

Chapter I

Introduction

Chapter I

Introduction

Water is one of the renewable resources essential for the sustenance of all forms of life, food production and economic development. Water is truly a unique gift to mankind from nature. It is impossible to substitute most of its uses and is expensive to transport¹. Many countries particularly those experiencing the impacts of climate change have started to make projections on their own water security, the most important reason being directly linked to social stability, economic growth and development of any country².

1.1 Importance of Water

Water is the most important factor for the existence of living organisms, next to oxygen. It is the undeniable sustenance constituent endowed upon our planet to grow and prosper³. Fresh water is found in atmosphere as water vapour and in landforms as surface and subsurface water, constituting 0.02 to 4% water by volume varying on location⁴. Over 90% of the world's potable water supply is derived from ground water⁵. Water circulates through the land by transporting, dissolving, replenishing nutrients and organic matter, also carrying away waste materials.

Unique characteristics of water are:

- * It plays an important role in maintaining protein structure by holding proteins in their peculiar folded conformations
- * It has high heat capacity per unit weight thereby absorbing large quantities of heat without producing huge changes in temperature
- * It has very low co-efficient of compressibility (5 pa^{-1}) at ordinary temperatures and pressure
- * Water is considered as universal solvent because of its high dielectric constant.

The quantity and quality of water available from varying resources have become inevitable for agricultural and industrial sectors. Agriculture is the backbone of the Indian economy and it receives an enhanced share of water allocation. Approximately 50% fresh water is utilized for agricultural activities, underground water is one of the major water

resources for agricultural use⁶. Every industry has its own water requirements, for example water containing least amount of nitrate and organic matter is essential for boiler use to prevent corrosion. In last three decades, rapid growth of industrialization and urbanization has caused serious impact on environment, large quantities of water are consumed for cooling and heating purposes in industries⁷.

1.2 Water Quality and Impacts

Water quality describes the condition of water including chemical, physical, biological and radiological characteristics, usually with respect to its suitability for a particular purpose. It contains dissolved substances, non-dissolved particulate matter and living organisms; indeed, such materials and organisms are necessary components of good – quality water, as they help to maintain vital biogeochemical cycles.

Water quality deserves increased attention alongside water quantity in its resource management. In general, water is considered to be fit for drinking, only when it possess the following characteristics⁸

- * Colorless, odorless and tasteless in nature
- * Free from turbidity and suspended impurities
- * Free of pathogenic and microorganisms
- * pH range →7 - 8.5
- * Hardness →50 to 150 mg/L
- * Anti-corrosive
- * Free from hazardous substances
- * Turbidity not to exceed 10 NTU
- * Free from objectionable dissolved gases like oxides of sulphur/ nitrogen, hydrogen sulphide and metal ions such as arsenic, lead, manganese and chromium salts
- * Total dissolved solids < 500 mg/L
- * Total organic content < 5 mg/L

- * Dissolved salts→ 50-500 mg/L
- * Free from disease producing microorganisms.

Inorganic minerals present in water can be classified as, requirements in

- * Large quantities on regular basis: K, Ca, Na and Mg
- * Smaller quantities: Co, Cu, Mn, Fe, Zn and Mo
- * Toxicants at very low concentrations: Ag, Bi, Be, Cd and Pb

Poor water quality has a direct impact on the ecosystem in a number of ways. Water pollution minimizes the surplus supply of water for drinking, bathing, industry, agriculture etc., Utilization of low-quality water (saline or brackish water) have direct impact on productive water use for irrigation, reflecting on land degradation, crop production, consequently, rural income and food security.

Over use of water resources for domestic use, agricultural/ industrial production, mining, power generation, forestry practices and other factors can deplete and alter their chemical, physical and biological characteristics which in turn disturb the ecosystem integrity. Pollution caused by these sources manifests water in the form of increased acidity and higher concentrations of nutrients, sediments, salts, trace metals, chemicals, and other toxicants as well as harmful pathogenic microorganisms. Nutrient enrichments has become one of the most widespread water quality problems severely degrading freshwater and coastal ecosystems.

1.3 Water Pollution

Pollution of water resources is due to the introduction of contaminants into the natural environment. For example, releasing inadequately treated wastewater into natural water bodies can lead to degradation of aquatic ecosystems, causing ill- effects to people living downstream. Water pollution may also occur because of inevitable changes in nature such as sedimentation from severe rainfall events, volcanic eruptions and natural calamities. It has been suggested that this pollution is the leading cause of death and diseases, worldwide. Adverse alteration in water quality result in large scale illness, where, approximately 14,000 people die per day globally⁹. Water pollution seems to be more directly correlated

to the demographic growth rather than simple population growth. Therefore, population growth and industrialization both go in hand synergistically, to increase the levels of pollution, implying that the extent of this pollution is directly related to industrialization, civilization and living standards. Serious consequences include species mortality, biodiversity reduction and loss of ecosystem services. The most problematic pollutants are microbes that induce disease, their sources may be considered as natural, but a preponderance of these instances result from human intervention in the environment or due to overpopulation¹⁰.

Contamination of water resources can be summarized as a consequence of the following factors¹¹

- * Natural process: erosion, volcanic activities, biological processes and human activities
- * Increasing erosion due to deforestation, wrong cultivation practices and urbanization
- * Washing of agrochemicals from agricultural and silvicultural production
- * Spillage accidents caused during the transport of fuel and other chemicals, especially through waterways
- * Untreated disposal of gaseous, liquid and solid wastes from industry, thermal and nuclear power generation, dwelling areas and subsequent leaching of land wastes
- * Infiltration of polluted water from terrestrial sources to the underground water table.

1.4 Water Pollutants - Classification

Water pollutants can be classified as physical (temperature), chemical (organic/inorganic substances) or biological (microorganisms) origin which leads to aesthetic or detrimental effects on aquatic life and consumers¹². Majority of water pollutants are, however, in the form of chemicals which remain dissolved or suspended in water whose environmental response is often objectionable. The adverse characteristics of water occur not only during the penetration through the atmosphere, soil and rocks but also due to the contact with vegetation canopy and cultivation practices.

1.4.1 Thermal pollution

Temperature adversely affects water quality and aquatic biota, majority of which is impacted by human activities. Some of the important sources of thermal pollution are nuclear power and electric power plants, petroleum refineries, steel melting factories, coal fire power plant, boiler from industries releasing large amounts of heat to the water bodies bringing about physical, chemical and biological changes of the latter. High temperature depreciates the oxygen content in water; disturbs the reproductive cycles, respiratory and digestive rates of aquatic population.

1.4.2 Organic pollutants

Insecticides and herbicides, organohalides and other forms of chemicals; bacteria from sewage and livestock farming; food processing wastes; pathogens; volatile organic compounds classified as organic toxicants pave way to pollute the water streams through the varied sources of origin.

1.4.3 Inorganic pollutants

Acid mine drainage; silt from surface run-off, logging, slash and burning practices and land filling; fertilizers from agricultural run-off inclusive of nitrates and phosphates and chemical wastes from industrial effluents, form the basis of inorganics resulting in their detrimental impact on water resources.

Table 1.1: Common Water Pollutants - Adverse Effects

Pollutants	Impacts
Organics i. Oxygen Demanding wastes ii. Synthetic Organic pollutants iii. Oil	Depletion of Dissolved Oxygen cause adverse effect in aquatic life, make water unfit for variable uses, responsible for endangering water birds and coastal plants due to coating of oils and also cause reduction of light transmission and photosynthesis.
Inorganics	Adverse effect on aquatic flora and fauna constituting public health problem.
Thermal	Rise in temperature leading to rapid decrease of Dissolved Oxygen altering spectrum of aquatic organisms.

Pollutants	Impacts
Radioactive	Toxic isotopes accumulate in the bones, teeth of living organisms, causing lethal effects.
Suspended solids and Sediments	Blocking of sunlight penetration into water retarding photosynthesis, and injures the gills of fishes causing asphyxiation.
Pathogens	Water borne diseases such as cholera, typhoid etc.,
Plant Nutrients	Affects aquatic life and causes groundwater pollution

1.5 Water Pollutants - Sources

1.5.1 Point Sources

Point sources of pollution comprise of harmful substances which come directly into a water body from an identifiable single source (fig 1.1), which may include discharge from pipe attached to a factory, oil spill from a tanker, effluents discharge from sewage treatment works, industries and power stations. Pollution from agriculture may include animal waste lagoons, animal feeding operations, fertilizers and pesticides. Municipal point sources might include landfills, motor pools, utility stations, wastewater treatment plants and fleet maintenance facilities.

1.5.2 Non-Point Sources

Non-point sources of water pollution serve as a platform for different sources of pollutants' origin and the number of ways by which these contaminants enter into groundwater or surface water (fig 1.2). This may originate from natural processes such as rainfall, snowmelt and human activities: crop irrigation or lawn maintenance. In some cases, pollution caused at one point of the environment leads to an extended effect at hundred or even thousands of miles away, referred to as transboundary pollution. Radioactive waste that travels through the oceans from nuclear reprocessing plants can be cited as an example ¹³.



