CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Superabsorbent polymers (SAPs)

2.1.1 Physical behavior of superabsorbent polymers

Superabsorbent polymers are crosslinked networks of flexible polymer chains characterized by both hydrophilicity and insolubility in water. They are interesting materials exhibiting both liquid-like and solid-like properties. The liquid-like properties result from that the major constituent of gels is usually a liquid. On the other hand, a gel can retain its shape since it has a shear modulus which becomes apparent when the gel is deformed. The modulus is due to the crosslinking of the polymers in the form of a network. They have the ability to absorb and hold large amounts of water. Their hydrophilicity increases because of water-solubilizing groups, such as –OH, -COOH, -$CONH_2$, -CONH-, -SO_3H, and so on. The insolubility increases from the presence of a three dimensional network. The crosslink may be covalent, electrostatic, hydrophobic, or dipole-dipole in character [11]. Superabsorbent polymers can be neutral or ionic in nature. The water absorption may exceed a factor of 100 based on dry gel weight. Superabsorbent polymers take up liquid by a diffusion mechanism whereas traditional absorbents, like cotton, show a convective mechanism. Diffusion is a molecular phenomenon wherein molecules move at random as a result of their thermal energy. Increasing the temperature makes the molecules move faster, and the diffusion processes occur at a faster rate.

Water moves into a particle of superabsorbent polymers because the activity of water is initially lower in the interior of the particle. As water diffuses into the particle, the particle volume increases and the polymer chains that form the superabsorbent polymer network must also move, generally in the direction opposite to that of the water molecules in order to accommodate the volume of the additional molecules of water. Because polymer molecules are much larger than water molecules, they diffuse much more slowly. Not only are polymer molecules larger, but they are also connected one to the other by the crosslinks, so that the polymer does not dissolve in the water and use as a superabsorbent [12].

2.1.2 Mechanism of swelling of superabsorbent polymers

When the superabsorbent polymers contact with water, the hydrophilic polymer backbone interacts with the solvent accompanied by energy decrease and entropy increase. Hydration and the formation of hydrogen bonds are two sources for such polymer/solvent interactions. The polymer chains also tend to disperse in the solvent. This leads to a higher number of allowed configurations for the system, which is equivalent to a higher degree of entropy.

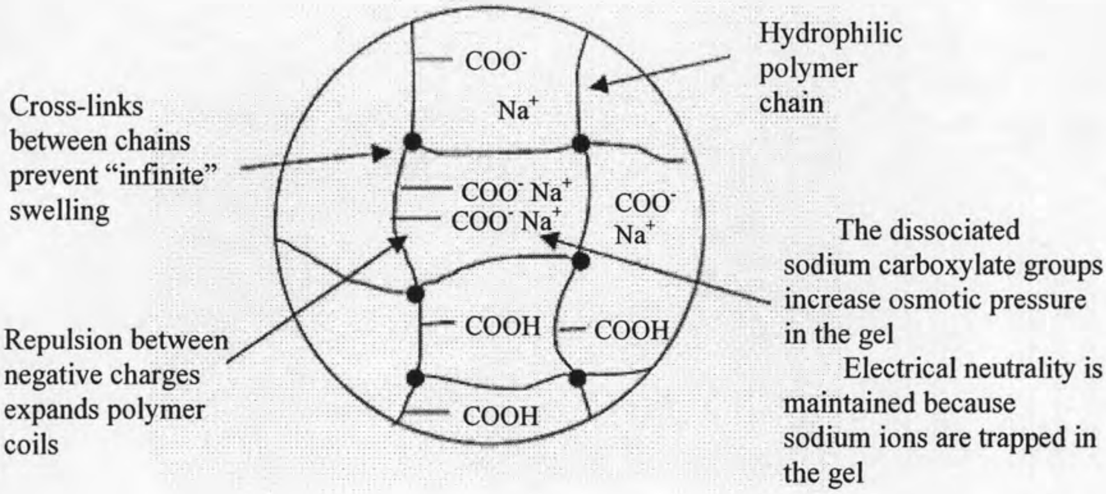

Figure 2.1 Mechanism of swelling of superabsorbent polymers

Due to that the presence of the crosslink polymer chains are restricted in swelling by elastic retraction forces of the network, the more chains separate from each other, the more stiffened the coiled polymer chains become. This decreases the entropy of the chains. Finally there is a balance between the infinite dilution of the chains and the retractive forces. Higher crosslink densities give network with stronger retractive forces and superabsorbent polymers with a lower degree of swelling at equilibrium.

