

CHAPTER II

LITERATURE SURVEY

2.1 TRIHALOMETHANES

2.1.1 Background and Regulatory History

In 1974, the Dutch scientist Johannes Rook was the first to identify chloro and bromotrihalomethanes (THMs), the first class of halogenated disinfection by products (DBPs) discovered in chlorinated drinking water (Rook, 1974). A year later, in 1975, the United States Environmental Protection Agency (USEPA) conducted a survey which identified chloroform as being dominant in most chlorinated drinking water (Symons *et al.*, 1975). Chloroform was identified in 1976 by the National Cancer Institute as a suspected human carcinogen (National Cancer Institute, 1978), which led the USEPA to set a maximum contaminant level (MCL) for total THMs (TTHMs) at 0.10 mg/L (USEPA, 1979). This standard applied to systems serving over 10,000 people. Due to wide occurrence and potential health risks of DBPs, the USEPA proposed the Disinfectants/Disinfection By-Products (D/DBP) Rule in two stages. Stage 1 of the D/DBP Rule was proposed in 1994 (USEPA, 1994b). It proposed TTHM MCLs of 0.080 mg/L. Stage 2 of the D/DBP Rule was proposed in 1994, which required even lower MCLs for DBPs than Stage 1 (0.040 mg/L). It was expected to be re-proposed in the year 2000.

2.1.2 Chemistry of THMs

THMs are organohalogen compounds that are named as derivatives of methane when three out of the four hydrogen atoms are substituted by three halogen atoms such as chlorine (Cl), bromine (Br), iodine (I) or a combination thereof. THM has a general formula, CHX_3 , where X is the halogen atom.

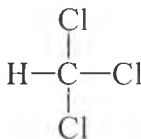
THMs are formed during the reaction between a chemical disinfectant (e.g., chlorine) and natural organic matter (NOM; as referred to as precursors) in water. The primary biochemical ancestors of THM identified by many researchers are humic substances including humic acid and fulvic acid (Rook, 1976; Trussell & Umphres, 1978; Oliver & Lawrence, 1979), algal materials mainly the chlorophyll-a, algal biomass and their extracellular products (Hoehn et al., 1980; Oliver & Shindler, 1980; Wachter & Andelman, 1984), proteins (Scully et al., 1985) assortment of aromatic substance (Copper et al., 1985) occurring naturally in the water. These materials also contribute to the natural color of the water.

Bromine (Loung et al., 1980; Amy et al., 1985) was also identified as precursors, since its presence in chlorinated water may be oxidized by chlorine to form hypobromous acid (HOBr), which led to the formation of brominated THM species. Iodine, to a lesser extent was also observed by Gould et al. (1985).

Four THM species of concern in drinking water are chloroform, bromodichloromethane, dibromodichloromethane and bromoform.

2.1.2.1 Chloroform

Chloroform or trichloromethane (CHCl₃) has a chemical structure as follow:



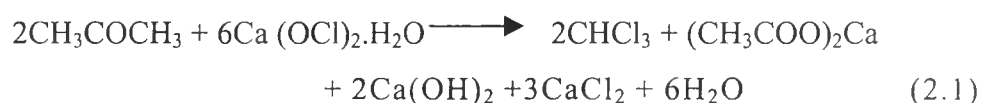
It has a molecular weight of 119.39 and other properties as listed below:

- i. colorless, highly refractive, heavy, volatile liquid, characteristic odor and sweet tasted;
- ii. miscible with alcohol, ether, benzene, carbon disulfide, carbontetrachloride and slightly soluble in water; and

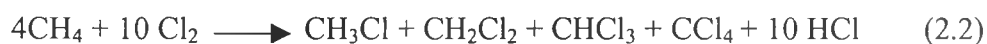
- iii. specific gravity of 1.485, boiling point of 61-62 °C, freezing point of –63 to –64 °C, refractive index of 1.4422 (25 °C), non-inflammable but will burn on prolonged exposure to flame or high temperature.

Preparation:

- i. Reaction of chlorinated lime with acetone, acetaldehyde or ethyl alcohol :



- ii. Byproduct from chlorination of methane:

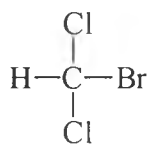


Purification: Extraction with concentrated sulfuric acid and rectification.

Uses: For starting materials of chlorodifluoromethane as refrigerant, solvent, fumigant, insecticides.

2.1.2.2 Bromodichloromethane

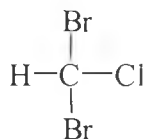
Bromodichloromethane or dichlorobromomethane (CHCl_2Br) has a chemical structure as follows:



It has a molecular weight of 163.82 and a boiling point of 90.1 °C

2.1.2.3 Dibromochloromethane

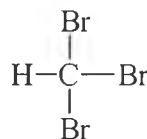
Dibromochloromethane or chlorodibromomethane (CHClBr_2) has a chemical structure as follow:



It has a molecular weight of 208.29 and a boiling point of 120°C , is a clear, colorless and heavy liquid with specific gravity of 2.38 and can be used as an organic synthesis.

2.1.2.4 Bromoform

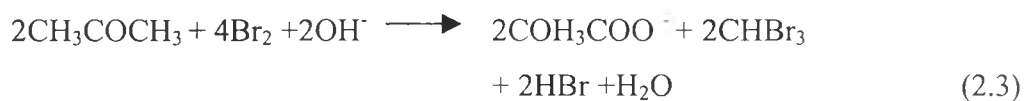
Bromoform or tribromomethane or methyl tribromide (CHBr_3) has a chemical structure as follows:



It has a molecular weight of 252.73 and processes other properties, such as:

- i. colorless and heavy liquid that smell and taste like chloroform;
- ii. soluble in alcohol, ether, chloroform, benzene, naphtha and slightly soluble in water;
- iii. specific gravity of 2.887, boiling point of 151.2°C , freezing point of -9°C and refractive index of 1.6005; and
- iv. Non-inflammable

It can be prepared by heating acetone or ethyl alcohol with bromine and alkali hydroxide, and recovered by distillation, as follows:

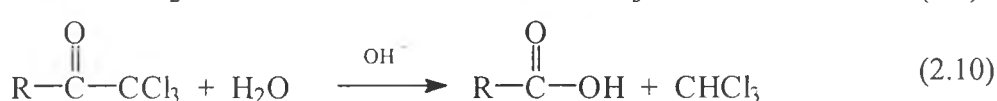
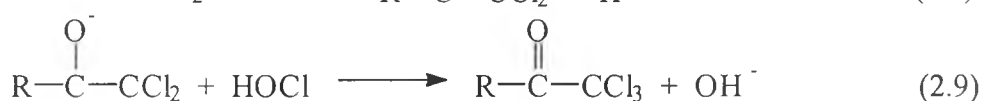
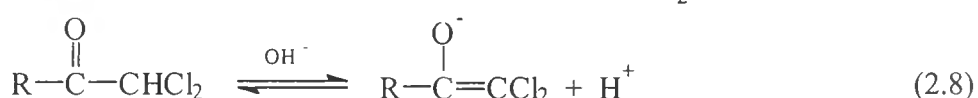
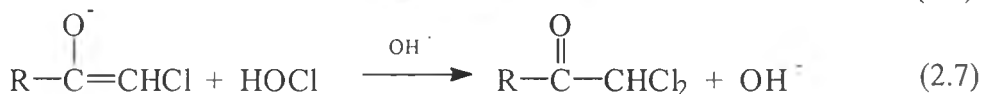
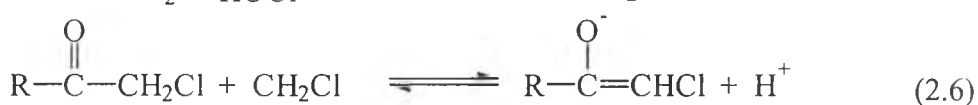
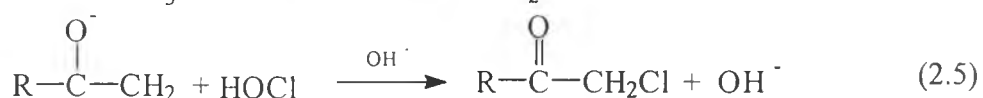
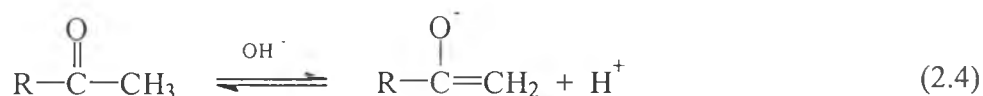


It is used as an intermediate in organic synthesis, a solvent for waxes, grease and oils, in medicine (as a sedative) and in geological assaying.