Figure 1.1 Point Source



Figure 1.2 Non- Point Source

Table 1.2 Characteristics of Point / Non-point Sources

Point Sources	Non - Point Sources
<ul style="list-style-type: none"> ✓ Wastewater effluent (municipal and industrial) ✓ Runoff and leachate from waste disposal sites, animal feedlots, mines, oil fields, unsewered ✓ Leakage in storage lagoons, underground storage tanks that contain chemicals or fuels ✓ Leachates from public and industrial wastewater treatment plants ✓ Storm sewer outfalls from cities with a population >100,000 ✓ Overflows of combined storm and sanitary sewers ✓ Runoff from construction sites >2 ha 	<ul style="list-style-type: none"> ✓ Runoff from agriculture (including return flow from irrigated agriculture), pasture and range, septic tank leachates, abandoned mines ✓ Urban runoff unsewered and sewer areas with a population <100,000 ✓ Atmospheric deposition over a water surface ✓ Pesticides, herbicides, and fertilizer from residential lawns, farmlands etc ✓ Activities on land that generate contaminants, such as logging, wetland conversion, construction, and development of land or waterways ✓ Precipitation containing air pollutants ✓ Oil, gasoline, animal feces and litter

1.6 Water Pollution - Control Measures

The key challenges towards better management of water quality include temporal and spatial variation of rainfall, uneven geographic distribution of surface water resources, persistent droughts, overuse of ground water, drainage and salinization, water quality

problems arising out of treated, partially treated and untreated wastewater from urban settlements, industrial establishments and runoff from irrigation sectors (CPCB Report, 2013). Thence, water quality maintenance is extremely needy to meet the and global scarcity of water resources.

1.6.1 Anionic Pollution

Anions combine with cations leading to salt formation, which are important for the human body. These ions play an inevitable role in many vital biological processes, starting from hormone production to DNA formation. Anions occur naturally in rock-forming and ore minerals which are associated with soils, sediments and waters. They can be considered as pollutants that affect human health and ecosystems if their concentrations reach certain levels. These anionic pollutants, including common anionic species as well as some anionic metal complexes are considered as important pollutants in most quality standards of water/wastewater. A number of common anionic species, including nitrate, nitrite, cyanide, phosphate, perchlorate, sulphate, and fluoride get introduced into the water bodies through various industrial activities viz., mining, refining ores, fertilizer industries, laundry units, tanneries, batteries, paper industries etc. These pollutants discharged into ecosystems from industries are of great concern worldwide due to their significant risks in environment and human health¹⁸. The most important anionic pollutants of water include phosphate, fluoride, nitrate and sulphate. Increasing concentrations of these anions in the water bodies result in severe health hazards due to their toxicity, accumulation and bio-magnification throughout the water bodies.

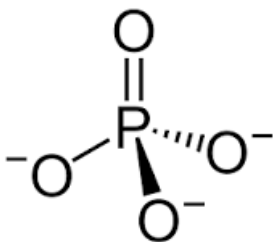
The regulatory limits for anions in drinking water and discharges from industrial wastewaters are shown in Table 1.3.

Table 1.3 Permissible limits of Toxic Anions

Anions	Drinking Water ^{15,16}			Industrial Effluent Discharge ¹⁷	
	BIS	WHO	USEPA	USEPA	
	mg/L	mg/L	mg/L	Inland Surface Water	Into Public Sewers
Phosphate	5	10	10	5	-
Nitrate	45	50	45	10	20
Sulphate	150	200	250	2.0	-
Fluoride	2.0	1.5	2.0	2.0	15
Chloride	250	300	250	600	-
Cyanide	0.05	0.2	0.05	0.2	2

1.6.2 Phosphate

Phosphate is an essential nutrient for the growth of plants, animals and humans. It is one of the twenty most abundant elements in the solar system, and the 11th most abundant in the earth's crust. Under natural conditions, phosphate is typically scarce in water. Human activities, however, have resulted in excessive loading of phosphorus into many freshwater systems¹⁹. This can cause water pollution by promoting excessive algal growth, particularly in lakes. Water quality can be impaired when bacteria consume dead algae and use up contaminated dissolved oxygen, leading to suffocation of fishes and other aquatic life. In some water bodies, minimal concentration of phosphorus limits algal growth and/or aquatic plants.



Formula: PO_4^{3-}

Molar mass: 94.9714 g/mol

Sources

- * Laundry units
- * Run off from fertilizers, pasture and croplands
- * Human and pet sewage
- * Chemical manufacturing
- * Vegetable and fruit processing units
- * Paper and pulp industry
- * Atmospheric deposition and stream bank erosion
- * Urban/non-agricultural/rural runoffs; seepage from individual / communal sewage systems
- * Municipal and industrial wastewaters

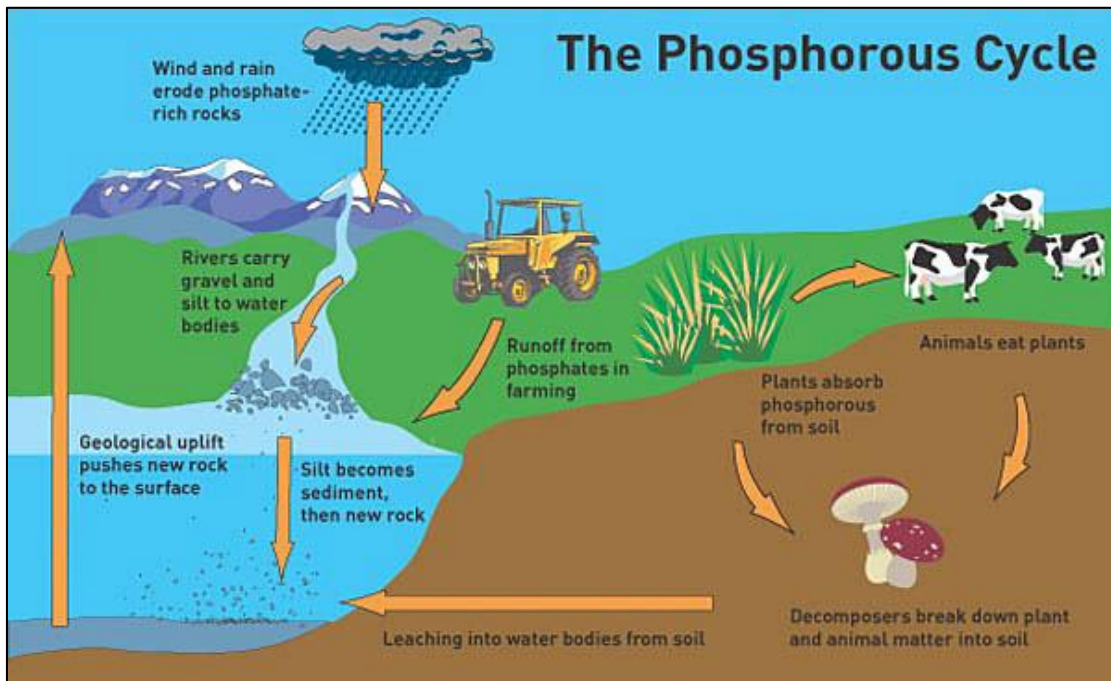
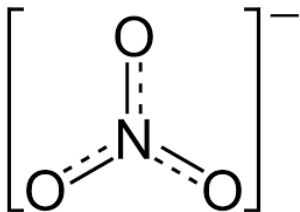


Figure 1.3 Phosphorus Cycle

1.6.3 Nitrate

It is a major constituent of earth's atmosphere and occurs in many different forms like elemental nitrogen, nitrate, and ammonia. Nitrate and Nitrite anions are ubiquitous in the environment. Both species are produced by denitrification process in which ammonia is oxidized by soil bacteria. However, nitrate is an essential component of proteins and DNA in living organisms. Drinking water is contaminated by inorganic nitrates such as potassium nitrate and ammonium nitrate, their sources are from fertilizers²⁰. Extensive use of fertilizers in agricultural practices in turn result in extended contamination of groundwater, leading to detrimental impact on cultivated food crops, affecting plant, animal and in turn human beings.



Formula: NO₃⁻

Molar mass: 62.0049 g/mol

Sources

- * Run-off from land
- * Sewage effluent
- * Manure deposits (Fertilizers and pesticides)
- * Animal feeds
- * Septic systems etc,
- * Broken sewage systems
- * Industrial wastes related to food processing

