CHAPTER 2
LITERATURE REVIEW

2.1 An Overview of Biological Wastewater Treatment

Biological processes are used to convert dissolved and suspended organic matter into flocculant settleable biological and inorganic solids that can be removed in subsequent solid separation stage mainly by gravity sedimentation. Biological conversion can be achieved either in presence or absence of oxygen according to the process are known as aerobic or anaerobic. The principal processes used for wastewater treatment are classified as suspended growth and attached growth or combined. Judd (2006) had described that, biological treatment demands the appropriate reactor conditions prevail in order to maintain sufficient levels of viable microorganisms to achieve removal of organics. The latter are normally measured as biological or chemical oxygen demand (BOD and COD, respectively).

According to Metcalf (2004), the removal of dissolved and particulate carbonaceous BOD and the stabilization of organic matter found in wastewater is accomplished biologically using a variety of microorganisms, principally bacteria. Microorganism are use to oxidize the dissolved and particulate carbonaceous organic matter into simple end product and addition biomass, as represented by the following equation for aerobic biological oxidation of organic matter.

$$\text{CHONS (organic material)} + O_2 + \text{Nutrients} \xrightarrow{\text{microorganisms}} C_5H_7NO_2\text{ (new cell)} + CO_2 + H_2O + \text{other end product} \qquad \textbf{(2.1)}$$

The most common process used for municipal wastewater treatment is the activated sludge process. The activated sludge processes make use of the suspended biomass to systematically stabilize the organic components of a wastewater in presence of oxygen. In activated sludge process, wastewater containing organic matter is aerated in an aeration basin in which microorganisms metabolize the suspended and soluble organic matter. The significant activity of activated sludge microorganisms is the rate of substrate (BOD or COD) removal. The liquid suspension of microorganisms in an aeration basin is generally referred to as mixed liquor, and the biological growth are called mixed liquor suspended solids (MLSS). Part of organic matter is synthesized into new cells and part is oxidized to CO_2 and water to derive energy. In activated sludge systems the new cells formed in the reaction are removed from the liquid stream in the form of flocculant sludge in settling tanks. A part of this settled biomass, described as activated sludge is returned to the aeration tank and the remaining forms waste or excess sludge.

2.2 Septic tank Wastewater

The most common subsurface disposal system for treatment of household wastewater consists of a septic tank for primary wastewater treatment and of a leaching bed for disposal and additional treatment of septic tank effluent. The household wastewater discharged into the septic tank usually contains the toilet wastes or the so called "black water" mixed with the "gray water" which includes the discharge from the kitchen sink, tub and shower, bathroom lavatory, dishwasher, and clothes washing machine. Conventional septic tank and soil absorption systems (STSAS) are often used for wastewater treatment in low population density areas because of the infrastructure costs associated with publicly owned treatment works (Zaveri *et al.*, 2002). The objective of the septic tank is to provide initial treatment to household wastewater by intercepting and separating solid fecal matter from the liquid part.

The quality of the septic tank effluent primarily depends on the duration of biological and chemical treatment of the waste water in the tank or on the detention time (in days), which represents the ratio between the volume of the septic tank and the volume of the daily wastewater discharged from the house. The quality of the effluent depends also on the contents of organic matter in the wastewater. Terpstra (1999) suggested that, most of the organic material, nutrients and pathogens in domestic wastewater are in black water (51% of COD, 91% of nitrogen, 78% of phosphorus). Average characteristics of domestic wastewater, black water and grey water are presented in Table 2.1.

Table 2.1 Average characteristics of domestic wastewater, black water and grey water from conventional flush toilets (Henze *et al.*, 2001)

Parameter (mg/L) water	**Domestic wastewater**	**Black water**	**Grey**
BOD	115–400	300–600	100–400
COD	10–740	900–1500	200–700
Total N	20–80	100–300	8–30
Total P	6–23	40–90	2–7

A septic tank system consists of the tank itself and if it discharges to land, a drainage field. The septic tank is a type of settlement tank intended to provide quiescent conditions for settlement of sludge and the development of anaerobic conditions for decomposition of organic matter. Raw sewage is fed to the tank, and settled sewage is discharged to the drainage field through the tank outlet. Sludge accumulates at the bottom of the tank and has to be removed periodically (Butler, 1995).

