

Simulated treatment set up

The simulated treatment system had hydraulic parameters clearly matching with the operational conditions of the plant. A constant head



(Stumm and Morgan 1996)

Figure 1.3.6. pH dependent speciation diagram of manganese.

Table 1.3.6. Typical Jar test experiment results

Sl No.	**Alum* alone**	**Alum+ Lime****	**Alum+ $KMnO_4$*****	**Alum+ Lime +$KMnO_4$**
Floc formation	Slow	Fast	Slow	Fast
Floc Type	Weak	Medium	Dense	Dense
Floc settling	Slow	Fast	Fast	Fast
% floc settled in first 10 minutes#	60-70	70-80	75-80	>90
Iron in supernatant	Present	Present	Present	Absent

*Alum: 15 mg/L

**Lime: quantity sufficient to correct the pH to 6.8

***$KMnO_4$ (0.01 N): 0.4 mL/L

maintained by an overflow tank specially fabricated for the purpose controlled the flow velocity. This ensured reasonably constant hydraulic characteristics in the experimental set up. From a calculation of a discharge through the clarifier column the nominal values of detention times were nearly as the same in the plant. The ultimate objective was to obtain desired level of iron removal and clarity at the clarifier overflow. The performance of the clarifier was monitored online to match the signal output from the LDR with turbidity units (NTU). Calibration runs were done with water of previously determined turbidity.

The column studies were performed to study the settling character of flocs under different chemical treatment schemes. Plant operations were simulated for the studies. For this purpose miniature version of dosing mechanism flocculator, and clarifier were fabricated.

A plastic crate of 80L capacity was taken and baffles were provided in it. Baffles were fabricated from stainless steel sheets of the required dimensions. Similar arrangement was done for clarifier also. The schematic diagram of the treatment set up is given in Figure 1.3.7. For settling study vertical column was fabricated. Dimensions and flow rates were simulated as in the actual plant. The schematic diagram of the settling column is given in Figure1.3.8.

The column was fabricated from high density PVC tube with a diameter of 0.2 m id. The length of the column was 3.0m. The bottom of the column was fitted with a three-way cock, which facilitated introduction of feed water and drainage of the column. An opening was given on the side at a

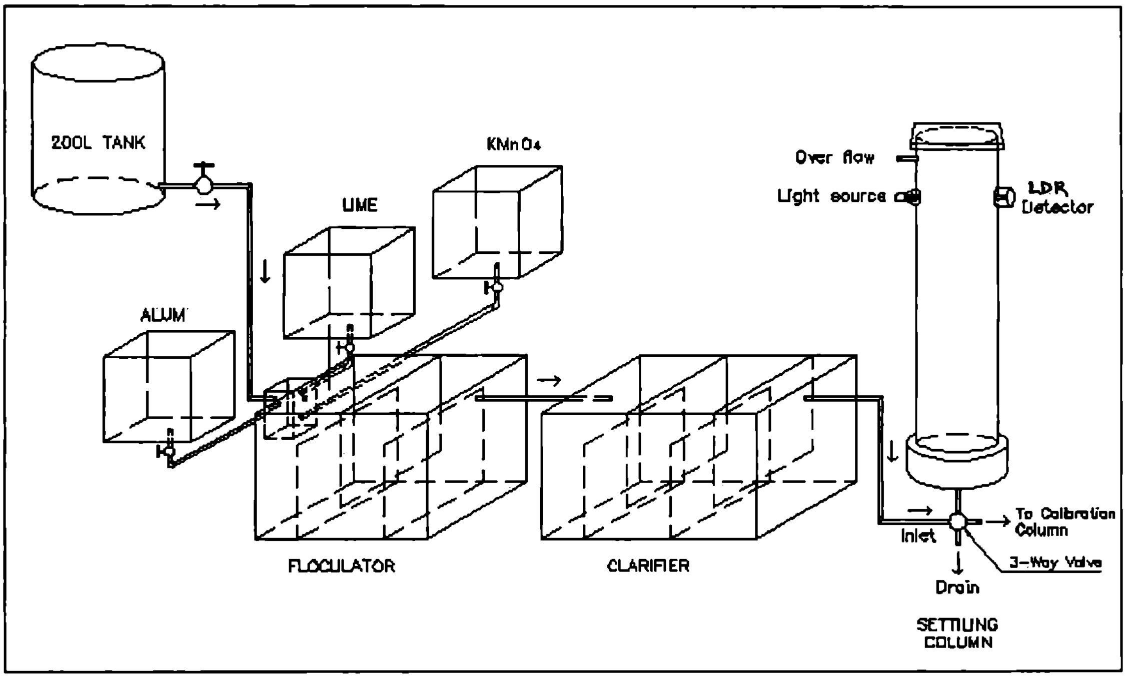


Figure 1.3.7 Schematic diagram of simulated treatment setup.

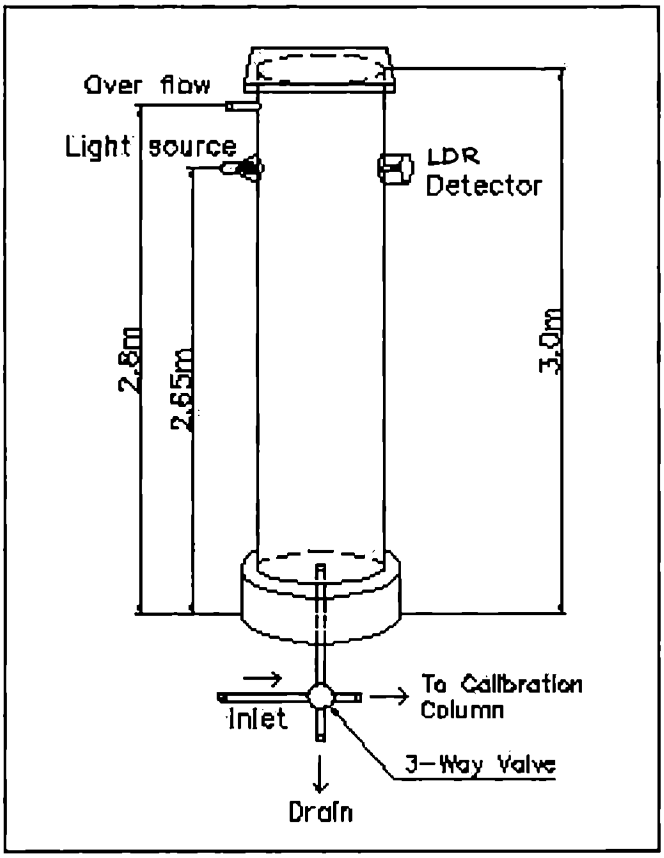


Figure 1.3.8. Schematic diagram of experimental Settling column.

height of 0.2m from the base of the column. This opening acts as an inlet for water. An opening for overflow is provided at a height of 2.80m from the base.

Settling studies were carried out by continuously monitoring the turbidity of effluent water at a particular height of the water column. For this two holes were provided diametrically opposite at a height of 2.60m. To monitor turbidity continuously a light source and an LDR detector with readout were used. These were placed at diametrically opposite points. The light beam passes through water column and falls on the detector. As the particles form and their concentration increases the light attenuation increases. This light attenuation is detected as increase in resistance in the LDR. This resistance is converted millivolts and can be recorded. By plotting millivolts against time the settling pattern is obtained.

1.3.10.**Operation**

The column was filled with intake water from the reservoir. Allowed the water to flow freely through the overflow tube and the intake valve to the column was closed. Detector signal was monitored and recorded at two-minute intervals.

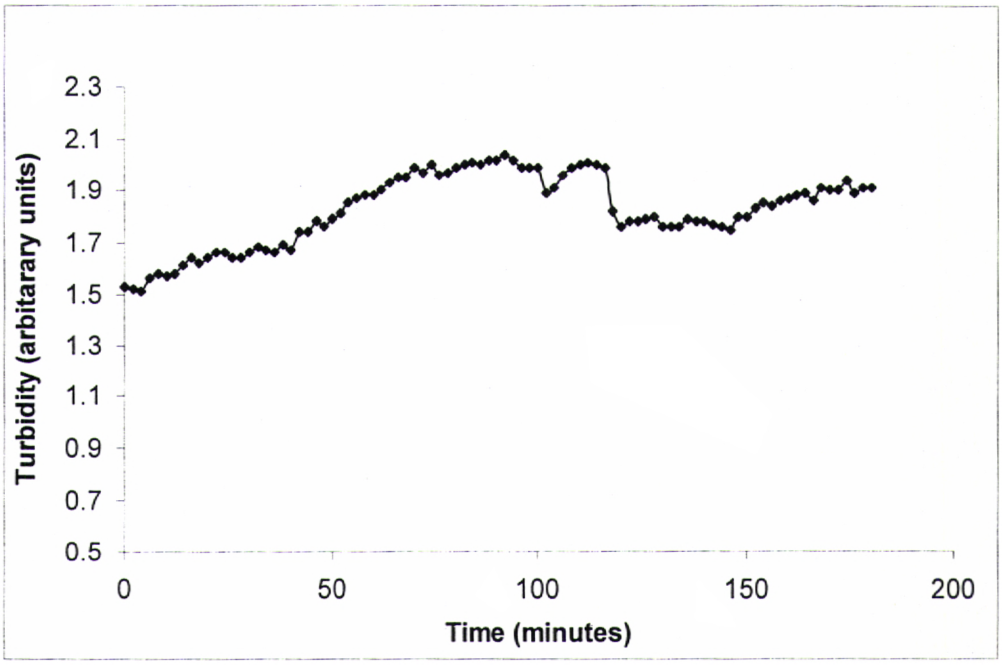
In another set of experiments alum and lime were added to the raw water in the form of slurry and passed through the simulated mixing and flocculation and clarifier basins before entering the settling column. In the settling column the growth and settling of flocs were monitored. The resistance caused by the suspended matter was read in millivolts change.

In the third set of experiments potassium permanganate was added as an auxiliary oxidant along with lime and alum. The water after treatment was directed to the column through the flocculator and clarifier. Settling pattern of the water was studied in the column.

The studies were performed when the raw water showed problem of iron. As can be seen in Figure1.3.9. aerated water had in fact a slow increase in turbidity as time increased. This can be easily accounted by the formation of Fe(III) by dissolved oxygen and its subsequent hydrolysis to $Fe(OH)_3$. At the concentration of iron observed in raw water (3 mg/L) raw water has turbidity below 5 NTU, which is acceptable for distribution. However this turbidity increases gradually, clarifier overflow contain unacceptable level of turbidity as well as iron.

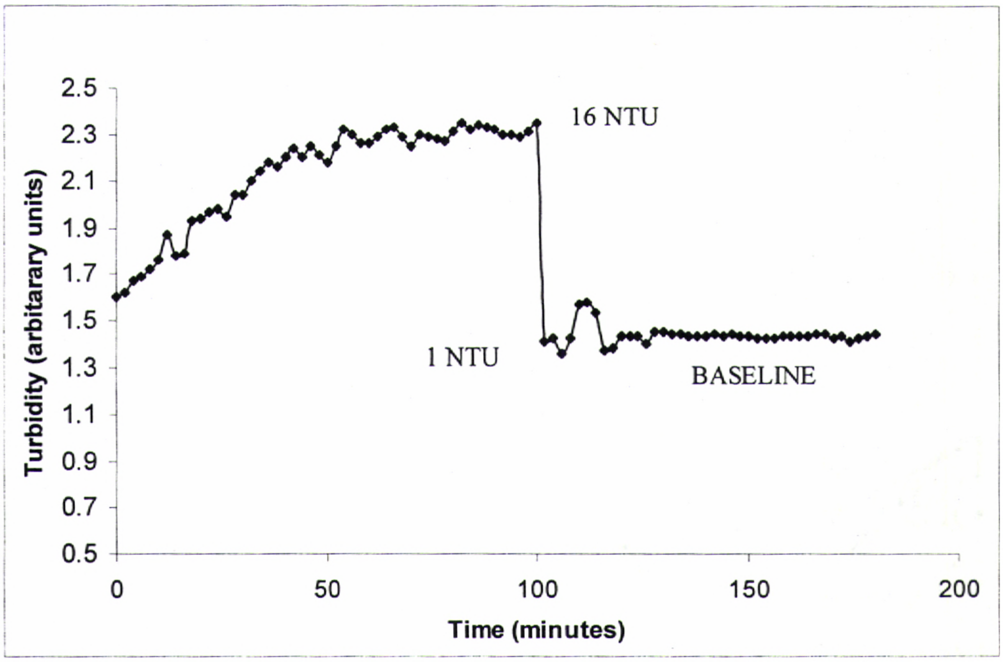
When inline oxidation of iron was amended with addition of alum (15 mg/L) and lime (10mg/L) initially there was an increase in turbidity. However at about 90-120 minutes there was a sudden decrease in turbidity. The settling pattern is shown in Figure.1.3.10. This is probably due to the alum aided separation of $Fe(OH)_3$ turbidity. Otherwise in neutral to alkaline medium $Fe(OH)_3$ particles are of small size and fairly stable. This also does not serve our point since only rapid removal of turbidity solves our problem.

