Treatment of Waste Water by Electrochemical Means

by

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CERTIFICATE

This is to certify that the research work embodying in this thesis has been carried out under my supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any university or institution.

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A thesis on

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has been accepted as satisfactory in partial fulfillment of the requirements for the degree of Master of Philosophy (M. Phil) in Chemistry and certify that the student has demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on April 27, 2011.

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Dedicated

To

My Beloved Parents

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S. M. Aktaruzzaman
Author

Abstract

Applying electrode potential, tape water and waste water (Dhanmondi Lake’s Water) were treated using platinum electrode in a three-electrode and double compartment electrolysis cell system.

Various electrolysis conditions such as electrode, electrolytes, potential (applying voltage) and electrolysis time were optimized. Stainless steel and platinum electrode, 3 V to 7 V potential, NaCl, Na_2SO_4 & H_2SO_4 electrolytes and 1 Hr to 3 Hr contact time were studied for the treatment of tape water.

Water quality parameters such as pH, Conductivity, Total Dissolved Solid (TDS), Total Hardness, Dissolved Oxygen (DO), Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) of tape water were measured for optimization. After optimizing, waste water of Dhanmondi Lake was treated. Satisfactory results regarding Total Hardness, Conductivity, DO, COD and BOD compare to Bangladesh Standard and United States Public Health (USPH) Standard were observed.

CHAPTER 1

INTRODUCTION

1.1 Background and Present State of the Problem

Environmental issues have become serious social concerns. The impact of water pollution is getting more serious because it is closely related to the health and lives of human beings. The substances in water, like organic matters, nitrogen, phosphorous and dyes are the most common pollutants caused by human activities. These substances are emitted not only by everyday life activities but also by agriculture, livestock raising and other industrial activities. Many researchers investigated the wastewater treatment technologies such as physical, chemical, biological process. Researchers also studied advanced oxidation process like ozonation, photo-catalytic oxidation [1-3] and electrochemical oxidation [4] etc for water pollution control. As a new water and wastewater treatment method, electrochemical process is an emerging technology because of its high efficiency and relatively simple system [5-8]. In the electrochemical treatment process, organic pollutants in wastewater are electrochemically oxidized or reduced to non-hazardous inorganic substances. In electrochemical wastewater treatment, electrode material is one of the important factors that affect treatment efficiency. In this study, water and wastewater from different sources will be treated electrochemically and scale up the sample water quality with the standard**.**

1.2 General Introduction

Water is a chemical substance with the chemical formula H_2O. Its molecule contains one oxygen and two hydrogen atoms connected by covalent bonds. Water is a liquid at ambient conditions, but it often co-exists on Earth with its solid state, ice, and gaseous state, water vapor or steam.

Water covers 70.9% of the Earth's surface [9] and is vital for all known forms of life [10]. On Earth, it is found mostly in oceans and other large water bodies, with 1.6% of water below ground in aquifers and 0.001% in the air as vapor, clouds (formed of solid and liquid water particles suspended in air), and precipitation [11]. Oceans hold 97% of surface water, glaciers and polar ice caps 2.4%, and other land surface water such as rivers, lakes and ponds 0.6%. A very small amount of the Earth's water is contained within biological bodies and manufactured products.

Water on Earth moves continually through a cycle of evaporation or transpiration (evapotranspiration), precipitation, and runoff, usually reaching the sea. Over land, evaporation and transpiration contribute to the precipitation over land.

Clean drinking water is essential to human and other life forms. Access to safe drinking water has improved steadily and substantially over the last decades in almost every part of the world [12-13]. There is a clear correlation between access to safe water and GDP per capita [14]. However, some observers have estimated that by 2025 more than half of the world population will be facing water-based vulnerability [15]. A recent report (November 2009) suggests that by 2030, in some developing regions of the world, water demand will exceed supply by 50% [16]. Water plays an important role in the world economy, as it functions as a solvent for a wide variety of chemical substances and facilitates industrial cooling and transportation. Approximately 70% of freshwater is consumed by agriculture [17].

1.3 Sources of Water : The Hydrologic Cycle

The water cycle (known scientifically as the hydrologic cycle) refers to the continuous exchange of water within the hydrosphere, between the atmosphere, soil water, surface water, groundwater, and plants.

Water moves perpetually through each of these regions in the water cycle consisting of following transfer processes:

- evaporation from oceans and other water bodies into the air and transpiration from land plants and animals into air.

- precipitation, from water vapor condensing from the air and falling to earth or ocean.
- runoff from the land usually reaching the sea.

Most water vapor over the oceans returns to the oceans, but winds carry water vapor over land at the same rate as runoff into the sea, about 36 Tt per year. Over land, evaporation and transpiration contribute another 71 Tt per year. Precipitation, at a rate of 107 Tt per year over land, has several forms: most commonly rain, snow, and hail, with some contribution from fog and dew. Condensed water in the air may also refract sunlight to produce rainbows.

Water runoff often collects over watersheds flowing into rivers. A mathematical model used to simulate river or stream flow and calculate water quality parameters is hydrological transport model. Some of water is diverted to irrigation for agriculture. Rivers and seas offer opportunity for travel and commerce. Through erosion, runoff shapes the environment creating river valleys and deltas which provide rich soil and level ground for the establishment of population centers. A flood occurs when an area of land, usually low-lying, is covered with water. It is when a river overflows its banks or flood from the sea. A drought is an extended period of months or years when a region notes a deficiency in its water supply. This occurs when a region receives consistently below average precipitation.

Hydrology is the study of the movement, distribution, and quality of water throughout the Earth. The study of the distribution of water is hydrographic. The study of the distribution and movement of groundwater is hydrogeology, of glaciers is glaciology, of inland waters is limnology and distribution of oceans is oceanography. Ecological processes with hydrology are in focus of eco-hydrology. The collective mass of water found on, under, and over the surface of a planet is called the hydrosphere. Earth's approximate water volume (the total water supply of the world) is 1,360,000,000 km^3

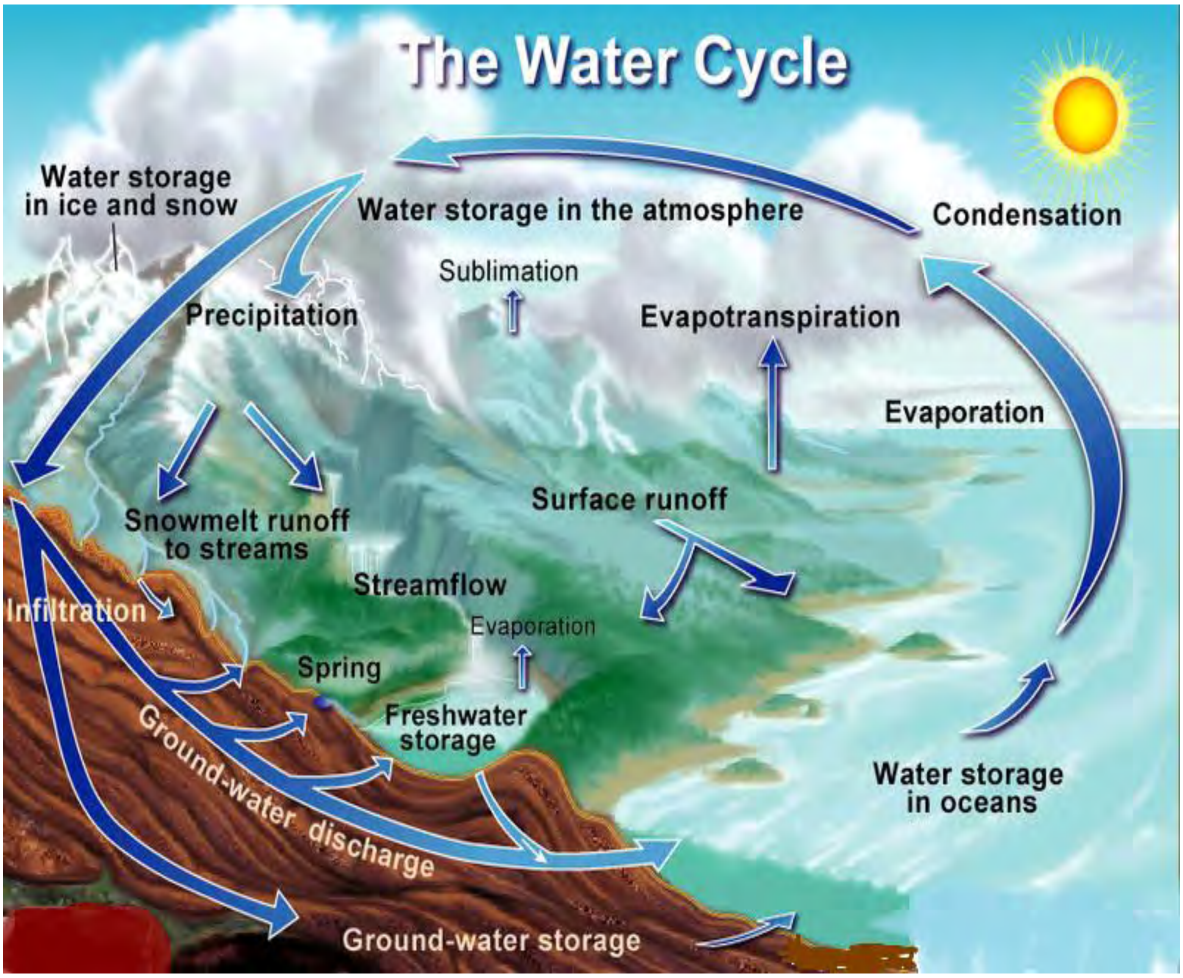


Fig. 1.1 Water cycle

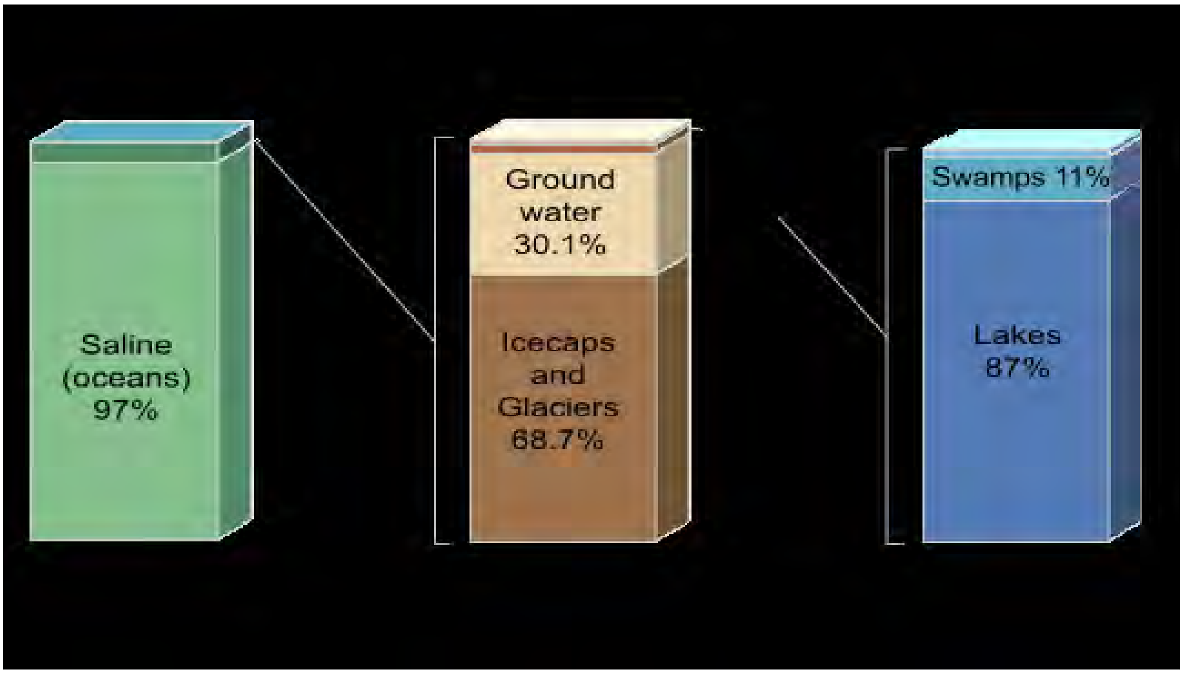


Fig 1.2 A graphical distribution of the locations of water on Earth.

Table 1.1 World water distribution [18]

Location	Volume, 10^{12} m^3	% of total
Fresh water lakes	125	0.009
Saline lakes and inland seas	104	0.008
Rivers	1.25	0.0001
Soil Moisture	67	0.005
Ground Water (above depth of 4000m)	8350	0.61
Atmosphere	13	0.001
Oceans	1320000	97.3

1.4 Physical and Chemical Properties of Water

The major chemical and physical properties of water are:

- Water is a tasteless, odorless liquid at standard temperature and pressure. The color of water and ice is, intrinsically, a very slight blue hue, although water appears colorless in small quantities. Ice also appears colorless, and water vapor is essentially invisible as a gas [19].

- Water is transparent, and thus aquatic plants can live within the water because sunlight can reach them. Only strong UV light is slightly absorbed.

- Water is a polar molecule with an electrical dipole moment. Water also can form an unusually large number of intermolecular hydrogen bonds (four) for a molecule of its size. These factors lead to strong attractive forces between molecules of water, giving rise to water's high surface tension [20] and capillary forces. The capillary action refers to the tendency of water to move up a narrow tube against the force of gravity. This property is relied upon by all vascular plants, such as trees.

- Water is a good solvent and is often referred to as the universal solvent. Substances that dissolve in water, e.g., salts, sugars, acids, alkalis, and some gases – especially oxygen, carbon dioxide (carbonation) are known as hydrophilic (water-loving) substances, while those that do not mix well with water (e.g., fats and oils), are known as hydrophobic (water-fearing) substances.

- All the major components in cells (proteins, DNA and polysaccharides) are also dissolved in water.

- Pure water has a low electrical conductivity, but this increases significantly with the dissolution of a small amount of ionic material such as sodium chloride.

- The boiling point of water (and all other liquids) is dependent on the barometric pressure. For example, on the top of Mt. Everest water boils at 68 °C, compared to 100 °C at sea level. Conversely, water deep in the ocean near geothermal vents can reach temperatures of hundreds of degrees and remain liquid.

- Water has the second highest molar specific heat capacity of any known substance, after ammonia, as well as a high heat of vaporization (40.65 $kJ \cdot mol^{-1}$), both of which are a result of the extensive hydrogen bonding between its molecules. These two unusual properties allow water to moderate Earth's climate by buffering large fluctuations in temperature.

- The maximum density of water occurs at 3.98 °C [21]. It has the anomalous property of becoming less dense, not more, when it is cooled down to its solid form, ice. It expands to occupy 9% greater volume in this solid state, which accounts for the fact of ice floating on liquid water.

- Water is miscible with many liquids, such as ethanol, in all proportions, forming a single homogeneous liquid. On the other hand, water and most oils are immiscible usually forming layers according to increasing density from the top. As a gas, water vapor is completely miscible with air.

- Water forms an azeotrope with many other solvents.

- Water can be split by electrolysis into hydrogen and oxygen.

- As an oxide of hydrogen, water is formed when hydrogen or hydrogen-containing compounds burn or react with oxygen or oxygen-containing compounds. Water is not a fuel, it is an end-product of the combustion of hydrogen. The energy required splitting water into hydrogen and oxygen by electrolysis or any other means is greater than the energy released when the hydrogen and oxygen recombine [22].

- Elements which are more electropositive than hydrogen such as lithium, sodium, calcium, potassium and cesium displace hydrogen from water, forming hydroxides. Being a flammable gas, the hydrogen given off is dangerous and the reaction of water with the more electropositive of these elements may be violently explosive.

1.5 Importance of Water

From a biological standpoint, water has many distinct properties that are critical for the proliferation of life that set it apart from other substances. It carries out this role by allowing organic compounds to react in ways that ultimately allow replication. All known forms of life depend on water. Water is vital both as a solvent in which many of the body's solutes dissolve and as an essential part of many metabolic processes within the body. Metabolism is the sum total of anabolism and catabolism. In anabolism, water is removed from molecules (through energy requiring enzymatic chemical reactions) in order to grow larger molecules (e.g. starches, triglycerides and proteins for storage of fuels and information). In catabolism, water is used to break bonds in order to generate smaller molecules (e.g. glucose, fatty acids and amino acids to be used for fuels for energy use or other purposes). Without water, these particular metabolic processes could not exist.

Water is fundamental to photosynthesis and respiration. Photosynthetic cells use the sun's energy to split off water's hydrogen from oxygen. Hydrogen is combined with CO_2 (absorbed from air or water) to form glucose and release oxygen. All living cells use such fuels and oxidize the hydrogen and carbon to capture the sun's energy and reform water and CO_2 in the process (cellular respiration).

Water is also central to acid-base neutrality and enzyme function. An acid, a hydrogen ion (H^+, that is, a proton) donor, can be neutralized by a base, a proton acceptor such as hydroxide ion (OH^-) to form water. Water is considered to be neutral, with a pH (the negative log of the hydrogen ion concentration) of 7. Acids have pH values less than 7 while bases have values greater than 7.

1.5.1 Aquatic Life Forms

Earth's surface waters are filled with life. The earliest life forms appeared in water; nearly all fish live exclusively in water, and there are many types of marine mammals, such as dolphins and whales. Some kinds of animals, such as amphibians, spend portions of their lives in water and portions on land. Plants such as kelp and algae grow in the water and are the basis for some underwater ecosystems. Plankton is generally the foundation of the ocean food chain.

Aquatic vertebrates must obtain oxygen to survive, and they do so in various ways. Fish have gills instead of lungs, although some species of fish, such as the lungfish, have both. Marine mammals, such as dolphins, whales, otters, and seals need to surface periodically to breathe air. Some amphibians are able to absorb oxygen through their skin. Invertebrates exhibit a wide range of modifications to survive in poorly oxygenated waters including breathing tubes (Diptera and some molluscs) and gills (Carcinus). However as invertebrate life evolved in an aquatic habitat most have little or new specialization for respiration in water.

1.5.2 Health and Pollution

Water fit for human consumption is called drinking water or potable water. Water that is not potable may be made potable by filtration or distillation, or by a range of other methods.

Water that is not fit for drinking but is not harmful for humans when used for swimming or bathing is called by various names other than potable or drinking water, and is sometimes called safe water, or "safe for bathing". Chlorine is a skin and mucous membrane irritant that is used to make water safe for bathing or drinking. Its use is highly technical and is usually monitored by government regulations (typically 1 part per million (ppm) for drinking water, and 1–2 ppm of chlorine not yet reacted with impurities for bathing water). Water for bathing may be maintained in satisfactory microbiological condition using chemical disinfectants such as chlorine or ozone or by the use of Ultra violet light.

In the USA, non-potable forms of wastewater generated by humans may be referred to as grey water, which is treatable and thus easily able to be made potable again, and black water, which generally contains sewage and other forms of waste which require further treatment in order to be made reusable. Grey water composes 50-80% of residential wastewater generated by a household's sanitation equipment (sinks, showers and kitchen runoff, but not toilets, which generate black water.) These terms may have different meanings in other countries and cultures.

This natural resource is becoming scarcer in certain places, and its availability is a major social and economic concern. Currently, about a billion people around the world routinely drink unhealthy water. Most countries accepted the goal of halving by 2015 the number of people worldwide who do not have access to safe water and sanitation during the 2003 G8 Evian summit [23]. Even if this difficult goal is met, it will still leave more than an estimated half a billion people without access to safe drinking water and over a billion without access to adequate sanitation. Poor water quality and bad sanitation are deadly; some five million deaths a year are caused by polluted drinking water. The World Health Organization estimates that safe water could prevent 1.4 million child deaths from diarrhea each year [24]. Water, however, is not a finite resource, but rather re-circulated as potable water in precipitation in quantities many degrees of magnitude higher than human consumption. Therefore, it is the relatively small quantity of water in reserve in the earth (about 1% of our drinking water supply, which is replenished in aquifers around every 1 to 10 years), that is a non-renewable resource, and it is, rather, the distribution of potable and irrigation water which is scarce, rather than the actual amount of it that exists on the earth. Water-poor countries use importation of goods as the primary method of importing water (to leave enough for local human consumption), since the manufacturing process uses around 10 to 100 times products' masses in water.

In the developing world, 90% of all wastewater still goes untreated into local rivers and streams [25]. Some 50 countries, with roughly a third of the world‘s population, also suffer from medium or high water stress, and 17 of these extract more water annually than is recharged through their natural water cycles [26]. The strain not only affects surface freshwater bodies like rivers and lakes, but it also degrades groundwater resources.

1.5.3 Human Uses of Water

1.5.3.1 Agriculture

The most important use of water in agriculture is for irrigation, which is a key component to produce enough food. Irrigation takes up to 90% of water withdrawn in some developing countries [27] and significant proportions in more economically developed countries (United States, 30% of freshwater usage is for irrigation) [28].

1.5.3.2 Water as a Scientific Standard

On 7 April 1795, the gram was defined in France to be equal to "the absolute weight of a volume of pure water equal to a cube of one hundredth of a meter, and to the temperature of the melting ice" [29]. For practical purposes though, a metallic reference standard was required, one thousand times more massive, the kilogram. Work was therefore commissioned to determine precisely the mass of one liter of water. In spite of the fact that the decreed definition of the gram specified water at 0 °C—a highly reproducible *temperature*—the scientists chose to redefine the standard and to perform their measurements at the temperature of highest water *density*, which was measured at the time as 4 °C [30].

The Kelvin temperature scale of the SI system is based on the triple point of water, defined as exactly 273.16 K or 0.01 °C. The scale is a more accurate development of the Celsius temperature scale, which was originally defined according the boiling point (set to 100 °C) and melting point (set to 0 °C) of water.

Natural water consists mainly of the isotopes hydrogen-1 and oxygen-16, but there is also small quantity of heavier isotopes such as hydrogen-2 (deuterium). The amount of deuterium oxides or heavy water is very small, but it still affects the properties of water. Water from rivers and lakes tends to contain less deuterium than seawater. Therefore, standard water is defined in the Vienna Standard Mean Ocean Water specification.

1.5.3.3 For Drinking

The human body is anywhere from 55% to 78% water depending on body size [31]. To function properly, the body requires between one and seven liters of water per day to avoid dehydration; the precise amount depends on the level of activity, temperature, humidity, and other factors. Most of this is ingested through foods or beverages other than drinking straight water. It is not clear how much water intake is needed by healthy people, though most advocates agree that 6–7 glasses of water (approximately 2 liters) daily is the minimum to maintain proper hydration [32]. Medical literature favors a lower consumption, typically 1 liter of water for an average male, excluding extra requirements due to fluid loss from exercise or warm weather [33]. For those who have healthy kidneys, it is rather difficult to drink too much water, but (especially in warm humid weather and while exercising) it is dangerous to drink too little. People can drink far more water than necessary while exercising, however, putting them at risk of water intoxication (hyper hydration), which can be fatal. The popular claim that "a person should consume eight glasses of water per day" seems to have no real basis in science [34]. Similar misconceptions concerning the effect of water on weight loss and constipation have also been dispelled [35].

An original recommendation for water intake in 1945 by the Food and Nutrition Board of the National Research Council read: "An ordinary standard for diverse persons is 1 milliliter for each calorie of food. Most of this quantity is contained in prepared foods [36]. The latest dietary reference intake report by the United States National Research Council in general recommended (including food sources): 2.7 liters of water total for women and 3.7 liters for men [37]. Specifically, pregnant and breastfeeding women need additional fluids to stay hydrated. According to the Institute of Medicine—who recommend that, on average, women consume 2.2 liters and men 3.0 liters—this is recommended to be 2.4 liters (10 cups) for pregnant women and 3 liters (12 cups) for breastfeeding women since an especially large amount of fluid is lost during nursing [38]. Also noted is that normally, about 20% of water intake comes from food, while the rest comes from drinking water and beverages (caffeinated included). Water is excreted from the body in multiple forms; through urine and faces, through sweating, and by exhalation of water vapor in the breath. With physical exertion and heat exposure, water loss will increase and daily fluid needs may increase as well.

Humans require water that does not contain too many impurities. Common impurities include metal salts and oxides (including copper, iron, calcium and lead) [39] and/or harmful bacteria, such as *Vibrio*. Some solutes are acceptable and even desirable for taste enhancement and to provide needed electrolytes [40]

The single largest (by volume) freshwater resource suitable for drinking is Lake Baikal in Siberia [41].

1.5.3.4 Washing

The propensity of water to form solutions and emulsions is useful in various washing processes. Many industrial processes rely on reactions using chemicals dissolved in water, suspension of solids in water slurries or using water to dissolve and extract substances. Washing is also an important component of several aspects of personal body hygiene.

1.5.3.5 Chemical Uses

Water is widely used in chemical reactions as a solvent or reactant and less commonly as a solute or catalyst. In inorganic reactions, water is a common solvent, dissolving many ionic compounds. In organic reactions, it is not usually used as a reaction solvent, because it does not dissolve the reactants well and is amphoteric (acidic *and* basic) and nucleophilic. Nevertheless, these properties are sometimes desirable. Also, acceleration of Diels-Alder reactions by water has been observed. Supercritical water has recently been a topic of research. Oxygen saturated supercritical water combusts organic pollutants efficiently.

1.5.3.6 As a Heat Transfer Fluid

Water and steam are used as heat transfer fluids in diverse heat exchange systems, due to its availability and high heat capacity, both as a coolant and for heating. Cool water may even be naturally available from a lake or the sea. Condensing steam is a particularly efficient heating fluid because of the large heat of vaporization. A disadvantage is that water and steam are somewhat corrosive. In almost all electric power stations, water is the coolant, which vaporizes and drives steam turbines to drive generators. In the U.S., cooling power plants is the largest use of water [28].

In the nuclear power industry, water can also be used as a neutron moderator. In most nuclear reactors, water is both a coolant and a moderator. This provides something of a passive safety measure, as removing the water from the reactor also slows the nuclear reaction down - however other methods are favored for stopping a reaction and it is preferred to keep the nuclear core covered with water so as to ensure adequate cooling.

1.5.3.7 Extinguishing Fires

Water has a high heat of vaporization and is relatively inert, which makes it a good fire extinguishing fluid. The evaporation of water carries heat away from the fire. However, only distilled water can be used to fight fires of electric equipment, because impure water is electrically conductive, or of oils and organic solvents, because they float on water and the explosive boiling of water tends to spread the burning liquid.

Use of water in fire fighting should also take into account the hazards of a steam explosion, which may occur when water is used on very hot fires in confined spaces, and of a hydrogen explosion, when substances which react with water, such as certain metals or hot graphite, decompose the water, producing hydrogen gas.

The power of such explosions was seen in the Chernobyl disaster, although the water involved did not come from fire-fighting at that time but the reactor's own water cooling system. A steam explosion occurred when the extreme over-heating of the core caused water to flash into steam. A hydrogen explosion may have occurred as a result of reaction between steam and hot zirconium.

1.5.3.8 Recreation

Humans use water for many recreational purposes, as well as for exercising and for sports. Some of these include swimming, waterskiing, boating, surfing and diving. In addition, some sports, like ice hockey and ice skating, are played on ice. Lakesides, beaches and water parks are popular places for people to go to relax and enjoy recreation. Many find the sound and appearance of flowing water to be calming, and fountains and other water features are popular decorations. Some keep fish and other life in aquariums or ponds for show, fun, and companionship. Humans also use water for snow sports i.e. skiing, sledding, snowmobiling or snowboarding, which requires the water to be frozen. People may also use water for play fighting such as with snowballs, water guns or water balloons.

1.5.3.9 Water Industry

The water industry provides drinking water and wastewater services (including sewage treatment) to households and industry. Water supply facilities include water wells cisterns for rainwater harvesting, water supply network, water purification facilities, water tanks, water towers, water pipes including old aqueducts. Atmospheric water generators are in development.

Drinking water is often collected at springs, extracted from artificial borings (wells) in the ground, or pumped from lakes and rivers. Building more wells in adequate places is thus a possible way to produce more water, assuming the aquifers can supply an adequate flow. Other water sources include rainwater collection. Water may require purification for human consumption. This may involve removal of undissolved substances, dissolved substances and harmful microbes. Popular methods are filtering with sand which only removes undissolved material, while chlorination and boiling kill harmful microbes. Distillation does all three functions. More advanced techniques exist, such as reverse osmosis. Desalination of abundant seawater is a more expensive solution used in coastal arid climates.

The distribution of drinking water is done through municipal water systems, tanker delivery or as bottled water. Governments in many countries have programs to distribute water to the needy at no charge. Others argue that the market mechanism and free enterprise are best to manage this rare resource and to finance the boring of wells or the construction of dams and reservoirs.

Reducing usage by using drinking (potable) water only for human consumption is another option. In some cities such as Hong Kong, sea water is extensively used for flushing toilets citywide in order to conserve fresh water resources.

Polluting water may be the biggest single misuse of water; to the extent that a pollutant limits other uses of the water, it becomes a waste of the resource, regardless of benefits to the polluter. Like other types of pollution, this does not enter standard accounting of market costs, being conceived as externalities for which the market cannot account. Thus other people pay the price of water pollution, while the private firms' profits are not redistributed to the local population victim of this pollution. Pharmaceuticals consumed by humans often end up in the waterways and can have detrimental effects on aquatic life if they are bioaccumulation and if they are not biodegradable.

Wastewater facilities are storm sewers and wastewater treatment plants. Another way to remove pollution from surface runoff water is bios wale.

1.5.3.10 Industrial Applications

Water is used in power generation. Hydroelectricity is electricity obtained from hydropower. Hydroelectric power comes from water driving a water turbine connected to a generator. Hydroelectricity is a low-cost, non-polluting, renewable energy source. The energy is supplied by the sun. Heat from the sun evaporates water, which condenses as rain in higher altitudes, from where it flows down.

Pressurized water is used in water blasting and water jet cutters. Also, very high pressure water guns are used for precise cutting. It works very well, is relatively safe, and is not harmful to the environment. It is also used in the cooling of machinery to prevent over-heating, or prevent saw blades from over-heating.

Water is also used in many industrial processes and machines, such as the steam turbine and heat exchanger, in addition to its use as a chemical solvent. Discharge of untreated water from industrial uses is pollution. Pollution includes discharged solutes (chemical pollution) and discharged coolant water (thermal pollution). Industry requires pure water for many applications and utilizes a variety of purification techniques both in water supply and discharge.

1.5.3.11 Food Processing

Water plays many critical roles within the field of food science. It is important for a food scientist to understand the roles that water plays within food processing to ensure the success of their products.

Solutes such as salts and sugars found in water affect the physical properties of water. The boiling and freezing points of water are affected by solutes, as well as air pressure, which is in turn affected by altitude. Water boils at lower temperatures with the lower air pressure which occurs at higher elevations. One mole of sucrose per kilogram of water raises the boiling point of water by 0.51 °C, and one mole of salt per kg raises the boiling point by 1.02 °C; similarly, increasing the number of dissolved particles lowers water's freezing point [42]. Solutes in water also affect water activity which affects many chemical reactions and the growth of microbes in food [43]. Water activity can be described as a ratio of the vapor pressure of water in a solution to the vapor pressure of pure water [43]. Solutes in water lower water activity. This is important to know because most bacterial growth ceases at low levels of water activity [43]. Not only does microbial growth affect the safety of food but also the preservation and shelf life of food.

Water hardness is also a critical factor in food processing. It can dramatically affect the quality of a product as well as playing a role in sanitation. Water hardness is classified based on the amounts of removable calcium carbonate salt it contains per gallon. Water hardness is measured in grains; 0.064 g calcium carbonate is equivalent to one grain of hardness [42]. Water is classified as soft if it contains 1 to 4 grains, medium if it contains 5 to 10 grains and hard if it contains 11 to 20 grains [42]. The hardness of water may be altered or treated by using a chemical ion exchange system. The hardness of water also affects its pH balance which plays a critical role in food processing. For example, hard water prevents successful production of clear beverages. Water hardness also affects sanitation; with increasing hardness, there is a loss of effectiveness for its use as a sanitizer [42].

Boiling, steaming, and simmering are popular cooking methods that often require immersing food in water or its gaseous state, steam. Water is also used for dishwashing.

1.6 Water Pollution

Water pollution is the contamination of water bodies (e.g. lakes, rivers, oceans and groundwater). Water pollution affects plants and organisms living in these bodies of water; and, in almost all cases the effect is damaging not only to individual species and populations, but also to the natural biological communities. Water pollution occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds.