However, septic tank effluent often fails to meet the effluent standard. Failure of conventional septic tank occurs due to several reasons, including lack of regular maintenance, unfavorable site topography and soil characteristics, poor design and construction, and inadequate capacity (Zaveri *et al.*, 2002). Such failures can result in nuisance odor and vector problems, as well as contaminate to surface water and groundwater causing serious environmental and health impacts. Because of septic tank effluent contains high concentrations of COD, ammonia, phosphorous, TSS, presence of number and type of bacteria (E. Coli) (Yaobo *et al.*, 2006).

2.3 Fundamental of Membrane Filtration

Membrane is defined as a thin film separation of two or more components from a fluid flow. The advantage of membrane techniques include continuous separation, low energy consumption, easy combination with other existing technique, easy up-scaling, and no additives used. The membrane filtration is divided into three narrower ranges based on particle size as follows,

Microfiltration is the coarsest size of the membrane filtration classes. Its applications are to separate suspended particles from dissolved substances. Microfiltration membranes are classified by pore diameter cut-off (PDCO) which has the diameter of the particles in the range of 0.1 to 10 μm (Cheryan, 1998).

Ultrafiltration is used for separation of large macromolecules such as proteins and starches and all types of microorganism, such as bacteria and virus. Ultrafiltration membranes are classified by molecular weight cut-off (MWCO) which is defined as the molecular weight of the smallest molecules. Ultrafiltration covers particle and molecules that range from 1,000 to 500,000 daltons in molecular weight (Cheryan, 1998).

Nanofiltration membrane retains solute molecules ranging from 100 to 1,000 daltons in molecular weight. Nanofiltration membranes are classified by molecular weight cut-off like ultrafiltration membranes or by percentage sodium chloride rejection like reverse osmosis membranes. It can also reject contaminants as small as 0.001 μm (Taylor, 1996).

Membranes can be manufactured by a wide variety of materials which include inorganic membranes (sintered metals and ceramics) and organic membranes (polymers). The inorganic membranes have better chemical, mechanical and thermal stabilities, but have disadvantages of being very fragile and more expensive than the organic membranes. The organic membranes are widely used in water and wastewater applications because they are more flexible and can be put into a compact module with very high surface area. The organic membranes can be made from cellulose, and all synthetic polymers which have relatively good chemical, mechanical and thermal stability tendencies, and also provide the membranes with better antifouling properties through the use of hydrophilic polymers (Cheryan, 1998).

Membranes can also be classified into two operation filtrations, such as dead-end filtration and cross-flow filtration (Figure 2.1). The filtration of coarse particles down to several micrometers is achieved by the conventional dead-end filtration. Particles retained by the filter in dead-end filtration build up with time as a cake layer resulting in an increased resistance to filtration. This requires frequent cleaning or replacement of filters. For cross-flow filtration, a fluid (feed) stream runs tangential to a membrane, establishing a pressure differential across the membrane. This causes some of the particles to pass through the membrane. Remaining particles continue to flow across the membrane. In contrast to the dead-end filtration, the use of a tangential flow prevents thicker particles from building up a "filter cake" by a high velocity gradient near the membrane surface, which assists in reducing the fouling and polarization effects.

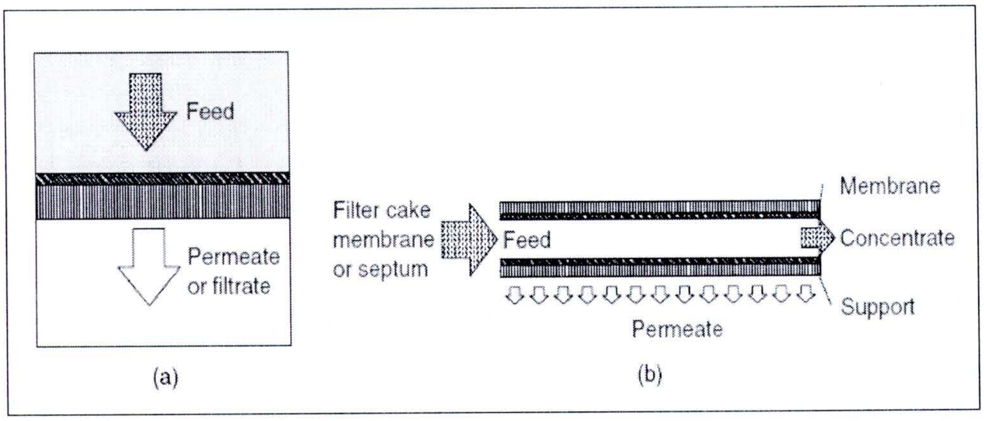

Figure 2.1 Schematic representation of (a) dead-end and (b) crossflow filtration (Judd, 2006)

