ASSESSMENT OF WATER QUALITY AROUND MINE SITES

A THESIS SUBMITTED IN PARTIAL FULLFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology

In

Mining Engineering

By

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108MN045

&

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DEPARTMENT OF MINING ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA – 769008
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This is to certify that the thesis entitled “Assessment of Water Quality Around Mine Sites” submitted by Sri Sukalyan Das (Roll No. 108MN043) and Sri Satyajit Rout (Roll No. 108MN045) in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Mining Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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ABSTRACT

Introduction:
One of the major impacts of mining processes is the contamination of water bodies through mine water drainage, leakage of water exposed to minerals, water from soil heaps, acid mine drainage and mine water rebound. Water is the most important element of eco-system and it is thus imperative to determine and mitigate the effects of mining operation on the same. Also, contaminated water has adverse physiological effects on human being and other animals. For this, it is important to identify the critical parameters in the water sample which is the scope of the study.

Sampling, Water quality parameters and their tests:
Samples were collected from different mines including both coal and metal mines spread over northern and western Odisha such as samples from Ib Valley coal mines of MCL, discharge of iron mines from Chhattisgarh and Koira region and were analysed through a series of experiments following standard procedure. The concentration of various physical, chemical, metallic and organic parameters were found which included determination of turbidity, conductivity, solids, iron, chromium content, pH, hardness, ammonia, nitrate, sulphate, phenol, fluoride, phosphate and organic parameters of importance such as Dissolved oxygen, Bio-chemical Oxygen Demand and Chemical Oxygen Demand.

Results and Discussions:
The results indicated that discharge of iron mine, Chhattisgarh, exceeds the contamination limits for physical and metal parameters but is within limits for others. Samples from the coal mining areas are having elevated concentrations of physical, chemical and organic parameters, such as solid content, turbidity and dissolved oxygen. Samples from metal mining region of Koira showed higher iron content and other nutrients. The results were quantified to determine the degree of contamination.
The values of degree of contamination ($C_d$) are given in the table-1. The $C_d$ values indicate that the water samples from coal mines, iron mines of Chhattisgarh, Barsuan and Bandhal from Koira region are heavily polluted.

Conclusion:
From the results obtained it may be concluded that water samples considered in the study are
polluted to a significant level and are not potable. The fact that these elevations in values of the parameters are observed during the winter season is a matter of sheer concern, because surface run-off is negligible during the same. Monsoon may inflict heavy pollution to the water bodies. Hence appropriate steps must be taken by the industry, State Pollution Control Board and the Government to prevent pollution of water. For water bodies near coal mines, primary water treatment, provision of retention tank for mine drainage can be helpful to lower the solids. In addition to treatment processes such as sedimentation and filtration, and allowing water through wetlands can decrease the metal and sediment content effectively and economically especially in Koiria region where large quantity of water must be treated.

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Chapter 1

INTRODUCTION
1. INTRODUCTION

The mining process impacts and many times deteriorates the environment in numerous ways. One of the aspects of environment, it harms the most, is the water resources. The main sources of such pollution are mine water drainage, leakage or flow of mineral exposed water to the surface or to nearby located aquifer system and surface water body, water from spoil heaps and spoil heap failures, acid mine drainage and mine water rebound. These run-offs may discharge directly into drainage ditches or to land around the periphery of the heap and infiltrate into aquifer. They can leach soluble salts, especially chlorides. These causes can be active in all mines whether working or abandoned. These types of sources result in various types of water pollution viz. acid mine drainage, heavy metal contamination and leaching, processing chemical pollution, or erosion and sedimentation.

The magnitude of pollution of water resources, mostly surface water bodies, due to discharge of contaminated water from mines and waste dumps is the most severe. The oxidation of sulphide minerals and sulphide-rich waste due to water and air exposure causes acid mine drainage (AMD). In addition to the acidity, the acidic water takes up salts and mobilizes metals from mine workings and residue deposits. Due to its content and reactivity it can turn an aquatic ecosystem to a biological wasteland and makes the water unusable. The persistency in the generation of AMD even after closure of the mine poses an ever mounting problem of groundwater and surface water pollution in the area nearby.

The release of mining waste to the environment can result in intense destruction of ecosystems, which in some cases may not be fully restored or rehabilitated. The impact of discharges containing metals and heavy metals on receiving streams is unexpectedly broad to comprehend. Health hazards of user of such water, destruction of aquatic flora and fauna, devastating aesthetic impact are some typical aspects of the broader view. Severe mine water discharges threaten water supply in many areas for house hold, irrigation or even construction purpose. It is therefore essential to carry out water quality studies and its fitness for various applications; otherwise its use may lead to disastrous consequences in the long run.

1.1 OBJECTIVES OF THE STUDY

Having mentioned the importance of assessing water quality, the work has been planned with the following objectives:
- Outline the mining activities that are responsible for water pollution and to study the impacts of such pollution of water.

- Collection of samples from water sources near mine sites.

- Analysis of the collected water samples for possible parameters

- Identification of the most polluting component and its source

- Quantification of the water quality and thereby assessing it

- Suggestion for possible remedial actions.
Chapter 2

LITERATURE REVIEW
2. LITERATURE REVIEW

The following is a brief review of scholarly work of different researchers in the field of water quality studies due to mining:

Singh (1997) carried out a number of experiments and concluded that the major impacts of mining are water pollution due to erosion, oil and grease, contamination of water bodies due to discharge of mine water effluents, leachates from wash-off dumps, solid waste disposal sites, broken rocks, toxic wastes, salinity from mine fires, acid mine drainage etc. He listed the major mitigation methods as follows: Overburden run-off collection and treatment with subsequent sediment control, Oil and grease separators, Collection/storage of leachates, seepages, wash-offs with subsequent treatment, Proper sanitation and provision of domestic and sewage effluents treatment, Treatment of mine water discharges.

He suggested that as there is acute shortage of water supply in mining areas, augmentation of underground pumped out mine water for various supplies can be provided. This is very economically cost-effective and provides savings towards water and energy conservation while giving environmental and social benefits.

Cherry et al (1999) carried out an integrative assessment of water sheds impacted by mines in south-western Virginia, USA and Ely Creek, a tributary to the North Fork of the Powell River was selected. The purpose of the study was to investigate the usefulness of integrative bio-assessments, which use several different types of assessment tools to obtain a broad, overall picture of the environmental impacts of pollutants in a given area. The parameters used in the study included: (1) water column chemistry; (2) sediment metal chemistry; (3) chronic sediment toxicity to a cladoceran (Daphnia magna) and midge (Chironomus tentans); (4) acute water column toxicity to another cladoceran (Ceriodaphnia dubia); (5) chronic in situ toxicity testing with Asian clams (Corbicula uminea); (6) in situ benthic macro-invertebrate sampling; and (7) habitat assessment and eco-toxicological rating (ETR) is determined. They found that when pH was consistently at or below 3.0, in situ benthic macro-organisms are very few. And at Acid mine drainage (AMD) sites where pH ranged from 3.5 to 6.0, some endpoints were insensitive to environmental stress. Their study showed that the abiotic sampling procedures, (water chemistry, habitat assessment and metals analysis) illustrated the extent of environmental stress.
**Jarvis and Younger** (2000) found that the impact of metalliferous discharges from mines and spoil heaps on receiving streams is detrimental. Aquatic flora and fauna are highly impoverished. Their study outlines the methodologies for mine water impact assessment used in the UK. Their methodology is to quantify mine water impacts by selecting/prioritising factors according to their effect. This was done by quantifying existing impacts via chemical, ecological, and visual characterization. The other methods include the following:

1. Method by the national rivers authority:
   a. Physicochemical assessment of watercourse
   b. Use of Benthic macro-invertebrates for second phase of assessment,

2. Chemical and ecological studies

Their study indicated that the above were not sufficient for assessing the effect of underground mining. The application of state-of-the-art hydro-geological and geochemical modelling techniques is mandatory. They suggested that for any EIA some of the factors that are to be considered are: Local knowledge that can provide an invaluable insight into the origins of mine water pollution and correctly instructed local community members.

In the experience of the authors, a collaboration of professional engineers and local community is an attractive proposition to potential funding bodies. Also local communities can assist with construction of remediation schemes, and perhaps more significantly can ensure day-to-day maintenance of such facilities.

**Roy et al.** (2003) after carrying out a number of experiments found out that mining affects huge area of the land and affect the quality of surface and underground water by adding contaminants and toxic compounds making it unsafe for drinking and industrial usage, disturbing the hydrology of the area. They discovered that the major sources of liquid effluents were: surface run-off, mine water pumped put during drainage operation, spent water from handling plants, dust extractors and dust suppression systems, effluents from preparation and beneficiation plants, and leaches/wash-off from waste/tailing dumps.

Also, according to their research Acid mine drainage is produced whenever in a mine of any type permeable formations interacts with the water table, aquifer, or perched water body, or where surface water finds its way into a mine where sulphides (particularly pyrites) are
present in the ore or country rock. Amongst objectionable features of the acid mine drainage are low pH and high levels of sulphates, iron, and total dissolved solids.

These deplete oxygen level in water, increase toxicity by rendering heavy metals soluble, and create corrosion problems. Acid mine drainage can be effectively controlled by preventing its formation at source, by diluting the acid mine drainage to acceptable affluent quality, and by employing standard waste water treatment methods for neutralization and removal of dissolved solids.

In addition to the acid mine drainage, they claim another source of water pollution to be the carry-off of the fine solid particles from the surface mining sites and coal preparation plants, especially during rainy seasons, into the streams and water-courses. Sometimes the overburden is dumped along the banks of the streams and water-courses, causing blockage of free flow and contamination of water. It has also caused a severe damage to the crops irrigated by the river water downstream.

Plant spillage, truck haulage, conveyor transfer points, and rail wagon loading areas, are common sources contributing fines to the surface run-offs. Abandoned mill tailings, coal refuse heaps, spoil heaps, and other waste dumps in mining area contain significant amounts of dissolved minerals, are chronic sources of stream pollution, apart from presenting eye-sore sights. Mining is also responsible for changing the hydrology of an area in many ways. Subsidence due to underground mining affects underground water, disruption of surface drainage patterns and resulting contribution to stream pollution. Sometimes it may change the river course and discharge, there by affecting the agriculture and flora and fauna of the area.

Lambert (2004) observed that in several areas of the Appalachian coal fields and in coal mining regions of the UK, mine water acidity and iron load are most severe in the first years after a discharge begins, but decreases steadily and substantially with time. Their study was to document the extent of water-quality changes in the Uniontown Syncline AMD discharges, and to investigate geochemical and hydraulic factors responsible for the changes. While in operation, the advantage of these mines was the fact that water did not pool and hinder mining activities, but rather travelled down slope and out of the mine. The discharge from Uniontown Syncline Pittsburgh Coal seam flow in to two major streams, or their tributaries: the Youghiogheny River in the north part of the Syncline, and Redstone Creek in the south part. But the method followed for this study included: Sample collection from 21 sites and
field measurements of pH, temperature, dissolved oxygen, conductivity, ferrous iron and flow. Results were recorded and compared with results from Scarlift study (1974). Thus Long-term changes in the quality of abandoned underground coal mine discharges were studied. The study presented clear evidence for natural improvement of the quality of drainage for abandoned mine discharges. They suggested that the type and magnitude of water-quality changes that occurred over time, mainly depends on the degree of flooding within the mine voids contributing to the discharges, and the time elapsed since mine abandonment. In flooded mines of the Uniontown Syncline, acidic discharges have become alkaline in less than 25 years. In the discharges from un-flooded mines, M59 and others north of the Youghiogheny River, improvements in water quality have also occurred over 25 years, but to a smaller extent than observed for the flooded mines. Thus their study proved that the availability of oxygen for AMD production is related to the extent of flooding in the mine voids.

