CHAPTER 1

The world demand for water is accelerating, as the standard of living is advanced, and as the world population is increasing. The growing needs of water for irrigation and industrial output require preservation of quality through waste treatment and recycling.

A cleaner technology is a source of reduction or recycles method applied to eliminate or significantly reduce the amount of any hazardous substance, or contaminant released to the environment. Pollution prevention occurs through source reduction, i.e., reductions in the amount of wastes generated, and source control (input material changes, technology changes, or improved operating practices).

Cleaner technologies include process changes that reduce the toxicity or environment impact of wastes or emissions. Processes that reduce waste toxicity by transferring pollutants from one environmental medium to another (e.g., from wastewater to sludge or from air emissions to scrubber wastes) are not inherently cleaner considered to be source reduction.

They include also the recycle methods, but recycling should be considered only after source reduction alternatives have been evaluated and implemented where technically feasible. Where they are used, recycling techniques should occur in an environmentally safe manner.

1.1. Metal Finishing

Surface finishing usually involves a combination of metal deposition operations and numerous finishing operations. Wastes typically generated during these operations are associated with the solvents and cleaners applied to the surface and the metal - ion bearing aqueous solutions used in plating tanks.

Metal ion-bearing solutions are commonly based on chromium, copper, gold, silver, cadmium, zinc, and nickel. Many other metals and alloys are also used, although less frequently.

Electroplating process is to prepare deposit metal ions which adhere well to the substrate and which has the required mechanical and physical properties. Moreover, it is of importance that the deposit properties meet their specification on all occasions. However, many metals may (by modification of the bath and plating conditions) be deposited with different properties.

A wide variety of materials, processes and products are used to clean, etch, and plate metallic and non–metallic surfaces. Typically, metal parts or work pieces undergo one or more physical, chemical and electrochemical processes. Physical processes include buffering, grinding, polishing, and blasting. Chemical processes include degreasing, cleaning, pickling, etching, polishing and electrolyses plating. Electrochemical processes include plating, electro polishing and anodizing.

The cleaners (e.g. acids) may appear in process of wastewater and the solvents may be emitted into air, released in wastewater, or disposed off in solid form; while other wastes, including paints, metal-bearing sludge and still bottom wastes, may be generated as solids.

1.2. Pollution problem

All metal finishing processes tend to create pollution problems and to generate wastes to varying degrees of particular importance. The most serious of them are those processes that use lightly toxic or carcinogenic ingredients that are difficult to destroy or stabilize and dispose off in an environmentally sound manner. Some of these processes are.

- Cadmium plating.
- Cyanide - based plating, especially zinc, copper, brass, bronze, silver plating.
- Chromium plating and conversion coating based on hexavalent chromium compounds.
- Lead and Lead -Tin plating.

1.3. Regulatory Environment

The metal finishing industry is heavily regulated under the law 93/1962 and 4/1994. The law emphasizes prevention of pollution at the source as the preferred alternative, with recycling and treatment and disposal identified as less describable options. Pollution prevention approach now requires certain categories of industrial facilities to prepare and submit pollution prevention plans detailing their efforts to reduce waste and prevention pollution.

1.4. Clay minerals

Clays are composed of fine- grained aluminosilicates of mostly monocline symmetry that may contain sodium, calcium and other ions The basic crystalline structure of clay minerals consists of two main structural units. The first unit is composed of layers of tetrahedral silicate, which are bonded over the oxygen atoms in one plain; the second structural are consists of octahedral (mainly aluminum and also

Fe^{3+}, Fe^{2+}, or, Mg^{2+}) is surrounded by OH^- ions. The clay crystal lattice is formed by layers of these octahedra (O), and tetrahedra (T). (1)

The most important clay mineral groups, which are used for environmental purposes, are kaolins, smectites, and illites. The kaolins belong to the two-layer minerals and have the approximate chemical composition.$Al_2O_3.2SiO_2.2H_2O$. The most common kaolins are kaolinite, which consists of a single-silica tetrahedral sheet and a single-alumina octahedral sheet, which form the kaolin unit layer.

A widely used smectite is montmorillonite, which occurs as Na-montmorillonite and Ca-montmorillonite. As the lattice exhibits unbalanced charge due to isomorphic substitution of alumina for silica in the tetrahedral sheet and of iron and magnesium for all octahedral sheets, the attractive force between the unit layers in the stacks is weak. The cations and polar molecules are able to enter between them and cause the layers to expand. Illite is used for a mica like clay whose basic structural unit is similar to that of montmorillonite. Illites are characterized by charge deficiency, which is balanced by potassium ions that bridge the unit layers.

The minerals in the clay fraction impart chemical and physical properties to soil which strongly influence its behavior, for example in adsorbing cations their properties can be understood from a knowledge of their structure.

All aluminosilicats in the clay fraction dissociate protons from broken and edge surfaces leaving the structure negatively charged. They therefore have pH-dependent negative charge (2). The total negative charge is responsible for the cation exchange properties of clay.

The cations Ca^{2+}, Mg^{2+}, Na^+ and K^+ are known as basic cations. The negative charge on clay is balanced by the charge on these cations and also by H^+ and aluminum ions (Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$). These cations pass into solution when the mineral hydrolyses.

$$(Ca, Mg, Na, K, Al)\ \text{silicate} + H_2O \rightarrow Ca^{2+} + Mg^{2+} + Na^+ + K^+ + Al(OH)_3 + Si(OH)_4 + OH^-$$

The products may include silicic acid, hydrous oxides of Al, and Fe or other clay silicates and the basic cations that pass into solution.

One of the most used methods of removing metals from wastewater is the adsorption of metal ions as metal hydroxides due to the hydrolyses of minerals

$$4KAlSi_3O_8 + 4H^+ + 18\,H_2O \longrightarrow Si_4Al_4O_{10}(OH)_8 + 4K^+ + 8\,Si(OH)_4$$

In all reactions soil components remove protons from the acidic feed solution and the pH will decrease to an extent that depends on the buffer capacity of the soil.

Metal ions such as Cu^{2+}, Zn^{2+}, $-Cr_2O_7^{2-}$ و Ni^{2+} and others form complex ions in solution. These metals form similar complexes at the surface that contain hydroxyl groups, especially those of hydrated iron, Mn and Al_2O_3 . The complex ions do not undergo cation exchange, and can be displaced by extraction with acids or complexing agents.

1.5. Pollution

Pollution is considered as a big problem especially in underdeveloped countries. Pollution is now classified into three types: air pollution, water pollution and soil pollution. To keep clean and healthy environment, various pollutants that may exist in different media must be removed by effective and efficient methods. For such purpose, it is often necessary to change the style of living to prevent or, at least decrease the wastes. The environmental problems require the cooperation of all people with the governmental organizations, non - governmental organizations and the centers of scientific research.

It is necessary to use new treatment operations and improve the action of the conventional processes. The treatment of water and wastewater requires a variety of techniques and processes involving unit operations, mass transfer, thermodynamics, and reaction kinetic. It is a dramatic situation when a human finds himself surrounded by water, which he cannot use. We must think it over and seriously consider the situation when water is brackish that its uses are restricted for health of course. Thus, pure and clean water becomes a valued commodity in locations where supply is limited.

