Chapter 1

Introduction

Chlorine is a highly effective disinfectant which removes or inactivates the pathogenic microorganisms in water. The protection of the public health from waterborne disease transmission by disinfection of water has been recognized since the turn of the century. Chlorine possesses many properties of a good disinfectant. Table 1.1 shows the properties of ideal disinfectants. It is also important to note that the disinfectants must be safe to handle and to apply and that their strength or concentration in treated water must be measurable. The process of disinfection is normally accomplished by using various chemicals such as chlorine and its derivatives, bromine, iodine, ozone, phenol and phenolic compounds, alcohols, heavy metal and related compounds, dyes, soaps and synthetic detergents, quaternary ammonium compounds, hydrogen peroxide and various alkalines and acids.

1.1 Disinfection with chlorine compounds[1]

The most common disinfectants are the oxidizing chemicals. Chlorine is one of the most universally used disinfectants as shown in Table 1.2. There are many modes of action for these disinfectants, i.e., to damage or to destruct the cell wall which inhibits the synthesis of the bacterial cell wall, to alter the permeability of the cytoplasmic membrane and then to destroy the selective permeability of the menbrane which allows vital nutrients such as nitrogen and phosphorus to escape, or to alter the chemical arrangement of enzymes and deactivate the enzymes.

Table 1.1 Comparison of ideal and actual characteristic of commonly used disinfectants.

Characteristic	Properties/response	Chlorine	Sodium hypochlorite	Calcium hypochlorite	Chlorine dioxide	Bromine chlorine	Ozone
Toxicity to microorganisms	Should be highly toxic at low concentration	High	High	High	High	High	High
Solubility	Must be soluble in water or cell tissue	Slightly Soluble	High	High	High	Slightly Soluble	High
Stability	Loss of germicidal action on standing should be low	Stable	Slightly stable	Relatively stable	Unstable	Slightly stable	Unstable
Nontoxic to higher form of life	Should be toxic to microorganisms and nontoxic to man and other animals	Highly toxic	Toxic	Toxic	Toxic	Toxic	Toxic
Homogeneity	Solution must be uniform in composition	Homo-geneous	Homo-geneous	Homo-geneous	Homo-geneous	Homo-geneous	Homo-geneous
Interaction with organic material	Should not be absorbed by organic material other than bacterial cells	Oxidizes organic matter	Active oxidizer	Active oxidizer	High	Oxidizes organic matter	Oxidizes organic matter
Noncorrosive and nonstaining	Should not disfigure metals or stain clothing	Highly corrosive	Corrosive	Corrosive	Highly corrosive	Corrosive	Highly corrosive
Penetrative	Should have the capacity to penetrate through surfaces	High	High	High	High	High	High

Table 1.2 Additional chemical applications in wastewater collection, treatment, and disposal

Application	Chemicals used	Remarks
Collection		
Slime-growth control	Cl_2 , H_2O_2	Control of fungi and slime-producing bacteria
Corrosion control (H_2S)	Cl_2 , H_2O_2, O_3	Control brought about by destruction of H_2S in sewers
Corrosion control (H_2S)	$FeCl_3$	Control brought about by precipitation of H_2S
Odor control	Cl_2 , H_2O_2, O_3	Especially in pumping stations and long , flat sewers
Treatment		
Grease removal	Cl_2	Added before preaeration
BOD reduction	Cl_2 , O_3	Oxidation of organic substances
pH control	KOH , $Ca(OH)_2$,NaOH	
Ferrous sulfate oxidation	Cl_2	Production of ferrous sulfate and ferric chloride
Filter - ponding control	Cl_2	Residual at filter nozzles
Filter - fly control	Cl_2	Residual at filter nozzles , used during fly season
Odor control	Cl_2 , H_2O_2, O_3	
Disposal		
Bacterial reduction	Cl_2 , H_2O_2, O_3	Plant effluent , overflows , and stormwater
Odor control	Cl_2 , H_2O_2, O_3	

1.2 Dosages for disinfection

Ranges of dosages of chlorine for various applications are reported in Table 1.3. Those dosages vary depending on the characteristics of the waste water. It is therefore of interest to determine the optimum chlorine dosages for each application.

Table 1.3 Typical dosages of chlorine for various applications in wastewater collection, treatment and disposal.

Application	Dosage range,mg/L
Collection	
Corrosion control (H_2S)	2-9
Odor control	2-9
Slime growth control	1-10
Treatment	
BOD reduction	0.5-2
Digester and Imhoff tank foaming control	2-15
Digester supernatant oxidation	20-140
Filter fly control	0.1-0.5
Filter ponding control	1-10
Grease removal	2-10
Sludge bulking control	1-10
Disposal (disinfection)	
Untreated wastewater (prechlorination)	6-25
Primary effluent	5-20
Chemical precipitation effluent	2-6
Activated sludge plant effluent	2-8

1.3 General characteristics of chlorine compounds

Chlorine has been used for various objectives other than disinfection in the wastewater treatment. It is used in the prechlorination process for the hydrogen sulfide control, for activated sludge bulking control and for odor control.