2.4 The Operational Parameters in Membrane Process

Transmembrane pressure, flux and resistances

Transmembrane pressure (TMP) influences the flux together with the back transport conditions and the thickness of the layer. This is one reason why the flux increase is not proportional to the pressure difference (Figure 2.2). With increasing pressure the flux is increased. The variation has an initial linear part, then exponential middle part and finally it becomes constant at very high pressures.

The transmembrane pressure is the driving force behind the filtration process. Equation 2.2 can be used to predict the permeate flux that remains proportional to hydraulic resistance for porous membrane system. The flux is the quantity of materials passing through a unit area of membrane per unit time and can be determined by both the driving force and the interfacial region adjacent to it. Under the simplest operating conditions, the resistance to flow is offered entirely by the membrane.

$$J = \frac{\Delta P}{\mu R_t} \qquad \textbf{(2.2)}$$

Where J : Permeate flux ($L/m^2.h$).
ΔP : Transmembrane pressure (kPa).
μ : Viscosity of the permeate (Pa.s); when Pa = N/m^2
R_t : Total resistance (1/m); $R_t = R_m + R_c + R_f$
R_m : Intrinsic membrane resistance.
R_c : Cake resistance from by the cake layer (reversible fouling)
R_f : Fouling resistance caused by solute adsorption into the membrane pore and gel formation (irreversible fouling)

All resistances shown in Equation 2.2 can be measured through a series of filtration experiments by comparing pure water filtration, sludge filtration, and pure water filtration after cake removal. However, the resistances are dependent on a number of experimental conditions, such as biomass characteristic, membrane material and temperature.

Judd (2006) concluded that the membrane resistance is governed by the membrane material itself, and mainly the pore size, the surface porosity (percentage of the surface area covered by the pores) and the membrane thickness. The fouling layer resistance is associated with the filtration mechanism, which is then dependent on the membrane and filtered solids characteristics.

For low concentrations and at modest operating pressure, the flux variation shows a linear relation with pressure. At higher operating pressures, the flux starts proportionally decreasing and finally the relationship level off. This leveling off is due to the compaction of deposition layer and densification of the membrane at higher pressures (Metcalf, 2004). Figure 2.2 shows a relationship between transmembrane pressure and flux. It is observed that the higher the transmembrane pressure and the flux, the faster the particles deposit on the membrane surface and to form a cake, then the flux is independent of the transmembrane pressure and remains constant.

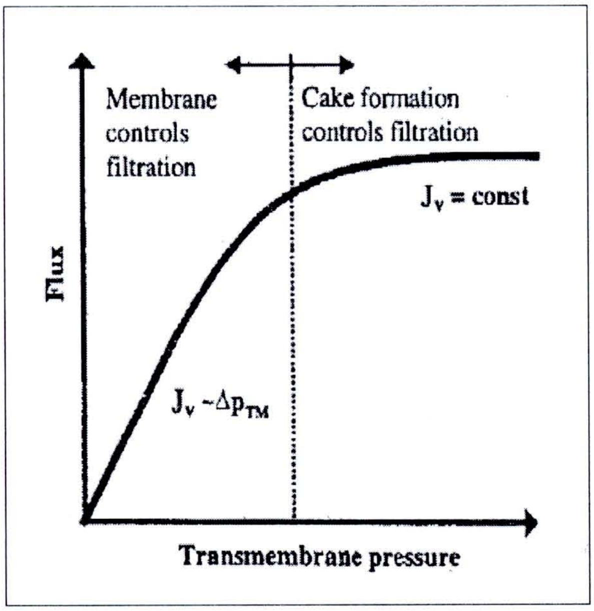

Figure 2.2 Relationship between transmembrane pressure and flux (Gender *et al.*, 2000)

2.5 Membrane Bioreactor

2.5.1 Definition of MBRs

A membrane bioreactor is a technology which combines the activated sludge process (bioreactor) with a membrane separation step. So it replaces and in some cases complements the solids separation function of secondary clarification and effluent filtration (Metcalf, 2004). Basically, a membrane is a material that allows some physical or chemical components to pass through more readily than others. It is perm-selective, which means that it is more permeable to those constituents passing through it (which then became permeate) than those which are rejected by it (which form the concentrate) (Judd, 2006).