The addition of predetermined chemical equivalent of $KMnO_4$ along with alum and lime gave very rapid decrease in turbidity as is shown in Figure1.3.11. It is known that MnO_4^- oxidation of iron(II) is instantaneous in acid, neutral and alkaline media. In neutral and alkaline media the reaction follows the equation



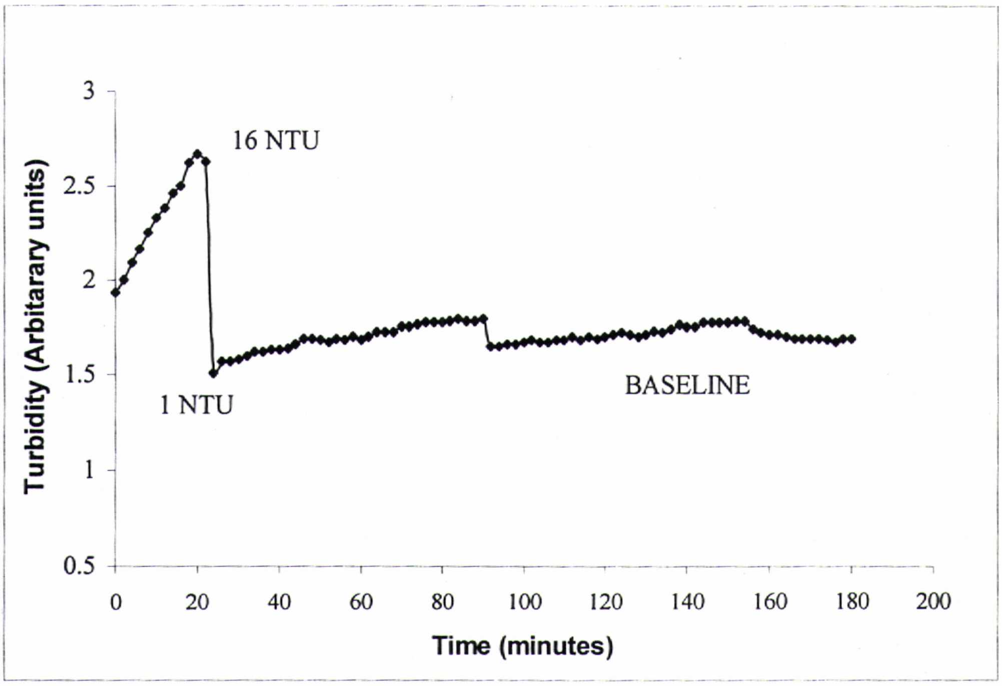
Iron - 3 mg/L

Figure 1.3.9. Typical settling curve with raw water alone.



Iron – 3 mg/L
Alum - 15 mg/L (15.5% Al_2O_3)
Lime - quantity sufficient to correct pH to 6.8
Baseline of the electronic signal not compensated.

Figure 1.3.10. Typical settling curve with alum and lime



Iron - 3 mg/L
Alum - 15 mg/L (15.5% Al_2O_3)
Lime - quantity sufficient to correct pH to 6.8
$KMnO_4$ - 0.4 mg/L (0.01N)
Baseline of the electronic signal not compensated.

Figure 1.3.11. Typical settling curve with alum, lime and permanganate

$$MnO_4^{-} + 3\ Fe^{3+} + 4\ H^{+} \rightarrow MnO_2 + 3\ Fe^{3+} + 2\ H_2O$$

There is a slight addition of alkalinity by permanganate oxidation. Moreover MnO_2 being denser and having a negative charge easily get flocculated by positively charged aluminium hydroxide species.

Removal of inadvertent excess of permanganate is likely to pose a problem since the raw water quality is likely to shift without any indication the optimal dosage fixed one time, either become excess or become inadequate at another point of time even during a shift. Excess permanganate problem is conventionally overcome by incorporating green sand filter.

$$Mn(II)_{(\text{trapped in silicate})} + MnO_4^{2-} \rightarrow 2\ MnO_{2\ (\text{solid trapped.})}$$

This necessitates the modification of the filter media, which is relatively expensive. The suggested method is a split stream treatment. The scheme is shown in Figure.1.3.12. Monitoring the redox potential at the flash mixer outlet and the flocculator outlet can regulate the dosage of permanganate. This scheme requires more of engineering fabrication with automatic control of auxiliary flow.

Hence it is concluded that dispensation of permanganate with alum and lime will be the most cost effective treatment in the existing plant.

Cost analysis of permanganate treatment

For the purpose of calculating the additional cost and accruing additional benefit, the unit of calculation may be one day. The cost will be adding up for the number of days during which the problem occurs, and the intensity of the problem. Resulting capital/consumable/control expenditure will be included in addition to existing facilities.

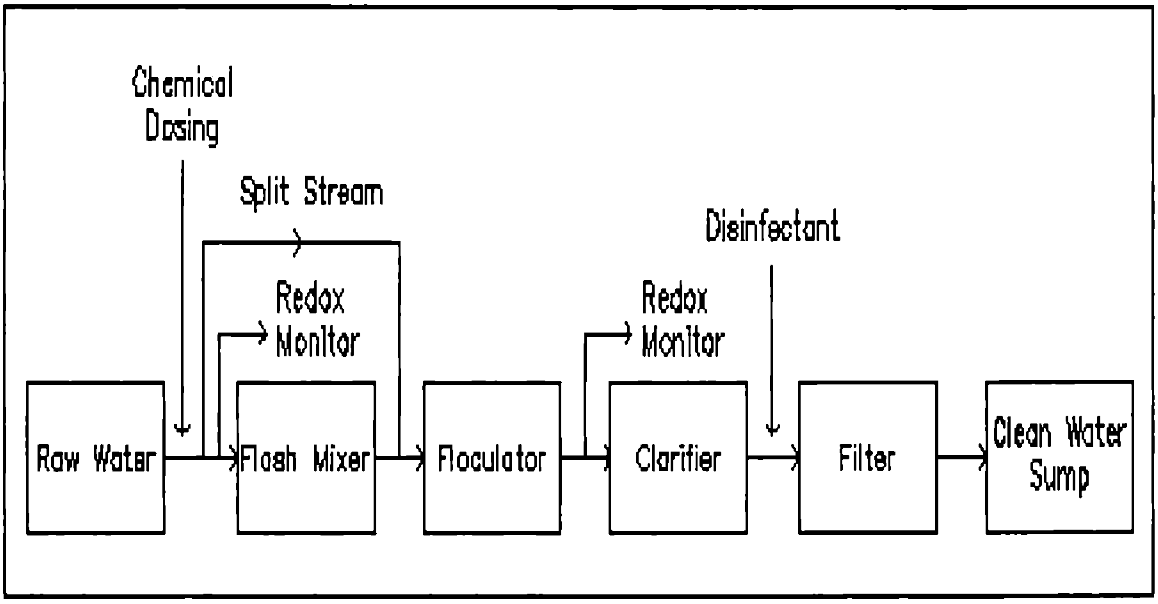


Figure 1.3.12. Split stream scheme for removal of excess $KMnO_4$

Engineering modifications required in the plant

A. Permanganate solution storage tank	
(200 L-ferrocement /brick-masonry with cement plastering)	Rs. 5000/-
Dosing pump for permanganate	Rs. 25,000/-
Eh monitors (2) with feed back control to dosing pump	Rs. 50,000/-
B. Consumables	
Iron test strip/solution	Rs. 1000/year
Maintenance of equipment	Rs. 5,000/year
Permanganate consumption for 50 MLD plant for 20 days at 3.0 mg/L of Fe(II)	84 kg
Cost of permanganate for 20 days	Rs. 210,000/ year
Cost of permanganate for 50 MLD plant	**Rs. 10,500/day**
C. Periodic training of operators	Rs. 10,000/year

Benefit

Water requirement for backwashing during non-problem period	1.2 MLD
Water requirement for backwashing during problem period	2.0 MLD
The loss in out put due to the increasing frequency of backwashing (20%)	10 MLD (Personal communication, KWA)
Total reduction in throughput	10.8 MLD
Cost of loss in throughput per day (at Rs. 7/- per m^3 of finished water)	**Rs.75600/-**

PART II

OXIDATION OF IRON(II) IN NATURAL WATERS

Abstract

This section summarizes the experiments and results obtained on the oxidation of iron (II) in natural raw water. The experiments were done without arbitrarily fixing solution conditions, so that the actual processes taking place during aeration in a water treatment plant could be simulated. This suffers from a limitation that kinetic parameters cannot be correlated with order of reaction. Order determining species like H^+ *and* HCO_3^- *change continuously. The results show that there is a lag in the oxidation at initial phase. Subsequently the rate follows a first order pattern. However results are important in evaluating iron removal processes in an aerated treatment process.*

2.1. **Iron in natural aquatic environment**

Iron is the second most abundant metal after Al and the fourth most abundant element on the earth's crust (Cotton *et.al.* 1999). The primary sources of iron in the hydrosphere are the iron minerals in igneous and metamorphic rocks. The major iron containing minerals include olivine, pyroxene and amphibolites (Deer *et al* 1992). Iron is largely mobilized and redistributed during the chemical weathering of the mineral. Mobilization is chiefly as dissolved Fe(II) under reducing conditions and as particulate Fe(III) oxyhydroxides in oxygenated environments (Langmuir 1997). In sedimentary rocks and soils exposed to atmosphere, iron is found chiefly as dissolved Fe(III) oxyhydroxides. In anaerobic systems, with decreasing Eh, iron occurs as Fe(II) oxyhydroxides, as its carbonate, siderite, and the sulfides. In oxidized surface waters and sediments, dissolved iron is mobile below about pH 3 as Fe^{3+} and its inorganic complexes (Langmuir 1997). Fe(III) is also mobile in many soils, and in surface and ground waters as ferric-organic complexes at pH 5 to 6, and as colloidal ferric oxyhydroxides between pH 3 to 8. Under reducing conditions iron is soluble and mobile as Fe(II) below about pH 7 – 8, when it occurs, usually as uncomplexed Fe^{2+} ion. However, where sulfur is present and conditions are anaerobic to cause sulfate reduction, Fe(II) precipitates almost quantitatively as sulfides (Langmuir 1997).

Iron is routinely found in most natural waters. Iron concentration is high in groundwater than in surface water. The natural concentration of iron in water sources varies widely. Iron concentration in natural waters largely depends on the soil type and mineralogical features of the area. Iron concentration is high in areas where laterite is abundant. In coastal areas and water logged areas iron is immobilized in the sediment due to the anoxic environment. The mobilization of iron depends largely on the existing pH and redox conditions.

Iron is a micronutrient for plant growth. Even though iron does not cause any physiological ill effects in organisms at concentrations observed in aerated natural waters, it affects the aesthetic quality of water. High concentrations of iron in water affect the distribution systems (Faust and Aly 1983). In extreme cases iron bacteria colonize the distribution lines and enhances corrosion of lines (Train 1979; AWWA 1995; McNeil and Edwards 2001). Iron is regulated as a secondary drinking water pollutant (Train 1979;

Faust and Ali 1983; Shulz and Okun 1984; Zuane 1990; BIS 1991; AWWA 1995; Badek et al. 1998). Excess iron in water imparts a metallic taste to it and causes the staining of fixtures and laundered clothes. According to WHO guidelines (WHO 1996) and Bureau of Indian Standards (BIS 10500) the maximum permissible level of iron in drinking water is regulated at 0.3 mg/L. However, in the case of non-availability of alternate sources the maximum permissible level is waived to 1.0 mg/L.