2.1.3 Possible Reaction Pathway of THMs in Water Treatment

Morris (1975) revealed the classical reaction of aqueous hypohalites with methyl ketones or compounds capable of oxidizing methyl ketone to yield haloforms. The pattern of reaction is by the replacement of hydrogen by a chlorine alpha, to a carbonyl group, followed by eventual hydrolysis to produce CHX_3 .

During water treatment, Onadera (1984) summarized a series of possible reactions that demonstrate the basic steps by which chloroform may be produced, as follows:-



2.1.4 Effect of THM Formation

Many studies have concluded that THM formation in drinking water depends upon various factors, such as pH, concentration of precursors, concentration of chlorine, temperature, and the most distinct, reaction time.

2.1.4.1 pH

Rook (1976) suggested that, the reaction increased evidently at pH values from 8 to 10. Much less influence was found when varying within pH 1-7, a feasible variation range during chlorinating.

Stevens et al. (1976) conducted an experiment with wider pH range of 6.5 to 11.5. The results show that the rate of formation of chloroform increases with the increase in pH. They explained that this was due to the increase in the humic acid reaction rate, since the rate-determining step of the classical haloform reaction is enolization of a ketone.

2.1.4.2 Precursor Concentration

Since the THM formation is a result of the reaction between chlorine and the THM precursors, it is obvious that the precursor concentrations would influence the THM concentrations. Rook (1976) in his series of experiments varied the concentrations of the organic precursors in order to study if TOC should be reduced before chlorinating. In this regard, it was found that the chloroform production from organic matter is linear in concentration up to 250 mg/l TOC. This clearly illustrates that precursor concentration is one of the factors affecting the THM formation.

2.1.4.3 Chlorine Dose

Chlorine dosage is one of the most important factors influencing the THM formation. Trussell&Umphres (1978) conducted a laboratory test with synthetic water prepared by adding 10 mg/l of humic acid, 1mg/l of NH_3Cl (as NH_3) and 10 mg/l of standard pH 7 buffer to demineralized water (TOC 0.2 mg/L). Different amount of chlorine was added to various portions. After 2 hours of contact time, the results show that higher THM concentration occurs within a certain range of chlorine dosages. At low dosage, presumably the chlorine is insufficient to react with the precursor to form THM as chlorine has been used up to react with ammonia, bacterial disinfection, etc.

2.1.4.4 Temperature

The effect of temperature on the rate of THM formation was investigated by Stevens et al. (1976) using the Ohio River water. The winter to summer temperature variation in Cincinnati, Ohio, of raw and finished water, is approximately 26°C. The result show that this temperature differential could easily account for most of winter to summer variations in chloroform concentration with a three to four days chlorine contact time was practiced.

2.1.4.5 Reaction Time

Reaction time is among the major factors influencing the THM formation. Recknow & Singer (1984) ran a few sets of experiments. One of these experiments was to study the formation of these chlorinated products as a function of the reaction time. They found that by varying the chlorine contact time, chloroform and total THM increases rapidly in the first few hours and then slowed to a generally steady rate of increase. This result is quite similar to that of previous researchers, which concluded that the active rate of reaction is within the first few hours of contact time.

2.1.4.6 Empirical Kinetic Model of THM formation

Since THM formation is influenced by a few parameters as mentioned above, several kinetic models of the THM formation have been predicted. McBride et al. (1978) reported that the change of [THM] could be empirically expressed by a semi-logarithmic relationship as in equation 2.11.

$$[\text{THM}] = A \log t + B \quad (2.11)$$

However, Somiya et al. (1980) reported that it could be better express with two semi-logarithmic equations as in equation 2.12., because at the initial stage when $t < 15$ min, the chlorine not only reacted with organic material to form THM, but was also used for bacterial disinfection, reacting with ammonia that may be present in the water, etc.

$$[\text{THM}] = A_1 \log t + B_1 \quad t \leq 15 \text{ min} \quad (2.12a)$$

$$= A_2 \log t + B_2 \quad t < 15 \text{ min} \quad (2.12b)$$

Urano et al. (1983) further improved the empirical kinetic model, taking into consideration all factors influencing the THM formation and suggested that the rate of THM formation in aqueous solution of humic acid can be represented as:

$$[\text{THM}] = k(\text{pH}-2.8) [\text{TOC}] [\text{C}_{12}]^{0.25} t^{0.36} \quad (2.13)$$

where k = rate constant (8.2×10^{-4} for humic acid as a reagent)

[TOC] = initial TOC concentration

[C_{12}] = initial chlorine concentration

t = contact time

2.1.5 Toxicity of THMs

THMs are chemicals with various industrial uses. Excessive exposure to each of them can cause adverse health effects, principally on the central nervous system. Industrial settings, exposure is usually by inhalation of vapor, but direct skin contact with their liquids also can have adverse local and systemic effects. Exposure to THMs from drinking water is typically at levels very much lower than the exposure, which might occur from the industrial use of individual THMs. Available studies indicate that the gastrointestinal absorption of all the THMs is high.

In 1975, it was recognized that the chlorination of water produced a number of by-product contaminants including THMs. Subsequently, many epidemiological studies have been conducted to investigate the association between the consumption of chlorinated drinking water and cancer. While the results of these studies have been inconsistent, some studies have indicated an association between the consumption of chlorinated drinking water and an increased risk of colon, rectal and bladder cancers. However, many of these studies have been of ecological design and studies of this type can not show a cause and effect relationship.

Pilotto (1995) has reviewed the epidemiology studies. One epidemiological approach to increase the statistical power of individual studies is to undertake a meta-analysis incorporating the results from a number of similar individual studies. A meta-analysis involving 10 of these studies found a positive association between consumption of chlorination by-products in drinking water and bladder and rectal cancer in humans (Morris et al. 1992). However, as the authors of that study indicated, this does not prove a cause and effect relationship, and in particular it does not show that THMs are the responsible agents. The authors speculated about the association, identifying a chlorinated hydroxy-furanone as a possible aetiological agent.

Showering has not been considered in epidemiological studies, but it is likely to result in significant exposure to organic contaminants through skin absorption and inhalation. It has been estimated that the absorbed dose of chloroform

from a 10 minute shower is equivalent to that from drinking 2 liters of chlorinated water (Jo et al., 1990)

IARC (The International Agency of Research on Cancer) has reviewed the carcinogenicity of chlorinated drinking water and the individual THMs by assessing the results of epidemiological studies and animal experiments. Chlorinated drinking water has been classified as Group 3, which means that the substances is not classifiable in regard to its carcinogenicity, based on the available human and animal data. Dibromochloromethane and tribromomethane have been classified individually in Group 3 also.