The membrane support facility require equipment, such as pumps, for activated sludge circulation and permeate extraction for constant flux filtrations, chemical storage tanks, chemical feed pumps, air-scour systems and a back-pulse water flushing system. The constituents in the feed-water tend to accumulate on the membranes increasing the inside pressure. Thus, the membrane flux starts to decrease and the transmembrane pressure increases. At a certain level of decreasing performance, the membranes must be backwashed and/or chemically cleaned (Metcalf, 2004).

2.5.2 Configuration of MBRs

The first general operation of MBR can be either configured in side-stream operation (as external) or submerged in the bioreactor (as internal) (Figure 2.3). In the case of side-stream system, the membrane is independent of the bioreactor. Feed wastewater enters the bioreactor where it contacts with biomass. The mixture of feed wastewater and biomass is then pumped around a re-circulation loop containing a membrane unit where the permeate is discharged and the retentate is returned to the bioreactor. Excess sludge is pumped out to maintain a constant sludge age. Backwash and chemical washing are used for cleaning the membrane. The use of re-circulation loops leads to an increase energy costs from 2 to 10 kWh/m^3 of the water produced, depending on the internal diameter of the tubes used (Côté *et al.,* 1997). The submerged system is no re-circulation loop as the separation occurs within the bioreactor itself. This system reduces the operation costs. The energy consumption rates are 0.2 to 0.4 kWh/m^3 of which more than 80% are for aeration (Chua *et al.*, 2002). The pressure across the membrane in this system can be applied either by suction through the membrane or by pressurizing the bioreactor. The cost considerations of side-stream and submerged MBRs were discussed by Gender *et al.*, (2002). Table 2.2 shows advantages and disadvantages of the submerged and side-stream MBRs.

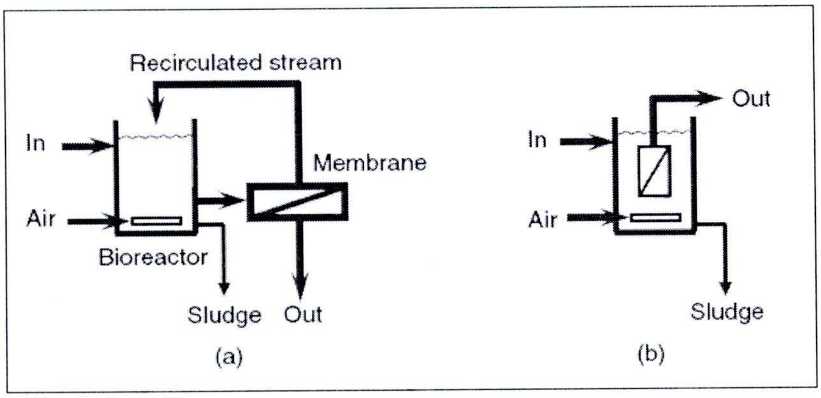

Figure 2.3 MBR configurations (a) Side-stream MBR (b) Submerged MBR (Judd, 2006).

Table 2.2 Advantages and disadvantages of MBR configurations (Stephenson *et al.*, 2000)

Submerged MBR	**Side-stream MBR**
Advantages • Small footprint • Feed-forward control of O_2 demand • Less frequent cleaning required • Lower operating costs • Low liquid pumping costs (28% of total costs) • Low energy consumption	**Advantages** • Small footprint • Complete solids removal from effluent • Effluent disinfection • High loading rate capability • Combined COD, solids and nutrient removal in a single unit • Low/zero sludge production • Rapid start up • Sludge bulking not a problem
Disadvantages • Susceptible to membrane fouling • High aeration cost	**Disadvantages** • Aeration limitations • Membrane fouling • Membrane costs • High operating costs • High pumping cost (60-80% of total costs) • High cleaning requirement • Process complexity

2.5.3 Membrane Types

Membranes have evolved with new materials and applications. The membranes primarily used in wastewater treatment are as follows,