1.5.1. Pollution in Egypt

The expansion of industrialization, overpolation, civilization, the presence of inhabitation and the absence of environmental perception have created pollution problems. Some of diseases such carcinoma, cirrhosis, nephritis, abortion, hypogenadism, etc. are due to air, water and soil pollution. The Egyptian government has existed laws and regulations. The ministry of housing and municipalities in the year of 1962 issued a decision no. 649 / 1962 concerned with wastewater disposal, ministerial decree 9 of 1989, as modified by decree 44 / 2000, law no.48 / 1982 and finally the Egyptian Environmental Affairs Agency **(EEAA)** issued the law no. 4 / 1994 to control these pollutions (3).

1.5.2. Wastewater characteristics

It is essential in the design and operation of treatment, collection, disposal facilities and in the engineering management of environmental quality to understand the nature of wastewater (4). Table (1.1) shows physical, chemical and biological characteristics of wastewater and their sources.

Table (1.1). The Physical, chemical and biological characteristics of wastewater and their sources.

Characteristic	Sources
Physical characteristics:	
Color	Domestic and industrial wastes, natural decay of organic material
Odor	Decomposing wastewater, industrial wastes
Solids	Domestic water supply, domestic and industrial wastes, Soil corrosion, inflow/infiltration
Temperature	Domestic and industrial wastes
Chemical characteristics:	
Organic:	
Carbohydrates	Domestic, commercial, and industrial wastes
Fats, oils and grease	Domestic, commercial, and industrial wastes
Pesticides	Agricultural wastes
Phenols	Industrial wastes
Priority pollutants	Domestic, commercial, and industrial wastes
Surfactants	Domestic, commercial, and industrial wastes
Volatile organic compounds	Domestic, commercial, and industrial wastes
Others	Natural decay of organic materials
Inorganic:	
Alkalinity	Domestic wastes, domestic water supply, groundwater infiltration
Chlorides	Domestic wastes, domestic water supply, groundwater infiltration
Heavy metal ions	Industrial wastes
Nitrogen	Domestic, commercial, and industrial wastes natural runoff
pH	Domestic, commercial, and industrial wastes
Phosphorous	Domestic, commercial, and industrial wastes
Priority pollutants	Domestic water supply, domestic commercial, and industrial wastes
Sulfur	
Gases:	
Hydrogen sulfides	Decomposition of domestic wastes
Methane	Decomposition of domestic wastes
Oxygen	Domestic water supply, surface water infiltration
Biological characteristic:	
Animals	Open watercourses and treatment plants
Plants	Open watercourses and treatment plants
Protista:	
Eubacteria	Domestic wastes, surface-water infiltration, treatment plants
Archaebacteria	Domestic wastes, surface-water infiltration, treatment plants
Viruses	Domestic wastes

1.5.3. Contaminants of concern in wastewater treatment

The important contaminants of concern in wastewater treatment are listed in Table (1.2). The removal of biodegradable organics, suspended solids, and pathogens are removed by the secondary treatment.

Table (1.2) Important contaminants of concern in wastewater treatment [(4)]

Contaminants	Reason for importance
Suspended solids	Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharged in the aquatic environment.
Biodegradable Organics	Composed principally of proteins, carbohydrates, and fats, biodegradable organics are measured most commonly in term of BOD (biochemical oxygen demand) and COD (chemical oxygen demand).If discharged untreated to the development of septic conditions.
Pathogens	Communicable diseases can be transmitted by the pathogenic organisms in wastewater.
Nutrients	Both nitrogen and phosphorous. along with carbon, are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the growth of undesirable aquatic life. When discharged in excessive amounts on land, they can also lead to the pollution of groundwater.
Priority pollutants	Organic and inorganic compounds selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity. Many of these compounds are found in wastewater.
Refractory organics	These organics tend to resist conventional methods of wastewater treatment, Typical examples include surfactants, phenols, and agricultural pesticides.
Heavy metal ions	Heavy metal ions are usually added to wastewater from commercial and industrial activities and may have to be removed if the wastewater is to be reused.
Dissolved inorganic	Inorganic constituents such as calcium, sodium, and sulfate are added to the organic domestic water supply as a result of water use and may have to be removed if the wastewater is to be reused.

1.5.4. Classification of wastewater treatment methods

The contaminants in wastewater are removed by physical, chemical and biological means, as shown in Table (1.3) and (1.4).

Table (1.3) represents the physical unit operation in wastewater treatment (5).

Contaminants	Reason for importance
Flow metering	Process control, process monitoring, and discharge reports
Screening	Removal of coarse and settleable solids by interception (surface straining).
Comminution	Grinding of coarse solids to a more or less uniform size.
Flow equalization	Equalization of flow and mass loading of BOD and suspended solids.
Mixing	Mixing chemicals and gases with wastewater, and maintaining solids in suspension.
Flocculation	Promotes the aggregation of small particles into larger particles to enhance their removal by gravity sedimentation.
Sedimentation	Removal of settleable solids and thickening of sludge's.
Flotation	Removal of finely divided suspended solids and particles with densities close to that of water. Also thickens biological sludge.
Filtration	Removal of fine residual suspended solids remaining after biological or chemical treatment.
Micro screening	Same as filtration also removal of algae from stabilization pond effluent.
Gas transfer	Addition and removal of gases.
Volatilization and gas stripping	Emission of volatile and semi-volatile organic compounds from wastewater.

Table (1.4) Applications of Chemical unit processes in wastewater (5)

Contaminants	Reasons for importance
Chemical Precipitation	Removal of phosphorus and enhancement of suspended-solids removal in primary sedimentation facilities used for physical-chemical treatment.
Adsorption	Removal of organics not removed by conventional chemical and biological treatment methods. Also used for dechlorination of wastewater before final discharge for treated effluent.
Disinfection	Selective destruction of disease-causing organism (can be accomplished in various ways).
Disinfection with Chlorine	Selective destruction of disease-causing organisms.
Dechlorination	Removal of chlorine residual that exists after chlorination (can be accomplished in various ways).
Disinfection with chlorine dioxides	Selective destruction of disease-causing organisms.
Disinfection with bromine chloride	Selective destruction of disease-causing organisms.
Disinfection with ozone	Selective destruction of disease-causing organisms.
Disinfection with ultraviolet light	Selective destruction of disease-causing organisms.
Other chemical application	Various other chemicals can be used to achieve specific objectives in wastewater treatment.

Biological treatment is used primarily to remove the Biodegradable organic substances (colloidal or dissolved) in wastewater. These substances are converted into gases that can escape to the atmosphere and into biological cell tissue that can be removed by nutrients (nitrogen and phosphorus) in wastewater (5).

1.5.5. Application of treatment methods

The purpose here is to introduce the different ways in which treatment can be accomplished. Wastewater processing includes "preliminary "and "primary" referred to physical operations, "secondary" referred to chemical and biological processes and "advanced" or "tertiary" referred to combinations of all three (4).

A. Preliminary wastewater treatment

It is defined as the removal of constituents that may cause problems with the process or equipment. It includes screening for removal of the coarse solids, suspended matter that may cause clogging of equipment and flotation for the removal of large quantities of oil and grease.

B. Primary treatment

It includes:

1- Equalization
2- Neutralization
3- Flocculation
4- Sedimentation
5- Filtration

C. Secondary treatment

Secondary treatment is used to remove organic matter through biochemical oxidation. The particular biological process selected depends upon such factors as quantity of wastewater, biodegradability of waste and suspended solids. Disinfections can be included in this secondary treatment.