**Heyden and New** (2005) carried out a number of experiments and observed that the use of wetlands to treat mine effluent has grown in popularity over the past two decades, although the processes by which the natural systems function are often poorly understood. This field-scale investigation utilises daily data over a 9-month period in assessing the processes leading to the remediation of mine effluent within a natural wetland on the Zambian Copper belt. The study differentiates effluent remediation through dilution from pollutant retention. Decreased wetland outflow concentrations of SO$_4$ and Na are due to dilution only, while Co (50%) and especially Cu (83%) are retained within the wetland. Retention was linked to adsorption onto new or primed surfaces during an initial period of effluent release into the system and to processes related to pH buffering to 7.5. The wetland’s acid buffering capacity was largely the result of carbonate-rich groundwater discharge into the wetland. Although this buffering capacity likely shows little seasonal fluctuation (20–80 kmol/day), the impact of acidic effluent input on the wetland itself probably varies markedly between seasons, owing to the temporal and spatial characteristics of discharge from the catchments aquifers. Assessment of other natural wetlands in the region indicated that some (circa 15%) showed similar catchment size, hydrochemical and hydrogeological characteristics as those of the New Dam wetland, likely demonstrating a similar effluent remediation potential as that described here.
Roychoudhury and Starke (2006) comprehended and assessed the potential threat of metal pollution from dewatering of Grootvlei Gold Mine effluent into the Blesbokspruit, a Ramsar certified wetland site, the Witwatersrand rock of this area contains sulphide minerals, like pyrite pyrrhotite, arsenopyrite, chalcopryrite, galena cobaltite, gersdorffite, Fe, Ni, Pb, Cu, Co, As and U-bearing leachable oxides (Scott). Groundwater seeps through the mineral reef, therefore, has high Fe, SO$_4$ and trace metal content. Effluent pumping subsequently resulted in disposal and dispersal of trace metals in the surface water system. Blesbokspruit stream recharges the local dolomite aquifer. The poor water quality therefore is likely to impact the freshwater resources in the area like Vaal River. The assessment was carried out by Surface water and sediment sampling, determination of Water chemistry by pH, electrical conductivity (EC), dissolved O$_2$ (DO), redox potential (Eh), temperature, ion Chromatograph (Dionex, DX500) and atomic absorption spectro-photometry test, which was followed by Leachate test using ICP-MS., CHN analyzer to determine the organic C in the sediment. They also assessed the Sediment quality by determining Enrichment factor (Ef), Geoaccumulation index (Igeo), Metal pollution index (MPI) and Sediment quality guideline index (SQG-I). For trace element analysis cluster analysis is performed. Cluster analysis was further used to identify the collective mobility behaviour of trace metals in Blesbokspruit.

It was found that the effect of mine water discharges is comparatively a smaller source because (1) the pH of the water is naturally high from flowing through the local dolomite aquifer, and (2) the mine water undergoes high density separation followed by lime treatment before it is discharged. Both of these factors promote precipitation of metals rather than dispersion and consequently the mobility of trace metals is relatively low in the studied area. Also the partition coefficient for all of the measured trace metals in Blesbokspruit is found to be high, which leads to their accumulation in the wetland.

Chen et al (2007) investigated the effect of acid mine drainage on the well water in the local areas of Daboashan mine area (Shangba village) and carried out an integrated research project. The study area is famous for copper, zinc, lead and iron mines. Most of the mines discharge their effluent in to a mud retaining impoundment (MRI) which is built for flood water. Since the MRI is overflowed the mine discharge is entering into a tributary. Their assessment method included sampling from 112 well out of which 6 were selected for long term studies. Then pH, electrical conductivity test, test for Cu, Pb, Zn, Cd, Fe and Mn by graphite furnace atomic absorption spectrometry and Al measurement by inductively coupled
plasma-atomic emission spectrometry (ICP-AES) were carried out. After wards toxicity test using Daphnia carinata was done. Analysis on statistical significance of difference between means was performed using pearson correlation. The results show that each chemical parameter was variable during the monitoring period. On average, pH was 2.9 ± 0.3. As a result, concentration of various metals of potential toxicity was also extremely high and was in order Zn > Cu > Pb > Cd. The concentration of these metals in the water was 1.6, 21, 1.76 and 13 times higher. Results of well water suggest that the groundwater in the Shangba floodplains have been affected by the acidic irrigation water and the lowest pH recorded in QL is attributable to its closest proximity to the inflowing irrigation water of AMD origin. Water collected from the location closest to the acidic irrigation water source was acutely toxic to the test organism (Daphnia carinata) even after 51 time dilution. It is likely that the extremely high mortality rate of the local population reported for the study area is at least partly related to the high levels of heavy metals, particularly Cd in the drinking well water.

Balistrieri et al (2007) tried to determine the composition of a river that is impacted by acid-mine drainage, and to evaluate dominant physical and geochemical processes controlling the composition. They assessed dissolved metal speciation and toxicity using a combination of laboratory, field and modelling studies. They found that values of pH increases from 3.3 to 7.6 and the sum of dissolved base metal (Cd + Co + Cu + Ni + Pb + Zn) concentrations decreases from 6270 to 100 mg/L in the dynamic mixing and reaction zones, downstream of the river’s confluence with acid-mine drainage. Mixing diagrams and PHREEQC calculations indicated that mixing and dilution affect the concentrations of all dissolved elements in the reach. Additionally, dissolved Al and Fe concentrations decrease due to mineral precipitation, whereas dissolved concentrations of Cd, Co, Cu, Ni, Pb and Zn decrease due to adsorption onto newly formed Fe precipitates. The uptake of dissolved metals by aquatic organisms depends on the aqueous speciation of the metals and kinetics of complexation reactions between metals, ligands and solid surfaces. Diffusive gradients in thin films (DGT) technique and the Biotic Ligand Model (BLM) are used to assess the metal contents. Data from DGT units indicate that almost all dissolved metal species are inorganic. BLM studies confirmed the DGT results. Calculated acute toxicity concentrations are below LC50 values. In contrast, labile Cu concentrations exceed LC50 values for the organisms as well as Criteria Continuous Concentration and Criteria Maximum Concentration at sites <30 m downstream of the confluence. These results suggest that environmental conditions at sites closest to the
confluence of the river and acid-mine drainage should not support healthy aquatic organisms. Their study demonstrated the importance of analytical modelling method and integrated geochemical water quality and toxicity indices to achieve an understanding of environmental impacts in complex ecosystem.

Bhuiyan et al (2010) assessed the heavy metal concentration in mine drainage (irrigation water) and groundwater systems in North-Western Bangladesh. They used pollution indices and different multivariate approaches (PCA and CA) to identify the pollution status and probable sources of pollutants in the study area. Their study involved evaluations of heavy metal pollution index (HPI), heavy metal evaluation index (HEI) and degree of contamination. In their assessment they collected thirty-two water samples, consisting of 20 from mine drainage and nearby wetlands (prefixed drainage water (DW)), 10 groundwater samples from boreholes, irrigation pumps and hand-dug wells (prefixed groundwater (GW)) and 2 samples from coal mine unaffected areas (prefixed river water) and performed temperature, pH and conductivity, DO, COD, AAS tests, thus determining physicochemical and elemental properties of water. Then pollution evaluation indices: heavy metal pollution indices, Heavy metal evaluation index, Degree of contamination (Cd) were determined which was followed by Statistical analysis. Then the water samples were classified and pollution source was identified. Spatial similarities and sampling site grouping was done and correlation matrix was formed.
CHAPTER 3

IMPACT OF MINING ON WATER
3. IMAPCT OF MINING ON WATER

Pollution of natural watercourses with mine drainage is a major environmental issue worldwide. Mining contributes to water pollution in numerous ways. The most common and significant mining related processes, which result in water pollution, are discussed below.

3.1 SOURCES OF WATER POLLUTION DUE TO MINING

3.1.1 Drainage Water from Mines: Water in the mines is contaminated due to the following reasons:

a. Mixing of different metals, sediments, minerals, salts to the water to be drained during drilling, blasting, transportation
b. Organic compound derived from spills of lubricating and hydraulic oils
c. During wet dust suppression variety of dusts get mixed with water

For coal mines: mine drainage water is generally hard, alkaline, moderately saline, and ferruginous. They generally have low oxygen demand but are rich in suspended matters associated with most of the coalmining. A high level of mineralisation is noticed via high values of electrical conductivity. Besides coal dust they contain high level of Na, K salts, strontium and barium. If the seam contains Fe, S then the mine water is acidic in nature and the pH value can be very low. Fe content may rise as high as several hundred mg/l. This iron in ferrous form is more stable underground but it oxidises itself in the presence of air and forms an orange precipitate termed Ochre.

3.1.2 Leakage or Flow of Mineral Exposed Water to the Surface or nearby Aquifer Systems: The physical changes such as de-lamination, bedding plane separation, fault reactivation and fissuring of rock masses caused by mining permit air to penetrate a much larger surface area than the immediate boundaries of the working faces and associated roadways. These changes also alter the hydro-geological conditions within the coalfield and allow wider movement of ground water through the rock masses than existed prior to mining. These factors mean that the ground water comes in contact with large surface area of rock and is exposed to oxidation. Hence the ground water becomes contaminated.

The mine water or ground water which are exposed to mining due to any reason have high salt content, and also high quantity of sulphates, iron, and other metals which are derived from natural resources or artificially introduced by mining equipment. Mine water from metal
mines may contain various metals, or heavy metals which may be toxic or non toxic. The salts are released into working by mining operations. In general, the salinity increases with depth below the surface.

3.1.3 Water from Spoil Heaps and Spoil Heap Failures: Surface water run-off can leach soluble salts, especially chlorides. These run-offs may discharge directly into drainage ditches or to land around the periphery of the heap and infiltrate into aquifer.

3.1.4 Acid Mine Drainage: It is most evident in seams with high Pyrite (or S) content. This is a type of drainage resulting from natural oxidation of sulphide minerals that occur in mine rock or waste that are exposed to air and water. This is a consequence of oxidation of sulphur in the material to a higher state of oxidation and if aqueous iron is present and unstable, the precipitation of ferric iron with hydroxide occurs. The acidic ferruginous water may contain high concentration of aluminium that precipitates as hydroxide as the pH value rises on entering a receiving body of water, giving a milky appearance. Concentration of heavy metals may be high in some acid water. This phenomenon does not occur if the S is in nonreactive state and the rock has sufficient alkaline material to neutralise the acidity. But still it may contain high amount of Calcium/ Magnesium Sulphate.

3.1.5 Mine Water Rebound: Mine water rebound means the comeback of the mine water to the mine worked out area or to the surface if pumping (drainage) is completely stopped. Mining subsidence is likely to have induced fractures in the overlying strata, enhancing their hydraulic conductivity, and creating new pathways for mine water to migrate upwards. This water may cause pollution of potable water supply abstractions. But many times the mine water is not harmful and the abandoned mines serve as aquifers.

3.2 EFFECTS OF WATER POLLUTION

Pollution of water sources is one of the major concerns of the environmentalists and people in general. The fact that a very limited amount of fresh water is available for human kind and many other life; both plants and organism, makes us to consider the effect of unbound pollution that human is responsible of.
The pollutants originating from mining is more than equal to the same caused by any other industry. Though the chemical agents exposed to water source may be less but different mining activities introduce minerals, heavy metals and solids to watercourses that can create problems for all kinds of life that are directly or indirectly dependent upon the water.

Water pollution due to mining activity is capable of rendering the water unusable as potable water source. The polluted water may have undesirable colour, odour, taste, turbidity, organic matter contents, harmful chemical contents, toxic and heavy metals, oily matters, radioactivity, high Total Dissolved Solids (TDS), acids, alkalis etc. The organic content may be biodegradable or non-biodegradable. Pollution of surface waters (rivers, lakes, and ponds), ground waters, and sea water are all harmful for human and animal health. Pollution of the drinking water and that of food chain is by far the most worry-some aspect as elements or constituents of polluted water can act as toxins and can create severe health hazard to organisms. Irrigation of such water introduces metals in the eatables and also contaminates the soil. Besides the obvious effects, other harms of water pollution are:

1. The high level of salt represents the most intractable water pollution problem with coal mining as they are not readily susceptible to treatment. Chlorides and sulphates are typical salts

2. Acid generation during acid mine drainage can lead to high levels of heavy metals and sulphate in the water that has detrimental effect on the quality like decrease in pH value, extinction of fish and amphibians from local water body as well as vegetation.

3. In case the pollutants are hydrocarbons and other organic materials, it is highly possible that the pollution will increase the BOD and COD of the water bodies nearby that are being polluted. This may lead to excessive growth of microorganism which will eventually lead to destruction of any other life in the water body.

4. High level of metal concentration in the domestic water derived from such polluted source may cause various serious health issues and diseases.

5. Heavy metals and radioactive substances may enter to our food chain via many paths and can be bio-magnified which will cause cancer and may even cause genetic problem.

6. Increase in oil content and oil waste pose a serious problem as it spreads on water quickly but are degraded very slowly. Birds and fishes ingest this oil which is toxic and thus enters the food cycle.

Again the oil slick prevents the Oxygen transfer and leads to a very low DO level.
3.2.1 Physiological effects on human beings and other animals: The constituents or pollutants that mining introduces to water bodies can have severe health hazard mentioned before. The health hazards, due to such, are broadly classified as given below:

**Geno-toxicity:** Many compounds that enter the body of an organism are known to cause damage to DNA. These compounds are called geno-toxins. Usually when pollutants damage DNA a natural repair system in an organism will return it to its usual state, if it fails for any particular reason cells with damaged DNA can divide. Mutant cells are than produced and the defect spreads, causing the offspring of the organism to have serious defects that are often very damaging to their health. Geno-toxins and their effects are given in table 2.1, 2.2, and 2.3.