1.6.1 Sources and Causes of Water Pollution

The causes of water pollution may be due to direct and indirect contaminant sources. The former are effluent outputs from refineries, factories and waste treatment plants. Fluids of differing qualities are emitted to the urban water supplies. In the United States and some other countries, these methods are controlled. However, still pollutants can be found in the water bodies. The latter are the water supply from soils/groundwater systems that have fertilizers, pesticides and industrial wastes. Also those through the atmosphere like bakeries, factories emission and automobile discharge. Contaminants can also be divided into inorganic, organic, acid/base and radioactive.

- Dumping of industrial wastes, containing heavy metals, harmful chemicals, by-products, organic toxins and oils, into the nearby source of water is one of the visible causes of water pollution.

- Another cause for the contamination of water is the improper disposal of human and animal wastes.
- Effluents from factories, refineries, injection wells and sewage treatment plants are dumped into urban water supplies, leading to water pollution.
- A number of pollutants, both harmful and poisonous, enter the groundwater systems through rain water.
- The residue of agricultural practices, including fertilizers and pesticides, are some of the major sources of water pollution.
- Untreated pollutants are drained into the nearest water body, such as stream, lake or harbor, causing water pollution.
- Another major source of water pollution comprises of organic farm wastes. When farm land, treated with pesticides and fertilizers, is irrigated, the excess nitrogen and poisons get mixed into the water supply, thereby contaminating it.
- Pathogens, sediments and chemical pollutants are other sources of water pollution.
- The corporeal wastes produced by humans and farmed organisms pollute rivers, lakes, oceans and other surface waters.
- The combustion of coal leads to the release of mercury in the atmosphere. This enters the rivers, lakes and groundwater. This is very hazardous for pregnant women and infants.
- Cattle and pig rearing causes a significant amount of nutrient-filled waste. Virulent pfiesteria toxin collects in the water masses.
- Fertilizers having a large quantity of nitrogen and phosphorus cause a high biological oxygen demand in the water. As oxygen is depleted, only anaerobic life-forms prosper.

- Human settlement along the banks of rivers causes human, animal and industrial waste to be discharged into it. In the developed world, sewage treatment plants are used to treat waste. However, in developing nations, the rivers are similar to open sewers.

Organic water pollutants are:

- Food processing waste, including pathogens
- Insecticides and herbicides, a huge range of organohalide and other chemicals
- Tree and brush debris from logging operations
- Bacteria from sewage or livestock operations
- Petroleum hydrocarbons like diesel, gasoline, jet fuels, fuel oils, motor oils
- Volatile organic compounds like industrial solvents

Inorganic water pollutants are:

- pre-production industrial raw resin pellets
- heavy metals including acid mine drainage
- chemical waste as industrial by-products
- acidity due to industrial discharges like sulphur dioxide
- silt in surface runoff due to logging, slash and burn practices, construction sites or land clearing sites
- fertilizers in runoff from agriculture including nitrates and phosphates

1.6.2 Effect of Water Pollution

- A number of waterborne diseases are produced by the pathogens present in polluted water, affecting humans and animals alike.

- Pollution affects the chemistry of water. The pollutants, including toxic chemicals, can alter the acidity, conductivity and temperature of water.

- Polluted municipal water supplies are found to pose a threat to the health of people using them.

- As per the records, about 14000 people perish or incur various communicable diseases due to the consumption of contaminated drinking water.
- The concentration of bacteria and viruses in polluted water causes increase in solids suspended in the water body, which, in turn, leads to health problems.
- Marine life becomes deteriorated due to water pollution. Lethal killing of fish and aquatic plants in rivers, oceans and seas is an aftereffect of water contamination only.
- Diseases affecting the heart, poor circulation of blood and the nervous system and ailments like skin lesion, cholera and diarrhea are often linked to the harmful effects of water pollution.
- Carcinogenic pollutants found in polluted water might cause cancer.
- Alteration in the chromosomal makeup of the future generation is foreseen, as a result of water pollution.
- Discharges from power stations reduce the availability of oxygen in the water body, in which they are dumped.
- The flora and fauna of rivers, sea and oceans is adversely affected by water pollution.

1.7 Admissible Limits of Contaminant in Water

Water is categorized based on the concentration of different constituents and other properties. As a result, it can be used in various purposes and having recommended value of constituents. However, the admissible limits recommended by Environmental Quality Standard (EQS) for Bangladesh [44], World Health Organization (WHO) [45] and United States Public Health (USPH) [46] for fresh water are given in Table 1.2.

Table 1.2 Admissible Limits of Contaminant in Water

Parameters	Bangladesh Standard	WHO Standard	USPH Standard
Color	Colorless	Colorless	Colorless
Odor	Odorless	Odorless	Odorless
Taste	Tasteless	Tasteless	Tasteless
pH	6.5 to 8.5	6.5 to 9.2	6.5 to 8.5
Specific Conductance	-----	-----	300 μ Siemens cm^{-1}
Total Dissolved Solids	1000 ppm	500 ppm	500 ppm
Suspended Solids	-----	5 ppm	5 ppm
Chloride	150 to 600 ppm	500 ppm	250 ppm
Sulphate	400 ppm	200 ppm	250 ppm
Cyanide	-----	0.05 ppm	0.05 ppm
Nitrate + Nitrite	10 ppm	45 ppm	Not more than 10 ppm
Fluoride	1 ppm	0.5 ppm	0.6 ppm
Phosphate	-----	0.1 ppm	0.1 ppm
Ammonia	0.5 ppm	0.5 ppm	0.5 ppm
Calcium	-----	100 ppm	100 ppm
Cadmium	0.005 ppm	0.01 ppm	0.01 ppm
Magnesium	30 ppm	150 ppm	30 ppm
Arsenic	0.05 ppm	0.01 ppm	0.05 ppm
Chromium (VI)	0.05 ppm	0.05 ppm	0.05 ppm
Copper	1 ppm	1.5 ppm	1.0 ppm
Iron	0.3 to 1 ppm	1.0 ppm	Not more than 0.03 ppm
Lead	0.05 ppm	0.1 ppm	Not more than 0.05 ppm
Manganese	0.1 ppm	0.5 ppm	Not more than 0.05 ppm
Zinc	0.5 to 5 ppm	5.0 ppm	5.0 ppm
Selenium	-----	0.01 ppm	0.01 ppm
Phenols	-----	0.002 ppm	0.001 ppm
DO	-----	4 to 6 ppm	4 to 6 ppm
BOD	-----	6 ppm	5 ppm
COD	4 ppm	10 ppm	4 ppm
Total Hardness	200-250 ppm	500 ppm	500
Coliform (Total)	0 N/100 mL	0 N/100 mL	0 N/100 mL

Characteristic and tolerance limits for inland surface water for fish culture and irrigation [46] are as follows in Table 1.3

Table 1.3 : Tolerance Limits for Inland Surface Water for Fish Culture and Irrigation.

Characteristics	Fish Culture	Irrigation
pH	6.0 to 9.0	5.5 to 9.0
Free CO_2 (ppm)	6.0	-----
Electrical Conductance at 25^0 C	1000×10^{-6} mhos	3000×10^{-5} mhos
Free Ammonia as N (ppm)	1.2	-----
DO (minimum)	40% saturation or 3 ppm, maximum whichever is higher	-----
Beta emitters, μ cmL^{-1}, maximum	10^{-8}	10^{-9}
Alpha emitters, μ cmL^{-1}, maximum	10^{-8}	10^{-9}
TDS (inorganic), ppm	-----	2100
Oil and Grease, ppm, maximum	0.1	-----
Boron as B , ppm, maximum	-----	2.0
Sulphate (ppm), maximum	-----	1000
Percent of Sodium, maximum	-----	60
Chloride (ppm), maximum	-----	60

1.8 Water Quality Parameters

1.8.1 Physical Parameters

1.8.1.1 Color

The appearance of color in drinking water is caused by the absorption of certain wavelengths of normal white light by dissolved or colloidally dispersed substances, by fluorescence in the visible wavelength region from substances that absorb white or ultraviolet light [49], by the presence of colored suspended solids, and by the preferential scattering of short wavelengths of light by the smallest suspended particles [49-50]. Color measured in water that contains suspended matter is defined as "apparent color"; "true color" is measured in water samples from which particulate matter has been removed by centrifugation [51-52]. In general, the true color of a given water sample is substantially less than its apparent color [52].

1.8.1.2 Taste and Odor

In the assessment of drinking water quality, the sensations of taste and odor are complementary. In general, the sense of taste is most useful in detecting the ionic, inorganic constituents of drinking water, and the sense of smell is most useful in detecting the covalent, organic constituents. Another way in which the senses of taste and smell complement each other is in their detection limits; much lower concentrations of matter can usually be detected by odour than by taste [47]. It is important to distinguish the taste of a substance from its flavour. The latter is a complex sensation affected primarily by taste, odour and temperature and secondarily by other factors such as texture and pungency. Formal theories and definitions of taste suggest that this sense is responsive only to the sensations of sweetness, sourness, saltiness and bitterness; nuances of taste are thought to be due to the degree to which various taste papillae respond to these sensations [48].

From a rigorous point of view, therefore, the taste of drinking water can be defined as the sensation that is due to the presence of substances in water that have negligible vapour pressures and negligible odours. It follows that taste tests should be performed only on water samples that are free of odour. Failure to make this distinction is responsible for much of the confusion that prevails in the older water quality literature on organoleptic testing.

1.8.1.3 Turbidity

Turbidity is a measure of the amount of particulate matter that is suspended in water. Water that has high turbidity appears cloudy or opaque. High turbidity can cause increased water temperatures because suspended particles absorb more heat and can also reduce the amount of light penetrating the water.

1.8.1.4 Temperature

Water temperature affects the ability of water to hold oxygen, the rate of photosynthesis by aquatic plants and the metabolic rates of aquatic organisms. Causes of temperature change include weather, removal of shading stream bank vegetation, impoundments, discharge of cooling water, urban storm water, and groundwater inflows to the stream.

1.8.1.5 Total Solids

Total Solids is a measure of the suspended and dissolved solids in a body of water. Thus, it is related to both conductivity and turbidity. To measure total suspended and dissolved solids, a sample of water is placed in a drying oven to evaporate the water, leaving the solids. To measure dissolved solids, the sample is filtered before it is dried and weighed. To calculate the suspended solids, the weight of the dissolved solids is subtracted from the total solids.

1.8.1.6 Total Suspended Solids

Total suspended solids is a water quality measurement usually abbreviated TSS. It is listed as a conventional pollutant in the U.S. Clean Water Act. This parameter was at one time called non-filterable residue (NFR), a term that refers to the identical measurement: the dry-weight of particles trapped by a filter, typically of a specified pore size. However, the term "non-filterable" suffered from an odd (for science) condition of usage: in some circles (Oceanography, for example) "filterable" meant the material retained on a filter, so non-filterable would be the water and particulates that passed through the filter. In other disciplines (Chemistry and Microbiology for examples) and dictionary definitions, "filterable" means just the opposite: the material passed by a filter, usually called "Total dissolved solids" or TDS. Thus in chemistry the non-filterable solids are the retained material called the residue.

1.8.1.7 pH

pH is a term used to indicate the alkalinity or acidity of a substance as ranked on a scale from 1.0 to 14.0. Acidity increases as the pH gets lower. A pH of 7.0 is neutral. Aquatic organisms differ as to the range of pH in which they flourish.

1.8.2 Chemical Parameters

1.8.2.1 Chlorophyll

Chlorophyll is the pigment that allows plants, including algae, to convert sunlight into organic compounds through photosynthesis. Measuring chlorophyll a concentrations in water is a surrogate for an actual measurement of algae biomass. Excessive amounts of chlorophyll a indicate the presence of blooms, which usually consist of a single species of algae - typically one that is not desirable for consumption by fish and other predators. Unconsumed algae sink to the bottom and decay, depleting deeper water of oxygen.

1.8.2.2 Suspended Minerals

Suspended minerals are a measure of the amount of sediment moving along in a stream. It is highly dependent on the flow of water and usually increases during and immediately after rain events. As the sediment settles out of the water, aquatic habitats are often destroyed.

1.8.2.3 Colored Dissolved Organic Carbon

Colored dissolved organic carbon, also referred to as fulvic acid and humic acid, contributes to the brownish tan color of a waterway. Tannins are one example of such compounds. In a nutrient-poor environment, it can serve as a nutrient allowing for the growth of algae whereas in a nutrient-rich environment, it can be given off as a byproduct from the decay of algae.

1.8.2.4 Dissolved Oxygen (DO)

Although water molecules contain an oxygen atom, aquatic organisms rely upon a small amount of oxygen that is actually dissolved in the water. In general, rapidly moving water contains more dissolved oxygen than slow or stagnant water and colder water contains more dissolved oxygen than warmer water. Bacteria consume oxygen as organic matter decays. As a result, an oxygen-deficient environment can develop in lakes and rivers with excess organic material. These conditions can eventually lead to fish kills.

The amount of Dissolved Oxygen (DO) in water is expressed as a concentration. A concentration is the amount of in weight of a particular substance per a given volume of liquid. The DO concentration in a stream is the mass of the oxygen gas present, in milligrams per liter of water. Milligrams per liter (mg/L) can also be expressed as parts per million (ppm).

The concentration of dissolved oxygen in a stream is affected by many factors:

- Temperature: Oxygen is more easily dissolved in cold water.
- Flow: Oxygen concentrations vary with the volume and velocity of water flowing in a stream. Faster flowing white water areas tend to be more oxygen rich because more oxygen enters the water from the atmosphere in those areas than in slower, stagnant areas.
- Aquatic Plants: The presence of aquatic plants in a stream affects the dissolved oxygen concentration. Green plants release oxygen into the water during photosynthesis. Photosynthesis occurs during the day when the sun is out and ceases at night. Thus in streams with significant populations of algae and other aquatic plants, the dissolved oxygen concentration may fluctuated daily, reaching its highest levels in the late afternoon. Because plants, like animals, also take in oxygen, dissolved oxygen levels may drop significantly by early morning.
- Altitude: Oxygen in more easily dissolved into water at low altitudes that at high altitudes.
- Dissolved or suspended solids: Oxygen is also more easily dissolved into water with low levels of dissolved or suspended solids.

- Human Activities Affecting DO:

➢ Removal of riparian vegetation may lower oxygen concentrations due to increased water temperature resulting from a lack of canopy shade and increased suspended solids resulting from erosion of bare soil.

- Typical urban human activities may lower oxygen concentrations. Runoff from impervious surfaces bearing salts, sediments and other pollutants increases the amount of suspended and dissolved solids in stream water.

- Organic wastes and other nutrient inputs from sewage and industrial discharges, septic tanks and agricultural and urban runoff can result in decreased oxygen levels. Nutrient input often leads to excessive algal growth. When the algae die, the organic matter is decomposed by bacteria. Bacterial decomposition consumes a great deal of oxygen.

- Dams may pose an oxygen supply problem when they release waters from the bottom of their reservoirs into streams and rivers. Although the water on the bottom is cooler than the warm water on top, it may be low in oxygen if large amounts of organic matter has fallen to the bottom and has been decomposed by bacteria.

Usually streams with high dissolved oxygen concentrations (greater than 8 mg/L for Ozark streams) are considered healthy streams. They are able to support a greater diversity of aquatic organisms. They are typified by cold, clear water, with enough riffles to provide sufficient mixing of atmospheric oxygen into the water.

In streams that have been impacted by any of the above factors, summer is usually the most crucial time for dissolved oxygen levels because stream flows tend to lessen and water temperatures tend to increase.

In general, DO levels less than 3 mg/L are stressful to most aquatic organisms. Most fish die at 1-2 mg/L. However, fish can move away from low DO areas. Water with low DO from 2 – 0.5 mg/L are considered hypoxic; waters with less than 0.5 mg/L are anoxic.

Because the temperature of the stream can vary daily and even hourly, it is important to factor out the effect of temperature when analyzing the DO levels in a sample of water. This is achieved by considering the saturation value. Saturation is the maximum level of DO that would be present in the water at a specific temperature, in the absence of other influences. Once anybody know the temperature of the water in stream he or she can use an oxygen saturation table to determine the maximum DO concentration. He or she can calculate the percent saturation by comparing the maximum saturation value (provided in the table) with his/her actual measured DO result. Simply divide the measured DO result by the maximum saturation value.

For example, if the stream temperature is 8 degrees C, then maximum saturation value would be 11.83 mg/L. If the DO reading is 8.5 mg/L, the percent saturation would be 8.50/11.83=71.9 percent. Since a healthy stream is considered to be 90-100 percent saturated, and then the sample indicates that something else besides temperature is affecting oxygen levels adversely (e.g. suspended or dissolved solids or bacteria decomposition).

Table 1.4 Maximum Dissolved Oxygen Concentration Saturation Table [53]

Temperature (°C)	DO (mg/L)	Temperature (°C)	DO (mg/L)
0	14.60	23	8.56
1	14.19	24	8.40
2	13.81	25	8.24
3	13.44	26	8.09
4	13.09	27	7.95
5	12.75	28	7.81
6	12.43	29	7.67
7	12.12	30	7.54
8	11.83	31	7.41
9	11.55	32	7.28
10	11.27	33	7.16
11	11.01	34	7.05
12	10.76	35	6.93
13	10.52	36	6.82
14	10.29	37	6.71
15	10.07	38	6.61
16	9.85	39	6.51
17	9.65	40	6.41
18	9.45	41	6.31
19	9.26	42	6.22
20	9.07	43	6.13
21	8.90	44	6.04
22	8.72	45	5.95

1.8.2.5 Acidity

Acidity of water is its quantitative capacity to react with a strong base to a designated pH. Acidity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known (19th Edition, Standard Methods, 1995)

1.8.2.6 Alkalinity

The Alkalinity or the buffering capacity of a stream refers to how well it can neutralize acidic pollution and resist changes in pH. Alkalinity measures the amount of alkaline compounds in the water, such as carbonates, bicarbonates and hydroxides. These compounds are natural buffers that can remove excess hydrogen (H^+) ions (1991, Streamkeeper's Field Guide: Watershed Inventory and Stream Monitoring Methods).

1.8.2.7 Biochemical Oxygen Demand (BOD)

The Biochemical Oxygen Demand is the amount of oxygen consumed by bacteria in the decomposition of organic material. It also includes the oxygen required for the oxidation of various chemical in the water, such as sulfides, ferrous iron and ammonia. While a dissolved oxygen test tells you how much oxygen is available, a BOD test tells you how much oxygen is being consumed.

BOD is determined by measuring the dissolved oxygen level in a freshly collected sample and comparing it to the dissolved oxygen level in a sample that was collected at the same time but incubated under specific conditions for a certain number of days. The difference in the oxygen readings between the two samples in the BOD is recorded in units of mg/L.

Unpolluted, natural waters should have a BOD of 5 mg/L or less. Raw sewage may have BOD levels ranging from 150 – 300 mg/L.

1.8.2.8 Carbonaceous Biochemical Oxygen Demand (CBOD)

Carbonaceous Biochemical Oxygen Demand measures the amount of demand that is oxidized by carbon. CBOD is a fraction of the BOD that excludes the nitrogenous oxygen demand by the addition of nitrogen inhibitors during the analysis (19th Edition, Standard Methods, 1995).

1.8.2.9 Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter. The test is useful for monitoring and control after correlation has been established.

Oxidation of most organic compounds is 95 to 100% of the theoretical value. Ammonia, present either in the waste or liberated from nitrogen-containing organic matter, is not oxidized in the absence of significant concentration of free chloride ions (19th Edition, Standard Methods, 1995).

1.8.2.10 Conductivity

Conductivity is a measure of how well water can pass an electrical current. It is an indirect measure of the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, phosphate, sodium, magnesium, calcium, iron and aluminum. The presence of these substances increases the conductivity of a body of water. Organic substances like oil, alcohol, and sugar do not conduct electricity very well, and thus have a low conductivity in water.

Inorganic dissolved solids are essential ingredients for aquatic life. They regulate the flow of water in and out of organisms‘ cells and are building blocks of the molecules necessary for life. A high concentration of dissolved solids, however, can cause water balance problems for aquatic organisms and decrease dissolved oxygen levels [54].

1.8.2.11 Fecal Coliform

Human and animal wastes carried to stream systems are sources of pathogenic or disease-causing, bacteria and viruses. The disease causing organisms are accompanied by other common types of nonpathogenic bacteria found in animal intestines, such as fecal coliform bacteria, enterococci bacteria, and escherichia coli (E. coli) bacteria.

Fecal coliform, enterococci, and E. coli bacteria are not usually disease-causing agents themselves. However, high concentrations suggest the presence of disease-causing organisms. Fecal coliform, enterococci, and E. coli bacteria are used as indicator organisms; they indicated the probability of finding pathogenic organisms in a stream.

To measure indicator bacteria, water samples must be collected in sterilized containers. The samples are forced through a filter and incubated at a specific temperature for a certain amount of time. The resulting colonies that form during incubation are counted and recorded as the number of colony producing units per 100 mL of water.

1.8.2.12 Hardness

Hardness is frequently used as an assessment of the quality of water supplies. The hardness of a water is governed by the content of calcium and magnesium salts (temporary hardness), largely combined with bicarbonate and carbonate and with sulfates, chlorides, and other anions of mineral acids (permanent hardness).

1.8.2.13 Metals

The effects of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Some metals are essential; others may adversely affect water consumers, wastewater treatment systems, and receiving waters. Some metals may be either beneficial or toxic, depending on concentration.

The primary mechanism for toxicity to organisms that live in the water column is by absorption to or uptake across the gills: this physiological process requires metal to be in a dissolved form. This is not to say that particulate metal is nontoxic, only that particulate metal appears to exhibit substantially less toxicity than does dissolved metal.

Dissolved: Those metals of an unacidified sample that pass through a 0.45 micrometer membrane filter and is thought to better represent the bioavailable fraction of metal in the water column than does total recoverable metal.

Recoverable: Those metals that are not tightly bound and are biologically available to aquatic organisms.

Total: Includes all metals, inorganically and organically bound, both dissolved and particulate. Will give a unrealistic high value of those metals that are biological available to aquatic organisms.

Not all metals are acutely toxic in small concentrations. The "heavy metals" include copper (Cu), iron (Fe), cadmium (Cd), zinc (Zn), mercury (Hg), and lead (Pb) and are the most toxic to aquatic organisms. Some water quality characteristics which affect metal toxicity include temperature, pH, hardness, alkalinity, suspended solids, redox potential and dissolved organic carbon. Metals can bind to many organic and inorganic compounds which reduces the toxicity of the metal.

1.8.2.14 Nitrogen

Nitrogen is important to all life. Nitrogen in the atmosphere or in the soil can go through many complex chemical and biological changes. It can be combined into living and non-living material and return back to the soil or air in a continuing cycle called the nitrogen cycle.

Nitrogen occurs in natural waters in various forms, including nitrate (NO_3), nitrate (NO_2), and ammonia (NH_3). Nitrate is the most common form tested. Test results are usually expressed as nitrate-nitrogen (NO_3-N), which simply means nitrogen in the form of nitrate. Ammonia is the least stable form of nitrogen and thus difficult to measure accurately. Nitrite is less stable and usually present in much lower amounts that nitrate.

These three compounds are interrelated through the process of nitrification, the biological oxidation of ammonia to nitrate. In this process nitrite is produced as an intermediate product.
Order of decreasing oxidation state:
Nitrate → Nitrite → Ammonia → Organic Nitrogen
(stable) → → →→ → →→ → →(Unstable)

In relatively stable, oxygenated natural water systems the oxidation of nitrite to nitrate is rapid, but the conversion of NH_3 to NO_2^- is the rate limiting step in the total process [54].

Ammonia (NH_3): It is one of the most important pollutants in the aquatic environment because of its relatively highly toxic nature and its ubiquity in surface water systems. It is discharged in large quantities in industrial, municipal and agricultural waste waters. In aqueous solutions, ammonia assumes two chemical forms: NH_4^+ - ionized (less/nontoxic) and NH_3 - unionized (toxic).

The relative concentration of ionized and unionized ammonia in a given ammonia solution are principally a function of pH, temperature and ionic strength of the aqueous solution. Total NH_3: Total ammonia is the sum of the NH_3 and NH_4^+ [55].

1.8.2.15 Phosphorus

Phosphorus is often the limiting nutrient for plant growth, meaning it is in short supply relative to nitrogen. Phosphorus usually occurs in nature as phosphate, which is a phosphorous atom combined with four oxygen atoms (PO_4^{-3}). Phosphate that is bound to plant or animal tissue is known as organic phosphate. Phosphate that is not associated with organic material is known as inorganic phosphate. Both forms are present in aquatic systems and may be either dissolved in water or suspended (attached to particles in the water column).

Inorganic phosphate is often referred to as orthophosphate or reactive phosphorous. It is the form most readily available to plants, and thus may be the most useful indicator of immediate potential problems with excessive plant and algal growth.

Testing for total phosphorous (both inorganic and organic phosphate) provides you with a more complete measure of all the phosphorus that is actually in the water [54].

1.8.3 Biological Parameters

1.8.3.1 Benthic Macroinvertebrates

Macroinvertebrates are organisms that are large (macro) enough to be seen with the naked eye and lack a backbone (invertebrate). Benthic refers to the bottom of a waterway. Examples of benthic macroinvertebrates include insects in their larval or nymph form, crayfish, clams, snails, and worms. Most live part or most of their life cycle attached to submerged rocks, logs, and vegetation. The basic principle behind the study of macroinvertebrates is that some are more sensitive to pollution than others. Therefore, if a stream site is inhabited by organisms that can tolerate pollution and the more pollution-sensitive organisms are missing a pollution problem is likely.

1.8.3.2 Submerged Aquatic Vegetation (SAV)

Submerged Aquatic Vegetation provides invaluable benefits to aquatic ecosystems. It not only provides food and shelter to fish and invertebrates but also produces oxygen, traps sediment and absorbs nutrients such as nitrogen and phosphorus. Whereas SAV are dependent upon the transmission of sunlight through the water, the location of individual species depends upon a variety of factors such as salinity, depth and bottom sediment.

Table 1.5 : Various Water Quality Parameters

Physical Parameters	Chemical Parameters	Biological Parameters
Color Taste and Odor Turbidity Temperature Total Solids Total Suspended Solids pH	Chlorophyll Suspended Minerals Colored Dissolved Organic Carbon, Dissolved Oxygen (DO) Acidity, Alkalinity Biochemical Oxygen Demand (BOD) Carbonaceous Biochemical Oxygen Demand (CBOD) Chemical Oxygen Demand (COD) Conductivity Fecal Coliform Hardness Metals Nitrogen Phosphorus	Benthic Macroinvertebrates, Submerged Aquatic Vegetation (SAV)

1.9 Fundamental Aspects of Electrochemical Process

1.9.1 Design of Electrochemical Techniques

Electrochemistry involves the study of spontaneous oxidation-reductions reactions that generate an electrical current and the study of non-spontaneous oxidation-reduction reactions that are forced to occur by the passage of an electrical current. In both cases, the conversion between chemical and electrical energy is carried out by electrochemical cell. The arrangement of an electrochemical cell is briefly discussed below:

1.9.1.1 Electrochemical Cell

The electrochemical cell consists primarily of the electrodes and the electrolyte, assembled in a compartment. Commonly a glass frit, separator, or membrane may be incorporated to isolate the anolyte from the catholyte. Three electrodes are commonly employed: a working electrode that defines the interface under study, a reference electrode which maintains a constant reference potential, and a counter (or secondary) electrode which supplies the current. The cell must be designed so that the experimental data are determined by the properties of the reaction at the working electrode.

1.9.1.2 Working Electrode

Design of working electrodes is diverse. Most commonly the working electrode is a small sphere, small disc, or a short wire, but it could also be metal foil, a single crystal of semiconductor or metal, an evaporated thin film, or a powder as pressed discs or pellets. An essential feature is that the electrode should not react chemically with the solvent or solution components. In principle, the electrodes can be large or small, but there are commonly experimental reasons why the electrode area should be relatively small ($<0.25\ cm^2$). Moreover, it should preferably be smooth, as the geometry and mass transport are then better defined. Wide ranges of solid materials are used as electrodes, but the most common ‗inert‘ solid electrodes are lead, vitreous carbon, gold and platinum. In order to obtain consistent results with solid electrodes, it is important to establish a satisfactory electrode pretreatment procedure that ensures a reproducible state of oxidation, surface morphology and freedom from adsorbed impurities. Electrodes are polished on cloth pads impregnated with diamond particles down to 1 μm and then with alumina of fixed grain size down to 0.05 μm.

1.9.1.3 Counter Electrode

The purpose of the counter electrode is to supply the current required by the working electrode without in any way limiting the measured response of the cell. It is essential that the electrode process is decomposition of the electrolyte medium or oxidation/reduction of a component of the electrolyte so that current flows readily without the need for a large overpotential.

The counter electrode should not impose any characteristics on the measured data, and in consequence it should have a large area compared to the working electrode. Moreover, as also noted above, its shape and position are important since these determine whether the working electrode is an equipotential surface, and consequently it is preferable to avoid a separator in the cell.

1.9.1.4 Reference Electrodes

The role of the reference electrode is to provide a fixed potential which does not vary during the experiment (e.g. it should be independent of current density). In most cases, it will be necessary to relate the potential of the reference electrode to other scales, for example to the normal hydrogen electrode (NHE), the agreed standard for thermodynamic calculations.

In potentiostatic experiments the potential between the working electrode and reference electrode is controlled by a potentiostat, and as the reference half cell maintains a fixed potential, any change in applied potential to the cell appears directly across the working electrode-solution interface. The reference electrode serves the dual purpose of providing a thermodynamic reference and also isolates the working electrode as the system under study. In practice, however, any measuring device must draw current to perform the measurement, so a good reference electrode should be able to maintain a constant potential even if a few microamperes are passed through its surface.

In practice the main requirement of a reference electrode is that it has a stable potential and that it is not substantially polarized during the experiment. Hence it is common to use the highly convenient aqueous saturated calomel electrode (SCE) in many experiments in all solvents. Even so, a very wide range of reference electrodes have been used in non-aqueous solvents.

Potential of some common reference electrodes are listed in Table 1.5.

Table - 1.6 Potential of Some Typical Reference Electrodes in Aqueous Solutions at 298K

Common name	Electrode composition	Potential / V *vs* NHE
SCE	Hg/Hg_2Cl_2, sat KCl	+0.241
Calomel	Hg/Hg_2Cl_2, 1 mol dm^{-3} KCl	+0.280
Mercurous sulphate	Hg/Hg_2SO_4, sat K_2SO_4 Hg/Hg_2SO_4, 0.5 mol dm^{-3} H_2SO_4	+0.640 +0.680
Mercurous oxide	Hg/HgO, 1 mol dm^{-3} NaOH	+0.098
Silver chloride	Ag/AgCl, sat KCl	+0.197

A great deal of modern electrochemistry is carried out in non-aqueous solvent media, and often aqueous reference electrodes can be used at the expense of an unknown aqueous-non aqueous junction potential. In acetonitrile, the calomel electrode is unstable, and the most frequently used reference electrodes are Ag/AgCl or Ag/Ag^+.

1.9.1.5 The Electrolytic Solution

The electrolytic solution is the medium between the electrodes in the cell, and it will consist of solvent and a high concentration of an ionised salt as well as the electroactive species; it may also contain other materials, complexing agents, buffers, etc. The supporting electrolyte is used (a) to increase the conductivity of the solution and hence to reduce the resistance between the working and counter electrodes (to avoid undue Joule heating), to help maintain a uniform current and potential distribution, and to reduce the power requirement on the potentiostat), and also to minimise the potential error due to the uncompensated solution resistance. With appropriate precautions, electrochemical experiments are possible in almost any medium. Table 1.6 lists some widely used media.

Table 1.7 Common Solvents and Media for Electrochemical Experiments**.**

1. Water
   Aqueous solutions of many salts and/or complexing agents at various pH. Buffered and unbuffered media.
2. Other Protonic Solvents
   e.g. acetic acid, ethanol, methanol, liquid HF.
3. Aprotic Solvents
   e.g. acetonitrile, dimethylformamide, dimethylsulphoxide, sulphur dioxide, ammonia, propylene carbonate, tetrahydrofuran. Many studies use as electrolytes $R_4N^+ X^-$, R= CH_3, C_2H_5 or C_4H_9, X= ClO_4^-, BF_4^-, PF_6^-, or halide ion. Media difficult to buffer.
4. Mixed Solvents
   Particularly mixtures of water with ethanol, acetronitrile, etc. Again, these media may be buffered or unbuffered, contain many electrolytes, etc.
5. Molten Salts
   e.g. NaCl, KCl/NaCl/LiCl eutectics etc.