Conventional secondary treatment is defined as the combination of processes used for the removal of these constituents and includes biological treatment by activated sludge or lagoon systems and sedimentation

D. Advanced treatment

Advanced or tertiary wastewater treatment is used to remove particular contaminants or prepare the water for use. Some common tertiary operations are the removal of heavy metal ions by precipitation, carbon adsorption and ion exchange, removal of phosphorous compounds by ammonia stripping with air or by nitrification - denitrification in biological reactors. Removal of residual organic and color compounds by adsorption on activated carbon and removal of dissolved solids by membrane processes (reverse osmosis and electro dialysis). The effluent water is often treated with chlorine or ozone to destroy pathogenic organisms before discharge into the receiving waters.

E. Industrial wastewater

Generally, industrial wastes occur in many forms but for waste treatment purposes the following classification will be used.

(i) Solids in suspension, (ii) Liquids in suspensions, (iii) Degradable organic matter in solution, (iv) Non degradable organic matter in solution, (v) Inorganic matter in solution.

Many industrial wastes contain a mixture of the above pollutants and the treatment system will consist of a series of treatment units to remove the pollutants given above. Solids or liquids in suspension are removed by physical separation with or without the aid of chemical coagulants as primary treatment. The precipitation and separation treatment will be classified as secondary treatment. The removal of fine particles by filtration, the adsorption of organic chemicals on carbon, and the removal of inorganic salts by ion exchange or other methods will also affect the treatment, whereas dilution of toxic materials in the receiving water was common. This practice is no longer possible and treatment plants should be designed to remove them, that can be broken down by biological treatment or metal ions that must be removed by chemical means.

Highly alkaline or acidic wastes must be neutralized before discharging to the receiving body of water or before biological treatment. This would be a pre treatment step.

Industrial wastes differ from one plant to another in one or more of the following aspects (6).

1- Extreme temperature, if high, that may need cooling.
2- Acidic or alkaline requiring neutralization.
3- Contains grease or oil.
4- Toxic substances such as
    (a) Salts of lead, chromium, copper and other heavy metals.
    (b) Cyanides, sulfides, etc.
5- large fluctuations in the dissolved and suspended solids contents.

The quantity and characteristics of industrial wastes are dependent on the measuring processes from where they originate. Before a study such as this can be carried out, some knowledge of the processes used and wastes produced by typical industries should be acquired. Statistical evaluation of the quantities and quantities of industrial wastes per product unit before treatment or byproduct recovery including flow, BOD, suspended solids, nitrogen phosphorus, COD and dissolved solids was given by Eckenfelder. (7).

1.6.1. Heavy metal ions pollution

The presences of heavy metal ions in the water/wastewater has a detrimental effect due to their toxicity. The most important feature thatdistinguishes heavy metal ions from other toxic pollutants is their nonbiodegradability and that they have even a tendency to accumulate in organs and tissues of aquatic organisms.

1. For the River Nile, the results obtained by Lasheen;(8) revealed that the trace elements had become accumulated in high concentrations in river sediments indicating the existence of localized pollution contamination (9).
2. The determination of toxic heavy metals in electroplating process by Fiber-Optic spectrophotometeric and partial least – squares calibration was reported (10). The heavy metal ions in wastewater is a major environmental pollution, it includes the accumulation in oceans, lakes, rivers and streams of physical, chemical and biological substances that are either directly harmful or result in secondary and long hang effects (11).
3. The potential hazard of waste disposal including heavy metal ions on the ecosystem has been argued by several investigators (12).

The heavy metal ions concentration in aquatic organisms can be taken as a good indicator of water quality. The content of 11 of heavy metal ions (Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, Cd^{2+}, Cr^{6+}, Co^{2+}, Fe^{3+}, Mn^{2+}, $Pb^{2+}$and Sr^{3+}), were determined in certain tissues and organs in fish species in the river (13). Other investigation (14,9) showed the selectivity of accumulation of heavy metal ions in organs and / or tissues varies in the fish group, and reported that diseases levels in fish were found to be higher in an area receiving sewage in comparison to adjacent control area.

Chemical toxicants enter the environment via air, water, soil as well as directly or indirectly into food, and can include categories such as food additives, pesticides, and industrial chemicals. It has been estimated that every year 10 - 20.000 new chemical substances become available throughout the world (15), many of which are produced in very large quantities (16). More than 300 of these newly synthesized compounds may be biologically active and reach man's environment in a controlled or uncontrolled way (17). Since 50-90% of cancer in man has been estimated to be caused by exposure to chemicals (18). Recent studies have found that high levels of aluminum in brain tissue cause a human disorder known as Alzheimer disease; hundreds thousands of americans and canadians suffer from this disorder each year (19). Therefore, the elimination of heavy metal ions from wastewater is an important subject for public health. According to some surveys from public Health Services of different countries, significant numbers of people have been exposed to hazards of excess metal ions in different ways (20).

1.6.2. Heavy metal ions removal

Most of the heavy metal ions found in wastewater are in the inorganic form. The most common method for removal of inorganic heavy metals is chemical precipitation (21), where metal ions precipitate at various pH levels depending on such factors as the metal ion itself, coagulation/flocculation (22) ion exchange (23), but it is expensive and requires recharge of the resin and disposal of a substantial volume of spent and contaminated regeneration solution. Adsorption (12) on activated carbon requires periodic regeneration of the carbon and as ion exchange, is also rather expensive because capacity of the carbon to remove heavy metals is very limited. There are some techniques to remove metal ions from aqueous solution such as solvent extraction (23), evaporation (24), filtration (25), reverse osmosis (26 - 27) and modified agricultural waste materials (28).

A. Removal by carbon adsorption

Numerous polluting materials can be successfully removed using carbon adsorption systems and it was the most economical methods for separating hazardous miscible liquid or dissolved solids especially when present at relatively low concentration (29).

Activated carbon should be considered within the matrix of treatment options in the following waste - treatment or detoxification situations:

- * Trace quantities of water.
- * Metal ions from industrial wastewater.
- * Removing COD, Color, phenol, etc.

The effect of pH on the removal of other heavy metal ions was also investigated and proved to be one of the important factors in determining the removal efficiency (30).
Kaolinite, coal and Nile Hyacinth were used for removing heavy metal ions such Cu^{2+}, Pb^{2+}, and Cd^{2+} (31) .Also Abdel Wahaab (32) revealed that the three adsorbents examined activated carbon; nile Hyacinth and waste tea can be successfully used for the removal of lead in a wide range of concentration.

B. Removal of metal by modified agricultural waste materials

Interest had arosen recently in the use of agricultural byproduct such as peanut skin (33) walnut expeller meal (34) modified cotton (35) and Coir pith carbon (36).

Investigations on the use of other inexpensive agricultural byproducts such as bagasses, flour waste, paddy husk, paddy straw, onion skin and garlic skin, showed the binding of toxic metal ions such as Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+}.

These agricultural byproducts are collected from locally available sources, dried, and thoroughly powdered in a grinder and treated with different chemicals, For example treated bagasse by NaOH, treated onion skin by CH_2O. The results obtained by these agricultural byproducts were as following; the percentage removal of copper ions was 64.8 % by garlic skin, 98.6 % by treated bagasse, 83.4 % by onion skin. Also the percentage removal of zinc ions by bagasse was 10 %, treated bagasse was 56 %, and by onion skin was 83 %.