- **Plate and Frame** – The plate and frame membranes consist of two flat sheets of membrane material, usually an organic polymer, stretched across a thin frame. The space between the membrane sheets is placed under vacuum in order to provide the driving force for filtration. Several plates are arranged in a cassette to allow for increased surface area and convenient modular design. The membrane cassette is immersed in the mixed liquor and the separation flow is from outside-in. For example, Kubota membranes have air induced liquid cross-flow along the plates. This creates turbulence and hinders cake formation and subsequent fouling. The organic polymer, polyethylene for example, has the required flexibility to move slightly in the cross-flow to allow three-dimensional dynamic forces to reduce cake formation. The cross-flow of air also acts to dissolve oxygen to and mix the contents of the reactor.

- **Hollow fiber** – Hollow fiber membranes consist of long strands, or fibers, of hollow extruded membrane. They are most often of organic polymer construction and are applied much the same as plate and frame membranes. The fibers are mounted to a supporting structure that serves as a manifold for permeate transport as well as an air delivery system. Similar to the plate and frame modules, air induced liquid cross-flow prevents excessive cake formation and increases the lifespan of the membrane. The fibers are most often employed in the outside-in arrangement. A vacuum is applied to the permeate manifold and this draws water from the reactor-side to the inside of the fiber and out of the system. As with the plate and frame membrane, hollow fiber membranes are also constructed in a cassette format to allow for the convenience of modular design.

- **Tubular** – As the name implies, tubular membranes are hollow tubes with the membrane placed on the surface of the tube. Below the membrane surface is a supporting structure with high porosity. In most cases, tubular membranes are made of inorganic material such as ceramic and have a metal oxide membrane surface to provide a small nominal pore size. Tubular membranes have a different separation driving force than the previous two. Rather than vacuum pressure, the material to be separated flows along the membrane at high velocity under pressure. The velocity provides a transverse force to drive the water through the membrane while leaving the larger diameter particles behind. A tubular membrane could be used in the outside-in arrangement with the feed water flowing along the centre of the tube and the permeate passing to the outside walls, or the inside-out arrangement where the influent travels along the centre of the tube and travels axially outward.

2.5.4 Advantages of MBRs

One of the major advantages of replacing a conventional settler with a membrane is its capability of producing high quality effluent with a smaller treatment process footprint. In addition the MBR has many other advantages over the conventional activated sludge (CAS) system. These include good disinfection capability, higher volumetric loadings and high mixed liquor concentration (or low F/M), independent control of solids and hydraulic retention times (SRT and HRT), which offers better protection against shock loading, and less mixed liquor production (Metcalf, 2004). Considering these advantages, MBR technology is becoming increasingly popular for wastewater treatment. The advantages of MBR are presented in Table 2.3. However, the high operating cost associated with the high energy demand and membrane replacement, is still a controlling factor for application of MBRs (Judd, 2006).

Table 2.3 Advantages of MBR (Visvanathan *et al.*, 2000)

Advantages	**Details**
High rate decomposition	- Treatment efficiency is improved by preventing leakage of undecomposed polymeric substances. If these polymers are biodegradable, they can be broken down with a reduction in the accumulation of substances within MBR. - Other dissolved organic substances with low molecular weights, which can be eliminated by membrane separation alone, can be broken down and gasified by various microorganisms or produced new bacteria cells.
Treated water Quality	- MBR produces the effluent ($BOD_5 <$ 5 mg/L). - MBR process is 15-20 fold higher in substrate conversion rate compared to CAS. - Solid/liquid separation is conducted by membrane filtration. Therefore, the final effluent does not contain suspended matters as CAS and enables the direct discharge into receiving sources and/or reuse of the effluent for cooling, toilet flushing, watering or process water.
Flexibility in operation	- SRT can be controlled completely independent so the system can be run at very long SRT providing favorable conditions for the growth of slow-growing microorganisms, which are able to degrade bio-refractory compounds and control fouling.
Compact plant	- Biomass concentration can be maintained up to 40 g/L in the reactor. Therefore, the system can stand for high Organic Loading Rate (OLR) resulting in the reduced size of the bioreactor. - Secondary clarifier, filter, sludge thickener or post treatment are not required for MBR process.

Table 2.3 Advantages of MBR (Con.)

