



CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Ceramic membrane filtration

Ceramic materials are generally very stable chemically, thermally and mechanically. They are ecologically friendly and more favorable than other separation technologies. No additives are necessary and the process temperature is not limited. Filtration with ceramics is a mild, highly selective process without phase transformation. Running costs are limited by closed production cycles and continuous processes. They are therefore ideal materials for many applications in the chemical and pharmaceutical industry or in water and wastewater processing. The membrane modules can withstand elevated temperatures, extremes of pH (0 to 14), and high operating pressures up to 10 bar (145 psi) without concern for membrane compaction, delaminating or swelling. This makes these membranes suitable for many applications where polymeric and other inorganic membranes cannot be used. Additionally, ceramic membranes are ideal for in-place chemical cleaning at high temperatures, while using caustic, chlorine, hydrogen peroxide, ozone and strong inorganic acids, and/or by using steam sterilization.

Materials

Ceramic membranes today run the gamut from A to Z in terms of materials (from alpha alumina to zircon). The most common membranes are made of Al, Si, Ti or Zr oxides, with Ti and Si being more stable than Al or Si oxides. In some less frequent cases, Sn or Hf are used as base elements. Each oxide has a different surface charge in solution. Other membranes can be composed of mixed oxides of two of the previous elements, or are established by some additional compounds present in minor concentration.

The supports for the membrane elements are made from γ -aluminium oxide or silicon carbide with open pores. This material can provide not only maximum permeability but can also fulfill high requirements relating to mechanical stability. These supports are either for a single channel or a multi-channel design. A membrane layer of a define texture only a few μm thick is applied to the inner side of the channels in a sandwich-type process and connected monolithically.

Structure

Ceramic membranes normally have an asymmetrical structure composed of at least two, mostly three, different porosity levels. Generally, there are two main layers assembled in ceramic membranes that are including of separation layer and support layer, as illustrated in Figure 2.1.

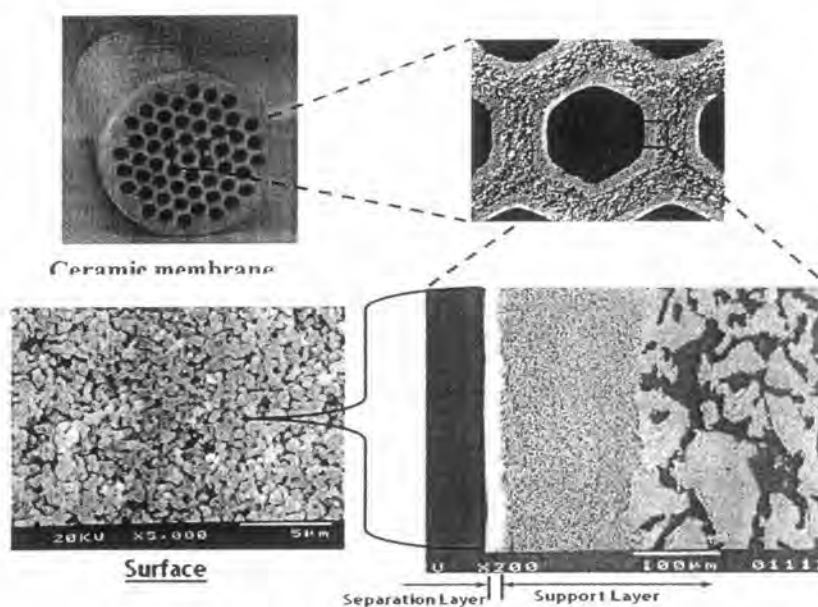


Figure 2.1 The magnification of ceramic membrane structure (Source: Meta Water Co., Ltd. Confidential Report, 2008)

The ceramic membranes are often formed into an asymmetric, multi-channel element. These elements are grouped together in housings, and these membrane modules can withstand high temperatures extreme acidity or alkalinity and high operating pressures, making them suitable for many applications where polymeric and other inorganic membranes cannot be used. Several membrane pore sizes are

available to suit specific filtration needs covering the microfiltration, the ultrafiltration, and nanofiltration ranges (from 5 μm down to 1000 Daltons).

