CHAPTER TWO

LITERATURE REVIEW

2.1 Wastewater in Malaysia

The degradation of water quality and production of wastewater increased in Malaysia with industrialization, as the volume of water used and wastewater generated increased (Rahani, 1995). To protect the environment, the government enacted the Environment Quality Act (EQA) 1974, with additions for industrial and sewage effluents in 1979. Two different standards were set, namely Standard A for wastewater discharged into inland waters within water catchment areas and Standard B for discharges into other inland waters as listed in **Table 2.1**.

Thus, water treatment is necessary for the removal of particulates and chemical pollutants, prevention of communicable disease transmission and improvement of aesthetic quality of water for consumption (Ong and Debbie, 1993).

2.2 Soap and Detergent Wastewater in Malaysia

The soap and detergent industry is growing rapidly as the population of the country and health awareness increases. Hence the generation of wastewater is on the increase. The wastewater characteristics of a typical soap and detergent factory are as given in **Table 2.2** for the years 1983 and 1993 to show the rapid change in the wastewater characteristics of the industry. The significant increase in the concentrations of these selected parameters is due to the formulation changes, more frequent cleaning of process equipment due to process changeovers, and new product lines (Dhileepan and Kumar, 1995).

The three main methods of water and wastewater treatment are physical, chemical and biological treatment, with the physico-chemical process being the primary treatment for water and wastewater. It is used to reduce the level of pollutants to levels that can be handled by microorganisms in biological treatment (Tebbutt, 1977). A diagram of a typical wastewater treatment plant for a soap and detergent factory is shown in **Figure 2.1** (Dhileepan and Kumar, 1995).

2.3 Physico-Chemical Methods of Treatment

Waters, polluted either by man or by nature, are likely to contain dissolved inorganic and organic substances, biological forms such as bacteria and plankton, and suspended inorganic material. To remove these substances, the usual unit processes include plain sedimentation, coagulation generally followed by filtration and chemical precipitation. These are used generally to remove dissolved minerals like hardness components, iron and manganese. Other processes such as adsorption, aeration, ion exchange, oxidation, and distillation are also important for the removal of dissolved substances (Black 1961; 1963).

2.3.1 Coagulation

Coagulation, generally followed by filtration, is by far the most widely used process to remove the substances producing turbidity in water. These substances

Table 2.1 : Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations 1979. Parameter limits of Effluent Standard A and B

Parameter	Unit	Standard A	Standard B
Temperature	° C	40	40
pH value	-	6.0-9.0	5.5-9.0
BOD$_5$ at 20°C	mg/l	20	50
COD	mg/l	50	100
Suspended solids	mg/l	50	100
Mercury	mg/l	0.005	0.05
Cadmium	mg/l	0.01	0.02
Chromium, hexavalent	mg/l	0.05	0.05
Arsenic	mg/l	0.05	0.10
Cyanide	mg/l	0.05	0.10
Lead	mg/l	0.01	0.50
Chromium, trivalent	mg/l	0.20	1.0
Copper	mg/l	0.20	1.0
Manganese	mg/l	0.20	1.0
Nickel	mg/l	0.20	1.0
Tin	mg/l	0.20	1.0
Zinc	mg/l	1.0	1.0
Boron	mg/l	1.0	4.0
Iron	mg/l	1.0	5.0
Phenol	mg/l	0.001	1.0
Free Chlorine	mg/l	1.0	2.0
Sulfide	mg/l	0.50	0.50
Oil and grease	mg/l	not detectable	10.0

(Environment Quality Act, 1974)

Table 2.2 : Typical Wastewater Characteristics

Parameters	1983	1993
pH	8.3	10.61
BOD	730	6593
COD	7340	18915
Suspended Solids	560	1345
Oil & Grease	528	15
Detergent	-	7600

(Dhileepan and Kumar, 1995).

All units in mg/l except for pH.

are largely of clay minerals and microscopic organisms and they occur in widely varying sizes, ranging from those large enough to settle readily to those small enough to remain suspended for very long times (Sen Gupta and Hashim, 1996; Sastry, 1995; Morales and Verela, 1994).