2.2. **Oxidation of iron in natural waters**

Iron occurs naturally in two oxidation states viz, the lower oxidation state, Fe(II) and the higher oxidation state, Fe(III). Both soluble and hydrolyzed iron species are present in natural waters. The transformation of Fe(II) to Fe(III) in water occurs in many geochemical environments, at the oxic/anoxic boundary in marine and freshwater basins, at the oxycline, which exists in sediments, at sediment water interfaces or in soils (Murray 1987). This transformation plays an important role in the mobilization of iron in seasonally anoxic lakes and reservoirs. Geochemical cycling of iron in oceanic and freshwater systems was studied in detail by various investigators. (Davison and Heaney 1978; Murray and Gill 1978; Davison 1979; Aller 1980; Verdouw and Dekkers 1980; Davison *et al.* 1980; Davison 1981; Elderfield *et al.* 1981; Spencer *et al.* 1981). Iron speciation and redox reactions have been discussed for synthetic and natural waters in detail by various investigators (Byrne and Kester 1976a, 1976b; Davison 1979). Since Fe(II) is soluble and hence mobile, Fe(III) is largely confined to the particulate phase, the rate of interconversion between these two plays an important role in the mobilization of iron in natural water bodies. The kinetics of oxidation has been studied in detail by various authors to elucidate the mechanism of oxidation process (Pankow and Morgan 1981; Millero 1989; Millero *et.al.* 1995; Stumm and Morgan 1996; Byrne *et.al.* 2000)

The oxidation of Fe(II) by dioxygen through aeration and separation of $Fe(OH)_{3(s)}$ is the most popular method for the removal of iron from anoxic lentic as well as groundwater sources. However, the method lacks universality since the rate of oxidation of Fe(II) depends on temperature, partial pressure of oxygen, and nature and concentration of anions present in the medium. In addition, it has been shown that photochemical redox cycling of iron occurs in natural waters under various conditions (Emmenegger *et al* 2001). The Fe(II) oxidation using dissolved oxygen has been studied extensively by different investigators (Morgan and Birkner 1966; Schenk and Weber 1968; Ghosh 1974; Sung and Morgan 1980; Davison, *et al.* 1982; Davison and Seed 1983; Roekens and van Grieken 1983; Milero 1989, 1990; Millero *et. a*l 1995; Byrne *et.al.* 2000; King and Farlow 2000; Santa-Casiano *et. al.* 2000). Measurements were also made in artificial media (Tamura et al. 1976; Sung and Morgan 1980; Millero and Izaguirre 1989). The stoichiometric relationship describing the oxidation of Fe(II) to Fe(III) and subsequent hydrolysis of Fe(III) in natural water is

$$2\ Fe^{2+} + 5\ H_2O + 1/2\ O_2 \rightarrow Fe(OH)_3 + 4\ H^+ \qquad (2.1)$$

In the pH range 5-7 the rate of Fe (II) oxidation is first order with respect to the concentration of both iron (II) and oxygen and second order with respect to hydroxide ion concentration over a wide range of temperature, ionic strength and ionic composition (Stumm and Lee 1961; Theis and Singer 1973; Higuchi *et al.* 1978; Millero *et al* 1987). Stumm and Lee proposed the rate law

$$-d[\text{Fe (II)}]/dt = k[\text{Fe (II)}][\text{OH}^-]^2 P_{O2} \qquad (2.2)$$

Millero *et al.* (1987) have shown that this equation is valid in water and seawater from 0^0C to 50^0C and for S = 0 40.where S is total ionic concentration.

Singer and Stumm (1968) concluded that oxidation rate is independent of pH below 3.0 and there is significant departure from the second order dependence of the rate on pH in the range 3.0 to 4.5. At constant pH and ionic strength, various anions were found to change the rates of oxidation of Fe(II). The rates were influenced by anions in the order $HCO_3^- >> Br^- > ClO_4^- > NO_3^- > Cl^- > SO_4^{2-} >> B(OH)_4^-$ (Millero 1989). A number of investigators have observed that alkalinity has an effect on the oxidation rate of Fe(II). Applebeaum, (1908) reported that high alkalinity and high solids generally favoured oxidation. Ghosh (1974) made some observations on the oxidation kinetics of iron (II) in natural ground waters. They observed first order dependence of the rate on pH. Stumm and Lee (1961) reported that the oxidation of Fe(II) was slower in solutions of lower alkalinity. The studies of Stumm Lee (1961) were carried out under designed conditions. They kept the medium buffered with a high concentration of HCO_3^- Hence the role of HCO_3^- as such and pH could not be assessed. Ghosh used natural ground water for his studies, but rate could not be readily evaluated.

Objectives of this study

This study is aimed at

1. Establishing the influence of constituents occurring in natural waters
2. Earlier investigations used buffered media for such studies. Hence the results could not be extrapolated to natural waters. In this study, natural buffering is used and the results could represent the processes taking place in actual treatment.

2.3. Materials

2.3.1. *Ground water*

Ground water samples were collected from boreholes located in Ochanthuruthu village of Vypeen Islands. Our earlier studies have shown that boreholes from these locales yield water of steady character (Peeter and Pillai 2001). The depth of the bores was 4-8 m. Water was collected in clean white polyethylene cans after washing and rinsing with the source water. The sampling was done according to EPA guidelines (EPA 1983). Samples were kept at 4°C in icebox and brought to the laboratory within one hour of sampling.

2.3.2. *Synthetic Water*

Synthetic water sample containing predetermined concentration of constituents was prepared in a way it matches in composition with Peechi reservoir water. Synthetic water was prepared as follows.

Thirty five liters of freshly distilled water was collected. Then nearly saturated sodium bicarbonate solution was prepared and standardized. Predetermined volume of this stock bicarbonate solution was added to distilled water and the alkalinity of the sample was determined by titration with standard hydrochloric acid (0.1N). A final alkalinity of 18-22 mg/L was maintained.

2.3.3. *pH meter*

pH measurements were done using Systronics digital pH meter (model 335). The meter was calibrated before each measurement using standard buffer.

2.3.4. *UV-VIS Spectrophotometer*

Varian UV-VIS dual beam spectrophotometer (Model Carey 50) was used for the spectrophotometric determination of iron.

2.4. **Chemicals.**

All chemicals used were of analytical reagent grade.

2.4.1. *Stock Fe(II) solution*

Accurately weighed $FeSO_4.6H_2O$ sample (100 mg) was dissolved in 100 mL distilled water. To prevent hydrolysis 0.5 mL con. H_2SO_4 was added before making up the solution.

2.4.2. *Ammonium acetate buffer*

Ammonium acetate buffer was prepared by dissolving 250 g ammonium acetate ($NH_4C_2H_3O_2$) in 150 mL distilled water and adding 750 mL glacial acetic acid to the ammonium acetate solution.

2.4.3. *1,10 phenanthroline solution*

1,10 phenanthroline reagent solution was prepared by dissolving 100 mg 1,10 - phenanthroline monohydrate, $C_{12}H_8N_2.H_2O$, in 100 mL distilled water and heating to 80^0C. The solution was cooled and stored in amber coloured glass bottles.

2.5. Experimental

Oxidation of Fe(II) in natural waters is influenced by other constituents present in water. To study the oxidation characteristics of iron (II) under different natural conditions, experiments were carried out using iron containing groundwater with low alkalinity, and synthetic water.

Reservoir water containing problematic concentration of iron occurs sporadically during the non-monsoon periods. The concentration of iron varies within hours. Hence synthetic water samples with nearly the same characteristics, as problematic reservoir water was prepared. The reservoir water is soft water type with alkalinity (as $CaCO_3$) in the range 12 – 40 mg/L. The typical values for various water quality parameters are already given in Table 1.3.2. It may be noted that the nature and concentration of NOM are irreproducible, and hence no attempt was made.

Procedure for the evaluation of oxidation pattern

Fe(II) oxidation studies were carried out under natural buffering conditions. Hence no pH correction was applied. Initial pH of the water was noted. The stock solution was kept in the thermostat for two hours. Desired volume of sample (2L) was transferred into a reaction vessel, which was a clean dry round bottom flask of 5L capacity, kept in the thermostat. Provisions were made for the addition of solution, withdrawal of aliquots, measurement of pH and aeration. Iron (II) in the form of $FeSO_4$ solution was added to the water (10 mg/L). Addition of $FeSO_4$ solution reduces alkalinity. Hence resultant alkalinity was measured in duplicate experiments. Immediately after addition of Fe(II) aeration was switched on. For aeration pure air was bubbled through the water, using fritted gas aerator at constant rate. In order to offset the influence of CO_2 on the pH, dust free air was bubbled through NaOH solution and two cascaded bubblers containing distilled water.

At predetermined intervals 20 mL –aliquots of the medium were withdrawn and added to 0.2 mL 1:2 HCl. Then 3 mL acetate buffer was added followed by 25 mL of 1, 10 - phenanthroline solution and shaken well. The coloured solution was kept in the dark. Then absorbance at 510 nm was measured after 5 minutes but not later than 10 minutes as instructed by Standard Methods (APHA 1998). Absorbance measurement was made at 510 nm. The measurements using aliquots were continued till steady absorbance was attained indicating completion of the reaction. Final pH of the medium was also measured.

In the case of ground water sample no further addition of Fe(II) was done. Immediately after reaching the laboratory 2 L of the sample was transferred to the reaction vessel. Then aeration was started and measurements were taken as in the case of synthetic water sample. Sample pre-treatments like filtration were not done, since our objective was to carry out the study under conditions of actual treatment.

2.6. **Results and Discussion**

The oxidation of iron (II) by dioxygen has been studied by various authors ((Morgan and Birkner 1966; Schenk and Weber 1968; Ghosh 1974; Sung and Morgan 1980; Davison *et al.* 1982; Davison and Seed 1983; Roekens and van Grieken 1983; Milero 1989, 1990; Millero *et. al* 1995; Byrne *et.al.* 2000; King and Farlow 2000). The classical study of Stumm and Lee

(1961) proposed a rate law in which oxidation rate is first order with respect to the concentration of both iron (II) and oxygen and second order with respect to hydroxide ion concentration over a wide range of temperature, ionic strength and ionic composition. The salient feature of this experiment was that it was carried out in a bicarbonate buffered medium, in which H^+ concentration practically does not change and bicarbonate concentration was high relative to Fe(II). Fe(II) forms a complex with bicarbonate (Cotton *et. al* 1999). However, the structure of this complex has not been elucidated.

The oxidation of Fe(II) with molecular oxygen is

$$4\,Fe^{2+} + O_2 + 4\,H^+ \rightarrow 4\,Fe^{3+} + 2\,H_2O \qquad (2.3)$$

This reaction consumes H^+ and in a weakly buffered medium a slight rise in pH is expected.

The medium used in the present study had alkalinity 0.44± 0.04 meq/L. At an iron concentration of 0.09 meq/L (5mg/L) for the complete oxidation of Fe (II) H^+ consumed according to this equation is 0.09 meq/L. Hence the change in alkalinity is significant. However when the oxidation starts there is an initial fall in pH, and this is reproducible. Subsequently pH rises to around 8.3. The medium had an initial pH of 6.5 which is the lower limit recommended for raw water for drinking water treatment.

In a buffered medium of the type used in this study the bicarbonate complex of iron(II) and the hydrolysis of Fe(III) formed play a complex role.

$$\text{Fe(II)-bicarbonate complex} \rightleftharpoons Fe^{2+} + HCO_3^- \qquad (2.4)$$

$$4\,Fe^{2+} + O_2 + 4\,H^+ \rightarrow 4\,Fe^{3+} + 2\,H_2O \qquad (2.5)$$

$$Fe^{3+} + 3\,H_2O \rightleftharpoons Fe(OH)_{3(solid)} + 3\,H^+ \qquad (2.6)$$

These three steps take place sequentially.

The time course of Fe(II) concentration when plotted shows a pattern shown as in Figure 2.1.