C. Removal of heavy metal ions from metal finishing works

The results of treatment based on full scale or pilot plant are listed as follows (37).

1. Sedimentation

Percentage removals of Cu^{2+}, Pb^{2+}, Hg^{2+}, and Zn^{2+} have been reported to be 98, 95, 50 and 95 % respectively for settling lagoon. In another report, for iron and steel industry, the following removal efficiency has been reported.

Metal	As^{3+}	Cu^{2+}	Pb^{2+}	Zn^{2+}
% Removal	77	92	99	99

The major factor affecting settling is the pH of the wastewater; lagooning for elongated period may be more successful than clarification in short periods.

2. Sedimentation with chemical additions

Lime, alum and ferrous / lime were used by Cecen and Gursoy (38) in adjusted doses with or without polymer additives to enhance settling of heavy metals. It has been found that the efficiencies of removing $-Cr_2O_7^{2-}$, Cu^{2+} and Ni^{2+} ions from acid pickling wastewater, using lime, are > 99, 98, 99 %, respectively. Doses adjustment is mandatory to have the desired removal efficiency.

More than 90 % of Cu^{2+} ion could be removed from solution with limestone and can be used as an alternative to replace activated carbon, which has similar metal ion removal efficiency (39).

3. Filtration

Filtration after pH adjustment had been reported to give excellent removal efficiencies (89 - 99 %) for $-Cr_2O_7^{2-}$, Cu^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+}.Pretreatment efficiency affects to a large extent the removal efficiency in filtration, as well as filter design and operational characteristics.

4. Ion-exchange

Ion exchange technique had been successfully applied for efficient removal in electroplating industry of Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, CN^-, Ag^+ and Zn^{2+} ions with percentages removal were > 99, 99, 98, 75, 99, 99, and 99%, respectively. Resin selectivity to specific ion or ions required special precautions including wastewater pretreatment and adjusting operation cycles of the resins.

Heavy metal ions are capable of binding smectite to clay in excess of its cation exchange capacity (40). The adsorption isotherms demonstrate that the complexes had a marked affinity for the clay surfaces in aqueous suspension. Also Reuter (41) reported a concept based on the high water and cation exchange capacity of clay minerals.

Elisabeta (42) Observed that the ionic exchange capacity for the considered authentic wastewater containing 0.05 M heavy metal ions have variable values depending on the dimensional compatibility of the involved cationic species with the a synthetic zeolite – type clioptilolite matrix and also on the mixing time.

5. Reverse osmosis

Reverse osmosis has been reported to give removal efficiency of up to 99 % for Cu^{2+} ion and 91 % for CN^{-1} using tubular membrane (43), operational factor including pretreatment of wastewater prior to membrane treatment and adjustment of operating pressure, temperature and pH should be considered carefully for successful separation.

6. Oxidation

Chlorination of cyanide waste under alkaline conditions produces cyanate. Sodium hypochlorite was used to destroy cyanides under alkaline conditions (pH = 9.5 - 10) for almost 30 minutes. Electrolytic oxidation of cupprocyanide electroplating wastewater in strong alkaline solution (pH >12) and copper oxide precipitation the anode was reported (44).

7. Electrochemical precipitation (ECP):

The economics of the ECP process was evaluated and compared with some conventional treatment processes for $-Cr_2O_7^{2-}$ removal from electroplating sources (45).

8. Adsorption

Wollband (46) showed that the adsorption studies of Co^{2+} using IR spectroscopy were used to probe the influence of the clay structure. Metal particle intercalated montomorillonite and aluminum pillared inter layered montomorillonite were prepared for these studies using reduction techniques.

Flemming (47) showed that significant quantities of Ag^{+},$Cu^{2+}$and Cr^{3+} were bound to isolated Bacillus subtitles 168 walls, Escherichia coli K-12 envelopes, kaolinite and smectite clays and the corresponding organic material-clay aggregates. The remobilization of the sorbet metal ions depends on the physical properties of the organic and clay surfaces and on the character and concern of the leaching agents.

Removal of -$Cr_2O_7^{2-}$, Ni^{2+} and Zn^{2+} from electroplating wastewater by adsorbing colloid flotation with a sodium dodecylsulfate /dodecanoic acid mixture compared with some conventional treatment processes for -$Cr_2O_7^{2-}$ removal were suggested by Sanciolo et.al (48).

Karathanasis (49) studied the subsurface migration of copper and zinc mediated by soil colloids. Cu^{2+} and Zn^{2+} solutions without colloids (controls) and combined with suspensions of montomorillonitic, mixed, illitic, and kaolinitic colloids with a range of surface properties were applied at a constant flux into undisturbed soil columns. The greatest metal ion transport potential was shown by colloids with high negative surface charge and organic carbon content and the lowest by colloids with large particle size, low negative surface charge, and high Fe- and Al-hydroxide contents. Although the dominant transport mechanism was metal ion sorption by colloids and contransport, the additional soluble Cu^{2+} and Zn^{2+} transported in the presence of colloids suggested involvement of physical exclusion, competitive sorption, or increased metal solubilization processes.

Duolite ES – 467 was used to treat wastewater containing heavy metal ions. Sorption experiments were carried out at varying pH values, agitation speeds, reaction time, and metal ions and sorbet concentrations. Each of the parameters affected the sorption behavior of individual metal ions. Copper sorption was greater compared with other metal ions such as zinc, nickel and cobalt. The presence of other metal ions affected copper sorption (50).

9-Biosorption:

Biosorption can be defined as the ability of biological materials to accumulate heavy metal ions from wastewater through metabolicatty mediated or physical-chemical pathways of uptake. Algae, Bacteria, fungi and yeasts had proved to be potential metal biosorbents (51).

The major advantages of biosorption over conventional treatment methods include (52):

- Low cost
- High efficiency
- Minimization of chemical and lower biological sludge
- No additional nutrient requirement
- Regeneration of biosorbent; and possibility of metal recovery.

Biosorption can be classified as transport across cell membrane, physical adsorption, ion exchange, complexation and precipitation.

More recently, biosorption of metals from aqueous solution using Rhizopus delmer Mycelia in free and Polyurethane – Bound forms was studied by Tsekova and Petrov (53), using a mixture of 0.5 – 5 mM $CuSO_4$, $CoCl_2$ and $FeSO_4$. Mycelia cells immobilized on polyurethane foam showed some times increase in uptake compared with that of free cells. Metal ions accumulation from a mixed solution decreased slightly for cobalt and iron and considerably for copper ions. Heavy metal uptake was examined in the immobilized column experiments and it was found that more than 92 % heavy metal removal from a mixed solution was achieved. During these experiments, the dry weight of the immobilized cells decreased by 2 %. These results showed that immobilized mycelia of Rhizopus delemer could be used repeatedly for removal of heavy metals from aqueous solution.

1.7. Chemical precipitation

This process transforms dissolved contaminants into an insoluble solid, facilitating the contaminant's subsequent removal from the liquid phase by sedimentation and filtration. The process usually uses pH adjustment, addition of a chemical precipitant and flocculation (25).