Coarser components, such as sand and silt, can be removed from water by simple sedimentation. Finer particles, however, will not settle in any reasonable time and must be flocculated to produce the larger particles that are settleable. The long-term ability to remain suspended in water is basically a function of both size and specific gravity (Powell, 1954). The importance of size is illustrated in **Table 2.3**, which shows the relative settling times of spheres of different sizes. It can be seen that the settling rates of the colloidal and finely divided (approximately 0.001 to 1 micron) suspended matter are so slow that removing them from water by plain sedimentation in tanks having ordinary dimensions is impossible. The enormous

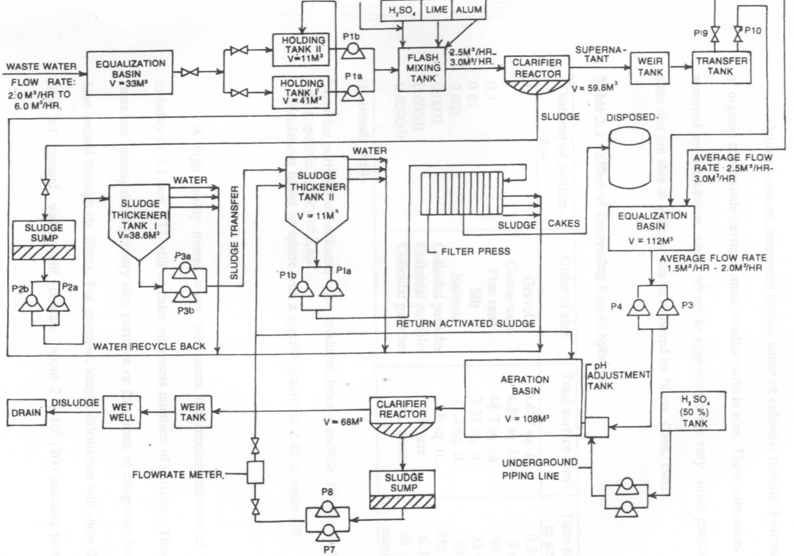


Figure 2.1 : Schematic diagram of industrial wastewater treatment plant

(Dhileepan and Kumar, 1995)

increase of surface area for a given weight of solids as the particles become smaller and more numerous is an important property of colloids (Heistand, 1964).

Color-producing substances consist either of colloidal metallic hydroxides or of organic compounds having a much smaller particle size. These substances can be removed by coagulation, which serves to agglomerate the very small particles into sizes that are able to settle or can be removed by filters (Ives, 1962).

Table 2.3 : Effect of Decreasing Size of Spheres

Diameter of particle, mm	Order of size	Total surface area^0	Time required to settle †
10	Gravel	0.487 sq. in.	0.3 sec
1	Coarse sand	4.87 sq. in.	3 sec
0.1	Fine sand	48.7 sq. in.	38 sec
0.01	Silt	3.38 sq. ft.	33 min
0.001	Bacteria	33.8 sq. ft.	55 hr
0.0001	Colloidal particles	3.8 sq. ft.	230 days
0.00001	Colloidal particles	0.7 acre	6.3 yr.
0.000001	Colloidal particles	7.0 acres	63 years minimum

(Heistand, 1964)

^{0}Area for particles of indicated size produced from a particle 10 mm in diameter with a specific gravity of 2.65.

† Calculations based on sphere with a specific gravity of 2.65 to settle 1 ft.

A high quality treated water that meets the recommendation of residual turbidity of 0.1 unit NTU still contains enormous numbers of particles. These either represent uncoagulated primary clay particles or fragments of coagulant floc which have passed through the filters. For example, simple calculation will show that each liter of treated water will contain about 2 x 10^8 (200 million) particles of insoluble alum coagulant, assuming a suspended solids content of 0.1 mg/l and spheres 1 μ in diameter with a specific gravity of 1.01. Experimental evidence on turbidity has confirmed that the computations and assumptions are valid, at least in the order of magnitude. A laboratory coagulation and filtration of turbid water produced a content of 0.06 mg/l. A count of the particles in the size range of 0.59 to 1.0 μ using an electronic particle counter revealed that each liter of this treated water contained 3.4 x 10^8 (340 million) particles, an experimental value that is quite consistent with the computed number (Lagvankar and Gemmell, 1968).

2.3.1.2 Mechanism of Coagulation

Settling velocities of finely divided and colloidal particles under gravity alone are so small that ordinary sedimentation is not practical. Therefore, it is necessary to use procedures which agglomerate the small particles into larger aggregates. The larger aggregates have the practical settling velocities required. Formation of larger particles from smaller ones is also required for their removal by filtration (Sen Gupta and Hashim, 1996).

The term's "coagulation" and "flocculation" have been used to describe the process of removal of turbidity from water. There is, however, a clear distinction between the two terms. The term "coagulation" comes from the Latin coagulare, meaning to drive together. This process describes the effect produced by the addition of a chemical to a colloidal dispersion, resulting in particle destabilization by a reduction of the forces tending to keep the particle apart.

In practice, coagulation is achieved by adding the appropriate chemical that causes particles to stick together when contact is made. Rapid mixing is important at this stage to obtain uniform dispersion of the chemicals and to increase the opportunity for particle-to-particle contact (Sen Gupta and Hashim, 1996). The entire process occurs in a very short time, probably less than a second and initially results in particles submicroscopic in size (Morgan and Stumm, 1962; Mackle, 1962).