Chloroform and bromodichloromethane are classified as Group 2B, which means they are possible human carcinogens, based on the available data. The other IARC groups are Group 1 (confirmed human carcinogens), Group 2A (probable human carcinogens) and Group 4 (data not indicate not a carcinogens)

As IARC has classified chloroform and bromodichloromethane in Group 2B, the Guideline Values for these contaminants in drinking water in the WHO Guidelines for Drinking-Water Quality (WHO, 1993) were derived by extrapolation of the results of positive animal experiments. Using the linearised multistage model, lifetime exposure to drinking water concentrations of 2000, 200 and 20 $\mu\text{g/L}$ for chloroform and 600, 60 and 6 $\mu\text{g/L}$ for bromodichloromethane correspond to excess lifetime cancer risks of 10^{-4} , 10^{-5} and 10^{-6} , respectively. In the other words, lifetime exposure to drinking water containing 200 $\mu\text{g/L}$ chloroform is estimated by this model to pose an added lifetime risk of cancer of 1 in 100,000. It should be noted that this model is likely to overstate the real risk, which, in fact, may be zero below a particular level (threshold) of exposure.



2.2 THM PRECURSORS

2.2.1. THM precursors in natural

THM precursors consist primarily of NOM (Natural Organic matter). NOM refer to precursors and nutrients in natural water as either allocthonous (derived from the surrounding watershed including land and sub-surface waterways) or autochthonous (derived from within the water body). Watershed run-off is a major contributor to allocthonous humic materials; dissolved and particulate organic substances are transported to a water body during run-off events (Cooke and Carlson, 1989). Algae and macrophytes are sources of organics within surface water bodies (Cooke and Carlson, 1989).

The organic carbon content of natural waters is comprised of humic and non-humic substances. Humic substances include humic and fulvic acids, while non-humic substances include hydrophilic acids, proteins, carbohydrates, carboxylic acids, amino acids, and hydrocarbons (Thurman, 1985; Amy, 1993).

The presence of humic substances causes not only color and odor problem, but also have potential to react readily with chlorine to yield THMs. Non-humic substances, such as algae and their extracellular products can also be THM precursors (Moriss and Baum, 1978; Oliver and Shindler, 1980)

Total organic carbon (TOC) is a collective measure of organic in water. It provides no information on the composition and distribution of the wide array of organic constituents. However, a large fraction of the TOC is humic substances, which usually contribute to the color in water.

Figure 2.1 describes the concentration of total organic carbon in natural water, and show that the TOC concentration is varies over wide range. The large fraction of TOC is humic substances, which are categorized as THM precursors.

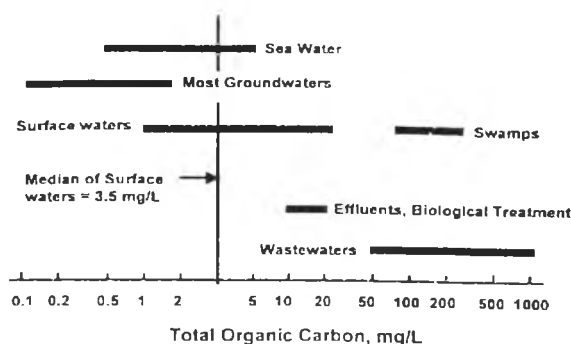


Figure 2.1 Range of Total Organic Carbon (TOC) in natural water.

(Source; Kavanaugh, 1978)

2.2.2 Characteristic of THM precursors

Aquatic humic substances as THM precursors are yellow to brown colored, polymeric acids which can be leached from soil and sediments, and are known to be natural by-products of vegetative degradation (Thurman, 1985). In most surface waters, the concentration of humic substances ranges from 100 $\mu\text{g/L}$ to 4 mg/L, with concentrations in bogs and marshes sometimes exceeding 100 mg/L (Thurman, 1985). Humic substances are comprised of humic and fulvic acids, which are differentiated by ultraviolet light absorbance (UVA), specific UVA (SUVA), and molecular weight ranges.

The molecular weights of fulvic acids typically range from 500 and 2,000 a.m.u. (Thurman, 1985; Amy et al., 1992). Fulvic acids have a higher charge density and are less amenable to coagulation by charge neutralization (Amy et al., 1992). Fulvic acids are also more prevalent and more soluble than humic acids. The SUVA of fulvic acids at 254 nanometers (nm) ranges from 2.9 to 4.3 L/mg-m (Reckhow et al., 1990).

Humic acids have a molecular weight greater than 2,000 a.m.u., and usually less than 100,000 a.m.u. The SUVA of humic acids ranges from 4.8 to 7.4 L/mg-m (Reckhow et al., 1990).

The molecular weight of precursors has also been correlated with THM formation potential (THMFP). Bell et al. (1996) indicated that organic molecules with molecular weights greater than 1 kilodalton (kd) contributed more THMFP than did the organics having molecular weights less than 1 kd. Recent work by Sinha et al. (1997) showed that THM precursors were predominately larger molecular weight humic materials.

There is no defined structure for humic substances. However, the humic acid is generally agreed to be a polymer containing varying numbers of substituted aromatic monomers. Christman and Ghassemi (1966) proposed that the structure consist of many carboxylic acids, hydroxyl and ketone function groups. It is because of these that humic substances are more soluble at high pH levels and are capable of complexing with divalent and trivalent cations.

Trussel and Umphres (1978) proposed a very simplified structure for the humic substances as shown in Figure 2.2. They proposed a hung amorphous mass of polyhetero condensate with functional groups protruding from its surface that react with chlorine to produce THMs i.e. the hydroxylated aromatic rings with two free meta-positioned OH-groups are active sites for haloform formation. Rook (1977) has also shown that meta-hydroxy aromatic rings, such as the ring on the top of Figure 2.2, are particularly effective in producing THMs.

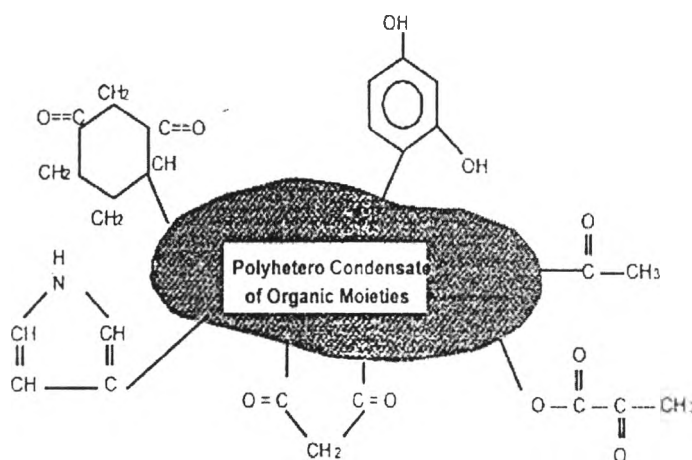


Figure 2.2 Model of Humic Compound

(Source; Trussel and Umphres, 1978)

2.2.3 Surrogate Parameters for monitoring THM precursors

Almost all the research worked with THM precursors (humic substances), Total Organic Carbon (TOC) and Ultraviolet absorbance (UVA) removal have been identified as the best surrogate for evaluating the reduction of THM precursors in water treatment (Schnitzer and Khan, 1972)

Under the terms of the D/DBP rule, removal of THM precursors will be monitored using total organic carbon (TOC) as a surrogate parameter; the percentage TOC removal required will depend on the TOC and alkalinity concentrations in the raw water (Table1).

Table 2.1. Percentage TOC removal requirements for enhanced coagulation

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as CaCO ₃)		
	0-60	>60-120	>120
2.0-4.0	40	30	20
4.0-8.0	45	35	25
>8.0	50	40	30

UV absorbance is also a good technique for measuring the presence of naturally occurring organic matter, such as humic substances, because they contain aromatic moieties and are the dominant form of organic matter in natural waters. As noted by Edzwald et al. (1985), humic aromatic compounds and molecules with conjugated double bonds absorb UV light, whereas simple aliphatic acids, alcohols, and sugars do not. Reckhow et al. (1990) measured the UVA and THM formations of the humic and fulvic fractions of five different sources. Humic acids had greater UVA, more aromatic rings, and higher molecular weight than fulvic acids. As the aromatic content increased (as in humic acids) the percentage of chlorine incorporation (i.e., THM formation) also increased.