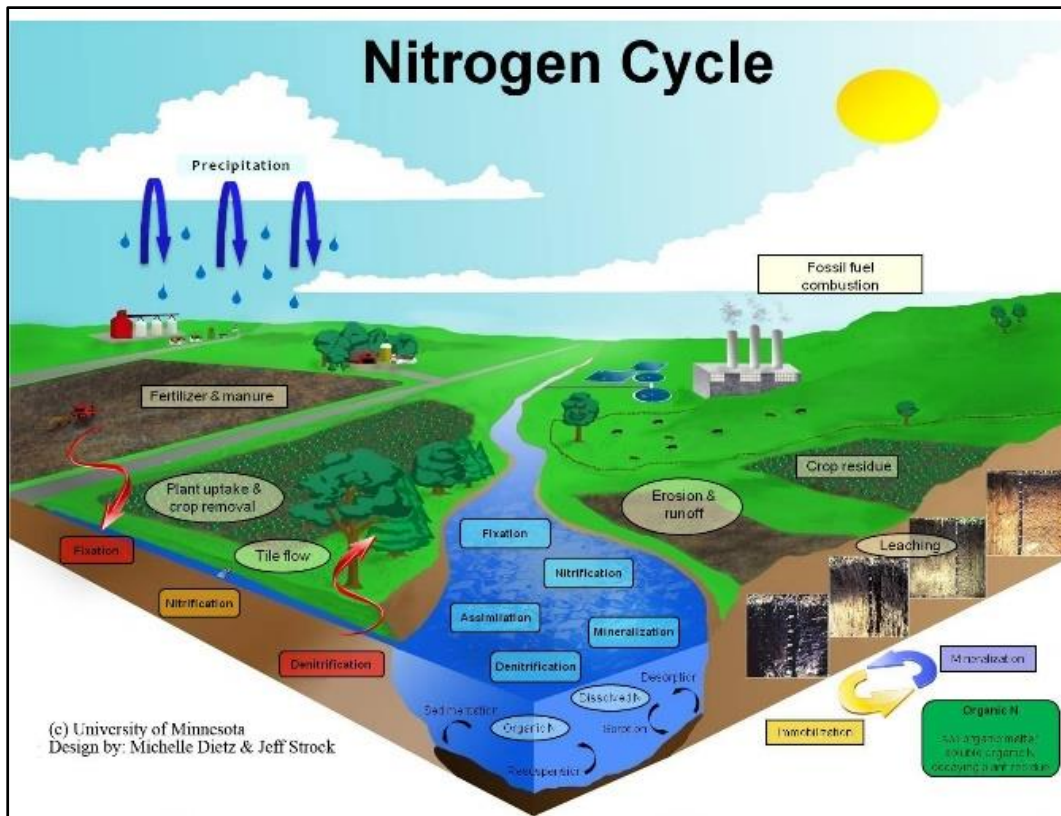
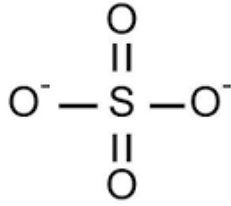


Figure 1.4 Nitrogen Cycle

1.6.4 Sulphate

Sulphate minerals are an essential for plant growth and development. Similar to nitrogen, sulphur is a mobile nutrient that moves rapidly downward through the soil, especially through sandy surface layers. It is present in the environment as a part of sulphur cycle. Sulphur cycle is a combination of atmospheric and terrestrial processes. The cycle begins with the erosion of sulphate (evaporites) and sulphide containing rocks and minerals. The stored sulphur is released into the environment, which contacts air and converted into sulphate (SO_4^{2-}). This sulphate is taken up by plants and microorganisms and converted into organosulphur compounds, in turn consumed by plants and animals, affecting the food chain²¹. When plants die, some sulphur is released back into the environment as sulphate. Breaking down of vegetation in swamps and tidal flats release hydrogen sulphide (H_2S) gas into the environment, which is converted to sulphate when is in contact with aqueous streams.



Formula: SO_4^{2-}

Molar mass: 96.06 g/mol

Sources

- * Production of fertilizers, fungicides, algae control and insecticides
- * Production of glass, paper and wood pulp
- * Soap and detergent industries
- * Medicine, Hide-skin processing
- * Burning of Fossil Fuels
- * Refuse Incineration
- * Metals/Minerals Processing
- * Burning of coal and petroleum in industries and power plants release huge amounts of toxic gases such as sulphur dioxide (SO_2) and sulphur trioxide (SO_3) which react with atmospheric water and oxygen to produce sulphuric acid (H_2SO_4), leading to soil acidity and increased sulphate levels of surface waters.

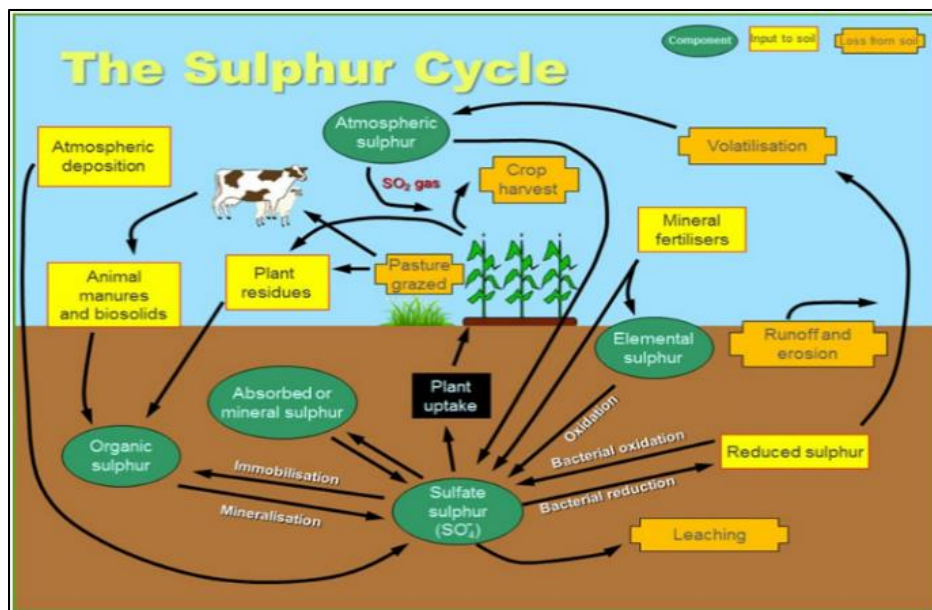


Figure 1.5 Sulphur Cycle

1.6.5 Fluoride

Fluorides is usually bound as inorganic compound but does not occur in elementary state due to its high reactivity. It is a part of natural environment, constantly connected to human life. However, concentration of fluoride can vary from one region to another. From chemical point of view, it is the most electronegative and reactive of all the elements due to its smaller atomic radius²². Fluoride content in drinking water and tooth paste are main sources of fluoride toxicity. On the one hand, fluoride is added to drinking waters in small quantities to prevent dental caries. On the other hand, fluoride is a bone seeker and is linked to hip fractures and brittle bones²². Fluoride normally enters into the human body through varied sources like water, food, drugs, cosmetics, etc.

Sources

- * Volcanic eruptions, rock dissolution
- * Numerous human activities (coal burning, ore processing, production, fertilizer usage and industrial plants)

1.6.6 Chloride

Chloride is a naturally occurring major anion found in all-natural waters. It is a conservative ion in most aqueous environments, as its movement is not retarded during the interaction of water with soils, sediments and rocks. Chloride is non-toxic to humans, but at elevated levels make water unpotable due to the salty nature²³. High chloride concentrations can act as an “advance warning” of presence of other toxic contaminants, beyond exceeding levels.

Sources

- * Human sewage
- * Livestock waste
- * Water conditioning salt
- * Synthetic fertilizer (primarily KCl)
- * Brine disposal pits associated with oil fields

- * Chemical industries/Snowy climes
- * Road salt runoff /Road dicers
- * Industrial Exposure

Table 1.4: Environmental Impacts of Anions

Anions	Health/ Environmental hazards
Phosphate	Kidney, liver, heart damage, Osteoporosis, nausea, stomach cramps and drowsiness, Eutrophication
Sulphate	Neurological effects and behavioural changes, Disturbance of blood circulation, Heart damage, Effects on eyes and eyesight, reproductive failure, damage to immune systems, liver and kidney functions stomach and gastrointestinal disorder, hearing defects, disturbance of the hormonal metabolism, dermatological effects, suffocation and lung embolism
Nitrate	Methemoglobinemia (Blue Baby Syndrome), damage to cardiovascular system, immune system, central nervous system and the peripheral nervous system. Decreased functioning of the thyroid gland (nitrate), vitamin shortages, Eutrophication of the aquatic streams.
Fluoride	Skeletal and neurological damage, tooth decay, Osteoporosis, Harmful to kidneys, bones, and muscles. Low birth-weights.
Chloride	Breathing small amounts of chlorine for short periods of time adversely affects the human respiratory system, irritates the skin, eyes and damage the respiratory system. Exposure to chlorine in air can affect the immune system, blood, heart and the respiratory system of animals.

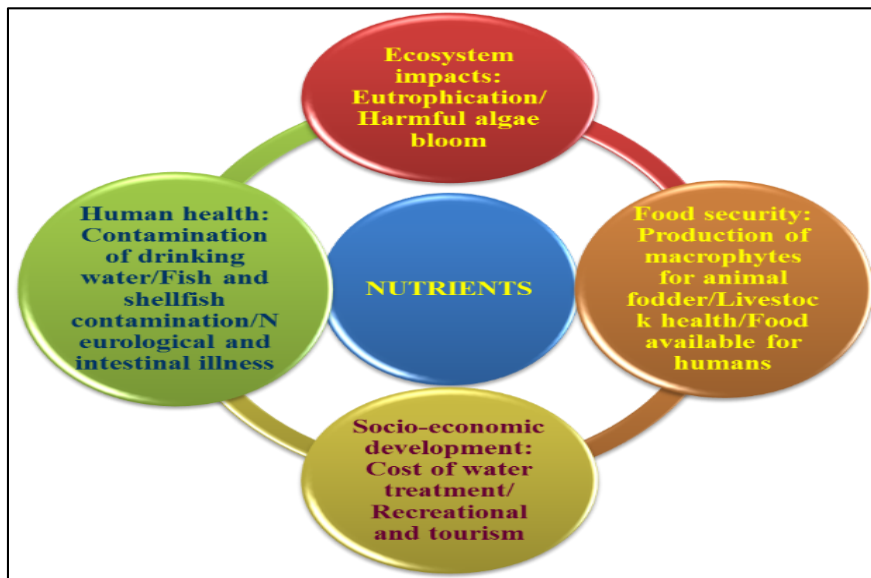


Figure 1.6 Impact of Excess Nutrients on Ecosystems

1.7 Physio-chemical Treatment Techniques

The purpose of wastewater treatment should ensure the removal of pollutants, so that the treated water meets the acceptable quality standards. This usually depends on, whether the water is to be reused or discharged into a receiving stream with lesser contamination²⁴. Finding appropriate remedial measures for the wastewater treatment is a complex task involving consideration of many factors: reliability of the process equipment, desired quality of treated water, space available for the construction of treatment facilities, waste disposal constraints and implementation. Treatment of wastewater to make it suitable for subsequent use include physical, chemical, biological and electrochemical processes.