Electrode reactions can be extremely sensitive to impurities in the solution; for example, organic species are often strongly adsorbed even at 10^{-4} mol dm^{-3} bulk concentration from aqueous solutions. Hence salts should be of the highest available purity and/or recrystallised, solvents should be carefully purified, and solutions must be carefully deoxygenated. Purification and drying of non-aqueous solvents have been described elsewhere [56-57] in some detail.

1.9.1.6 Instrumentation

The electrochemist‘s armory is based on electronic apparatus designed to control/measure the charge passed (coulostat/integrator), current (galvanostat/current follower) and potential (potentiostat/high impedance voltmeter) in an electrochemical cell.

Potentiostat : The potentiostat is a device for controlling the potential between the working electrode and the reference electrode at a fixed and selected potential (commonly we also wish to programme this potential with time).

Galvanostat : The simplest way to obtain a constant current is to apply a voltage from a low output impedance voltage sources across a large resistor in series with the cell. The current will be given by the ratio E_{in}/R (provided resistance R is very large compared with the impedance of the cell).

1.9.2 Processes at Electrode Surface

A solid conducting material must be present to provide the site for each electrochemical reaction. These materials are called electrodes. The electrodes at which oxidation occurs is termed as the anode. The other electrode, the cathode, is the site of the reduction process.

1.9.2.1 Electrode Reactions

An electrode reaction is a heterogeneous chemical process involving the transfer of electrons to or from a surface, generally a metal or a semiconductor. The electrode reaction may be an anodic process whereby a species is oxidised by the loss of electrons to the electrode, e.g.

$$2\,H_2O - 4e^- \rightarrow O_2 + 4H^+ \qquad 1.1$$

$$Ce^{3+} - e^- \rightarrow Ce^{4+} \qquad 1.2$$

$$2Cl^- - 2e^- \rightarrow Cl_2 \qquad 1.3$$

$$Pb + SO_4^{2-} - 2e^- \rightarrow PbSO_4 \qquad 1.4$$

$$2Al + 3H_2O - 6e^- \rightarrow Al_2O_3 + 6H^+ \qquad 1.5$$

By convention [58], the current density, *I* , for an anodic process is a positive quantity. Conversely, the charge transfer may be a cathodic reaction in which a species is reduced by the gain of electrons from the electrode, e.g.

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \qquad 1.6$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu \qquad 1.7$$

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \qquad 1.8$$

$$PbO_2 + 4H^{+} + SO_4^{--} + 2e^{-} \rightarrow PbSO_4 + 2H_2O \qquad 1.9$$

$$2CH_2 = CHCN + 2H_2O + 2e^{-} \rightarrow (CH_2CH_2CN)_2 + 2OH^{-} \qquad 1.10$$

and the current density for a cathodic process is a negative quantity. The diversity of electrode reactions can already be seen from Equation (1.1.–1.10): the electroactive species may be organic or inorganic, neutral or charged, a species dissolved in solution, the solvent itself, a film in the electrode surface, or indeed, the electrode materials itself. Moreover, the product may be dissolve in solution, in a gas, or a new phase on the electrode surface. The many type of electrodes reactions are also illustrated in Fig. 1.3.

Electrolysis is only possible in a cell with both an anode and a cathode, and, because of the need to maintain an overall charge balance; the amount of reduction at the cathode and oxidation at the anode must be equal.

1.9.2.2 Mass Transport

In general, in electrochemical systems, it is necessary to consider three modes of mass transport; namely,

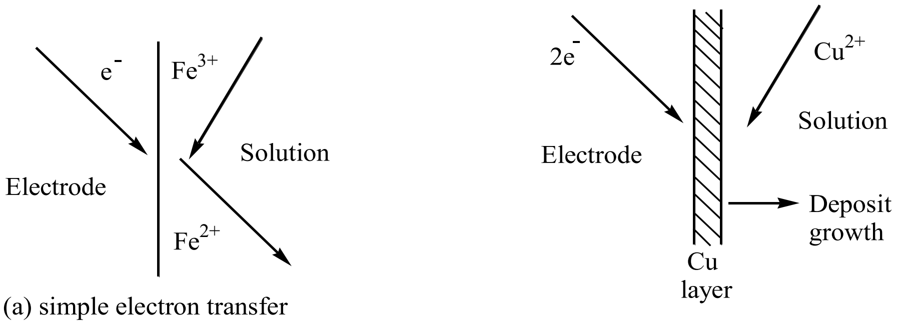
(a) Diffusion: Diffusion is the movement of a species down a concentration gradient, and it must occur whenever there is a chemical change at surface. An electrode reaction converts starting material to product (O→R), and hence close to the electrode surface there is always a boundary layer (up to 10^{-2} cm thick) in which the concentrations of O and R are a function of distance from the electrode surface. The concentration of O is lower at the surface than in the bulk, while opposite is the case for R, and hence O will diffuse towards and R away from the electrode.

(b) Migration: Migration is the moment of charged species due to a potential gradient, and it is the mechanism by which charge passes through the electrolyte; the current of electrons through the external circuit must be balanced by the passage of ions through the solution between the electrodes (cations to the cathode and anions to the anode).

It is, however, not necessarily an important form of mass transport for the electroactive species even if it is charged. The forces leading to migration are purely electrostatic, and hence the charge can be carried by any ionic species in the solution. As a result, if the electrolysis is carried out with a large excess of an inert electrolyte in the solution, this carries most of the charge, and little of the electroactive species is transported by migration.

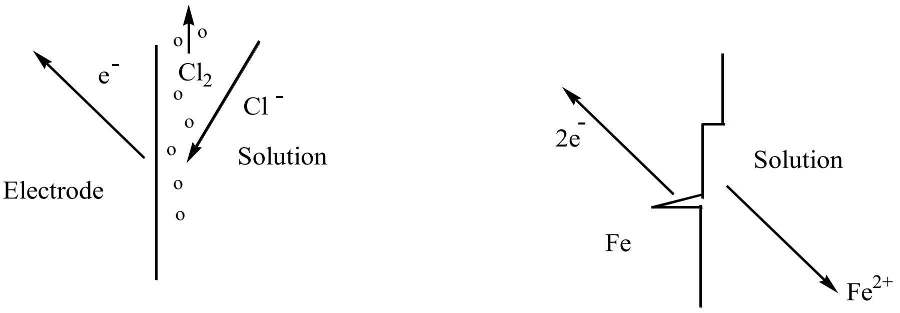
1.9.2.3 Convection

Convection is the moment of a species due to mechanical forces. It can be eliminated, at least on a short timescale (it is difficult to eliminate natural convection arising from density difference on a longer time, i.e.> 10s) by carrying out the electrolysis in a thermostat in the absence of stirring or vibration. In industrial practice, it is much more common to stir or agitate the electrolyte or to flow the electrolyte through the cell. These are all forms of forced convection and, when present, they have a very large influence on the current density.



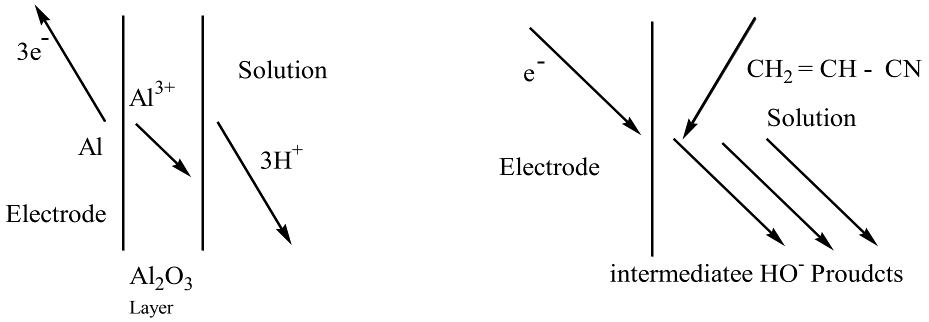
(a) simple electron transfer
$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$

(b) metal deposition
e.g. $Cu^{2+} + 2e^{-} \rightarrow Cu$



(c) gas evolution
e.g. $2Cl^{-} - 2e^{-} \rightarrow Cl_2$

(d) corrosion
e.g. $Fe - 2e^{-} \rightarrow Fe^{2+}$



(e) oxide film formation
$2Al + 3\,H_2O - 6e^{-} \rightarrow Al_2O_3 + 6H^{+}$

(f) electron transfer with coupled chemistry
$2CH_2 = CH - CN + 2H_2O + 2e^{-}$
$\rightarrow (CH_2 - CH_2 - CN)_2 + 2OH^{-}$

Fig. 1.3: Schematic view of some types of electrode reactions met in applied and fundamental electrochemistry.

1.10 Some Important Electrode Materials

1.10.1 Metals

Metals are crystalline solid materials consist of metal atoms distributed in a definite pattern resulting from their close packing. The types of close packing arrangement depend upon the size and electronic configuration of the atoms involved in the formation of crystal lattice. Since the metal atoms are all in direct contact with one another in the lattice and their valence electrons are in identical energy states, it is believed that the electrons are free to migrate between atoms. Metal atoms have an excess of low energy orbital vacancies. These vacancies enable valence electrons to move from near a certain nucleus to near any other nucleus where their position remains indistinguishable from the first. Thus, metals may be pictured as a collection of positive atomic cores embedded in a fluid of electrons or sea of electrons. For this fluid of electrons, metals are good conductors of electricity and heat. Metals have metallic luster; they are malleable, ductile and high melting points.

Metals have simple crystal lattices since metallic bonding envisages closest packing of atoms-one layer above another. Metals may have any system of seven common crystal systems. Fe, Cu, Al, Ag, Au etc are the most common metals which are very useful to us.

1.10.2 Metal Oxide : Semiconductors

Semiconductors are special kind of materials which have the properties of semiconductivity, an electrical property of materials. A relatively small group of elements and compounds have an important electrical property, semiconduction, in which they are neither good electrical conductors nor good electrical insulators. Instead, their ability to conduct electricity is intermediate. Si, Ge, impure ZnO, impure NiO are some examples of semiconductors.

The magnitude of conductivity in the simple semiconductors fall within the range 10^{-6} to 10^{-1} Ω^{-1} cm^{-1}. This intermediate range corresponds to band gaps of less then 2 eV. Both conduction electrons and electron holes are charge carriers in a simple semiconductor.

In a semiconductor element, the energies of the valence electrons, which bind the crystal together, lie in the highest filled energy band, called the valence band. The empty band above, called the conduction band, is separated from the valence band by an energy gap. The magnitude of the energy gap or the width of the forbidden energy zone is characteristic of the lattice alone and varies widely for different crystals.

The transfer of an electron from the valence band to the conduction band requires high excitation energy to overcome the potential barrier of the forbidden energy zone. Consequently, such elements behave like an insulator at low temperatures. The application of heat or light energy may give enough energy to some electrons in the valence band to excite them across the forbidden zone into the conduction band. These electrons in the conduction band are now free to move and can carry electricity (Fig. 1.4).
Semiconductors are of two kinds such as

(i) Intrinsic semiconductor
(ii) Extrinsic semiconductor

(i) Intrinsic semiconductors : If a pure, elemental substance shows the semiconducting properties, it is called intrinsic semiconductor. Pure Si, Ge shows these semiconducting properties. For these, semiconduction results from the thermal promotion of electrons from a filled valence band to an empty conduction band . There, the electrons are negative charge carriers. The removal of electrons from the valence band produces electron holes which are positive charge carrier and identical to the conduction electrons (Fig. 1.4 a). This overall conduction scheme is possible because of the relatively small energy band gap between the valence and conduction bands in silicon. If δ is the conductivity of semiconductor then for intrinsic semiconductor, we can write:

$$\delta = nq\,(\mu_e + \mu_n) \qquad 1.11$$

Where, n → density of conduction electron

q → charge of single carrier

μ_e → carrier mobility of electron

μ_n → carrier mobility of hole

(ii) Extrinsic semiconductors: Extrinsic semiconduction results from impurity additions known as dopants, and the process of adding these components is called doping. These types of semiconductors are extrinsic semiconductors. At room temperature, the conductivity of semiconductors results from electrons and holes introduced by impurities in the crystal. The presence of an impurity lowers considerably the activation energy necessary to transfer an electron from the valence band to the conduction band. This indicates that the ground state energies of such easily excited electrons must lie in the forbidden energy region. Two such discreate energy levels, known as donor levels and acceptor levels, may be introduced into the forbidden energy zone at a small interval of energy below the conduction band or above the valance band (Fig.1.4 b). Donor levels give rise to electrons in the conduction band, whereas acceptor levels lead to the formation of holes in the valence band. Impurity of Si, with B, P, NiO, ZnO, are the examples of extrinsic semiconductors. Extrinsic semiconductors are of two kinds such as p-type extrinsic semiconductor and n-type extrinsic semiconductor.

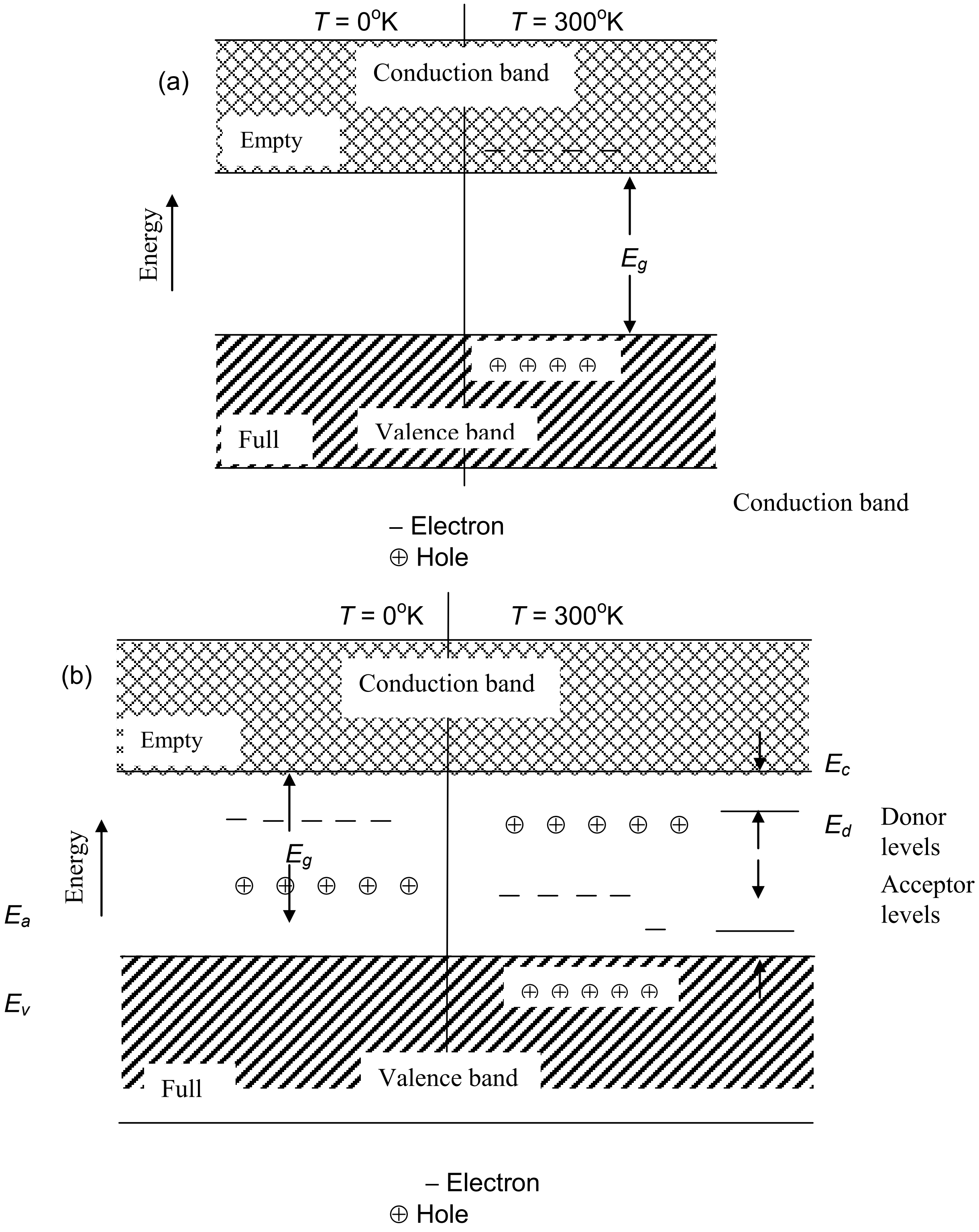


Fig. 1.4 A pictorial representation of an (a) intrinsic and (b) extrinsic semiconductor.

p-type Extrinsic Semiconductors: The p-type semiconductor is obtained when the impurity atoms have fewer valence electrons than the silicon or germanium atoms of the original crystal. When a trivalent element such as B, Al, Ga, In is substituted for Si atom, the structure will be locally incomplete and the impurity atom will acquire an extra electron from a nearly bond in the lattic to approximate the terahedral cloud distribution of the lattice. This creates a positive hole localized near the impurity, which will attempt to neutralize itself by taking an electron from another neighboring bond. Then, again a hole is formed in place of this electron and it will neutralize itself by taking another electron from the next neighboring bond. Such way the positive holes carry electricity in the extrinsic semiconductor. So it is called p (i.e. positive) type semiconductor (Fig. 1.5) Cu_2O also p-type semiconductor.

n-type Semiconductors: The n-type semiconductor arises from substitution of impurity atoms having more valence electrons than Si or Ge atoms. Elements such as P, As, Sb, and Bi have five valence electrons. When such an element is substituted for a silicon atom, four of its five electrons will enter the inter-atomic bonds, but the fifth electron will be only slightly attracted by the excess of the positive charge on the nucleus. Thermal agitation even at room temperature is sufficient to transfer this electron to the conduction band. Since conductivity is due to the motion of electrons in the conduction band, this semiconductor is called n-type and the impurity is called the donor (Fig. 1.5). Titanium dioxide or titania is a non-stoichiometric transition metal oxide and behaves as n-type semiconductor [59].

There are three naturally occurring crystal phases of titanium dioxide: rutile, anatase, and brookhite. Most of the electrochemical and photocatalytic work to date have been performed on rutile or anatase, or a mixture of the two. Both rutile and anatase have tetragonal unit cells, and both structures contains slightly distorted TiO_6 octahedral. Rutile is thermodynamically more stable than anatase at room temperature; the free energy change for antatase to rutile is –5,4 kJ/mol [60].

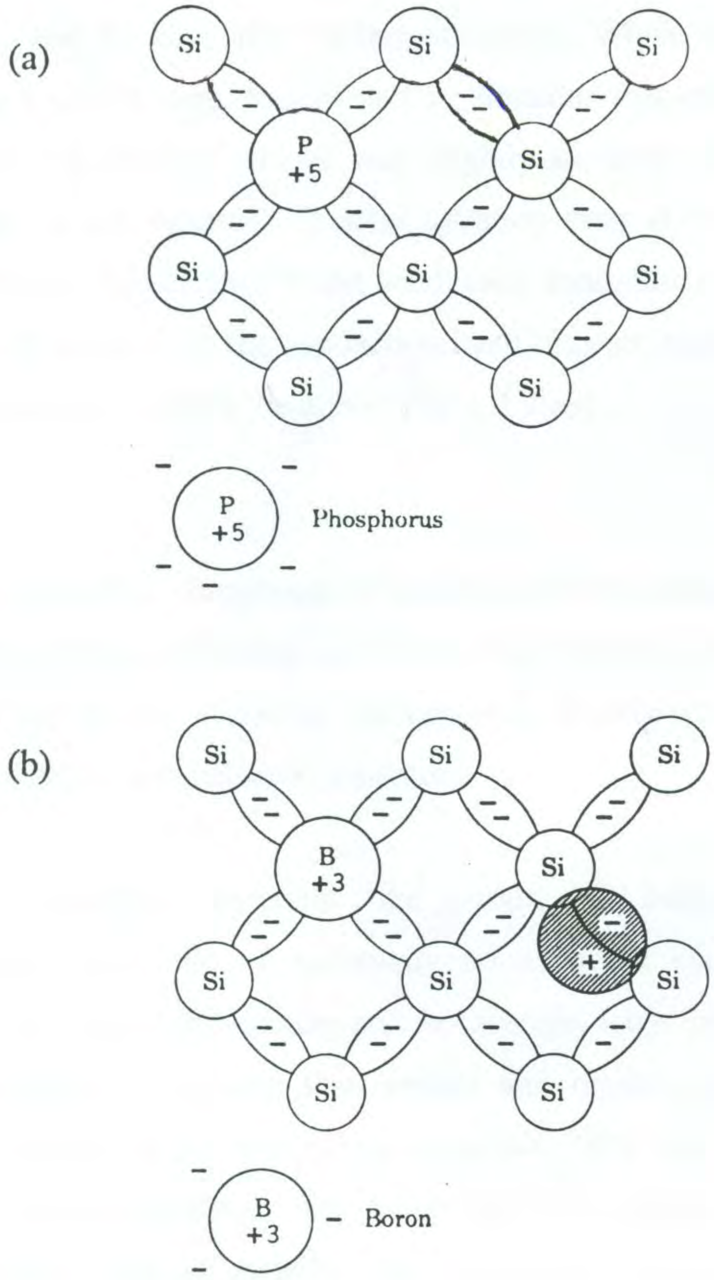


Fig. 1.5: Types of Impurity Semiconductors (a) n-type (b) p- type.

The absorption and reflection properties of rutile have been studied extensively. At 4K, the short wavelength absorption edge for rutile is 410 nm (bandgap energy = 3.05 eV) [61-62]. The lowest energy electronic absorption at 3.05 eV is an indirect transition. On the other hand, the bandgap of anatase is reported as 3.2 eV [63]. The absorption coefficients for both crystal phases are reported as ~10^5 cm^{-1} at 340 nm [64].

Ultraviolet radiation below ~390 nm stimulates valence-band electrons in TiO_2 particles that are suspended in contaminated water. These electrons are promoted to the conduction band (e^-_{cb}), creating holes in the valence band (h^+_{vb}). These electron / hole pairs can either recombines, producing thermal energy, or interact with the external environment to perform oxidation and reduction reactions.

$$TiO_2 \xrightarrow{hv} TiO_2\ (e^-_{cb},\ h^+_{vb})$$

1.10.3 Composites

Since 1965 a distinct discipline and technology of composite materials had begun to emerge. That is 80% of all research and development on composites have been done since 1965 when the Air Force launched its-all out development program to make high performance fiber composites a practical reality. There are two major reasons for the revived interest in composite materials. One is that the increasing demands for higher performance in many product areas specially in the aerospace, nuclear energy and aircraft fields is taxing to the limit our conventional monolithic materials. The second reason, the most important for the long run is that the composites concept provides scientists and engineers with a promising approach to designing, rather than selecting, materials to meet the specific requirements of an application.

The term ‗composite' refers to something made up of various parts or elements. In definition of composite depends on the structural level of the composite we are thinking about. At the submicroscopic level that of simple molecules and crystal cells all materials composed of two or more different atoms or elements would be regarded as composites. This would include compounds, alloys plastics and ceramics. Only the pure elements would be excluded. At the microscopic level (or microstructural level) that of crystals, polymers, and phases a composite would be a material composed of two or more different crystals, molecular structures, or phases. By this definition, most of our traditional materials, which have always been considered monolithic, would be classified as composites. At the macro structural level which is most useful for composites, the definitions of composites is that they are a mixture of macro constituent phase composed of materials which are in a divided state and which generally differ in form and/or chemical composition. Note that, contrary to a widely held assumption, this definition does not require that a composite be composed of chemically different materials, although this usually the case. The more important distinguishing characteristics of a composite are its geometrical features and the fact that its performance is the collective behavior of the constituents of which it is composed. A composite material can vary in composition, structure, and properties from one point to the next inside the material.

The major constituents used in structuring composites are fibers, particles, laminas, flakes, filters and matrix. The matrix, which can be thought of as the body constituent, gives the composite its bulk form. The others four which can be referred to as structural constituents, determine the characters of the composites‘ internal structure. A special type of composite, fiberglass embedded in a polymer matrix is a relatively recent invention but has in a few decades, become a commonplace material. Characteristic of good composites, fiberglass, provides the ‗best of both worlds‘, it carries along the superior properties of each component, producing a product that is superior to either of the components separately. The high strength of the small diameter glass fibers is combined with the ductility of the polymer matrix to produce a strong material capable of withstanding the normal loading required of a structural material.

1.11 Theoretical Aspects of Experimental Techniques

1.11.1 Cyclic Voltammetry

Electrochemical process is widely used in the polymerization of organic polymer. Most of the system for electrochemical polymerization consists of a compartment where three electrodes are dipped into the solution containing monomer and electrolyte solution. Appropriate potential is applied to the working electrode for polymerization of the monomers. The potential of the working electrode, where deposition of the polymer film takes place, is controlled versus the reference electrode using a feed-back circuit or a potentiostat. Feed-back circuit drives the current between the working and counter electrodes while ensuring that none passed through the reference electrode circuit.

The nature of the working electrode is a critical consideration for the preparation of these films. Since the films are produced by an oxidative process, it is important that the electrode is not oxidized concurrently with the aromatic monomer. For this reason, most of the available films have been prepared using a platinum or a gold electrode.

Potentiostatic, galvanostatic and potential sweep techniques such as cyclic voltammetry are widely used for electrochemical polymerization of aromatic compounds. In potentiostatic technique, a constant potential is applied to the working electrode which is sufficient to oxidize the monomers to be polymerized on the electrode. In galvanostatic process, a constant current density is maintained to polymerize the monomers while film thickness can be controlled in the similar way as described for potentiostatic technique. On the other hand, cyclic voltammetry involves sweeping the potential between potential limits at a known sweep rate. On reaching the final potential limit, the sweep is reversed at the same scan rate to the initial potential and the sweep may be halted, again reversed, or alternatively continued further. In such experiments, cell current is recorded as a function of the applied potential.

1.11.2 d. c. Conductivity

The conductivity of polymer or polymeric composites depends on dopant level, protonation level of an oxidized matrix and moisture content of the sample. Electrical resistivity of the polymer samples may be measured by two probe and four probe techniques. However, the electrical conductivity measurement employed the ohm‘s law

$$E/I = R \qquad 1.12$$

where I is the current in amperes, E is the potential difference in volts, R is the resistance in ohms. The reciprocal is termed the conductance, this is measured in Siemens (S) which is reciprocal of ohms (ohm^{-1}). The resistance of a samples of length L, and cross-sectional area A, is given by

$$R = \rho L/A \qquad 1.13$$

where ρ is a characteristic property of the material termed as resistivity. L and A will be measured respectively in cm and then ρ refers to cm cube of the material and

$$\rho = RA/L \qquad 1.14$$

The reciprocal of resistivity is the conductivity, (formerly specific conductance)

$$K = 1/\rho \qquad \text{or} \qquad K = L/RA \qquad 1.15$$

which is in SI units, is the conductance of a one cm cube of substance and has the units ohm^{-1} cm^{-1} or S cm^{-1} [65].

In this experiment, the powdered samples were pressed to rigid solid mass by pressing from the both sides of the mass. The two electrodes of microvolt were then connected with solid mass and resistivity was measured directly from the microvolt

1.12 Literature Review

Oturan M.A. [66] showed that the electrochemical production of Fenton's reagent by simultaneous reduction of dioxygen and ferric ions on a carbon felt electrode, permits a controlled, in situ generation of hydroxyl ($OH^{\cdot}$) radicals. The possibility of using electrochemically produced OH· radicals for solving environmental problems is investigated. Continuous and controlled production of hydroxyl radicals was achieved by electrochemical reduction of O_2 in the presence of a catalytic amount of ferric or ferrous ion. These radicals are used for remediation of water containing toxic-persistent-bioaccumulative organic pollutants through their transformation into biodegradable compounds or through their mineralization into H_2O and CO_2. A widely used herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D), was selected as a model for a toxic organic pollutant. High pressure liquid chromatography (HPLC) was used to quantify the distribution of the hydroxylated products obtained. Rate constants for the hydroxylation reactions of 2,4-D, 2,4-dichlorophenol (2,4-DCP), 2,4-dichlororesorcinol (2,4-DCR) and 4,6-dichlororesorcinol (4,6-DCR) were determined. The mineralization of 2,4-D and its derivatives was followed by total organic carbon (TOC) measurements. More than 95% of 2,4-D and the intermediates generated during the electrolysis can be mineralized.

Kariyajjanavar P. et al. proved [67] the removal of pollutants from effluents by electrochemical degradation has become an attractive method in recent years. Their paper deals with the removal of reactive textile dye Cibacron Navy W-B (CNWB) from an aqueous medium by the electrochemical method using graphite carbon electrodes. Electrochemical behavior of reactive azo dye CNWB was performed with cyclic voltammetry in sulphuric acid medium using glassy carbon as working electrode. The potential range selected for the dye was in the range +700 mV to –450 mV. The voltammetric curve of CNWB shows cathodic peaks at +50 mV, –155 mV and –317 mV and anodic peaks at +382 mV and +547 mV, respectively. The decolorization efficiency was assessed through UV-Visible studies. The LC-MS of the dye were analyzed before and after electrochemical treatment and confirmed that the azo groups and aromatic rings were destroyed. The effect of pH and nature of supporting electrolytes on the electrochemical degradation of dye was also studied. The maximum Chemical Oxygen Demand (COD) removal efficiency was ~100% for the dye solutions at 5 gL^{-1} of NaCl concentration. The results revealed the suitability of the present process for the effective degradation of dye effluents.

Ghangrekar M.M. [68] did the performance of mediator-less and membrane-less microbial fuel cell (ML–MFC) was evaluated to treat synthetic wastewater and actual sewage. The ML–MFC gave COD and BOD removal efficiencies of 88% and 87%, respectively, and TKN removal was around 45–50%. Biomass granulation was observed in the anode compartment of ML–MFC. Effect of distance between the electrodes and total surface area of anode on electricity production was evaluated under variable external resistance. Maximum power density of 10.9 and 10.13mW/m^2 was observed at lower spacing between the electrodes (20 cm) and for lesser surface area of the anode, respectively. With variation in the carbon source in the feed, variation in power production was observed.

Abu Ghalwaa N.M. [69] showed a modified electrode, which can be used as an anode for electrocatalytic oxidation processes of dyestuff in aqueous solutions, was fabricated by the electrodeposition of a lead oxide layer on a titanium substrate. The modified electrode was used for the electrochemical degradation of an acid green dye. The results of the electrocatalytic oxidation process of the dyestuff solutions were expressed in terms of the remaining dye concentration and chemical oxygen demand (COD) values. The different operating conditions of the treatment process were studied. The optimum operating conditions for the dye and modified electrode were determined, where good results for complete removal of the dye and COD were achieved. The optimum conditions were applied to the treatment of a sulfur black dye in true wastewater solutions.

Idris A. [70] represented the degradation of phenol in wastewater using anolyte, which is generated from electrochemical activation process. Anolyte consists of reactive ions and free radicals, which contribute to its oxidizing behavior. The optimum conditions, which facilitate a complete degradation of phenol, were found using variation of dosage of anolyte and reaction time. It was found that about 20% of anolyte was the optimal dosage which corresponded to 98% degradation of phenol after a reaction time of 60 minutes. The main products during degradation of phenol by anolyte were found to be benzoquinone, hydroquinone, catechol, maleic acid, fumaric acid and oxalic acid.

Bensalah Nasr [71] explained the electrochemical oxidation of aqueous wastes polluted with 4-chlororesorcinol has been studied on boron-doped diamond electrodes on acidic medium. The voltammetric results showed that in the potential region where the supporting electrolyte is stable, reactions occur, resulting in the loss of activity due to electrode fouling. Galvanostatic electrolysis study showed that the oxidation of these wastes in single-compartment electrochemical flow cell with boron doped diamond anodes deal to the complete mineralization of the organics but is no indication of electrode fouling. Resorcinol, 1,2,4-trihydroxybenzene, benzoquinone, maleic, fumaric, and oxalic acids have been detected as soluble organics and chlorides (Cl^-) and hypochlorites (ClO^-) as mineral products during the electrolysis of 4-chlororesorcinol. The electrochemical oxidation of 4-chlororesorcinol consists of a sequence of steps: Release of Cl and/or hydroxylation of the aromatic ring; formation of quinonic compounds; oxidative opening of aromatic ring to form carboxylic acids; and oxidation of carboxylic acids to carbon dioxide. Both, direct oxidation at boron doped diamond surface and mediated oxidation by powerful oxidants electrogenerated from electrolyte oxidation at anode surface are involved in these stages.