Metal ions precipitation from contaminated water involves the conversion of soluble heavy metal salts to insoluble salts that will precipitate. The precipitate can then be removed from the treated water by physical methods such as clarification (settling) and filtration. The process usually uses pH adjustment, addition of a chemical precipitant and flocculation. Typically, metal ions precipitate when chemical precipitants, coagulants, and flocculations are used to increase particle size through aggregation. The precipitation process can generate very fine particles that are held in suspension by electrostatic surface charges. These charges cause clouds of counter-ions to form around the particles, giving rise to repulsive forces that prevent aggregation and separation processes. Therefore, chemical coagulants are often added to overcome the repulsive forces of the particles (54).

The three main types of coagulants are inorganic electrolytes (such as alum, lime, ferric chloride, and ferrous sulfate), organic polymers, and authentic polyelectrolytes with anionic or cationic functional groups (55).

A. Hydroxides precipitation

Heavy metal ions are generally precipitated as the hydroxide through the addition of lime or caustic to attain the pH of minimum solubility. However, several metal ions are amphoteric and exhibit a specific pH zone of minimum solubility. The addition of 100 mg / l of lime was found effective for removal of Pb^{2+}, Cu^{2+}, Zn^{2+} and Co^{2+} at pH of 9.5 .

The process of precipitation is readily automated and controlled. By raising pH the value of a solution with a common alkaline material such as lime or sodium hydroxide, the corresponding metallic hydroxide compounds become insoluble and precipitate from solution.

B. Ammoniacal complexes

Most heavy metal ions precipitate by raising the pH of solution forming the respective metal hydroxide compound. Certain metal ions, primarily copper, zinc and cadmium readily form metallic complexes with ammonia (56). The ammoniacal metal complexes remain soluble at the higher pH values prohibiting the precipitation of the respective metal hydroxide There are several methods conventionally used to destroy the ammoniacal complex and precipitate the metallic ion.

The ammonium ion may be destroyed by oxidation with chlorine or ozone; eliminating the ammonia destroys the complex. However, the cost is prohibitive when compared to other methods.

The additions of soluble ferrous ions as either ferrous sulfate or ferrous chloride will co-precipitate the metallic ion with the iron hydroxide.

C. Sulfide precipitation

The most economical method is to add soluble sulfide ions and break the ammoniacal complex by precipitating the metallic sulfide compounds (30). Sulfide precipitation was an excellent technique for precipitating heavy metal ions since proper control can be achieved.

1.8. Electroplating processes

The objective of an electroplating process is to prepare a deposit which adheres well to the substrate and which has the required mechanical, chemical and physical properties. Moreover, it is of overriding importance that the deposit properties meet their specification on all occasions, i.e. the process is both predictable and reproducible.

On the other hand, many metals may (by modification of the bath and plating conditions) be deposited with different properties (57). For this reason it is not possible to define a single set of conditions for electroplating each metal, the bath, current density, temperature, and etc. will depend to some extent on the deposit properties required.

It is important that the plating bath is stable for a long period of time because of the importance of reproducibility of the deposit. It is also necessary that the quality of deposit is maintained over a range of operating conditions, since some variations in concentrations and current density are bound to occur, particularly when different objects are to be plated. Tolerance of the bath to carry over from previous process liquors or mishandling during operation on the factory floor is an additional advantage.

The principle components of an electroplating process are shown as.

1- An electroplating bath containing a conducting salt and the metal to be plated in a soluble form, as well as perhaps a buffer and additives.

2- The electronically conducting cathode i.e. the work piece to be plated.

3- The anode (also electronically conducting) which may be soluble or insoluble.

4- An inert vessel to contain 1-3, typically, e.g. steel, rubber and PVC.

The process sequence of electroplating line is shown in Figure 1.1. It comprises the following two main treatment processes.

(a) Pretreatment process before electroplating; for example degreasing, rinsing, neutralization with acid and rinsing.

(b) Post – treatment process; for example copper, zinc, chromium and nickel plating.

Figure 1.1. Shows the process sequence of electroplating.

Table 1.5. Shows the chemicals and function of different processes in an electroplating line which effecting operation and discharged to waste process solutions.

The following is a summary of Table 1.5.

Degreaser: Anodic cleaning is preferred for stainless steel; tank capacity is 2.5 m^3, contained alkaline solutions of sodium hydroxide, (15 Kg / $2m^3$) to remove lubricant and passive oxide film that is present.

Care should be taken to see that alkalinity, current density and temperature of cleaning bath is kept as low as possible.

Desmutt: This solution contains from 5-10 % H_2SO_4 and was not designated for discharge. It is used to remove the rust.

Cu Plating: Copper in cyanide baths is monovalent and copper is bound mostly as complex cyanides. Two moles of sodium cyanide combine with one mole of copper cyanide to form a complex.

$$2NaCN + CuCN = Na_2[Cu(CN)_3]$$

This bath was made up 120 g / l of NaCN + CuCN

Brass plating: The brass alloy most often plated is a yellow colour and contains about 70 to 80 % Cu with the balance of Zn. This bath was made up 100 g / l of CuCN + Zn $(CN)_2$ + NaCN at pH 10- 11 and 25 - 35 °C for 2 to 3 min.

Ni Plating: Nickel is mainly electro - deposited from nickel sulphate solution containing a certain minimum of chloride ions.

A typical basic composition is the following; 250g/l $NiSO_4$,60 g /l $Nicl_2$ and 40 g/l H_3BO_4 at 60 - 70 °C and 5 amp. / dm^2 for 15 min.

Cr plating: Hard chromium plating had found its use in all industries; it makes a wide use of chromium plated for long life anc resistance to corrosion. The bath is made up of 250g/l CrO_3, 2.5 g/l $K_2Cr_2O_7$ and activator at 25-40 °C for 1 min.

Zn plating: Depositions from easily Zinc electro plating baths of acid chloride or alkaline zincate's have a very dull and finish. Today bright Zinc electrodeposits can be obtained from most Zinc electroplating baths.

Alkaline bath contains 25-40 g / l Zn $(CN)_2$, 35-80 g / l NaCN at 30 - 60 °C with 2 – 80 amp./ ft. Acid bath was made up from 20-25 g / l $ZnCl_2$, 25 - 30g / l KCl