2.3.1.3 Chemistry of Metal Coagulants

Although the coagulation process using aluminum and iron salts as coagulants is ancient and has been in continuous use for the past 100 years, knowledge of the precise mechanism is not well understood. It is known that, when added to water, aluminum and iron salts will react with the water or with alkalinity present in the water. This reaction was thought to yield the insoluble material, aluminum or ferric hydroxide, represented as $Al(OH)_3$ or $Fe(OH)_3$. In the reaction, an acid is produced which reduces the pH of the solution and consumes alkalinity in approximately the ratio of 1 mg/l of alkalinity for each 2 mg/l of commercial alum (Sen Gupta and Hashim, 1996; Hammer 1977). Discrepancies in this ratio and the fact that the aluminum hydroxide floc frequently contained ions other than aluminum and hydroxyl ions, notably sulfate, suggests that the reaction is not, in fact, as simple as represented. The hydrolytic chemistry of aluminum and iron is exceedingly complex (Pokras,1956).

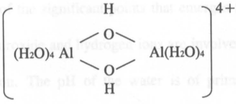
A series of reactions occurs when an aluminum salt is added to water. The current view is that, aluminum ions, almost instantly after addition to water, enter into a series of hydrolytic reactions with water to form a series of multivalent charged hydrous oxide species. Depending on pH, these compounds may range from positive at the lower pH values to negative at the more basic pH values. These reactions can be represented as follows:

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H_3O^+$$

$$[Al(H_2O)_5OH]^{2+} + H_2O \rightleftharpoons [Al(H_2O)_4(OH)_2]^{+} + H_3O^+$$

These reaction can proceed until the neutral species $[Al(H_2O)_3(OH)_3]$ or a negatively charged species $[Al(H_2O)_2(OH)_4]^-$ is formed (Walters,1972).

Evidence also suggests that the monomeric species, i.e. those compounds containing only one aluminum ion, are at best transient, and that a second type of reaction called "olation" has great importance in coagulation process. In the process of olation, a series of polymerization reactions occurs, resulting in complexes containing several aluminum ions bridged by two hydroxyl groups. A model of a simple complex containing two aluminum ions can be illustrated as shown below:



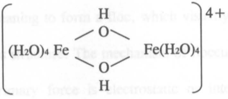
It has also been suggested that a polynuclear complex is important in the coagulation process at low concentrations of aluminum. The complex, containing eight aluminum ions carrying a tetrapositive charge, takes the form of :

$$[Al_8(OH)_{20}]^{4+}$$

The hydrolysis of iron is similar to that of aluminum. Thus iron undergoes a series of hydrolytic and olation reactions with the formation of ferric hydroxo and polynuclear complexes. The hydrolytic type of reaction yields the following:

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5 OH]^{2+} + H_3O^+$$

Iron has a greater tendency than aluminum to polymerize through the olation reaction to form metal hydroxo polymers of the type (Walters, 1972):



One of the significant points that emerges from the study of these reactions is that both hydroxide and hydrogen ions are involved. Thus pH plays an important role in coagulation. The pH of the water is of primary importance in establishing the average charge of the hydrolysis products and consequently is significant in determining the rate of coagulation (Sastry, 1995). In addition to pH, the chemical composition of water also influences the species of complex produced, since negative ions other than hydroxide, particularly the di- and trivalent ions, may enter the complex and significantly change its properties. Thus in the presence of, for example sulfate, one or more sulfate ions may substitute for hydroxide ions in the manner shown below:

$$[Al(H_2O)_6]^{3+} + SO_4^{2-} \rightleftharpoons [Al(H_2O)_4\,SO_4]^{+} + 2H_2O$$

In this case, the divalent sulfate ion has substituted two hydroxide ions yielding a monopositive aluminum complex.

2.3.2 Flocculation

Flocculation is the second stage of the formation of settleable particles from destabilized colloidal-sized particles. This term also has its derivation from the Latin, *flocculare*, meaning to form a floc, which visually resembles a tuft of wool or highly fibrous porous structure. The mechanism of flocculation is different from coagulation, where the primary force is electrostatic or inter-ionic. Flocculation occurs by a chemical bridging or physical enmeshment mechanism. Flocculation is operationally obtained by gentle and prolonged mixing which converts the submicroscopic coagulated particles into discrete, visible, suspended particles. At this stage, the particles are large enough to settle rapidly under the influence of gravity and may be removed from suspension by filtration (Haney, 1956; Morales and Verela, 1994; Sastry, 1995).

2.3.2.1 Floc Formation Mechanism

The mechanism of floc formation in turbid waters can be explained from the physical and chemical behaviour of the colloids initially present and of the colloids formed from the external addition of aluminum or iron salts.