1.7.1 Physical Treatment Process

Flotation, reverse osmosis/membrane filtration, adsorption are few common methods employed.

1.7.2 Reverse osmosis (RO)

Reverse osmosis (RO) traps anions under pressures ranging between 300 - 1,500 psi to reverse the normal osmotic water flow. The most commonly used membranes are made up of cellulose acetate, polyamides and composite materials. When the water is passed through the membrane, most of the impurities are filtered²⁵. RO is the most common method of anion removal in various sectors.

1.7.3 Flotation

Flotation is a separation process, based on the introduction of gas bubbles as the transport medium. Suspended particulate matter, either hydrophobic or conditioned, gets attached to the bubbles and approaches the surface of water solution in contrary to the direction of gravity²⁶.

Flotation is classified into various type of which DAF (Dissolved – air flotation) is the most commonly used one, for the treatment of metal-contaminated wastewater. Metal pollutants are trapped through foaming effect in the adsorptive bubble separation. The floating target substances are locked within the foaming phase kept away from the liquid phase.

1.7.4 Membrane Filtration

Membrane Filtration method is used to remove suspended solids, organic compounds and inorganic contaminants. Ultra-filtration, nano filtration and reverse osmosis are employed for anion removal, depending on the size of the retainable particle²⁷.

1.7.5 Ultra-Filtration

This method involves the separation of heavy metals, macromolecules and suspended solids from inorganic solutions on the basis of pore size (5-20 nm) and molecular weight of the separating compounds (1000-100,000 Da). Low molecular solutes and water molecules can pass through the membrane, whilst macromolecules are retained, since their pore sizes are larger than that of the membrane pore size²⁸.

1.7.6 Nano Filtration

The separation mechanism involves steric and electrical effects. A potential is created between the charged anions in the nano filtration membrane and the co-ions in the effluent to reject the latter. The membrane significance is accounted on its small pore size and nature of the membrane's surface charge²⁹.

1.7.7 Chemical Treatment Process

Chemical treatment process involves certain chemical reaction or reactions to improve the water quality. General chemical processes, cover chemical precipitation, ion-exchange, coagulation/flocculation, ozonation etc.

1.7.8 Chemical Precipitation

In this method anions, metals and dyes are precipitated from water. It is mainly employed to minimize the hard nature of potable waters loaded with calcium and magnesium ions. Addition of alkaline reagents such as limestone, lime, ferrous salts or other compounds are commonly used to increase pH level from acidic to alkaline, later anions are removed by precipitation³⁰.

1.7.9 Ion Exchange

Ion exchange reaction is the one in which free mobile ions of a solid, the ion exchanger, are exchanged for different ions of similar charge in solution. The exchanger

must have an open network structure, either organic or inorganic, which carries the ions and allows to pass through it³¹. An ion exchanger is a water-insoluble substance exchanging few ions for similarly charged ions of a medium of contact. This exchange unit operates in alike to a household water softener.

1.7.10 Coagulation-flocculation

Coagulation is the process in which colloidal particles are destabilized through addition of coagulant, resulting in sedimentation. Flocculation occurs, following coagulation, in turn, used to increase the particle size and form bulky floccules, at adjusted pH³². Color removal, reduction of suspended solids and COD using Fe³⁺/Cr³⁺, alum with lime etc., are carried out using this process.

1.7.11 Ozonation

Ozone is an extremely powerful oxidant and an efficient disinfectant. Ozone reacts with various organic and inorganic compounds in aqueous media, either by direct oxidation of molecular ozone or through secondary radical type reaction involving production of hydroxyl radical due to the ozone decomposition in water³³.

1.8 Biological Treatment Process

Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by microbial (living or dead) biomass and bioremediation systems are commonly applied for the treatment of industrial effluents³⁴. Bacteria, algae, yeast and fungi are the important biomasses most widely studied for their pollutant degrading ability.

1.9 Electrochemical Treatment Techniques

1.9.1 Electrochemical Precipitation

This technique concentrates on the applicability of potential electrical charges replacing regular chemical precipitation, favoring heavy metal removal a lot, from specific discharges³⁵.

1.9.2 Electro-Coagulation

Electrical charge is employed to a contaminated water to remove anions, suspended solids, dissolved metals, tannins and dyes. When these ions and other charged particles are

neutralized with ions of opposite electrical charges, they become destabilized and get precipitated into a stable form³⁶.

1.9.3 Photocatalysis

Photocatalysis refers to the acceleration of a photoreaction in the presence of a catalyst. Photochemical oxidation has many advantages, viz., mild reaction conditions (ambient temperature and pressure), powerful oxidizing ability, fast kinetics etc. This technology involves the destruction of a lot of organic pollutants whose structures are stable and difficult to degrade biologically³⁷.

1.9.4 Membrane Electrolysis

This is a chemical process driven by an electrolytic potential, applied to remove impurities from metal finishing wastewaters. Two types of cathodes are involved: a conventional metal cathode and a high surface area cathode. When an electrical potential is applied across an ion exchange membrane, occurrence of reduction–oxidation reaction is envisaged at the electrodes³⁸.

1.9.5 Electrodialysis

Selective transport of ions through alternately aligned anion exchange and cation-exchange membranes is the principle of electrodialysis. Transport of ions is caused by direct electric current potential applied between two electrodes³⁹. Ionic transfer membranes from a lower to more concentrated solution is foreseen by application of direct electric current. Selective removal of undesirable ions through a semi permeable membrane is possible. Merits and demerits of the aforementioned methods are tabulated in Table 1.5

Table 1.5 Treatment Methods – Merits / Demerits

Methods	Merits	Demerits
Membrane Filtration	<ul style="list-style-type: none"> ✓ Small space requirements ✓ No chemical is required ✓ Low solid waste generation 	Sludge generation incapable for largescale treatments, Expensive and high energy requirements
Ion Exchange	<ul style="list-style-type: none"> ✓ Simple equipment's ✓ Easy control and maintenance 	Maintenance cost, Regeneration time consuming and Clogging of the reactors.
Membrane Electrolysis/ Photocatalysis	<ul style="list-style-type: none"> ✓ Mild rection conditions 	<ul style="list-style-type: none"> ✓ More energy consumption ✓ Not ideal for highly concentrated wastewaters
Electrolysis	<ul style="list-style-type: none"> ✓ Varying degree of success in colour removal low solid waste, no chemicals required 	<ul style="list-style-type: none"> ✓ Not tested in full scale operations ✓ Generate undesirable by-products ✓ Limited flow rates
Coagulation/ Flocculation	<ul style="list-style-type: none"> ✓ Simple, Economically feasible, ✓ Very efficient of colloidal particles 	<ul style="list-style-type: none"> ✓ Produce high sludge ✓ High amounts of chemicals required ✓ Incomplete removal of ions
Sedimentation	Produces clean materials	Produce high sludge
Ultra-Filtration	<ul style="list-style-type: none"> ✓ No chemicals are used ✓ Inexpensive methods ✓ Simple, rapid and efficient at higher concentrations 	<ul style="list-style-type: none"> ✓ Odour of the water remains the same ✓ Soluble materials are not filtered ✓ High maintenance and operation costs
Reverse Osmosis	<ul style="list-style-type: none"> ✓ Produces high quality treated effluents ✓ No chemicals required ✓ Low solid waste 	<ul style="list-style-type: none"> ✓ Limited flow rates ✓ It is determined by specific applications like hardness reduction etc., ✓ Low throughput, limited flow rates

Methods	Merits	Demerits
Incineration	<ul style="list-style-type: none"> ✓ Simple process, highly efficient, ✓ Eliminates all the organic Compounds ✓ High production of Energy 	<ul style="list-style-type: none"> ✓ Transport and storage of effluents ✓ High running costs ✓ High initial cost of equipment
Ozonation	<ul style="list-style-type: none"> ✓ Strongest oxidizer (larger compound can be broken into Simpler) 	Release carcinogenic molecules
floatation	<ul style="list-style-type: none"> ✓ Efficient for removal of small particles and can remove low density particles which would require long settling period ✓ low retention time 	<ul style="list-style-type: none"> ✓ Energy cost ✓ High initial capital cost ✓ Maintenance and operation cost no negligible
Biological methods	<ul style="list-style-type: none"> ✓ Application of microorganisms for the biodegradation of organic contaminants are simple and economically feasible ✓ large number of species are used in mixing culture 	<ul style="list-style-type: none"> ✓ Necessary to create an optimally favourable environment ✓ Requires management and maintenance of the microorganisms ✓ Slow process ✓ Necessity to had a good knowledge of the enzymatic process governing the decomposition of the substance.