SUVA (which is the UVA divided by the dissolved organic carbon concentration) can be used as an indicator of the ability of coagulation (or softening) to remove THM precursors. Edzwald et al.(1985) reported SUVA at 254 nm and 260 nm are excellent surrogate parameter for estimating raw water concentrations of organic carbon as Non-Purgable Total Organic Carbon (NPTOC) and THM precursors as TTHMP.

2.3 APPROCH FOR THM PRECURSORS REMOVAL

2.3.1 Coagulation

The term “coagulation,” narrowly defined, refers to the destabilization of a colloidal suspension, but it is often used in a broader sense that includes the addition of a coagulant and perhaps one or more coagulant aids (e.g., acid or base for pH adjustment) as well as the process used to remove the destabilized particles.

Coagulants typically used for treating drinking water include metal-salt coagulants (e.g., alum, ferric sulfate, ferric chloride), polymerized metal-salt coagulants (e.g., polyaluminium chloride, PACl), and organic polymers that may be cationic, anionic, and nonionic. These coagulants not only destabilize particles, but also remove a fraction of the natural organic matter present in natural waters.

In general, as the coagulant dosage increases, the precursor removal increases; however if the pH is not independently controlled, restabilization can occur (due to very low pH) and precursor removal will be less than optimal. Coagulant dose is one of the most common variables studied during jar tests, and results from numerous studies are cited in the literature, and results are specific to the water source and season being tested.

The solution pH during coagulation is a significant variable which can be controlled to maximize precursor removal under a given set of conditions. Coagulation using iron or aluminium salts in the pH range of 4.5 to 6.0 generally corresponds to maximum precursor removal; however the optimum pH for iron salts is typically 0.5 to 1.0 pH unit lower than for alum.

The ability of commonly used coagulants to remove TOC is discussed below:

i) Precursor Removal by Aluminium Sulfate Coagulation.

It is well known that TOC removal by $\text{Al}_2(\text{SO}_4)_3$ coagulation is superior at solution pH values near 5.5 to 6. The TOC removal achieved within this pH range can be substantial: TOC removals of greater than 50 percent have been widely reported in the literature. Alum coagulation is also effective for DBPP removal. Cheng et al. (1993)

observed approximately 30 percent THM precursor and 30 percent HAA precursor removal with 20 mg/L $\text{Al}_2(\text{SO}_4)_3$ at pH 5.5 to 6.3 for State Project and Colorado River water in southern California.

ii) Precursor Removal by Ferric Sulfate Coagulation.

Ferric sulfate coagulation can effectively reduce TOC, THMFP, and TOXFP. In studies by Sinsabaugh et al., 1986, a 20 mg/L $\text{Fe}_2(\text{SO}_4)_3$ dosage removed nearly half of the THMFP and the TOXFP. Increasing the dosage to 50 mg/L $\text{Fe}_2(\text{SO}_4)_3$ increased these removals to approximately 70 percent. The pH during coagulation was maintained near 5.0.

iii) Precursor Removal by Ferric Chloride Coagulation.

Ferric chloride is also very effective for NOM removal. Dryfuse et al. (1995) optimized TOC removal using bench-scale FeCl_3 coagulation for three different water sources. The percentage DOC removal ranged from 46 to 71 percent and the removal of THMFP and HAAFP was slightly greater, ranging from 59 to 90 percent. Ferric chloride coagulation was found to preferentially remove the high molecular weight, humic fraction of organics; non-humics were also removed by FeCl_3 coagulation, but to a lesser extent.

iv) Precursor Removal by Polyaluminium Chloride Coagulation.

Polyaluminium chloride is a partially hydrolyzed metal coagulant prepared by adding a base to the coagulant to "pre-form" the polymeric aluminium species that may be more effective in achieving organics removal. Dempsey et al. (1984) reported that PACl outperformed $\text{Al}_2(\text{SO}_4)_3$ for fulvic acid removal. The PACl coagulant was better at all pH values above and below those for optimum alum coagulation.

Many researchers have shown that coagulation preferentially removes the higher molecular weight organics from solution (e.g., Edzwald, 1993; Vilage et al., 1997). Kavanaugh (1978) reported that the differences in molecular weight and charge densities between humic acids and fulvic acids resulted in a higher coagulant dosage required for fulvic acid removal. Weber and Jodellah (1985), however, found that $\text{Al}_2(\text{SO}_4)_3$ coagulation (50 mg/L) removed greater than 80 percent of both humic and fulvic acids. Many have found that coagulation preferentially removes the more

hydrophobic and more highly humified organics (e.g., Owen et al., 1993; Bell et al., 1996), which have also been found to be the most reactive THM precursors (Collins et al., 1986).

2.3.2 Membranes

Membranes in water treatment serve as a physical, and sometimes chemical, barrier between particles and other colloidal and dissolved contaminants and treated water. The four major membrane types used for potable water treatment are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Their pore size and the required pressure for treating water generally characterize membrane systems. MF systems have larger pore sizes (typically 0.075 to 0.8 μm) than UF systems (typically 0.0015 to 0.09 μm). Similarly, NF systems are considered "loos" RO, and because the pore size of NF and RO systems is very small, these membranes are characterized by the molecular weight cut-off (MWCO) as determined with test compounds.

Precursor removal by MF and UF alone is typically less than 20 percent. Scanlan et al. (1997) reported that MF without coagulant addition achieved 6.5 percent TOC removal from a surface water supply in Wyoming (average raw water TOC and turbidity near 4.5 mg/l and 3.1 NTU, respectively). The UF system achieved 19 percent TOC removal. Jacangelo et al. (1995) reported that TOC removal by UF from three different surface water supplies was less than 22 percent. Huey et al. (1999) reported that Memcor MF and Aquasource UF systems achieved only 11 to 12 percent TOC removal in studies at Tempe, AZ. In general, the pore sizes of MF and UF membranes do not reject the majority of precursors in surface water.

NOM compounds exist in all size fractions, however in surface waters, the majority of the organics are usually between 1,000 and 100,000 d. NF and RO have pore sizes with MWCOs ranging from very small (200 d) to large (approximately 1,000 d.), therefore, NF and RO systems can potentially removes significant

concentrations of TOC. For example, NF with a MWCO of 1,000 d. achieved approximately 80 percent TOC rejection in studies by Nilson and DiGiano (1996).

2.3.3 Membrane with PAC or Coagulant Addition

Many investigators have studied the addition of powdered activated carbon (PAC) or coagulant upstream of MF or UF membranes for improved organics removal, and the results have been mixed. The addition of a modest coagulant dosage (15 to 35 ml/L alum or ferric-salt coagulant) improved TOC removal from 6.5 percent to 19 to 38 percent in studies by Scanlan et al., 1997 and Freeman et al. 1997. PAC addition (20 mg/L) upstream of MF, however, achieved only 11 percent TOC removal in one trial, and 0 percent TOC removal in another trial. Both the coagulant and PAC additions shortened the duration of water production between cleanings.

Combining a cross-flow, polysulfone UF system with PAC to treat a softened-water (pH approximately 9) containing from 2.5 to 6.1 mg/L TOC resulted in only about 10 percent TOC removal (Crozes and Seacord, 1999). In this study, PAC was selected based on kinetics and capacity for atrazine removal, rather than TOC removal.