Flow

Ceramic membranes are operated in the cross flow filtration mode. This mode has the benefit of maintaining a high filtration rate for membrane filters compared with the direct flow filtration mode of conventional filters. Cross flow filtration is a continuous process in which the feed stream flows parallel (tangential) to the membrane filtration surface and generates two outgoing streams. A small fraction of feed, called permeates or filtrates, separates out as purified liquid passing through the membrane. The remaining fraction of feed, called concentrate contains particles rejected by the membrane. The separation is driven by the pressure difference across the membrane, or the trans-membrane pressure. The parallel flow of the feed stream, combined with the boundary layer turbulence created by the cross flow velocity, continually sweeps away particles and other material that would otherwise build up on the membrane surface.

Element shapes

Ceramic membranes are available from several manufacturers in different shapes, mainly round and hexagonal, and with various channel diameters. A multi-channel construction provides a higher membrane packing density than a tubular element of the same length. A typical industrial installation will have several of these modules arranged in series and/or parallel configuration.

2.1.1 Membrane filtration for DOM removal

Lee *et al.*, (2004) reported that the ceramic tight-UF membranes exhibited the potential to more effectively remove DBP precursors than natural organic matter in terms of DOC, versus the tested polymeric membranes proved to be very effective at removing DBP precursors, compared with DOM with respect to DOC and UVA. Filtration using ceramic membranes is rarely used in drinking water compared to

polymeric membranes, though a titanium dioxide nanofiltration (NF) membrane was tested to effectively reject mono- and di-valent anions by charge interaction between the negative-charged membrane surface and the anions (Puhlfur *et al.*, 2000).

Many researches showed the advantages of using pre-coagulation combined with membrane filtration over using membrane filtration alone. Maartens *et al.* (1999) reported treatment of the natural brown water with pre-coagulation increased DOM adsorption and decreased hollow-fiber UF (made from polysulfone) performance. Laine *et al.* (1990) found that, without some kind of chemical pretreatment, UF is not effective in removing DOM, with DOC removals of less than 20%. While much potential has been shown by nanofiltration (Conlon *et al.*, 1989), ultrafiltration without pretreatment has shown only limited potential (Laine *et al.*, 1992).

A combination of coagulation and membrane filtration has been developed, since the coagulation rate is very fast and the aggregates rapidly reach sizes larger than the membrane's pore size after coagulant is added (Matsushita *et al.*, 2005) therefore; long-duration mixing is probably not needed in the coagulation-membrane filtration hybrid system (Judd *et al.*, 2001). Moreover, the addition of a coagulant as a pretreatment prior to membrane filtration has been proposed for the purpose of not only improving the removal of DOMs but reducing membrane fouling (Wiesner *et al.*, 1989; and Jacangelo *et al.*, 1995)

Guigui *et al.* (2002) reported that good conventional coagulation conditions in terms of coagulant type, dose and pH should also provide good performance and final water quality for in-line coagulation with UF. UF membranes also shown to remove DBP precursors up to 30% and addition of organic polymers and chemical coagulants upstream of UF enhances DOM removal (Siddiqui *et al.*, 2000). A hybrid process of ultrafiltration with in-line coagulation improved the removal of natural humic acids greatly compared to direct UF, such as pre-coagulation at pH 7, DOC and UV removals were increased from 28% to 53% and 40% to 78% respectively and In-line coagulation also reduced the rate of membrane fouling and resulted in more constant permeate flux and very slight increase of transmembrane pressure during a filtration cycle. (Wang *et al.*, 2006).

Bian *et al.* (1997, 1999) suggested that the combination of high flux and good water quality were achieved when they used a lower dose of coagulant prior to membrane filtration than the optimal dose for removal of humic substances during conventional treatment that shown the effective DBP precursor reductions can be achieved by membrane separation. Precoagulation (PC) with either ferric or aluminium coagulants also improve DOM removal and lead to reduced trihalomethane (THM) formation (Judd *et al.*, 2001).

Comparison between DOC removal by conventional clarification and PC-MF revealed decrease of around 40% in DOC passage achieved by the PC-MF system with ferric chloride, polyaluminium chloride and aluminium sulphate (Pikkarainen *et al.*, 2004).

A ceramic tight-ultrafiltration (UF) membrane showed the same potential as a similar nanofiltration (NF) polymeric membrane, in terms of the minimization of haloacetic acid (HAA) formation. Moreover, a ceramic UF membrane with a MWCO of 8000 Daltons showed almost the same behavior as an equitable polymeric UF membrane with a MWCO of 8000 Daltons in terms of NOM removal (Sangyoun *et al.*, 2004).