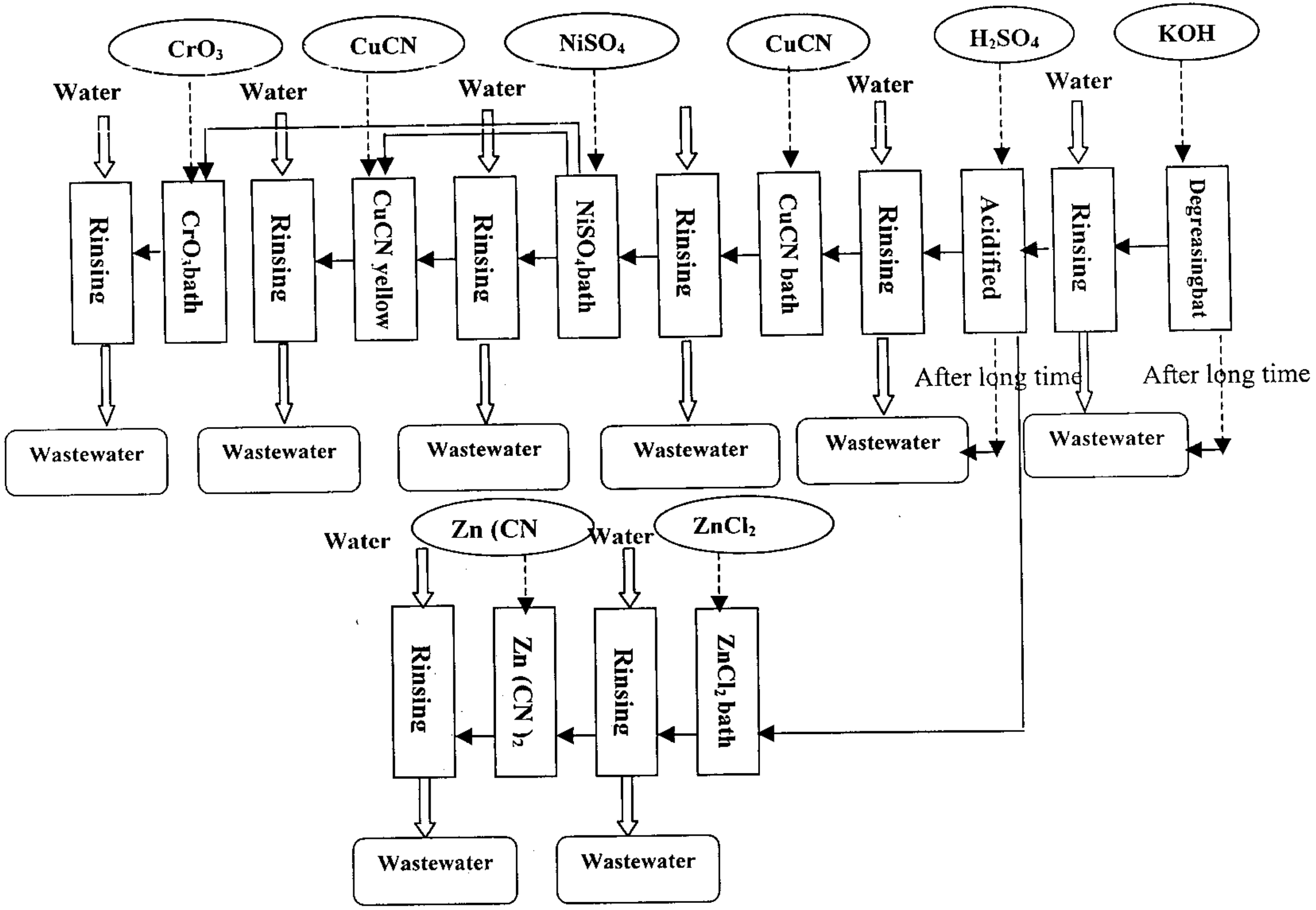


Figure 1.1. Shows the processes sequent of electroplating and rinsing of wastewater

Table 1.5. The chemicals and function of different processes in an electroplating line.

Process	Chemicals	pH	Temp. °C	Life time	Function
Degrease	Alkaline solution 15 kg/2m^3	9	70-90	3 months	Removal of lubricants
Rinsing	Water polluted	7.28	30	Continuous over flow 20 l / min	Remove any trace of NaOH
Desmutt	H_2SO_4 5-10%	acidic	25-30	Long life	Remove passive film of Fe_2O_3
Rinsing	Water polluted	5.65	18- 25	Continuous over flow 20 l / min	Remove trace of acid
Cu Bath	CuCN +NaCN = 120g/l	8-9	60-70	Long life	To improve anode corrosion
Rinsing	Water polluted	6-7.5	25	Continuous over flow 20 l / min	Remove trace of Cu^+ ion
Ni Bath	1-$Nicl_2$ 60 g/l 2-$NiSO_4$ 250 g/l 3- H_3BO_4 40 g/l with 5 amp./dm^2	3-4	55-65	Long life	Ni^{2+} ions deposit- ions have good brightness and more resistance for corrosion
Rinsing	Water polluted	7.27	25	Continuous over flow 20 l / min	Remove trace of Ni^{2+}ions
Cu Brass	CuCN +Zn $(CN)_2$ + NaCN =100 g/l	10-11	25-35	Long life	To improve yellow color
Rinsing	Water polluted	8.08	25	Continuous over flow20 l / min	Remove trace of Cu^+ ions
Cr Bath	CrO_3 250 g/l +$K_2Cr_2O_7$ 2.5 g/l	2-3	25-40	Long life	Faster rate of deposition
Rinsing	Water polluted	6.8	25	Continuous over flow 20 l / min	Remove trace of -$Cr_2O_7^{2-}$ions
Zn Bath (acidic)	Zncl2 2-2.5 g/l + KcL 25- 30 g/l+ H_3BO_4 25 g/l	4-5	30-55	Long life	Zn^{2+} ions depositions have good brightness and ductility.
Rinsing	Water polluted	5.57	25	Continuous over flow 20 l / min	Remove trace of Zn^{2+} ions
Zn Bath (alkaline)	Zn $(CN)_2$ 25-45 g/l+NaCN 35-105 g/l	9	18-25	Long life	Rate of deposition is rapid giving high throwing power
Rinsing	Water polluted	7.2	18-25	Continuous over flow20 l / min	Remove trace of Zn^{2+} ions

1.8.1 Rinsing water

Water is used to clean the profiles of steel after each process. The specification of water used in rinsing must be as the potable water or deionized water. The system uses a mixture of drag-out rinses, for a variety of rinsing requirements. For health and environmental benefits, it is required to decrease water use, reduce water pretreatment and reduce water post treatment for pollution prevention actions (58).

Rinsing water from the treatment tanks is installed after the treatment tanks. This waste outlet was continuous i.e. the water enters the rinsing tanks in constant flow rate and leaves in a continuous flow, thus creating the waste outlet itself.

1.8.2. Wastes of electroplating process

During the electroplating process waste streams as well as emission develop, which may have an impact on our environment. The most important waste fluids are:

1. Alkaline fluid with steel in solution.
2. Acid fluid with steel in solution.
3. Wastewater containing heavy – metal ions.
4. Cyanide fluid from Cu and Zn solution.

The first waste fluid arises at the pre - treatment, where the second waste during treatment and the third waste during the pre-treatment and post treatment.

The wastes are created as the spent baths are changed when the effective strength of the chemical solution weakens or is exhausted or when the solution is partially renewed in order to keep the limit of polluting substances in the waste within a minimum level of acceptability able to achieve a correct process (59).

The volumes of these wastes are almost never large, but the concentrations of polluting substances discharged their massive addition to the depuration plant by modest and steady flow rate technologies for the recovery of wastes are used (60).

The success in treating such wastes lies in the necessity of contineous monitoring of the process variables; as an example treating chemicals, temperature, dipping time inside the tank, quality of water, analysis and characteristics of wastewater coming to treatment plant, flow rate and sequence of treatment (61).

1.9. Flocculation

Flocculation means formation of a floc, which visually resembles a tuft of wool or highly fibrous porous structure. Flocculation occurs by a chemical bridging or physical enmeshment mechanism.

Flocculation is operationally obtained by gentle and prolonged mixing, which converts the submicrospic-coagulated particles into discrete, visible, suspended particles. At this stage the particles are large enough to settle rapidly under the influence of gravity and be removed from suspension by filtration (62).