Jack and Clark (1998) reported that a PAC dosage of 10 mg/L prior to UF (Aquasource BCDA, hollow-fiber membrane) achieved from 27 to 38 percent TOC removal and from 17 to 30 percent DOC removal from the Vermilion River in Illinois. The 1997 average raw-water quality was TOC 3.9 mg/L; turbidity 4.9 NTU; alkalinity 164 mg/L and hardness 254 mg/L.

Jacangelo et al. (1995) reported modest increases in TOC removal (0 to 7 percent) by PAC addition (at 10 and 40 mg/L) to UF. Only at higher PAC dosages (> 100 mg/L) did substantial improvements in TOC removal (>55 percent) occur. This increase in precursor removal, however, resulted in higher bromide-to-TOC ratios in the permeate, which affected the speciation of DBPs to the brominated compounds.

Robert et al (1999) showed that conventional softening and filtration followed by NF resulted in effluent TOC concentrations near 0.5 mg/L. MF followed

by NF (300 d MWCO) and in-line coagulation followed by UF and NF achieved similar TOC removal. Subsequent simulated distribution system chlorination procedures yielded THM concentration well below the stage MCLs for the D/DBP Rule. In-line coagulation with from 10 to 30 mg/L ferric chloride prior to UF (20,000 d MWCO) and NF did not result in prohibitive fouling conditions in these studies, and membrane-cleaning frequencies were not excessive.

PAC and coagulant addition to membrane systems will affect the hydraulics of the system and could potentially shorten the available time for water production. Huey et al. (1999) studies the hydraulic impact of PAC addition on Memcor (dead-end flow pattern) and Aquasource system (cross-flow pattern) membranes in studies at Tempe, AZ. The run length of the Memcor system was significantly impacted by PAC addition. The impact of PAC addition on run length was less dramatic for the cross-flow pattern of the Aquasource system. Likewise for coagulation, Lahoussine-Turcaud et al. (1990) reported that the membrane flux (i.e. water production) was least affected when coagulation also resulted in higher rejection of organics by a polysulfone membrane.

The characteristics of the organic compounds remaining in solution after PAC or coagulant addition will affect TOC removal by membranes. Nilson and DiGiano (1996) reported that contact with PAC resulted in the removal of mid-sized organics, in the feed water. NF of this PAC treated water resulted in flux decline by the remaining higher molecular weight, hydrophobic fractions. The organics in the effluent collected during a membrane cleaning cycle had MWCOs greater than 30,000 d, indicating that the larger molecular irreversible membrane fouling.

2.3.4 GAC and BAC

Granular activated carbon (GAC) is widely used in drinking water for the removal NOM, taste and odor causing compounds, and specific trace organic compounds. It is often used as pre-adsorber (i.e., filter cap) or as post-adsorber (i.e., post-filter reactor). The ability of GAC to adsorb NOM depends on many factors. The type of carbon, empty-bed contact time (EBCT), bed depth, hydraulic loading

rate, pH, extent of pretreatment, and presence of biological activity influence NOM removal by GAC.

GAC can remove a significant amount of precursors (approaching 100 percent) if the EBCT is sufficient. However, as TOC is adsorbed with continued use, the carbon's adsorptive capacity becomes exhausted, and the effluent TOC concentration steadily increases. For this reason, side-stream treatment is often used for GAC contacting. GAC should also be placed in the treatment train at a location where precursor concentrations are low (such as after sedimentation or filtration). Optimization of coagulation for precursor removal prior to GAC filtration has been shown increase the run time of the GAC by over 100 percent (Owen et al. 1998). The economics of GAC installation for precursor removal often dictate its feasibility at WTPs, because GAC is relatively expensive to be less efficient and less economical for removal of THM precursors than for removal of taste and odor control or trace organic removal.

Biologically activated carbon (BAC) prevails in systems using ozone. Ozone reacts with some organics, and makes them more biodegradable. This is a concern because it clouds lead to re-growth in the distribution system. If GAC absorbers are used following ozone application, and if the GAC contractor is not disinfected, the microbiological population will effectively remove some of the biodegradable organic carbon, as well as remove other disinfection-by-products of ozone (i.e., aldehydes). This biological activity also removes a portion of THM precursors: the removal is typically about 20 to 30 percent.

Wang et al. (1995) showed that biologically active GAC (over sand) filters removed from 21 to 29 percent TOC while biologically active anthracite/sand filters achieved from 16 to 20 percent TOC removal. The THM formation potential was reduced by 27 to 40 percent by BAC, whereas the anthracite/sand filters only achieved 23 percent removal of THM formation potential. GAC media can support significantly more biomass than anthracite or sand media. Most of the biomass, as well as TOC removal, occurred in the upper layers of the GAC, thus indicating that TOC removal can be achieved by BAC with short EBCTs.

GAC caps on filters can remove some TOC, but the duration of effective adsorption is dependent on the GAC type and water quality of the feed water. They are primarily used for taste and odor control or removal of trace organics. At start-up, there is usually an initial adsorption of organics by GAC caps, which will result in reduced TOC. This initial phase is typically short in duration, as the caps are of shallow depth (12 to 15"), and the adsorption sites soon become saturated with NOM.

2.4 PELLETIZATION PROCESS

2.4.1 Introduction

There are many approaches for controlling or minimizing THMs formation during the reaction between chlorine and NOM (act as THM precursors) such as enhanced coagulation, granular activated carbon (GAC) and membrane. Enhanced coagulation has several advantages over GAC and membrane including little required capital investment, minimal increase in unit operating cost and well-know technology. However, enhanced may not be effective enough to achieve the required precursor (organic) reduction to allow chlorination and still meet the proposed THM standard.

In this study is proposed a new approach to THM precursor removal, which called pelletization processes. The major advantages of the pelletization process, that are low operation and maintenance costs, high purity produced, and produced pellets have extremely low water content which can easily to disposal.

2.4.2 Concept of Pelletization process

In a conventional flocculation process, charge neutralized elementary particles collide randomly with one another and form bulky agglomerates. These are called "random floc" particles. In the course of floc size growth through the random flocculation, the density of floc decreases with increase of the floc size, entrapping much more void water in the agglomerates. This relationship was formulated by Tambo *et al.* (1979) and named as the floc density function as shown in the following equation:

$$\rho_e = \rho_s - \rho_o = a / (d_f / l)^k \quad (2.14)$$

where: ρ_e = the effective density of floc (g/cm^3):
 ρ_s, ρ_o = the density of floc and water, respectively (g/cm^3):
 a, k = constants. (g/cm^3)
 (d_f / l) = dimensionless floc diameter

If much higher density floc particles with large size can be formed, settling velocity of the particles will increase drastically. A process of “pellet flocculation” based upon metastable state concept is thus proposed in this paper.

A supersaturated solution for a labile concentration forms a precipitation spontaneously. However, a metastable solution may not form any precipitation over a relatively long period of time. It needs an “aging” time to reach an equilibrium state. However, if a large amount of the same kind of solids phase is introduced into the metastable state, precipitation of the solute upon the introduced solid surface occurs very often.

This kind of treatment has already been devised for hard water softening in The Netherlands (Graveland, 1983). This kind of process has much wider application if we handle the metastable state with a much broader sense of understanding.