2.1.2 Membrane filtration for microbial removal

MF, typically with pore sizes 0.1 μm have showed lower removal of virus, and in some cases, could not at all act as physical barrier to viruses (Sondhi *et al.*, 2003). UF can achieve more than 6 log (99.9999%) virus removal; MF cannot efficiently remove viruses when the filtration mechanism relies on physical sieving alone. The addition of coagulant, the most commonly used methods for the removal of suspended solids in water, is one of the selection to be the pretreatment process before a membrane filtration process to increase permeate quality.

Previous researches have been presented that some viruses have tendency to adsorb on to the aluminum floc particles, which are finally retained by the membrane to form the cake layer (Clesceri *et al.*, 1998). Other researchers have reported that the formation of a cake layer may enhance the removal of viruses by membrane filtration

(Jacangelo *et al.*, 1995; Madaeni *et al.*, 1995; Farahbakhsh *et al.*, 2004) because the PACl accumulated in the membrane compartment would consequently increase with time and could inactivate the viruses there (Matsushita *et al.*, 2005).

Matsui *et al.*, 2005 concluded that coagulant dose, membrane pore size, and coagulation time affected virus removal. Increasing coagulant dosage was most effective for virus removal. Extending time probably improved the low removal resulting from the low coagulant dose. The effect of membrane pore size was more clearly observed at the beginning of filtration where the caked layers have not fully developed. MF with nominal pore size of 0.1 μm after coagulation pretreatment with the PACl dose of 1.08 mg/l Al and 2.4-s mixing time achieved over 6.4 log reduction in virus load. The MF whose pore size were 0.5 and 0.1 μm showed about 1 log less removal than by the 0.1- μm pore-size.

2.2 Polyaluminium Chloride (PACl) coagulation

The term "poly-aluminum chloride" or "PACl" refers to a class of soluble aluminum products in which aluminum chloride has been partly reacted with base. The relative amount of OH-, compared to the amount of Al, determines the basicity of a particular PACl product. The chemistry of PACl is often expressed in the form $\text{Al}_n(\text{OH})_m\text{Cl}_{(3n-m)}$. Basicity can be defined by the term $m/(3n)$ in that equation. Solutions of PACl are not as acidic as alum; consequently they do not tend to decrease the pH as much as an equivalent amount of alum. Another difference is that PACl is formulated so that it already contains some of the highly cationic oligomers of aluminum - materials that are especially effective for the modification of colloidal charges. A particularly stable and important ionic species in PACl and related soluble aluminum chemicals has the formula $\text{Al}_{12}(\text{OH})_{24}\text{AlO}_4(\text{H}_2\text{O})^+_{127}$.

Polyaluminium chloride (PACl) is increasingly used for water treatment. Against the conventional use of aluminium sulphate (alum), it is showing distinct advantages. PACl are synthetic polymers dissolved in water. They react to form insoluble aluminium poly-hydroxides which precipitate in big volumetric flocs. The

flocs absorb suspended pollutants in the water which are precipitated with the PACl and can together be easily removed. PACl can be used as a flocculant for all types of water treatment, drinking water, industrial waste water, urban waste water and in the paper industry.

The advantages of PACl over Alum

- Lower dosage requirement
- No requirement for any neutralising agent (soda, lime)
- Shorter flocculation time
- Smaller amount of sludge
- Reduced number of back washing steps
- Higher quality of the treated water
- Alum can contain any type of hazardous metals in some conditions

2.3 Dissolved Organic Matter (DOM) and their surrogates

DOM is a complex mixture of various compounds with widely different chemical properties from simple structure to very complex polymers in natural water (Henze, 1992). DOM consists of humic substances, amino acids, sugar aliphatic acids, and a large number of organic molecules (Pirnie Inc., 1993). Leenheer and Croue (2003) defined DOM as a complex mixture of aromatic and aliphatic hydrocarbon structures with attached amide, carboxyl, hydroxyl, ketone, and various mineral functional groups. Generally, natural water source such as river, reservoir and groundwater, are utilized as the source of raw water to produce water supply.

DOM has been commonly quantified by using surrogate, nonspecific parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at wavelength of 254 nm (UV-254), specific ultraviolet

absorbance (SUVA) and trihalomethane formation potential (THMFP) (USEPA, 1999).