Logan B.E. [72] proved that it is possible to directly generate electricity using bacteria while accomplishing wastewater treatment in processes based on microbial fuel cell technologies. When bacteria oxidize a substrate, they remove electrons. Current generation is made possible by keeping bacteria separated from oxygen, but allowing the bacteria growing on an anode to transfer electrons to the counter electrode (cathode) that is exposed to air. In this paper, several advances are discussed in this technology, and a calculation is made on the potential for electricity recovery. Assuming a town of 100,000 people generate 16.4-106L of wastewater, a wastewater treatment plant has the potential to become a 2.3 MW power plant if all the energy is recovered as electricity. So far, power densities are low, resulting in power generation rates of ,150 kW/m^2. Progress is being made that we believe may result in as much as 0.5MW from wastewater treatment. The generation of electricity during wastewater treatment may profoundly affect the approach to anaerobic treatment technologies used in wastewater treatment.

Hong Liu [73] examined that microbial fuel cells (MFCs) have been used to produce electricity from different compounds, including acetate, lactate, and glucose. We demonstrate here that it is also possible to produce electricity in a MFC from domestic wastewater, while at the same time accomplishing biological wastewater treatment (removal of chemical oxygen demand; COD). Tests were conducted using a single chamber microbial fuel cell (SCMFC) containing eight graphite electrodes (anodes) and a single air cathode. The system was operated under continuous flow conditions with primary clarifier effluent obtained from a local wastewater treatment plant. The prototype SCMFC reactor generated electrical power (maximum of 26 mW m^{-2}) while removing up to 80% of the COD of the wastewater. Power output was proportional to the hydraulic retention time over a range of 3-33 h and to the influent wastewater strength over a range of 50-220 mg/L of COD. Current generation was controlled primarily by the efficiency of the cathode. Optimal cathode performance was obtained by allowing passive air flow rather than forced air flow (4.5-5.5 L/min). The Coulombic efficiency of the system, based on COD removal and current generation, was <12% indicating a substantial fraction of the organic matter was lost without current generation. Bioreactors based on power generation in MFCs may represent a completely new approach to wastewater treatment. If power generation in these systems can be increased, MFC technology may provide a new method to offset wastewater treatment plant operating costs, making advanced wastewater treatment more affordable for both developing and industrialized nations.

Parsaa J. B. [74] showed his paper the decolorization and degradation of synthetic and real wastewater by electrochemical oxidation method were investigated. Synthetic wastewater consisting of Mordant Red 3 (MR3) was used as a model compound. Electrochemical degradation processes were performed using Pt as an anode and Stainless Steel 304 as a cathode. In the bulk solution, the strong oxidizing potential of the chemicals were produced when the wastewater was passed through the electrolytic cell the organic pollutants were oxidized too little or harmless organic molecules, carbon dioxide and water. The results indicated that the removal of chemical oxygen demand (COD) and color were 86% and 100% respectively. The removal of COD and color increased by increasing voltage and chloride concentration at low pH.

Hyunsoo Moon [75] optimized a microbial fuel cell (MFC) which in terms of MFC design factors and operational parameters for continuous electricity production using artificial wastewater (AW). The performance of MFC was analyzed through the polarization curve method under different conditions using a mediator-less MFC. The highest power density of 0.56 W/m2 was achieved with AW of 300 mg/l fed at the rate of 0.53 ml/min at 35^{0}C. The power per unit cell working volume was 102 mW/l, which was over 60 times higher than those reported in the previous mediator-less MFCs which did not use a cathode or an anode mediator. The power could be stably generated over 2 years.

Lidia Szpyrkowicz [76] treated the tannery wastewater by the electrochemical method using Ti/Pt and Ti/Pt/Ir electrodes is investigated. The aim of a satisfactory elimination of NH^+_4 from wastewaters of different strength was achieved using both types of electrodes. A Ti/Pt/Ir anode proved to have the electrocatalytical properties for NH^+_4 removal, but it resulted to be more sensitive to poisoning by H_2S contained in the wastewater. For both types of the electrodes NH^+_4 removal followed pseudo-first order kinetics, with the rate decreasing in function of the presence of organic substances. A concurrent removal of COD was observed particularly with a Ti/Pt anode, but its magnitude was not sufficient to ensure the discharge limits to be met while treating the raw wastewater only by the electrochemical process. In conclusion the electrochemical process can be applied successfully as a final polishing or an alternative to biological nitrification, but cannot substitute completely the traditional treatment of tannery wastewater.

Oliver J. Murphy [77] used a single cell electrochemical reactor that utilizes a proton exchange membrane (PEM) as a solid electrolyte was investigated for the treatment of waters with low or negligible electrolyte content. The electrochemical reactor concept, test system design, the role of the proton exchange membrane and the principle of organic impurity oxidation at PEM/electrocatalyst interfacial reaction zones are outlined. Test data and kinetic analysis are presented. The feasibility and application for water reclamation processes in controlled ecological environments (e.g. lunar/Mars habitats) are discussed. The approach has potential as a terrestrial water pollution control method.

Marco Panizza [78] explained the disposal of industrial wastewater containing naphthalene- and anthraquinone-sulphonic acids by electrochemical methods has been studied in this paper. It was found that only a small fraction of the organics was oxidised by direct electrolyses, while complete mineralisation of the organics was obtained with the indirect process, electrogenerating hypochlorite from chloride oxidation. The effects of operating factors, such as anode materials and chloride concentration, were also investigated. The experimental data suggested that the Ti/Pt anodes had the highest electrocatalytic activity and increasing the chloride concentration in the electrolyte resulted in an increasing of COD and colour removal.

Polcaro A.M [79] investigated the performance of BDD electrodes during oxidation of aqueous solutions of phenol. The main reaction intermediates are identified, the effect of operating conditions on the faradic yield of the process, and the degree of mineralization achievable under different experimental conditions are evaluated. Due to the crucial role of mass transfer in the process, an impinging jet cell is used for the experiments. The results indicate that if a minimum value of current density is imposed, suitable initial conditions can be set at which the removal of the reactant is always under mass transfer control and the process is carried out at a faradic yield of about unity, up to the near-complete disappearance of total organic load. High current density and high mass transfer coefficient must be used in order to carry out the process with high space-time yield. The performance of BDD is compared to that obtained at Ti/RuO_2 anodes.

Active carbon fiber was used as electrodes to treat several simulated dyeing wastewater and factual textile-dyeing wastewater from a textile-dyeing operation at Shanghai in Jinping Jia‘s experiment [80]. This method was found to be quite effective and highly competitive in contrast with Fenton's reagent. Several operating variables, such as voltage, pH and salt added were studied to ascertain their respective effect on the treatment efficacy. According to the experiment, nearly all the wastewater's chromaticity removals were higher than 90%, with COD removals within *ca.* 40–80%.

Different anode materials were tested by Eduardo Arevalo [81] to evaluate their suitability to eliminate organotin compounds electrochemically from shipyard process waters. The capacity of two types of anode materials was investigated: niobium coated with boron-doped diamond (BDD) and titanium coated with iridium dioxide, (Ti/IrO_2). The aim of this work was to characterize the performance of the process using both anode materials at different current densities, and also to evaluate the generation of by-products. A further objective of this work was to evaluate if operating at low potentials with BDD anodes (to avoid the generation of elemental oxygen) the consumption of energy for degradation of pollutants could be minimized. The processes were tested on synthetic and real shipyard water containing approximately 25,000 ng L^{-1} of tributyltin (TBT) (as Sn) and 5000 ng L^{-1} dibutyltin. The range of current densities was between 6 and 70mAcm^{-2}. The results showed that electrochemical treatment is suitable to eliminate organotins down to very low concentrations following a stepwise debutylation mechanism. Both anode materials exhibited a similar performance with energy consumption in the range of 7–10 kWhm^{-3} in order to decrease organotins down to 100 ng L^{-1} (as Sn). For the water composition tested, BDD did not outperform Ti/IrO_2 as initially expected, most probably because organotins were not only oxidized by •OH, but also by active chlorine compounds generated by the oxidation of chloride present in the wastewater (1.6 g L^{-1}, Cl^-) with both anode materials. It was also found that the residual oxidants remaining in the treated effluent had to be eliminated if the water is to be discharged safely in the aquatic environment.

The electrochemical oxidation of phenol for waste water treatment was studied by Comninellis, Ch. [82] on doped SnO_2 anodes. Analysis of reaction intermediates and a carbon balance has shown that the main reaction is oxidation of phenol to CO_2. This unexpected behaviour of the SnO_2 anode is explained by a change of the chemical structure of the electrode surface during anodic polarization.

Wastewater treatment by electrochemical oxidation of soluble organic wastes represents an attractive way of water purification, using only electrons as a reactant and is thus of major importance to the environmental science in Igor Cretescu‘s experiment [83]. For this purpose, the electrochemical behaviour of phenol in diluted aqueous acid and alkaline solutions was studied. Phenol was chosen as a test compound, because pollutants such as phenols and their derivatives are very common and present a low biodegradation character. Cyclic voltammetry on the platinum and platinum oxide electrodes and absorption spectrophotometry were used as investigation methods.

José L. Nava [84] showed the electrochemical oxidation of Alphazurine A (azA) has been studied in Na_2SO_4 media at Ti/IrO_2, Pb/PbO_2 and boron-doped diamond (Si/BDD) electrodes by bulk electrolysis experiments under galvanostatic control at j = 30 and 60 mA cm^{-2}. The obtained results have clearly shown that the electrode material plays an important role for the electrochemical incineration of azA, where Pb/PbO_2 and Si/ BDD lead complete mineralization of dye, while Ti/IrO_2 disfavoured such process. The complete mineralization of ±zA on Pb/PbO_2 and Si/BDD is due to the production of hydroxyl radicals on these materials surfaces. Current efficiencies obtained at Ti/IrO_2, Pb/PbO_2 and Si/ BDD gave values of 3, 24 and 42%, for each electrode material, at 30 mA cm^{-2}, respectively. These values were higher than those obtained at 60 mA cm^{-2}. Energy consumption values from the electrolyses performed at 30 mA cm^{-2} were 254, 124 and 51 kWh m^{-3}, for Ti/IrO_2, Pb/PbO_2 and Si/BDD, respectively. UV spectrometric measurements showed faster azA elimination at the Si/BDD electrode than those obtained on Ti/IrO_2 and Pb/PbO_2.

Karuppan Muthukumar [85] treated textile dye house wastewater from a reactive dye processing unit by using an electrochemical oxidation technique. The experiments were carried out in an electrochemical bipolar disc reactor using RuO_2 coated on titanium as anode and titanium as cathode. The sodium chloride present in the effluent was used as supporting electrolyte.

Operating parameters such as current density, reservoir hold-up and electrolysis time were studied for maximum Chemical Oxygen Demand (COD) reduction and other relevant parameters such as current efficiency and power consumption per kg of COD removal were calculated. The higher flow rate and lower reservoir hold-up resulted in improved COD removal. The applied current density was also found to significantly influence the reduction of COD. A suitable mathematical model is also proposed to illustrate the relationship between the basic parameters. Pseudo mass transfer coefficients were also evaluated for different experimental conditions.

A. G. Vlyssides [86] showed wastewater from total dyeing and finishing stages (TDFW) and wastewater only from dyeing stage (DW) from a Textile cellulosic reactive azo dyeing process were treated separately by an electrochemical method using Ti/Pt as anode and Stainless Steel 304 as cathode. In this technique, sodium chloride was used as an electrolyte and the mixture was passed through an electrolytic cell. Due to the strong oxidizing potential of the chemicals produced (chlorine, oxygen, hydroxyl radicals and other oxidants) the COD, BOD of the wastewaters were substantially decreased using this electrochemical technique. A number of experiments were run in a batch 5 liter apparatus and the results of the electrochemical treatment on the two kinds of wastewaters are reported here. The results indicate that the electrochemical method used is feasible for treatment of textile dyeing wastewaters.

D. Rajkumar [87] worked on the electrochemical oxidation of phenol using a Ti/TiO_2-RuO_2-IrO_2 anode in the presence of chloride as the supporting electrolyte was investigated. The experiments were performed in an undivided batch reactor. Preliminary investigations showed that only a small fraction of phenol was oxidized by direct electrolysis, while complete degradation of phenol was achieved by indirect electrochemical oxidation using chloride as a supporting electrolyte. The effect of operating parameters such as initial pH, supporting electrolyte concentration, phenol concentration, and charge input was studied using Box-Behnken second order composite experimental design. The effect of current density on COD removal was studied separately. TOC removal and AOX formation were studied for selected conditions. It was found that the formation of chlorinated organic compounds was pronounced at the beginning of electrolysis, but it was reduced to lower levels by extended electrolysis.

Chih-Ta Wang‘s experiment showed [88] the removal efficiency of COD in the treatment of simulated laundry wastewater using electrocoagulation/ electroflotation technology is described. The experimental results showed that the removal efficiency was better, reaching to about 62%, when applying ultrasound to the electrocoagulation cell. The solution pH approached neutrality in all experimental runs. The optimal removal efficiency of COD was obtained by using the applied voltage of 5 V when considering the energy efficiency and the acceptable removal efficiency simultaneously. The Cl^{-} concentration of less than 2500 ppm had a positive effect on the removal efficiency. The performance of the monopolar connection of electrodes was better than that of the bipolar connection in this work. In addition, the removal efficiency of using Al electrodes was higher in comparison with using Fe electrodes in the study. The highest COD removal amount per joule was found to be 999 mg dm^{-3} kW h^{-1} while using two Al electrodes, although the removal efficiency increased with the number of Al plates.

MUFF J. [89] studied the use of p-nitrosodimethylaniline (RNO) as a selective probe compound for hydroxyl radical detection in electrochemical oxidation studies. In the applied recirculation experimental setup with a Ti/Pt90-Ir10 anode, oxidation of RNO was found in both inert sulphate, phosphate, and nitrate electrolytes and electroactive chloride electrolytes, where the rate of oxidation was dramatically enhanced due to the indirect hypochlorous acid/hypochlorite oxidation. No influence on the rates of oxidation was found by addition of excess amounts of t-BuOH as hydroxyl radical scavenger, and hence the oxidation of RNO can be entirely contributed to the oxidative abilities of the lattice active oxygen of the Ti/Pt90-Ir10 anode and the chlorine species. The reaction kinetics changed from standard first order kinetics in the inert electrolytes to second order kinetics in the chloride electrolyte. Comparison of the oxidative performance of the electrochemical oxidation in a chloride electrolyte and the chemical oxidation by sodium hypochlorite under similar conditions showed a superior oxidation power of the in-situ electrochemical oxidation of RNO.

Krishna P [90] worked on the performance of a prototype up-flow single-chambered microbial fuel cell (MFC) for electrical power generation using brewery wastewater as fuel is reported. The designed reactor consisted of three zones, namely a lower anaerobic digestion zone, a central MFC zone, and an upper effluent clarifier zone. Tests were conducted in batch mode using a beer wastewater as the fuel/electron donor (COD concentration: 430 mg/L) and mixed consortia (both sewage microflora and anaerobic sludge) as a source of electrogenic bacteria. A stable current density of ~2,270 mA/m^2 was generated under continuous polarization with a constant external resistance (0.01 kΩ) and cell polarization gave a peak power density of 330 mW/m^2 at a current density of 1,680 mA/m^2. Electrochemical impedance analysis showed that the overall internal resistance of the reactor was quite low, that is, 8.0 Ω. Cyclic voltammetric analysis of the anodic biofilm at low scan rate revealed quite complex processes at the anode, with three redox peaks, at potentials of 116, 214, and 319 mV (vs. NHE).

E. M. Elsayed [91] investigated a method to electro reduce toxic hexavelent chromium to trivalent state using rotating disc electrode (RDE) and rotating cylinder electrode (RCE) cell. Electrolysis of acidic hexavalent chromium solution using a rotating lead cathode reduces the hexavalent chromium Cr6+ to trivalent chromium. The effect of chromium, sulphuric acid concentration, current density, time and speed of cathode rotation on current efficiency has been investigated under galvanostatic and linear sweep voltammetric techniques. The effect of these parameters on cell voltage and energy consumption has been also studied. It was found that the efficiency of the reduction method is directly proportional to the hexavalent chromium and sulphuric acid concentration. Trivalent chromium is successfully obtained from acidic industrial wastewater containing 1.5 g l-1 $Cr6^+$. High current efficiency is attained at current density 225 mA cm^{-2} for 80 minutes.

Huu D Doan [92] explained that the simulated wastewater containing propylene glycol methyl ether, Ni^{2+} and Zn^{2+} was treated using an aerated packed column. An electrochemical cell was also installed beneath the packing support in the bottom section of the column. The flowrate of water through the column was maintained at 8.94 kg m^{-2} s^{-1}. For 72 h of treatment using aeration alone, the BOD_5 was reduced by 43%, 56%, and 54% for air flowrates of 0.00094, 0.00141, and 0.00188 kg m^{-2} s^{-1} respectively. On the other hand, when the electrochemical cell was activated without aeration, the BOD_5 was reduced by 15%, 17%, and 23% at the applied voltages of 8, 16, and 25 V respectively. When both aeration of the wastewater and a voltage of 25 V were used, the percentage removal of BOD_5, on the average, was about 65% for all air flowrates used. The concentrations of Ni^{2+} and Zn^{2+} were also reduced by 57% and 61% respectively, in the absence of the supporting electrolyte. The addition of potassium chloride (100 ppm) as the supporting electrolyte enhanced the metal removal by 30%.

Choon Hwan Shin [93] proved that it is getting difficult to secure various kinds of usable water due to the worsening quality of water resources. Along with other regions, in Busan various measurements are considered to resolve the problems with increasing water consumption and limited water resources. In this point of view, a greywater treatment system (GTS) will be developed in this study as an alternative to reuse sewage/wastewater and its applicability will be confirmed to meet the demand. The GTS basically consists of an electrolytic cell which has shown highly effective in organic matter oxidation and nitrification, and its performance is investigated by assessing the treatment method and the water quality in both influent and effluent. A candidate system of electrolysis apparatus, which is the first reactor in the GTS, was selected and operated in batch and continuous types with real dye wastewater. The highest removal rates of BOD and COD were obtained with current density of 1.0 A/dm^2 and 10 % of electrolyte level. Also the removal rates of T-N and T-P were found to be moderate and could be improved with recycleratios of between 20 and 50 once.

Xuemingchen [94] showed that electroflotation (EF) is an attractive method in wastewater treatment. The heart of EF is the dimensionally stable oxygen evolution anode that is usually expensive. They present a stable anode by coating IrO x-Sb_2O_5- SnO_2 onto titanium. Accelerated life test showed that the electrochemical stability of the Ti/IrO x-Sb_2O_5-SnO_2 anode containing only 2.5 mol % of IrO x nominally in the activated coating was even higher than that of the conventional Ti/IrO xanode. Its service life for electroflotation application is predicted to be about 20 yr. Voltammetric investigation demonstrated that the Ti/IrO x-Sb_2O_5-SnO_2 anode could provide fast electron transfer. Moreover, the present anode was designed to be fork-like and arranged interlockingly at the same level as the cathode with a similar shape. Such an innovation in electrode configuration and arrangement allows bubbles produced at both electrodes to be dispersed into wastewater flow quickly and, therefore, enhances the effective contact between bubbles and particles, favorable for high flotation efficiency. In addition, the novel electrode system reduces the inter electrode gap to 2 mm, a spacing that is technically difficult for a conventional electrode system. This small gap results in a significant energy saving. Easy maintenance is found to be another advantage of this novel electrode system.

Wu Chen [95] discovered a method using three-dimensional electrode is applied to treat wastewater in oil fields, which contains polyacrylamide (PAM), for analogue. A best condition for electrolysis (I = 1.0 A, t=90 min, c=0.1%, m=980 g, ϕ=5 mm, d=5.0 cm) has been determined, under which the COD removal efficiency reached 96.0%, COD containing in wastewater reduced to 64.3 mg/L from 1 622.9 mg/L, the figure before treatment. Three categories of PAM-containing wastewater in production practice have been treated with the COD removal ratios being 87.5%, 82.4% and 84.7% respectively. Presence of H_2O_2 and ·OH are detected by means of Ti(IV)-5-Br-PADAP technique and colorimetry respectively. The concentration is positively proportional to the COD removal ratio and increases in accordance with increment of time of electrolysis and current.

Nabil S. Abuzaid [96] shown the efficiency of nitrite removal in an electrochemical cell was investigated in this study using stainless steel electrodes. The experiments were designed to study the effects of current input, volume of the solution, initial pH, and number of electrodes on removal of nitrite at a concentration typical to aquaculture system effluents. Current variation causes opposite trends, while an increase in current would increase the oxidizing efficiency of the system, the voltage induced increase in pH due to hydrogen evolution would decrease the efficiency of the oxidizing agent formed. However, the highest nitrite removal was achieved at a current of 2 A and a complete removal was attained after a duration of ten minutes. A first order reaction model was developed to predict the effect of current on nitrite removal. The energy consumption was directly proportional to the initial pH and the solution volume, while it was inversely proportional to the number of electrodes.

In Nabil S. Abuzaid‘s [97] experiment, the study dealt with colloids separation from ground water in the Eastern Province of Saudi Arabia. The water was found to have a conductivity of 4400 μ Siemens cm^{-1} and chloride and sulfate concentrations of 834 and 550 mg/L respectively. The turbidity of the water was increased to 76 nephlometric turbidity unit NTU by the addition of bentonite. The efficiency of using soluble stainless steel electrodes for the in-situ formation of ferric hydroxide has been investigated. The electrical current input was found to be inversely proportional to the residual turbidity in the test water. At a contact time of 5 min and a natural chloride content, the highest turbidity removal efficiency of 95% was achieved at a current of 1 A. When the current was reduced to 0.5 A and the contact time was increased to 10 min, the residual turbidity was reduced from 4.0 to 1.6 NTU. Furthermore, similar turbidity removals were achieved at a much shorter contact time 2 min when 1 g/L sodium chloride was added to the test water. Due to the importance of pH variation with regard to coagulation, the phenomenon of voltage-induced hydrogen evolution was investigated as well. While the solutions final pH increased with the increase in current and contact time, it decreased with the increase in sodium chloride concentration.

Seok J. D. [98] has developed the TiO_2/Indium_tin_oxide (ITO) electrode for the electrochemical system. Oxide conductor such as ITO has electrical and chemical stability compared to metal conductor. We also investigated the electrochemical oxidation process using TiO_2/ITO electrode for the industrial dye wastewater treatment. We found that the efficiency of electrochemical process using TiO_2/ITO electrode was sufficiently high for industrial dye waste-water treatment.

1.13 Objectives with Specific Aims and Possible Outcome

The quality of water supplies has gradually declined, largely because of high and often excessive consumption of natural water and the abuse of the ground soil as a recipient of wastewater. It is impossible to specify a precise method for treating waters because of the various qualities of waters that exist. Nevertheless, a series of conventional processes can be identified; such as screening, straining, oxidation, clariflocculation and filtration. These can be followed by specific stages for the removal of particular pollutants. To efficiently handle the wastewater without damaging the environment, in this work, attempt will be made to treat water and wastewater electrochemically.

It is expected to

- get insight about the electrochemical behavior of the treated and untreated water.
- control pH, specific conductance, DO, minerals, BOD, COD, TDS and TSS.
- investigate the BOD/COD ratio.
- establish a low cost efficient electrochemical technique for water purification.
- optimize low cost new electrode system for water purification.

1.14 Sampling Spot : The Dhanmondi Lake

Dhanmondi Lake, a prominent depression within Dhaka metropolitan area, is situated in the middle of Dhaka City (about 23°43'N latitude and 90°26'E longitude). It lies within the vicinity of Dhanmondi residential area. Originally Dhanmondi Lake was an abandoned channel of the 'Karwan Bazar Nadi' ('Karwan Bazar' is commonly spelled and pronounced as 'Kawran Bazar'), previously known as the 'Carevan River', whose alignment was possibly along Begunbari Khal-Green Road-Kalabagan-Dhanmondi Lake to the TURAG river. Part of this lake still functions as a storm water drain and falls into the Begunbari Khal. Expansion of urbanisation in this area during Pakistan period has changed the natural water system in this place. Dhanmondi residential area was developed in 1956 with 240.74 ha of land including the lake. The lake is about 16% of the total area of Dhanmondi and has been playing a vital role in maintaining the only drainage system of Dhanmondi and adjacent areas. It also shows some trellis pattern together with the dendritic pattern of drainage system. The lake offers attractive panoramic views to many thousands of people who live in the vicinity.

Beginning from Jigatola (Dhanmondi Road # 2) the lake extends up to Road # 27 (new I6A), and bounded by the Mohammadpur-Lalmatia area in the north, Satmasjid Road in the west, BDR (BANGLADESH RIFLES) Gate

(Dhanmondi Road # 2) in the south and in the east by Kalabagan residential area. It is 3 km in length, 35-100m in width, with a maximum depth of 4.77m and the total area of the water body is 37.37 ha. There is one box culvert in the lake near Sukrabad area, which is the only outlet of the lake. Excess floodwater due to heavy rainfall passes through this outlet. So water level in the lake remains almost the same in all seasons [99].

Fig 1.6 Dhanmondi Lake near Road 4/A of Dhanmondi, Dhaka.

Fig 1.7 Dhanmondi Lake near Kalabagan, Dhaka.

CHAPTER 2

EXPERIMENTAL

2.1 **Chemicals**

Analytical grade chemicals and solvents were used throughout the work and were used as received unless stated otherwise. Doubly distilled water (H_2O) was used as solvent to prepare most of the solutions utilized in this work. The important chemicals and solvents utilized throughout the experiments are listed below:

i. Aniline [E. Merck, Germany]
ii. Sulfuric Acid (97%) [E. Merck, Germany]
iii. N, N-dimethyl formamide [E. Merck, Germany]
iv. KH_2PO_4 [Merck, India]
v. K_2HPO_4 [Merck, India]
vi. $Na_2HPO_4.10H_2O$ [Merck, India]
vii. NH_4Cl[E. Merck, Germany]
viii. $MgSO_4.7H_2O$ [Aldrich, England]
ix. $CaCl_2$ [E. Merck, Germany]
x. $FeCl_3.6H_2O$[Merck, India]
xi. NaOH [Aldrich, England]
xii. Anhydrous Potassium Iodide (KI) [E. Merck, Germany]
xiii. Anhydrous Mercuric Iodide [E. Merck, Germany]
xiv. $MgCl_2.6H_2O$ [E. Merck, Germany]
xv. $Na_2H_2O_8N_2.2H_2O$[Aldrich, England]
xvi. HCl [Aldrich, England]
xvii. NaCl [Uni-chem, China]
xviii. Ag_2SO_4 [E. Merck, Germany]
xix. Hg_2SO_4 [E. Merck, Germany]
xx. Potassium Hydrogen Phthalate [E. Merck, Germany]

2.2 Instruments

Analysis of the samples performed in this work employed the following devices:

- i) Potentiostat / Galvanostat / Coulomb meter [HABF 501, Hokuto Denko, Japan]
- ii) X-Y recorder [F–5C, Riken Denshi Co. Ltd, Japan]
- iii) Auto ranging microvolt [Keithley 197 A, USA]
- iv) Digital balance [FR-200, Japan]
- v) H-Series H280G DO Probes [HACH, Colorado, USA]
- vi) DO meter [HACH, Colorado, USA]
- vii) COD reactor [HACH, Colorado, USA]
- viii) DR 4000/U Spectrophotometer [HACH, Colorado, USA]
- ix) Compressor [HACH, Colorado, USA]
- x) pH meter [Hanna, pH209, India]
- xi) Conductivity meter [HACH, Colorado, USA]
- xii) BOD Incubator [HACH, Colorado, USA]
- xiii) Furnance [DK, Chino, China]

2.3 Preparation of Different Solutions

2.3.1 Reagents

2.3.1.1 Buffer Solution (pH=10)

Dissolve 4.716g of Na-salt of EDTA and 3.12g of $MgSO_4.H_2O$ or 2.576g of $MgCl_2.6H_2O$ in 50mL of water. Add this solution to 6.706g NH_4Cl and 570mL of concentrated ammonium with mixing and diluting to 1.0L.

2.3.1.2 0.1 M EDTA Solution

Disodium dihydrogen ethylene diamine tetra acetate of analytical reagent quality is available commercially but this may contain a trace of moisture. After drying the reagent at 80^{o}C its composition agrees with the formula

$Na_2H_2O_8N_2.2H_2O$ (relative molar mass 372.24). But it should not be used as primary standard. If necessary, the material may be purified by preparing a saturated solution at room temperature, this requires about 20g of salt per 200 mL of water. Add ethanol slowly until a permanent precipitate appears, filter. Dilute the filtrate with an equal volume of ethanol, filter the resulting precipitate through a sintered glass funnel, wash with acetone and then with diethyl ether. Air-dry at room temperature overnight and then dry in an oven at 80^oC for at least 24 hours. Pure disodium dihydrogen ethylene diamine tetra acetate 3.7224g was dissolved in 1L volumetric flask with double distilled water and made up to the mark with same water.

2.3.1.3 6N Hydrochloric Acid Solution

32% hydrochloric acid 143 mL was diluted to 250 mL with double distilled water to prepare 6n hydrochloric acid.

2.3.1.4 2N Sodium Hydroxide Solution

Sodium hydroxide 40g was taken into a beaker and then 500mL double distilled water was added and mixed to obtain 2N sodium hydroxide solution.

2.3.1.5 0.02N Sodium Hydroxide Solution

Sodium hydroxide 0.4g was taken into a beaker and then 500mL double distilled water was added and mixed to obtain 0.02N sodium hydroxide solution.

2.3.1.6 18N H_2SO_4 Solution

98% conc. H_2SO_4 486.4 mL was taken into a 1 L volumetric flask and made up to the mark with double distilled water.

2.3.1.7 8N H_2SO_4 Solution

98% conc. H_2SO_4 216.2 mL was taken into a 1 L volumetric flask and made up to the mark with double distilled water.

2.3.1.8 0.02N H_2SO_4 Solution

8N H_2SO_4 2.5 mL was taken into a 1 L volumetric flask and made up to the mark with double distilled water.

2.3.1.9 Alkaline Potassium Iodide Solution

Prepared from 49g of sodium hydroxide, 20g of potassium iodide and 0.5g of sodium azide made up to 100mL with double distilled water.

2.3.1.10 Phosphate Buffer (pH 7.2) Solution

0.85g of KH_2PO_4, 2.175g of K_2HPO_4, 4.013g of $Na_2HPO_4.10H_2O$ and 0.17g of NH_4Cl dissolved in 100mLvolumetric flask and made up to the mark with double distilled water.

2.3.1.11 Magnesium Sulphate Solution

2.25g of $MgSO_4.7H_2O$ dissolved in 100mL volumetric flask and made up to the mark with double distilled water.

2.3.1.12 Calcium Chloride Solution

2.75g of $CaCl_2$ dissolved in 100mL volumetric flask and made up to the mark with double distilled water.

2.3.1.13 Ferric Chloride Solution

0.025g of $FeCl_3.6H_2O$ dissolved in 100mL volumetric flask and made up to the mark with double distilled water.

2.3.1.14 48% $MnSO_4$ Solution

48g of $MnSO_4$ dissolved in 100mL volumetric flask and made up to the mark with double distilled water.

2.3.1.15 0.25N Sodium Thiosulphate Solution

Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) is not suitable as a primary standard because of its efflorescent nature. It is reducing agent:

$2\ Na_2S_2O_3 + I_2 \quad = \quad Na_2S_4O_6 + NaI$

$I_2 + 2e \quad = \quad 2I^-$

Thus its equivalent weight is its molar weight which is 248g. An approximate 0.25N solution was prepared by dissolving 6.025g of it in 1 L of double distilled water. Then it was standardization with standard potassium dichromate solution.

2.3.1.16 0.05N Sodium Hydroxide Solution

Sodium hydroxide 1g was taken into a beaker and then 500mL double distilled water was added and mixed to obtain 0.05N sodium hydroxide solution.

2.3.1.17 0.25N Potassium Dichromate Solution

The equivalent weight of potassium dichromate is = 294/6 g = 49g. So, potassium dichromate 6.125g was taken into a 500mL volumetric flask and made up to the mark with double distilled water.