For ionic polymers, there is the solvent/polymer interactions include more simple mixing term. These gels bear electrical charges along the polymer chains. The negative charge of the carboxyl groups repel one another and are compensated for the positive charges of the sodium ions, in order to maintain electrical neutrality. When the polymer contacts with water, the solvent diffuses into the polymer network and solvates the sodium ions. Water with high dielectric constant lowers the attractive forces between the sodium ions and the negative charge of carboxylate groups. As in salt solutions, the sodium ion are released and become freely moveable within the gel. The mobile positive sodium ions cannot leave the gel because they are still weakly attracted to the negative carboxylate ions along the polymer backbone and so behave like they are trapped by a semi-permeable membrane. So the driving force for swelling is the difference between the osmotic pressure inside and outside the gel. Increasing the salinity outside of the gel will lower the osmotic pressure and reduce the swelling capacity of the gel. The maximum swelling of the gel will occur in deionised water [13].

2.1.3 Factors affecting the swelling of ionic hydrogel

2.1.3.1 Effect of ionic content

Since increasing in ionic content in SAPs increases the hydroplilicity, therefore, the higher equilibrium swelling can occur. Anionic or cationic SAPs containing the carboxylic groups swell at pH which is higher than the pK_a of the gel due to ionization. Opposite behavior is observed in the case of cationic or basic gels containing amine groups. For the gel containing both acidic and basic groups (called ampholyte), an isoelectric pH is the deciding factor [14].

2.1.3.2 Effect of ionization equilibrium

The degree of ionization of ionizable groups in the polymer is controlled by the pK_a of the gel. At equilibrium swelling, the chemical potential of the ion inside and outside (external swelling medium) of the gel is equal. In addition, the electroneutrality condition also applied inside the gel as well as in the external swelling medium. The presence of fixed charges on the polymer chains excludes any sorption of co-ion because of the electroneutrality. The concentration of counterions is always higher in the gel phase than that in the external swelling medium which resulting in the electrostatic potential difference between the two phases. The internal counterion concentration is high when the gel has a high content of ionizable groups and is highly crosslinked. Therefore, the efficiency of co-ion exclusion increases with decreasing the concentration of solution and increasing the ionic content and degree of crosslinking [14].

2.1.3.3 Effect of ionic interaction

The various kind of ionic interaction in the gel affect the counterion concentration inside the gel. In the ionic gel, ion pair formation between counterion and fixed charge on the polymer chain can localize the counterion and reduces the co-ion exclusion efficiency.

In the case of multivalent counterions, they associate strongly with the fixed ionic groups. The transformation of anionic to cationic in the gel can occur by complex formation which affects the swelling properties [14].

2.1.3.4 Effect of electrostatic attraction

The interaction between counterions and fixed ionic groups is electrostatic attraction of two opposite charges. The strength of the interaction depends on the ionic charge and the distance between the counterion and fixed ionic groups. The higher valence counterions are more strongly because the electrostatic attraction is proportional to the ionic charge and inversely proportional to the square of the distance between charges [14].

2.1.4 Application of superabsorbent polymers

Since the superabsorbent polymers (SAPs) have excellent properties, absorb and hold a large amount of water, therefore, they have been used in many different applications. The most application of SAPs are in the personal hygiene products including disposable infant diapers, adult incontinence product, and feminine sanitary napkins. These products must hold the liquid under pressure from the babies or adults.

In addition, SAPs are used to release the water to the surrounding as vapor in the agriculture and horticultural application, such as soil additives.

Pharmaceuticals and fertilizers may be incorporated into SAPs to produce controlled release products that release water-soluble substances from within the network structure into solution surroundings.

In a wastewater treatment process, SAPs were used as flocculants, such as polyacrylamide and its copolymer. Moreover, polymeric flocculant which called microparticle/polymer flocculants have been attractive because they give better flocculation than conventional polymer systems.

Another characteristic of SAPs is rubbery nature that employed the sealing properties for electrical and optical cables [12, 13]. The summarized application of SAPs is shown in Table 2.1.

Table 2.1 The applications of SAPs

Application Fields	Products
1. Personal hygiene products	- infant diapers - adult incontinence product - feminine sanitary napkins
2. Agriculture	- soil conditioner - seed coating
3. Medical	- contact lenses - blood compatible hydrogel - wound dressings, plasters
4. Food packaging	- agents for preservation of freshness of vegetable and fruit storage packaging
5. Electronic and cabling	- water- blocking tapes for cables (prevent water penetration into the cable)
6. Water absorbing construction materials	- water-blocking construction filler - concrete additive
7. Controlled release	- delivery systems for pharmaceuticals - reservoir for insecticide
8. Wastewater treatment	- polymeric flocculants

2.2 Preparation of superabsorbent polymers

Several techniques have been reported for the synthesis of hydrogels: free radical polymerization and step polymerization. The monofunctional and multifunctional monomers are mixed together and the polymerization reaction is initiated by chemical initiator. Crosslinks are formed as multifunctional monomers which are incoporated into two or more growing chains. Some of the commonly crosslinking agents include *N, N'*-methylenebisacrylamide, divinyl benzene, and ethylene glycol dimethacrylate. The polymerization reaction can be carried out in bulk, in solution, or in suspension. Moreover, crosslinking of linear polymers by irradiation is used in the preparation of the ionic polymer network containing an ionizable group [14]. The monomers and the crosslinking agents used in the preparation of hydrogels are given in Table 2.2.