DOMs can be distinguished by fluorescent spectrometry wavelengths scanning of both excitation and emission, and obtained three-dimensional fluorescent spectroscopy results (fluorescent excitation-emission matrix, FEEM). FEEM provides information on the putative origin of fluorescent organic matter in water. It may identify the matter as a tyrosine-like substances, tryptophan-like substances, humic acid and fulvic acid-like substances, and so on (Nakajima *et al.* 2002; Chen *et al.* 2003; and Sierra *et al.* 2005).

2.3.1 Dissolved Organic Carbon (DOC)

TOC is the measure of all organic substances contained in water samples including suspended fractions that could be removed by coagulation and sedimentation. DOC is defined as the fraction of TOC that passes through a 0.45 μm filter paper. Since some types of 0.45 μm filter paper are produced using cellulose nitrite or cellulose acetate membrane, organic substances could leach from these filter papers after the filtration process. Thus, GF/F filter paper with a pore size of 0.7 μm is used in DOC analysis.

2.3.2 Ultraviolet absorbance at wavelength 254 nm (UV-254)

UV-254 is used to provide an indication of the aggregate concentration of UV-absorbing organic constituents, such as humic substances and various aromatic compounds (APHA, AWWA, WEF, 1995). As noted by Edzwald *et al.* (1985), humic aromatic compounds and molecules with conjugated double bonds absorb UV light, whereas simple aliphatic acids, alcohol, and sugars do not. Most research has utilized the measurement at the UV-visible at the wavelength of 254nm as the representative for the relative quantity of aromatic-humic organic substances (Leenheer and Croue 2003). UV absorbance is a well-known technique for measuring the presence of naturally occurring organic matter such as humic substances. UV analysis is also affected by pH and turbidity (Edzwald *et al.*, 1985). UV absorption is a useful

surrogate measure for DOM or precursor of THMs because humic substrates strongly absorb ultraviolet radiation (Eaton, 1995).

2.3.3 Specific Ultraviolet Absorption (SUVA)

The ratio between UV absorbance to DOC, referred to as specific ultraviolet absorbance (SUVA) (L/mg-m) demonstrates a relative index of humic content (Edzwald, 1993; and Owen *et al.*, 1993). SUVA could suggest the nature of DOM and its consequent THM formation (Krasner *et al.*, 1996). Higher SUVA values tend to indicate higher humic content. The SUVA of a humic sample depends upon the molecular weight of the substance (Pettersen *et al.*, 1995). SUVA can be used as an indicator of its coagulation (or softening) ability to remove THM precursors. Water having a high SUVA value (SUVA > 3 L/mg-m) has been found to contain organic matter that is more humic-like in character, higher in AMW, and more readily removed by coagulation (Edzwald, 1993) whereas lower SUVA values (< 3 L/mg-m) indicate the presence of organic matter of lower AMW that is more fulvic-like in character and more difficult to remove. With regard to wastewater treatment plants, Fukushima *et al.* (1996) reported that the SUVA of total DOM increased as the lake water, influenced by pedogenic DOC, was allowed to further stabilize through biodegradation over a long period of time. Imai *et al.* (2002) reported that since a biological treatment was employed in sewage treatment plants, it should produce effluent water with higher SUVA values than that of influent wastewater.

2.3.4 Trihalomethanes Formation Potential (THMFP)

Trihalomethanes (THMs)

Trihalomethanes (THMs) were formed when chlorine reacted with naturally occurring humic substances in water treatment plants and water distribution systems. The first identification of chloro- and bromo-trihalomethanes (THMs) was done by Johannes Rook in 1974. The first class of halogenated disinfection by-products (DBPs) discovered in chlorinated drinking water. Since that time, the reduction of

THMs has been the subject of intensive investigation in the water treatment field. Symon *et al.* (1975) described a survey of halogenated organic compounds from 80 water supply plants. THMs have been found to be the most widespread organic contaminants in drinking water, and occur at higher concentrations than other disinfection by-products. The four THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) are formed when chlorine-based disinfectants are added to source water with fairly high organic content, such as surface water. THMs are included among the 25 volatile organic compounds regulated under the Safe Drinking Water Act (SDWA) of 1987. These compounds are persistent and mobile, and pose a cancer risk to humans (Pereira, 1983; Munro *et al.*, 1986). Chloroform (CHCl_3), the most common THM, is a proven animal carcinogen and a suspected human carcinogen.