At low bicarbonate concentration the dissociation of Fe(II)-bicarbonate complex is likely to be complete. In that case there is no influence for the dissociation of bicarbonate complex on the oxidation Fe(II). Fe(II) oxidation kinetics approaches first order with respect to Fe(II). The initial lag observed in the time course of Fe(II) oxidation in at high bicarbonate concentrations as shown in Figure 2.2. The lag can be explained as due to the slow dissociation of Fe(II)- bicarbonate complex.

It is known that in aqueous medium iron forms two species $FeCO_3^0$ and $FeHCO_3^+$(Langmuir 1997). $FeCO_3^0$ has a narrow stability range and its log β value is + 5.1, where β is formation constant. If we consider $FeHCO_3^+$, its log β is +2.0, which has a larger stability range (Langmuir 1997). So under the condition of study the species that exists in solution is $FeHCO_3^+$ which decomposes according to the equation given below. This leads to initial depression in pH.

$$FeHCO_3^+ \rightarrow FeCO_3 + H^+ \qquad (2.7)$$

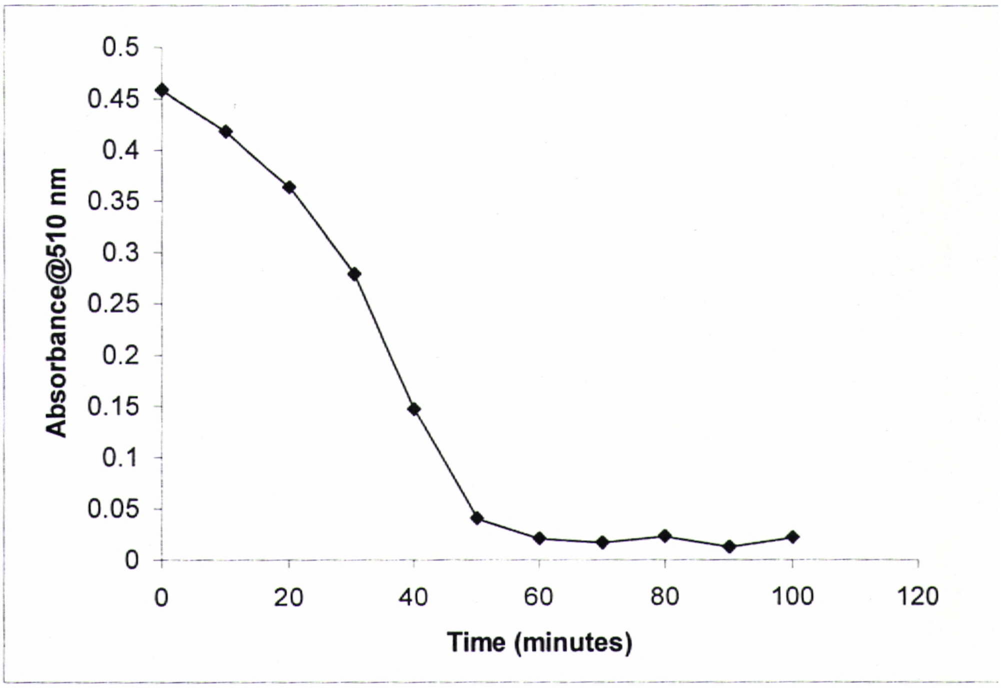
$$Fe(HCO_3)_2 \rightarrow FeCO_3 + CO_2 + 2\,H_2O$$

The dissociation of $Fe(HCO_3)_2$, oxidation of Fe(II) and hydrolysis of Fe(III) are given by the following equations.

$$Fe(HCO_3)_2 \rightleftharpoons Fe^{2+} + 2HCO_3^- \qquad (2.8)$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (2.9)$$

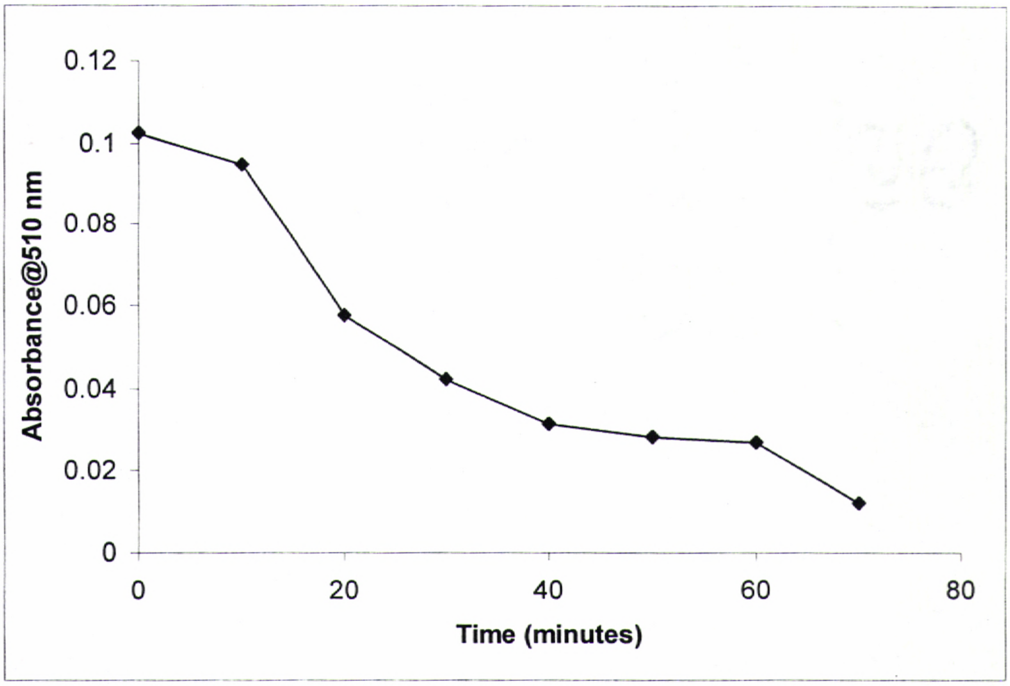
$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ \qquad (2.10)$$



Origin: bore hole, Vypeen

Fe(II) 8.2 mg/L	Initial pH 6.4	Final pH 8.3
Alkalinity 14 mg/L as $CaCO_3$	Total hardness 8 mg/L as $CaCO_3$	

Figure 2.1. Air oxidation pattern of natural water



Fe(II) 10 mg/L	Initial pH 6.5	Final pH 8.3
Alkalinity	22 mg/L as $CaCO_3$	
Total hardness	14 mg/L as $CaCO_3$	

Figure 2.2. Air oxidation pattern of synthetic water

Hence at intermediate times both processes (2.8) and (2.9) contribute to the velocity of reaction. When the dissociation reaction is assumed to be the rate-determining step occurring initially, the rate of dissociation can be calculated. Since it is obtained from analyzing expanded initial part of the graph as recommended by Ekenfelder, the results are only empirical in character. Moreover, as the reaction proceeds further $Fe(OH)_{3(s)}$ in the suspended form renders the medium heterogeneous, and application of kinetic concepts developed for homogeneous medium become less applicable.

Bicarbonate species liberated by the dissociation of ferrous bicarbonate further dissociates according to the scheme

$$2\ HCO_3^- \rightarrow CO_3^{2-} + CO_2 + H_2O \qquad (2.11)$$

This dissociation can account for the rise in pH during oxidation of iron (II) in natural waters containing bicarbonate.

Natural waters especially from sources containing organic carbon have significant concentration of natural organic matter (NOM). Fulvic acid and humic acid are the major constituents. These have ligand functional groups like OH^- and COO^-. The molecular species of varying molecular mass in the range 500 to 2000 daltons are found in fulvic acids and 2000 to 10^6 daltons are found in humic acids (Drever 1997). These form stronger complexes with Fe (II) than that by bicarbonate with iron (II). Their dissociation and subsequent oxidation may have different pattern. Hence the oxidation pattern of Fe(II) by O_2 in natural water containing high concentrations of NOM may have a different pattern.

However, if it is simply the NOM complex of iron that is getting oxidized, pH is not likely to rise to a significant level during oxidation process.

$$3\ (\text{Fe-COOR})_2 \rightleftharpoons \text{Fe}^{2+} + 6\ \text{RCOO}^- \qquad (2.12)$$

$$3\ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 3\ e^- \qquad (2.13)$$

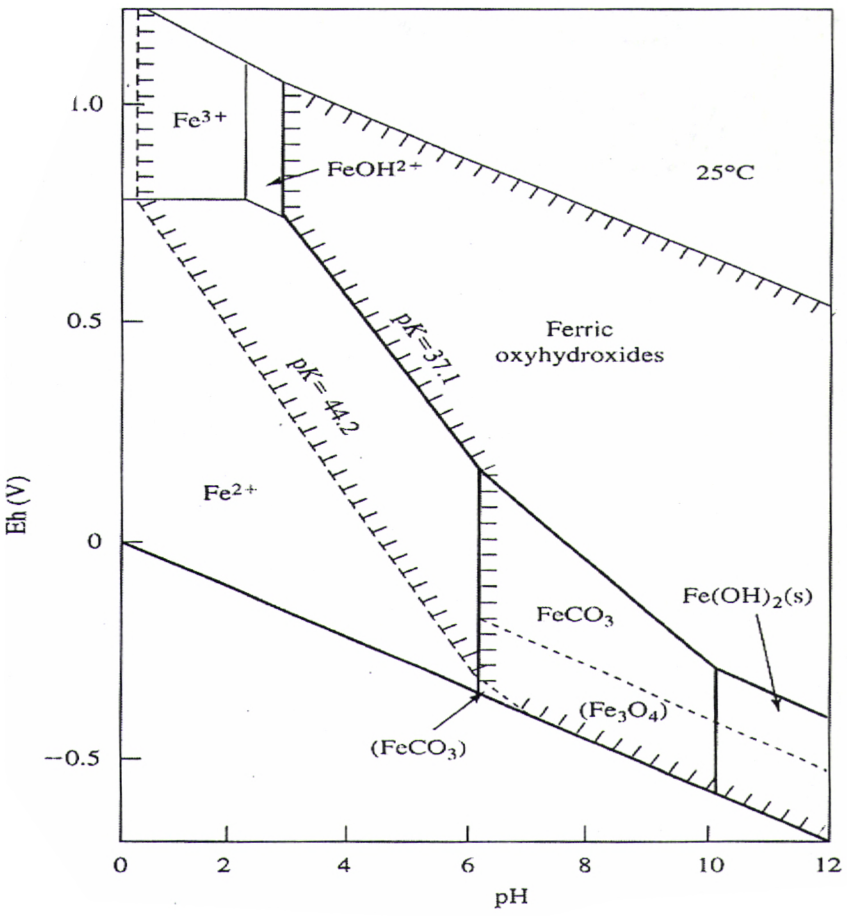
$$3\ \text{Fe}^{3+} + 6\ \text{RCOO}^- \rightleftharpoons 3\ \text{Fe}(\text{COOR})_2^+ \qquad (2.14)$$

$RCOO^-/RCOOH$ species would act as a buffer. But the mechanism given cannot explain the increase in pH observed in the present case. So if at all the complex is there, it is present only in small proportions.

Ferrous carbonate is transient under the prevailing pH conditions, as can be seen from the species diagram of iron given in Figure 2.3. Fe(II) is oxidized by molecular oxygen with subsequent hydrolysis. But in the absence of buffering i.e. at low bicarbonate concentration $FeHCO_3^+$ species may undergo transformation, which approximately follows zero order kinetics.