The metastable state products are those particles that have already possessed elementary structures of the final aggregate, but do not have enough size and/or concentration to form the desirable aggregates in a very short time. These metastable state products are simply referred to as the “elementary particles” in the following discussion. If high-concentration solids having the same activity to the metastable state compounds are introduced into the metastable state system, very quick association of the elementary particle with the active solid surface will occur in accordance with the mode of one-by-one attachment of the elementary particle onto the introduced solids. Random collision among various size flocs inevitably introduces large void volume into the produced aggregates. However, this mode of one-by-one attachment of the elementary particle onto the introduced solid particles may form much denser agglomerates. These agglomerates are composed of regularly

arranged elementary particles covering the active core material, i.e. the introduced solid particle, and show the highest density among aggregates generated from the elementary particles (Figure 2.3)

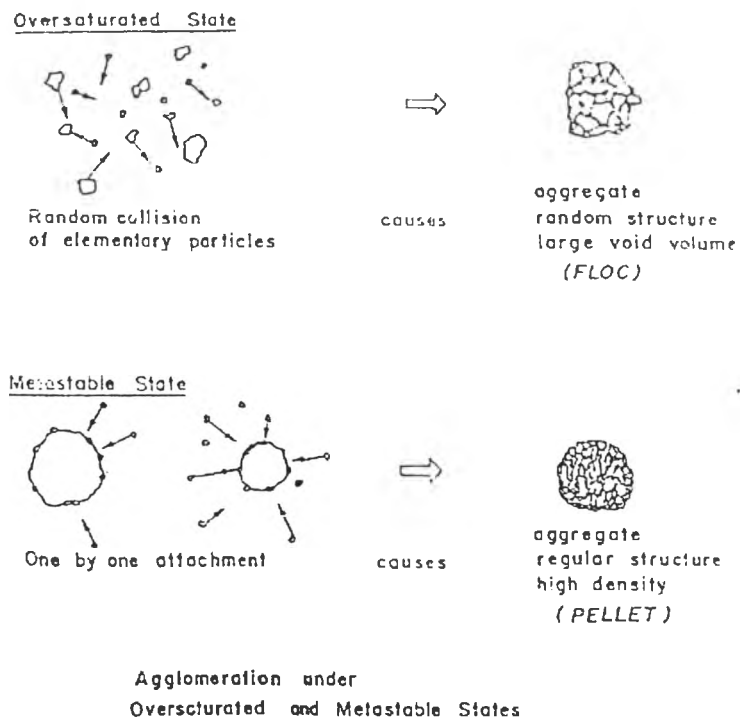


Figure 2.3 Agglomeration under oversaturated and metastable state
(Tambo, N. and Matsui, Y., 1989)

2.4.3 Theoretical Ways to Make Compact Floc

The goal of pelletization process is to make compact floc. To understand how the density of a floc changes during its growth in multiple steps, a simplified mathematical model is imagined as follows.

Supposing the first step of particle agglomeration is the combination of primary particles to form so-called first level aggregates, the effective density of the aggregate ρ_1 can be calculated by the effective density of the primary particle ρ_0 and the void ratio of the aggregate ε_1

$$\rho_1 = \rho_0 (1 - \varepsilon_1) \quad (2.15)$$

Because $\varepsilon_1 > 0$, the density of the first-level aggregate is less than that of the primary particle by a coefficient of $(1 - \varepsilon_1)$ which is the substantial ratio of the aggregate.

Then if the second step of agglomeration is considered to be a combination of the first level aggregates to form so-called second-level aggregates, the effective density of the second-level aggregate ρ_2 can be calculated in a similar way:

$$\rho_2 = \rho_1 (1 - \varepsilon_2) \quad (2.16)$$

where ε_2 is the ratio of the void water among the first-level aggregates in a second-level aggregate. A combination of equation 1 and 2 yields

$$\rho_2 = \rho_0 (1 - \varepsilon_1) (1 - \varepsilon_2) \quad (2.17)$$

With the increase in void water in the second agglomeration step, the substantial part of the second-level aggregate becomes the product of $(1 - \varepsilon_1)$ and $(1 - \varepsilon_2)$.

Further, if agglomeration progresses in a stepwise way to the i th level, the density of an i th level aggregate becomes

$$\begin{aligned}\rho_i &= \rho_{i-1} (1-\rho_i) \\ &= \rho_0 (1-\varepsilon_1) (1-\varepsilon_2) \dots (1-\rho_{i-1}) (1-\rho_i)\end{aligned}\quad (2.18)$$

where, the parameters with subscripts $i-1$ and i are those connecting with the $(i-1)$ th and the i th steps of agglomeration, respectively. The density of the agglomeration step.

Figure 2.4 is a schematic explanation of the above mentioned multilevel agglomeration process.

Practical process of flocculation, of course, will not take place in such an idealized way. However, with its simplicity, equation. 2.18 can help to understand the relationship between floc structure and floc density.

There are two possible ways to make compact floc. The characteristic of the first way is to form flocs with the same density directly regardless of the agglomeration level. The characteristic of the second way is to exude the higher-level void water entrapped in the already formed multilevel flocs to generate denser aggregate gradually through an extended period. Figure 2.5 is a comparison of these two pathways for pelletizing.

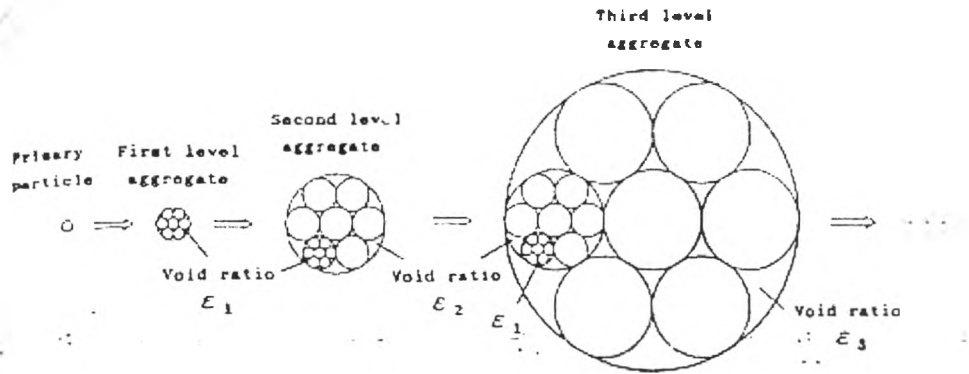


Figure 2.4 Stepwise formation of a multilevel floc.
(Tambo and Wang 1993)

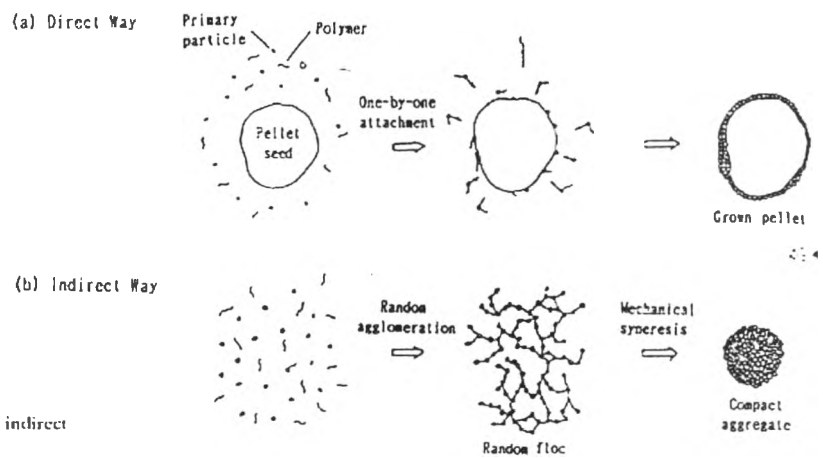


Fig. 4. (a) Direct and (b) indirect ways of pelletizing.

Figure 2.5 Pathways for pelletizing (a) Direct and (b) indirect ways of pelletizing.

(Tambo and Wang 1993)

2.4.4 Advantages of Pelletization Process

Many researchers reported that the pelletization process have several advantages over the convention process in water treatment, which can be summarized as follows:

i. High Efficiency

The pelletization process produced high quality effluent. Panswad and Channarong (1998) found that this process could removed turbidity as high as 98%. In wastewater treatment, Shimizu et al. (1994) found that the process could removed suspended solid, total COD and Total nitrogen in wastewater 99, 95 and 78%, respectively.

ii. Simple to Operate

The process is fully automated, simple to operate and maintenance. It required very limited operator attention.