**Carcinogenity:** Several pollutants are carcinogenic, which means they can induce cancer in the body of humans and animals. Carcinogenic pollutants are pollutants that play a role in one or more of the stages of cancer development in an organism. They can also be promoters, which mean that they promote the growth of cells that have cancer-forming properties. Finally, they can be progressors, which mean that they stimulate unrestrained division and spreading of cancer cells. When one of these substances is absent cancer cannot be induced. When cancer cells are malignant, they can spread through the human body rapidly, causing defects to healthy cells and immunity mechanisms. They will destroy normal body cells and cause cancer in organs and systems. Carcinogens and their effects are given in table 2.1, 2.2, and 2.3.

**Neurotoxicity:** The nervous system of organisms is very sensitive to toxic effects of chemicals, both naturally occurring and man-made. Chemicals that cause neurological effects are called neurotoxins. Neurotoxins all somehow disturb the normal transmission of impulses along nerves or across synapses. The consequences of neurotoxicity vary. They can be uncoordinated muscular tremors and convulsions, malfunction of nerves and transmissions, dizziness and depression, or even total malfunction of body parts. Neurotoxicity can be so serious, that synapses are blocked. Synaptic block causes death as a result of paralysis of the diaphragm muscles and respiratory failure. Neurotoxins and their effects are given in tables.

**Reproductive failure:** Pollutants that cause reproductive failure due to damage to the reproductive organs are called endocrine disruptors. There are several ways in which a pollutant can act as an endocrine disruptor. The first is an oestrogenic chemical. This is a chemical that can imitate an oestrogen by binding to the oestrogen receptor. This results in
the induction of oestrogenic processes, causing an organism to experience reproductive failure due to a disturbance in the reproductive system. An oestrogenic chemical can also block the effects of endogenous oestrogens by binding to the oestrogenic receptor. This causes masculization of female organisms. It is also possible that female reproductive chemicals are found in male organisms. This causes hermaphrodites. Another series of problems is caused when chemicals block the hormone receptor sites. In this case, the normal action of the hormone is inhibited, as it cannot react with the receptor. This can cause infertility when it occurs over a longer period of time.

Table 3.1: Effects of Different Physical Parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Possible Sources</th>
<th>Health and Environmental Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity</td>
<td>Caused by the presence of suspended matter such as clay, silt, and fine particles of organic and inorganic matter, plankton, and other microscopic organisms.</td>
<td>Objectionable for aesthetic reasons. Indicative of clay or other inert suspended particles in drinking water. May not adversely affect health but may cause need for additional treatment. Following rainfall, variations in ground-water turbidity may be an indicator of surface contamination.</td>
</tr>
<tr>
<td>Colour</td>
<td>Can be caused by decaying leaves, plants, organic matter, copper, iron, and manganese, which may be objectionable. Indicative of large amounts of organic chemicals, inadequate treatment, and high disinfection demand. Potential for production of excess amounts of disinfection by-products.</td>
<td>Presence of colour suggests that treatment is needed. No health concerns. Aesthetically unpleasing.</td>
</tr>
</tbody>
</table>
pH
Indicates, by numerical expression, the degree to which water is alkaline or acidic. Represented on a scale of 0-14 where 0 is the most acidic, 14 is the most alkaline, and 7 is neutral.

High pH causes a bitter taste; water pipes and water-using appliances become encrusted; depresses the effectiveness of the disinfection of chlorine, thereby causing the need for additional chlorine when pH is high. Low-pH water will corrode or dissolve metals and other substances.

Odour
Certain odours may be indicative of organic or non-organic contaminants that originate from municipal or industrial waste discharges or from natural sources.

Loss of potability of the water if odour is objectionable

Taste
Many substances such as certain organic salts produce a taste without an odour or with odour and can be evaluated by a taste test.

Loss of potability of the water if taste is objectionable

Table 3.2: Effects of Organic Contaminant in Water

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Potential health and other effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile organic compounds</td>
<td>Can cause cancer and liver damage, anaemia, gastrointestinal disorder, skin irritation, blurred vision, exhaustion, weight loss, damage to the nervous system, respiratory tract irritation, cancer and liver damage.</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Can cause poisoning, headaches, dizziness, weakness, and cancer, gastrointestinal disturbance, numbness. Destroys nervous system, thyroid, reproductive system, liver, and kidneys.</td>
</tr>
<tr>
<td>Plasticizers, chlorinated</td>
<td>Causes cancer. Damages reproductive and nervous systems,</td>
</tr>
</tbody>
</table>
solvents, benzo[a]pyrene, kidney, stomach, and liver.

Table 3.3: Effects of Different Metals Present in Water

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Potential health and environmental effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>Aluminium oxide is very toxic specially for brain, sometimes may lead to Alzheimer’s disease in humans</td>
</tr>
<tr>
<td>Antimony</td>
<td>Decreases longevity, alters blood levels of glucose and cholesterol in laboratory animals exposed at high levels over their lifetime.</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Causes acute and chronic toxicity, kidney and liver damage; decreases blood haemoglobin. Possible carcinogen.</td>
</tr>
<tr>
<td>Barium</td>
<td>Excess of Ba (more than 100 mg) in human body may cause excessive salivation, diarroha, tremors, paralysis of muscles or nervous system, colic, vomiting, damage to heart and blood vessels, a variety of cardiac, gastrointestinal, and neuromuscular effects, associated with hypertension and cardio-toxicity in animals.</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Causes acute and chronic toxicity; can cause damage to lungs and bones. Possible carcinogen.</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd is very toxic, 50 mg may cause vomiting, diarroha, abdominal pains, loss of consciousness. It takes 5–10 years for chronic Cd intoxication. During first phase, discolouration of teeth, loss of sense of smell, mouth dryness occurs. Afterwards it may cause decrease of red blood cells, softening of bones, fractures, skeletal deformations, damage of kidney, hypertension, tumour formation, heart diseases, impairment of bone marrow, lumber pains, disturbance in calcium metabolism, impaired reproductive function, genetic mutation, etc. Replaces zinc biochemically in the body and causes high blood pressure, liver.</td>
</tr>
<tr>
<td>Chloride</td>
<td>Above secondary maximum contaminant level, taste becomes noticeable.</td>
</tr>
<tr>
<td>Chromium</td>
<td>Chromium III is a nutritionally essential element. Chromium VI is much more toxic than Chromium III and causes liver and kidney</td>
</tr>
</tbody>
</table>

19
<table>
<thead>
<tr>
<th>Substance</th>
<th>Health Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Excess of Cu in human body (more than 470 mg) is toxic, may cause hypertension, uraemia, sporadic fever and coma. Copper also produces pathological changes in brain tissue. However, Cu is an important cell component in several metalloenzymes. Lack of Cu causes growth inhibition and blood circulation problem, stomach and intestinal distress, liver and kidney damage, anaemia in high doses. Imparts an adverse taste. Essential trace element but toxic to plants and algae at moderate levels.</td>
</tr>
<tr>
<td>Cyanide</td>
<td>Poisoning is the result of damage to spleen, brain, and liver. May have an influence on the acceptability of water in general. May be indicative of the presence of excess concentrations of specific substances not included in the Safe Water Drinking Act, which would make water objectionable. High concentrations of dissolved solids shorten the life of hot water heaters. Decreases incidence of tooth decay but high levels can stain or mottle teeth. Causes crippling bone disorder (calcification of the bones and joints) at very high levels.</td>
</tr>
<tr>
<td>Dissolved solids</td>
<td>May have an influence on the acceptability of water in general. May be indicative of the presence of excess concentrations of specific substances not included in the Safe Water Drinking Act, which would make water objectionable. High concentrations of dissolved solids shorten the life of hot water heaters.</td>
</tr>
<tr>
<td>Fluoride</td>
<td>Decreases the lather formation of soap and increases scale formation in hot-water heaters and low-pressure boilers at high levels.</td>
</tr>
<tr>
<td>Hardness</td>
<td>Imparts a bitter astringent taste to water and a brownish colour to laundered clothing and plumbing fixtures. It is one of the essential mineral for humans and animals. It is a component of blood cells and liveral metalloenzymes. However, more than 10 mg per kg of body weight causes rapid respiration and pulse rates, hypertension, congestion of blood vessels and drowsiness. It increases hazard of pathogenic organisms, as many of them require Fe for their growth.</td>
</tr>
<tr>
<td>Iron</td>
<td>More than 400 mg of lead in human body can cause brain damage, vomiting, loss of appetite, convulsions, uncoordinated body movements helplessly amazed state, coma. It is retained in liver, brain, muscle, soft tissues, kidney, and bones. Leads to high rate of</td>
</tr>
<tr>
<td>Lead</td>
<td>damage, internal haemorrhaging, respiratory damage, dermatitis, and ulcers on the skin at high concentrations.</td>
</tr>
</tbody>
</table>
miscarriages, affects skin, and respiratory system, damages kidney, and liver and brain cells. It disturbs endocrine system, causes anaemia, and long term exposure may cause even death. Affects red blood cell chemistry; in babies and young children. Causes slight deficits in attention span, hearing, and learning in children delays their normal physical and mental development. Can cause slight increase in blood pressure in some adults. Lead is also a probable carcinogen.

Relatively non-toxic to animals but toxic to plants at high levels. Mn is essential for mammals but in concentration greater than 100 ppm, is toxic, and causes growth retardation, sexual impotence, muscles fatigue, fever and eye blindness

Mercury is very toxic. Excess mercury in human body (more than 100 mg) may cause headache, abdominal pain, diarrhoea, destruction of haemoglobin, tremors, very bad effects on cerebral functions and central nervous system, hyper coagulability of blood, Mimamata disease, paralysis, inactivates functional proteins, damage of renal tissues, and even death. It may cause impairment of vision and muscles and even coma. It disturbs reproductive and endocrine system. Also causes insomnia, memory loss, gum inflammation, loosening of teeth, loss of appetite, etc.

Damages the heart and liver of laboratory animals exposed to large amounts over their lifetime. More than 30 mg may cause changes in muscle, brain, lungs, liver, and kidney and can also cause cancer, tremor, paralysis and even death.

Toxicity results from the body’s natural breakdown of nitrate to nitrite. It causes “bluebaby disease,” or methemoglobinemia, which threatens oxygen-carrying capacity of the blood.

Toxicity results from the body’s natural breakdown of nitrate to nitrite. Causes “bluebaby disease,” or methemoglobinemia, which threatens oxygen-carrying capacity of the blood. Causes acute and chronic toxic effects in animals--”blind staggers” in cattle. Nutritionally essential element at low doses but toxic at high doses. Signs of Se poisoning (more than 4 mg) are fever,
nervousness, vomiting, falling of blood pressure, causes damage to liver, kidney and spleen, loss of nails and hair, causes blindness to animals. Cats are most susceptible. It affects enzyme systems and interferes with sulphur metabolism. It can cause growth inhibition, skin discolouration, bad teeth, psychological problem, gastrointestinal problems, but trace amount of Se is protective against poisoning by Hg, Cd, and Ag.

Causes pathological change in kidney, liver and may even damage kidney. May cause Argyria (discolouration of skin). Effects mucous membranes and eyes. In high doses, it may be fatal to humans.

Can be a health risk factor for those individuals on a low-sodium diet.

Forms hard scales on boilers and heat exchangers; can change the taste of water, and has a laxative effect in high doses.

Damages kidneys, liver, brain, and intestines in laboratory animals when given in high doses over their lifetime.

Zinc is essential element for humans, animal and plants. It is also an important cell component in several metalloenzymes, aids in the healing of wounds. Causes no ill health effects except in very high doses. Imparts an undesirable taste to water. Toxic to plants at high levels. Infants need 3–5 mg/day, adult males 15 mg/day, pregnant and lactating females 20–25 mg Zn/day. However, heavy doses of Zn salts (165 mg) for 26 days causes vomiting, renal damage, cramps, etc.

---

**Table 3.4: Effects of Radio-nuclear Material Present in Water**

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Potential health and environmental effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross alpha-particle activity</td>
<td>Damages tissues and destroys bone marrow.</td>
</tr>
<tr>
<td>Combined radium-226</td>
<td>Causes cancer by concentrating in the bone and skeletal tissue.</td>
</tr>
</tbody>
</table>
and radium-228

Beta-particle and photon radioactivity Damages tissues and destroys bone marrow.
Chapter 4

SAMPLING

General aspects of sampling

Sample collection procedure
4. SAMPLING

4.1. GENERAL ASPECTS OF SAMPLING

The objective of sampling is to collect representative sample. Representative sample means a sample in which relative proportions or concentration of all pertinent components will be the same as in the material being sampled. Moreover, the same sample will be handled in such a way that no significant changes in composition occur before the tests are made. The following points should be kept in mind while collecting water samples (Nollet, 2007):

4.1.1 Initial Considerations: An appropriate sampling design must be chosen on the basis of the situation, temporal and spatial processes of the part of the ecosystem under investigation. Preservation and storage of the samples should be adapted to protect necessary information.

4.1.2 Spatial Aspects: The location of sampling must be kept in mind. In addition to that currents in flowing water must be considered. Stratification crucially affects the distribution of particles, especially in lakes. Different distances downstream of a sewage effluent discharge point must be carefully sampled. Choosing the appropriate depth is also required by the sampler.