1.10 Adsorption

Adsorption finds to be an inevitable alternate in trapping toxic environmental pollutants. Adsorbent is a porous material with high surface area possessing the ability to sequester substances by the way of intermolecular forces onto its surface. Material being adsorbed or attached, is termed as adsorbate. Uptake of gases by charcoal and clay were the first set of experiments reported using the process. Interaction of H^+ and anions between the solid and the surrounding aqueous solution is the main focus. Diffusion controlled

adsorption mechanism is presented in figure 1.3. Three basic steps involved in the performance of porous adsorbents are ⁴⁰,

- * Transport of adsorbate molecules from the whole lot to the exterior of the sorbent surface (External diffusion)
- * Migration of these externally sorbed species into sorbent pores (Gradual adsorption stage)
- * Interaction of the adsorbate moieties with the available interior sorption sites, with functional group binding onto capillary sorbent spaces (Intra particle diffusion)

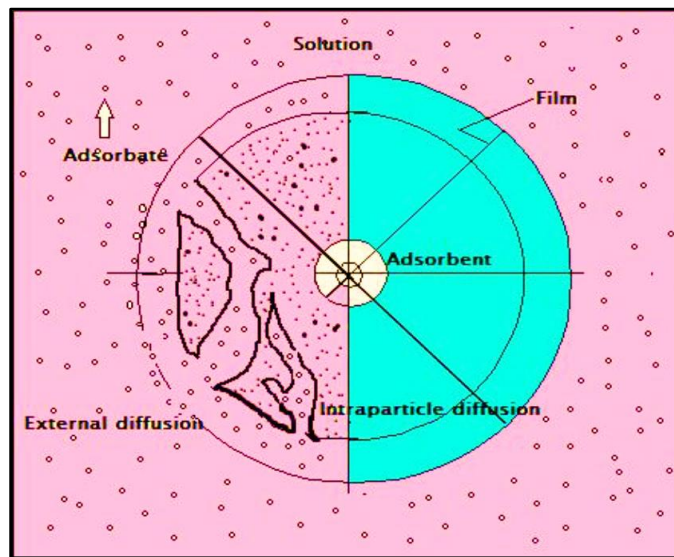


Figure 1.7 Adsorption Mechanism

Adsorption is widely used for various industrial applications / water purification. Adsorption kinetics is defined as the speed at which sorbate species are shifted from the aqueous phase to solid matrix. Preference of adsorption technique over other conventional treatment methods shall be due to the following reasons:

- * Economical & efficient method for toxicants' removal
- * Minimization of chemical and biological sludge, low cost, high efficiency, schematic regeneration of exhausted materials with possibility of ions recovery
- * Selective chelation of toxicants even at lower concentrations
- * Prevention of secondary pollution

- * Wider pH ranges (2-9) for the systems' operation
- * Lower sensitivity to diurnal variation
- * Minimal capital investment/operational cost
- * Greater flexibility in the design, operation and superior removal of organic contaminants
- * Effluent discharge concentrations meet the government regulation (CPCB).

1.10.1 Types of Adsorption

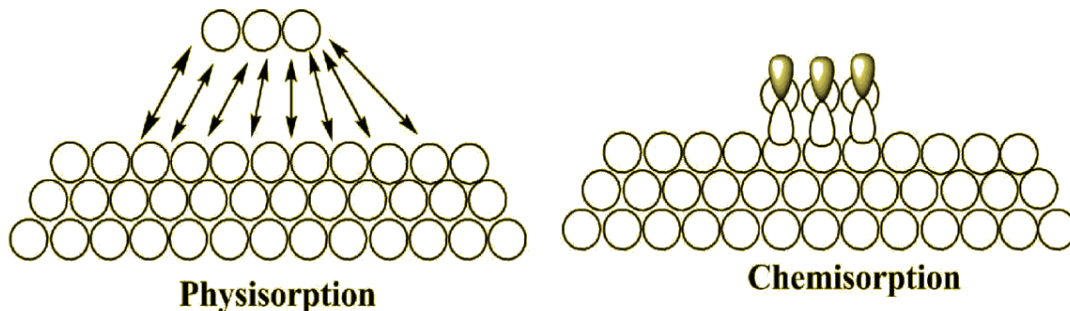
The prime types of adsorption process can be classified as, physical adsorption (physisorption) and chemical sorption (chemisorption)

1.10.2 Physical adsorption

Intermolecular forces of attraction play an inevitable role between solid molecules, sorbent and the substance being adsorbed in physical adsorption. It is a readily reversible phenomenon, which comes in handy for industrial operations, wherein it supports the recovery of adsorbent/ adsorbed substance⁴¹. This type of adsorption is characterized by comparatively low heats of adsorption viz., 20-40 kcal/ mol.

1.10.3 Chemisorption

Chemical interaction between the solid adsorbent matrix and the adsorbed substance substitutes chemisorption. The adhesive force, exothermic nature and irreversible property⁴² are the key observables in this process.



1.10.4 Adsorbents

Materials containing many miniscule internal pores can be grouped as adsorbents. Activated carbon is the universal adsorbent suggested for the removal of diversified toxicants. It is manufactured by roasting and decomposing organic material obtained from different sources into carbon granules their surface areas varying between 300 - 500 m²/g.

Materials with sorption characteristics may be summarized based on their availability and nature.

- * Naturally occurring materials (wood, peat, coal, lignite etc.) industrial/agricultural/domestic wastes or byproducts (slag, sludge, fly ash, red mud etc), synthesized products, organic/inorganic material
- * Bio based naturally / occurring materials viz., chitin/chitosan, zeolite, bentonite, coconut coir pith, rice bran, wheat bran, rice husk, saw dust, sugarcane bagasse, walnut shell, almond shell, corn cob powder have been reported^{43,44}, by and large as effective sequestrants
- * Although, different low-cost adsorbents from a variety of sources have been explored due to enormous surface areas per unit weight, in recent times, the search for low cost/ no cost adsorbents that have anion binding capacities have intensified.

1.11 Review of Literature

Agro Derived Materials

Jibing Xiong et al.,⁴⁵ reported about the sequestering ability of freshwater mussel shells for trapping phosphate ions, where the surface modified mussel shell powder exhibited effective interaction with sorbate than natural mussel shell powder and the spent sorbents were utilized as fertilizers for acidic soils.

Shaik Basha et al.,⁴⁶ investigated phosphate ion removal from aqueous solutions employing red seaweed *Kappaphycus alvarezii* and reported that maximum sorption on red seaweed to be 82.28%. The sorption system was described to follow pseudo second order model, involving both chemisorption and physisorption.

Moussa Amrani et al.,⁴⁷ studied phosphate sorption onto chemically modified Aleppo pine sawdust, where phosphate binding was rapid indicative of probable sorption on cell walls of sawdust.

Deepak Yadav et al.,⁴⁸ adopted Batch process employing rice husk and fruit juice residues to trap phosphate ions from aqueous solutions. The findings reveal diffusion or external mass transfer or both are responsible for the sorption process. Phosphate loaded material was used for biogas generation in an eco-friendly manner.

Efficacy of seagrass *Cymodocea rotundata* beads on the removal of excessive nutrients in shrimp aquaculture wastewater was experimented by **P.Santhanam et al.,**⁴⁹ where beads density was observed to be responsible for effective trapping. Exhausted seagrass was used as feedstock for production of biofertilizers and biofuel aiming zero waste management.

Sorption efficiency of lemon peel for phosphate removal from simulate wastewater was studied by **Lahieb Faisal Muhaisen,**⁵⁰ with maximum chelation occurring at pH 5.5 and higher temperatures.

Employment of *Ficus carica*, *Moringa oleifera* and Sawdust for phosphate removal from wastewaters were assessed by **E.Subha et al.,**⁵¹ Batch results revealed that among the tested materials *Ficus carica* exhibited 77 % anion removal efficiency.

Impact of sulphuric acid activated coir pith on phosphorous uptake from aqueous matrix was observed to be pH dependent by **Kumar et al.,**⁵²

Eberhardt and Min⁵³ experimented the influence of Aspen wood on phosphate adsorption. Results suggested larger wood particles demonstrated better phosphate adsorption owing to the possession of higher number of carboxylates to complex ions.

Biswas et al.,⁵⁴ explored that foreign anions such as sulphates, chlorides and carbonates seldom registered any substantial influence on phosphate adsorption by La (III) loaded orange waste.

M. Chitan et al.,⁵⁵ reported the efficiency of chitin in the uptake of nitrate ions from aqueous solutions, as pH independent and temperature dependent, recording the system to be endothermic in nature.

Findings of **Wasse Bekele et al.**,⁵⁶ nitrate removal from aqueous solution by modified Ethiopian bentonite clay revealed 80% of the former and the system was favoured Langmuir isotherm model.

Anni Keranen et al.,⁵⁷ analysed the effect of temperature and coexisting anions on Nitrate - employing modified pine saw dust system, where nitrate removal recorded a moderate at higher temperatures. Also, SO_4^{2-} and PO_4^{3-} ions played a significant role, in minimizing nitrate chelation by the saw dust.

Efficacy of banana peel as nitrate sequestrant was explored by **Ch. Adisheshu reddy et al.**,⁵⁸ A minimum of 0.05g peel recorded 80 % nitrate removal at an agitation period of 0.5 hours.

R C Jagessar et al.,⁵⁹ studied the concentration of nitrate ions present in the wastewaters collected from nine selected areas of coastal Guyana. Analysis was performed in UV-vis spectrophotometer using phenol disulphonic acid reagent and many of the samples recorded nitrate concentrations within the permissible level.