2.3.1.18 Digestion Solution

Digestion solution was prepared by adding the following chemicals in a 500 mL round bottom flask

$K_2Cr_2O_7$	2.458g
Distilled water	250mL
Conc. H_2SO_4	83.5mL
$HgSO_4$	16.65g

2.3.1.19 Sulfuric Acid Reagent

Sulfuric acid reagent was prepared by adding 2.75g Ag_2SO_4 to 271.7mL of conc. H_2SO_4 and the solution was then diluted to 500mL and stand the solution for 1 to 2 days to dissolved Ag_2SO_4.

2.3.1.20 Potassium Hydrogen Phthalate (PHP) Standard

425mg of PHP was dissolved in double distilled water, and diluted to 1000mL. This solution had a theoretical COD of 500 mg/L.

2.3.1.21 Seed Water

Mix sewerage water and some rotten things like food in a bottle and keep it for few days.

2.3.2 Indicator Preparation

2.3.2.1 Eriochrome Black T (EBT) Indicator

Eriochrome Black T (EBT) also called solo chrome black or mordant black. Grind 0.05g of EBT with 100g of powder NaCl or KNO_3. Store it in dark colored bottle. This powder has an approximate life of one year.

2.3.2.2 Starch Indicator

To make the paste of 1g of starch with some double distilled water. To add this paste with 100mL of boil double distilled water with continuous stirring. Cool this solution. Then 3g of potassium iodide and 5g of mercuric iodide were added. The life time of this indicator is 2-3 months.

2.4 Measurement of Water Parameters

2.4.1 Measurement of pH

The samples were taken to the laboratory and the pH was measured with a pH meter.

2.4.2 Measurement of Conductivity

The samples were taken to the laboratory and the conductivity was measured with a conductivity meter within one hour. The instrument was standardized by 0.01M KCl solution.

2.4.3 Measurement of Total Hardness

Measurements of total hardness were carried by following points:

a) Take 50 mL sample in a conical flask. In presence of organic matter in nature and waste water, add 2-4 drops of 30% hydrogen peroxide. Adjust the pH 8-10. Boil for 15 minutes and cool.
b) Add 5 mL buffer (pH 10) solution.
c) Add 30-40 mg of Eriochrome Black T indicator. EDTA solution till the solution changes its color from wine red to blue.
d) **Calculation** : 1 mL 0.01 M EDTA = 1.0mg of $CaCO_3$

2.4.4 Measurement of Total Dissolved Solid (TDS)

Measurements of total dissolved solids were carried by following points (known as Gravimetric Method):
a) Filtered 50 mL of the water sample
b) Evaporated the filtrate on water bath in a previously weighted beaker.
c) The residue was dried in the oven at 105^0 C for 40 minutes and cooled in desiccators and weighted again

2.4.5 Measurement of Dissolved Oxygen

Dissolved Oxygen (DO) is the term used for the measurement of the amount of oxygen dissolved in a unit volume of water. We use DO Probes for measuring dissolved oxygen. Dissolved Oxygen (DO) is usually displayed as mg/L or ppm, DO sensors do not measure the actual amount of oxygen in water, but instead measure partial pressure of oxygen in water. Oxygen pressure is dependent on both salinity and temperature.

There are two fundamental techniques for measuring DO— galvanic and polarographic. Both probes use an electrode system where the DO reacts with the cathode to produce a current. If the electrode materials are selected so that the difference in potential is -.5 volts or greater between the cathode and anode, an external potential is not required and the system is called galvanic. If an external voltage is applied, the system is called polarographic.

- Galvanic probes are more stable and more accurate at low dissolved oxygen levels than polarographic probes.
- Galvanic probes often operate several months without electrolyte or membrane replacement, resulting in lower maintenance cost.
- Polarographic probes need to be recharged every several weeks of heavy use.

Galvanic DO sensors consist of two electrodes, an anode and cathode which are both immersed in electrolyte (inside the sensor body). An oxygen permeable membrane separates the anode and cathode from the water being measured. Oxygen diffuses across the membrane. It interacts with the probe internals to produce an electrical current (more detail is shown below the DO sensor graphic). Higher pressure allows more oxygen to diffuse across the membrane and more current to be produced. The actual output from the sensor is in millivolts. This is achieved by passing the current across a thermistor (a resistor that changes output with temperature).

$V = i * R$,
V is output in Volts, i = current
R is resistance from thermistor in ohms

The thermistor corrects for membrane permeability errors due to temperature change. In other words, increasing permeability at higher temperature allows more oxygen to diffuse into the sensor, even though the oxygen pressure has not changed. This would give falsely high DO if the thermistor were not used.

To represent sensor output in ppm or mg/L, the temperature of the water must be known. A separate temperature sensor can be used or one can built into the sensor. This is independent from the thermistor connected between the anode and cathode to compensate for membrane permeability changes due to temperature change.

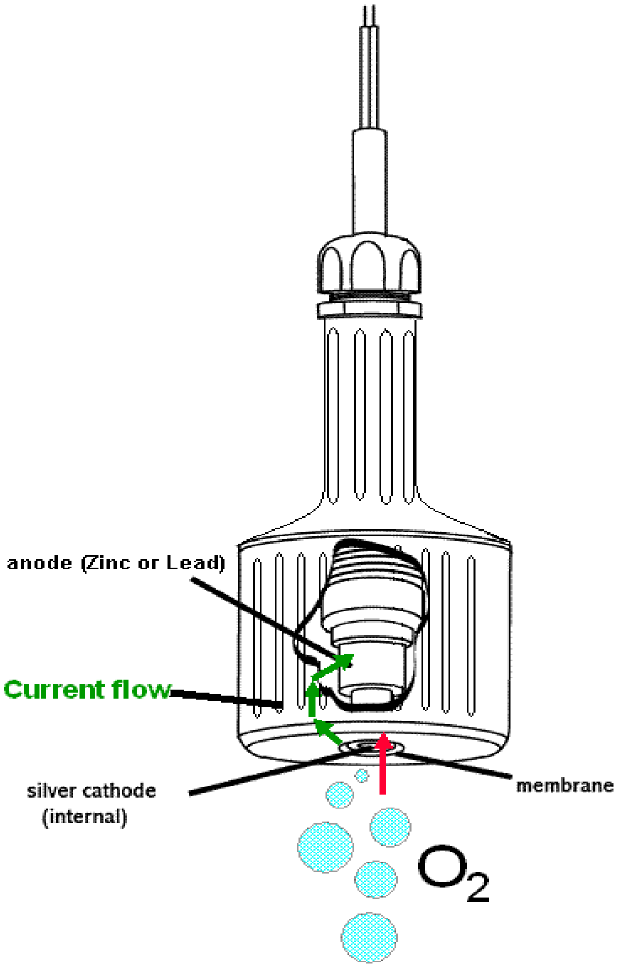


Fig. 2.1 DO Probe

Some characteristics of membrane DO probes are:

- The pH of the solution does not affect the performance of membrane probes.
- Chlorine and hydrogen sulfide (H_2S) cause erroneous readings in DO probes.
- Atmospheric pressure (altitude above sea level) affects the saturation of oxygen. DO probes must be calibrated for the barometric pressure when reading in mg/l (ppm).
- Membrane thickness determines the output level of the probe and the speed of response to change in DO levels.
- Salinity correction must be made

The cathode is a hydrogen electrode and carries a negative potential with respect to the anode. Electrolyte surrounds the electrode pair and is contained by the membrane. With no oxygen, the cathode becomes polarized with hydrogen and resists the flow of current. When oxygen passes through the membrane, the cathode is depolarized and electrons are consumed. The cathode electrochemically reduces the oxygen to hydroxyl ions:

$O_2 + 2\ H_2O + 4\ e^- = 4\ OH^-$

The anode reacts with the product of the depolarization with a corresponding release of electrons.

$Zn + 4OH^- = Zn\ (OH)_4^{2-} + 2e^-$

The electrode pair permits current to flow in direct proportion to the amount of oxygen entering the system. The magnitude of the current gives us a direct measure of the amount of oxygen entering the probe.

Because all of the oxygen entering the probe is chemically consumed, the partial pressure of oxygen in the electrolyte is zero. Therefore, a partial pressure gradient exists across the membrane and the rate of oxygen entering the probe is a function of the partial pressure of oxygen in the air or water being measured.

Since the partial pressure of dissolved oxygen is a function of temperature of the sample, the probe must be calibrated at the sample temperature or the probe‘s meter must automatically compensate for varying sample temperature. Note that this thermal effect is different from the thermal response of the membrane discussed above.

The reading of a DO probe must be corrected for the amount of salt in the sample. As seen in the chart below, the salt in solution will reduce the actual concentration of oxygen.

In all DO Probes; the membrane/sample interface should have a few cm/sec flow of the sample for precision performance. Without flow at the interface, the surrounding oxygen will be consumed and the local reading drops. The output of the probe increases(up to a point) with relative movement between the probe and sample.

Table 2.1 Solubility of solutes as a function of temperature (mg of solutes per liter of water).

Solute	Temperature (^{O}C)					
	0	20	40	60	80	100
O_2	69	43	31	14	0	
CO_2	3350	1690	970	580		
NaCl	357,000	360,000	366,000	373,000	384,000	398,000
KCl	276,000	340,000	400,000	455,000	511,000	567,00

With stationary, continuously monitoring Dissolved Oxygen Probes, the source of the oxygen being measured is air. Thus, Dissolved Oxygen in air or saturated water (mg/l or ppm) as a function of temperature is determined by:

Solubility (ml/L) x Density (mg/ml) x % in air = saturated DO in mg/L (ppm)

Solubility (mg/L) x % in air = saturated DO in mg/L (ppm)

Increasing temperature usually increases the solubility of solids and liquids whereas it reduces the solubility of gases. Also keep your units straight--mg/L, ppm, ml/L, % saturation.

Fig. 2.2 pH, Conductivity, DO Meter Starter Kit

2.4.6 Measurement of Chemical Oxygen Demand (COD)

For the measurement of COD, closed reflux, colorimetric methods are used. A calibration curve is prepared. In the project a spectrophotometer was used, which covered essentially 380 to 750 nm, but might be included some of the UV near infrared region.

2.4.6.1 Formation of a Light-Absorbing Species

For the specific determination of any given substance, a reagent should be used to form a new colored substance. The color forming substance should be selective in its reaction, and should not form interfering colors with foreign substances likely to be present. The reaction of the reagent, and the substance to be measured should be quick and quantitative, or at least reproducible.

The sample was refluxed in strongly acidic solution with an excess of potassium dichromate. Straight chain aliphatic compounds were oxidized more effectively when silver sulphate was added as a catalyst.

2.4.6.2 Selection of Wavelength

In absence of interferences, the wavelength chosen for a quantitative determination was the wavelength of maximum absorbance. Use of the wavelength was not always possible. It was common for color forming reagent to absorb somewhat at the wavelength of maximum absorbance of the complex being measured. For COD determination the wavelength was set at 600nm.

2.4.6.3 Preparation of Calibration Curve

Seven standard forms of PHP solution with COD equivalent of 10, 20, 50, 100, 200, 300 and 500 mg/L were prepared.

30mL culture tubes and caps were washed with 20% H_2SO_4 before first used to prevent contamination. PHP solution was placed in 30 mL ampoules and then digestion solution was added with it. Sulfuric acid reagent was run carefully inside of the ampoules. The composition of different samples for COD calibration curve is present in table 2.2. The ampoules were tightly capped and inverted several times to mix completely. Ampoules were placed in an oven preheated to 150 ^{o}C and refluxed for two hours. Ampoules were then cooled to room temperature and absorbance was measured by spectrophotometer.

Table 2.2 Composition of Different Samples for COD Calibration Curve

COD	KHP solution (mL)	Digestion solution (mL)	H_2SO_4 Reagent (mL)	Double Distilled water (mL)
10	0.167	5.0	11.67	8.163
20	0.334	5.0	11.67	8.070
50	0.835	5.0	11.67	7.500
100	1.670	5.0	11.67	6.670
200	3.340	5.0	11.67	5.000
300	5.000	5.0	11.67	3.330
500	8.330	5.0	11.67	0.000

By measuring the absorbance of the sample solution the COD could immediately be read from the calibration curve.

2.4.7 Measurement of Bio-chemical Oxygen Demand (BOD)

Biochemical oxygen demand or BOD is a chemical procedure for determining the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. It is not a precise quantitative test, although it is widely used as an indication of the organic quality of water [100].

It is most commonly expressed in milligrams of oxygen consumed per litre of sample during 5 days of incubation at 20 °C and is often used as a robust surrogate of the degree of organic pollution of water.

BOD can be used as a gauge of the effectiveness of wastewater treatment plants. It is listed as a conventional pollutant in the U.S. Clean Water Act.

2.4.7.1 Preparation of Dilution H_2O

Place 1200 ml of distilled water in a 2 L beaker, add 1.2 ml phosphate buffer, add 1.2 ml $FeCl_3$, add 1.2 ml $MgSO_4$, add 1.2 ml $CaCl_2$, add 1.2 ml seed water and then air bubble for half an hour for mixture.

2.4.7.2 Dilution Technique and Measuring the BOD

B_1 (DO) : Take 285 ml dilution water in a bottle. Then measure the DO by DO probe. It is blank DO.

D_1 (DO) : Place 10 ml of sample in a 285 ml measuring bottle. Fill up with dilution water. Then measure the DO by DO probe.

Then the two bottles put in an incubator at 20°C for 5 days. After 5 days by using DO probe measure the DO‘s. The results become B_2 and D_2 respectively.

2.4.7.3 Calculation

$$BOD = 29.5 [(D_1-D_2)-(28.5/29.5) (B_1-B_2)] \text{ ppm}$$

Fig. 2.3 Incubator for measuring BOD

2.5 Design of Electrochemical Cell

The electrolysis of waste water was carried out at room temperature in a standard three-electrode one-compartment electrolysis cell. A schematic representation of the electrochemical cell employed in this work is illustrated in Fig. 2.4. The cell consisted of a 8 cm^2 working electrode (WE) made of platinum (Pt) and also stainless steel (SS), a 8 cm^2 Pt and also stainless steel foil counter electrode (CE) and a saturated calomel electrode (SCE) as the reference (RE). Prior to each experiment, the working Pt (and stainless steel) electrode was carefully polished with fine–grained abrasive paper, followed by rinses in distilled water and 5 min immersion in concentrated nitric acid (HNO_3), before it was finally dried on clean laboratory tissues. The reproducibility of experimental results was greatly improved with this pretreatment of the working electrode. The films were grafted onto the working Pt electrode either by sweeping the potential or constant potential mode. Voltammetric sweeps were always started in the anodic direction from 0.0V at 100 mV/s, unless stated otherwise. A Hokuto Denko (HABF 501] electrochemical measurement system provided necessary potential and current control.

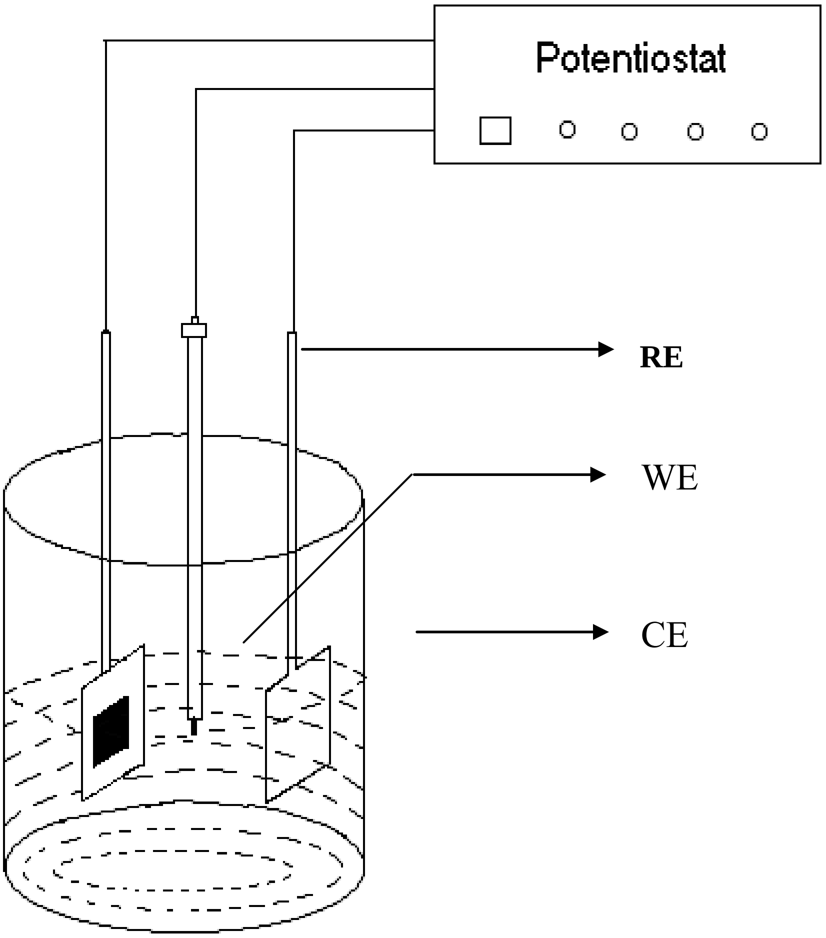


Fig. 2.4 : Three electrode system for electrochemical measurements.

2.6 Optimization of the Condition for Water Treatment

Water purification conducted electrochemical method. As a result, voltage, electrode, electrolytes and contact time were necessary to optimize. For this purpose, firstly, we studied on tape water and optimized the conditions of voltage, electrode, electrolyte and contact time.

2.6.1 Optimization of Voltage

3 volt, 5 volt and 7 volt of potential were applied to treatment of tape water. In these experiments, the following parameters were fixed :

Electrode : Platinum (Pt)
Contact Time : 1 Hour
Electrolyte : NaCl

Using above conditions, some water quality parameters of tape water were measured before and after electrolysis. The water quality parameters are pH, Conductance, Total Hardness, Total Dissolved Solid (TDS), Dissolved Oxygen (DO), Chemical Oxygen Demand (COD) and Bio-chemical Oxygen Demand (BOD). Voltage is optimized considering the value of after electrolysis of above mentioned water quality parameters comparing with the value of standards.

2.6.2 Optimization of Electrode

Platinum and Stainless Steel (Surface Area 8 cm^2) were used to treatment of tape water. In these experiments, the following parameters were fixed :

Applied Voltage : 5 V
Contact Time : 1 Hour
Electrolyte : NaCl

Using above conditions, the above water quality parameters of tape water were measured before and after electrolysis. Electrode is optimized considering the value of after electrolysis of above mentioned water quality parameters comparing with the value of standards.

2.6.3 Optimization of Electrolyte

H_2SO_4, NaCl and Na_2SO_4 electrolytes were used to treatment of tape water. In these experiments, the following parameters were fixed :

Electrode	:	Platinum (Pt)
Contact Time	:	1 Hour
Applied Voltage	:	5 V

Using above conditions, the above water quality parameters of tape water were measured before and after electrolysis. Electrolyte is optimized considering the value of after electrolysis of above mentioned water quality parameters comparing with the value of standards.

2.6.4 Optimization of Time

1 Hour, 2 Hour and 3 Hour of contact time were used to treatment of tape water. In these experiments, the following parameters were fixed :

Electrode	:	Platinum (Pt)
Electrolyte	:	NaCl
Applied Voltage	:	5 V

Using above conditions, the above water quality parameters of tape water were measured before and after electrolysis. Contact time is optimized considering the value of after electrolysis of above mentioned water quality parameters comparing with the value of standards.

2.6.5 Summary of Optimized Parameters

After proper optimization of voltage, electrode, electrolytes and time we finally chose the following conditions:

Applied Voltage : 5 V
Electrode : Platinum (Pt)
Electrolyte : NaCl
Contact Time : 1 Hour

Then the above water quality parameters of the Dhanmondi Lake‘s water were measured before and after electrolysis. In electrolysis process, the above conditions (voltage, electrode, electrolyte and time) were applied.

2.7 Study Area

2.7.1 Sampling Site

Water samples were collected from Dhanmondi Lake of Dhaka City. The location is shown in Fig. 2.5 (Indicate through red # sign)

Fig. 2.5 Map of Dhaka City showing collection point of water from Dhanmondi Lake

2.7.2 Sample Container

Sample container of high density polyethylene (HDPE) was first cleaned by using detergent. The containers (1L/2L) were rinsed with double distilled water. Finally, the containers were soaked in 8M HNO_3 for 2 days and were rinsed with double distilled water to make it ready for sample collection.

2.7.3 Preservation of Sample [101]

It is essential to protect sample from changes in composition and deterioration with aging due to various interactions. The optimum sample - holding times range from zero for parameters such as pH, temperature and dissolved oxygen. to one weak for metals.

The preservation techniques for various parameters are summarized in table as mentioned below, these are essential for retarding biological action, hydrolysis of chemical compounds and complexes and reduction of volatility of constituents. It is desirable for accurate results, that analysis must be undertaken within 4 hours for some parameters and 24 hours for others, from the time of collection and it must be concluded with a week.

Table 2.3 Water Sample Preservation

Parameter	**Container**	**Preservation Technique**
pH	Polythene	No Preservation Measure with 0-4 hours
Conductivity	Polythene	No Preservation Measure with 0-4 hours
Total Hardness	Polythene	No Preservation Measure with 0-4 hours
Total Dissolved Solid (TDS)	Polythene	No Preservation Measure with 0-4 hours
Dissolved Oxygen (DO)	Polythene	No Preservation Measure with 0-4 hours
Chemical Oxygen Demand (COD)	Polythene	Add H_2SO_4 to pH 2, Refrigerate
Bio-chemical Oxygen Demand (BOD)	Polythene	No Preservation Measure with 0-4 hours

CHAPTER 3

RESULTS

&

DISCUSSION

3.1 Analysis of Various Water Quality Parameters of Tape Water

Various water quality parameters such as pH, Conductivity, Total Hardness, Total Dissolved Solid, Dissolved Oxygen, Chemical Oxygen Demand and Biochemical Oxygen Demand of tape water were measured carefully before and after electrolysis. Then we chose the optimized condition of voltage, electrode, electrolyte and contact time. After choosing the optimized conditions we treated the waste water of Dhanmondi Lake.

3.1.1 pH Analysis

pH value of a sample indicates either it is acidic or basic. Pure water should be neutral with pH value of 7. For pH > 7, water is basic and for pH < 7, water is acidic. The standard pH of drinking water quality of Bangladesh is 6.5 to 8.5. More the hydrogen ions present in solution pH value will lower. Similarly, more the hydroxyl ions present in solution pH value will higher.

3.1.1.1 Effect of Variation of Voltage

The pH values of tape water with the variation of cell voltage, using platinum electrode, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.1 and data are given in Table A, in appendix section. At 3 V and 5 V the pH maintains with the above standard. The concentration of hydrogen ion decreases. More the voltage, more H^+ ion deposits onto cathode and reduces to H_2 gas. Hence, the concentration of H^+ ion decreases from the solution. So, pH increases. And for the same reason, the studied cell voltage, 7 V is not suitable for this experiment. Moreover, water can be splited at the cathode to produce OH^- that ultimately increases the pH value of the solution. [102]

<u>Reactions :</u>

Anode : $2H_2O = O_2 + 4H^+ + 4e^-$

Cathode : $4H_2O + 4e^- = 2H_2 + 4OH^-$

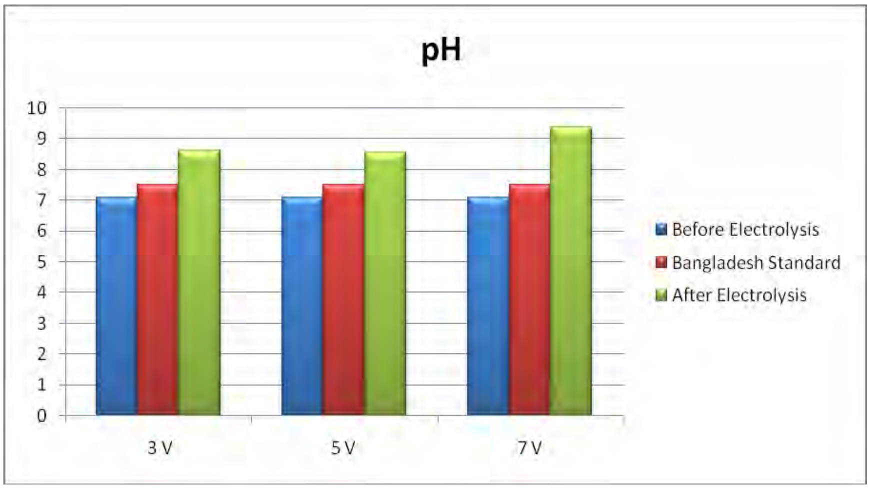


Fig 3.1 pH of tape water with the variation of voltage, using platinum electrode, NaCl as electrolyte and 1 Hr as contact time

3.1.1.2 Effect of Variation of Electrode

The pH values of tape water with the variation of electrode, using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.2 and data are given in Table B, in appendix section. The deposit amount of H^+ ion onto stainless steel is less than that of platinum. Na^+ and H^+ ions exist in NaCl aqueous solution. Using platinum as a cathode in NaCl solution, H^+ ion produces H_2 gas firstly rather than Na^+. At both electrodes used, the values of pH are slightly larger than those of before electrolysis and Bangladesh Standard. This may be due to the splitting water at the cathode to produce OH^-, which ultimately increases the pH value of the solution. [102]

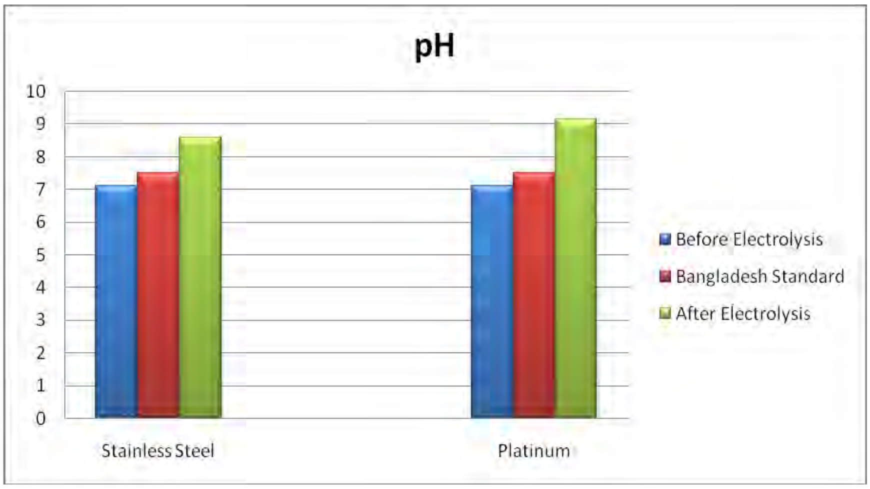


Fig 3.2 pH of tape water with the variation of electrode using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time

3.1.1.3 Effect of Variation of Electrolyte

The pH values of tape water with the variation of electrolyte, using platinum electrode, 5 Volt potential and 1 Hr as contact time, have been shown graphically in Figure 3.3 and data are given in Table C, in appendix section. The values are closer to standard when we use NaCl and Na_2SO_4 as electrolytes. And, H_2SO_4 decreased the pH value of the sample.

$NaCl = Na^+ + Cl^-$

$Na_2SO_4 = 2Na^+ + SO_4^{2-}$

$H_2SO_4 = 2H^+ + SO_4^{2-}$

Cl^- discharges firstly rather than that of SO_4^{2-} .

$Cl^- = \frac{1}{2} Cl_2 + e^- \quad E = -1.36$

$SO_4^{2-} = SO_2 + O_2 + 2e^- \quad E = -2.05$

$2H_2O + 2e = H_2 + 2OH^- \quad E = -0.83$

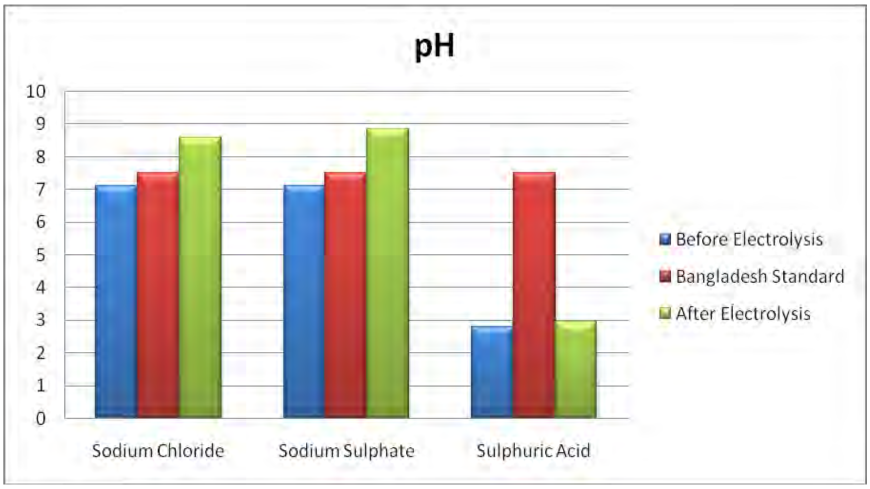


Fig 3.3 pH of tape water with the variation of electrolyte using platinum electrode, 5 Volt potential and 1 Hr as contact time

3.1.1.4 Effect of Variation of Time

The pH values of tape water with the variation of time, using platinum electrode, 5 Volt potential and NaCl as electrolyte, have been shown graphically in Figure 3.4 and data are given in Table D, in appendix section. If we treat water for 1 hour then the pH value is closer to standard. According to Faradays' second law of electrolysis, if electrolysis time is more, the generation of OH^- species will be more. As mentioned before, H_2O may be electrolyzed to form OH^- that enhances the value of pH. Again, bubbles were formed at 3 hour contact time.

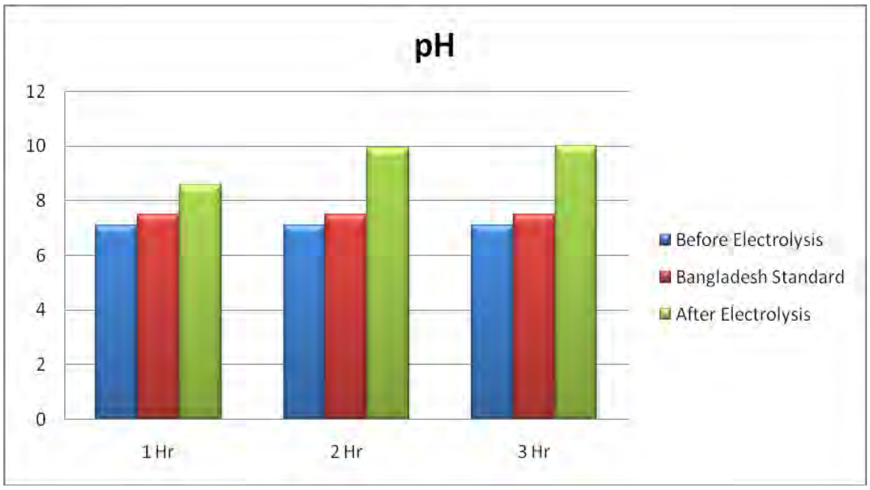


Fig 3.4 pH of tape water with the variation of time using platinum electrode, 5 Volt potential and NaCl as electrolyte

3.1.2 Conductivity Analysis

Electrolytes conductivity in water as dielectric constant of water is higher. It can be dissolve most of the salt with it. So, conductivity results the concentration of salts in water. The admissible limit of conductivity of drinking water recommended by United States Public Health (USPH) is 300 micro Siemens /cm. Presence of various salts in water and OH^- & H^+ ions are the sources of Conductivity.

3.1.2.1 Effect of Variation of Voltage

The conductivity values of tape water with the variation of voltage, using platinum electrode, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.5 and data are given in Table A, in appendix section. Tap water contains various minerals/various ions, i.e., Cu^{2+}, Fe^{3+}, Fe^{2+}, Ca^{2+} and Mg^{2+} etc. By applying potential some ions may be deposited onto electrode that reduces conductivity. At 7 Volt, more OH^- ion produces. Hence, conductivity slightly increases than that of 5 Volt. So, 5 Volt is preferable.