Turbid water contains dissolved and settleable solids, in addition to colloids that are electrically charged. The charges induce the formation of electrical double layers, and stability of the colloidal system is established by the forces of repulsion existing in the interaction between double layers (Sastry,1995).

Upon addition of aluminum or iron salts to the water, reactions with water and other ions occur, resulting in the production of multipositive hydroxo and polynuclear species of compounds. The coagulant species are rapidly adsorbed onto the surface of the turbidity particles, which ultimately become "coated" with coagulant. The electrostatic attraction between the negatively charged particles and the positively charged hydrolysis products enhances the deposition. The net result is that the electrical charges on the particles are reduced. Depending on pH and coagulant dose, the charge on the particle as measured by zeta potential may vary from slightly negative to neutral or to slightly positive. The suspension is considered to be destabilized and the process of flocculation, where the particles can agglomerate to settleable size, can proceed unhindered. Mixing or turbulence promotes collisions and as the particles have been destabilized, each collision results in a lasting union (Sen Gupta and Hashim, 1996).

In addition to the above process, that is dependent on electrostatic forces for adsorption and attraction, a purely physical or mechanical process may be taking place concurrently. Under the proper conditions for coagulation and even in the absence of turbidity, coagulants will hydrolyze and form progressively larger masses of flocculent materials. In the process of this formation, and during its settling when sufficient size has been attained, the floc may also physically enmesh the turbidity particles and simply act like a "sweep" as it settles. In any coagulation-flocculation system, both the electrostatic and enmeshment mechanisms play an important role (Hsiao-Wei et al., 1994).

A slightly modified mechanism has been suggested for the destabilization of hydrophilic colloids compared to the coagulation of hydrophobic particles. An important example is natural color in water. A characteristic of hydrophilic colloids is that they contain polar groups such as hydroxyl, carboxyl or phosphate groups that are negatively-charged. These colloids are thus able to combine chemically rather than by electrostatics, with the positively charged coagulant hydrolysis products forming an insoluble product that is electrically neutral or destabilized. The process of flocculation to settleable size then proceeds as described for hydrophobic colloids (Walters 1972).

Practically, the unit processes of coagulation-flocculation, sedimentation and filtration have been physically separated (Morales and Verela, 1994; Sastry, 1995). There have been efforts to condense these processes by reducing flocculation time and shortening or even eliminating the sedimentation basin, thus relying on the filters to replace the sedimentation process (Hudson, 1965).

2.3.3 Coagulant Aids

Coagulant aids improve floc properties formed by reaction of turbidity in water and wastewater with the hydrolysis products of trivalent aluminum or iron coagulants. Polymeric flocculants, termed polyelectrolytes or coagulant aids, are hydrophilic macromolecular compounds used in wastewater clarification primarily as a coagulant aid.

2.3.3.1 Types of Polymeric Flocculants

Polymeric flocculants may be inorganic or organic, natural or synthetic and cationic, anionic or non-ionic in nature. **Table 2.4** gives a scheme of classification of some well-known flocculants based on the origin of the compounds and their ionic character (Kitchener, 1972).

There is an enormous number and variety of natural and synthetic polymers potentially suitable for use in water and wastewater treatment. A wide range of natural polymeric flocculants have potential for use in water and wastewater treatment. However only three materials have been developed commercially. They are modified starch, sodium alginate and tannin (Carr, 1967).

Potato starch is a mixture of the polysaccharide amylopectin which are comprised of glucose units. Substitution in the glucose units enables modified starches to carrying either a positive or negative charge. Starch based polymers have

Table 2.4 Classification of Flocculants

Origin	Non-ionic	Anionic	Cationic	Amphoteric
Natural products	Gum guar, starch			Gelatin, albumen
Derivatives of natural products	Dextrin	Sodium alginate, phosphated starch sodium carboxy methyl cellulose		Cross-linked gelatin, aminated tannin
Synthetic polymers	Polyacrylmide Polyethylene oxide Polyvinylalcohol	Hydrolyzed polyacrylamide	Polyethyleninimine, inylpyridineacryl-amide co-polymers	

[a]Or substantially non-ionic: a trivial proportion of carboxylic acid (or phosphate) groups may be present.
(Kitchener, 1972)

molecular weights ranging up to 1 x 10^6. Alginate is obtained from seaweed. Certain seaweeds contain alginic acid, a long-chain polysaccharide comprised of L-guluronic acid and D-mannuronic acid. Alkaline treatment of the seaweed yields a crude alginate solution, which after suitable refining is marketed as powdered sodium alginate. The commercial tannin product is a partially condensed polymer of wattle tannin extract modified to produce active amine groups along the polymer molecule. It carries a positive charge and has a molecular weight of approximately 5 x 10^4 (Schaffer, 1963).