4.1.3 Temporal Aspects: The temporal variation must be considered carefully during sampling as it is of great importance if the environment to be sampled shows changes. If many samples are to be taken over a period of time, it is appropriate to match the sampling rate to the expected variation in pattern. Samples containing identical volumes are taken at constant time intervals if sampling is time proportional.

4.1.4 Number of Samples: The number of samples required largely depends on the problem at hand. To get an average concentration several samples are collected as per a general calculation of the necessary number of samples.

4.1.5 Sample Volume: The sample volume depends on the elements or substances required to be analyzed on their expected concentration in the sample. For trace metal analysis sample volume of about 100 ml is sufficient in most cases. For the analysis of organic parameters 1 L samples are commonly used.

4.1.6 Storage and Conservation: To prevent any kind addition of contaminants, loss of determinants by sorption or other means, and any other unintended changes that effect the
concentrations of determinants of interest proper preservation must be carried out. For this purpose, long-term storage with negligible composition change must be preferred.

4.1.7 Contamination: There are always chances of contamination of samples during the sampling process, either from external sources or from contaminated sampling or storage equipment. Polyethylene or Teflon bottles must be used for inorganic analysis, and glass or quartz bottles in organic trace analysis.

4.2. SAMPLE COLLECTION PROCEDURE

Collection of sample:

- It is ensured that all sampling equipment is clean and quality-assured before use. Use sample containers that are clean and free of contaminants.
- Sample containers were filled without pre-rinsing with sample; pre-rinsing results in loss of any pre-added preservative.
- Special precautions are necessary for samples containing trace metals.
- Since many constituents may be present at low concentrations, they may be totally or partially lost or easily contaminated when proper sampling and preservation procedures are not followed.
- The followings were recorded during sample collection
  - General information
  - Sample identification number
  - Location
  - Sample collector
  - Date and hour
  - Sample type (Grab or composite)

Grab sampling is followed during the sampling. Grab samples are collected at a specific spot at a site over a short period of time (typically seconds or minutes). Thus, they represent a “snapshot” in both space and time of a sampling area. Discrete grab samples are taken at a selected location, depth, and time.

Grab samples sampling is followed as it is known that the composition of the water source near mines changes frequently depending upon weather and also waste discharge interval.
When a source is known to vary with time, grab samples collected at suitable intervals and analyzed separately can document the extent, frequency, and duration of these variations. The sampling is done by manual method. The details of the sample collected are as presented in table 4.1.

**Table 4.1: Samples with their respective Locations and Identity**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample Id</th>
<th>Location</th>
<th>Date of Collection</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>S-1</td>
<td>Coal mine main sump discharge, MCL, Ib Valley area</td>
<td>30-01-2012</td>
</tr>
<tr>
<td>2.</td>
<td>S-2</td>
<td>Iron mines, Chhattisgarh</td>
<td>30-12-2011</td>
</tr>
<tr>
<td>3.</td>
<td>S-3</td>
<td>Coal mine sump discharge, MCL, North Central Ib Valley Nallah nearby Iron mines receiving its discharge</td>
<td>21-01-2012</td>
</tr>
<tr>
<td>4.</td>
<td>S-4</td>
<td>Nallah in between two iron mines</td>
<td>25- 02-2012</td>
</tr>
<tr>
<td>5.</td>
<td>S-5</td>
<td>Nallah in between two iron mines</td>
<td>25- 02-2012</td>
</tr>
<tr>
<td>7.</td>
<td>S-7</td>
<td>Nallah Adjacent to Manganese and Iron Mines</td>
<td>25- 02-2012</td>
</tr>
<tr>
<td>8.</td>
<td>S-8</td>
<td>Post mine stream (Manganese and Iron mines) of the nallah</td>
<td>25- 02-2012</td>
</tr>
<tr>
<td>9.</td>
<td>S-9</td>
<td>Nallah, 100 mtrs from the Iron Mine</td>
<td>26- 02-2012</td>
</tr>
<tr>
<td>10.</td>
<td>S-10</td>
<td>Nallah flowing downhill from a Iron Mine</td>
<td>26- 02-2012</td>
</tr>
</tbody>
</table>
Figure 4.1: Source of sample S-6

Figure 4.2: Source of sample S-7
Chapter 5

WATER QUALITY TESTS

Physical parameters

Metals

Inorganic non-metallic parameters

Organic parameters
5. WATER QUALITY TESTS

Water quality is the physical, chemical and biological characteristics of water. In the present work, these characteristics are determined following the guidelines prescribed by American Public Health Association (APHA, 1985) and Central pollution control board (CPCB).

The various parameters of interest present in water are broadly placed in four categories, namely Physical parameters, Metals, Inorganic Non-metallic contents or chemical compounds, Organic parameters.

Physical Parameters: This deals primarily with measurement of the physical properties of a sample. Many of the determinations included here are turbidity, conductivity, solids and temperature.

Metals: The effect of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Some metals are essential; others may adversely affect aquatic life. Some metals may be either beneficial or toxic, depending on their concentrations.

Chemical parameters and Inorganic Non-metallic Constituents: Acidity, pH, hardness, alkalinity, various forms of chlorine, nitrogen and phosphorous are the concerned parameters while analysing for inorganic constituents present in water. These constituents affect the quality of water in numerous ways.

Organic parameters: Direct determination of the Organic diversity and the ability of water to sustain life are troublesome. Hence parameters like Dissolved Oxygen content, Bio-chemical Oxygen Demand, Chemical Oxygen Demand and Total Organic Carbon content helps in deducing inference regarding ability of the water to sustain life in it. Therefore these parameters are determined with utmost accuracy and given importance in this work.

5.1 PHYSICAL PARAMETERS

The physical parameters include:
1. Colour
2. Turbidity
3. Conductivity
4. Solids
5. Odour
6. Temperature

Out of these parameters except odour, all others bear specific significance and the determination of which is necessary. The present study included determination of turbidity, conductivity and solids.

5.1.1. Determination of Turbidity: Turbidity can be measured by its effect on the scattering light, which is termed as Nephelometry. Turbidity meter can be used for sample with moderate turbidity and Nephlometer for sample with low turbidity. Higher the intensity of scattered lights higher the turbidity. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. Results from nephelometric measurements are expressed as nephelometric turbidity units (NTU).

**Procedure:**
1. Calibration curves are prepared using standard solutions of known turbidity.
2. Sample is subjected to test to find out the intensity of scattering light and as per the calibration curve turbidity is determined.

5.1.2. Determination of Conductivity: This method is used to measure the conductance generated by various ions in the solution/water. Rough estimation of dissolved ionic contents of water sample can be made by multiplying specific conductance (in mS/cm) by an empirical factor which may vary from 0.55 to 0.90 depending on the soluble components of water and on the temperature of measurement.

**Apparatus and Equipment:**
1. Self-contained conductance instruments: Conductivity meter.
2. Thermometer, 10-50°C.
3. Conductivity cells

**Reagents and standards:**
1. Standard potassium chloride 0.01M.

**Procedure:** Conductivity can be measured as per the instruction manual supplied with the instrument and the results may be expressed as mS/m or mS/cm. The temperature at which measurement is made is noted down.

5.1.3. **Determination of Solids:** The term ‘solid’ refers to the matter either filterable or non-filterable that remains as residue upon evaporation and subsequent drying at a defined temperature. Water with high dissolved solids results in unfavourable physiological reaction in the consumer. It is also unsuitable for many industrial applications. High suspended solids in waters may be aesthetically unsatisfactory. Analysis of total solids is important to decide upon the various unit operations and processes in physical and biological wastewater treatment.

**Principle:** Residue left after the evaporation and subsequent drying in oven at specific temperature 103-105°C of a known volume of sample are total solids. Total solids include “Total suspended solids” (TSS) and “Total dissolved solids” (TDS). Whereas loss in weight on ignition of the same sample at 500°C, 50°C, in which organic matter is converted to CO₂ volatilisation of inorganic matter as much as consistent with complete oxidation of organic matter, are volatile solids.

**Apparatus:**
1. Electrically heated temperature controlled oven
2. Monopan balance
3. Evaporating dish (200mL)
4. Pipettes
5. Measuring cylinder (100mL)

**Procedure:**
1. A known volume of a well-mixed sample is taken in a tarred dish ignited to constant weight (W1)
2. The sample is evaporated to dryness at 103-105°C for 24hrs.
3. Then it is cooled in desiccators, weighed and the reading is recorded. (W2)
4. The concentration is calculated in percent by weight.
**Calculation:**
The total solids is expressed as:

Total solids, mg/L = (W2 - W1) x 1000 / mL of sample

**Total dissolved solids:** It is the filterable residue is the material that passes through a standard glass filter disk and remains after evaporation and drying at 180°C.

Procedure
1. The well-mixed sample is filtered under vacuum through membrane filter or Gooch Crucible.
2. 100mL or more filtrate is taken in a weighed evaporating dish.
3. Then it is evaporated to dryness on steam bath for at least 1 hour in an oven at 180±2°C and is cooled in a desiccator and weighed.

Calculation:
Total filterable residue at 180°C = (A – B) x 1000 / C
Where:
A = weight of dried residue + dish
B = weight of dish
C = mL of filtrate used

**Total suspended solids:** It is found out by subtracting the total dissolved solids from the total solids.

5.2. DETERMINATION OF METALS

Metal content of water can be determined through various ways, such as Atomic Absorption Spectrometric Method, Phenanthroline Method, and Titration Method. Out of which the Atomic Absorption Spectrophotometry (AAS) is the most sensitive, rapid and modern method. The accuracy of this method is very high. So in this work for determination of metals AAS is used.

5.2.1 Atomic absorption spectrophotometry: In flame atomic absorption spectrometry, a sample is aspirated into a flame and atomized. A light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element in the flame. For some metal, atomic absorption exhibits superior sensitivity over flame emission. Because each metal has got its own characteristic absorption wavelength a source lamp composed of the elements is used, this marks the method relatively
free from spectral or radiation interference. Most atomic absorption instruments also are equipped for operation in an emission mode, which may provide better linearity for some elements.

There is always a chance of “chemical interference” which arises when the flame is not strong enough to dissociate the molecules resulting in lack of absorption by atoms.

**Apparatus and Reagents:**
1. Atomic absorption spectrometer
2. Burner
3. Readout
4. Lamps
5. Pressure reducing valves
6. Vent
7. Air and acetylene
8. Metal free water
9. Standard solution

**Procedure:**
1. Sample is digested for the use during estimation.
2. Appropriate hollow cathode lamp is installed as per the metal whose content is desired to be found and proper wave length is selected for the different metals. The table of wavelength as per metal and sensitivity is given below.
3. Slit width is set according to manufacturer-suggested setting for the element being measured and then current is turned on and adjusted as suggested by the manufacturer, and then the instrument is left to warm-up until energy source stabilises for about 10 to 20 min.
4. Wavelength is optimised by adjusting wavelength dial until optimum energy gain is obtained.
5. After installing suitable burner head, and allowing air flow as per maximum sensitivity acetylene is allowed and flame is ignited.
6. Calibration is performed by aspirating blank samples and standard samples and recording the absorbance of the respective ones.
Table 5.1: Suggested Wavelength for Different Metals during the use of Atomic Absorption Spectrophotometry:

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>328.1</td>
</tr>
<tr>
<td>Cd</td>
<td>228.8</td>
</tr>
<tr>
<td>Cr</td>
<td>357.6</td>
</tr>
<tr>
<td>Cu</td>
<td>324.7</td>
</tr>
<tr>
<td>Fe</td>
<td>248.3</td>
</tr>
<tr>
<td>Mn</td>
<td>279.5</td>
</tr>
<tr>
<td>Ni</td>
<td>232.0</td>
</tr>
<tr>
<td>Pb</td>
<td>283.3</td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
</tr>
</tbody>
</table>

7. After getting the calibration plot between concentration and absorbance, sample is analysed for the particular metal.
8. The concentration of the metal is directly recorded from the digital display or read out.
9. The flame is then extinguished by turning off the acetylene first followed by air.

*Calculation:*

The results are directly noted from the instrument.
5.3 CHEMICAL AND INORGANIC NON METALLIC PARAMETERS

Chemical and inorganic non-metallic parameters cover the followings:

1. pH
2. Hardness
3. Ammonia
4. Nitrate
5. Sulphate
6. Phenol
7. Fluoride
8. Phosphate

5.3.1 pH determination: The pH is determined by measurement of the electromotive force (EMF) of a cell comprising of an indicator electrode (an electrode responsive to hydrogen ions such as glass electrode) immersed in the test solution and a reference electrode (usually a calomel electrode). Contact is achieved by means of a liquid junction, which forms a part of the reference electrode. The EMF of this cell is measured with pH meter.