Nitrate removal from aqueous solution using ZnCl_2 and phosphoric acid activated carbon derived from pomogranate peel was examined by **Moussa Amrani et al.**,⁶⁰ who reported that the adsorption process was pH dependent of (7.5 – 9.5) and followed monolayer sorption with adsorption capacity being 78.125 mg/g.

Hassan A Hanafi⁶¹ employed activated carbon derived from rice straw for the removal of nitrate and nitrite anions from wastewater. The nitrate sorption by the carbon was due to the competitive effect extended by nitrite ions.

Mohammad Hassan Shahmaradi et al.,⁶² compared the nitrate sorption efficiencies of activated carbons obtained from pyrolysis of rice husk and primary sludge of paper industry wastewater. The adsorption affinity was found to be 93.5mg/g for rice husk and 79.5mg/g for the sludge.

N Osturk et al.,⁶³ tested the impact of HCl activated sepiolite, slag and activated carbon as adsorbents for NO_3^- removal. It was observed that activated sepiolite exhibited better sorption capacity of (38.16mg/g) against the other two sorbents studied.

Hakan P emiral et al.,⁶⁴ recorded the observations for trapping nitrate ions using activated carbon generated from sugar beat baggase as the latter possessed significant pore volume ($0.966\text{m}^3/\text{g}$) and notable BET surface area ($1826\text{ m}^2/\text{g}$).

FTIR spectrum of NO_3^- - acid treated sunflower seed husk reported by **M.Moyo et al.,**⁶⁵ aided the interaction of nitrate ions with the hydroxyl, carbonyl, amino carboxyl groups present in the sorbent.

Cengelogu et al.,⁶⁶ examined the removal of nitrate ions from aqueous solution using original and activated red mud (HCl treated) and reported that the activated red mud shows better sorption ability to that of original red mud. This statement is supported by the chemical nature of modified red mud and the subsequent interaction between metal oxide surface and NO_3^- ions.

Kanchan et al.,⁶⁷ proposed a simple method for the determination of nitrite ion concentration in water samples. The method involves diazotization of nitrite with metoclopramide in acid medium followed by coupling with ethyl acetoacetate (EAA) in basic medium to form an azo dye. The absorbance reading of this dye exposed the concentration of nitrite ion in water samples. Different variables affecting the reactions are optimized and the results obtained by the proposed method agree well with the standard established method.

Chinnaiya Namasivayam et al.,⁶⁸ examined the applicability of surfactant modified coir pith for the removal of sulphate ions from aqueous solutions. Results revealed that the reaction was pH driven suggesting the feasible that recovery of sulphate from the spent sorbent. Also, quantitative removal of sulphate ion from fertilizer industry wastewater was achieved.

Agriculture residue rice straw chemically converted into a strong basic anion exchanger had been utilized for trapping sulphate ions from aqueous solution by **Wei cao et al.,**⁶⁹ The prepared material registered notable regeneration of exhausted cycles and was find to exhibit high selectivity for sulphate ions.

Alena Kuptakova et al.,⁷⁰ established that synthetic sorbent slovakite as a good alternate for the uptake of sulphates from acid Mine Drainage (AMD). They tested the

ability of slovakite as an anaerobic bacterial sulphate reduction using Sulphate Reducing Bacteria (SRB) *genera Desulfovibria* achieved 84% removal efficiency.

Bagasse pith cellulose-based adsorbents were used to treat Cu^{2+} and SO_4^{2-} enriched aqueous solution by **Xin Gao et al.**,⁷¹ Sorption capacities were highly influenced by pH and the maximum uptake of both the ions had occurred at pH 5. The reaction mechanism was speculated to follow ion exchange, complexation and electrostatic interactions between the bio sorbents and sorbate ions.

A. Naga babu et al.,⁷² identified the potentiality of red mud as effective lead ions sequestrant after treating with hydrazine sulphate and further doping with calcium alginate beads. Isothermal studies reveal that the system exhibited linearity for Langmuir plot. Regeneration of the spent material using 0.1M HCl registered least changes in sorption nature. Further, the immobilization of activated red mud in the beads facilitated, easy filtration. Chelating capacity of the material was found to be 138.6 mg/g.

Yosep Han et al.,⁷³ studied the removal of SO_2 , fine particulates and heavy metals present in the plant sewage sludge, utilizing Ca-based bead sorbents. Sorption characteristics is favoured 3 – D network pore structure, high surface area and gas permeability of the bead. Experimental results confirmed that SO_2 gas, fine particulates and heavy metals had been simultaneously removed with increasing efficiency over the time of operation.

Phosphate removal from synthetic water employing Fe cross – linked alginate beads was achieved by **Mohammad E. Hossain et al.**,⁷⁴ The maximum sorption capability of the beads was found to be 79 mg/g. Freundlich isotherm correlates well with experimental data supporting multilayer adsorption of the system.

Akeem Adeyemi Oladipo et al.,⁷⁵ fabricated magnetic biocomposite of palm seed-based biochar in the presence of Fe_3O_4 particles through co-precipitation method for the removal of nickel from aqueous solution. The results revealed an intermediate micro-mesoporous character and high saturation magnetization value of the nickel laden sorbent enabling it to be easily separated from experiment run solution using a bar magnet.

Sankaran Meenakshi et al.,⁷⁶ studied the removal efficiency of phosphate and nitrate ions using Zr^{4+} ions embedded chitosan soya bean husk activated bio – char composite beads (Zr-CS-SAC). The adsorption equilibrium models of Langmuir, Freundlich and DKR isotherms were studied and the results described that the Freundlich model was the best for the studied anions with respective sorption capacities of 90.09 and 131.29mg/g. The authors had reported that Zr-CS-SAC composite beads possessed good anion removal efficiency.

Chitosan biosorbent modified with Zirconium ion beads (ZCB) was prepared and employed for the chelation of phosphate ions from aqueous solutions by **Lingfan Zhang et al.,**⁷⁷ The results revealed that the adsorption mechanism was possibly attributed to the electrostatic and ion exchange reaction between ZCB and phosphate ions.

Mohan et al.,⁷⁸ investigated the adsorption nature towards phosphate from water using zirconium treated fine red mud impregnated in Zn- alginate beads (ZRMAB). The extraction conditions were optimized for the maximum trapping of phosphate by the beads whose sorption ability is reported as 13.64 mg/g. The developed procedure was extended to the phosphate removal from polluted ground water samples.

Hanna siwek et al.,⁷⁹ produced alginate/goethite hydrogel composite beads by crosslinking sodium alginate and $CaCl_2$ suspensions and investigated the beads for phosphate uptake from aqueous solutions and field samples. Experimental results for the goethite gelation exhibited almost complete swelling while using deionized water and 50% swelling in contaminated water against least swelling in raw goethite granules. The test results concluded that the proposed sorbent had potential for the removal of phosphate from contaminated water.

Y. Fan et al.,⁸⁰ synthesized goethite anchoring regenerated graphene oxide (α -FeOOH@rGO) nanocomposite for the chelation of fluoride ion from the drinking water. From the experimental studies, it is evident that α -FeOOH@rGO possessed good difluorination ability in a wide pH ranges and pose a strong anti-interference ability in the presence of high concentrated foreign anions.

Dae Sung Lee et al.,⁸¹ studied the phosphate removal from aqueous solution using chitosan/Ca organically modified montmorillonite (chitosan/Ca-OMMT) beads through

batch and fixed – bed column systems. Thomas, Yoon-Nelson and Adams-Bohart models were applied to the experimental data to predict the breakthrough curves using nonlinear regression. Yoon-Nelson model recorded best agreement with the breakthrough curves. These findings demonstrated that chitosan/CaOMMT beads can be used as a cost effective and eco-friendly material.

Column validation of acid blue 113 an anionic dye was examined by **S. Tamilselvi et al.**,⁸² The results when applied to varied models, Yoon-Nelson model provided excellent fit with notable R^2 values for all the range of dye concentrations, flow rate and bed height.

The continuous fixed bed column performances of arsenate and arsenite with organic modified spent grains (OSGs) were evaluated by **Chen Yunnen et al.**,⁸³ at varying flow rates and initial concentrations of the sorbate ions. The column reports confirmed that the rate constant for the Yoon Nelson model reduced at higher with increase in both initial influent arsenic ions concentration and flow rate.

S.P. Shukla et al.,⁸⁴ fabricated column bed device packed with Plaster of Paris (POP) pellets for the removal of polycyclic aromatic hydrocarbon (pyrene). Data derived from column studies were fitted to three well established models; Thomas, Adams-Bohart and Yoon Nelson, in support of the pellets' efficiency in pyrene chelation.