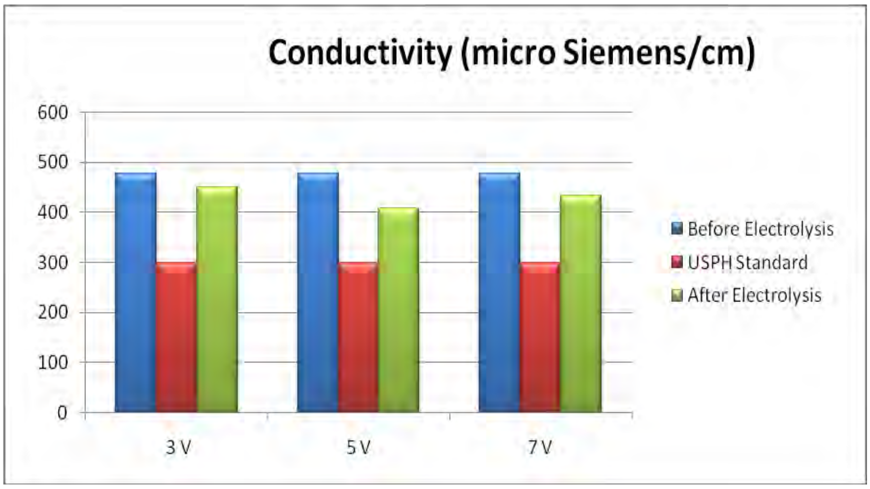


Fig 3.5 Conductivity of tape water with the variation of voltage using platinum electrode, NaCl as electrolyte and 1 Hr as contact time

3.1.2.2 Effect of Variation of Electrode

The conductivity values of tape water with the variation of electrode, using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.6 and data are given in Table B, in appendix section. Platinum electrode is found more suitable than stainless steel. The decrease rate of conductivity by Platinum is higher than that of stainless steel. The deposit amount of electrolytes onto stainless steel is less than that of platinum. So, if we use stainless steel as electrode, then the amount of electrolytes that presence in solution will be higher than that of platinum. Being more electrolytes presence in solution in case of stainless steel, conductivity will be higher than that of platinum. So, platinum is preferable rather than stainless steel.

<u>For Pt Electrode</u>

$O_2 + 4e^- + 4H^+ = 2H_2O$

$2Cl^- - 2e^- = Cl_2$

$Fe^{2+} + 2e^- = Fe$

<u>For Other Electrode</u>

$O_2 + 2e^- + H_2O = HO_2^- + OH^-$

$2Cl^- - 2e^- = Cl_2$

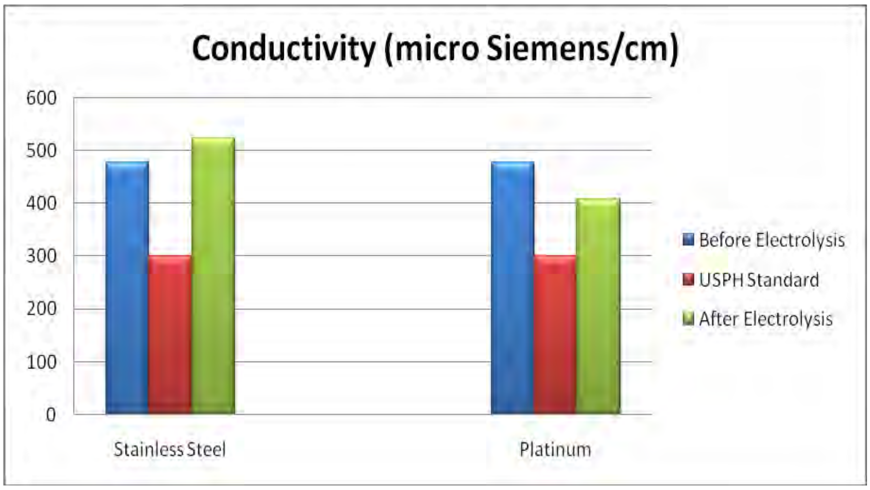


Fig 3.6 Conductivity of tape water with the variation of electrode using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time

3.1.2.3 Effect of Variation of Electrolyte

The conductivity values of tape water with the variation of electrolytes, using platinum electrode, 5 Volt potential and 1 Hr as contact time, have been shown graphically in Figure 3.7 and data are given in Table C, in appendix section. The values are closer to Bangladesh Standard if we use NaCl and Na_2SO_4 as electrolytes.

Cl^- discharges firstly rather than that of SO_4^{2-}.

$Cl^- = \frac{1}{2} Cl_2 + e^-$ $E = -1.36$

$SO_4^{2-} = SO_2 + O_2 + 2e^-$ $E = -2.05$

$2H_2O + 2e = H_2 + 2OH^-$ $E = -0.83$

So, in solution, using NaCl as electrolyte, the remaining amount of NaCl in solution is less than that of Na_2SO_4 and H_2SO_4. As a result, conductivity will be lower in case of NaCl. Again, comparison between Na^+ ion & H^+ ion, the mobility of H^+ ion is higher than that of Na^+. As a result, conductivity will be higher if we use H_2SO_4 as electrolyte.

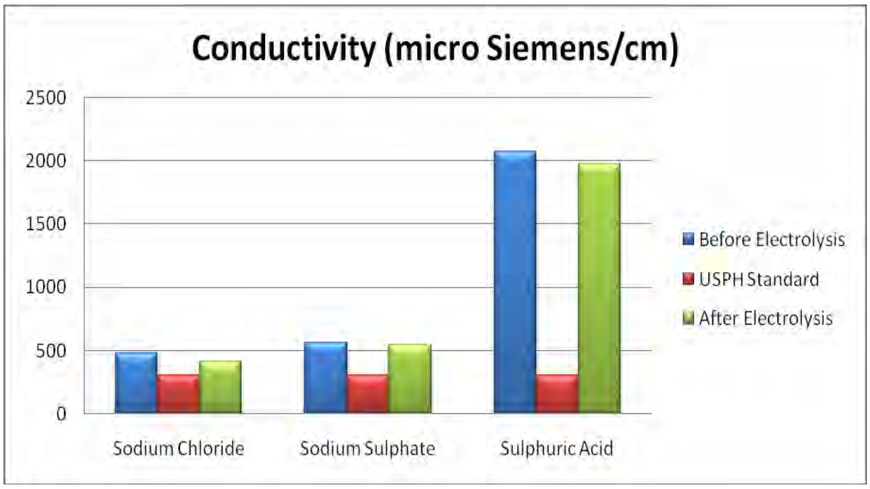


Fig 3.7 Conductivity of tape water with the variation of electrolyte using platinum electrode, 5 Volt potential and 1 Hr as contact time

3.1.2.4 Effect of Variation of Time

The conductivity values of tape water with the variation of time, using platinum electrode, 5 Volt potential and NaCl as electrolyte, have been shown graphically in Figure 3.8 and data are given in Table D, in appendix section. Treatment of water for 1 or 2 hour(s) the conductivity values found less than before. At 3 Hr contact time, more OH^- ion produces. Hence, conductivity increases than that of 2 Hr.

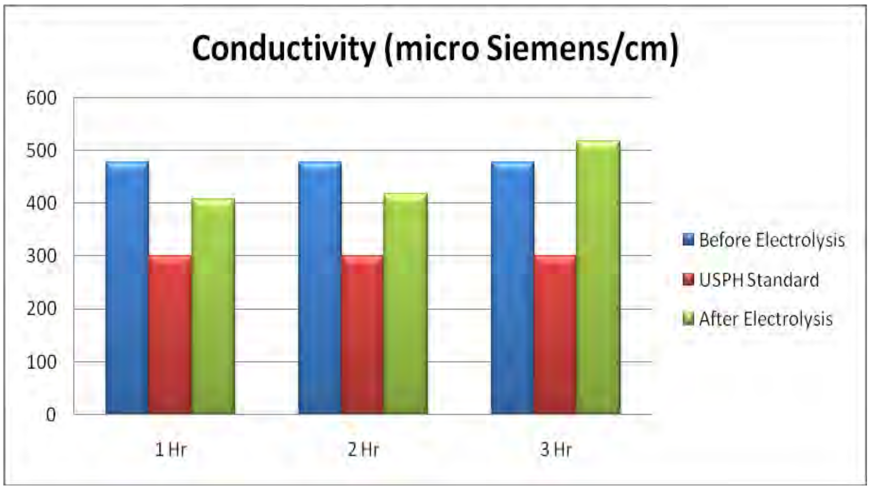


Fig 3.8 Conductivity of tape water with the variation of time using platinum electrode, 5 Volt potential and NaCl as electrolyte

3.1.3 Analysis of Total Hardness

The hardness of the samples has been calculated as $CaCO_3$ in ppm. hardness results from the presence of divalent metallic cations of which Ca & Mg are most abundant one in lake water. The standard Hardness of drinking water quality of Bangladesh, World Health Organization (WHO) and United States Public Health (USPH) is 250, 500, 500 ppm, respectively. However, there are certain ranges which can be delineated and these are shown in the table 3.1 [102].

Table 3.1 Hardness range and the quality of water

Hardness (ppm)	Description
0-40	Soft
40-100	Moderately Hard
100-300	Hard
300-500	Very Hard
500-Up	Extremely Hard

3.1.3.1 Effect of Variation of Voltage

The Total Hardness values of tape water with the variation of voltage, using platinum electrode, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.9 and data are given in Table A, in appendix section. The total hardness of tape water is closer to Bangladesh standard. The decrease rate of total hardness applying 5V & 7V is suitable. If voltage increases, more ions deposit onto electrode. Hardness occurs if Ca^{2+}, Mg^{2+}, SO_4^{2-} and CO_3^{2-} ions present in water. Applying more voltage, these ions deposit onto electrodes. As a result, hardness will be decreased.

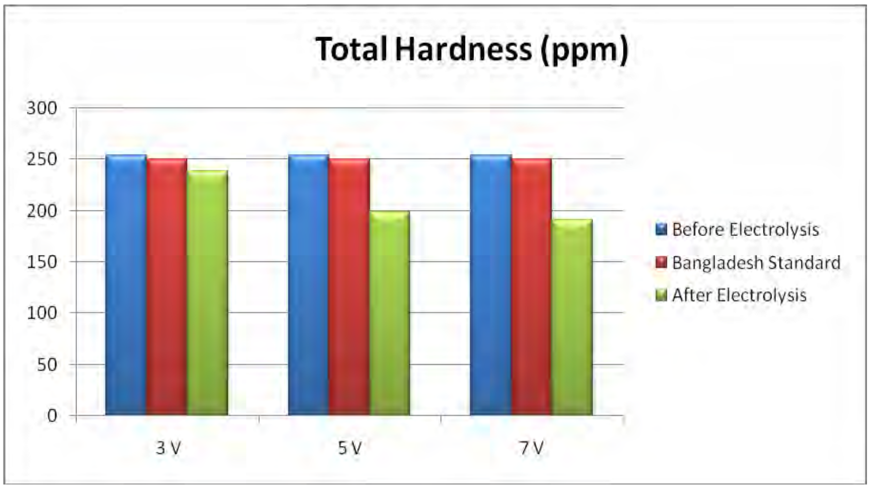


Fig 3.9 Total Hardness of tape water with the variation of voltage using platinum electrode, NaCl as electrolyte and 1 Hr as contact time

3.1.3.2 Effect of Variation of Electrode

Total Hardness values of tape water with the variation of electrode, using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.10 and data are given in Table B, in appendix section. Platinum electrode is more suitable than stainless steel because its decrease rate is high. The deposit amount of electrolytes onto stainless steel is less than that of platinum. So, if we use stainless steel as electrode, then the amount of electrolytes presence in solution that responsible for hardness will be higher than that of platinum. As a result, hardness will be lower in case of platinum rather than that of stainless steel.

<u>For Pt Electrode</u>

$Ca^{2+} + 2e^- = Ca$

$Mg^{2+} + 2e^- = Mg$

$Fe^{2+} + 2e^- = Fe$

<u>For Other Electrode</u>

$O_2 + 2e^- + H^+ = H_2O_2$

$2Cl^- - 2e^- = Cl_2$

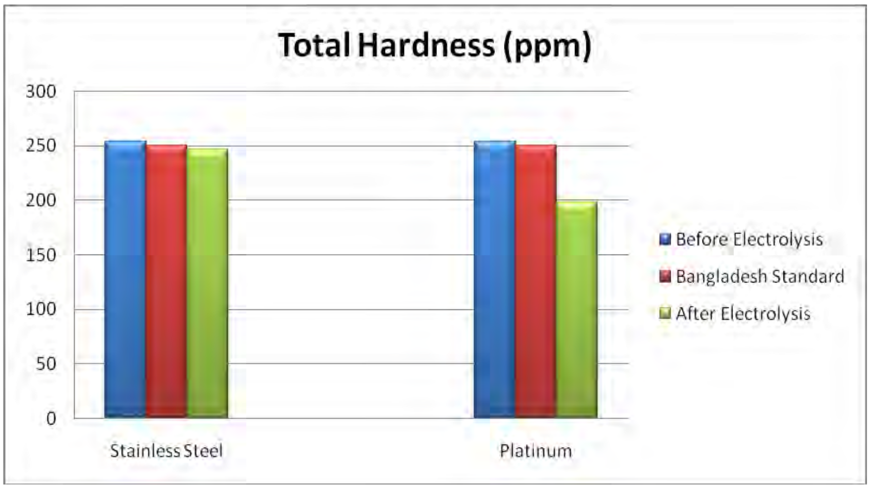


Fig 3.10 Total Hardness of tape water with the variation of electrode using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time

3.1.3.3 Effect of Variation of Electrolyte

Total Hardness values of tape water with the variation of electrolytes, using platinum electrode, 5 Volt potential and 1 Hr as contact time, have been shown graphically in Figure 3.11 and data are given in Table C, in appendix section. The values are closer to standard when we use NaCl and Na_2SO_4 as electrolytes. Also the decrease rate of total hardness of tape water for NaCl is the best.

$NaCl = Na^+ + Cl^-$

$Na_2SO_4 = 2Na^+ + SO_4^{2-}$

$H_2SO_4 = 2H^+ + SO_4^{2-}$

If we use Na_2SO_4 and H_2SO_4 as electrolytes then more SO_4^{2-} ions exist in solution. The SO_4^{2-} ions reacted with Ca^{2+}, Mg^{2+} and as a result hardness was increased.

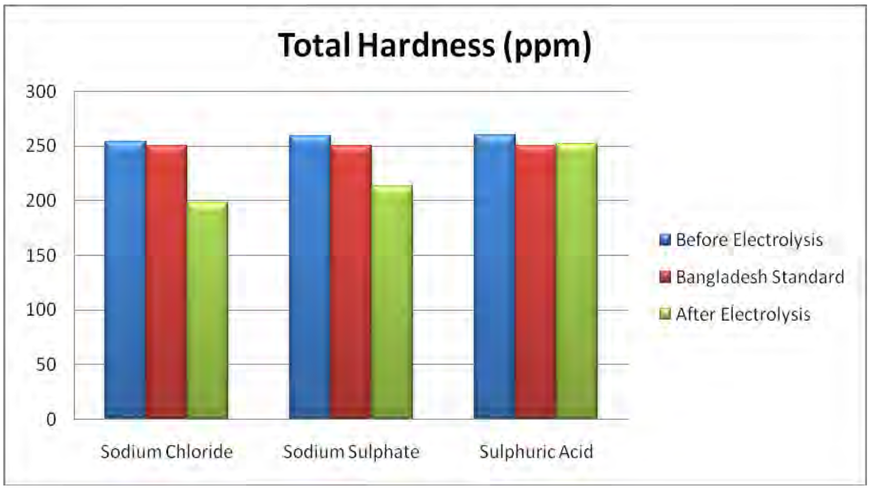


Fig 3.11 Total Hardness of tape water with the variation of electrolyte using platinum electrode, 5 Volt potential and 1 Hr as contact time

3.1.3.4 Effect of Variation of Time

Total Hardness values of tape water with the variation of time, using platinum electrode, 5 Volt potential and NaCl as electrolyte, have been shown graphically in Figure 3.12 and data are given in Table D, in appendix section. In all experiments the decrease rate of total hardness found closer to Bangladesh standard. According to Faradays‘ second law of electrolysis, if electrolysis time is more, the deposit onto electrode will be more. So, hardness decreases with the increasing of time. Again, at 3 Hr contact time, more OH^- ion produces. Hence, conductivity increases than 2 Hr contact time. Here, the reaction rate in basic solution may be differing.

Fig 3.12 Total Hardness of tape water with the variation of time using platinum electrode, 5 Volt potential and NaCl as electrolyte

3.1.4 Analysis of Total Dissolved Solid

Waters which are high in total dissolved mineral substances are objectionable both to water consumers and the manufacturers of many commodities. The standard TDS of drinking water quality of Bangladesh, World Health Organization (WHO) and United States Public Health (USPH) is 1000, 500, 500 ppm respectively. Total dissolved solid is not charged particle. It may be as colloidal format in solution.

3.1.4.1 Effect of Variation of Voltage

The TDS values of tape water with the variation of voltage, using platinum electrode, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.13 and data are given in Table A, in appendix section. At 3V and 5V the TDS maintains with the above standard. Total dissolved solid is not charged particle. There may be colloid particles in solution. Applying more potential, colloid particles can behave as charged particle. And, by electrophoresis process, colloid particles from solution can remove. As a result, applying more voltage, total dissolved solid will be decreased.

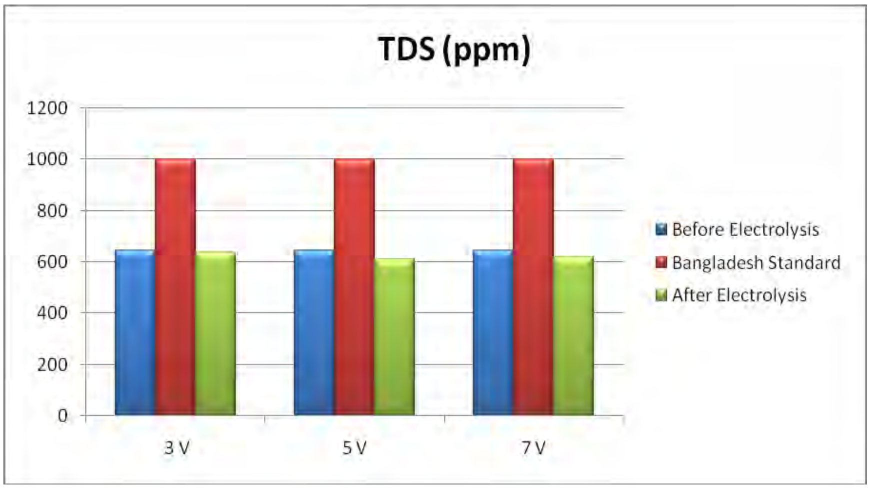


Fig 3.13 Total Dissolved Solid of tape water with the variation of voltage using platinum electrode, NaCl as electrolyte and 1 Hr as contact time

3.1.4.2 Effect of Variation of Electrode

The TDS values of tape water with the variation of electrode, using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.14 and data are given in Table B, in appendix section. Platinum electrode is more suitable than stainless steel because its value is close to Bangladesh standard. The deposit amount of electrolytes onto stainless steel is less than that of platinum. So, if we use stainless steel as electrode, then the amount of electrolytes that presence in solution will be higher than that of platinum. As a result, total dissolved solid will be lower in case of platinum rather than that of stainless steel.

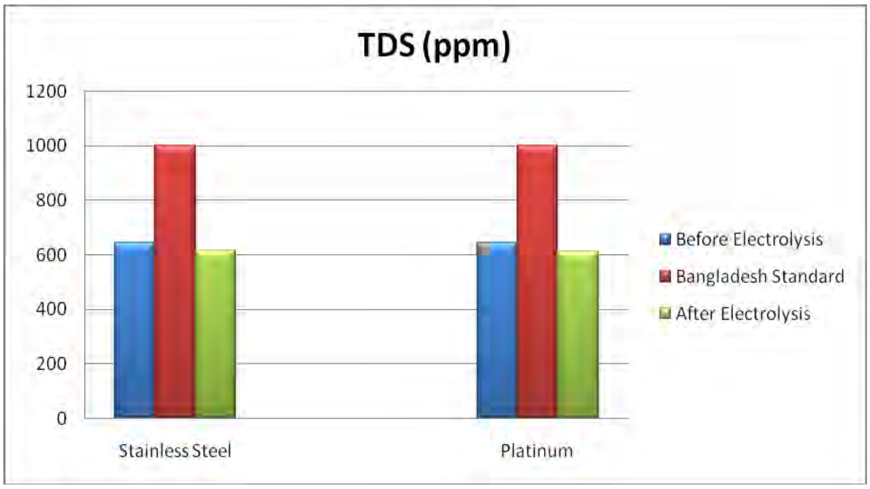


Fig 3.14 Total Dissolved Solid of tape water with the variation of electrode using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time

3.1.4.3 Effect of Variation of Electrolyte

The TDS values of tape water with the variation of electrolytes, using platinum electrode, 5 Volt potential and 1 Hr as contact time, have been shown graphically in Figure 3.15 and data are given in Table C, in appendix section. The molecular weight of NaCl, Na_2SO_4 and H_2SO_4 are not same. After adding electrolyte we have measured TDS. For this, the initial readings of TDS of the sample were found different. The TDS values of sample after electrolysis are closer to standard when we use NaCl and Na_2SO_4 as electrolytes.

$NaCl = Na^+ + Cl^-$ $Na_2SO_4 = Na^+ + SO_4^{2-}$ $H_2SO_4 = H^+ + SO_4^{2-}$

Cl^- discharges firstly rather than that of SO_4^{2-} .

$$Cl^- = \frac{1}{2} Cl_2 + e^-$$

$$SO_4^{2-} = SO_2 + O_2 + 2e^-$$

So, in solution, using NaCl as electrolyte, the remaining amount of NaCl in solution is less than that of Na_2SO_4 and H_2SO_4. As a result, total dissolved solid will be lower in case of NaCl than that of Na_2SO_4 and H_2SO_4.

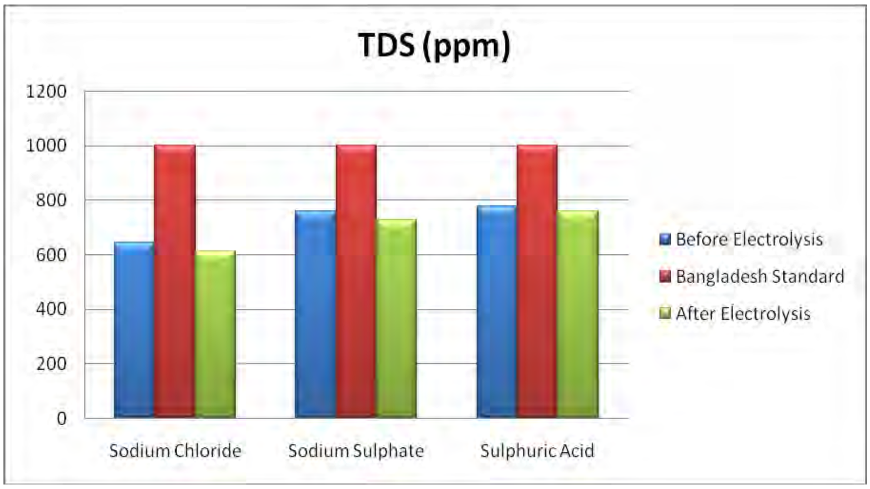


Fig 3.15 Total Dissolved Solid of tape water with the variation of electrolyte using platinum electrode, 5 Volt potential and 1 Hr as contact time

3.1.4.4 Effect of Variation of Time

The TDS values of tape water with the variation of time, using platinum electrode, 5 Volt potential and NaCl as electrolyte, have been shown graphically in Figure 3.16 and data are given in Table D, in appendix section. If we treat water for 1 hour then the TDS value is closer to standard. According to Faradays' second law of electrolysis, if electrolysis time is more, the deposit onto electrode will be more. So, total dissolved solid decreases with the increasing of time.

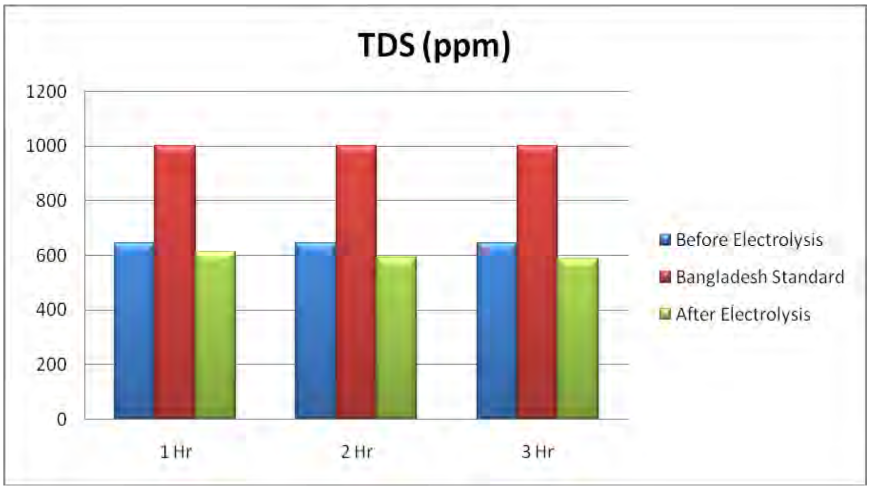


Fig 3.16 Total Dissolved Solid of tape water with the variation of time using platinum electrode, 5 Volt potential and NaCl as electrolyte

3.1.5 Dissolved Oxygen Analysis

Dissolved oxygen of samples was determined after taken the samples from the site to the laboratory. The standard DO value of drinking water quality is 4 to 6. Deviation from this value indicates the pollution of water.

3.1.5.1 Effect of Variation of Voltage

The DO values of tape water with the variation of voltage, using platinum electrode, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.17 and data are given in Table A, in appendix section. At 3V and 5V the DO maintains with the above standard. Applying more voltage, more O_2 reduces to O_2^{2-} or H_2O. [105-106]

$O_2 + 4e^- + 4H^+ \quad = \quad 2H_2O$ (Platinum Electrode)

$O_2 + 2e^- + H^+ \quad = \quad H_2O_2$ (Other Electrode)

The concentration of O_2 decreases from the solution. So, dissolved oxygen decreases. At 7 Volt, the decreasing rate is high.

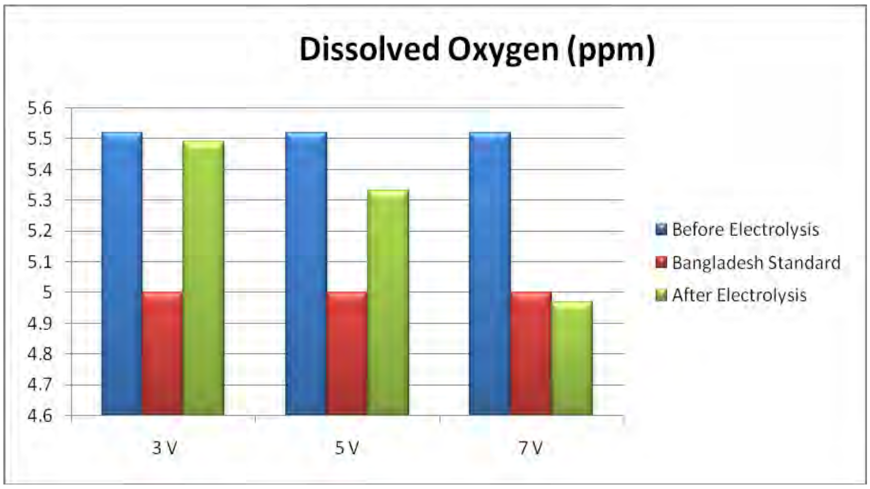


Fig 3.17 Dissolved Oxygen of tape water with the variation of voltage using platinum electrode, NaCl as electrolyte and 1 Hr as contact time

3.1.5.2 Effect of Variation of Electrode

The DO values of tape water with the variation of electrode, using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.18 and data are given in Table B, in appendix section. Platinum electrode is more suitable than stainless steel because its value is close to Bangladesh standard. Applying more voltage, more O_2 reduces to O_2^{2-} or H_2O. [105-106]

$O_2 + 4e^- + 4H^+ = 2H_2O$ (Platinum Electrode)

The concentration of O_2 decreases from the solution. So, dissolved oxygen decreases.

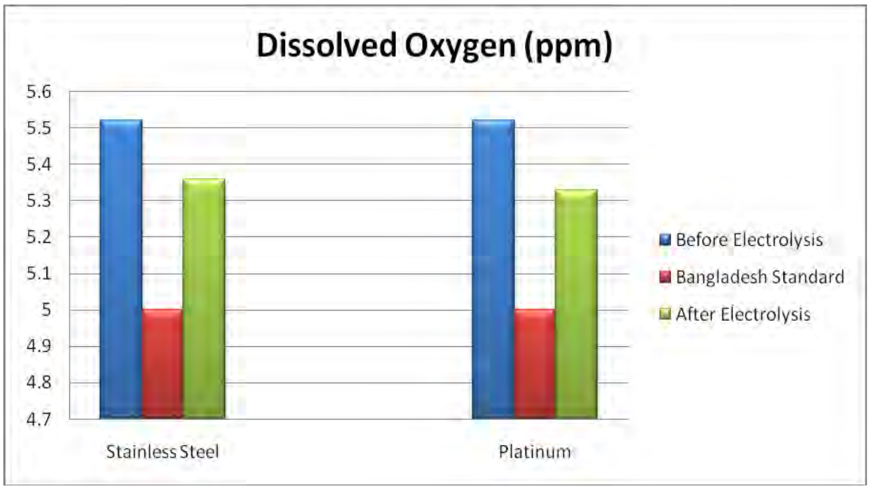


Fig 3.18 Dissolved Oxygen of tape water with the variation of electrode using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time

3.1.5.3 Effect of Variation of Electrolyte

The Dissolved Oxygen values of tape water with the variation of electrolytes, using platinum electrode, 5 Volt potential and 1 Hr as contact time, have been shown graphically in Figure 3.19 and data are given in Table C, in appendix section. The values are closer to standard when we use NaCl.

Cl^- discharges firstly rather than that of SO_4^{2-}.

$$Cl^- = \frac{1}{2} Cl_2 + e^-$$

$$SO_4^{2-} = SO_2 + O_2 + 2e^-$$

SO_4^{2-} produces oxygen gas. As a result, the values of dissolved oxygen were higher after electrolysis in case of Na_2SO_4 and H_2SO_4. Using H_2SO_4, the amount of dissolved oxygen after electrolysis was found the highest. Also, H_2SO_4 is an oxidizing agent. For this, the initial reading of DO of the sample was found highest. For these grounds, H_2SO_4 and Na_2SO_4 can‘t be used for Dissolved Oxygen measurement. Thus, NaCl is more suitable as an electrolyte.

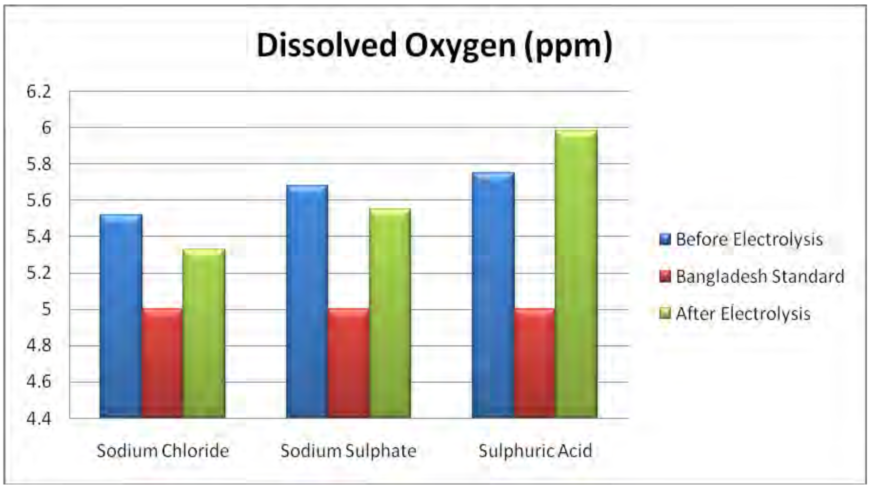


Fig 3.19 Dissolved Oxygen of tape water with the variation of electrolyte using platinum electrode, 5 Volt potential and 1 Hr as contact time

3.1.5.4 Effect of Variation of Time

The DO values of tape water with the variation of time, using platinum electrode, 5 Volt potential and NaCl as electrolyte, have been shown graphically in Figure 3.20 and data are given in Table D, in appendix section. If we treat water for 1 hour, then DO value found closer to standard. More time, more oxygen dissolves in water. Also, bubbles were formed at 3 hr contact time. We can make conclusion that dissolved oxygen increases with the increasing of time.