Table 2.2 Structure of monomers used in the preparation of SAPs

Types of monomers	Name
1. Ionic monomers	
1.1 Anionic monomers	Acrylic Acid Methacrylic Acid
1.2 Cationic monomers	Vinyl pyridine 2-methacryloyloxy- trimethylammonium chloride
1.3 Neutral monomers	Acrylamide 2-hydroxyethyl methacrylate
2. Polyfunctional crosslinking monomers	*N,N'*-methylenebisacrylamide Ethylene glycol dimethacrylate

2.2.1 Bulk polymerization

Bulk polymerization is the simplest technique which involves only monomer and monomer-soluble initiators. High rate of polymerization and degree of polymerization occur because of the high concentration of monomer. However, the viscosity of reaction increases with the conversion which generates the heat during polymerization. These problems can be avoided by controlling the reaction at low conversions.

The advantage of bulk polymerization is that it produces high molecular weight polymer with high purity.

2.2.2 Solution polymerization/crosslinking

In solution co-polymerization/crosslinking reactions, the ionic or neutral monomers are mixed with the multifunctional crosslinking agent. The polymerization is initiated thermally, by UV-irradiation, or by a redox initiator system. The presence of solvent serves as heat sink is the major advantage of solution over bulk polymerization. The prepared hydrogels need to be washed with distilled water to remove the unreacted monomers, oligomer, crosslinking agent, the initiator, and other impurities. The phase seperation occurs and the heterogeneous hydrogel is formed when the amount of water during polymerization is more than the water content corresponding to the equilibrium swelling [14]. The best example is preparation of poly(2-hydroxyethyl methacrylate) hydrogels from hydroxyethyl methacrylate, using ethylene glycol dimethacrylate as crosslinking agent. Using this method, a great variety of hydrogels have been synthesized [15]. The hydrogels can be made pH-sensitive or temperature-sensitive by incorporating methacrylic acid [16], or *N*-isopropylacrylamide as monomers [17].

2.2.3 Suspension polymerization

Suspension polymerization is method to prepare spherical hydrogel microparticles with size range of 1 μm to 1 mm. In suspension polymerization, the monomer solution is dispersed in the non-solvent forming fine droplets, which are stabilized by the addition of stabilizer. The polymerization is initiated by thermal decomposition of free radicals. The prepared microparticles then washed to remove unreacted monomers, crosslinking agent, and initiator. Hydrogel microparticles of poly(vinyl alcohol) and poly(hydroxy ethyl methacrylate) have been prepared by this method [14].

2.2.4 Polymerization by irradiation

The high energy radiation, like gamma and electron beam, has been used to prepare the hydrogels of unsaturated compounds. The irradiation of aqueous polymer solution results in the formation of radicals on the polymer chains. Also, radiolysis of water molecules results in the formation of hydroxyl radicals, which also attack the polymer chains, resulting in the formation of macroradicals. Recombination of the macroradicals on different chains results in the formation of covalent bonds, and finally a crosslinked structure is formed. Examples of polymers crosslinked by radiation method are poly(vinyl alcohol), poly(ethylene glycol) and poly(acrylic acid). The major advantage over chemical initiation is the production of relatively pure and residue-free hydrogels.

2.3 Characteristics of the polymerization

2.3.1 Monomer concentration

The monomer concentration in the polymerization mixture is one of the key parameters affecting both the properties and the economics of the process. Higher monomer concentrations allow higher throughputs and require less energy for drying the polymer.

Polymerization at high temperature favors the termination step of the propagating radical chains, which leads to the low molecular weight. On the other hand, grafting reaction can occur preferably at higher polymer concentrations and temperatures. When the monomer concentration is high, the polymerization is achieved at lower conversion and the reaction temperature may increase more rapidly due to the lower heat capacity of polymer compared to water [3].

2.3.2 Initiator

The polymerization is initiated by free radicals in the aqueous phase using thermal initiators, redox initiators or combinations. Redox systems used for the crosslinking polymerizations include the couples of persulphate/bisulfite, persulphate/thiosulphate, persulphate/ascorbate and hydrogen peroxide/ascorbate. Thermal initiators include persulphates, 2,2'-azobis-(2-amidinopropane)-dihydrochloride and 2, 2'-azobis-(4-cyanopentanoic acid). Combinations of initiators are used when the polymerization takes place over a board temperature range. Appropriate concentrations of multi-initiators can achieve the desired constant rate of polymerization [13, 18].

2.3.3 Neutralization

The acrylic acid usually is partially neutralized before the polymerization is initiated, but the crosslink polymer can be neutralized after polymerization is completed. Usually, sodium hydroxide and sodium carbonate are used as the neutralizing agent [3].