The commonly used chlorine compounds at the wastewater treatment plants are chlorine (Cl_2), chlorine dioxide (ClO_2), sodium hypochlorite (NaOCl) and calcium hypochlorite [$Ca(OCl)_2$]. The chlorination process is known as "hypochlorination".

1.3.1 Chlorine

Chlorine is supplied as a liquefied gas under high pressure in various size containers, i.e., 50, 68, 100, 1000 kg cylinders or 5-25 ton tank truck. Selection of the size of the pressurized chlorine vessel should depend on analysis of the rate of chlorine usage, the cost of chlorine, the facility's requirement and the availability of supply.

1.3.2 Chlorine dioxide

Chlorine dioxide (ClO_2 , O=Cl=O) is a powerful oxidizing agent with nearly 2.5 times the oxidizing power of chlorine. The disinfection efficiency of chlorine dioxide does not vary with pH while the disinfection efficiency of chlorine does. Chlorine dioxide is also superior to chlorine because it can oxidize iron and manganese. For the removal of iron and manganese, chlorine dioxide is added as a treatment preceding flocculation and sedimentation.[2]

1.3.3 Sodium hypochlorite

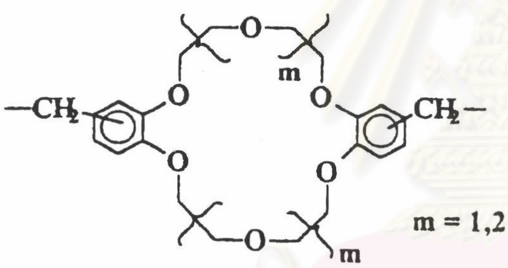
Sodium hypochlorite solution can be 12 to 15 percent of available chlorine. The solution decomposes more readily at high concentration and its decomposition is affected by light and heat. A 16.7 percent solution stored at 26.7 °C will lose 10 percent of its strength in 10 days, 20 percent in 25 days and 30 percent in 43 days. It must therefore be stored in a cool location in a corrosive - resistant tanks. Several proprietary systems are available for the generation of sodium hypochlorite from sodium chloride (NaCl) or seawater. These systems use high voltage electricity and in the case of seawater, result in a very dilute solution, a maximum of 0.8 percent hypochlorite is generated.

1.3.4 Calcium hypochlorite

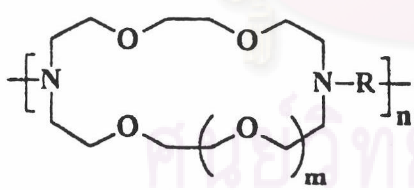
Calcium hypochlorite is available commercially in either a dry or a wet form. High test calcium hypochlorite contains 65-70 percent available chlorine . In dry form, it is available as powder or as granules, compressed tablets or pellets. Calcium hypochlorite granules or pellets are readily soluble in water and under proper storage conditions are relatively stable. Because of its oxidizing potential, calcium hypochlorite should be stored in a cool, dry location away from other chemicals in corrosion resistant containers. Because it tends to crystallize, calcium hypochlorite may clog metering pumps, piping and valves.

Among four types of chlorine precursors, calcium hypochlorite is the most widely used because it can be kept for a long time and it is easy to handle however it has more sediment when it dissolves in water resulting from the formation of calcium carbonate. The general method that can prevent calcium carbonate precipitation is by chelating with the chelating agent. EDTA is the common complex formation reagent.

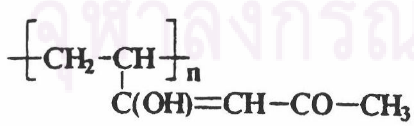
This organic ligand can form up to six bonds with a metal ion. EDTA combines with metal ions on a 1:1 ratio regardless of the charge on the metal ion. This study intends to solve the precipitation problem of calcium carbonate in an aqueous solution by using chelating polymers which are highly selective and are rapid to chelate with the metal ions. The chelating polymers have gained numerous attention from research scientists in the fields of polymer chemistry, analytical, inorganic and organic chemistry. The chelating polymers have received considerable attention due to their high selectivity to metal ions in the adsorption processes. They have been used in water treatment, pollution control and recovery of metals. The selective adsorption depends on a stability constant of a complex forming between a particular polymer ligand with a particular metal ion. Some groups of chelating polymers that have been used in the adsorption of various metal ions are shown as follows[3]:



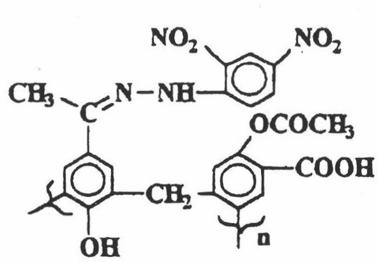
[Poly(Dibenzo-18-crown-6)][4]
for selective separation of K^+, Pb^{2+} and Cs^+.