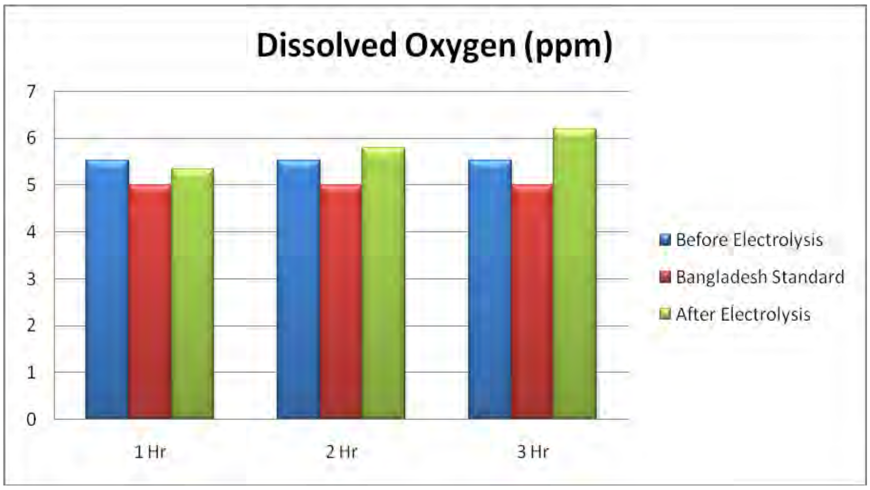


Fig 3.20 Dissolved Oxygen of tape water with the variation of time using platinum electrode, 5 Volt potential and NaCl as electrolyte

3.1.6 Chemical Oxygen Demand (COD) Analysis

The higher COD values indicate the presence of higher organic load in the water sample. It is preferable to BOD. COD value of a sample indicates either it is acidic or basic. The standard COD of drinking water quality of Bangladesh, World Health Organization (WHO) and USPH is 4, 10, 4 ppm respectively.

3.1.6.1 Effect of Variation of Voltage

The COD values of tape water with the variation of voltage, using platinum electrode, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.21 and data are given in Table A, in appendix section. At 3V and 5V the COD maintains with the above standard. Applying more potential, more carbonious compounds may be degraded. As a result, COD decreases with the increasing of potential. At 7 Volt, more OH^- ion produces. It can increase the COD value by reacting with carbonious compounds.

$O_2 + 2H_2O + 4e^- = 4OH^- \quad E = +0.40$

$O_2 + 4e^- + 4H^+ = 2H_2O \quad E = +1.23$

$2H_2O - 2e^- = H_2O_2 + 2H^+ \quad E = +1.78$

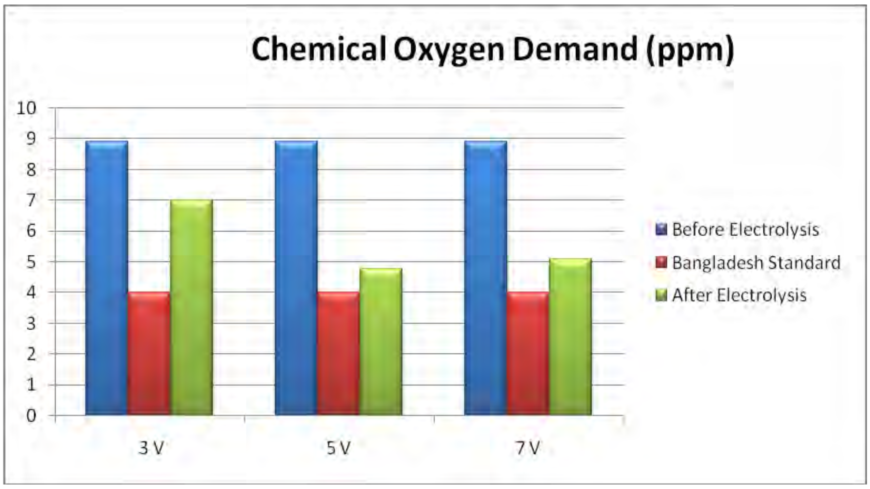


Fig 3.21 Chemical Oxygen Demand of tape water with the variation of voltage using platinum electrode, NaCl as electrolyte and 1 Hr as contact time

3.1.6.2 Effect of Variation of Electrode

The COD values of tape water with the variation of electrode, using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.22 and data are given in Table B, in appendix section. Platinum electrode is more suitable than stainless steel because its value is close to Bangladesh standard. Using platinum electrode, more carbonious compounds may be degraded. As a result, COD decreases.

$O_2 + 4e^- + 4H^+$ = $2H_2O$ (Platinum Electrode)

$O_2 + 2e^- + 2H^+$ = H_2O_2 (Other Electrode)

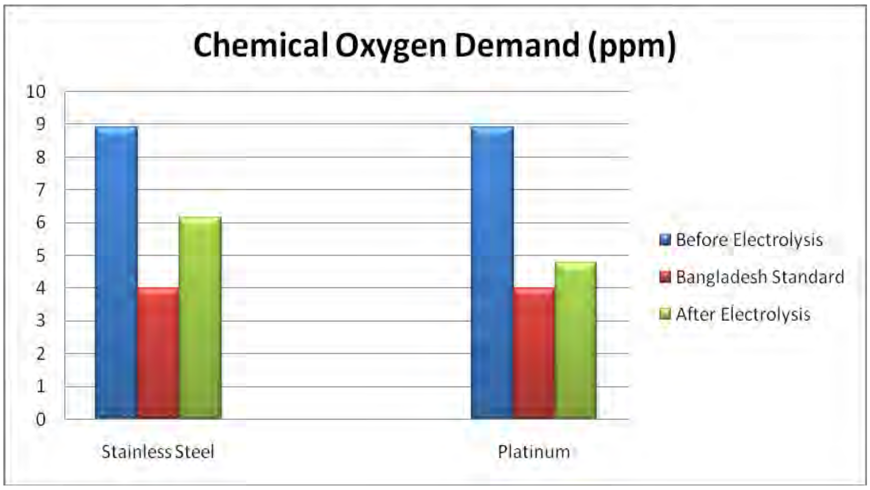


Fig 3.22 Chemical Oxygen Demand of tape water with the variation of electrode using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time

3.1.6.3 Effect of Variation of Electrolyte

The COD values of tape water with the variation of electrolytes, using platinum electrode, 5 Volt potential and 1 Hr as contact time, have been shown graphically in Figure 3.23 and data are given in Table C, in appendix section. The values are closer to standard when we use NaCl and Na_2SO_4 as electrolytes. For measuring COD, a certain range of pH is essential. But, H_2SO_4 decreases the pH value. As a result, using H_2SO_4 as electrolyte, initial COD value found highest [74, 76, 78, 95]. Though the initial COD value is high in case of using H_2SO_4, we can avoid H_2SO_4 as electrolyte.

$NaCl = Na^+ + Cl^-$

$Na_2SO_4 = 2Na^+ + SO_4^{2-}$

$H_2SO_4 = 2H^+ + SO_4^{2-}$

$Cl^- = Cl_2 + e^-$ E = -1.36

$SO_4^{2-} = SO_2 + O_2 + 2e^-$ E = -2.05

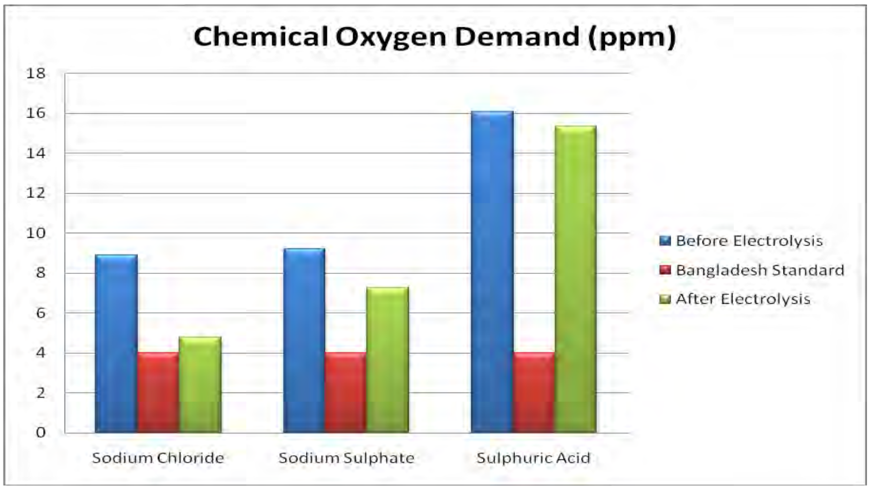


Fig 3.23 COD of tape water with the variation of electrolyte using platinum electrode, 5 Volt potential and 1 Hr as contact time

3.1.6.4 Effect of Variation of Time

The COD values of tape water with the variation of time, using platinum electrode, 5 Volt potential and NaCl as electrolyte, have been shown graphically in Figure 3.24 and data are given in Table D, in appendix section. If we treat water for 1 hour then the COD value found closer to standard. At 2 hour or 3 hour the COD value is nearly same. But, bubbles were formed. So, contact time 1 hour is more suitable.

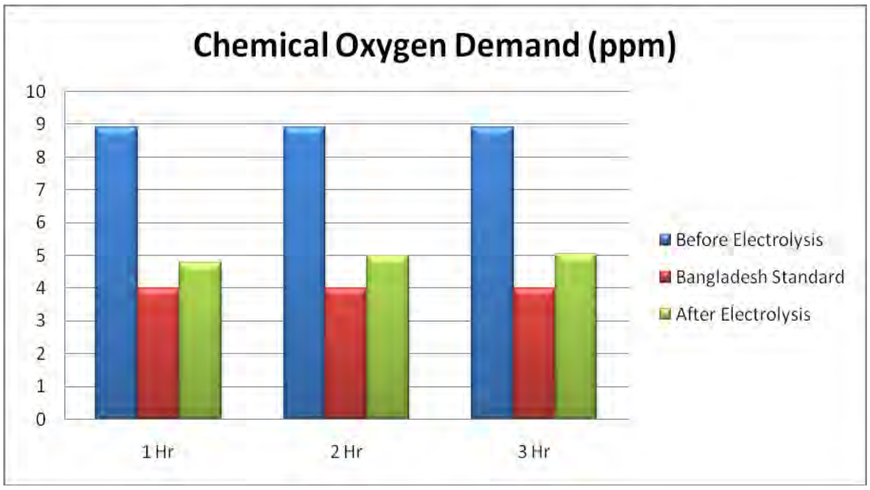


Fig 3.24 COD of tape water with the variation of time using platinum electrode, 5 Volt potential and NaCl as electrolyte

3.1.7 Bio-chemical Oxygen Demand (BOD) Analysis

BOD is defined as —the quantity of dissolved oxygen, in milligrams per liter, required during stabilization of the decomposable organic matter by aerobic biochemical action”. Higher the BOD value, higher the presence of micro bacterial agents which use dissolved oxygen for their metabolic purposes. BOD values are very important, when they signify : 1) that oxygen supply dissolved in water will be so greatly reduced that fish no longer survives in water, 2) that conditions for the propagation of dangerous bacteria exist. The standard BOD of drinking water quality of World Health Organization (WHO) and USPH is 6 & 5 ppm respectively.

3.1.7.1 Effect of Variation of Voltage

The BOD values of tape water with the variation of voltage, using platinum electrode, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.25 and data are given in Table A, in appendix section. At 3V and 5V the BOD maintains with the above standard. Applying more potential the living organism in water may be destroyed. Thus, BOD value decreases. When 7V potential was applied, it disturbed for several times to find a result.

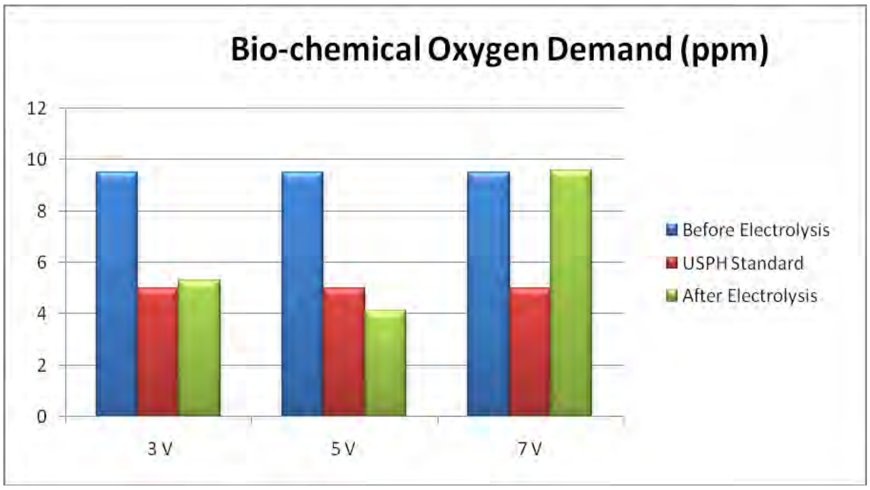


Fig 3.25 Bio-chemical Oxygen Demand of tape water with the variation of voltage using platinum electrode, NaCl as electrolyte and 1 Hr as contact time

3.1.7.2 Effect of Variation of Electrode

The BOD values of tape water with the variation of electrode, using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time, have been shown graphically in Figure 3.26 and data are given in Table B, in appendix section. Platinum electrode is more suitable than stainless steel because its value is close to Bangladesh standard. Previous experiment shown that, the DO value decreased in case of using platinum electrode. Ultimately, BOD value may be decreased.

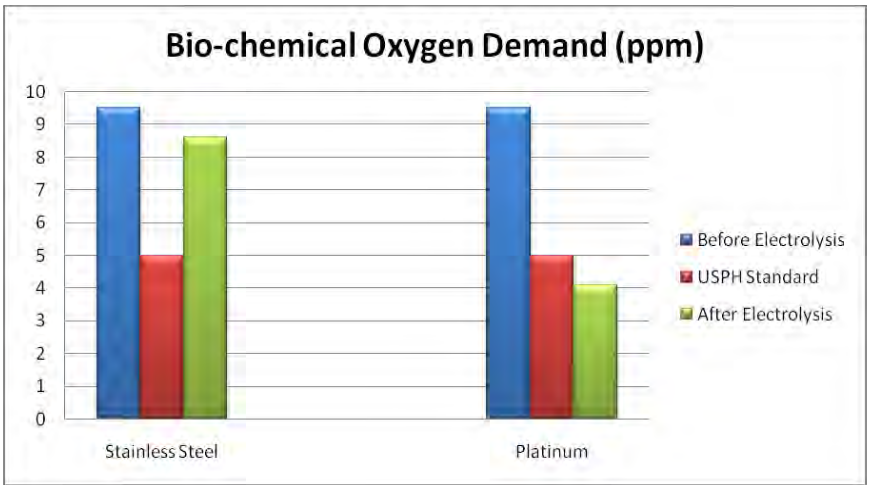


Fig 3.26 Bio-chemical Oxygen Demand of tape water with the variation of electrode using 5 Volt potential, NaCl as electrolyte and 1 Hr as contact time

3.1.7.3 Effect of Variation of Electrolyte

The BOD values of tape water with the variation of electrolytes, using platinum electrode, 5 Volt potential and 1 Hr as contact time, have been shown graphically in Figure 3.27 and data are given in Table C, in appendix section. The values are closer to standard when we use NaCl. The decrease rate is not suitable in case of Na_2SO_4. Cl^- discharges firstly rather than that of SO_4^{2-}.

NaCl = $Na^+ + Cl^-$

Na_2SO_4 = $2Na^+ + SO_4^{2-}$

H_2SO_4 = $2H^+ + SO_4^{2-}$

Cl^- = $Cl_2 + e^-$ E = -1.36

SO_4^{2-} = $SO_2 + O_2 + 2e^-$ E = -2.05

Again, SO_4^{2-} produces oxygen gas. As a result, the amount of dissolved oxygen will be higher in case of Na_2SO_4 that increase the BOD value. So, Na_2SO_4 can‘t be used. Thus, NaCl is more suitable as an electrolyte. In case of H_2SO_4 no significant result of BOD was found. So, H_2SO_4 must be avoided as electrolyte.

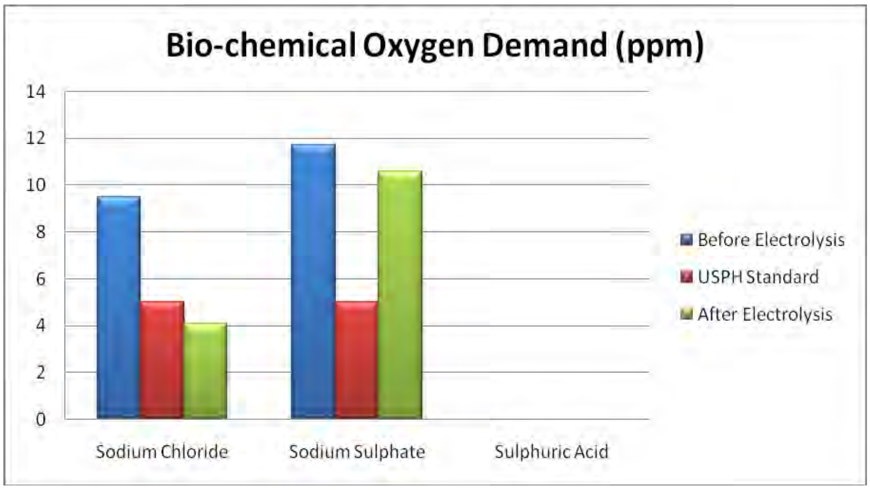


Fig 3.27 Bio-chemical Oxygen Demand of tape water with the variation of electrolyte using platinum electrode, 5 Volt potential and 1 Hr as contact time

3.1.7.4 Effect of Variation of Time

The BOD values of tape water with the variation of time, using platinum electrode, 5 Volt potential and NaCl as electrolyte, have been shown graphically in Figure 3.28 and data are given in Table D, in appendix section. If we treat water for 1 hour then the BOD value is closer to standard. Increasing the time, DO value is increasing which may suitable for living organism. So, BOD may increase for this reason.

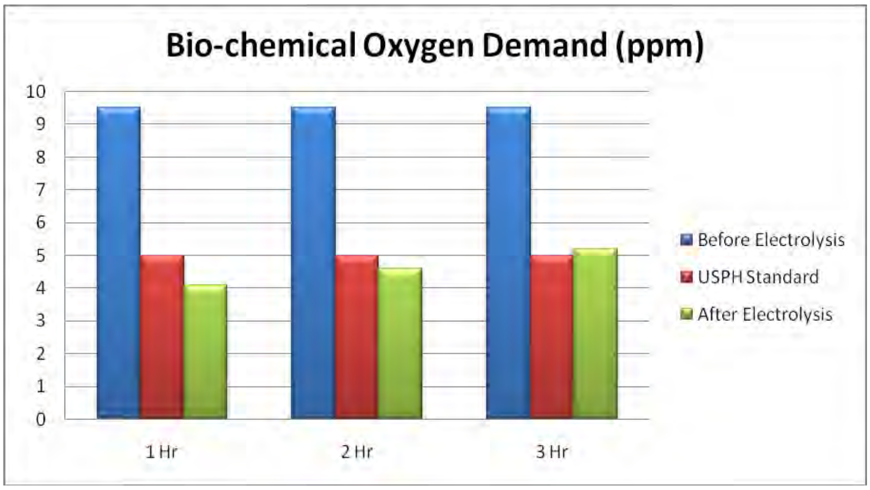


Fig 3.28 Bio-chemical Oxygen Demand of tape water with the variation of time using platinum electrode, 5 Volt potential and NaCl as electrolyte

3.2 Optimized Condition for Electrochemical Treatment of Waste Water

a) Voltage : At 3 V, the conductivity value, total hardness and the COD value are not suitable comparing with Bangladesh Standard. At 7 V, the pH value, conductivity value and BOD value are not suitable. Specially, for BOD measurement, we can‘t apply 7 V potential. Also, at 7 V potential, bubbles are formed and water is splited out. We can‘t reproduce the exact result in case of applying 7 V potential. So, comparing these potential, 5 V potential is appropriate.

b) Electrode : Comparing stainless steel electrode and platinum electrode, only DO value is close to Bangladesh Standard and thus suitable for both electrode. But, for others parameters, platinum electrode is more suitable than stainless steel, especially for BOD, COD and total hardness measurement. So, we chose platinum as electrode.

c) **Electrolyte :** H_2SO_4 is not suitable at all for measuring COD, BOD. Also, it increases the conductivity value and decreases pH value. So, for water treatment, using H_2SO_4 as electrolyte must be avoided. Comparing NaCl and Na_2SO_4, NaCl is more preferable for measuring conductivity, total hardness, COD and BOD. Especially for BOD and COD, using NaCl electrolyte is more acceptable. So, for choosing electrolyte, we favor NaCl solution.

d) **Contact Time :** At 3 hour contact time, the pH, conductivity, DO, COD, BOD values are high which are not apposite for standard water quality. Also, bubbles are formed at higher contact time. Comparing 1 hour and 2 hour contact time, the values of all parameters are close to each other. But, time consuming is not appropriate for water treatment as well as chemical experiment. So, we chose 1 hour as contact time.

3.3 Treatment of Dhanmondi Lake Water

In the last few decades, Dhaka has been greatly changed with rapid urbanization and industrialization, especially through garments manufacturing, establishment of small and large-scale business enterprises, increase of multinational business and trade firms, increasing participation of international organization in the local and national development process etc. Unfortunately, this rapid urbanization process has not taken place in a formal and planned manner. This unplanned approach of development has made this city ―aland of unhealthy life". Water of the surrounding rivers and lakes has already exceeded the standard limits of many water quality parameters, for example, DO, BOD, COD, pH. The table 3.2 indicates deterioration of the lake water quality.

Table 3.2 Concentration of water quality indicators of Dhanmondi lake water of Dhaka city in November, 2001 [103]

Parameters	pH	Conductivity (µS/cm)	Total Hardness (ppm)	TDS (ppm)	DO (ppm)	COD (ppm)	BOD (ppm)
Value	6.95	843	523	498	6.1	7.9	1.9

3.3.1 Water quality parameters before electrolysis

Water quality of Dhanmondi Lake decreases day by day. So, it is essential to save the water. Also purification is needed now a day. The table 3.3 indicates the pollution of the lake water.

Table 3.3 Various water quality parameters of Dhanmondi Lake water in November 2010 (Before Electrolysis)

Parameters	pH	Conductivity (μS/cm)	Total Hardness (ppm)	TDS (ppm)	DO (ppm)	COD (ppm)	BOD (ppm)
Value	9.12	1109	657	876	7.57	10.3	9.08

3.3.2 Water quality parameters after electrolysis

The above water quality parameters of Dhanmondi Lake were measured using platinum electrode, 5 V potential, NaCl electrolyte and 1 Hr contact time. The values are shown in Table 3.4.

Table 3.4 Various parameters of Dhanmondi Lake water in November 2010 (After Electrolysis)

Parameters	pH	Conductivity (μS/cm)	Total Hardness (ppm)	TDS (ppm)	DO (ppm)	COD (ppm)	BOD (ppm)
Value	8.8	437	322	356	5.93	4.68	4.76

3.3.3 Removal efficiency of the water quality parameters

Satisfactory results were found especially for Conductivity, Total Hardness, TDS, COD and BOD. The results of removal efficiency are shown in Table 3.5 and also Figures 3.29 to 3.35.

Table 3.5 Various parameters of Dhanmondi Lake water in November 2010 (After Electrolysis)

Parameters	pH	Conductivity (μS/cm)	Total Hardness (ppm)	TDS (ppm)	DO (ppm)	COD (ppm)	BOD (ppm)
% of Removal	3.51	60.6	50.99	59.4	21.66	54.6	47.58

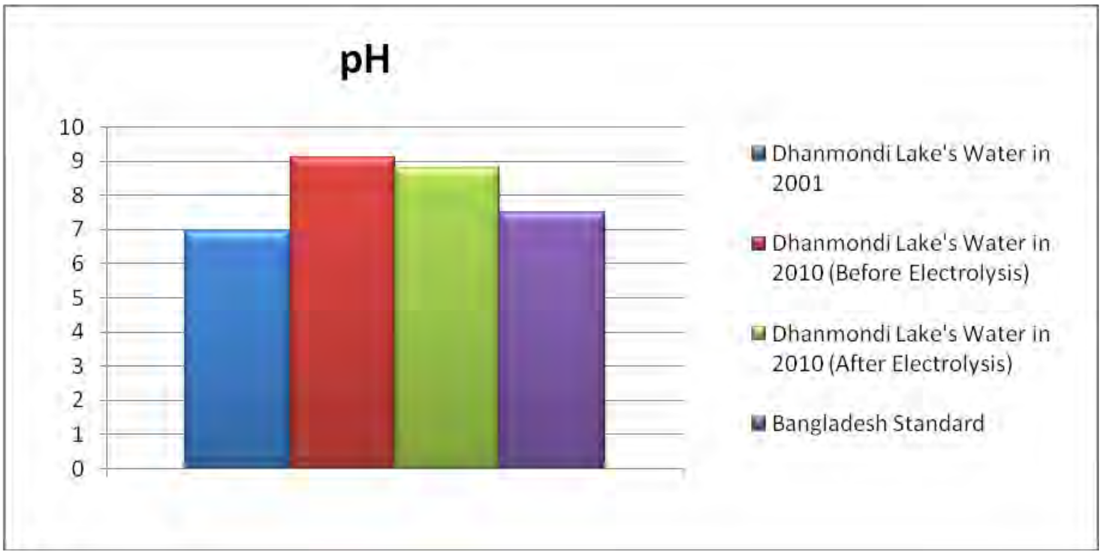


Fig 3.29 pH of Dhanmondi Lake‘s Water in 2001, in 2010 (Before Electrolysis), in 2010 (After Electrolysis using platinum electrode, 5 V potential, NaCl electrolyte and 1 Hr contact time) and Bangladesh Standard.

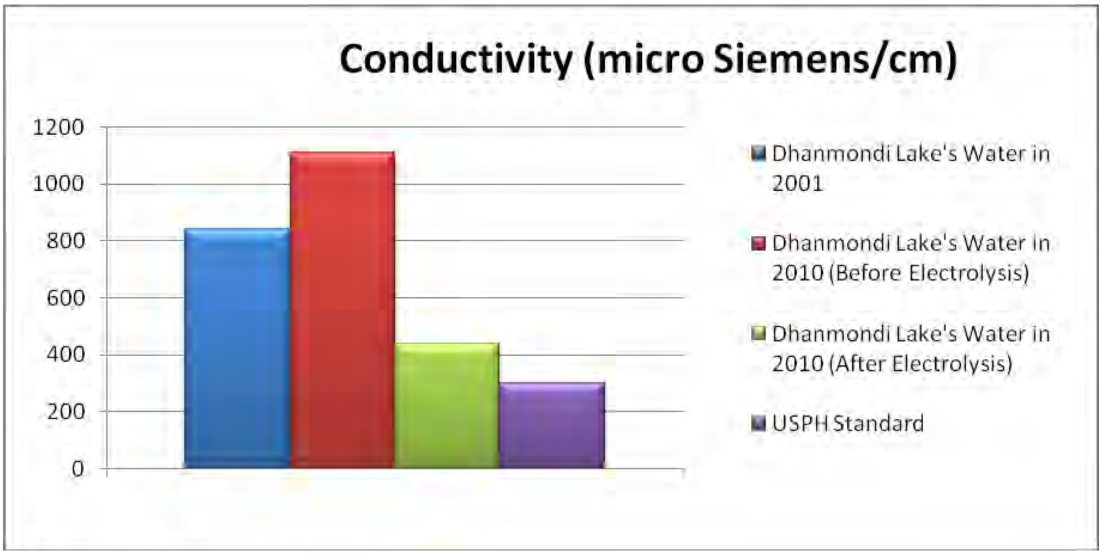


Fig 3.30 Conductivity of Dhanmondi Lake‘s Water in 2001, in 2010 (Before Electrolysis), in 2010 (After Electrolysis using platinum electrode, 5 V potential, NaCl electrolyte and 1 Hr contact time) and USPH Standard.

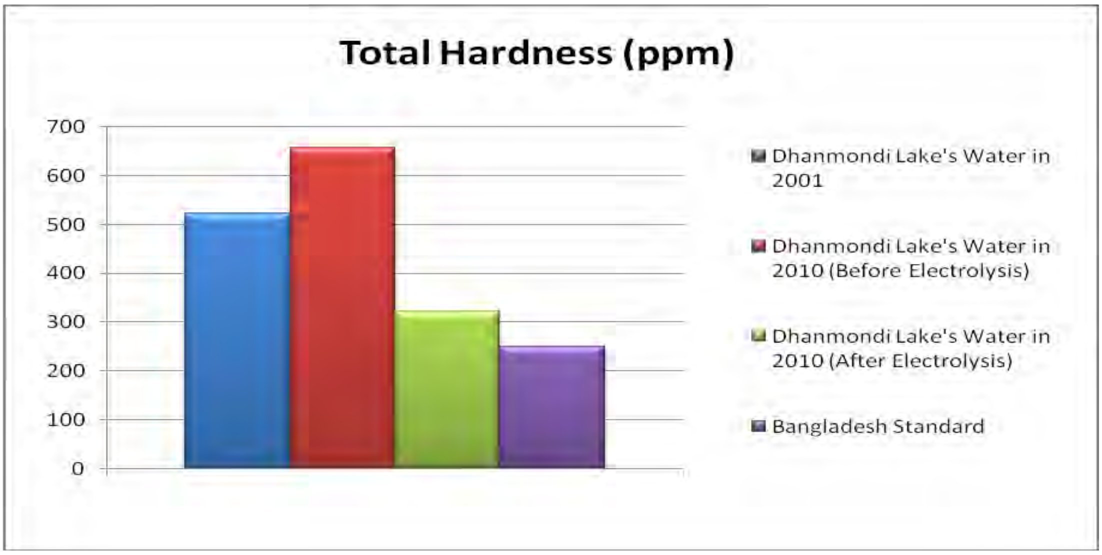


Fig 3.31 Total Hardness of Dhanmondi Lake‘s Water in 2001, in 2010 (Before Electrolysis), in 2010 (After Electrolysis using platinum electrode, 5 V potential, NaCl electrolyte and 1 Hr contact time) and Bangladesh Standard.

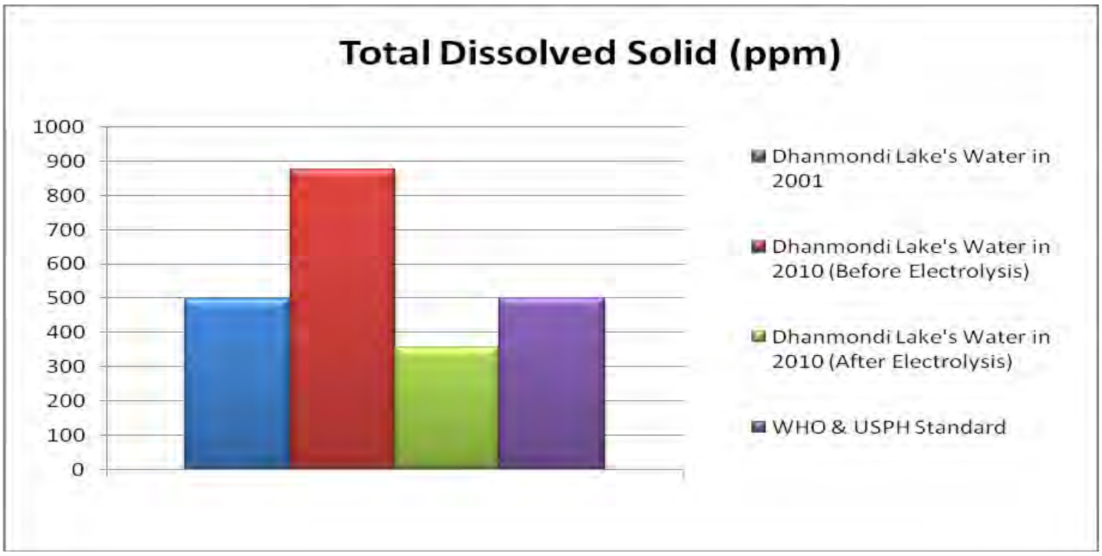


Fig 3.32 Total Dissolved Solid (TDS) of Dhanmondi Lake‘s Water in 2001, in 2010 (Before Electrolysis), in 2010 (After Electrolysis using platinum electrode, 5 V potential, NaCl electrolyte and 1 Hr contact time) and WHO & USPH Standard.