Since the pH is defined operationally on a potentiometric scale, the measuring instrument is also calibrated potentiometrically with an indicating (glass) electrode and a reference electrode using standard buffers having assigned pH value so that

\[
\text{pH}(B) = \log_{10} [H^+] \\
\text{Where,} \\
\text{pH}(B) = \text{assigned pH of standard buffer.}
\]

The operational pH scale is used to measure sample pH and is defined as:

\[
\text{pH}s = \text{pH}B + F (\text{Es} – \text{EB}) / 2.303 \text{ RT} \\
\text{Where,} \\
\text{pH}s = \text{potentiometrically measured sample Ph} \\
F = \text{Faraday 9.649 x 104 coulomb/mole} \\
\text{Es} = \text{Sample EMF V} \\
\text{EB} = \text{Buffer EMF V} \\
R = \text{Gas constant 1.987 cal deg-1 mole-1} \\
T = \text{absolute temperature, °K}
\]
**Apparatus and reagents required:**

1. pH meter
2. reference electrode
3. sensor electrode
4. beaker
5. stirrer
6. pH 4 buffer
7. pH 7 buffer
8. pH 10 buffer

**Calibration:**
Before use, remove the electrodes from the water and rinse with distilled or demineralised water. Dry the electrodes by gentle wiping with a soft tissue. Calibrate the electrode system against standard buffer solution of known pH. Because buffer solution may deteriorate as a result of mould growth or contamination, prepare fresh as needed for work or use readily available pH buffers. Use distilled water a conductivity of less than 2μ Siemens at 25°C and distilled and pH 5.6 to 6.0 for the preparation of all standard solutions. For routine analysis, commercially available buffer tablets, powders or solutions of tested quality also are permissible. Buffer having pH 4.0, 7.0 and 9.2 are available. In preparing buffer solutions from solid salts, dissolve all the material; otherwise, the pH calibration will be incorrect. Prepare and calibrate the electrode system with buffer solutions with pH approximating that of the sample, to minimise error resulting from nonlinear response of the electrode.

**Procedure:**
1. The electrodes are removed from storage solutions (recommended by manufacturer) and rinse with distilled water.
2. Electrodes are dried by gently blotting with a soft tissue paper, and are standardised using a buffer solution within 2 pH units of sample pH.
3. Electrodes are removed from buffer, and rinsed thoroughly with distilled water; then dried.
4. Same standardisation is followed with pH 10 buffer.
5. For samples analysis, equilibrium is established between electrodes and sample by stirring sample to ensure homogeneity and measure pH.

**Calculation:** The pH value is obtained directly from the instrument.
5.3.2 Determination of hardness: Water hardness is a traditional measure of the capacity of water to precipitate soap. It is caused by dissolved polyvalent metallic ions. In fresh water, the principal hardness causing ions are calcium and magnesium which precipitate soap. Total hardness is defined as the sum of the calcium and magnesium concentration, both expressed as CaCO$_3$, in mg/L.

**EDTA titration method**

**Principle:**
Hardness is determined by the EDTA method in alkaline condition. EDTA and its sodium salts from a soluble chelated complex with certain metal ions. Calcium and Magnesium ions develop wine red colour with Eriochrome black T in aqueous solution at pH 10.0 ± 0.1. When EDTA is added as a titrant, divalent ions of Calcium and Magnesium get complexed resulting in sharp change from wine red to blue which indicates end-point of the titration. Magnesium ion must be present to yield satisfactory point of the titration. Hence, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer. The sharpness of the end point increases with increasing pH. However, the specified pH of 10.0 ± 0.1 is a satisfactory compromise. At a higher pH i.e. at about 12.0 Mg$^{++}$ ions precipitate and only Ca$^{++}$ ions remain in solution. At this pH murexide (ammonium purpurate) indicator forms a pink colour with Ca$^{++}$. When EDTA is added Ca$^{++}$ gets complexed resulting in a change from pink to purple which indicates end point of the reaction. To minimise the tendency towards CaCO$_3$ precipitation limit the duration of titration period to 5 minutes

**Apparatus:**
1. Conical flasks 100mL
2. Burette
3. Pipette
4. Spatula
5. Buffer solution
6. Inhibitor
7. Eriochrome black T indicator
8. Murexide indicator
9. Sodium hydroxide 2N
10. Standard EDTA solution 0.01 M
11. Standard calcium solution

**Procedure:**

1. 25 or 50mL well mixed sample is taken in porcelain dish or conical flask.
2. 1-2mL buffer solution is added followed by 1mL inhibitor.
3. A pinch of Eriochrome black T is added and then titrated with standard EDTA (0.01M) till wine red colour changes to blue, the volume of EDTA required (A) is noted.
4. A reagent blank is run and the volume of EDTA (B) was found.
5. Volume of EDTA required by sample, C = (A - B) is calculated.

**Calculation:**

Total hardness as CaCO$_3$ mg/L = C x D x 1000 / mL sample.

where, C = volume of EDTA required by sample

D = mg CaCO$_3$ equivalent to 1mL EDTA titrant

**5.3.3. Determination of Ammonia Content:** Ammonia is mainly produced by microbial action of organic nitrogenous matter. Hence ammonia may be found in the water bodies near to coal deposits as coal itself contains nitrogenous material. Concentration of ammonia above a certain level is toxic to fish and other aquatic animals.

Ammonia is determined by colorimetry (nesslerisation) or by titration method.

**Titration method:** The titrimetric method is used only on samples that have been carried through preliminary distillation. This method is used especially for ammonia concentration up to 5 mg/L. Distillation with sulphuric acid is mandatory when interferences are present.

**Apparatus:**

1. Distillation Apparatus
2. pH meter

**Reagents:**

1. Mixed indicator solution
2. Indicating boric acid solution
3. Standard Sulphuric acid titrant, 0.02 N
**Procedure:**

1. Sample is taken as per the given table. Since ammonia content is expected to be low in the samples, 250 ml of samples is used.
2. The ammonia was titrated in distillate with standard 0.02 N \( \text{H}_2\text{SO}_4 \) titrant until indicator turned pale lavender.

<table>
<thead>
<tr>
<th>Ammonium nitrogen in sample (mg/L)</th>
<th>Sample volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-10</td>
<td>250</td>
</tr>
<tr>
<td>10-20</td>
<td>100</td>
</tr>
<tr>
<td>20-50</td>
<td>50</td>
</tr>
<tr>
<td>50-100</td>
<td>25</td>
</tr>
</tbody>
</table>

**Calculation:**

The ammonia content is measured by using the following:

\[ \text{mg of } \text{NH}_3 \text{ (N/L) = (A-B)} \times 280/ \text{ml sample} \]

Where,

A= Volume of \( \text{H}_2\text{SO}_4 \) titrated for sample, ml

B= Volume of \( \text{H}_2\text{SO}_4 \) titrated for blank, ml

**5.3.4. Determination of Nitrate content:** Nitrate is the highest oxidised form of nitrogen compounds that are present in natural waters. Chemical fertilizers, decayed vegetable and animal matter, domestic effluents, sewage sludge disposal to land, industrial discharge, leachates from refuse dumps and atmospheric washout are the significant sources of nitrate.

Though it can occur in all kinds of water bodies but it concentration may go higher in areas near coal mines due to their organic origin.

**Phenol Disulphonic Acid (PDA) method**
**Principle:**
Nitrate reacts with Phenol disulphonic acid and produces a nitro-derivative which in alkaline solution develops yellow colour due to rearrangement of its structure. The colour produced follows Beer’s law and is intensity proportional to the concentration of NO$_3$ present in the sample.

**Apparatus:**
1. Colorimetric or spectrophotometer having a range of 300-700nm.
2. Nessler tubes, capacity, 100mL.
3. Beakers, capacity, 100mL.
4. Water bath

**Reagents:**
1. Standard silver sulphate (1ml=1mg )
2. Phenol disulfonic acid (PDA)
3. Ammonium hydroxide NH$_4$OH conc
4. Potassium hydroxide, 12N
5. Standard nitrate solution(1ml=10 μg N)
6. EDTA reagent
7. Aluminium hydroxide

**Procedure:**
1. Calibration: the colorimeter is calibrated using standard nitrate solution and calibration curve (absorbance Vs. Concentration) is plotted.
2. Colour development:
   a. The clarified sample is neutralised to pH 7.0.
   b. Suitable aliquot of the sample is taken in a beaker and evaporated to dryness on water bath.
   c. The residue is dissolved using glass rod with 2mL phenol disulphonic acid reagent. Then is diluted and transferred to Nessler’s tubes.
   d. 8-10mL 12N KOH is added. If turbidity develops the EDTA reagent is added drop-wise till it dissolves.
   e. The solution is filtered and made up to 100mL. To avoid turbidity 10mL conc. NH$_4$OH is added instead of KOH.
   f. Blank is prepared in the same way using distilled water in place of sample.
g. Then the sample is subjected to colorimetry and the intensity of colour developed at 410nm with a light path of 1cm is read.

**Calculation:**
The concentration of Nitrate is calculated from the standard calibration curve and the values are reported in mg/L.

5.3.5. **Determination of Sulphate:** Sulphate occurs in natural waters in soluble form. They originate from oxidation of sulphate ore, presence of shale, from organic compounds. Sulphur-bearing mineral are common in most sedimentary rocks. In humid region, sulphate is readily leached from the zone of weathering by infiltrating waters and surface run off. Sulphate concentration is expected to be higher in areas near coal mines as minerals containing sulphur occur in coal deposits.

Ingestion of water containing high concentration of sulphate can have a laxative effect, which is enhanced when sulphate is consumed in combination with magnesium. Water containing magnesium sulphate at levels about 1000 mg/L acts as a purgative in human adults. Taste threshold concentrations for the most prevalent sulphate salts are 200-500mg/L for sodium sulphate, 250-900mg/L for calcium sulphate, and 400-600mg/L for magnesium sulphate.

**Gravimetric Method with Ignition of Residue**

**Principle:**
Sulphate is precipitated in a hydrochloric acid (HCl) solution as barium Sulphate (BaSO₄) by the addition of barium chloride (BaCl₂). The precipitation is carried out near the boiling temperature, and after a period of digestion the precipitate is filtered, washed with water until free of chloride ion, ignited or dried, and weighed as (BaSO₄). The gravimetric determination of Sulphate is subject to many errors, both positive and negative. Interferences leading to high results-suspended matter, silica, nitrite and occluded mother liquor in the precipitate are the principal factors in positive errors. Interferences leading to low results-alkali metal Sulphates frequently yield low results.

**Apparatus:**
1. Steam bath
2. Drying oven
3. Muffle furnace
4. Desiccator
5. Analytical Balance
6. Filter
7. Filtering apparatus

**Reagents:**
1. Methyl red indicator solution
2. Hydrochloric acid
3. Barium chloride solution
4. Silver nitrate-nitric acid
5. Silicone fluid

**Procedure:**
1. Ba(+II) is added in excess under acidic conditions, BaSO₄ is precipitated quantitatively. The reaction is allowed to continue for 2 hours or more at 80-90˚C. This is to encourage the formation of BaSO₄ crystals (non-filterable) from the initially formed colloidal precipitate (partially filterable).
2. The precipitate is washed, and then dried at 800˚C for 1 hour. Low pH is needed to avoid the precipitation of BaCO₃ and Ba₃(PO₄)₂. Positive bias may result from acid-resistant insoluble matter such as silica, Sulphites which may oxidize to Sulphate, and nitrate and chloride which will associate with barium and co-precipitate to a small extent with the barium Sulphate. Negative bias may result from the presence of certain heavy metals (e.g., Cr, Fe) which can form soluble complexes with Sulphate.

**Calculation:**

\[ \text{mg SO}_4^{2-}/\text{L} = \text{mg BaSO}_4 \times 411.6/\text{mL sample} \]

**5.3.6. Determination of phenol:** Phenols, detergents and other organic materials may be toxic to phyto and zoo-plankton beyond certain levels. Organic compounds may enter water environment through human waste disposal and industrial discharges. Phenols are defined as hydroxyl derivatives of benzene, and its condensed nuclei occur in domestic and industrial wastewaters, natural wastes and potable water supplies. Odoriferous and objectionable tasting chlorophenols are formed as a result of chlorination of water containing phenol. Phenols may be present in raw water owing to the discharge of wastewaters from coke distillation plants, the petrochemical industry and numerous other industries where phenols serve as intermediates.

**Chloroform extraction method:**
**Principle:**
The steam distillable phenols react with 4-aminoantipyrine at a pH of 7.9 in presence of potassium ferricyanide to form a coloured antipyrine dye. The dye is extracted from aqueous solution with chloroform and the intensity is measured at 460 nm. This method is applicable in the concentration range of 1 μg/L to 250 μg/L with a sensitivity of μg/L.