THMs can be taken in by drinking the water and breathing its vapours (for example when showering). They are then metabolised and eliminated rapidly. Most THMs are metabolised into a less-toxic form, but some are transformed into more reactive substances, especially at high concentrations. The THMs are absorbed, metabolized and eliminated rapidly by mammals after oral or inhalation exposure. Following absorption, the highest tissue concentrations are attained in the fat, liver and kidneys. THMs induce cytotoxicity in the liver and kidneys of rodents exposed to doses of about 0.5 mmol/kg of body weight. A maximum contaminant level (MCL) of 100 $\mu\text{g/L}$ for total trihalomethanes (TTHMs) in finished drinking water was established by the US. Environmental Protection Agency (USEPA) in the National Interim Primary Drinking Water Regulations in 1979. The USEPA has set a new MCL of 80 $\mu\text{g/L}$ for stage 1 of the disinfection by product rule (D/DBP Rule; USEPA 1998). In stage 2, the D/DBP Rule may lower the MCL for THMs to 40 $\mu\text{g/L}$.

Trihalomethanes Formation Potential (THMFP)

Total trihalomethanes (TTHM_T) is the sum of all four compound concentrations, chloroform, dichlorobromomethane, dibromochloromethane and bromoform, produced at any time T (usually measured in days). TTHM_0 is the total THMs concentration at the time of sampling. It can range between non-detectable to

several hundred micrograms per liter if the samples have been chlorinated. $TTHM_7$ is the total concentration of all four THMs compounds produced during the reactions of the sample precursors with excess free chlorine over a 7-day reaction time at the standard reaction conditions, which were as follows: free chlorine residual at least 3 mg/L and not more than 5 mg/L at the end of a 7-day reaction (incubation) period with sample incubation temperature of $25 \pm 2^\circ\text{C}$, and pH controlled at $7 \pm 0.2^\circ\text{C}$ with phosphate buffer. THMFP or $\Delta THMFP$ is the difference between the final $TTHM_7$ concentration and the initial $TTHM_0$ concentration. For samples that do not contain chlorine at the time of sampling, $TTHM_0$ will be close to zero. Therefore the term THMFP may be used. For samples that contain chlorine at the time of sampling, a $TTHM_0$ value will be detected. Therefore the term $\Delta THMFP$ may be used when reporting the difference between the TTHM concentrations (Standard method, 1995).

THMFP has also only been commonly employed to measure the DOM in water at drinking water supply facilities. The THMFP of treated wastewater has not been widely evaluated due to treated wastewater being perceived as less aromatic (Aieta, 1998). Nevertheless, treated wastewater seems to have much higher DOC concentrations than most surface water used as drinking water supplies. A survey of five wastewater treatment plants in southern California, USA demonstrated that DBPs in treated wastewater was found to be higher than that of influent wastewater (National Research Council, 1998). Musikavong *et al.* (2005) reported that the level of THMFP in the treated wastewater of the industrial estate in northern Thailand was moderately high when compared with other surface waters in Thailand (Wattanachira *et al.* 2003, Homklin 2004, Janhom 2004, Panyapinyopol *et al.* 2005; and Phumpaisanchai 2005).

2.3.5 Fluorescent Excitation-Emission Matrix, FEEM

Chen *et al.* (2003) defined excitation and emission boundaries into five regions based largely upon supporting literature. FEEM peaks have been associated with humic-like, tyrosine-like, tryptophan-like, or phenol-like organic compounds. In general, peaks at shorter excitation wavelengths (<250 nm) and shorter emission wavelengths (<350 nm) are related to simple aromatic proteins such as tyrosine

(Regions I and II). Peaks at intermediate excitation wavelengths (250 nm - 280 nm) and shorter emission wavelengths (<380 nm) are related to soluble microbial byproduct-like material (Region IV). Peaks at longer excitation wavelengths (>280 nm) and longer emission wavelengths (>380 nm) are related to humic acid-like organics (Region V). For fulvic acids, FEEM with minimum excitation wavelengths of 250 nm indicated shoulders of FEEM peaks located at shorter excitation wavelengths. Therefore, peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials (Region III).

Janhom (2004) characterized the fluorescent organic matter in reservoir water of the Northern-Region Industrial Estate, Lumphun province, Thailand. A fluorescent peak at 275nmEx/410nmEm representing humic-like substances was detected.