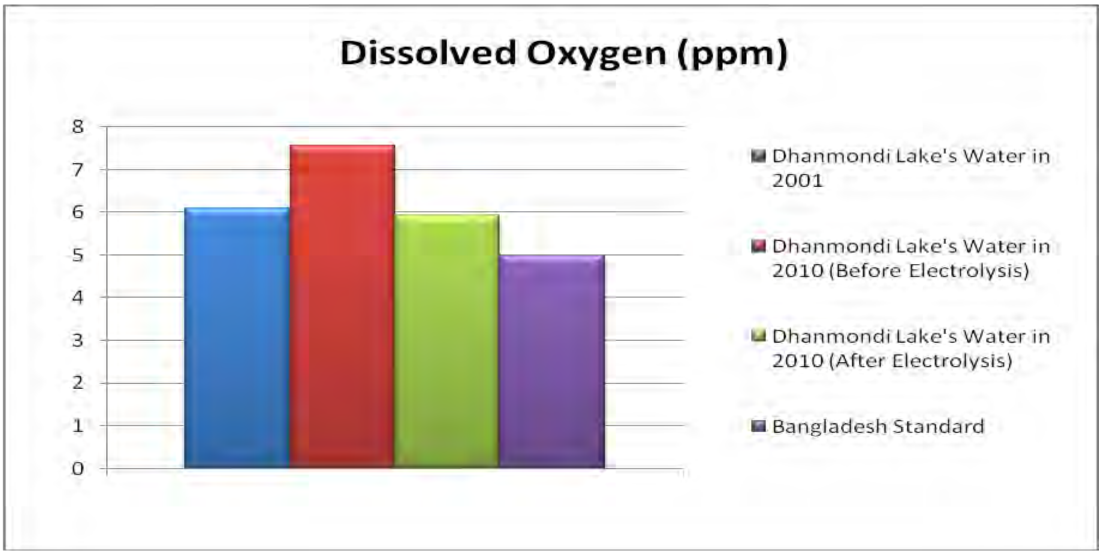


Fig 3.33 Dissolved Oxygen (DO) of Dhanmondi Lake‘s Water in 2001, in 2010 (Before Electrolysis), in 2010 (After Electrolysis using platinum electrode, 5 V potential, NaCl electrolyte and 1 Hr contact time) and Bangladesh Standard.

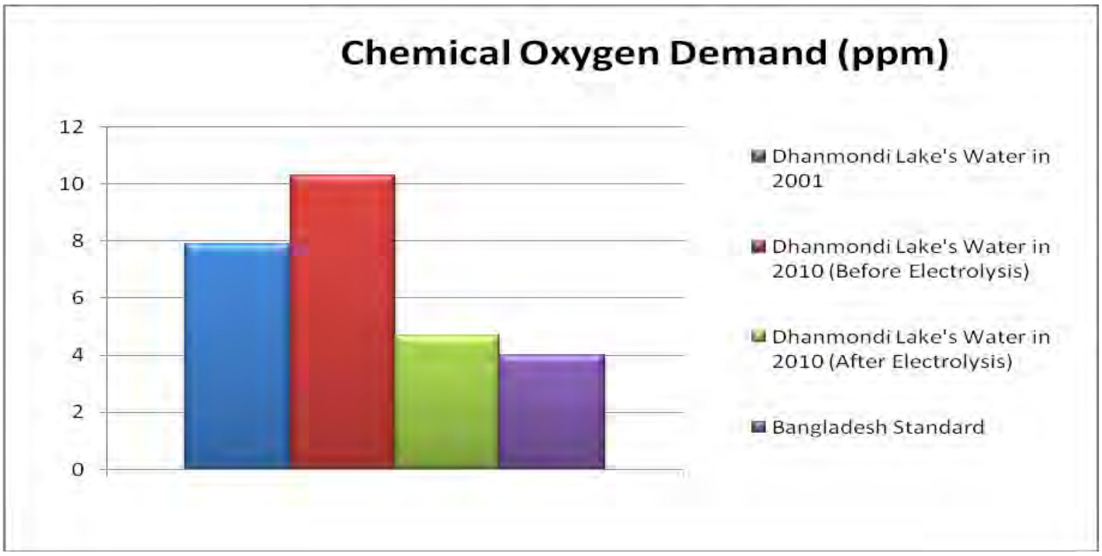


Fig 3.34 Chemical Oxygen Demand (COD) of Dhanmondi Lake‘s Water in 2001, in 2010 (Before Electrolysis), in 2010 (After Electrolysis using platinum electrode, 5 V potential, NaCl electrolyte and 1 Hr contact time) and Bangladesh Standard.

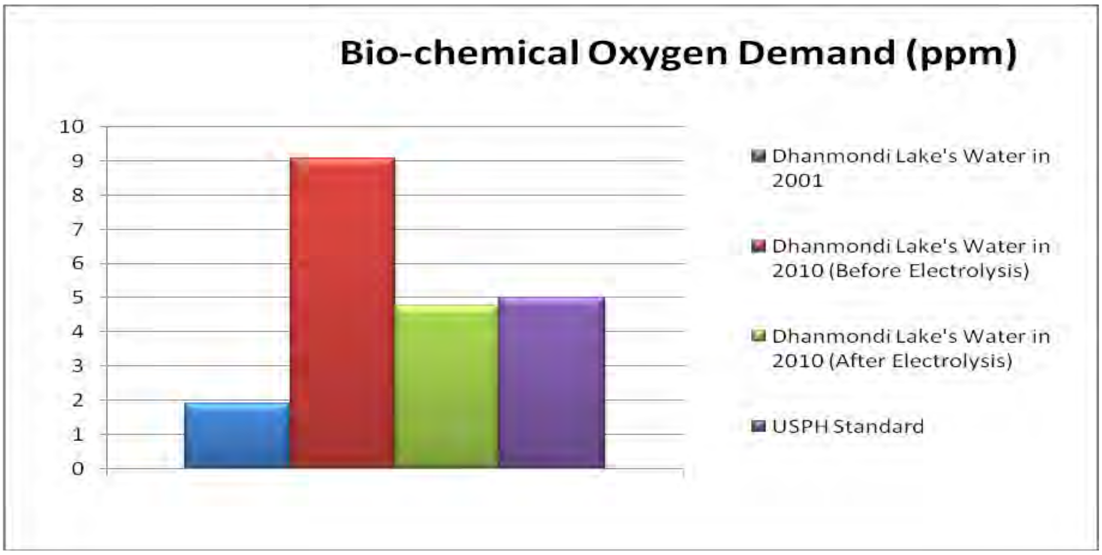


Fig 3.35 Biochemical Oxygen Demand (BOD) of Dhanmondi Lake‘s Water in 2001, in 2010 (Before Electrolysis), in 2010 (After Electrolysis using platinum electrode, 5 V potential, NaCl electrolyte and 1 Hr contact time) and USPH Standard.

Conclusion

As a new water and wastewater treatment method, electrochemical process is an emerging technology because of its high efficiency and relatively simple system. In electrochemical wastewater treatment, electrode material is one of the important factors that affect treatment efficiency. To efficiently handle the wastewater without damaging the environment, in this work, attempt has made to treat water and wastewater electrochemically.

Applying electrode potential, tape water and waste water (Dhanmondi Lake‘s Water) were treated using platinum electrode in a three-electrode and double compartment electrolysis cell system.

Various electrolysis conditions such as electrode, electrolytes, potential (applying voltage) and electrolysis time were optimized. Stainless steel and platinum electrode, 3 V to 7 V potential, NaCl, Na_2SO_4 & H_2SO_4 electrolytes and 1 Hr to 3 Hr contact time were studied for the treatment of tape water.

Water quality parameters such as pH, Conductivity, Total Dissolved Solid (TDS), Total Hardness, Dissolved Oxygen (DO), Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) of tape water were measured for optimization. After optimizing, waste water of Dhanmondi Lake‘s water was treated. Satisfactory results regarding Total Hardness, Conductivity, DO, COD and BOD were observed. The values of these parameters were decreased and found close to Bangladesh Standard and United States Public Health (USPH) Standard.

The water from Dhanmondi Lake was found polluted. The pH, conductivity, TDS and BOD are increasing day by day that indicates degraded water quality resulting in (a) loss of aquatic biodiversity, (b) hamper of fish culture, (c) adverse impact on agricultural users and consumers and (d) increase water borne diseases.

This study can facilitate the water quality model for Dhanmondi Lake as well as Dhaka city and help in formulating the strategy for water abstraction and water supply for Dhaka city.

This study suggest a low cost, less time consuming and efficient electrochemical process which can purify wastewater from different water sources of Dhaka city. Also it can be a new era for wastewater treatment in Bangladesh by electrochemical procedure.

References

1. Prevot A.B., Baiocchi C., Brussino M.C., Pramauro E., Savarino P., Augugliaro V., Marci G., and Palmisano L., —Mineralization and discoloration of textile wastewater by TiO_2 nanoparticles”, *Environ. Sci. Technol.,* **35** (2001) 971.
2. Stylidi M., Kondarides D.L., and Verykios X.E., —Enhancement of photo induced hydrogen production from irradiated Pt/TiO_2 suspensions with simultaneous degradation of azo-dyes”, *Appl. Catal. B: Environ.,* **40** (2003) 271.
3. Zhang W., An T., Xiao X., Fu J., Sheng G., Cui M., and Li G., —Photo electrochemical oxidation behavior of organic substances on TiO_2 thin-film electrodes”, *Appl. Catal. A: General,* **255** (2003) 221.
4. Rajkumar D., and Kim J.G., —Color and COD removal using a three-dimensional stacked Pt/Ti screen anode”, *J. Hazard. Mater. B,* **136** (2006) 203.
5. Chen X., Chen G., Gao F., and. Yue P. L., —High Performance Ti/BDD Electrodes for Pollutant Oxidation”, *Environ. Sci. and Technol.*, **37** (2003) 5021.
6. Rodrigo M. A., Michaud P. A., Duo I., Panizza M., Cerisola G., and Comninellis C, —Oxidation of 4-Chlorophenol at Boron-Doped Diamond Electrode for Wastewater Treatment”, *J. Electrochem. Soc.,* **148** (2001) 60.
7. Kraft A., Stadelmann M. and Blaschke M., —Anodic oxidation with doped diamond electrodes: a new advanced oxidation process*”, J. Hazard. Mater.,* **103** (2003) 247.
8. Zu-cheng W.U., Ming-hua Z., Zhi-wei H., Da-hui W., —electrolysis method for wastewater treatment using a novel beta-lead dioxide anode”, *J. Zhejiang Uni. Sci.*, **3** (2002) 194.
9. "CIA- The world fact book". Central Intelligence Agency. https://www.cia.gov/library/publications/the-world-factbook/geos/xx.html Geo. Retrieved 2008-12-20.

10. "United Nations". Un.org. 2005-03-22. http://www.un.org/ waterforlife decade/ background.html. Retrieved 2010-07-25.
11. Water Vapor in the Climate System, Special Report, [AGU], December 1995 (linked 4/2007). Vital Water UNEP.
12. Lomborg, Björn (2001). *The Skeptical Environmentalist*. Cambridge University Press. p. 22. ISBN 0521010683. http://www.lomborg.com/ dyn/files/basic_items/69-file/skeptenvironChap1.pdf.
13. "MDG Report 2008". http:// mdgs.un.org/ unsd/mdg/ Resources/Static/ Products/Progress2008/MDG Report 2008 En.pdf page 44. Retrieved 2010-07-25.
14. "Public Services", Gapminder video
15. Kulshreshtha, S.N., "A Global Outlook for Water Resources to the Year 2025". *Water Resources Management* **12** (3),167–184, 1998.
16. ""Charting Our Water Future: Economic frameworks to inform decision-making"" (PDF). http://www.mckinsey.com/ App Media/ Reports/ Water/ Charting Our Water Future Full Report 001.pdf. Retrieved 2010-07-25.
17. Baroni, L.; Cenci, L.; Tettamanti, M.; Berati, M., "Evaluating the environmental impact of various dietary patterns combined with different food production systems". *European J. of Clinical Nutrition* **61** (2), 279–286, 2007.
18. Peavy, H.S. Rowe, D.R. and Tchobanoglous, G., *Environmental Engineering*, McGraw-Hill Inc., New York (1985).
19. Braun, Charles L.; Sergei N. Smirnov, "Why is water blue?". *J. Chem. Educ.* **70** (8): 612,1993
20. Campbell, Neil A.; Brad Williamson; Robin J. Heyden (2006). *Biology: Exploring Life*. Boston, Massachusetts: Pearson Prentice Hall. ISBN 0-13-250882-6. http://www.phschool.com/el_marketing.html.
21. Kotz, J. C., Treichel, P., & Weaver, G. C. (2005). *Chemistry & Chemical Reactivity*. Thomson Brooks/Cole. ISBN 053439597X.

22. Ball, Philip (14 September 2007). "Burning water and other myths". *Nature News*. http://www.nature.com/news/2007/070910/full/070910-13.html. Retrieved 2007-09-14.
23. "G8 "Action plan" decided upon at the 2003 Evian summit". G8.fr. 2003-06-02. http://www.g8.fr/evian/ english/ navigation/ 2003 g8 summit/summit_documents/water a g8 action plan.html. Retrieved 2010-07-25.
24. "World Health Organization. Safe Water and Global Health". Who.int. 2008-06-25. http://www.who.int/features/qa/70/en/. Retrieved 2010-07-25.
25. UNEP International Environment (2002). *Environmentally Sound Technology for Wastewater and Stormwater Management: An International Source Book*. IWA Publishing. ISBN 1843390086. OCLC 49204666.
26. Ravindranath, Nijavalli H.; Jayant A. Sathaye (2002). *Climate Change and Developing Countries*. Springer. ISBN 1402001045.
27. "WBCSD Water Faacts & Trends". http://www.wbcsd.org/includes/getTarget.asp?type d&id MTYyNTA. Retrieved 2010-07-25.
28. Water Use in the United States, National Atlas.gov
29. *Decree relating to the weights and measurements*
30. *L'Histoire Du Mètre, La Détermination De L'Unité De Poids*
31. Re: What percentage of the human body is composed of water? Jeffrey Utz, M.D., The MadSci Network
32. "Healthy Water Living". BBC. http://www.bbc.co.uk/health/ healthy living/nutrition/ drinks water.shtml. Retrieved 2007-02-01.
33. Rhoades RA, Tanner GA (2003). *Medical Physiology* (2nd ed.). Baltimore: Lippincott Williams & Wilkins. ISBN 0781719364. OCLC 50554808.
34. "Drink at least eight glasses of water a day." Really? Is there scientific evidence for "8 × 8"? by Heinz Valdin, Department of Physiology, Dartmouth Medical School, Lebanon, New Hampshire

35. Drinking Water How Much?, Factsmart.org web site and references within.
36. *Food and Nutrition Board, National Academy of Sciences. Recommended Dietary Allowances.*. National Research Council, Reprint and Circular Series, No. 122. 1945. pp. 3–18.
37. Dietary Reference Intakes: Water, Potassium, Sodium, Chloride, and Sulfate, Food and Nutrition Board
38. "Water: How much should you drink every day? –". Mayoclinic.com. http://www.mayoclinic.com/health/water/NU00283. Retrieved 2010-07-25.
39. "Conquering Chemistry" 4th Ed. Published 2008
40. Maton, Anthea; Jean Hopkins, Charles William McLaughlin, Susan Johnson, Maryanna Quon Warner, David LaHart, Jill D. Wright (1993). *Human Biology and Health*. Englewood Cliffs, New Jersey, USA: Prentice Hall. ISBN 0-13-981176-1. OCLC 32308337.
41. Unesco (2006). *Water: a shared responsibility*. Berghahn Books. p. 125. ISBN 1845451775. http://books.google.com/ id=1cV8tziHZ5 sC&pg PA125.
42. Vaclavik, Vickie A. and Christian, Elizabeth W (2007). *Essentials of Food Science*. Springer. ISBN 0387699392. http://books.google.com/ id=iCCsvwZrguUC&printsec=frontcover
43. DeMan, John M (1999). *Principles of Food Chemistry*. Springer. ISBN 083421234X.http://books.google.com/id kDYJ7a1Hb D0C & p g PA 434.
44. Montogomery, J.M., *Water Treatment Principles and Design*, Consulting Engg. Inc., John Wiley and sons, New York 75, 2nd edition (1985).
45. DE, A.K., *Environmental Chemistry,* Weily Eastern, New Delhi, 3rd ed., P-171(1994)
46. Kudesia, V.P., *Water Pollution*, Pragati Prakashani, Meerat India.
47. Rosen, A.A. and Booth, R.L. Taste and odour control. In: Water quality and treatment; a handbook of public water supplies. 3rd edition.

American Water Works Association. McGraw-Hill, Toronto. p. 225 (1971).

48. Suffett, I.H. and Segall, S. —Detecting taste and odor in drinking water", *J. Am. Water Works Assoc.*, **63**: 605 (1971).
49. Black, A.P. and Christman, R.F. —Characteristics of colored surface waters", *J. Am. Water Works Assoc.*, **55**: 753 (1963).
50. Black, A.P. and Hannah, S.A. —Measurement of low turbidities", *J. Am. Water Works Assoc.*, **57**, 901 (1965).
51. Sawyer, C.N. and McCarty, P.L. *Chemistry for sanitary engineers*. 2nd edition. McGraw-Hill Book Company, Toronto. p. 299 (1967).
52. American Public Health Association/American Water Works Association/Water Pollution Control Federation. Standard methods for the examination of water and wastewater. 14th edition. Washington, DC (1976).
53. 1991, *Streamkeeper's Field Guide*: Watershed Inventory and Stream Monitoring Methods.
54. 1991, Streamkeeper's Field Guide: Watershed Inventory and Stream Monitoring Methods.
55. Fundamentals of Aquatic Toxicology, 1985.
56. H. Lund, *Inorganic Electrochemistry*, Eds., M. M. Baizer and H. Land, Marcel Dekker, (1983)
57. S. Barnartt, *J. Electrochem. Soc.*, **99**, 549 (1952).
58. Reports on the IUPAC Convention on Electrochemistry, *Electrochim. Acta,* **27**, 629 (1982) and *Pure and Appl. Chem.*, **37**, 503 (1974), **51**, 1159 (1979)
59. L. Smart and E. Moore, *Solid State Chemistry*, Chapman and Hall, 126, (1992).
60. *The Oxide Handbook,* G. V. Samsonov, Ed.; IFI / Plenum, New York, 23, (1982).
61. F. A. Grant, *Riv. Modern Phys.*, **31**, 646 (1959**)**.
62. D.C.Cronemeyer, Phys. Rev. **87**, 876 (1952).
63. R. I. Bickley, *Chem. Phys. of Solids and Their Surface* **7**, 118 (1978).

64. P. Salvador, *Solar Energy Matter.*, **6**, 241 (1982).
65. G. Zhang, X. Bi and G. Peng, J. Appl. Polym. Sci., **56**, 1683 (1995).
66. Oturan M.A., "An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants: Application to herbicide 2,4-D", *J. of Appl. Electrochem*. **30** (2000) 475.
67. Kariyajjanavar P., Narayana J., Nayaka Y. A., Umanaik M., "Electrochemical Degradation and Cyclic Voltammetric Studies of Textile Reactive Azo Dye", *Portugaliae Electrochimica Acta* 2010, **28**(4), 265-277
68. Ghangrekar M.M., Shinde V.B., "Performance of membrane-less microbial fuel cell treating wastewater and effect of electrode distance and area on electricity production", *Bioresource Technol*. **98**(15), 2007, 2879-2885
69. Abu Ghalwaa N.M., Abdel-Latifb M.S., "Electrochemical Degradation of Acid Green Dye in Aqueous Wastewater Dyestuff Solutions Using a Lead Oxide Coated Titanium Electrode", *J. of the Iranian Chem. Soc.*, **2**(3), 2005, 238-243.
70. Idris A., Saed K., "Degradation of phenol in wastewater using anolyte produced from electrochemical generation of brine solution*", Global Nest: the Int. J.* **4**(2-3), 139 -144, 2002
71. Bensalah Nasr, Gadri Abdelatif, "Electrochemical treatment of wastewaters containing 4-chlororesorcinol using boron doped diamond anodes" , *The Canadian J. of Chem. Eng.* **87**(1), 78–84, 2009.
72. Logan B.E., "Simultaneous wastewater treatment and biological electricity generation", *Water Sci. & Technol.*, **52**(1-2), 31–37, 2005.
73. Hong Liu, Ramanath A. N., Brucee L., "Production of Electricity during Wastewater Treatment Using a Single Chamber Microbial Fuel Cell", *Environ. Sci. Technol*. **38**, 2281-2285,2004.

74. Parsaa J. B., Abbasib M., "Decolorization of Synthetic and Real Wastewater by Indirect Electrochemical Oxidation Process", *Acta Chim. Slov*. 2007, **54**, 792–796.
75. Hyunsoo Moon 1, In Seop Chang, Byung Hong Kim, —Continuous electricity production from artificial wastewater using a mediator-less microbial fuel cell", *Bioresource Technol.* **97** (2006) 621–627
76. Lidia Szpyrkowicz, Jeremi Naumczyk, Francesco Zilio-Grandi , —Electrochemical treatment of tannery wastewater using Ti/Pt and Ti/Pt/Ir electrodes" *Water Research*, **29**(2), 1995, 517-524.
77. Oliver J. Murphy, G. Duncan Hitchens, Lamine Kaba, Charles E. Verostko, —Direct electrochemical oxidation of organics for wastewater treatment", *Water Research*, **4**, 1992, 443-451.
78. Marco Panizza , Cristina Bocca, Giacomo Cerisola —Electrochemical treatment of wastewater containing polyaromatic organic pollutants" *Water Research*, **34** (9), 2000, 2601-2605
79. Polcaro A.M., Vacca A., Palmas S., Mascia M. —Electrochemical treatment of wastewater containing phenolic compounds: oxidation at boron-doped diamond electrodes", *J. of App. Electrochemistry* , **33**, 10, 885-892,
80. Jinping Jia, Ji Yang, Jun Liao, Wenghua Wang and Zijian Wang, —Treatment of dyeing wastewater with ACF electrodes", *Water Research*, **33**(3), 1999, 881-884.
81. Eduardo Arevalo, Wolfgang Calmano., Studies on electrochemical treatment of wastewater contaminated with organotin compounds, *Journal of Hazardous Materials* 146 (2007) 540–545
82. Comninellis, Ch. ; Pulgarin, C. , Electrochemical oxidation of phenol for wastewater treatment using SnO_2, anodes , Chemistry and Materials Science , *Journal of Applied Electrochemistry*, **23**, 2, 108-112.
83. Igor Cretescu1, Harold Braunstein, Matei Macoveanu, STUDY OF PLATINUM ELECTRODES APPLIED IN THE TREATMENT OF

PHENOLIC WASTEWATER, *Environmental Engineering and Management Journal*, 2002,**1**(4), 551-556.

84. José L. Nava, Marco A. Quiroz, Carlos A. Martínez-Huitle, Electrochemical Treatment of Synthetic Wastewaters Containing Alphazurine A Dye: Role of Electrode Material in the Colour and COD Removal, *J. Mex. Chem. Soc.* 2008, **52**(4), 249-255
85. Karuppan Muthukumar, P Shunmuga Sundaram, N Anantharaman, C Ahmed Basha, ―Treatment of textile dye wastewater by using an electrochemical bipolar disc stack reactor" , *Journal of Chemical Technology & Biotechnology*, **79**(10), 1135–1141, 2004.
86. G. Vlyssides, D. Papaioannou, M. Loizidoy, P. K. Karlis and A. A. Zorpas, ―Testing an electrochemical method for treatment of textile dye wastewater" *Water Research*, 20(7), 2000, 569-574.
87. D. Rajkumar, J. Guk Kim, K. Palanivel, ―Indirect Electrochemical Oxidation of Phenol in the Presence of Chloride for Wastewater Treatment" *Chemical Engineering & Technology*, Volume **28**, Issue 1, pages 98–105, January, 2005.
88. Chih-Ta Wang, Wei-Lung Chou and Yi-Ming Kuo**,** ―Removal of COD from laundry wastewater by electrocoagulation/electroflotation", Journal of Hazardous Materials, Volume 164, Issue 1, 15 May 2009, Pages 81-86.
89. MUFF J., BENNEDSEN L.R., SØGAARD E.G., ―Detailed parameter study on the mechanisms in electrochemical oxidation of p-nitrosodimethylaniline in chloride electrolyte" EAAOP 2 2009
90. Krishna P. Katuri, K. Scott, ―Electricity generation from the treatment of wastewater with a hybrid up-flow microbial fuel cell", Biotechnol. and Bioengg., 107(1), 52–58, 2010
91. E. M. Elsayed, A. E. Saba ―The Electrochemical Treatment of Toxic Hexavalent Chromium from Industrial Effluents using Rotating Cylinder Electrode Cell", Int. J. Electrochem. Sci., 4 (2009) 627 – 639
92. Huu D Doan, Jianning Wu, Edwin Boithi, Megan Storrar, ―Treatment of wastewater using a combined biological and electrochemical

technique”, *Journal of Chemical Technology & Biotechnology*, Volume **78**, Issue 6, pages 632–641, June 2003.

93. Choon Hwan Shin, Jun-Seok Bae, —Operational Performance of an Electrolytic Reactor in Configurating a Greywater Treatment System for Sewage/Wastewater Reuse”, *J. Ind. Eng. Chem.,* Vol. **13**, No. 7, (2007) 1091-1097
94. Xueming Chen, Guohua Chen, Poloc Kyue, —Novel Electrode System for Electroflotation of Wastewater”, *Environ. Sci. Technol.*2002, **36**,778-783.
95. Wu Chen, Changzhu Yang, Ping Mei and Xianqing Yin, —Treatment of wastewater containing polyacrylamide using three dimensional electrodes”, *Wuhan University Journal of Natural Sciences* Volume **12**, Number 2, 353-360.
96. Nabil S. Abuzaid, Zakariya Al-Hamouz, Alaadin A. Bukhari and Mohamed H. Essa, —Electrochemical Treatment of Nitrite Using Stainless Steel Electrodes”, *Earth and Environmental Science Water, Air, & Soil Pollution* , **109**, 1-4, 429-442.
97. Nabil S. Abuzaid_, Alaadin A. Bukhari, Zakariya M. Al-Hamouz , —Ground water coagulation using soluble stainless steel electrodes”, *Advances in Environmental Research*, **6** (2002), 325-333.
98. Seok J. D., Cham K., Se Geun Lee, Sung J. L., Ho Young Kim, Sang-Jun Ahn, Seog-Jin Jo, Jang Seung Choi, "Industrial dye waste-water treatment by electrochemical catalytic process using TiO2/ITO electrode", *Advanced Nanomaterials Research T.* **711**(1999), 703-834.
99. Banglapedia
100. Clair N. Sawyer, Perry L. McCarty, Gene F. Parkin (2003). *Chemistry for Environmental Engineering and Science* (5th ed.). New York: McGraw-Hill.
101. DE, A.K., *Environmental Chemistry,* Weily Eastern, New Delhi, 3rd ed., P-171 (1994)

102. Md. Mominul Islam, Taheyoshi Okajima, Shimpei Kojima, Takeo Ohsaka, Water electrolysis : an excellent approach for the removal of water from ionic liquids, *Communication*, 2008, 5330-5332

103. Dwight G. Ballinger, Leonard D. Pagnot, Robert L. Bunch, John B. Pate, Treatise on Analytical Chemistry, Part 3, Section B, Volume 2

104. *DOE in Majed and Rahman,* 2002

105. M.M. Islam and T. Oshaka, *J. Phys. Chem. C,* 2008, **112**, 1269

106. P.S. Singh and D.H. Evans, *J. Phys. Chem. B,* 2006, **110**, 637

Appendices

Table A : Investigated result for before and after electrolysis of tap water with the variation of voltage and compare with EQS for Bangladesh, World Health Organization (WHO), United States Public Health (USPH)

Sl	Parameter	Tap Water	Before Electrolysis	After Electrolysis using 3V	After Electrolysis using 5V	After Electrolysis using 7V	Bangladesh Standard	WHO Standard	USPH* Standard
1	**pH**	7.1	7.1	8.63	8.57	9.37	6.5-8.5	6.5-9.2	6.5-8.5
2	**Conductivity** (micro Siemens/cm)	423	478	451	408	434	-	-	300
3	**Total Hardness** (ppm)	253	254	239	198	191	250	500	500
4	**Total Dissolved Solid** (ppm)	641	644	636	612	618	1000	500	500
5	**Dissolved Oxygen** (ppm)	4.10	5.52	5.49	5.33	4.97	4-6	4-6	4-6
6	**Chemical Oxygen Demand** (ppm)	8.2	8.9	7.01	4.77	5.08	4	10	4
7	**Bio-chemical Oxygen Demand**	6.2	9.5	5.3	4.1	9.58	-	6	5

Table B : Investigated result for before and after electrolysis of tap water with the variation of working electrodes and compare with EQS for Bangladesh, World Health Organization (WHO), United States Public Health (USPH)

Sl	Parameter	Tap Water	Before Electrolysis	After Electrolysis using SS	After Electrolysis using Pt	Bangladesh Standard	WHO Standard	USPH* Standard
1	**pH**	7.1	7.1	9.76	8.57	6.5-8.5	6.5-9.2	6.5-8.5
2	**Conductivity** (micro Siemens/cm)	423	478	524	408	-	-	300
3	**Total Hardness** (ppm)	253	254	247	198	250	500	500
4	**Total Dissolved Solid** (ppm)	641	644	618	612	1000	500	500
5	**Dissolved Oxygen** (ppm)	4.10	5.52	5.36	5.33	4-6	4-6	4-6
6	**Chemical Oxygen Demand** (ppm)	8.2	8.9	6.16	4.77	4	10	4
7	**Bio-chemical Oxygen Demand**	6.2	9.5	8.6	4.1	-	6	5

Table C : Investigated result for before and after electrolysis of tap water with the variation of electrolytes and compare with EQS for Bangladesh, World Health Organization (WHO), United States Public Health (USPH)

			Using NaCl		Using Na_2SO_4		Using H_2SO_4				
Sl	Parameter	Tap Water	Before Electrolysis	After Electrolysis	Before Electrolysis	After Electrolysis	Before Electrolysis	After Electrolysis	Bangladesh Standard	WHO Standard	USPH* Standard
1	**pH**	7.1	7.1	8.57	7.1	8.85	2.81	2.94	6.5-8.5	6.5-9.2	6.5-8.5
2	**Conductivity** (micro Siemens/cm)	423	478	408	563	542	2070	1970	-	-	300
3	**Total Hardness** (ppm)	253	254	198	259	213	260	252	250	500	500
4	**Total Dissolved Solid** (ppm)	641	644	612	761	727	777	760	1000	500	500
5	**Dissolved Oxygen** (ppm)	4.10	5.52	5.33	5.52	5.55	5.75	5.98	4-6	4-6	4-6
6	**Chemical Oxygen Demand** (ppm)	8.2	8.9	4.77	9.2	7.26	16.09	15.35	4	10	4
7	**Bio-chemical Oxygen Demand** (ppm)	6.2	9.5	4.1	11.73	10.6	Can’t be Measured	Can’t be Measured	-	6	5

Table D : Investigated result for before and after electrolysis of tap water with the variation of contact time and compare with EQS for Bangladesh, World Health Organization (WHO), United States Public Health (USPH)

Sl	Parameter	Tap Water	Before Electrolysis	After Electrolysis Time-1 Hr	After Electrolysis Time-2 Hr	After Electrolysis Time-3 Hr	Bangladesh Standard	WHO Standard	USPH* Standard
1	**pH**	7.1	7.1	8.57	9.94	10.02	6.5-8.5	6.5-9.2	6.5-8.5
2	**Conductivity** (micro Siemens/cm)	423	478	408	417	518	-	-	300
3	**Total Hardness** (ppm)	253	254	198	167	179	250	500	500
4	**Total Dissolved Solid** (ppm)	641	644	612	592	588	1000	500	500
5	**Dissolved Oxygen** (ppm)	4.10	5.52	5.33	5.79	6.2	4-6	4-6	4-6
6	**Chemical Oxygen Demand** (ppm)	8.2	8.9	4.77	4.98	5.04	4	10	4
7	**Bio-chemical Oxygen Demand**	6.2	9.5	4.1	4.6	5.19	-	6	5