Timofeeva et.al (63) tested the purpose of acrylamide substitution in the gravity sedimentation of metal hydroxides from electroplating effluents.

1.10. Polyurethanes

Few polymer – forming systems had received as much attention, or been applied in so many branches of technology as polyurethanes when one consider the properties available in such materials. The end products of polyurethanes have widely diverse character, such as fibres, filmforming, thermoplastics, thermosetting, or elastomeric materials. It is the ability to synthesize polymers containing not only the urethane link, $-NH-\overset{\|}{C}-O-$ (the basis for this classification) but also to include other groups as integral units in or on the polymer chains, which leads to this versatility. There can be introduced, in a controlled manner, specific chemical structures displaying chains stiffness. Or flexibility, an ability to orient or crystallize, and interchain attraction or chemical cross-linking, all of paramount importance in determining the ultimate physical and mechanical properties.

Polyurethane synthesis can be affected by the reaction of chloroformic esters with diamines and carbamic esters with diols:

$$- RNH_2 + Cl\,COOR' \longrightarrow RNHCOO\,R'$$

$$- ROH + ZOOCNH\,R' \longrightarrow ROOCNH\,R'$$

Development of isocyanate chemistry was directed to polymer formation when [(64)], during research on fibre-forming polymers analogous to the polyamides, prepared a number of linear polyurethanes from diisocyanates and diols. One of these, the polyurethane from 1,4 – butane diol and hexamethylene diisocyanate:

$$HO(CH_2)_4OH + OCN(CH_2)_6NCO \longrightarrow$$

$$-\!\!\left[O(CH_2)_4OOCNH(CH_2)_6NHCOO\right]_x\!\!-$$

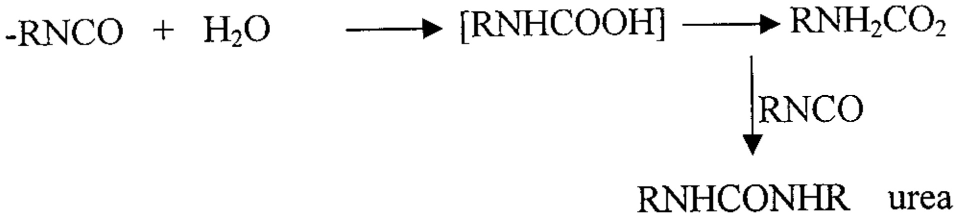
The NCO group can react generally with compounds containing active hydrogen atoms, according to the following:

a) $-RNCO + R'OH \longrightarrow RNHCOO\,R'$ urethane

b) $-RNCO + R'NH_2 \longrightarrow RNHCONH\,R'$ urea

c) $-RNCO + R'\,COOH \longrightarrow RNHCO\,R' + CO_2$ amide

d)

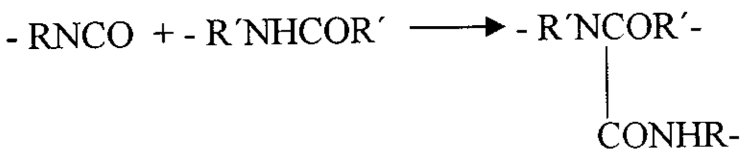


$$-RNCO + H_2O \longrightarrow [RNHCOOH] \longrightarrow \begin{array}{c} RNH_2CO_2 \\ \Big\downarrow {\scriptstyle RNCO} \\ RNHCONHR \end{array} \quad \text{urea}$$

Thus, if the reagents are di- or poly- functional, polymer formation can take place. While these reactions normally occur at different rates, reaction (b) being the most rapid, they can be influenced appreciably and controlled by the use of catalyst. Reactions (c) and (d) give rise also to carbon dioxide, a feature of value when forming foamed products. In the reactions noted, there is the advantage that, unlike polycondensation; the processes normally give rise to no by-products requiring removal as the macromolecules are built up. Again, additional reaction of the isocyanate with urea, urethane, and amide groups, already introduced during the initial polymer formation, is also possible.

Chain branching or crosslinking then occurs, due to the formation of acylurea, biuret, and allophanate links onto the main chain as follows:

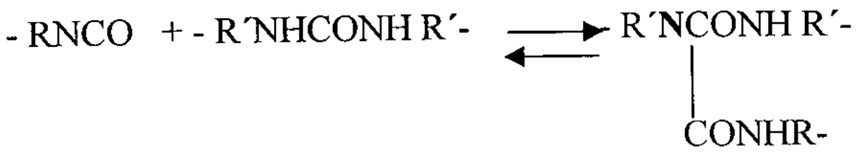
e)



$$-RNCO + -R'NHCOR' \longrightarrow \begin{array}{c} -R'NCOR'- \\ | \\ CONHR- \end{array}$$

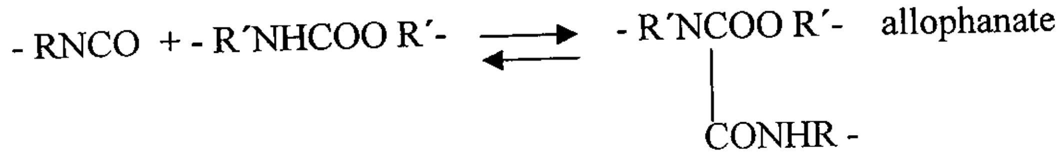
acylurea

f)



$$-RNCO + -R'NHCONH\,R'- \rightleftarrows \begin{array}{c} R'NCONH\,R'- \\ | \\ CONHR- \end{array}$$

biuret

g) 

$$-\mathrm{RNCO} + -\mathrm{R'NHCOO\,R'}- \rightleftharpoons -\mathrm{R'}\underset{|\atop \mathrm{CONHR}-}{\mathrm{N}}\mathrm{COO\,R'}- \quad \text{allophanate}$$

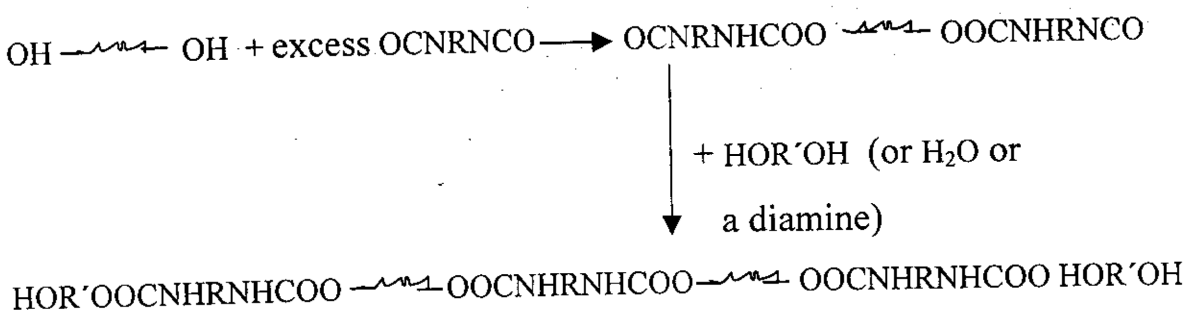
The initial studies on urethane synthesis were based on simple diisocyanates and diols but the main importance of the reaction is now concerned with the use of intermediates, which are often themselves polymeric in character (polyesters, polyethers) and carry terminal groups (usually –OH or –NCO) capable of further reaction and thus of increasing the molecular size, often during the actual fabrication processing, by either chain extension, branching, or crosslinking.