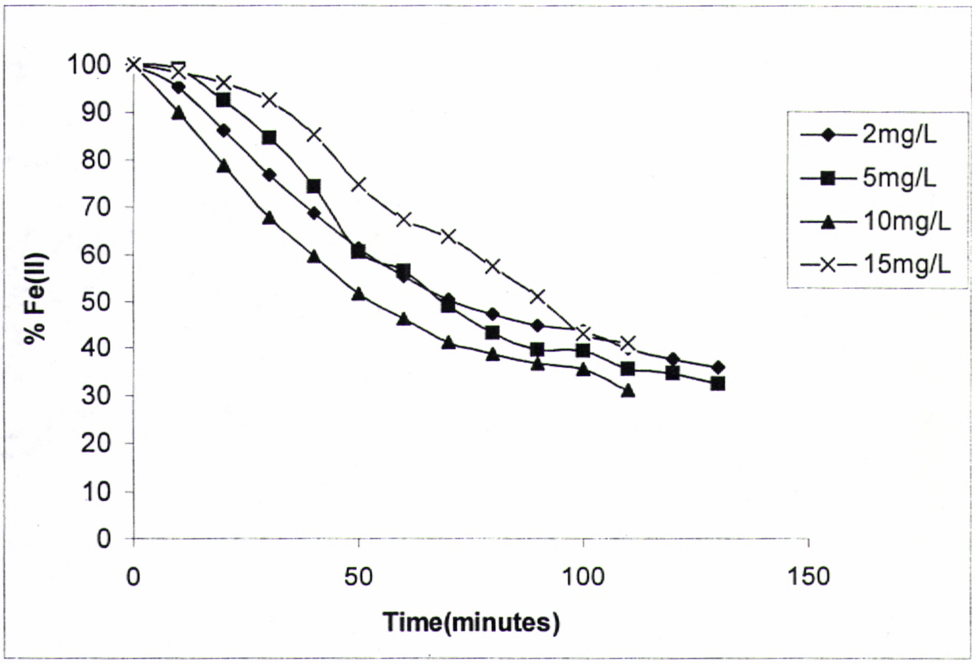
$$d\text{Fe(II)}/\,dt = k\ \text{Fe(II)}^0 \qquad (2.14)$$

Low concentrations of chloride, sulphate and nitrate does not change the nature of the concentration – time profile during oxidation of Fe(II) with dioxygen. Typical plots are given in Figures 2.4 to 2.6. Lack of agreement for the kinetic parameter may be due to the heterogeneity of the reaction. The suspended solids formed during oxidation viz., ferric hydroxide introduce this heterogeneity. Moreover it is known that light can catalyze the oxidation of iron (II) (Emmenegger 2001). Light was not excluded in our experiments.



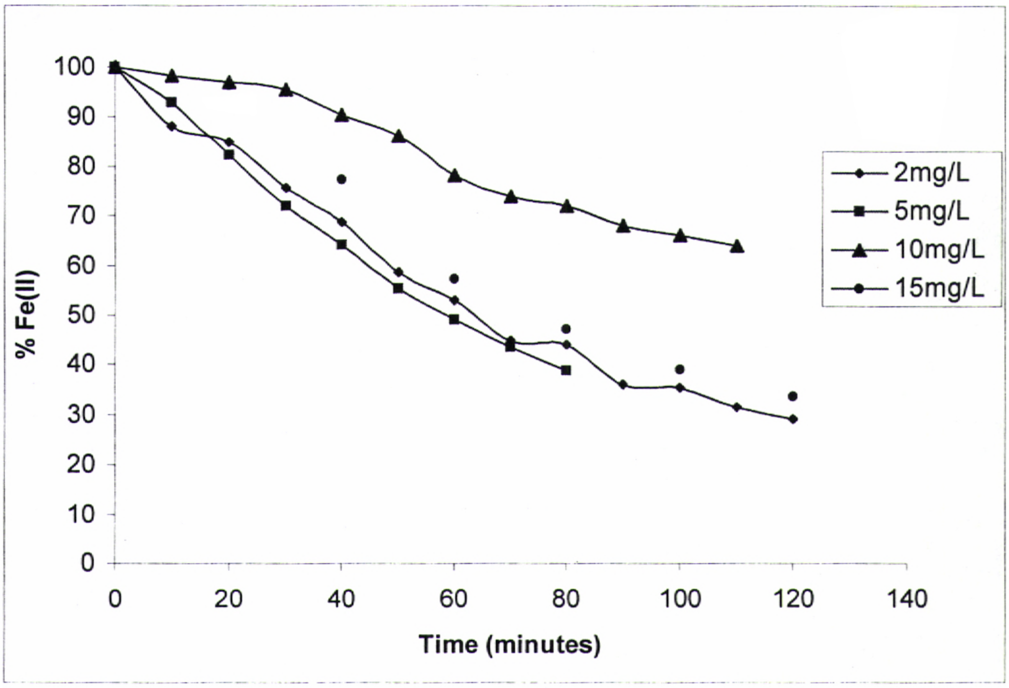
(Langmuir 1997)

Figure 2.3. Eh – pH dependant speciation diagram of iron



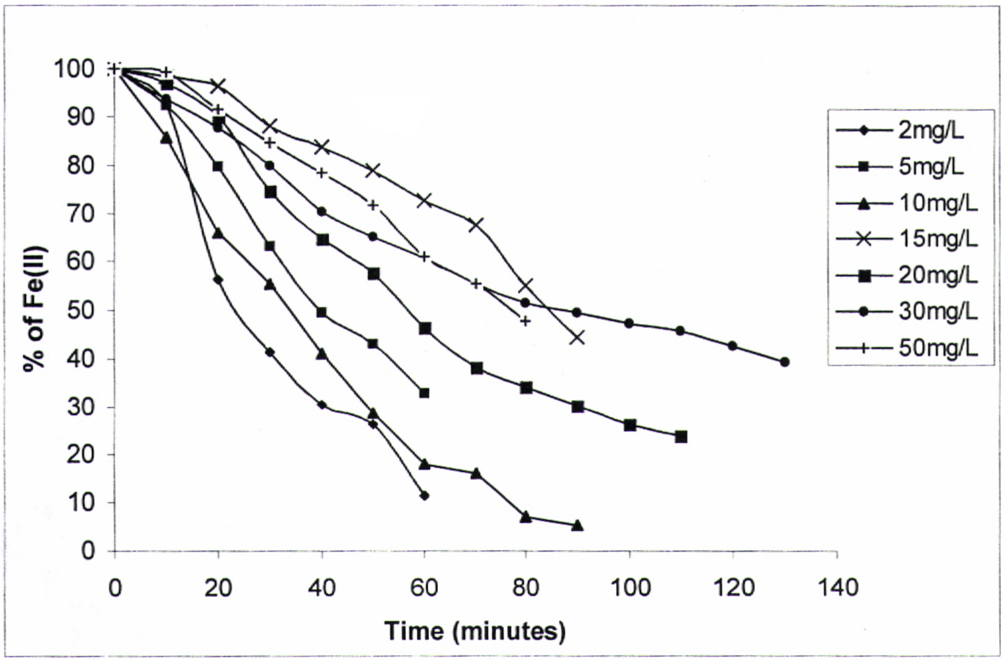
Fe(II) – 5 mg/L

Figure 2.4. Influence of nitrate ion on Fe(II) oxidation



Fe(II): 5mg/L

Figure 2.5. Influence of sulphate ion on Fe(II) oxidation



Fe(II): 5 mg/L

Figure 2.6. Influence of chloride ion on Fe(II) oxidation

The exact evaluation of kinetic parameter is not possible since there is concomitant change in the concentration of H^{+}. However this rate is more appropriate to be considered while designing or evaluating a treatment plant. The behaviour of Fe(II) under similar alkalinity conditions in a synthetic water sample follows more or less the same pattern. There can be concentration dependent variations. Since there is no change in pattern in natural water with moderately high DOC ($SUVA_{254}$= 0.156) the presence of NOM does not modify the oxidation kinetics to a significant extent.

Part III

CONVERSION OF Cr (III) TO Cr(VI) BY DIOXYGEN

Abstract

Presence of "occluded chromate" is a problem encountered with iron-chromium mixed oxide catalyst. In an effort to avoid this undesirable constituent the mechanism of its formation and occlusion was investigated. Chromium(III) hydroxide in alkaline medium does not adsorb Cr(VI). Adsorption pattern of Cr(VI) on freshly precipitated $Fe(OH)_3$ *is irregular. When a mixture of* $Fe(OH)_3$ *and* $Cr(OH)_3$ *is aerated Cr(VI) is formed. There is an incubation period following which a gradual increase in Cr(VI) occurs. It is shown that carefully dried mixed oxide catalyst does not contain Cr(VI). However, if Cr(VI) is provided in solution it is adsorbed on the mixed oxide with regular adsorption pattern.*

For the first time we have given conclusive proof for the oxidation of Cr(III) with molecular oxygen in alkaline medium. A plausible theoretical explanation is given.

3.1. Introduction

On the earth's crust chromium is the 21st most abundant element (Barnhart 1997). Chromium is one of the most widely used metals. It is used as *in situ* formed thin deposits for decorative finish and protection of metals from corrosion and wear, as insoluble Cr(VI) salts in pigments and corrosion inhibitors. Cr(III) oxide is extensively used in pigments because, its stability helps protect materials from degradation by the environment (Zachara et. al.

1987; Barnhart 1997). Chromium finds wide application in metallurgical processes. Chromium imparts the luster and makes steel stainless. It is the major constituent of mixed catalysts, which find wide use in petroleum cracking. On a world-wide basis, about 80% of the mined chromium goes into metallurgical applications. About 15% is used in refractory applications.

Chromium can exist in oxidation states of –2, +4, +5 and +6. However only the trivalent and hexavalent forms of chromium are of biological significance (Schroeder and Lee 1975; Bartlett and James 1998). Trivalent chromium is an essential element in animals playing a role in glucose and lipid metabolism (Casarett and Doull 1980). Deficiency of trivalent chromium results in glucose intolerance, inability to use glucose and other metabolic disorders (Mertz 1974; NAS 1980). Other forms will tend to be converted to the trivalent oxide when in contact with the natural environment. Unlike Cr (III), which behaves as a hard Lewis acid, and forms insoluble $Cr(OH)_3$, Cr(VI) is a Lewis base and is present in aqueous solution as anion. It has very little affinity for soil constituents and hence easily percolates through soil when disposed, thus contaminating groundwater.

Redox reactions affect the aqueous concentrations of chromium. Oxidation of Cr(III) to Cr(VI) by Mn oxides is thermodynamically possible in soil and aquatic systems. Under favourable conditions, reduction of Cr(VI) to Cr(III) by organic matter and Fe(II) derived from iron containing minerals will occur, which drastically decreases the toxicity and mobility of Cr(VI). Under acidic conditions, Cr(VI) can be reduced to Cr(III) by activated carbon, Fe(II) (Eary & Ray 1991) and organic matter. Chromate reduction by ferrous ions is spontaneous. Eary and Rai (1991) have reported that Cr(VI) can be readily reduced to Cr(III) by Fe(II) ions derived from Fe(II) containing minerals such as hematite and biotite in acid media. They have also demonstrated that the rate of Cr(VI) reduction by Fe(II) derived from hematite and biotite increases with reducing pH values. Bartlett and James (1979) discovered that certain forms of Cr(III) may be oxidized to Cr(VI) in soils, and that Cr(VI) may be reduced to Cr(III) in the same soil. This opposing solubility and reaction characteristic of Cr(III) and Cr(VI) and the potential for Cr(III) oxidation in soils represent a unique challenge for the establishment of protective, health based clean up standards for chromium contaminated soils (Proctor *et al* 1997).

Hexavalent chromium is a Class A human carcinogen by inhalation and is acutely toxic or irritating to living cells (Nriagu and Nieboer 1988; Katz 1993; Proctor *et. al.* 1997). Cr(VI) is of great concern due to its potential for groundwater contamination due its high mobility in the aquatic environment (Pagilla and Canter 1999).The regulatory maximum limit for Cr(VI) in drinking water is 0.01 mg/L. In contrast, Cr(III) is non toxic, essential for human health, and found predominantly in insoluble forms in the environment. Trivalent chromium is naturally occurring and environmentally pervasive element that has low acute and chronic toxicity and has been recognized as an essential micronutrient for many years (Mertz 1969). Hexavalent chromium rarely occurs naturally, and is acutely toxic at high doses, and is recognized as a human respiratory carcinogen (USEPA 1984; IARC 1990; ATSDR 1994). Chromate is also teratogenic causing birth defects to mammals including humans (Keith and Tilliard 1979; Pettrilli and Miller 1977). Cr(VI) has been shown to be a skin irritant and to induce allergic contact dermatitis (Adams 1990). This may occur primarily from occupational exposures (Paustenbach *et al.* 1992; Nethercott *et al.* 1994). Since the different valence states have different toxicological properties environmental action levels are set separately. Cr(III) and Cr(VI) have different fate and transport characteristics. The leachability of Cr(VI) is enhanced under alkaline conditions where as the leachability of Cr(III) is enhanced under acidic conditions.