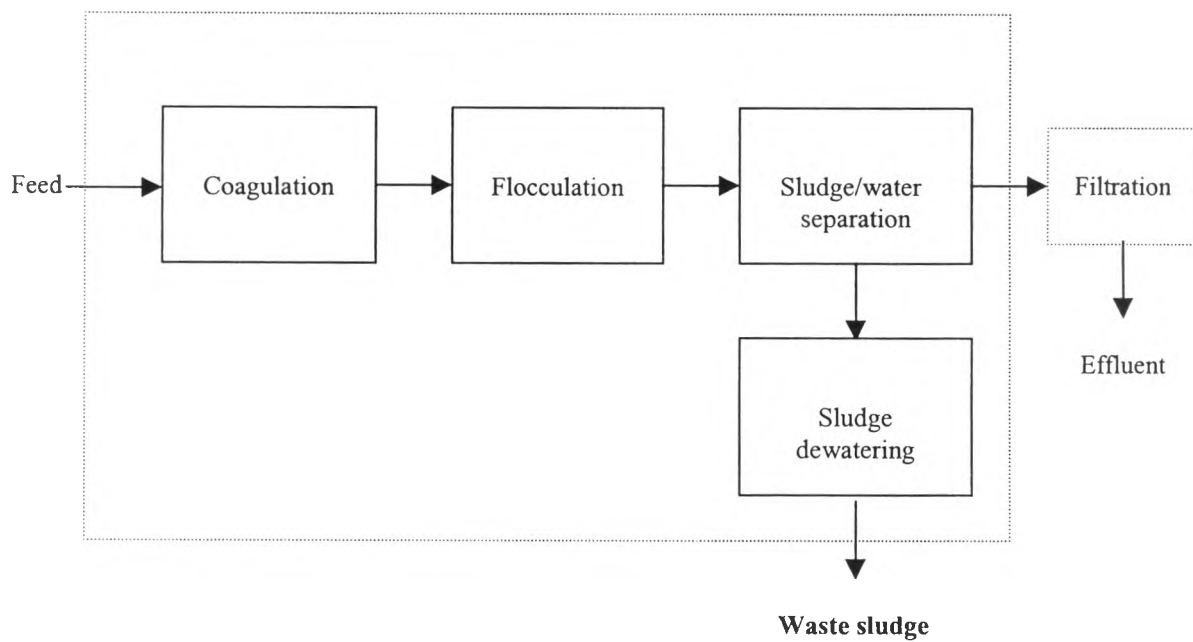
iii. Low Cost

The cost including investment costs, operation and maintenance costs, chemical costs and waste disposal costs are lower than the convention process. In investment costs are lower since the coagulation, flocculation, separation and dewatering process are combined into one by the pelletization process (Figure 2.6). Costs for energy are low, only requiring electricity for pumping.

iv. Low Waste Product

The pelletization process produced small quantity of waste product when compared with the convention process. Moreover, wastes also easy to dispose because produced pellets have low water content (low cost for dewatering).

Conventional



Pellet Reactor

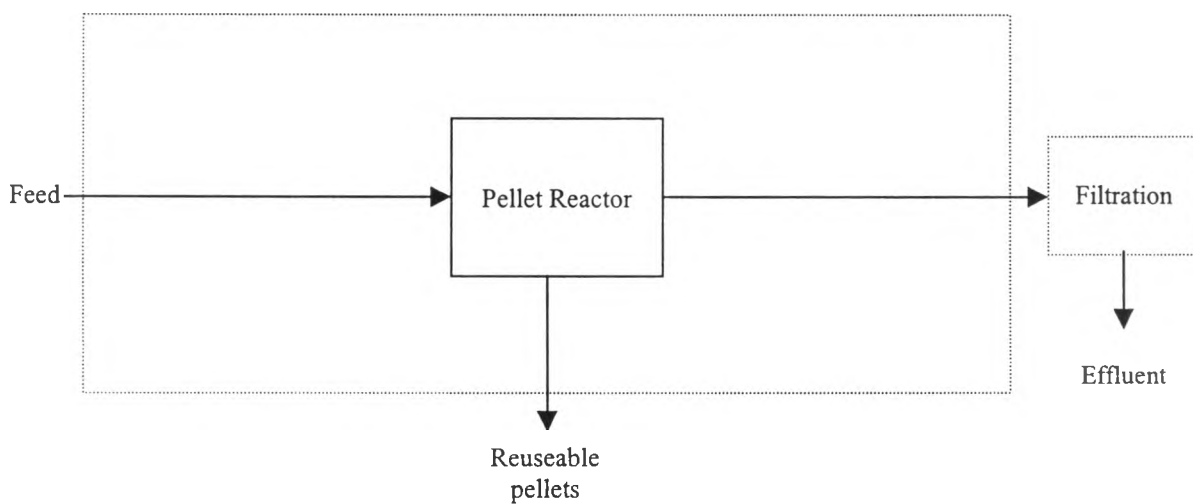


Figure 2.6 The four steps found in conventional treatment process are combined into one by the pelletization process. (Giesen, 1999)

2.6 COAGULANTS

2.6.1 Introduction

The most widely used coagulants in water treatment are aluminium and iron salts. Aluminium salts are employed more frequently than iron salts because they are usually cheaper. Iron salts have an advantage over aluminium salts because they are effective over a wider pH range. The principle factors affecting the coagulation and flocculation of water or wastewater are turbidity; suspended solids; temperature; pH; cationic and anionic compositions and concentrations; duration and degree of agitation during coagulation and flocculation; dosage and nature of the coagulant; and, if required, the coagulant aid. The selection of a coagulant requires the use of laboratory or pilot plant coagulation studies, since a given water or wastewater may show optimum coagulation results for a particular coagulant. Usually laboratory studies using the jar test are adequate for selecting a coagulant for a water treatment plant, whereas laboratory and frequently pilot studies are required for wastewater.

2.6.2 Polyaluminium chloride (PACl)

2.6.2.1 The Nature of PACl

PACl is a coagulant developed in Japan. It has been used in Asia, Australia and Europe for water treatment since the late 1960's and rapidly expanding into commercial in mid 1980's. PACl is a coagulant that consists of partially hydrolyzed aluminium chloride (AlCl_3) produced by the addition of base to concentrated AlCl_3 solution under specified conditions. The general formula of PACl may be expressed as;



The simplest polyaluminium form is shown in Figure 2.7, the dimer has two octahedrally coordinated aluminium ions joined together by two shared hydroxyl groups that displaced four water molecules.

PACl can be prepared by mixing a hot aqueous solution of AlCl_3 with a small amount of a solution or suspension of aluminium hydroxide, which in turn can be obtained by precipitation of a solution of AlCl_3 or sulfate by sodium carbonate. The composition of PACl will depend on the concentration of the stock AlCl_3 solution, degree of neutralization (r), type of base, mixing technique, presence of sulfate, temperature, pressure, and on occasion, age of the solution. PACl is supplied as a liquid with the equivalent of 10% Al_2O_3 . Dilutes solution of concentration 4-3% show evidence of slow hydrolysis.

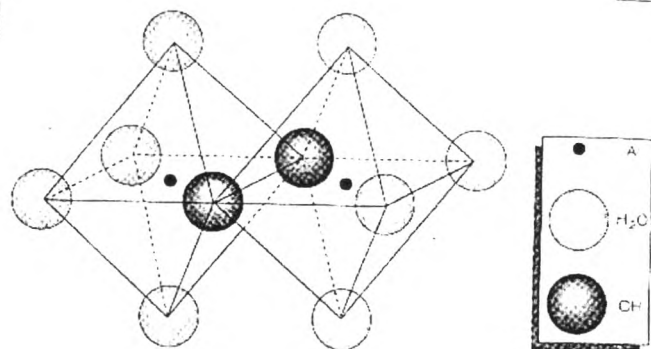


Figure 2.7 The simplest polyaluminium form.