1.12 References

- [1] Mohammad Zakir Hossain, Water: The Most Precious Resource of our Life, *Global Journal of Advanced Research*, 2(9) (2015) 1436 – 1445
- [2] Dursun Yıldız, The Importance of Water in Development, *World Water Diplomacy & Science News*, (2017)
- [3] Martin F. Chaplin, Water: its Importance to life, *Biochemistry and Molecular Biology Education*, 29 (2001) 54-59
- [4] Mehtab Haseena, Muhammad Faheem Malik, Asma Javed, Sidra Arshad, Nayab Asif, Sharon Zulfiqar and Jaweria Hani, Water pollution and human health, *Environmental Risk Assessment Remediation*, 1(3) (2017) 16-19
- [5] Sivaranjani S, Amitava Rakshit and Samrath Singh, Water Quality Assessment with Water Quality Indices, *International Journal of Bioresource Science*, 2 (2) (2015) 85 – 93
- [6] Khalid S. Hashima,b, Rafid Al Khaddara , Nisreen Jasimb , Andy Shawa , David Phippsa , P. Kota , Montserrat Ortoneda Pedrolaa , Ali W. Alattabia,c , Muhammad Abdulredhaa,d , Reham Alawsh, Electrocoagulation as a green technology for phosphate removal from river water, *Separation and Purification Technology*, 210 (2019) 135 -144.
- [7] Jain & Jain, Dhanpat Rai, Engineering chemistry, *Publishing company (P) Ltd.*
- [8] Indian Standard Drinking, *Water- Specification* (BIS 10500:1991)
- [9] Pollution Control Acts, Central Pollution Control Board, Ministry of Environment and Forests, New Delhi, India (1998)
- [10] Registry of toxic effects of chemical Substances. National toxicology information Program, National Library of Medicine, Bethesda, MD (1993)
- [11] Kanamadi R.D.Ahalya, N.Ramachandra, Biosorption of Heavy metals by Low cost adsorbents. *Technical Report*: 112 (2006)
- [12] Scientific facts on water; State of the Resource, Green facts website (2008)

- [13] The cost of meeting the Johannesburg targets for Drinking Water, Water Academy Organization (2004)
- [14] Aboyeji, Oyebanji Oluseun, Freshwater Pollution in Some Nigerian Local Communities, Causes, Consequences and Probable Solutions, *Academic Journal of Interdisciplinary Studies*, 2(13) (2013)
- [15] Al-Shammiri, M, Al-Saffar. A, Bohamad. S and Ahmed. M, Waste Water Quality and Reuse in Irrigation in Kuwait using Microfiltration Technology in Treatment, *Desalination and Water Treatment*, 185 (3) (2005) 213-225
- [16] N.Muthulakshmi Andal, Studies on the adsorption of Iron(III), Copper(II), Zinc(II) and Chromium(VI) using naturally occurring polymers, Ph.D., thesis, Gandhigram Rural Institute-Deemed University, Tamil Nadu, India (2003)
- [17] O.D.Tyagi, M.Mehra, A Text Book of Environmental Chemistry, 1stEdition, 3rd Reprint, Anmol Publications Private Ltd, New Delhi, India (2000)
- [18] A. Bhatnagar and M Sillanpaa., Utilization of Agro-Industrial and Municipal Waste Materials as Potential Adsorbents for Water Treatment A review, *Chemical Engineering Journal*, 157 (2-3) (2010) 277-296
- [19] M. Sarioglu, S. Akkoyun and T. Bisgin, Inhibition Effects of Heavy Metals (Copper, Nickel, Zinc, Lead) on Anaerobic Sludge, *Desalination and Water Treatment*, 23 (1-3) (2010) 55-60
- [20] Y. Fu and T. Viraraghavan, Fungal Decolorization of Dye Wastewaters: A Review, *Bioresource Technology*, 79 (3) (2001) 251-262
- [21] T. Kikuchi and S. Tanaka, Biological Removal and Recovery of Toxic Heavy Metals in Water Environment, *Critical Reviews in Environmental Science and Technology*, 42 (10) (2012) 1007- 1057.
- [22] V. J. Inglezakis, A. A. Zorpas, M. D. Loizidou and H. P. Grigoropoulou, The Effect of Competitive Cations and Anions on Ion Exchange of Heavy Metals, *Separation and Purification Technology*, 46 (3) (2005) 202 – 207

- [23] C. Escobar, C. Soto-Salazar and M. Inés Toral, Optimization of the Electrocoagulation Process for the Removal of Copper, Lead and Cadmium in Natural Waters and Simulated Wastewater, *Journal of Environmental Management*, 81 (4) (2006) 384 - 391
- [24] A. Groffman, S. Peterson and D. Brookins, Removing Lead from Wastewater using Zeolite, *Water Environmental Technology*, 4 (1992) 54-59
- [25] Sultan Ahmed, Shiraz Chughtai, Mark A.Keane, The Removal of Cadmium and Lead from Aqueous Solution by Ion Exchange with NaY Zeolite, *Separation and Purification Technology*, 13 (1) (1998) 57-64
- [26] V. J. Inglezakis, A. A. Zorpas, M. D. Loizidou and H. P. Grigoropoulou, The Effect of Competitive Cations and Anions on Ion Exchange of Heavy Metals, *Separation and Purification Technology*, 46 (3) (2005) 202 – 207
- [27] L. Charerntanyarak, Heavy metals removal by chemical coagulation and precipitation, *Water Science Technology*, 39 (1999) 135-138
- [28] A. Papadopoulos, D. Fatta, K. Parperis, A. Mentzis, K.J. Harambous, M. Loizidou, Nickel uptake from a Wastewater stream produced in a Metal finishing Industry by Combination of Ion-exchange and Precipitation Methods, *Separation and Purification Technology*, 39 (2004) 181-188
- [29] S. D. Faust and O. M. Aly, Chemistry of Water Treatment, 2nd Edition, Ann Arbor Press, New York, (1998)
- [30] R. F. Saad, Selected Heavy Metal and Organic Removal from Wastewater by Precipitation and Ozonation Process, Master of Applied Science thesis, University of Ottawa, Canada (1998)
- [31] R.Y. Ning, Arsenic removal by reverse osmosis, *Desalination*, 143 (2002) 237-241
- [32] S.Babel, T. A.Kurniawan, Low cost adsorbents for heavy metals uptake from contaminated water, A review. *Journal of Hazardous Material*, 97 (2003) 219 –243

- [33] S.S. Sablani, M.F.A. Goosen, R. Al-Belushi, M. Wilf, Concentration polarization in ultrafiltration and reverse osmosis: A critical review, *Desalination*, 141 (2001) 269-289
- [34] K.H. Ahn, K.G. Song, H.Y. Cha, I.T. Yeom, Removal of ions in nickel electroplating rinse water using low-pressure nanofiltration, *Desalination*, 122 (1999) 77-84
- [35] G. McKay, M. S. Otterburn and A. G. Sweeney, The Removal of Colour from Effluent using various Adsorbents III. Silica: Rate processes, *Water Research*, 14 (1) (1980) 15-20
- [36] G. Raj, Surface Chemistry, Krishna Prakashan, (2002)
- [37] J. Toth, Adsorption, Taylor and Francis, CRC Press, (2002)
- [38] F. L. Slejko, Adsorption Technology: A Step-By-Step Approach to Process Evaluation and Applications, Marcel Dekker Incorporated (1985)
- [39] Noll, K. E., Gounaris, V. & Hon, W. S, Adsorption Technology for Air and Water Pollution Control, Lewis, Chelsea, U.S.A. (1992) 3-6
- [40] Oscik J, Adsorption, John Willey and Sons, New York (1982)
- [41] J. Weber, Walter & M. McGinley, Paul & Katz, Lynn, Sorption phenomena in subsurface systems: Concepts, models and effects on contaminant fate and transport. *Water Research*, 25 (1991) 499-528
- [42] Bhatnagar A, Jain AK., A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water, *Journal of Colloid and Interface Science*, 281(1) (2005) 49-55
- [43] A. K. Jain, V. K. Gupta, A. Bhatnagar & Suhas, A Comparative Study of Adsorbents Prepared from Industrial Wastes for Removal of Dyes, *Separation Science and Technology*, 38(2) (2007) 463-481
- [44] Jibing Xiong, Yong Qin, Ejazul Islam, Min Yue, Wenfeng Wang, Phosphate removal from solution using powdered freshwater mussel shells, *Desalination*, 276 (2011) 317 – 321

- [45] Manali Rathod, Kalpana Mody, Shaik Basha, Efficient removal of phosphate from aqueous solutions by red seaweed, *Kappaphycus alvarezii*, *Journal of Cleaner Production*, XXX (2014) 1-10
- [46] Salah Benyoucef, Moussa Amrani, Adsorption of Phosphate ions onto low-cost Aleppo pine adsorbent, *Desalination*, 275 (2011) 231 – 236
- [47] Deepak Yadav, Meghna Kapur, Pradeep Kumar, Monoj Kumar Mondal, Adsorptive removal of phosphate from aqueous solution using rice husk and fruit juice residue, *Process Safety and Environmental Protection*, 482 (2014) 1-8
- [48] G. N. Soumyaa, N. Manickavasagama, P. Santhanamb and S. Dinesh Kumarb, Efficacy of Seagrass *Cymodocea Rotundata* Beads on the Removal of Excessive Nutrients in Shrimp Aquaculture Wastewater, *Biological Methods of water Treatment*, 39, (2017) 250 – 255
- [49] Lahieb Faisal Muhaisen, Lemon Peel as Natural Biosorbent to Remove Phosphate from Simulated Wastewater, *Journal of Engineering and Development*, 20 (2016) 163 – 173
- [50] E. Subha, S.Sasikala, G.Muthuraman, Removal of Phosphate from wastewater using natural adsorbents, *International Journal of ChemTech Research*, 7(7), (2015) 3095 - 3099
- [51] Pradeep Kumar, S. Sudha, Shri Chand & Vimal Chandra Srivastava, Coir pith Phosphate Removal from Aqueous Solution Using Coir-Pith Activated Carbon, *Separation science and Technology*, 45(10), (2010), 1463 - 1470
- [52] Dan Chen, Xuelian Xiao, Kai Yang, Egg shell Removal of phosphate and hexavalent chromium from aqueous solutions by engineered waste eggshell, *Royal Society of Chemistry Advances*, 6 (2016), 35332-35339
- [53] Thomas L.Eberhardt, Soo-HongMin, James S.Han., Aspen wood Phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride, *Bioresource Technology*, 97(18), (2006) 2371 - 2376