**Apparatus and equipment:**
1. Distillation assembly with graham’s condenser
2. Spectrophotometer for use at 460 nm
3. pH meter
4. Separatory funnels and beakers

**Reagent:**
1. Phosphoric acid (0.45%)
2. Methyl orange indicator
3. Sulphuric acid 1N
4. Sodium chloride crystals
5. Chloroform or ethyl ether
6. Sodium hydroxide (2.5N)
7. Standard phenol solution (1ml=1mg of phenol)
8. Bromate bromide solution (0.1N)
10. Standard sodium thiosulphate (0.025N)
11. Starch solution
12. Ammonium hydroxide (0.5N)
13. Phosphate buffer solution
14. 4-Aminoantipyrine solution
15. Potassium ferricyanide solution
16. Sodium sulphate
17. Potassium iodide

**Procedure:**
1. Calibration: By titration the concentration of standard phenol is to be measured.
2. Distillation: 500 mL sample is taken in a beaker, and 50 mL phenol-free distilled water is added, and so the pH is lowered to 4.0 with H$_3$PO$_4$ solution using methyl orange as an indicator. 5 mL of CuSO$_4$ solution is added. The solution is transferred to distillation flask and 500 mL of distillate is collected using measuring cylinder as receiver.

3. Extraction and colour development:
   - 500 mL of the distillate is taken containing more than 50 mg phenol and is diluted to 500 mL in 1 litre beaker.
   - 500 mL of distilled water blank and a series of 500 mL phenol standards containing 5, 10, 20, 30, 40 and 50 μg phenol is taken in respective beakers.
   - 12 mL 0.5 N NH$_4$OH solution is added and the pH of each is adjusted to 7.9 ± 0.1 with phosphate buffer. About 10 mL phosphate buffer is required. Then it is transferred to 1 litre separating funnel, and 3.0 mL 4-aminooantipyrine solution in each separatory funnel is added and mixed well. 3.0 mL of potassium ferricyanide is added and the colour is allowed to develop for 15 min.
   - 25 mL chloroform is added in each separatory funnel and is shaken for at least 10 times. CHCl$_3$ extract is filtered through filter paper containing 5 g layer of anhydrous Na$_2$SO$_4$.
   - The dried extract clean cells are extracted and the absorbance is measured of the sample and standard against the blank at 460 nm.
   - Absorbance against mg phenol concentration is plotted and a calibration curve is drawn. Phenol content is measured from photometric reading by using a calibration curve.

**Calculations:**

Use of calibration curve,

μg/L, phenol = [(A / B) x 1000]

Where:

A = μg phenol in sample (estimated from calibration curve)
B = mL original sample

5.3.7 Determination of Fluoride: Fluoride has significant role and optimum concentration of it is desired within limits as excess of it causes fluorosis and when of less concentration it results in dental caries.

SPANDS, a colorimetric method, and Ion Selective Electrode method are generally used to determine Fluoride content.
**Ion selective electrode method:**

**Principle:**

When the fluoride electrode is dipped in sample whose concentration is to be measured, a potential is established by the presence of fluoride ions by any modern pH meter having an expanded millivolt scale. Measuring the developed potential helps in finding the concentration.

**Apparatus:**

1. Ion meter (field/laboratory mode) or pH/mV meter
2. Reference electrode (calomel electrode)
3. Fluoride-sensitive electrodes
4. Magnetic stirrer
5. Plastic lab ware

**Reagents:**

1. Standard fluoride solution
2. Total Ionic Strength Adjustment Buffer (TISAB)

**Procedure:**

1. Calibration: the electrode is calibrated using the standard fluoride solution.
2. Connection of the electrodes to meter and for further operations of the instrument is done as per the instruction manual supplied by the manufacturer.
3. The electrode slope is checked with the ion meter (59.16mV for monovalent ions and 29.58mV for divalent ions at 25°C).
4. 50 to 100mL of sample is taken in a 150mL plastic beaker. TISAB is added.
5. Electrode is rinsed, blotted dry and placed in the sample. Stirring is done thoroughly and the steady reading on the meter is noted.
6. Recalibration is done in every 1 hour.
7. Direct measurement results can be verified by a known addition procedure. The known addition procedure involves adding a standard of known concentration to a sample solution. From the change in electrode potential before and after addition, the original sample concentration is determined.
**Calculation:**
The concentration in mg/L is obtained directly from the specific ion meter.

**5.3.8 Determination of phosphate:** Various forms of Phosphates get into water source mainly via waste water from residential area or from fertiliser and cleaning industry. The presence of phosphate in large quantities in fresh waters indicates pollution through sewage and industrial wastes. It promotes growth of nuisance causing micro-organisms. Though phosphate poses problems in surface waters, its presence is necessary for biological degradation of wastewaters.

**Stannous chloride method:**

**Principle:**
In phosphate analysis the phosphorous in any form is tried to convert into orthophosphate form mainly via acid hydrolysis. In acidic condition, orthophosphate reacts with ammonium molybdate to form molybdophosphoric acid. It is further reduced to molybdenum blue by adding reducing agent such as stannous chloride or ascorbic acid. The blue colour developed after addition of ammonium molybdate is measured at 690 or 880nm within 10-12 minutes after development of colour by using blank. The concentration is calculated from the standard graph. The intensity of the blue coloured complex is measured which is directly proportional to the concentration of phosphate present in the sample.

**Apparatus:**
1. Colorimeter for use at 690nm and 880nm providing 0.5cm light path.
2. Nessler tubes, 100mL

**Reagents:**
1. Stock phosphate solution
2. Ammonium molybdate solution
3. Strong acid reagent (concentrated H$_2$SO$_4$+ 4ml of HNO$_3$)
4. Sodium hydroxide 6N
5. Phenolphthalein indicator
6. Stannous chloride reagent I
7. Dilute stannous chloride reagent II
8. Potassium antimonyl tartrate solution
9. Ascorbic acid
10. Combined reagent(combination of the reagents 2, 3, 8, 9)

Procedure:
1. Absorbance vs. Phosphate concentration is plotted for the colorimeter using working phosphate solution and blank solution and so the instrument is calibrated.
2. For Total phosphate: Organically combined phosphorus and all phosphate including polyphosphate as first converted to orthophosphate by digestion as given below.
3. 100mL of well mixed sample is taken in a 150mL conical flask and one drop of phenolphthalein indicator is added. If red colour develops, sulphuric acid solution is added drop wise to just discharge the colour.
4. Then 1mL sulphuric acid solution in excess is added and boiled gently for at least 90 minutes, adding distilled water to keep the volume between 25 and 50mL. One drop of phenolphthalein indicator is added after it cooled and is neutralized to a faint pink colour with hydroxide solution.
5. 50 ml of the solution is taken in colorimetry and then concentration of phosphate is read from calibration curve.

Calculation:
The concentration is found out from the absorbance vs. Concentration plot.

5.4. DETERMINATION OF ORGANIC PARAMETERS

The most important parameters that bear importance to the organic activity and the life in the aquatic media are Dissolved Oxygen, Bio-chemical Oxygen Demand, Chemical Oxygen Demand and the Total Organic Carbon. Hence these parameters are given equal importance with that of the metal content and are determined in this work.

5.4.1 Determination of dissolved Oxygen: Dissolved Oxygen is the oxygen content of any water body. All aquatic organisms depend on this to sustain. So DO level helps to assess quality of raw water to keep check on pollution.

Winkler method with Azide modification:

Principle:
Oxygen present in sample rapidly oxidises the dispersed divalent manganous hydroxide to its higher valency, which is precipitated as a brown hydrated oxide after the addition of NaOH/KOH and KI. Upon acidification, manganese reverts to divalent state and liberates iodine from KI equivalent to the original DO content. The liberated iodine is titrated against Na2S2O3 (N/40) using starch as an indicator. The chemical reactions involved in the method are given below:

1. \( \text{MnSO}_4 + 2\text{KOH} \rightarrow \text{Mn(OH)}_2 + \text{K}_2\text{SO}_4 \) (white ppt)
2. \( 2\text{Mn(OH)}_2 + \text{O}_2 \rightarrow 2 \text{MnO(OH)}_2 \) (Brown ppt)
3. \( \text{MnO(OH)}_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{Mn(SO}_4)_2 + 3\text{H}_2\text{O} \)
4. \( \text{Mn(SO}_4)_2 + 2 \text{KI} \rightarrow \text{MnSO}_4 + \text{K}_2\text{SO}_4 + \text{I}_2 \)
5. \( 2\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O} + \text{I}_2 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaCl} + 10\text{H}_2\text{O} \)
6. \( 2\text{NaN}_3 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HN}_3 + \text{Na}_2\text{SO}_4 \)
7. \( \text{HNO}_2 + \text{HN}_3 \rightarrow \text{N}_2 + \text{N}_2\text{O} + \text{H}_2\text{O} \)

**Apparatus and reagents:**

1. BOD bottles, capacity 300mL
2. Sampling device for collection of samples
3. Manganese sulphate
4. Alkali iodide-azide reagent
5. Sulphuric acid
6. Starch indicator
7. Standard sodium thiosulphate (0.025N)

**Procedure:**

1. Sample is collected in a BOD bottle.
2. 1mL MnSO4 is added followed by 1mL of alkali-iodide-azide reagent to a sample collected in 250 to 300mL bottle up to the brim and then is repeatedly inverted to mix well.
3. The precipitate is allowed to settle. (It is white if the sample is devoid of oxygen, and becomes increasingly brown with rising oxygen content.)
4. 1mL conc. H2SO4 is added and the stopper is replaced and mixed well till precipitate goes into solution.
5. 201mL of this solution is taken in a conical flask and is titrated against standard Na2S2O3 solution using starch (2mL) as an indicator. When 1mL MnSO4 followed by 1mL alkali-
iodide-azide reagent is added to the samples as in (2) above, 2mL of original sample is lost. Therefore 201mL is taken for titration which will correspond to 200mL of original sample. 200 x 300/ (300-1) = 201mL

**Calculation:**

1mL of 0.025N Na$_2$S$_2$O$_3$ = 0.2mg of O$_2$

DO in mg/L = (0.2 x 1000) x (0.025N) ml of thiosulphate / 200

**5.4.2 Determination of Biochemical Oxygen Demand:** The Biochemical Oxygen Demand (BOD) is the oxygen requirement for aerobic oxidation of decomposable organic matter and certain inorganic materials in water, polluted waters and wastewater under controlled conditions of temperature and incubation period.

**Principle:**

This test measures the oxygen utilised for the biochemical degradation of organic material (carbonaceous demand) and oxidation of inorganic material such as sulphides and ferrous ions during a specified incubation period. It also measures the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. Temperature effects are held constant by performing a test at fixed temperature. The methodology of BOD test is to compute a difference between initial and final Do of the samples incubation. Minimum 1.5 L of sample is required for the test. DO is estimate by iodometric titration.

**Equipment, apparatus and reagents:**

1. BOD bottles 300mL capacity
2. Incubator or water-bath to be controlled at 20ºC or at any desired temperature 1ºC.
3. Phosphate buffer
4. Magnesium sulphate
5. Calcium chloride
6. Ferric chloride
7. Sodium sulphate solution 0.025N
8. Acid and Alkali solutions 1N
9. Glucose-glutamic acid solution
10. Nitrification inhibitor
11. Alkali iodide-azide reagent
12. Sulphuric acid
13. Starch indicator
14. Standard sodium thiosulphate (0.025N)

**Procedure:**

**Preparation of dilution water:**
1. Distilled water, tap or receiving-stream water free of biodegradable organics and bio-inhibitory substances such as chlorine or heavy metals are used.
2. The required volume of dilution water is aerated in a suitable bottle by bubbling clean-filtered compressed air for sufficient time to attain DO saturation at room temperature or at 20ºC/27ºC.
3. 1mL each of phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride are added to solutions in that order for each Litre of dilution water.
4. For wastes which are not expected to have sufficient microbial population, seed is essential. BOD of the seeding material is determined.

**Sample preparation:**
1. The sample is neutralised to pH 7, if it is highly acidic or alkaline.
2. The sample is freed from residual chlorine using Na$_2$S$_2$O$_3$ solution.
3. Samples are brought down to 20 ± 1ºC before making dilutions.
4. If nitrification inhibition is desired, 3mg 2-chloro-6-(trichloromethyl) pyridine (TCMP) is added to each 300mL bottle before capping or sufficient amount to the dilution water is added to make a final concentration of 30mg/L.
5. Samples having high DO contents, DO ≥ 9mg/L are treated to reduce the DO content to saturation at 20ºC. The sample is agitated or aerated with clean, filtered compressed air.
6. Dilutions that result in a residual DO of at least 1mg/L and DO uptake of at least 2mg/L produces reliable results. So several dilutions are made to pre-treated sample so as to obtain about 50% depletion of DO or DO uptake of 2mg/L.

**Sample processing:**
1. The diluted or undiluted sample is siphoned in three labelled bottles and stopper immediately.
2. DO of 1 bottle is determined initially and the other 2 bottles are kept at 20°C for 3days.
3. The O₂ consumption is measured in dilution water.
4. BOD of seed blank is determined for correction of actual BOD.
7. DO in a BOD test can is determined in the blank on initial day and end of incubation period by Winkler method as described for DO measurement.