[Poly(1,10-diaza-4,7,13,16-tetraoxacyclooctadecane][5]
for binding of alkali metal ions.



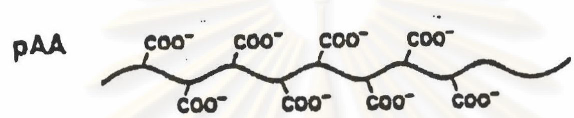
[Polyacryloyacetone][6]
for binding of various metal ions.



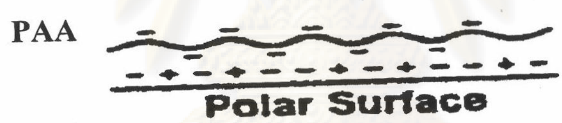
[2,4-dinitro phenylhydrazone of 4-hydroxy acetophenone, acetyl salicylic acid-formaldehyde][7]
for adsorption of bivalent metal ions.

The above polymers have complex structures when they chelate to metal ions. The other common chelating polymers are acrylate polymers which are widely used in the world for many application such as in industrial and institutional detergent because they can prevent or disperse inorganic salt precipitation, sequester multi-valent cations and prevent soil redeposition.

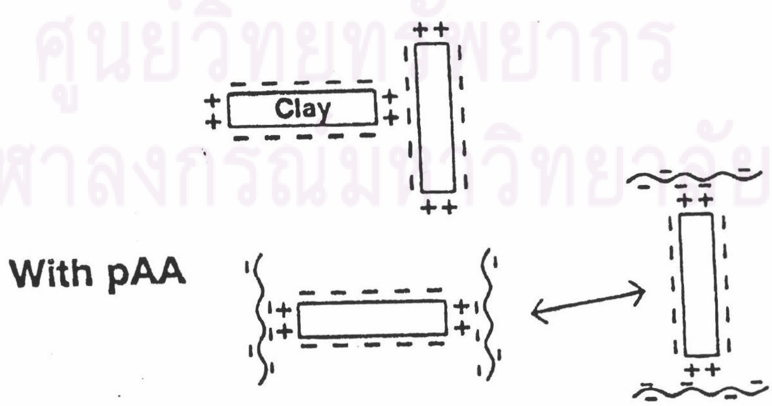
Polyacrylic acid contains polar carboxyl groups as pendant groups. Thus the interaction of polyacrylic acid with the substrate involves a dipole - dipole interaction[8].



The chemisorption process takes place when polyacrylic acid reacts with the polar surface of clays.



This chemisorption process involves an electrostatic interaction between the surface of polyacrylic acid and the surface of clay.



The acrylate polymers provide a number of major benefits to the industrial and institutional detergent formulators. The acrylate polymers improve the detergency ability by reducing soil redeposition which lead to graying on fabrics and increasing the overall negative charge of the fabric / soil system. A soil particle must overcome the coulombic repulsive barrier to redeposit onto the surface of a fabric. London – Van der Waals attractive forces bind the particle to the surface. The higher the repulsive barrier (or the greater the Zeta potential), the more difficult it will be for the soil particle to redeposit. For example, the acrylate polymers absorb on the negative charges of the kaolin clay and the polyester fibers. This makes the kaolin clay more negatively charged. The higher surface charge increase the coulombic repulsive barrier and makes the deposition of the kaolin clay on the polyester more difficult.

1.4 Objective and scope of the research

1.4.1 Objective

Since the acrylate polymers are cheap and can be modified easily, they are chosen to use in this study. The principal objective of this thesis is to study the reactions of calcium ion with sodium salt of polyacrylate and acrylate copolymers and the conditions to improve the solubility of calcium ions in an aqueous solution.

1.4.2 Scope of the research

The follows are the scope of this research;

1.4.2.1 Study the prevention of calcium salt precipitation by polyacrylate.

1.4.2.2 Determination of the weight ratios of the mixed solution of a) and b) to be clear solution (less insoluble matter).

a) Calcium oxide and polyacrylate (acrylate copolymers).

b) Calcium hypochlorite and polyacrylate (acrylate copolymers).

1.4.2.3 Characterization of the chelation complexes by Fourier - Transform Infrared Spectrophotometry (FTIR).

1.4.2.4 Determination of the effect of solvents , pH , temperature and the thermal stability of the mixing material.