Sierra *et al.* (2005) used single-scan and FEEM techniques to identify the fluorescent fingerprints of fulvic and humic acids from various origins. They noted that in the case of fulvic acids, the Ex/Em pairs were approximately 260nmEx/460nmEm and 310nmEx/440nmEm, whereas in the case of humic acids, their excitation and emission maxima were red-shifted. The corresponding Ex/Em pairs were located at approximately 265nmEx/525nmEm and 360nmEx/520nmEm.

Phumpaisanchai (2005) used the FEEM to characterize the fluorescent organic matter in water from the Mae-Hia reservoir, Chiang Mai province and Bhumibol Dam reservoir in Tak province, Thailand. Fluorescent peaks at 260nmEx/420nmEm and 330nmEx/400nmEm were detected in the water from the Mae-Hia reservoir, whereas fluorescent peaks at 260nmEx/420nmEm and 330nmEx/410nmEm were found in the water from the Bhumibol Dam reservoir. These observations lead to the conclusion that, humic acid-like and fulvic acid-like substances were the major fluorescent organic matter in both the Mae-Hia reservoir and Bhumibol Dam reservoir.

Musikavong *et al.* (2005) demonstrated correlations of THMFP and fluorescent intensity of the influent wastewater and water samples from each pond at the wastewater treatment plant of the Northern Region Industrial Estate, Lamphun,

Thailand. Their reported results showed that FEEM could be used to quantify the THMFP in the water source.

2.4 Viral Indicators

The most significant virus group affecting water quality and human health originates in the gastrointestinal tract of infected individuals, called enteric viruses. The enteric viruses cause a wide range of diseases and symptoms. Viral etiology is rarely identified, even though viruses are believed to cause a majority of water borne illness (Griffin *et al.*, 2003). The numbers of pathogenic microorganisms presented in surface waters are generally few and difficult to identify and isolate. The methods to detect pathogens are relatively laborious, require specialized personnel, and not well suited for monitoring purpose. Similarly, in case of enteric viruses in water is difficult; interest has focused on indicator organisms that are nonpathogenic, rapidly detected, easily enumerated, similar survival characteristics to those of the pathogens and able to associate with the presence of pathogenic microorganisms.

Total and fecal coliforms have been used extensively for many years as indicators for determining the sanitary quality of surface, recreational, and shellfish growing waters. The term "total coliforms" includes several genera of gram-negative, facultative anaerobic, non-spore-forming, rod-shaped bacteria, some of which occur naturally in the intestinal tract of animals and humans. *Escherichia coli* (*E. coli*) has also long been used as an indicator of fecal pollution. It has good characteristics of a fecal indicator, such as not normally being pathogenic to humans, and is present at concentrations much higher than the pathogenic it predicts. However, some studies have shown that these indicators do not provide adequate information about viruses particularly in term of their fate in the environment (Skraber *et al.*, 2002; Jofre *et al.*, 1995), because the coliform ecology, prevalence, and resistance to stress is differ from those of viruses and other pathogenic microorganisms (Desmarais *et al.*, 2002). Treatment processes and watershed management strategies designed on the basis of bacteriological criteria do not necessarily protect against virus infection because viruses are generally more persistent in water environment and are not removed well

by treatment processes (Havelaar *et al.*, 1993); therefore many current studies have been directed toward identifying more specifying more specific indicators of viral contamination.

The bacteriophages(bacterial viruses) have been proposed as useful alternative viral indicator, as their morphology and survival characteristics closely resemble that of some of the important human virus groups. Several researches have been published on the use of bacteriophages as viral indicators for the presence of human enteric viruses in fresh water, fecal pollution of treated or untreated drinking water, or indicators of treatment efficiency.

Three types of bacteriophages have been proposed as specific indicators of viral contamination: the somatic coliphages, the F-specific RNA phages, and bacteroides fragilis phages (Morinigo *et al.*, 1998; Havelaar *et al.*, 1985; Jofre *et al.*, 1989). Somatic coliphages are bacteriophages which consist of a capsid containing single or double stranded DNA as the genome. They are violent phages which attach to lipopolysaccharide or protein receptors in the bacterial cell wall. Natural host strains of somatic coliphages include besides *Escherichia coli* or other closely related bacterial species. F-specific RNA bacteriophages are consisting of a simple capsid of cubic symmetry of 21-30 nm in diameter and contain single stranded RNA as the genome. They are infectious for bacteria which possess the F- or sex plasmid originally detected in *Escherichia coli* K-12. Bacteroides fragilis phages are DNA virus, about 60 nm in diameter, infecting by attachment to bacterial cell wall.