The synthetic polymers are based on polyacrylamide or polyacrylic acid or on acrylamide/acrylate co-polymers. The acrylamide based polymers have molecular weights ranging between 1 x 10^4 and 2 x 10^7. They may have anionic or cationic character, depending on whether hydrolysis of polyacrylamide or co-polymerization with sodium acrylate was employed or whether cationic esters of acrylic acid were involved. The important polymer characteristics are chain length, number and type of active groups (Schaffer,1963).

In addition to the organic polymeric flocculants referred to above, there are products based on aluminum, termed polyaluminium chlorides. Originally developed in Japan, they are compounds obtained by the partial neutralization of aluminum chloride. In use they behave in a similar nature to aluminum sulfate plus a polymer, giving more rapid flocculation and larger, more resilient floc. They are high molecular weight polymers (Packham, 1967).

2.3.3.2 Polymer Properties and Mechanism

Polymeric flocculants can act by either coagulation or flocculation or both of the above mechanisms, and certain cationic polymers may, in addition to coagulation and flocculation, form insoluble complexes with dissolved humic and fulvic acids. The three most important characteristics of polymeric flocculants influencing flocculation are the type of charge they carry, the charge density and the molecular weight.

Most suspended matter in water is negatively charged and it might be expected that cationic polymers would tend to be more effective than anionic polymers. However in practice this is not necessarily the case. When used in conjunction with primary coagulants whose initial hydrolysis products are positively charged, the relevance of polymer charge is uncertain, although differing results will be obtained using polymers with a range of characteristics. Classical particle charge neutralization is possible following electrostatic adsorption of polymers, reducing the surface potential and therefore the stability of the particles. The polymer potential determining ion is specifically adsorbed, resulting in coagulation (Hilson and Richards, 1980).

This mechanism, however, fails to explain the interaction of cationic polymers with negatively charged dispersed colloids where aggregation occurs despite minimal reduction in zeta potential, or the destabilization of negatively charged clays with non-ionic or anionic polymers where charge neutralization is impossible (Pressman, 1967). A polymer with high charge density is more likely to be extended than non-ionic polymers. For most applications, a coiled or condensed configuration is undesirable (Minz,1964).

Molecular weight or chain length can be crucial factor in flocculation. It is often found that polymers of a higher molecular weight give better results in sedimentation. High molecular weight polyacrylamide flocculants may consist of as many as 250000 monomer units and if fully extended can be several μm in length. When added to suspensions, the polymer chains are rapidly and irreversibly adsorbed. The longer the chain the greater will be the probability of bridging. Efficient polymer use therefore requires rapid and uniform dispersial of the flocculants solution in the water being treated. Extended polymeric molecules can be of a length comparable to, or well in excess of the dimensions of particles. Thus bridging between particles is possible with different segments of polymer being adsorbed on to the separate particle surfaces and acting as anchor points for the bridges.

Polymeric flocculants find application in primary treatment, in filtration and in sludge treatment and they may supplement, partially replace or even substitute conventional coagulants. In comparison to the dose of primary coagulant the required polymer dose may be very small; for example, the dose of acrylamide polymer required as a coagulant aid in sedimentation may be only 0.1mg/litre and in filtration only 0.01 mg/liter. The dose of polymer used may be critical and over dosing can result in severe problems particularly during filtration (Kruize, 1981; Letterman and Prasit, 1982). Excessive quantities of polymer have been shown to irreversibly stabilize colloidal suspensions. At low polymer concentrations, inter-particle bridging results in flocculation but at increasingly higher polymer concentrations the particle surfaces can become progressively covered with polymer, minimizing bridging and eventually stabilizing the suspension by protective colloid action. This protective action at higher polymer concentrations requires very careful attention to the control of polymer dosing in respect to the quantity of polymer added and the efficiency of polymer dispersion (Kruize, 1981). **Table 2.5** lists some of the advantages and disadvantages resulting from the use of polymeric flocculants in water treatment (Lewis, 1980).

Although progress has been made in the theory of colloid stability, the description of even relatively simple ideal systems requires complex mathematical formula and computer-aided calculations and the application of this theory to practical water systems is limited or inappropriate. Therefore, the destabilization processes that occur in water clarification, including the action of polymeric flocculants, is normally explained in quantitative terms.

2.3.3.3 Polymers as Primary Coagulants

The use of polymers as the sole coagulant has often been claimed to be highly effective. One of the advantages over the use of traditional inorganic hydrolyzing coagulants is that the amount of sludge produced for subsequent treatment and disposal is greatly reduced. Certain cationic polymers possess the ability to precipitate certain organic acids, which are the colored constituent of peaty upland waters. It has however, been found that the floc particles are capable of being toughened by the addition of a small dose of an anionic polymer in the same way as alum floc particles can be modified. The costs of such a process, however, may be several times the costs for similar color removal using aluminum sulfate, together with a small dose of an anionic coagulant.