Due to its toxicity Cr(VI) is classified as a priority pollutant and its conversion into non toxic Cr(III) form is mandatory before its disposal. The anionic Cr(VI) species is readily reduced to cationic Cr(III) species by organic matter and inorganic reducing agents in soil. Both soil organic acids and inorganic species such as Fe(II)/Fe(III) influence the extent and rate of Cr(VI) reduction to Cr(III) (Eary and Rai 1991; Wittbrodt and Palmer 1996). The cationic forms of Cr(III) form stable complexes with negatively charged inorganic or organic particles in soils and are retained in soil by adsorption.

Chromium is widely used in petrochemical processes as a catalyst. Another industry, which uses chromium in large quantities, is tanning industry. In all these industries chromium-containing wastes are a serious pollution problem. Speciation and associated solubility of metal species in wastes, which contain metals, determine the mobility of metals in the soil or water environment. The pH of the medium acts as a master variable in the speciation of chromium in the environment.

Hexavalent chromium is found in wastewater from various industries. The treatment of these waters to get rid of Cr(VI) is mandatory (KSPCB 1997). The permissible limit of chromium in industrial discharge is 0.1 mg/L (KSPCB 1997). Existing methods of Cr(VI) removal include adsorption (Bailey *et al* 1992), floatation (Lin and Huang 1990), and reduction/precipitation (Patterson *et al* 1994). Of these the most commonly used method is the reduction /precipitation method. Hexavalent chromium is reduced by low cost reducing agents like Fe(II) or sulphite. Raising the pH by alkali treatment precipitates insoluble hydroxide. The hydroxide containing sludge is dewatered and disposed as landfill. In order to prevent leaching of metal from the sludge liners are provided.

In United States alone the annual use of chromium amounts to 110,000 tonnes of sodium dichromate equivalent. Sector wise uses of chromium for various industrial purposes are as follows. Leather tanning accounting for 40%. Metal finishing (17%), pigments (15%), wood preservation (15%), refractory compounds (3%) and other uses (10%). In chromium consuming industries chromium is used extensively for the manufacture of various catalyst mixtures. In the manufacture of iron/chromium mixed oxide catalyst presence of Cr(VI) is observed in the fresh catalyst and spent catalyst (solid waste).

In the manufacturing process of mixed iron-chromium oxide catalyst Fe(II) is used as reductant as well as source for iron. Scrap iron is dissolved in sulphuric acid and the resulting ferrous sulphate is used in catalyst manufacture. Solid sodium dichromate is dumped into the reaction vessel and stirred. Ferrous sulphate reduces the Cr(VI) to Cr(III). Then caustic soda solution is added to the reaction mixture. Mixed hydroxide is generated. This mixed hydroxide is roasted at around 500^0C. The hydroxides are converted to respective oxides. The finished catalyst contains traces of Cr(VI), which is "occluded". Presence of Cr(VI) in the sludge makes it hazardous and treatment of the waste is mandatory before disposal.

Presence of Cr(VI) in the catalyst reduces the efficiency of the catalyst. Moreover, leaching of Cr(VI) from the catalyst cause environmental hazard. Sud Chem Industries, Edayar, referred this problem to us. The task assigned was to identify the origin of the problem and to suggest remedial measures. We tried to ascertain the origin of the problem by answering the following questions.

1. What is the role of individual oxides and the mixed oxide in the adsorption of Cr(VI)?
2. Whether residual Cr (VI) from the manufacturing process is occluded in the catalyst by co-precipitation?

Adsorption of anions by hydrous oxides and silicates has been a topic of interest among soil scientists, chemists and water treatment professionals (Schwertmann and Cornell 1991). Recent investigations have focused on identification of anionic pollutants and an evaluation of their interactions with oxide surfaces. (Davis and Leckie 1980; Benjamin and Leckie 1981; Zachara et. al. 1987).

As part of our studies on the efficiency of iron hydroxide/oxyhydroxide as an adsorbent for the removal of heavy metal anions from wastewater we studied the adsorption of CrO_4^{2-} on iron oxide, iron hydroxide/oxyhydroxide. To find out the effect of aging of the adsorbent on the characteristics, experiments were conducted using freshly precipitated (*in situ.* generated) as well as aged precipitates as adsorbents.

Iron compounds are widely used as coagulants in water treatment plants. Iron oxyhydroxides are known adsorbents for heavy metals and are effective in the removal of heavy metals (Benjamin and Leckie 1981; Zachara et. al. 1987). Mineral phases with proton specific surface sites, particularly those with high points of zero charge (e.g., iron and aluminium oxides) effectively adsorb CrO_4^{2-} at pH 3 – 7. It may be noted that this argument cannot be extended to low pH range since $Fe(OH)_3$ and $Al(OH)_3$ are amphoteric and soluble. Amorphous iron oxide ($Fe_2O_3.H_2O$ or ferrihydrite) has particularly high capacity for Cr(VI).

3.2. **Materials and Methods**

The adsorption of heavy metal anions on ferric hydroxide/ oxyhydroxides were done using specially designed adsorption devices. The experimental set up for adsorption studies consisted of a 50 mL Corning glass impinger tubes placed in a thermostat (± 0.5^0C). Impinger tubes were provided with inlets for bubbling air. Passing air through the medium at constant rate provided uniform mixing of adsorbate and adsorbent. Mechanical stirring of the mixture will cause accretion of particles. This will affect the particle size and shape, and hence surface area, especially for soft particles. Stirring by air bubbles is ideal because it causes minimum accretion of particles.

In order to avoid the influence of CO_2 on the pH and ionic composition of the reaction mixture, carbon dioxide free air was passed through the reaction mixture. The sequential bubbling of air through NaOH solution and distilled water made it CO_2 and dust free, and saturated with water vapour so that volume of the medium remained constant.

All the chemicals used in the study were of analytical reagent grade unless otherwise mentioned.

Cu(III) sulphate solution

Cr(III) solution was prepared by reducing potassium dichromate solution with sodium metabisulfite solution in dilute sulfuric acid medium. Excess of metabisulfite was oxidised by boiling with HNO_3.

Fe(II) sulphate solution

Iron (II) solution was prepared by dissolving fresh ferrous sulphate in distilled water. The solution was acidified with sulphuric acid.

$Cr(OH)_3$

Chromium (III) hydroxide was prepared by adding sufficient quantity of sodium hydroxide solution (15% w/v) to Cr(III) solution till precipitation was complete (pH > 12).

$Cr_2O_3.Fe_2O_3$.

Mixed Cr (III) – Fe (III) hydroxide was prepared as follows. Measured volume of Cr(VI) (0.4N) solution was acidified with 6 M sulfuric acid. Enough Fe(II) solution was added to keep Fe/Cr ratio at the desired level. The ratios selected were such that Fe(II)/Cr(VI) ratio was >5. This is the usual ratio used in industrial catalysts. The solution was made alkaline with sodium hydroxide solution till precipitation was complete (pH>12).

3.3. Procedure

In adsorption experiments Fe(II) /Cr(VI) solutions were taken in impinger tubes in different ratios. Metal hydroxides were precipitated by adding predetermined quantity of sodium hydroxide solution (pH >12). Air scrubbed with 20% sodium hydroxide was bubbled through distilled water and then fed to the test solutions for desired length of time at uniform rate. After aeration the contents were centrifuged for 10 minutes at 1200 rpm. The centrifugate was analyzed for of Cr (VI) using 1, 5 – Diphenylcarbazide reagent (APHA 2000). The method is specific for Cr(VI) under a wide variety of conditions including moderate concentrations of iron.

Non-interference of iron and chromium salts in the determination of Cr(VI) within the concentration range employed was confirmed by preparing calibration curves with solutes spiked separately and collectively with Fe and Cr solutions. Different adsorbent/adsorbate ratios were used in the experiments. Reliability of determination of Cr(VI) was assured by standard addition method. All the experiments were replicated and reproducibility was established.

3.4. Results and Discussion

The observation that in iron oxide/chromium oxide catalyst is invariably contaminated with "occluded chromate" was subjected to investigation. There are two hypotheses that can be put forth to explain the presence of Cr(VI) in the catalyst.

(1) The medium itself contains Cr(VI) which is incorporated by co-precipitation or post precipitation.

(2) During the handling of the mixture in the alkaline medium and exposing to air, Cr(III) is oxidized to Cr(VI).

To prove the hypotheses false or true the following experiments were done.

(a) Chromium hydroxide was precipitated from chromate free chromium(III) salt.

(b) Adsorption experiments were done to test the possibility of adsorption of Cr(VI) on $Cr(OH)_3$. Freshly precipitated $Cr(OH)_3$ and dried $Cr(OH)_3$ (Cr_2O_3) were used in these experiments.

(c) Adsorption isotherms were studied with freshly precipitated $Fe(OH)_3$ as adsorbent and CrO_4^{2-} as adsorbate. The same was repeated with dried ferric hydroxide $Fe(OH)_3$, (Fe_2O_3) (Schwertmann and Cornell 1991).

(d). A mixture of freshly precipitated $Cr(OH)_3$ and $Fe(OH)_3$ were investigated for the adsorption of Cr(VI).

(e). Dried iron oxide/chromium oxide mixture was investigated for the adsorption isotherm of CrO_4^{2-}

The studies on the adsorption of CrO_4^{2-} on the materials listed above were carried out at low concentrations (50 to 150-mg/L). Metal ions and other species are known to get adsorbed on glass surface. This contributes to large errors in such measurements, especially when measurements are done at low concentrations. Hence it was necessary to statistically evaluate the contribution of such errors.

Cleaning the vessel using warm nitric acid and rinsing with distilled water controlled possibility of determinate errors by adsorption/desorption. Effect of matrix on the measured value was determined by standard addition method.

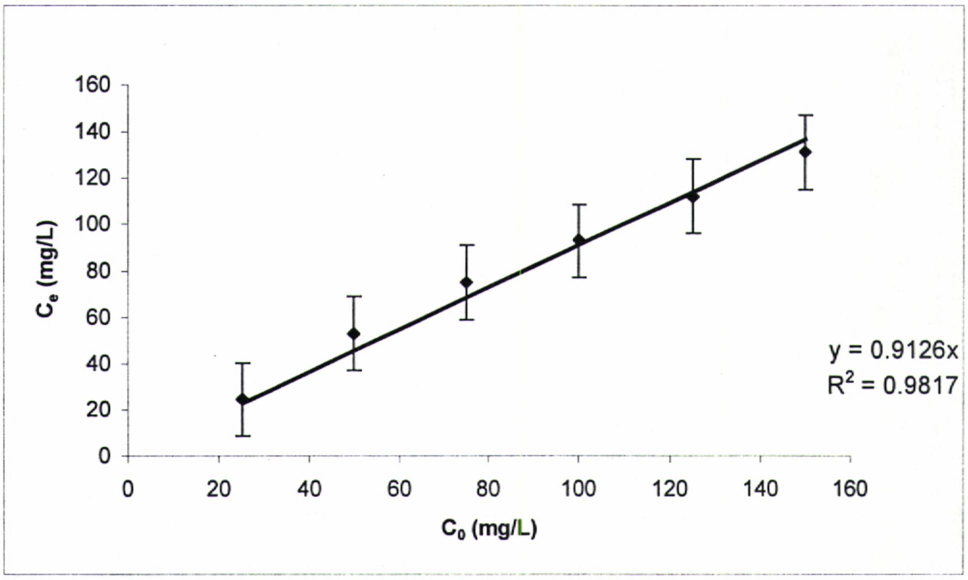
3.4.1. Adsorption of Cr(VI) on $Cr(OH)_3$.

The results of the experiments to verify the adsorption of CrO_4^{2-} on freshly precipitated $Cr(OH)_3$ are given in Figure 3.1. To account for the uncertainity of measurements, results are presented with whiskers indicating standard deviation.