(Wortley, 1990)

2.6.2.2 Theory of the Action of PACl

Different reactions may occur when PACl is added to polluted water, depending upon the impurities in the water. The aluminium species can act both as coagulants (destabilizing agents) in stable colloid suspensions and as precipitants of soluble contaminants. According to Stumm and O'Melia (1968), PACl can function as a coagulant for the destabilization of colloid and particle mainly in two ways:

- a) Positively charged aluminium polymers adsorb onto the negatively charged particles, neutralizing their charge and permitting effective aggregation when sufficient contact opportunities are provided. This process works well for concentrated suspensions where flocculation is fast and at pH levels where cationic polymers are formed rapidly (pH \approx 5-6). Increasing concentration of organic matter require increasing amounts of destabilization chemical for charge neutralization by adsorption; stoichiometry is observed.
- b) $\text{Al}(\text{OH})_3$ (s) can be precipitated before charge neutralization occurs. This will typically happen in low organic matter water at pH >5-6. The colloidal matter is removed as a consequence of entrapment to the "stick" hydroxide precipitate, the "sweep floc". Increasing concentration of colloidal matter requires fewer contact opportunities, so that coagulant requirement can even decrease slightly with increasing colloidal concentration; stoichiometry is not observed.

2.6.2.3 Advantages of PACl

Many researchers indicated that PACl coagulants have several advantages over the traditional metal salt coagulants in most waters, which can be summarized as follows:

- Better overall purification efficiency.
- Better floc separation.
- Wider working pH range.
- Less sensitive to low temperatures.
- Lower residual aluminium concentration.

In addition, there are effects that normally are favorable, such as lower alkalinity consumption resulting in less pH drop when added to the water. The following are briefly discussing these effects based on references from the literature both on drinking water and wastewater treatment.

i. Improved Overall Purification Efficiency

PACl are used extensively in the treatment of turbid waters for drinking water preparation. Especially in France, the development of these coagulants in the seventies led to improve treatment. Later references from England, USSR, USA, Sweden and Canada show that PACl seems to give lower residual turbidity values than alum at a given dosage, corresponding to lower Al dosage in order to obtain the same treatment result.

Most of reports on turbidity removal also conclude that the removal of organic matter was improved. In addition there are several reports where specifically soft, humic waters have been treated, demonstrating that a PACl gave better color removal efficiency at equivalent Al doses. Storrvik (1986) demonstrated that a PACl gave better color removal than aluminium sulfate.

For wastewater treatment, several studies reports have shown PACl to give better result than aluminium sulfate with respect to particle separation. Diamadopoulus and Benedek (1984) found, however, that phosphate removal was poorer the higher the basicity of the coagulant.

ii. Better Floc Separation Effect

Several authors have found that PACl have given flocs with improved floc separability, with respect to settleability, filterability and sludge dewaterability.

Diamadopoulus and Benedek (1984) found better settling rates in wastewater coagulation with PACl than with alum. The higher the basicity, however, the lower was the settling rate. These authors also studied the dewaterability of the sludge. It is difficult to draw absolute conclusion from their work, but their result seem to indicate a higher specific resistance for the PACl coagulated sludge than for that coagulated by alum.

In coagulation / direct filtration experiments of a humic water, Eikebrokk and Fetting (1990) reported that one could achieve a higher net water production with PACl than with alum as a consequence of the higher optimum filter velocity that could be achieved with the PACl.

iii. Wider Working pH Range

Invariably, it seems that the pH range which coagulation is successful is considerably wider with PACl than with alum coagulation. This was the case in turbidity removal, in humic substance removal and in wastewater treatment.

Dentel (1988) hypothesizes that the advantage of PACl at the pH extremes stems from the circumvention of solubility limitations. In other words, the positively charged insoluble aluminium hydroxide species, which act as destabilization agents, are preformed and do not depend on pH conditions within the water to be treated.

Since PACl give less pH drop for a given Al dosage, one can normally operate at a lower Al dosage in order to obtain a given result. This is also of importance in pre-coagulation before biological nitrification in wastewater treatment, both because the nitrification velocity is highest at $\text{pH} \approx 8-8.5$ and because nitrification itself consumes alkalinity.

iv. Less Sensitive to Low Temperatures

It is well known that the performance of coagulation plants deteriorates at very low temperatures due to an efficiency loss in all the treatment steps (coagulation, flocculation, settling and filtration). Several authors have reported that PACl is more efficient at low temperatures than the basic metal salts.

v. Lower Residual Al concentration

Simpson et al.(1988) demonstrated that in all three full scale drinking water plants, the residual Al concentration was lower with the use of PACl than with alum at equivalent dosages. This is relevant in the discussion about aluminium having an influence on the occurrence of Alzheimer disease.

2.7 COAGULANT AIDS

2.7.1 Introduction

In water treatment coagulant aids are compounds that useful either in reducing interference from organic material or improving floc characteristics. They are usually added with metal coagulants to produce a quick-forming, dense, rapid-settling floc and to insure optimum coagulation. In some case, they also used as primary coagulants.

2.7.2 Polyelectrolytes

2.7.2.1 The Nature of Polyelectrolytes

Polyelectrolytes are widely accepted as coagulant aids both in water and wastewater treatment. In general, polyelectrolytes are water-soluble organic or inorganic polymers with ionizable groups. They may be of natural origin such as starch or polysaccharide gums, or they are may be synthetic in origin. Most polyelectrolytes used in water and wastewater treatment are synthetic organic chemicals. These aids are usually classified according to their ionic characteristics. There are anionic (negatively charged), cationic (positively charged), and nonionic polymers. The nonionic and anionic polyelectrolytes are normally used as coagulant aids. As such, they speed up the coagulation process, but they do not replace the metal salts, which are acting as the primary coagulants. It also appears that a minimum molecular weight of the polymer is necessary for successful coagulation. The minimum molecular weight also depends on such factors as the relative number of charged groups, the degree of branching of the polymeric structure, the charge of colloidal particles and the ionic strength of the solution. The cationic polyelectrolytes may well be used in the future as primary coagulants, but this use has not developed significantly at the present time as no technical or economic advantages have been demonstrated.

Polyelectrolytes are frequently in powder form and may require specific procedures to prepare aqueous solutions for feeding. Usually the dosage is less than about 0.3 mg/L

2.7.2.2 Theory of the Action of Polyelectrolytes

The most acceptable model for the explanation of the ability of polyelectrolytes to destabilize colloidal dispersion seems to be provided by the bridging theory.

According to the bridging theory, polyelectrolytes must contain chemical groups, which can interact with adsorption sites on the surface of the colloidal particle. When polyelectrolytes molecule comes into contact with a colloidal particle, some of the active groups are adsorbed at the particle surface. The pliable coiled threads remaining extended in the solution can attach other vacant adsorption sites of several colloidal particles. A particle-polyelectrolyte-particle complex is thus formed. Thus optimum destabilization only occurs when a small fraction of the available adsorption sites on the surface of the particles are covered. If the dosage of polyelectrolyte is sufficiently large to saturate the particle surface a restabilized colloid can be produced, since no sites are available for the formation of polyelectrolyte bridges.

The bridging theory provides an explanation for the effective destabilization and aggregation of colloids by polyelectrolytes having the same charge as the particle. This theory is confirmed by the fact that under certain conditions a system which has been destabilized and aggregated can be restabilized with extended agitation, which gives rise to the breaking of particle polyelectrolyte bonds.