Table 2.5 : Advantages and Disadvantages of Polymeric Flocculation in Water Treatment

Advantages	Disadvantages
Improved clarification as a result of larger, tougher, denser, more rapidly settling floc.	Polymer dose is often critical and therefore more attention must be given to the control of dosing.
Significant increases in plant throughput can be obtained.	Some polymers require special handling procedures to protect treatment plant operators.
Filtrate quality frequently improved, particularly residual turbidity and coagulant cation concentration.	Is poorly soluble requiring careful attention to ensure they are completely dissolved prior to use.
Certain polymers can replace or partially replace primary coagulant.	Polymers can be costly, often 50 times more expensive than primary coagulants.
Longer filter runs and less sludge may result.	Commercial products are seldom well characterized making polymer selection difficult and laboratory and plant evaluation essential.
Increased sludge solids concentrations and improved sludge dewatering characteristics can be obtained.	There is evidence that different batches of certain products may vary in physical and chemical characteristics.
Improved treatment efficiency at low temperatures may be possible.	

(Lewis, 1980)

So, unless improved cationic polymers are developed or the cost of the products reduced, there is little chance in the immediate future of such materials replacing in significant quantities the traditional hydrolyzing coagulants (Gregory, 1977).

2.3.4 Stability of Colloidal Suspension

It is necessary to consider the factors which cause particles to remain in suspension and that result in coagulation. Stability refers to the inherent property of colloidal particles to remain dispersed despite the passage of time, whereas instability describes the tendency of particles to coalesce whenever particle-to-particle contact is made. Two theories have been proposed to explain the mechanisms involved. The chemical theory assumes that colloids acquire electrical charges on their surfaces by ionization of chemical groups present at the surface and that coagulation or destabilization is accomplished by chemical interactions between colloid particles and coagulant. The physical theory, on the other hand, emphasizes such physical factors as electrical double layer and counterion adsorption where destabilization occurs through reduction of forces such as zeta potential. It now appears that the mechanisms are not mutually exclusive and both theories are applicable in the process of coagulation in wastewater plant systems where a heterogeneous mixture of colloid systems exists (Gregory, 1977).

2.3.4.1 Stability Forces

The objective of coagulation is to destabilize particles to permit formation of aggregates. In hydrophilic colloid systems, stability is maintained by the phenomenon of hydration. Water molecules are attracted to the surface of the particles and act as a barrier of contact between particles.

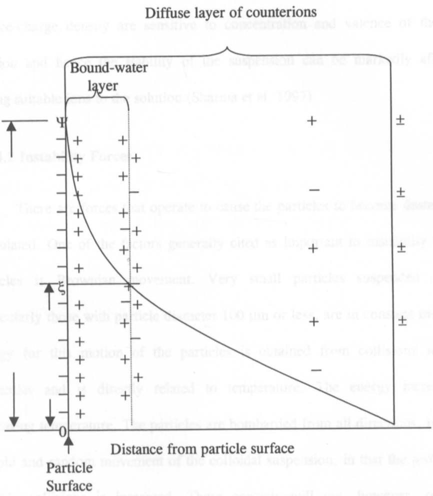
The stability of hydrophobic particles is due largely to the phenomenon of the electrical double layer consisting of the charged-particle surface and a surrounding sheath of ions charge opposite to that of the particle surface. Several theories have been advanced to quantitatively describe the concept of the electrical double layer. The theory states that hydrophobic particles suspended in water carry electrical charges at their surfaces. For particles in natural waters, the charge is usually negative. These electrical charges may arise through ionization of atoms at the particle surface, by replacement of elements in a crystal lattice, by elements having a different charge or particles may acquire the charge through adsorption of ions, particularly hydroxide ions, from the water itself. These ions are tightly bound to the surface of the particle and attract ions of opposite charge from the mixture of positive and negative ions in the water. This layer of oppositely charged ions (called "counterions") is held near the particle surface into the bulk solution. As shown in **Figure 2.2**, the potential decays exponentially from the particle surface and eventually becomes zero where equal concentrations of cations and anions are present (Grantham, 1992).

Particles in water are not considered as discrete portions of matter suspended or moving in a liquid. Each particle is a complicated entity consisting of several components in addition to the primary particle. Several distinct layers can be described. These are schematically illustrated in **Figure 2.2.** The particle surface is shown as a plane containing negatively charged ions. Cations from the bulk solution are attracted to this surface. At increasing distances from the particle, the forces of attraction quickly decrease, and there arises a diffuse layer of ions trailing out into the bulk solution. At some distance from the particle and within the diffuse layer there is a plane of shear representing the portion of bound water and ions that will remain attached to the particle as it moves through the suspending liquid. The bound-water layer can be considered as an integral part of the charged-particle surface (Grantham, 1992).