2.3.4 Crosslinking agent

Crosslinking is the formation of chemical links between molecular chains to form a three-dimensional network. The small amounts of crosslinking agents play the major role in modifying the properties of superabsorbent polymers. The crosslinking agents typically used in the superabsorbent polymers are di-, tri-acrylate esters such as diethylene glycol acrylate and 1,1,1,-trimethylolpropanetriacrylate. In addition to modify the swelling and mechanical properties, the crosslinking agents are used. The crosslinking agent affects the amount of soluble polymer formed during the polymerization. The tendency of a crosslinking agent to be depleted earlier in the polymerization is reflected in its reactivity ratio with the monomer. The degree of crosslinking and the details of the molecular structure quantified in terms of the crosslink density which have a profound impact on the swelling characteristics of the crosslinked system [3].

2.3.4.1 Chemical crosslinked hydrogels

Polymers containing functional groups like -OH, -COOH and -NH_2 are soluble in water. The presence of these functional groups on the polymer chain can be used to prepare hydrogels by forming covalent linkages between the polymer chains and complementary reactivity, such as amine-carboxylic acid and isocyanate-OH/NH_2.

Polymers that are water soluble can be converted to hydrogels, using bi- or higher-functional crosslinking agents like divinylsulfone, and 1,6-hexanedibromide. The crosslinking agents react with the functional groups present on the polymer, via addition reaction. These crosslinking agents are highly toxic, and hence unreacted agents have to be extracted. Moreover, the reaction has to be carried out in organic solvent, as water can react with the crosslinking agent. The drugs have to be loaded after the hydrogels are formed, as a result the release will be typically first order.

Crosslinking between polymers through hydrogen bond formation occurs as in the case of poly(methacrylic acid) and poly(ethylene glycol). The hydrogen bond formation takes place between the oxygen of poly(ethylene glycol) and carboxylic acid group of poly(methacrylic acid).

2.3.4.2 Physical crosslinked hydrogels

Most of the covalent crosslinking agents are known to be toxic, even in small traces. A method to overcome this problem and to avoid a step of purification, is the prepare hydrogels by reversible ionic crosslinking. Chitosan, a polycationic polymer can react with positively charged components, either ions or molecules, forming a network through ionic bridges between the polymeric chains. Among anionic molecules, phosphate bearing groups, particularly sodium tripolyphosphate is widely studied.

Ionic crosslinking is a simple and mild procedure. In contrast to covalent crosslinking, no auxiliary molecules such as catalysts are required. Chitosan is also known to form polyelectrolyte complex with poly(acrylic acid). The polyelectrolyte complex undergoes slow erosion, which gives a more biodegradable material than covalently crosslinked hydrogels.

2.4 Wastewater treatment process

2.4.1 Coagulation and flocculation

In wastewater treatment operations, the processes of coagulation and flocculation are employed to separate suspended solids from water.

Finely dispersed solids (colloids) suspended in wastewaters are stabilized by negative electric charges on their surfaces, causing them to repel each other. Since this prevents these charged particles from colliding to form larger masses, called flocs, therefore they do not settle. To assist in the removal of colloidal particles from suspension, chemical coagulation and flocculation are required. These processes, usually done in sequence, are a combination of physical and chemical procedures.

Chemicals are mixed with wastewater to promote the aggregation of the suspended solids into particles large enough to settle or be removed.

Coagulation refers to the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs). Rapid mixing is required to disperse the coagulant throughout the liquid. Overdose the coagulants can cause a complete charge reversal and restabilize the colloid complex [18]. The advantages and disadvantages of inorganic coagulants are given in Table 2.3.

Table 2.3 The advantages and disadvantages of inorganic coagulants

Inorganic coagulants	Advantages	Disadvantages
Aluminium sulphate (alum)	Easy to handle and apply, most commonly used, most effective between pH 6.5 and 7.5	Adds dissolved solids (salts) to water, effective over a limited pH range
Sodium aluminate	Effective in hard water, small dosage usually needed	Often used with alum, high cost, ineffective in soft water
Ferric sulphate	Effective between pH 4-6 and 8.8-9.2	Adds dissolved solids (salts) to water, usually need to add alkalinity
Ferric chloride	Effective between pH 4 and 11	Adds dissolved solids (salts) to water, consumes twice as much alkalinity as alum
Ferrous sulphate	Not as pH sensitive as lime	Adds dissolved solids (salts) to water, usually need to add alkalinity
Lime, $Ca(OH)_2$	Commonly used, very effective, may not add salts to effluent	Very pH dependent, produces large quantities of sludge, overdose ca result in poor quanlity

Flocculation refers to the action of polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregate. An anionic flocculant will react against a positively charged suspension, adsorbing on the particles and causing destabilization either by bridging or charge neutralization. In this process, it is essential that the flocculating agent be added by slow and gentle mixing to allow for contact between the small flocs and to agglomerate them into larger particles. The newly formed agglomerated particles are quite fragile and can be broken apart by shear forces during mixing. Anionic polymers are lighter than water. As a result, increasing the dosage will increase the tendency of the floc to float and not settle.