Calculations:
BOD of the sample is calculated as follows:
a. When dilution water is not seeded
   \[ \text{BOD as O}_2 \text{ mg/L} = \frac{(D1 - D2) \times 100}{\% \text{ dilution}} \]

b. When dilution is seeded
   \[ \text{BOD O}_2 \text{ mg/L} = \left\{ \frac{(D1 - D2) - (B1 - B2) \times 100}{\% \text{ dilution}} \right\} \]
Where,
D1 = DO of sample immediately after preparation, mg/L
D2 = DO of sample after incubation period, mg/L
B1 = DO of blank (seeded dilution water) before incubation, mg/L
B2 = DO of blank (seeded dilution water) after incubation, mg/L

5.4.3 Determination of Chemical Oxygen Demand: Chemical Oxygen Demand (COD) test determines the oxygen requirement equivalent of organic matter that is susceptible to oxidation with the help of a strong chemical oxidant. It is an important, rapidly measured parameter which provides the means of measuring organic strength for streams and polluted water bodies. The test can be related empirically to BOD, organic carbon or organic matter in samples from a specific source taking into account its limitations. This test is relatively easy, precise, and fast.

Open Reflux method:
This method uses potassium dichromate for oxidation. The organic matter gets oxidised completely by potassium dichromate (K₂Cr₂O₇) with silver sulphate as catalyst in the presence of concentrated H₂SO₄ to produce CO₂ and H₂O. The excess K₂Cr₂O₇ remaining after the reaction is titrated with ferrous ammonium sulphate [Fe (NH₄)₂ (SO₄)₂]. The dichromate consumed gives the oxygen (O₂) required for oxidation of the organic matter. The chemical reactions involved in the method are as under:
1. \[2\text{K}_2\text{Cr}_2\text{O}_7 + 8 \text{H}_2\text{SO}_4 \rightarrow 2 \text{K}_2\text{SO}_4 + 2 \text{Cr}_2\text{(SO}_4)_3 + 8 \text{H}_2\text{O} + 3\text{O}_2\]
2. \[\text{C}_6\text{H}_12\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}\]
3. \[\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}\]

**Apparatus:**

1. 250 or 500mL Erlenmeyer flask with standard (24/40) tapered glass joints
2. Friedrich’s reflux condenser (12 inch) with standard (24/40) tapered glass joints
3. Electric hot plate or six-unit heating shelf
4. Volumetric pipettes (10, 25, and 50mL capacity)
5. Burette, 50mL with 0.1mL accuracy
6. Burette stand and clamp
7. Analytical balance, accuracy 0.001
8. Spatula
9. Volumetric flasks (1000mL capacity)
10. Boiling beads, glass
11. Magnetic stirrer and stirring bars

**Reagents and standards:**

1. Standard potassium dichromate solution, 0.25N (0.04167 M)
2. Sulphuric acid reagent
3. Standard ferrous ammonium sulphate approx. 0.25N (0.25M)
4. Ferroin indicator
5. Mercuric Sulphates
6. Potassium hydrogen phthalate (KHP) Standard

**Procedure:**

Sample Preparation:

1. All samples high in solids are blended for 2 minutes at high speed and stirred when an aliquot is taken for analysis.
2. Proper volume of sample is selected based on expected COD range. (e.g. for COD range of 50-500 mg/L take 25-50mL of sample)

Reflux of Samples:

1. 0.4g HgSO₄ is added to a 250mL reflux sample.
2. 20mL sample or an aliquot of sample diluted to 20mL with distilled water is added to it and is mixed well.

3. Clean pumice stones or glass beads are added.

4. 10mL 0.25N (0.04167M) K₂Cr₂O₇ solution is added and mixed.

5. 30mL concentrated H₂SO₄ containing Ag₂SO₄ is added slowly and thoroughly. This slow addition along with swirling prevents fatty acids to escape due to generation of high temperature. Alternatively a flask is attached to condenser with water flowing and then H₂SO₄ is added slowly through condenser to avoid escape of volatile organic substance due to generation of heat.

6. Mixing is performed and if the colour turned green, either fresh sample is taken with lesser aliquot or more potassium dichromate and acid is added.

7. The flask is attached condenser. The contents are mixed before heating.

8. The sample is left to be refluxed for a minimum of 2 hours. And then is cooled.

9. The reflux condenser is disconnected and the mixture is diluted to about twice its volume with distilled water. After cooling down to room temperature the excess K₂Cr₂O₇ is titrated with 0.1M FAS using 2-3 drops of ferroin indicator. The sharp colour change from blue green to reddish brown indicated the endpoint.

10. The same quantity of ferroin indicator is used for all titrations.

11. Blank is also refluxed in the same manner using distilled water instead of sample.

**Calculations:**
COD as mg/L = (a – b) x N x 8000 / mL sample
Where, a = mL FAS used for blank
b = mL FAS used for sample
N = normality of FAS
8000 = Milieq. wt. of O₂ x 1000
Chapter-6

RESULTS AND DISCUSSIONS
6. RESULTS AND DISCUSSION

6.1 RESULTS

The values of different physical parameters obtained after performing the above mentioned experiments are tabulated as follows.

Table 6.1: Results for Different physical Parameters

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Turbidity (NTU)</th>
<th>Conductivity (µS/cm)</th>
<th>Total Suspended Solids (mg/L)</th>
<th>Total Dissolved Solids (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max value in effluent** (#)5-WHO</td>
<td>-</td>
<td>**100</td>
<td>**2100</td>
<td></td>
</tr>
<tr>
<td>Max (BIS) limit¹</td>
<td>10</td>
<td>300</td>
<td>100</td>
<td>2000</td>
</tr>
<tr>
<td>S-1</td>
<td>21</td>
<td>3080</td>
<td>198</td>
<td>3.41</td>
</tr>
<tr>
<td>S-2</td>
<td>136</td>
<td>3090</td>
<td>172</td>
<td>5.66</td>
</tr>
<tr>
<td>S-3</td>
<td>80</td>
<td>2000</td>
<td>133</td>
<td>7.46</td>
</tr>
<tr>
<td>S-4</td>
<td>46</td>
<td>1800</td>
<td>78</td>
<td>4.6</td>
</tr>
<tr>
<td>S-5</td>
<td>3</td>
<td>1920</td>
<td>22</td>
<td>5.2</td>
</tr>
<tr>
<td>S-6</td>
<td>2</td>
<td>1950</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>S-7</td>
<td>25</td>
<td>1970</td>
<td>05</td>
<td>3.8</td>
</tr>
<tr>
<td>S-8</td>
<td>23</td>
<td>2180</td>
<td>11</td>
<td>4.2</td>
</tr>
<tr>
<td>S-9</td>
<td>9</td>
<td>2070</td>
<td>02</td>
<td>2.4</td>
</tr>
<tr>
<td>S-10</td>
<td>14</td>
<td>1910</td>
<td>25</td>
<td>3.3</td>
</tr>
</tbody>
</table>
Table 6.2. Experimental Results for Metal contents of Different samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Iron Content (mg/L)</th>
<th>Chromium hexavalent(mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max value in effluent**</td>
<td>**3</td>
<td>**0.1</td>
</tr>
<tr>
<td>Max (BIS) limit(^1)</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>S-1</td>
<td>1.2</td>
<td>Not traceable</td>
</tr>
<tr>
<td>S-2</td>
<td>80</td>
<td>Not traceable</td>
</tr>
<tr>
<td>S-3</td>
<td>1.2</td>
<td>Not traceable</td>
</tr>
<tr>
<td>S-4</td>
<td>8</td>
<td>Not traceable</td>
</tr>
<tr>
<td>S-5</td>
<td>0.94</td>
<td>Not traceable</td>
</tr>
<tr>
<td>S-6</td>
<td>1.12</td>
<td>Not traceable</td>
</tr>
<tr>
<td>S-7</td>
<td>42</td>
<td>Not traceable</td>
</tr>
<tr>
<td>S-8</td>
<td>1.2</td>
<td>Not traceable</td>
</tr>
<tr>
<td>S-9</td>
<td>2.20</td>
<td>Not traceable</td>
</tr>
<tr>
<td>S-10</td>
<td>2.4</td>
<td>Not traceable</td>
</tr>
</tbody>
</table>

Table 6.3. Experimental results of various inorganic Parameters

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>pH</th>
<th>Total Hardness(mg/L)</th>
<th>Calcium Hardness (mg/L)</th>
<th>Ammonia(mg/L)</th>
<th>Nitrate(mg/L)</th>
<th>Sulphate(mg/L)</th>
<th>Phenol(mg/L)</th>
<th>Fluoride(mg/L)</th>
<th>Phosphate(mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max value in effluent**</td>
<td>5.5-9</td>
<td>600</td>
<td>**50</td>
<td>**10</td>
<td>**1000</td>
<td>**1.0</td>
<td>**2.0</td>
<td>**5.0</td>
<td></td>
</tr>
<tr>
<td>Max (BIS) limit(^1)</td>
<td>6.5-8.5</td>
<td>#500-1000</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td>NT</td>
<td></td>
</tr>
<tr>
<td>S-1</td>
<td>6.5</td>
<td>120</td>
<td>0.18</td>
<td>0.8</td>
<td>459</td>
<td>0.08</td>
<td>0.35</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>S-2</td>
<td>5.5</td>
<td>650</td>
<td>0.31</td>
<td>0.5</td>
<td>NT</td>
<td>NT</td>
<td>0.05</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>S-3</td>
<td>6.5</td>
<td>-</td>
<td>2.22</td>
<td>23</td>
<td>41</td>
<td>NT</td>
<td>0.33</td>
<td>NT</td>
<td></td>
</tr>
</tbody>
</table>
### Table 6.4. Experimental Results for Organic Parameters:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Dissolved Oxygen (mg/L)</th>
<th>Bio-chemical Oxygen Demand (5) (mg/L)</th>
<th>Chemical Oxygen Demand (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max value in effluent**</td>
<td><strong>Min 5.0 mg/L</strong></td>
<td><strong>30 for 5 days</strong></td>
</tr>
<tr>
<td>Max (BIS) limit¹</td>
<td>Min 5.0mg/L</td>
<td>30</td>
<td>250</td>
</tr>
<tr>
<td>S-1</td>
<td>3.0</td>
<td>12</td>
<td>47</td>
</tr>
<tr>
<td>S-2</td>
<td>5.1</td>
<td>14</td>
<td>33</td>
</tr>
<tr>
<td>S-3</td>
<td>3.1</td>
<td>17</td>
<td>22</td>
</tr>
<tr>
<td>S-4</td>
<td>3.6</td>
<td>12</td>
<td>43</td>
</tr>
<tr>
<td>S-5</td>
<td>4.2</td>
<td>14</td>
<td>151</td>
</tr>
<tr>
<td>S-6</td>
<td>3.5</td>
<td>18</td>
<td>258</td>
</tr>
<tr>
<td>S-7</td>
<td>3.2</td>
<td>20</td>
<td>194</td>
</tr>
<tr>
<td>S-8</td>
<td>5.2</td>
<td>13</td>
<td>150</td>
</tr>
<tr>
<td>S-9</td>
<td>4.2</td>
<td>10</td>
<td>161</td>
</tr>
<tr>
<td>S-10</td>
<td>4.1</td>
<td>17</td>
<td>75</td>
</tr>
</tbody>
</table>

**The maximum permissible values of individual parameters are as provided in the Schedule VI of Environment (Protection) Rules, 1986.**

# The maximum value of parameters are as given in standard for drinking water by World Health Organisation (WHO).

¹is the maximum allowable limit for drinking water as stated in IS: 10500, 1991 and as accepted by Bureau of Indian Standards.
6.2 DISCUSSION

6.2.1 Physical parameters:

**Turbidity:** Turbidity of different water samples are compared with the WHO standard in the figure 6.1.

![Figure 6.1: turbidity of water samples](image)

From figure 6.1 it is observed that the turbidity of all samples except for S-5 and S-6 is higher than that of the maximum value as provided by the BIS/WHO for drinking purpose. Sample S-2, which is collected from the discharge location of iron mine showed maximum value which even crosses the effluent limit of turbidity. It shows the water has large amount of suspended material which is responsible for its high turbidity.

More over the samples collected from general body of water such as S-4, S-7, S-8 and S10 also have more turbidity than that of the standard. This indicates that though the sources may or may not be directly contaminated by the mining operation but are affected by it and so have high turbidity.

**Conductivity:** Conductivity of different samples are compared with the standard value as shown in figure6.2.
From the figure it may be concluded that the conductivity of all water samples are far more than that of the standard value as provided in Indian standards. Water samples from an Open cast coal mine of Ib Valley area, MCL and discharge location of an Iron mine showed maximum value as the solids in form of ions are expected to be higher in the discharge location.

Other samples also show a significant rise in the values attributing to the fact that most of the samples are collected near the metal mines.

**Total suspended solids and total dissolved solids:** Total suspended solids and total dissolved solids are compared to the maximum values in the effluent of the same as provided in schedule vi of Environment (protection) rule, 1986 (EP,1986) and maximum permissible limit of BIS.