A consequence of the electrical double layer surrounding each particle in water is to create regions of electrical potential in a bulk solution that nominally has a zero potential. The electrostatic work required to transport a unit charge from this bulk solution through the phase boundaries of each layer surrounding a particle to any point measures the potential at that point. The potential increases sharply with increasing approach to the primary particle surface. The potential at the surface of the particle, also called the "total potential" or Nernst potential, is represented by Ψ (Wang and Wen, 1998). For certain surfaces of known composition, Ψ can be calculated. However, its value is unobtainable for impure colloids of interest in water and wastewater treatment. The second potential of interest is called the "zeta potential" (ζ) and is located at the "plane of shear", that is, at the boundary between the solvent adhering to the particle in its motion and that which can move with respect to it. This "plane of shear" essentially separates the water of hydration from free water.

The zeta potential is the electrical potential in the slipping plane between the fixed and flowing liquid. The slipping plane is located somewhere in the liquid and not exactly at the solid-liquid phase boundary. When an electric field is applied across an electrolyte, charged particles suspended in the electrolyte are attracted towards the electrode of opposite charge. Viscous forces acting on the particle tend to oppose this movement and when an equilibrium is reached the particles move with constant velocity. The velocity is dependent on the strength of the electric field or voltage gradient, the dielectric constant and the viscosity of the medium and the zeta potential. The particle velocity in a unit electric field and is referred to as its electrophoretic mobility.

Approximate values of zeta potentials can be calculated from easily measured electrophoretic mobilities. Zeta potential does not measure the total potential, but only a portion of it. Zeta potential is important because it is related to particle stability (Hunter, 1981).



Note: ψ is at the particle surface, and ξ is at the hydrodynamic plane of shear. (Grantham, 1992)

Figure 2.2. : Structure of a double layer and the corresponding potentials.

The net effect of the existence of electrical double layers around particles is to inhibit the close approach of particles to each other, and hence the double layers confer stability to the suspension. Both the thickness of the double layer and the surface-charge density are sensitive to concentration and valence of the ions in solution and hence the stability of the suspension can be markedly affected by adding suitable ions to the solution (Sharma et al. 1997).

2.3.4.2 Instability Forces

There are forces that operate to cause the particles to become destabilized or coagulated. One of the factors generally cited as important to instability of colloid particles is Brownian movement. Very small particles suspended in water, particularly those with particle diameter 100 μm or less, are in constant motion. The energy for this motion of the particles is obtained from collisions with water molecules and is directly related to temperature. The energy increases with increasing temperature. The particles are bombarded from all directions, resulting in a rapid and random movement of the colloidal suspension, in that the probability of particle collisions is increased. These contacts will not, however, result in a sufficient number of lasting unions unless the colloidals have already been destabilized. Moreover, for larger particles, Brownian movement becomes a negligible factor (Grantham, 1992). A more effective way of promoting particle collisions is to establish hydraulic gradients by mixing or by creating areas of turbulence.

Another force of attraction between particles and leads ultimately to instability is the London-Van der Waals force. It is an atomic cohesive force and exists between all atoms. This force is generally considered to operate within distances of the order of atomic dimensions for colloidal particles. The aggregate effect of the attractive force is to extend the range of effectiveness to the order of colloidal dimensions.

If the electrical forces of repulsion between particles are sufficiently reduced to permit particle-to-particle contact, then the London-Van de Waals force will cause particles to stick to each other, leading to progressive agglomeration of particles.

Because an approximate value for the zeta potential of particles is readily determined by electrophoretic mobility measurements, attempts have been made to correlate zeta potential with coagulation. Experimental evidence generally leads to the conclusion that coagulation of colloids in water is often obtained well before complete reduction of the zeta potential to zero, the value generally ranging from -5 to -10 mV or less. This lack of exact correlation of zeta potential and coagulation is explainable. As indicated in **Figure 2.2,** the zeta potential denotes the potential at the "plane of shear" between the particle complex and the bulk solution; but the forces of attraction extend appreciably beyond this point, so that a measurement of zeta potential cannot be a complete indication of stability. However, an empirical relationship can often be established between zeta potential and instability or coagulation (Grantham, 1992). This experimentally derived value then becomes useful to control the coagulation under those specific conditions. The optimum zeta potential value is usually negative with the usual systems in water (Sen Gupta and Hashim, 1996).