Once suspended particles are flocculated into larger particles, they can usually be removed from the liquid by sedimentation, provided that a sufficient density difference exists between the suspended matter and the liquid. Such particles can also be removed or separated by filtration, straining or flotation.

2.4.2 Hydrolysis of aluminium salts

Hydrolyzing metal salts, based on aluminium or iron, are widely used as coagulant in water treatment. They play a vital role in the removal of many impurities from polluted waters including inorganic particles, such as clays and dissolved natural organic matter.

The titration of aluminium salts with base as shown in Figure 2.2 gives four forms of product depending on the degree of neutralization value, B [19].

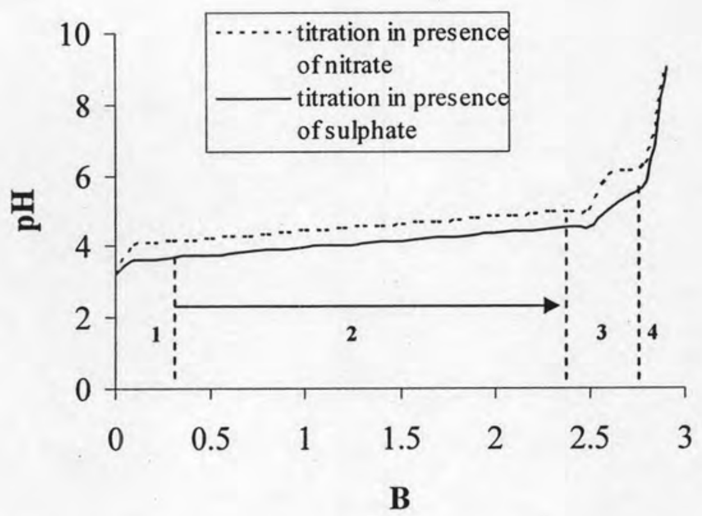

Figure 2.2 The titration curves for neutralization of aluminium salt solutions

1. At monomeric products (region 1), the B value is less than 0.25. The value of pH increases rapidly because the base neutralize free acid by spontaneous hydrolysis, such as $AlOH^{2+}$, $Al(OH)_2^+$

2. At polynuclear species (region 2), the B value is in the range of 0.25-2.4. The pH increases slowly (about 4) since added base is consumed by hydrolysis, for example $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$

3. At precipitate formation (region 3), the B value is in the range of 2.4-2.8. Amorphous $Al(OH)_3$ can be formed and precipitation occurs rapidly.

4. For the value of B above 2.8 (region 4), the added base reduces the positive charge of hydroxide particles. Further addition of base gives a rapid increase in pH.

2.4.3 Polymeric flocculants

Polymeric flocculants are very widely used in many industrial applications, such as water and wastewater treatments, paper making, thickening and dewatering, mineral processing and others.

In the recent years, polymeric flocculants have been particularly attractive. Polymeric flocculants may be anionic, cationic, or non-ionic, depending on the application. Many flocculation systems have been developed including single polymer systems [9], dual polymer systems [5] and microparticle/polymer flocculants [10]. The most common is the single polymer systems based on polyacrylamide, with molecular weights up to about 20 million. However, there are many applications which low molecular weight polyelectrolytes are effective. High molecular weight linear polymers are effective because they are able to bridge particles together [13].

Today there are a lot of polymeric flocculants commercially available for the applications. Polyacrylamide and their copolymers are the most common product used. [18].

2.4.4 Mechanism of polymer flocculation

1. Bridging flocculation

Polymer bridging occurs because segments of polymer chain adsorb on different particles and link the particles together. The floc of bridging flocculation can be much stronger than destabilized particles by simple salts. Binding by polymer chains gives stronger attachments between particles than by Van der Waals attraction.

In order to form effective bridging, there must be sufficient adsorbed polymer which extends far enough from the particle surface to attach other particles as shown in Figure 2.3. When excess polymer is adsorbed, bridging flocculation becomes less effective and the particle can be restabilized. At low concentrations, there is insufficient polymer to provide adequate bridging links and a large amount of restabilization can occur.

However, it is found that anionic polymers are able to flocculate negatively charged particles. In these systems, counterions (such as Ca^{2+}) are required to facilitate the bridging of anionic polymer segment onto the negatively charged surface. Counterions act as "bridges-with-bridges" to induce the flocculation [20].

Many commercial polymeric flocculants are used, such as anionic and cationic polyelectrolytes. They can form bridging flocculation by charge neutralization. The presence of charge segments along a polymer chain has a significant effect on bridging flocculation [13].