- [54] Biplob Kumar Biswas, Katsutoshi Inoue, Kedar Nath Ghimire, Shingo Ohta, Hiroyuki Harada, Keisuke Ohto, Hidetaka Kawakita, The Adsorption of Phosphate from an Aquatic Environment Using Metal-Loaded Orange Waste, *Journal of Colloid and Interface Science*, 312(2):2, (2007) 14 - 23
- [55] M. Morghi, F. Abidar, A. Soudani, M. Zerbet, M. Chiban, H. Kabli and F. Sinan, Removal of nitrate ions from aqueous solution using chitin as natural adsorbent, *International Journal of Research in Environmental Studies*, 2 (2015) 8 – 20
- [56] Wasse Bekele, Gezahegn Faye and Nestor Fernandez, Removal of Nitrate ion from Aqueous Solution by Modified Ethiopian Bentonite Clay, *International Journal of Research in Pharmacy and Chemistry*, 4 (2014) 192 – 201
- [57] Anni Keranen, Tiina Leiviska, Osmo Hormi, Juha Tanskanen, Removal of Nitrate by Modified Pine Sawdust: Effects of Temperature and Co-existing anions, *Journal of Environmental Management*, 147 (2015) 46 -54
- [58] Ch. Adishesu Reddy, N. Prashanthi, P. Hari Babu, Jyoti S Mahale, Banana Peel as a Biosorbent in Removal of Nitrate from Water, *International Advanced Research Journal in Science, Engineering and Technology*, 210 (2015) 94 – 98
- [59] R.C.Jagessar &L.Sooknundun, Determination of nitrate anion in waste water from nine selected areas of coastal Guyana via a spectrophotometric method, *IJRRAS* 7 (2), (2011) 203-212
- [60] Ammar Touil & Moussa Amrani, Removal of Nitrate (NO_3^-) from Aqueous Solution using Adsorbent from Agricultural Residues: Equilibrium and Kinetic Studies, *Environment SIHE Ouargla*, (2013) 593 – 600
- [61] Hassan A Hanafi and sami M Abdel Azeema, Removal of Nitrate and Nitrite Anions from Wastewater using Activated Carbon Derived from Rice Straw, *Journal of Environmental and Analytical Toxicology*, 6 (2016) 1 - 6
- [62] Mohammad Hassan Shahmoradi, Behnoush Amin Zade, Ali Torabian and Mahdi Seyed Salehi, Removal of Nitrate from Ground Water using Activated Carbon prepared from Rice Husk and Sludge of Paper Industry Wastewater Treatment, *ARPN Journal of Engineering and Applied Sciences* 10 (17) (2015)

- [63] Öztürk, N., Bektas., T.E., Nitrate removal from aqueous solution by adsorption onto various materials. *J. Hazard. Mater.* B112, (2004) 155-162
- [64] Demiral, Gul Gunduzoglu, Removal of Nitrate from Aqueous Solutions by Activated Carbon prepared from Sugar Beet Bagasse Hakan, *Bioresource Technology*, 101 (2010) 1675 – 1680
- [65] M. Moyo, A. Maringe, F. Chigondo, B. C. Nyamunda E. Sebata, M. Shumba, Adsorptive Removal of Nitrate Ions from Aqueous Solutions Using Acid Treated Sunflower Seed Husk (*Helianthus annuus*), *International Journal of Advances in Science and Technology*, 5(6) (2012) 47 – 66
- [66] Cengeloglu, Y., Tor, A., Ersoz, M., Arslan, G., Removal of nitrate from aqueous solution by using red mud. *Sep. Purif. Technol.* 51, 374-378 (2006)
- [67] Kanchen Nemedede, Sanyay Atterde, Development And Validation Of UV Spectrophotometric Method for Simultaneous Estimation of Nitrate and Nitrite In Water, Soil, Drug and Vegetable Samples, *International Journal of Advanced Chemistry*, 2, (2) (2014) 74-79.
- [68] Chinnaiya Namasivayam, Molagoundampalayam and V. Sureshkumar, Removal of Sulfate from Water and Wastewater by Surfactant Modified Coir Pith, an Agricultural Solid Waste by Adsorption Methodology, *Journal of Environmental Engineering Management*, 17 (2007) 129 -135
- [69] Wei Caoa, Zhi Danga, Xing-Qiu Zhoua, Xiao-Yun Yi, Ping-Xiao Wu, Neng-Wu Zhu, Gui-Ning Lu, Removal of sulphate from aqueous solution using modified rice straw: Preparation, characterization and adsorption performance, *Carbohydrate Polymers*, 85 (2011) 571 – 577
- [70] Alena Luptáková, Eva Mačingová, Ingrida Kotuličová, Dominika Rudzanová, Sulphates Removal from Acid Mine Drainage, IOP Conference Series: *Earth and Environmental Science* 44 (2016) 1 – 6
- [71] Xin Gao, Heng Zhang , Keli Chen, Jiali Zhou , Qixing Liu, Removal of heavy metal and sulfate ions by cellulose derivative-based biosorbents, *Cellulose* 25 (2018):2531–2545

- [72] G.V. Krishna Mohan, A. Naga Babu, K. Kalpana and K. Ravindhranath, Zirconium-Treated Fine Red Mud Impregnated in Zn-Alginate Beads as Adsorbent in Removal of Phosphate from Water, *Asian Journal of Chemistry*, 29 (2017) 2549 – 2558.
- [73] Yosep Han, Gukhwa Hwang, Donghyun Kim, Soyeon Park, Hyunjung Kim, Porous Ca-based bead sorbents for simultaneous removal of SO₂, fine particulate matters, and heavy metals from pilot plant sewage sludge incineration, *Journal of Hazardous Materials*, 283, (2015) , 44 - 52
- [74] Mohammad E. Hossain, Cody L. Ritt, S.M.ASCE, Talal B. Almeelbi; and Achintya N. Bezbaruah, A.M.ASCE,., Biopolymer Beads for Aqueous Phosphate Removal: Possible Applications in Eutrophic Lakes, *Journal of Environmental Engineering*, 144(5), (2018) 1 - 11
- [75] Mustafa Gazi, Akeem Adeyemi Oladipo & Kola A. Azalok, Highly efficient and magnetically separable palm seed-based biochar for the removal of nickel, *Separation Science and Technology*, (2016) 1 -28
- [76] H. Thagira Banu, P. Karthikeyan, and Sankaran Meenakshi, Zr⁴⁺ ions embedded Chitosan-Soya bean husk Activated Bio-char Composite Beads for the Recovery of Nitrate and Phosphate Ions from Aqueous Solution, *International Journal of Biological Macromolecules*, (2019) 1 -44
- [77] Lingfan Zhang, Removal of phosphate anions using the modified chitosan beads: Adsorption kinetic, isotherm and mechanism studies, *Powder Technology*, (2015), 1- 9
- [78] Mohan et al., Zirconium-Treated Fine Red Mud Impregnated in Zn-Alginate Beads as Adsorbent in Removal of Phosphate from Water, *Asian Journal of Chemistry*, 29(11) (2017) 2549-2558
- [79] Hanna Siwek, Artur Bartkowiak and Małgorzata Włodarczyk, Adsorption of Phosphates from Aqueous Solutions on Alginate/Goethite Hydrogel Composite, *Water* 11 (2019) 1 – 13
- [80] Yunfang Fan, Dandan Fu, Siqi Zhou, Yiqing Lu, Xiaoxi Zhao, Wei Jin & Yaping Zhao, Facile synthesis of goethite anchored regenerated graphene oxide nanocomposite and its application in the removal of fluoride from drinking water, *Desalination and Water Treatment*, (2016) 1–12

- [81] Jiseon Jang and Dae Sung Lee, Effective Phosphorus Removal Using Chitosan/Ca Organically Modified Montmorillonite Beads in Batch and Fixed-bed Column Studies, *Journal of Hazardous Materials*, (2019) 1 - 40
- [82] S. Tamilselvi and M. Asaithambi, Column Mode Adsorption Studies of Acid Dye using a Novel Adsorbent, *Rasayan Journal of Chemistry*, 8 (1) (2015) 84-91
- [83] Chen Yunnen, Wu Ye, Liu Chen, Guo Lin, Nie Jinxia, Ren Rushan, Continuous fixed-bed column study and Adsorption Modelling: Removal of Arsenate and Arsenite in Aqueous Solution by Organic Modified Spent Grains, *Pollution Journal of Environmental Studies*, 26 (4) (2017), 1847-1854
- [84] Anusha D.L. Wickramasinghe, S.P. Shukla, A.K. Balange, K. Pani Prasad and Sanath Kumar, A Novel Fixed Column Bed Device for Removal of Polycyclic Aromatic Hydrocarbon (Pyrene) from Water: Performance Evaluation and Thermodynamic Modelling, *International Journal of Current Microbiology and Applied Sciences*, 7(3) (2018) 94 -111.