Experiments were replicated for different concentrations of the adsorbates. It conclusively proves that there is no adsorption of CrO_4^{2-} on freshly precipitated $Cr(OH)_3$. This is expected since $Cr(OH)_3$ adsorbs/reacts with OH^- giving CrO_2^-. CrO_2^- and CrO_4^{2-} being Lewis bases, there is little probability of adsorption type of reaction.

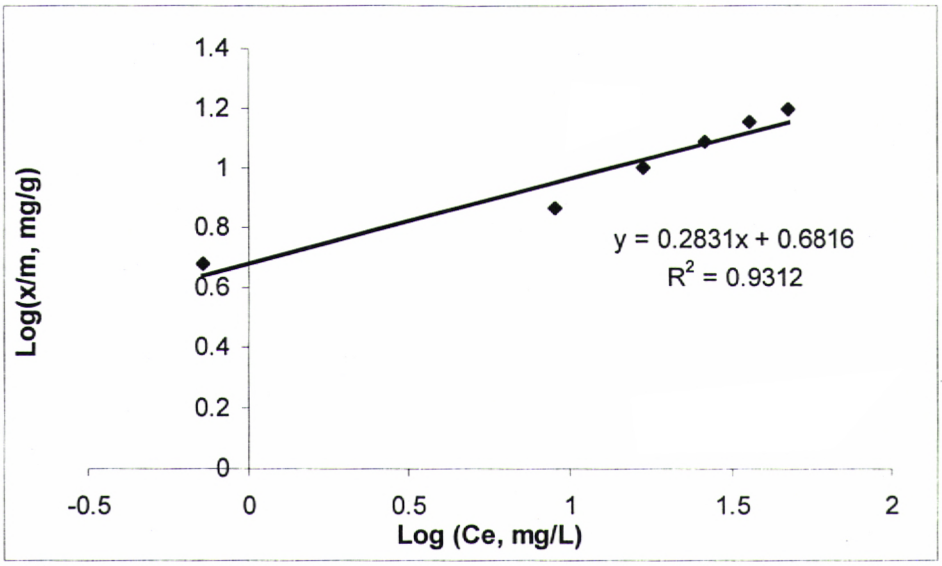
Metal hydroxides are known to undergo slow transformation in standing or on heating (Schwertmann and Cornell 1991). Hence experiments were repeated with samples of metal hydroxides filtered, washed and dried at 105^0C. The adsorption pattern of Cr(VI) on dried chromium (III) hydroxide [Cr_2O_3] is shown in Figure 3.2. The results were fitted to Freundlich and Langmuir isotherms. Typical results show a better fit to Freundlich isotherm. It is clear that there is normal adsorption taking place on dried metal hydroxide (metal oxide).

The difference in isotherm pattern is better understood by the net charge residing on the adsorbent. $Cr(OH)_3$ either contains adsorbed OH^- or is

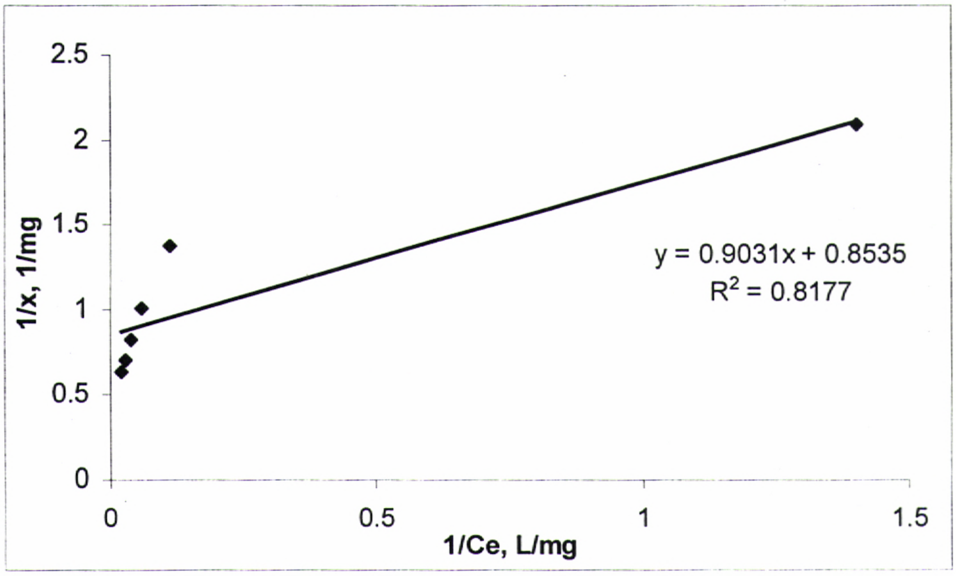


Adsorbent fresh $Cr(OH)_3$)	0.1 g
Temperature	35 ± 0.2 °C
pH	>12
Aeration time	6 hours.

Figure 3.1. Adsorption of Cr(VI) on fresh $Cr(OH)_3$



(a) Freundlich plot for adsorption of Cr(VI) on dried $C_r(OH)_3$



(b) Langmuir plot for adsorption of Cr(VI) on dried $C_r(OH)_3$

Adsorbent (dried $Cr(OH)_3$) - 0.1 g
Temperature - 35 ± 0.2 °C
pH - >12
Aeration time - 6 h.

Figure 3.2. Isotherm plots of Cr(VI) adsorption on dried $Cr(OH)_3$

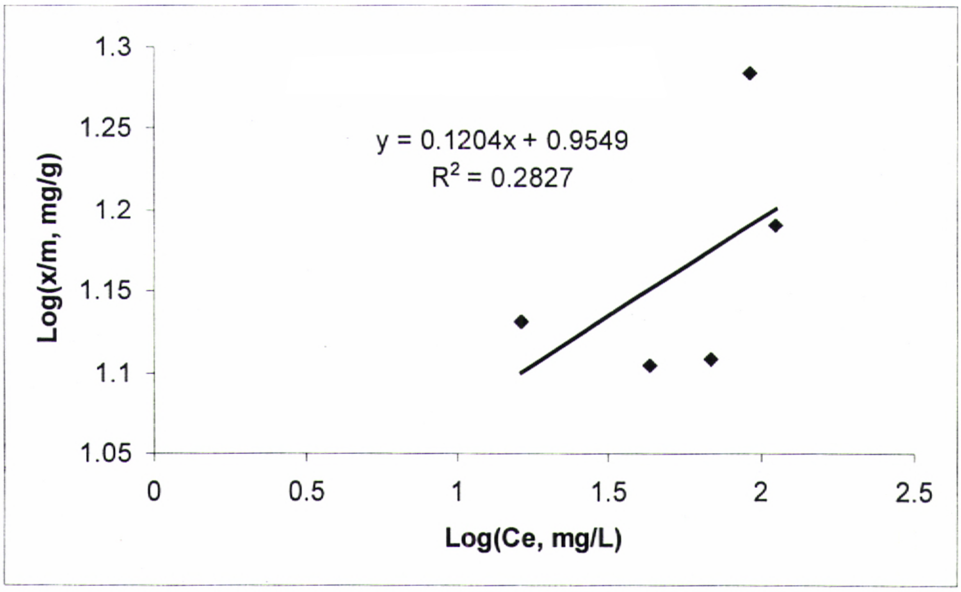
converted to CrO_2^-, whereas dried $Cr(OH)_3$, (Cr_2O_3), has only neutral or acidic sites.

3.4.2. **Adsorption of Cr(VI) on ferric hydroxide**

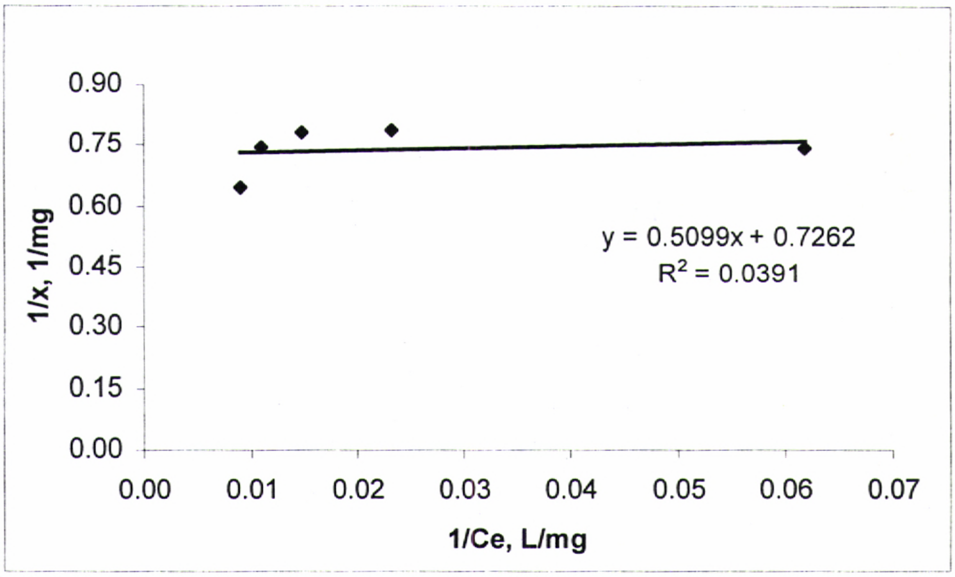
Adsorption experiments were conducted with both *in situ* formed ferric hydroxide and dried ferric hydroxide. Depending on the conditions of drying $Fe(OH)_3$ is converted to different crystalline forms. Accordingly surface area also changes. This happens slowly even when $Fe(OH)_3$ is kept in the medium ((Schwertmann and Cornell 1991). In the case of dried adsorbent, the adsorption follows an irregular pattern and does not fit into any of the isotherm equations as given in Figure 3.3. Replicated experiments also gave similar results.

3.4.3. **Adsorption on freshly precipitated Cr(III)/Fe(III) mixed hydroxide.**

Individual adsorption characteristics of $Fe(OH)_3$ and $Cr(OH)_3$ were discussed above. Individually they show some difference in the freshly precipitated state. The experimental design of adsorption studies of Cr(VI) on mixed oxides in various compositions are shown in Table 3.1. There is an increase in concentration of CrO_4^{2-} in the medium with increasing time and value exceeded the initial concentration. This points to the fact that during aeration there is a slow generation of Cr(VI) either by desorption or by oxidation of Cr(III) to Cr(VI). The results show that Cr(III) undergoes oxidation to Cr(VI) with dioxygen in alkaline medium in presence of $Fe(OH)_3$. A plausible mechanism for the process is given in the following sections.



(a) Freundlich plot for adsorption of Cr(VI) on dried Fe(OH)$_3$



(b) Langmuir plot for adsorption of Cr(VI) on dried Fe(OH)$_3$

Adsorbent (dried Cr(OH)$_3$) - 0.1 g
Temperature - 35 ± 0.2 °C
pH - >12
Aeration time - 6 h.