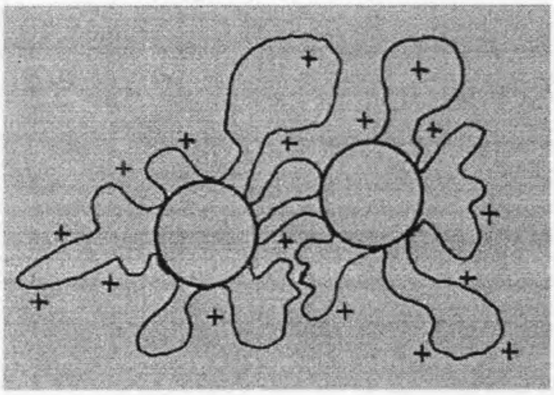

Figure 2.3 Bridging flocculation of colloidal particles by polymeric flocculants

2. Charge neutralization

Particles in a wide range of industrial suspensions are negatively charged. The most effective flocculants are often found to be cationic polyelectrolytes, which adsorb strongly on opposite charged particles. However, both charge density and molecular weight of cationic polymers play important roles. High molecular weight cationic polymers, such as dimethylaminoethyl methacrylate (DMAEMA) are prepared as copolymers of acrylamide.

3. Electrostatic patch effect

When particles with low negative surface charge densities adsorb highly charged cationic polymers, it may not be physically for each surface charge to be neutralized by cationic polymer segment. The distance between surface sites may be less than that between cationic sites along the polymer chain. In such cases, although charge neutralization may occur, there will be local heterogeneity of charge, giving an electrostatic patch arrangement, as shown in Figure 2.4. The attraction caused by patchwise adsorption can give stronger flocs than those produced by simple salts. These effects are dependent on ionic strength, since increasing of salt concentration causes the electrical attraction between opposite charge to be reduced.

A useful combination of charge effect and bridging interaction can be achieved by a dual polymer system, especially in paper making applications.

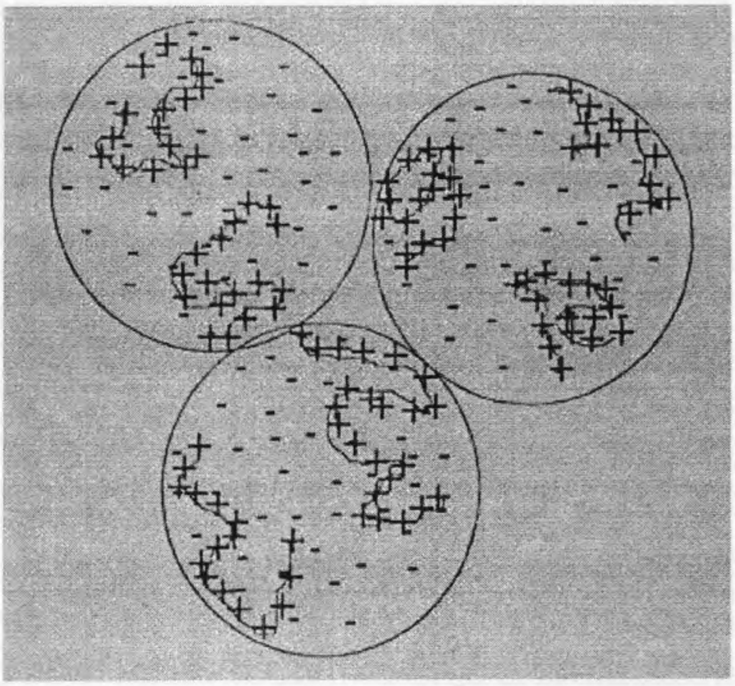

Figure 2.4 Electrostatic patch interactions

2.5 Adsorption mechanism

The adsorption is a process which atoms or molecules move from a bulk phase (that is solid, liquid, or gas) onto a solid or liquid surface. An example is purification by adsorption where impurities are filtered from liquids or gases by their adsorption onto the surface of a high-surface-area solid such as activated charcoal [21].

Adsorption distinguished from absorption, a process in which atoms or molecules move into the bulk of a porous material, such as the absorption of water by a sponge. Sorption is a more general term that includes both adsorption and absorption.

Molecules that have been adsorbed onto solid surfaces are referred to generically as adsorbates, and the surface to which they are adsorbed as the substrate or adsorbent.

2.5.1 Adsorbent

Generally, the adsorbent must have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties. That is it must be capable of transferring adsorbing molecules rapidly to the adsorption sites. In the most applications, the adsorbent must be generated after use and the regeneration can be carried out and without damage the adsorptive properties. The raw materials and method for producing adsorbents must be inexpensive and give the high efficiency for adsorption process. There are many types of adsorbents as follows:

Activated carbon

Carbonaceous materials have been known to provide adsorptive properties. At the earliest application, activated carbons could be used to remove tastes, colors and odours from water. Now they are used widely in industrial applications such as solvent recovery, hydrogen purification and water treatment. The activated carbons comprise elementary microcrystallites stacked in random orientation and are made by the thermal decomposition of various carbonaceous materials followed by an activation process.

Polymeric adsorbents

A board range of synthetic, non-ionic polymers is available particularly for analytical chromatography applications. For preparation and industrial applications, commercially available resins in a bead form are based on copolymer of styrene/divinyl benzene and acrylic acid, esters/divinyl benzene.