Some of the reactions are reversible under the action of heat, thus introducing the possibility of molecular rearrangement during processing. The "Polyurethanes" can therefore have a preponderance of other linking groups, i.e. be essentially copolymers such as polyester urethanes or polyether urethanes and be branched or cross linked through groups formed in reactions (e) or (g).

The whole macromolecular system in these polymers can accordingly be designed so as to incorporate links or chain segments which will provide the required molecular flexibility or rigidity, and the chain order, branching, or crosslinking necessary to give the properties required in the finished products.

The polyurethanes are used in a wide variety of applications but relatively few isocyanates are employed commercially in their manufacture. The most important are the toluene diisocyanates (TDI), diphenylmethane diisocyanat (MDI), naphthylene diisocyanate (NDI), and hexamethylene diisocyanate (HDI), although other types are now being developed industrially. Although most widely used, the aromatic diisocyanates lead to polyurethanes which turn yellow on exposure to light, and recent developments have been directed to intermediates in which the NCO groups are aliphatic and not attached directly to an aromatic nucleus (65). An interesting and most useful feature of the isocyanates lies in their ability to: (i) form thermally labile adducts, (ii) give higher molecular weight adducts in which some free isocyanate groups remain; and (iii) give rise to cyclic dimmers and trimers.

Linear polyurethanes formed from the reaction of diols with diisocyanates are crystalline, fibre-forming polymers but are lower-melting than the corresponding polyamides, and non has become of real importance either as a synthetic fibre or as a thermoplastic material. However, replacement of the simple diols by polymeric analogues has resulted in much commercial development. This arose from the finding that linear polyesters, of molecular weight 2000 and carrying terminal OH groups, would react with hexamethylene diisocyanate or toluene diisocyanates (66).



It will be seen that the initial polyester of modest molecular weight is converted into a high polymer through rigid linking units arising from the naphthylene diisocyanate and butane diol, and then slightly crosslinked. It is essentially a copolymer in which flexible polyester segments are joined by short urethane units.

The concept of molecular tailing so as to introduce units giving the required mechanical and physical properties has led to the provision of a variety of linear and branched polyesters and polyethers for polyurethane production. These intermediates may have molecular weights of the order of 500- 3000, be crystalline or amorphous, contain a groups which contribute to molecular flexibility or stiffness, and be linear or branched according to the requirements for use in elastomers, flexible or rigid foams, coatings.. etc.

1.10.1.Structure – property relationships of polyurethanes:

Linear polyurethanes prepared from α, ω- diols and diisocyanates are usually thermoplastic crystalline polymers having melting points intermediate between those of the aliphatic polyesters and polyamides of comparable unit structure. The -NHCOO- group is highly polar and capable of hydrogen bonding, having a cohesive energy value comparable to that of an amide, but greater flexibility arising from the additional oxygen atom.

As with the simple urethane, the type of linking atoms or groups present will be important. Oxygen will reduce melting point, aromatic rings increase it, and groups which are capable of hydrogen bonding will increase melting point and strength. Crystallization potential, leads to increase in hardness and strength but reduction in flexibility and extensibility. A small number of crosslinks can reduce crystallization tendencies by restricting chain rotation, thus enabling a polymer to be more elastomeric in behaviour. On the other hand, crosslinking to a higher degree increases rigidity and modulus but reduces extensibility.

A series of metal–containing polyurethane ureases having ionic links in the main chain, were synthesized by Rajalingam and radhakishnan (67), with Mn, Cu, Co and Pb salts of mono (hydroxyl ethyl)- phthalate and a bisurea. The polymer obtained was brown to green. These polymers were well characterized by solubility, viscometry, spectral studies (IR, UV and NMR) and thermo gravimetric analysis.

Semi crystalline segmental polyurethanes based on hydrogenated polybutadiene soft segments and butanediol or di-B-hydroxyethyl hydroquinones as chain extenders were synthesized by Leon and Pascault (68), under different conditions of preparation of polyurethane induce various characteristics and tensile properties of the corresponding polyurethane.

A number of polyurethanes was synthesized by reacting caster oil with TDI and HMDI and varying the NCO/OH ratio. All these PUs were reacted with some acrylic monomers like ethyl acrylate, n- butylacrylate, ethylmethylacrylate, and butylmethacrylate using a cross linker ethylene glycol dimethyl-acrylate and benzoyl peroxide as initiator. The physicochemical properties of interpenetrating polymer networks (IPNs) we reported. The thermogravimetric analysis was used to study the thermal behavior of IPNs and the evaluation of kinetic parameters. Degradation mechanism has also been investigated. Some of the mechanical properties viz tensile strength, share-A hardness, elongation and break… etc. we also reported by Mishra etal (69). Electronic- ionic conducting interpenetrating polymer networks based on (caster oil-polyethylene glycol) PU and polyvinyl pyridine (VP) we synthesized by coupling caster oil and PEG with TDI and by radical polymerization of VP with caster oil simultaneously (70). The crystalinity and water absorbency of IPNs increased with increasing molecular weight of PEG.

Studies have been carried out on polyurethane elastomer based on modified caster oil in combination with different molecular weight of PEG and polymeric methylene diphenyl–4,4-prime-diisocyanate (PMDI). The resulting polymers were cast into molds and the moldings were characterized by scanning electron microscopy and thermo gravimetric analysis. Mechanical properties such as tensile, strength, elongation and hardness were measured. There was an increase in the flexibility of PU with increase in molecular weight of PEG, added to modify caster oil (71).

A series of interpenetrating polymer networks (IPN) of PU /PS has been synthesized by condensation reaction of caster oil with MDI and styrene, employing benzoyl peroxide as initiator (72).

A series of poly (ester – urethane – urea) s containing pendant methacrylate functionality has been prepared by opera et.al (73) which were characterized and formulated into polyurethane methacrylate elastomers using a prepolymer process. They we synthesized in two – step process: synthesis of an isocyanate terminated prepolymers prepared from an excess molar concentration of a diisocyanate reacted with a polyether or a polyester diol average molecular weight (1000-3000) to form an isoganatic–terminated prepolymer in bulk or in the solvent to form polyurethane- urea (PUU) with an aliphatic diamine. Also these anthans(73) studied the stress and strain, which are closer to the values of the conventional linear urethane block copolymer.

Calcium containing poly (urethane–ether) (PUE) were synthesized by the reaction of hexamethylene diisocyanate or toluylene 2.4-diisocyanate (HMDI orTDI) with a mixture of calcium salt of mono(hydroxy butyl) phthalate (Ca (HBP) $_2$) and polyethylene glycol (PEG$_{200}$ or PEG $_{400}$). A series of calcium containing PUEs having different compositions were synthesized by taking the mole ratio of Ca $(HBP)_2$: PEG_{200} or PEG_{400}: diisocyanate (HMDI or TDI) as 3: 1: 4, 2: 2: 4 and 1: 3: 4 to study the effect of calcium content on the properties of the copolymer. The structure of the polymers were confirmed by IR and NMR spectra .The polymer was soluble in DMF and DMSO. The viscosity of the calcium containing PUEs increased with increase in the soft segment content as well as its length and decrease with increase in calcium content (74).