2.3.5. Factors Influencing Coagulation

2.3.5.1. Effect of Coagulant

The type of coagulant selected greatly influences the effectiveness of the wastewater plant. While alum is by far the most commonly used coagulant, iron salts can be used as well and in some instances have advantages over alum. The significant advantage of iron salts over aluminum is the boarder pH range for good coagulation. Thus, in the treatment of soft colored waters where color removal is required, the use of iron salts is preferable. The greater insolubility of ferric hydroxide at alkaline pHs, in contrast to aluminum salts which form soluble aluminate ions at basic pHs, suggest that iron salt should be considered under these conditions. Sodium aluminate is, however, used for coagulation of softening precipitates at high pH. For alum, the pH zone for optimum coagulation is quite narrow, ranging from about 5 to 7; the comparable range for ferric sulfate is considerably broadened, to a pH range of 8 to 11 (Sen Gupta and Hashim, 1996; Sastry, 1995).

2.3.5.2 Effect of Mixing

Two stages of mixing or other means to create turbulence are generally used in a wastewater plant. Rapid mixing to distribute the coagulant throughout the water being treated is frequently called "flash mixing." This rapid mixing is essential to uniformly disperse the coagulant and to promote collisions of coagulant particles with turbidity particles. Such high turbulence conditions should be maintained for 30 to 60 seconds, at the end of which the coagulant is hydrolyzed and adsorbed on the turbidity particles (Sastry, 1995).

The second stage of floc growth or flocculation is accomplished by gentle stirring. Immediately following the addition of coagulant and during the flash mixing step, coagulation and precipitation produce finely divided suspensions. In a quiescent fluid, Brownian movement and the differences in settling velocities of various-sized particles would result in ever-increasing size of floc. But floc growth can, however, be hastened by stirring the water. This increases the number and opportunities for particle contact by collision. The degree of agitation must be great enough to keep the floc particles suspended and in motion, but not too great that the floc is disintegrated by shearing forces. This process is called "flocculation." Detention times between 20-60 minutes are frequently adequate to produce a floc that will settle in a reasonable time (Sen Gupta and Hashim, 1996).

2.3.5.3 Effect of pH

pH plays an important role in determining effectiveness of the coagulant selected for the wastewater treatment. The important aspect of coagulation with aluminum salts is the solubility of $Al(OH)_3$, which depends on the pH and is low in the pH range of 5.0 – 7.5. When using ferric salts such as $FeCl_3$ and $Fe_2(SO_4)_3$, the pH of water should be more that 4.5. A Ferrous salt such as copperas, $FeSO_4$, is only effective at pH more than 9.5. It is customary to add lime while using copperas to maintain the alkalinity of the solution (Sen Gupta and Hashim, 1996; Sastry 1995).

2.4 Adsorption in Wastewater Treatment

Adsorption is a process mainly used for removal of small amounts of non-biodegradable toxic or potentially bio-accumulating compounds. Activated carbon is a popular choice as an adsorption material. It has a relatively non-polaric character and is well suited for the removal of non-polaric organics (Sastry,1995). Granulated carbon has been widely used in filters. Powdered activated carbon has also been used together with flocculants. Activated carbon are made from different plants, animal residues and bituminous coal. Gharaibeh et al. (1998) reported that some types of carbon may be more suitable compared to others depending on the type and composition of wastewater.

2.4.1 Adsorption in Color Removal

Dyeing and finishing wastewaters in the textile industry have high color and organic content. Many researchers have reported color removal using different methods with varying degrees of successful removal. Davis et al. (1982) reported significant color removal using hydrogen peroxide at pH 12. Grau (1991) in his study reported that chlorine efficiency of color removal was higher at low pH whereas color removal using ozone was independent of pH. Ganjidoust et al. (1995) used various minerals and found that a rise in temperature lowered adsorption efficiency. Most researchers found that removal of color with carbon is most successful (Gharaibeh et al., 1998; Yeh et al., 1993; Meyer et al., 1992). Adsorption varies with the type and forms of carbon. Activated carbon and other forms such as wood charcoal gives different results (Davis et al.,1982; Yeh et al., 1993; Mehrotra et al.,1995).

2.4.2 Adsorption in Surfactant Removal

Atsuko et al. (1990) reported that both anionic and nonionic surfactant could be removed by adsorption. They reported that the efficiency of removal was 80 % for anionic surfactant and 70 % for nonionic surfactant using activated carbon. However, the same study using coagulation precipitation with calcium hydroxide and ferrous sulfate could only remove 50% of anionic surfactant and gave no reduction of nonionic surfactants. However, Dhileepan and Kumar (1995) found that carbon adsorption was unsuccessful in treating surfactant wastewater to reduce COD and BOD to the desired level of COD lower than 100 mg/l and BOD lower than 50 mg/l.