From figure 6.3 and 6.4 it is quite clear that all the samples contained high amount of suspended solids (as indicated by high turbidity) but do not have dissolved solids to a significant level whose limit for effluents is 2100mg/L as per EP, 1986.

Sample S-1, S-2, and S-3 being the samples from the discharge location have the maximum suspended and dissolved solids. Other samples from the general sources of water do not have significant solids in them.
Figure 6.3: Total Suspended solids

Figure 6.4: TDS of different samples
6.2.2 Metallic Parameters: Results of the metal content of the sample water are shown and discussed below.

**Iron content:** The Iron contents of all the samples are shown in the figure 6.5 and are compared with the maximum value for effluent as provided in EP, 1986 as well as with maximum limit for drinking water as suggested by BIS.

From the figure it can be easily deduced that except S-2, S-4 and S-7 all other samples have less iron than the given limit. S-2, sample from discharge location of Chhattisgarh iron mines, shows the maximum iron content as expected. The S-4 sample being taken from a water source, which serves as sink to discharge of another Iron mine of Koirat region, shows higher iron content than the limit. Still the Fe content does not over exceed the limit as discharge of drainage water had been stopped and was not necessary in winter when sample was collected. S-7 sample, which is collected from a water source that crosses 2 iron mines and a manganese mine, is expected to have high values. But the content over exceeds the limit even in winter time.

![Figure 6.5: Iron Content of different water samples](image)

**Hexavalent Chromium:** None of the samples contained hexavalent Chromium, or at least the Cr\(^{6+}\) is in non traceable amount in all the samples.
6.2.3 Inorganic Chemical or Non-metallic Parameters:

**pH:** Figure 6.6 clearly indicates that all the samples are within the pH limit for effluent, which is 5.5-9. But the samples such as S-2, S-4, and S-6 are at the lower limits and so seek attention. Though the pH is within effluent limit, the water from these sources cannot be used as drinking water as they have lower pH than the BIS limit.

![Figure 6.6. pH content of the different samples and standard range of pH](image)

**Hardness:** The figure 6.7 shows the hardness of different samples and compares them with the maximum allowable value in drinking water as provided by WHO and BIS.

From figure 6.7 it can be clearly visualised that except sample S-2 all other samples show lower hardness than that of the maximum value. Discharge of Iron mine must be having high amount of carbonate salt of calcium and magnesium that caused the elevated hardness in the water.
Figure 6.7. Total and Calcium Hardness of different water samples

**Ammonia:** The ammonia content of different water sample is shown in the figure 6.8.

The maximum allowable concentration of ammonia in any water body is specified to be 50mg/L. From the figure it can be seen that all the water samples have almost negligible quantity of ammonia except for the water sample collected from the sump discharge of north-east Ib Valley deposit (Coal mine).
**Nitrate:** From figure 6.9 it may be inferred that the nitrate concentration in the sample of north-east Ib Valley deposit (Coal mine) is much more than that another deposit of Ib Valley. Only sample S-3 exceeds the permissible limit, whereas the concentration in other samples can be ignored unanimously.

**Figure 6.9. Nitrate content in different samples**

**Figure 6.10. Sulphate content in different samples.**
**Sulphate:** Figure 6.10 shows the sulphate content in the samples.

Apart from the samples collected from the coal mines, the sulphate content in every other water sample is untraceable. Presence of the sulphate concentration in the water sample S-1 from Ib Valley area is indicative of the sulphur content in coal in the form of pyrite. This fact is supported by the spontaneous heating, which is observed in that deposit. However, the sulphate concentration in sample S-3, which is also from a coal mine, is well under limit.

**Phenol:**

![Figure 6.11. Phenol content of water samples](image)

The phenol contents of different samples are shown in the figure 6.11 and are compared to the standard value as provided for effluents in EP, 1986. From the figure it is quite clear that phenol content in all the water samples is next to negligible. Only sample S-1 contains some amount of phenol whose source is unknown but may be due to the organic origin of the coal deposit.

**Fluoride:** The figure 6.12 represents the fluoride levels of various samples:

The maximum allowable fluoride content in water sample is 2.9mg/L as per EP, 1986. Figure 6.12 clearly indicates that the water samples contain significantly less amount of fluoride than that of the maximum limit.
Phosphate: Phosphate, which is significantly present in water source that serves as the discharge of laundering industry and domestic waste, is present in very low concentration in all the water samples since there are no such polluting sources. The present concentration is due to its natural origin.
6.2.4 Organic Parameters:

**Dissolved Oxygen:** Figure 6.14 represents the Dissolved oxygen content of all the water samples and compares them with the standard provided by EP, 1986 for the effluents. It can be easily deduced that except for S-2 and S-8 all other samples lack DO content. But the deficiency is not very high except for S-1, S-3 and S-7. The first two being discharge of coal mines certainly contain more organic nutrients and micro-organism owing to their less DO. S-7 which is contaminated by iron and manganese mines must be rich in nutrients because of which the DO is low.

![Dissolved Oxygen (mg/L)](image)

**Figure 6.14. DO in various samples.**

**Biological Oxygen Demand:** In figure 6.15 Bio- Chemical Oxygen Demand of all the water samples are shown and compared to the maximum permissible (BOD5) value for effluent as provided in EP, 1986. All samples have lower BOD than the limit (BOD3 limit value is 21.5mg/L). Only BOD of S-7, though less than the limit, almost equals to the maximum limit, which indicates and supports the fact that the source of S-7 is rich in nutrients.

**Chemical oxygen demand:** Figure 6.16 shows the Chemical Oxygen Demand of different water samples and compares them with the standard value. It is evident from the figure that most of the water samples have less COD than the maximum value except S-6. Which implies S-6 is rich in organic matter or equivalent to organic matter that can be oxidised by strong agents.
Since BOD of S-6 is low, so it can be said that they are not easily bio-degradable. Hence higher COD may not pose any problem. Though S-7 shows less COD than S13, still its COD is comparable and supports the fact that the source is contaminated with high amount of nutrients and may have micro-organism in plenty.
6.3. QUANTIFICATION OF THE RESULTS:

To quantify the pollution of the water sources, various parameters that are being analysed are combined to form a single index. Degree of contamination (Hakanson, 1980), (Backman et al., 1998) is one of such index that combines the parameters of concern, which can be defined as the summation of ratios of difference between maximum permissible value and observed value to that of maximum permissible value. The mathematical representation is as follows.

\[ C_d = \sum_{i=1}^{n} C_{fi}, \quad C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1 \]

Where, \( C_{Ai} \) and \( C_{Ni} \) are measured value and Maximum Allowable Concentration respectively and \( C_{fi} \) is contamination factor. The quality classification of water as per its \( C_d \) is given in table 6.5.

Table 6.5. classification of water sample as per C\(_d\) value

<table>
<thead>
<tr>
<th>( C_d )</th>
<th>Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td>Low pollution</td>
</tr>
<tr>
<td>1-3</td>
<td>Medium</td>
</tr>
<tr>
<td>&gt;3</td>
<td>Heavily polluted</td>
</tr>
</tbody>
</table>

Degree of contamination (\( C_d \)) is calculated using 14 parameters excluding pH, BOD and Phosphate and is tabulated below.

Table 6.6. \( C_d \) values of water samples

<table>
<thead>
<tr>
<th>Sl no</th>
<th>Sample Id</th>
<th>Degree of Contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S-1</td>
<td>39.76</td>
</tr>
<tr>
<td>2</td>
<td>S-2</td>
<td>93.4</td>
</tr>
<tr>
<td>3</td>
<td>S-3</td>
<td>4.85</td>
</tr>
<tr>
<td>4</td>
<td>S-4</td>
<td>6.253</td>
</tr>
<tr>
<td>5</td>
<td>S-5</td>
<td>-4.766</td>
</tr>
<tr>
<td>6</td>
<td>S-6</td>
<td>-4.1726</td>
</tr>
<tr>
<td>7</td>
<td>S-7</td>
<td>38.84</td>
</tr>
<tr>
<td>8</td>
<td>S-8</td>
<td>-1.784</td>
</tr>
<tr>
<td>9</td>
<td>S-9</td>
<td>-2.7</td>
</tr>
<tr>
<td>10</td>
<td>S-10</td>
<td>-2.39</td>
</tr>
</tbody>
</table>

From table 6.6 it is clear that the sample S-2, S-1, S-7 are ultra high polluted where as S-5 and s-6 are least polluted.
Chapter 7

CONCLUSION
7. CONCLUSION

Significant growth in metal and power industry and the rapid increase in demand of raw material have enhanced extent of the mining industry like never before. Both coal mining and metal mining have seen a huge transformation during the past decades. No wonder it has led to growth in economy and development of many localities and the country in general but the toll it has taken on the environment and ecology cannot and should not be ignored. The impact of mining activity on natural water bodies is wide and extensive. It has become a recent challenge for the industry, government and the environmentalist to prevent the water pollution due to various mining activity which may be direct or indirect cause for such pollution.

For the cause of which, in the present work water samples from regions belonging to the mining belt of western Odisha were collected and analysed. Samples from large coal mines (S-1 and S-3) open cast mines of Ib Valley area, MCL were subjected to analysis for the parameters like turbidity, conductivity, solids, iron, chromium content, pH, hardness, ammonia, nitrate, sulphate, phenol, fluoride, phosphate and organic parameters of importance such as Dissolved oxygen, Bio-chemical Oxygen Demand and Chemical Oxygen Demand. Koira mining zone, which has been producing a large amount of iron, bauxite and manganese for the country, has been a host for number of such mines for the last 30 years. Because of that contamination of the water body in and around the locality is highly probable. Hence water samples (S-4, S-5, S-6, S-7, S-8, S-9, and S-10) from around the metal mines from Koira zone are subjected to the same kind of analysis. Also water sample (S-2) from effluent discharge location of another iron mines, Chhattisgarh was collected for analysis.

From the results and discussions the following conclusions are drawn:

All the samples, that are being analysed and compared to the maximum permissible limit posed by Bureau of Indian Standard for potability, are found to exceed the limits and so are not suitable for drinking purpose. Despite the fact that many of them are critically polluted the water sources are used in day to day work of the local people of the concerned areas. The pollution extents can be summarised as follows: Turbidity, conductivity and solid content of S-1, S-2, S-3, S-4 and S-7 are higher than others and exceed the maximum permissible values. Iron content of S-2 and S-7 are far too greater than the limits. Though S-2 is collected from iron ore mine discharge, still the iron content is very high and treatment is necessary. On the contrary S-7 is considered to be heavily polluted for a general water stream. Iron
toxication may arise from it. None of the samples has significant Cr$^{6+}$ in them. pH of samples S-2, S-4 and S-6 is to be bothered as it is at its lower limit for effluents and below the minimum pH limit as per BIS. Hardness of S-2, the only sample, exceeds the limit posed by WHO and Indian Standard. Nitrate contents of all samples except S-3 are well below limits. S-3 has both higher ammonia (but within limits), nitrate. Sulphate, phenol, phosphate and fluoride contents of all the samples are within the permissible limit. S-2 and S-8 are having desired DO level. But all other samples lacked DO, the minimum of which are S-1 and S-2 which are nutritionally rich and also contain high solids hindering the oxygen transaction rendering them unsuitable for direct discharge to water bodies. Almost all samples have lower BOD$_3$ than the maximum limit except for S-7. S-7, which is rich in Iron, must be rich in other nutrients which are responsible for its higher BOD. COD of all samples are below the maximum value even for S-7 which showed highest BOD. S-6 has slightly elevated value than that of maximum indicates that it is rich in equivalent organic matter. The quantification of the experimental results via degree of contamination also supports the fact that S-1, S-2 and S-7 are highly polluted.

From the above it is observed that S-2 exceeds the contamination limits for physical and metal parameters but is within limits for others. Primary water treatment such as provision of retention tank before discharging the drainage can be helpful to lower solid and metal content. S-1 and S-3, samples from the coal mining areas, are having elevated concentrations of physical, chemical and organic parameters. Sedimentation and filtration may help in decreasing the solids. The same can be useful for Koira region that showed elevated solids and metals; such as sample S-1, S-7, which is having higher iron content and other nutrients. Since very large quantity of water to be handled in Koira zone, formation of wetlands and allowing water through them can decrease the metal and sediment content effectively and economically.

The fact that these elevations in values of the parameters are observed during the winter season is a matter of sheer concern, because surface run-off is negligible during this time. And contamination is only due to occasional discharge. So during monsoon and post monsoon period, introduction of heavy amount of contamination is expected and the resultant pollution will be far beyond the limiting values. This calls for a more detailed study of the water quality in the region mentioned. Based on the assessment of the key hydrological and geochemical attributes of mine water discharges, a rational decision-making framework can be developed for deciding which of these options to implement for control of water pollution.
due to mining. It is suggested that appropriate steps must be taken by the industry, State Pollution Control Board and the Government to prevent pollution of water. Implementation of preventive measures proposed can be helpful to a great extent.
8. REFERENCES