Selective adsorption properties are obtained from the structure, controlled distribution of pore sizes, high surface areas and chemical nature of the matrix. Regeneration can be achieved by variety methods including steam desorption, solvent elution, pH change and chemical extraction.

Silica gel

Siliga gel is a partially dehydrated polymeric form of colloidal silicic acid with the formular $SiO_2.nH_2O$. The surface comprises mainly SiOH and Si-O-Si groups which indicate the polarity. Therefore, it can adsorb water, alcohols, amines, etc. by a hydrogen bonding mechanism.

Zeolites

Zeolites are porous crystalline aluminosilicates which comprise of SiO_4 and AlO_4 tetrahedral joined together through the sharing oxygen atoms. The process of adsorption and desorption of molecules in zeolites are based on differences in molecular size, shape, and other properties such as polarity.

2.5.2 Adsorption Isotherm

Adsorption isotherm is the relationship between the amount of a substance adsorbed and its concentration in the equilibrium solution. There are many types of adsorption isotherm as follows [22]:

2.5.2.1 Langmuir adsorption isotherm

Langmuir theory is the basic assumption that the sorption takes place at the specific homogeneous sites within the adsorbent. This isotherm describes adsorbate-adsorbent systems which the extent of adsorbate coverage is limited to monolayer on the adsorbent surfaces. The Langmuir equation can be given as Eq. (2.1)

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2.1}$$

The constant q_{max} and K_L can be determined from a linearized form of Eq. (2.2)

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{2.2}$$

where K_L $(=a_R)$ is the Langmuir adsorption constant (l mg^{-1}) related to the energy of adsorption and q_m $(=K_R/a_R)$ signifies adsorption capacity (mg g^{-1}).

2.5.2.2 Freundlich adsorption isotherm

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of adsorption on the surface as shown in Eq. (2.3)

$$q_e = K_F C_e^{1/n} \tag{2.3}$$

The linear form of Eq. (2.3) can be given as Eq. (2.4)

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2.4}$$

where $K_F = K_R/a_R$ is the Freundlich constant (l mg^{-1}), and $(1/n) = (1-\beta)$ is the heterogeneity factor.

2.6 Literature survey

Omidian et al. [23] prepared the superabsorbent polymer by inverse suspension and solution polymerization techniques using different acrylic monomer composition and different amounts of crosslinking agents. The particle size distribution of product which made by inverse suspension polymerization were determined and the dependence of absorption characteristics on the particle size was investigated. They found that both the rate of absorption and the ultimate degree of absorption increased as the particle size became smaller. Moreover, the effect of salinity of the water on absorption was determined. It was shown that as the salinity of the water was increased, the absorption decreased.

Zhao et al. [24] prepared a polyacrylamide-polyacrylic acid copolymer hydrogel by the controlled hydrolysis of polyacrylamide in an alkaline solution of 10% sodium hydroxide. The structure and composition of the resulting copolymer hydrogel were approximately two acrylic acid units for every acrylamide unit. The capacity of the copolymer hydrogel to bind various metal ions was tested with varying uptake time, pH, and ionic strength. At pH > 5, Cu^{2+} and Cd^{2+} were bound more strongly than the competing ions of Na^+, K^+, Ca^{2+} and Mg^{2+} due to the increased acidity of these transition metal ions. The copolymer had an equilibrium swelling ratio of 120 at pH > 6 with an ionic strength equivalent to 0.01 M NaCl, and swelling ratio of 265 at low ionic strength. This material should be of uses for the recovery and separation of Cu^{2+} and Cd^{2+} ions and trace environmental analysis applications such as diffusive gradients in thin film (DGT) technique.

Solpan et al. [5] prepared acrylamide-acrylic acid hydrogels. These hydrogels were found to be effective in adsorption of cationic dyes. Among the two common textile dyes tested, Janus Green B (JGB) has shown the highest adsorption capacity while Congo Red (CR) was not adsorbed by these hydrogels. Adsorption capacity of the hydrogel at $pH < 5$ provides a great advantage in utilization for the treatment of acidic textile dyes from wastewater.

Karadag et al. [25] synthesized acrylamide/itaconic acid hydrogels by irradiating with gamma rays. They were used for removal of cationic dyes, such as basic red 5 (BR-5), basic violet 3 (BV-3), and briiliant cresyl blue (BCB). This study found that the adsorption of dyes was increased with increasing the content of itaconic acid in the hydrogels and irradiation dose.

Qian et al. [26] synthesized a novel flocculant based on hybrid $Al(OH)_3$-polyacrylamide (HAPAM) by polymerization of acrylamide in $Al(OH)_3$ colloid solution. They found that an ionic bond exists between $Al(OH)_3$ colloid and polyacrylamide (PAM) chain in the HAPAM. The flocculation efficiency of HAPAM is much better than that of commercial PAM and the PAM/$AlCl_3$ blend used for kaolin suspension.