Figure 3.3. Isotherm plots of Cr(VI) adsorption on dried Fe(OH)$_3$

Table 3.1. Experimental design of adsorption studies of Cr(VI) on mixed oxides

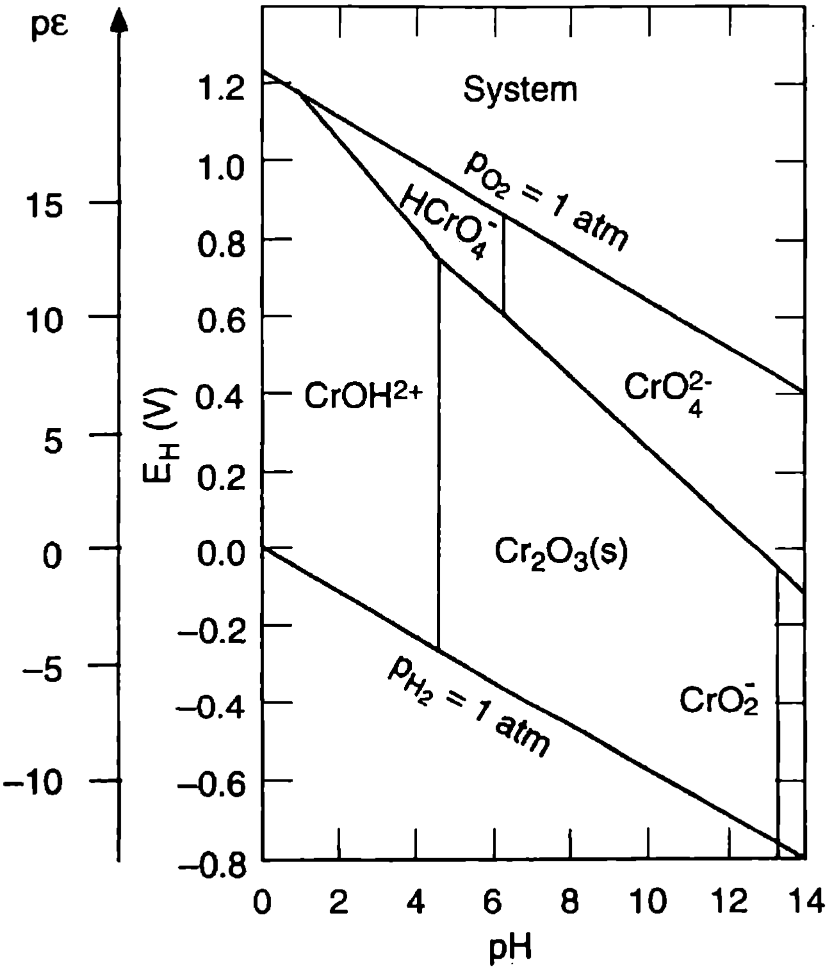
Adsorbent	Adsorbate	Temperature	Stirring	Observed phenomenon	Remarks
Dried $(FeOH)_3$	Cr(VI)		Air	Reproducible Adsorption	
In situ generated $Fe(OH)_3$	Cr(VI)	35 ± 0.5	Air	Non-reproducible adsoprtion	
Ex situ generated $Fe(OH)_3$	Cr(VI)	35 ± 0.5	Air	Appreciable adsorption	
In situ generated $Fe(OH)_3$	Cr(VI)	45 ± 0.5	Air	Appreciable adsorption	
In situ generated modified $Fe(OH)_3$ Cl_2 treated	Cr(VI)	45 ± 0.5	Air	Low adsorption	
In situ generated $Cr(OH)_3$	Cr(VI)	45 ± 0.5	Air	Concentration more than added	
In situ generated mixed hydroxides.	Cr(VI)	35± 0.5	Air	Adsorption	
Dried iron oxide powder	Cr(VI)	35± 0.5	Air	Adsorption	
Dried mixed oxide powder	Cr(VI)	35± 0.5	Air	Adsorption	
Dried mixed oxide powder	Cr(VI)	35± 0.5	Air	Adsorption	
Aid washed iron oxide	Cr(VI)	35± 0.5	Air	Adsorption	
In situ generated $Fe(OH)_3$		35± 0.5	Air	No Cr(VI) formation	
In situ generated $Cr(OH)_3$		35± 0.5	Air	No Cr(VI) formation	
Fe(II):Cr(III) hydroxide mixture(6:1 ratio)		35± 0.5	Air	Cr(VI) formation	
Fe(II):Cr(III) hydroxide mixture(6:1 ratio		35± 0.5		No Cr(VI) formation	
Fe(II):Cr(III) hydroxide mixture(10:1 ratio)		35± 0.5	Air	Cr(VI) formation	
Fe(II):Cr(III) hydroxide mixture(10:1 ratio)		35± 0.5		No Cr(VI) formation	

3.4.4. **pH-Eh dependent speciation of Cr(III)**

It is known that metal hydroxides can form complex with anions at high concentrations of hydroxides (high pH) (Davis and Leckie 1980; Cotton et.al. 1999). The pH-Eh dependant speciation diagram of Cr(III) is given in Figure 3.4. The diagram shows that Cr(III) forms CrO_2^- species and the concentration of the species increases with increasing pH. In all experiments described above pre determined quantities of alkali were added, even though pH cannot be measured precisely for solutions with pH values greater than 12 due to alkaline error of the glass electrode. However, a reproducible concentration of OH^- ions was maintained in the medium. Concentration of alkali was maintained at a level such that Cr(III) hydroxide was available as suspended solid. When the concentration of OH^- reached a much higher level Cr(III) species dissolves appreciably (Cotton *et.al* 1999). Hence it is reasonable to assume that at the alkali concentrations maintained in the medium there is a large proportion of $Cr(OH)_3$ and small proportion of CrO_2^- .When the redox potential Eh increases dissolved oxygen present in the medium can covert $Cr(OH)_3$ or CrO_2^- to CrO_4^{2-}

3.4.5. **Formation of Cr(VI) in alkaline medium catalyzed by mixed $Fe(OH)_3$. $Cr(OH)_3$**

When the adsorption of Cr(VI) on freshly prepared $Fe(OH)_3$. $Cr(OH)_3$ was tried, the equilibrium concentration of adsorbate was found to be irregular. Repetition of the experiments under different conditions confirmed this behaviour. Hence it was thought worthwhile to investigate the phenomenon further. When chromium(III) hydroxide alone was aerated



(Stumm and Morgan, 1997)

Figure 3.4. pH-Eh dependant speciation diagram of Cr(III)

Cr(VI) was not formed. $Fe(OH)_3$. $Cr(OH)_3$ was stirred continuously with air and blank measurements were done for Cr(VI). As time increased Cr(VI) started appearing slowly. On further stirring with air the concentration of Cr(VI) increased with time. To eliminate the possible presence of Cr(VI) in the adsorbent, the material was tested for Cr(VI) at the start of the experiment. Different mole ratios of $Cr(OH)_3$ and $Fe(OH)_3$ were used. In all cases aerated samples showed the formation of Cr(VI) whereas non aerated mixtures did not produce any Cr(VI). The increase in the concentration of Cr(VI) upon aeration of $Fe(OH)_3.Cr(OH)_3$ is illustrated in Figures 3.5 and 3.6.

The formation of Cr(VI) was further confirmed by extracting the peroxochromium species in diethyl ether and comparing it with that obtained with standard dichromate solution (Cotton *et.al* 1999).

It is not surprising that dioxygen oxidizes Cr(III) to Cr(VI). The speciation diagram of Cr(III) – Cr(VI) system indicates that at elevated pH oxidation of Cr(III) to Cr(VI) by dioxygen is thermodynamically feasible (Drever 1997). The speciation diagram of iron indicates that in terms of standard potential it falls between the chromium system and dioxygen. E^0 of Cr(VI)/Cr(III) in alkaline medium is –0.13 V (Cotton *et.al* 1999). Now the conditions are favourable for Fe(III) to act as a catalyst for the oxidation of Cr(III).

$$CrO_4^{2-} + n\,H_2O + 3\,e^- = Cr(OH)_{3\,(s)} + 5\,OH^-;\ E^0=-0.13\ V \qquad (1)$$

Iron (III) hydroxide can act as a catalyst and effect the conversion of Cr(III) to Cr(VI) with dioxygen.

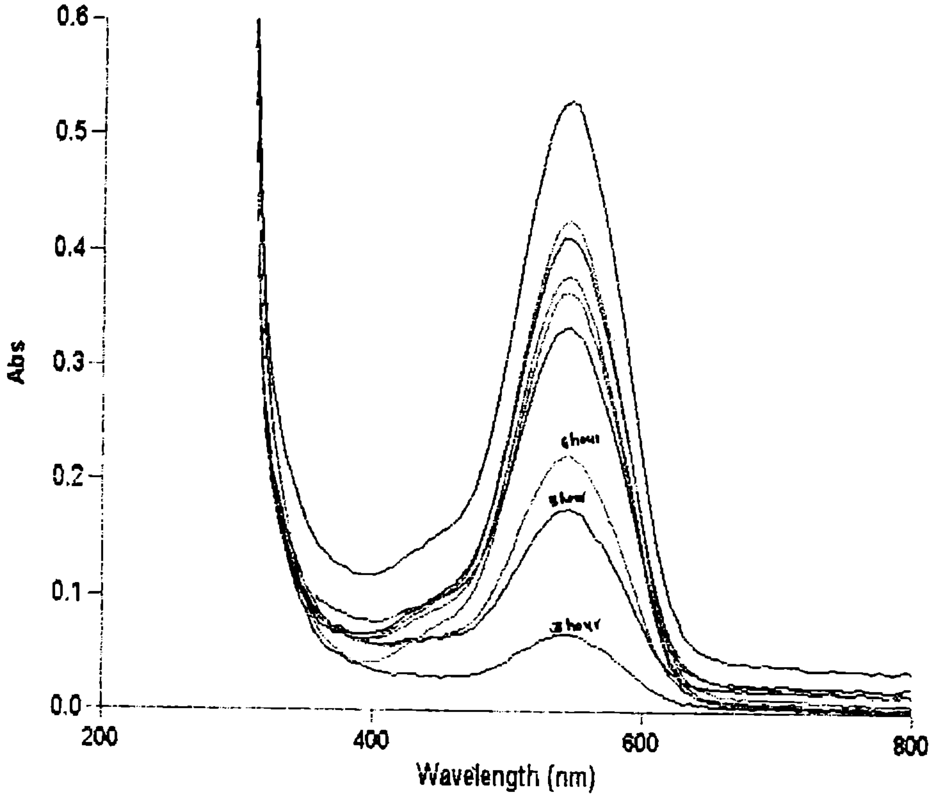
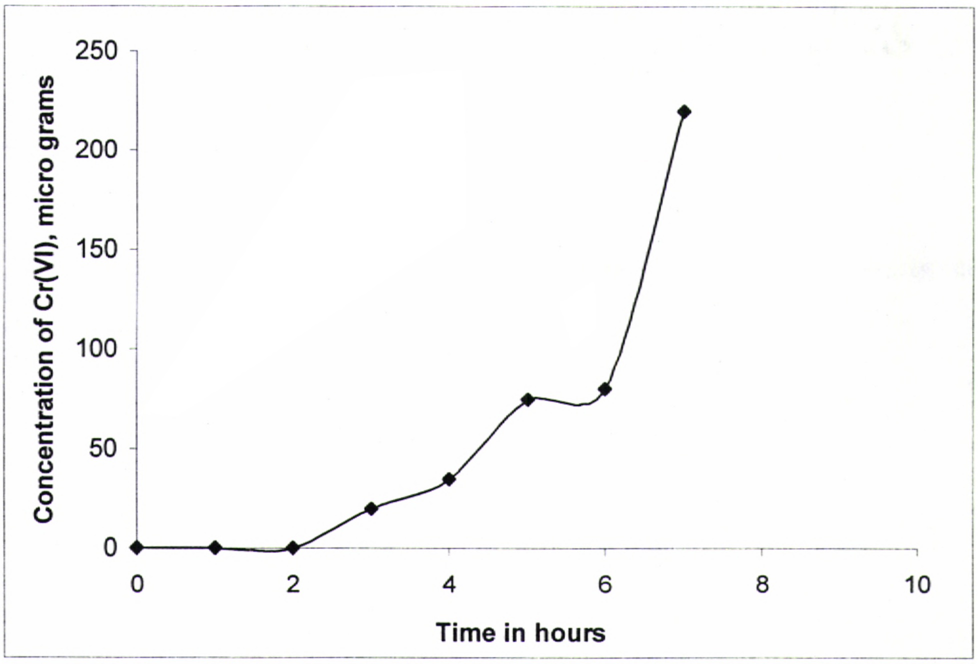


Figure 3.5. Wavelength scan of di-phenyl carbazide-Cr(VI) complex at one hour intervals



$Fe(OH)_3$. $Cr(OH)_3$ mole ratio 1:8
Stirred with CO_2 – free air

Figure 3.6. Concentration of Cr(VI) with aeration time

Separately prepared ferric and chromium oxides when dried at 85^0C, mixed together and aerated under the same conditions did not give Cr(VI). The fact is that Cr(III) hydroxide and iron(III) hydroxide when occurring together at elevated pH and, when contacted with air forms Cr(VI), though slowly. Industrial sludge containing iron and chromium precipitated as their hydroxides is usually disposed in landfills. Iron compounds co-occur with Cr(III) in most instances and there is a definite chance for the iron-catalyzed oxidation of Cr(III) to Cr(VI). This necessitates a new look at the feasibility of disposing chromium hydroxide sludge.

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