Zemaitaitis et al. [27] proposed the mechanism of dye removal from textile wastewater using poly(quaternary ammonium salt) as a flocculant. It was shown that the cationic polymer tends to react with anionic textile dye, forming intermolecular complexes. These complexes are able to incorporate the dye ion or molecules and precipitate together. Electrostatic interactions are responsible for transferring dye particles to the polymer chain. Chemical binding with hydrophilic sites, which preserve their negative charges during interaction with dye ions or molecules, facilitate their transfer from water environment to the polymer.

Gao et al. [28] investigated the coagulation efficiency and residual aluminium content of poly(aluminium silicate chloride) (PASC) in water treatment. A series of PASC, which have diferrent OH/Al and Al/Si molar ratios, were prepared by a copolymerization and composite technique. A coagulation efficiency and residual aluminium content of PASC were compared with poly(aluminium chloride) (PAC). They found that PASC had a better coagulation efficiency and lower residual aluminium content than PAC, and the PASC prepared by the copolymerization gave a better coagulation efficiency than that prepared by the composite technique. With an increasing OH/Al molar ratio and a decreasing Al/Si molar ratio, the residual turbidity and residual aluminium content in treated water diminished. Moreover, there is low residual aluminium content in the neutral pH range of the water sample.

Gao et al. [29] prepared a poly(aluminium chloride) (PAC) coagulant from $AlCl_3.6H_2O$ and Na_2CO_3. The Al_{13} species in PAC was separated and purified by the SO_4^{2-}/Ba^{2+} deposition-replacement method, and characterized by ^{27}Al NMR and XRD. The coagulation experiment results show that PAC- Al_{13} give better results for turbidity, humic acid and color removal effect, and achieves higher charge-neutralizing ability than PAC and $AlCl_3$. Al_{13} species is a higher positive-charged and the most effective polymeric Al species in water and wastewater treatment.

Ozkan et al., [30] investigated coagulation and flocculation of celestite using $CaCl_2$, $MgCl_2$, $AlCl_3$, anionic (A-150), cationic (C-573) and non-ionic (N-100) flocculants, respectively. They were determined that the Mg^{2+} was more effective on the celestite suspension than Ca^{2+} and Al^{3+} at high pH levels. Anionic and non-ionic polymers strongly flocculated the celestite suspension with respect to cationic polymer. The non-ionic polymer gave little effect by pH changes of the suspension, but the flocculation by the anionic polymer decreased in an acidic region. The higher polymer concentrations caused the lower flocculation. The flocculation of celestite suspension decreased sharply, especially for magnesium ion.

Teng et al. [9] investigated the flocculation performance of cationic and anionic polyacrylamide with the difference molecular weights and charge densities. The results showed that the cationic polyacrylamide with very high molecular weight and low charge density gives the highest flocculation efficiency in the treatment of the paper mill waste water.

Tor et al. [31] studied the effect of contact time, pH, adsorbent dosage and initial dye concentration on the Congo red removal from water using the acid activated mud. The effective pH was 7.0 for adsorption on the activated red mud. It was found that the sufficient time to attain equilibrium was 90 min. The adsorption isotherms were analyzed using the Langmuir, the Freundlich, and the three parameters Redlich-Peterson isotherms. The Langmuir isotherm was the best-fit adsorption isotherm model for this experiment.

Pavan et al. [32] synthesized the hybrid anilinepropylsilica xerogel by the sol-gel method. It was used as adsorbent for removing Congo red from aqueous solution. The pH, contact time and initial dye concentration were changed to obtain the best experimental conditions. The dye adsorption equilibrium was attained after 20 min of contact time. The experiment data were best fitted to Sips and Redlich- Peterson isotherm, attaining a maximum adsorption capacity of 22.62 mg g^{-1} of Congo red.

Dogan et al. [33] investigated the removal of reactive blue 221 and acid blue 62 anionic dyes on sepiolite from aqueous solutions using calcinations temperature, pH, ionic strength and temperature parameters. The amount adsorbed of reactive blue 221 and acid blue 62 on sepiolite increased with increasing ionic strength and temperature, and decreasing pH. The sepiolite calcinated at 200 °C had a maximum capacity. However, calcinations at higher temperature caused a decrease in the amount adsorbed of dye. The experiment datas were best fitted to Freundlich isotherm model.

Qian et al. [34] investigated the flocculation performance of four kinds of polyacrylamide (PAM) with different chain end groups, namely, PAM, star-PAM, PGS-PAM and $Al(OH)_3$-PAM hybrid, in kaolin suspensions. It was found that the optimum dosage of polymer flocculant was proportional to the critical concentration of polymer flocculant in solution and the suspension solid content in kaolin suspension. The flocculation efficiency decreased in the order: PGS-PAM > $Al(OH)_3$-PAM hybrid ~ star-PAM > PAM.