Advantages	Details
Low sludge production	- Excess sludge from MBR is lower than CASP about one fifth fold (0.22-0.53 kgSS/kgBOD$_5$). - Low F/M ratio and longer SRT (50-100 d) causes low sludge production rate. - SRT increased causes reduction in filaments, increase in rotifiers and nematodes.
Disinfection and odor control	- The removal of bacteria and viruses can be achieved without any chemical addition. - All the process equipment can also tightly close, no odor dispersion occurs.

2.6 Membrane Fouling

2.6.1 Fouling

Membrane fouling is characterized as reduction of permeate flux through the membrane, which results from an increased flow resistance due to pore blocking, concentration polarization and cake formation. Fouling is attributed to many factors such as sludge particle deposition, adhesion of macromolecules to the membrane surface and pore clogging by small molecules, among which the cake layer formation by sludge particle deposition is the most common reason for the flux decline. Fouling will not be observed when the flux is maintained below "critical flux", but beyond this critical value, the particles start to deposit on membrane surface as a cake layer. The cake layer is readily removable from the membrane by physical washing protocol, this being classified as reversible fouling. On the other hand, internal fouling caused by adsorption of dissolved matter into the membrane pore, and pore blocking is considered irreversible, and is generally removed by chemical cleaning. In addition, formation of the gel layer on a membrane surface is often irreversible, although it is theoretically reversible. This is because it forms a cake layer and reduces membrane lifetime.

The mechanisms of membrane fouling are shown in Figure 2.4. Three accepted mechanisms are gel/cake formation caused by concentration polarization, pore plugging, and pore narrowing.

- Gel or cake layer formation is an extreme case of concentration polarization where a large amount of matter has accumulated on the membrane surface due to size exclusion from pores.

- Pore plugging is caused by insertion of organic macromolecules (or extracellular polymeric substances, EPS) into membrane pores and some metal ions might function as a fastener. Smaller bacteria can also be a contributor to pore plugging.

- Some foulants, particularly small bacteria and soluble EPS (or soluble microbial product, SMP) enter the membrane pores and further build up on the pore wall, leading to a reduction of total section area of membrane pore and eventually an increase of filtration resistance. This mechanism is called pore narrowing. It has been hypothesized that once the pore size is reduced the concentration polarization is amplified further, this causing an increase in fouling (Bourgeous *et al.*, 2001).

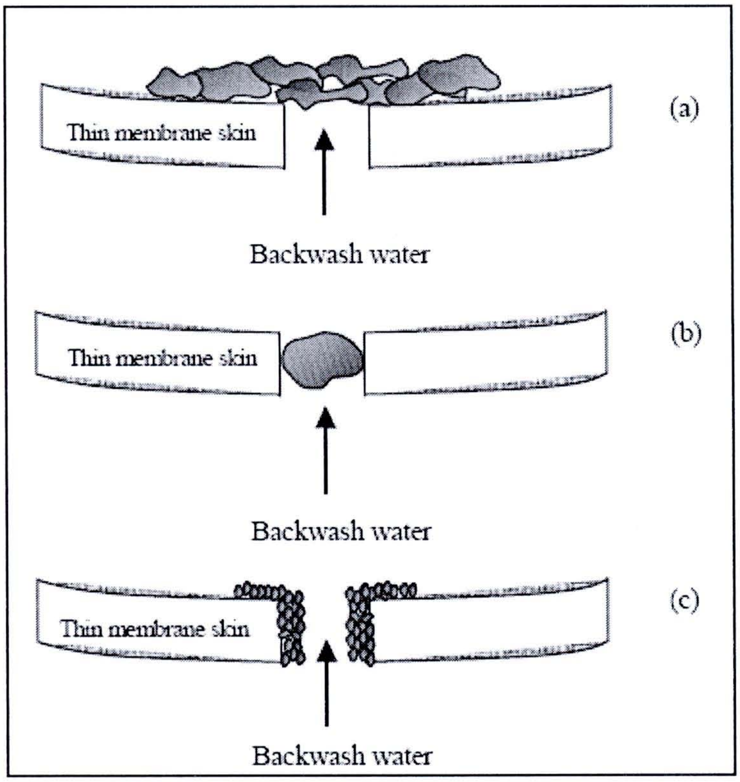

Figure 2.4 Mechanisms of membrane fouling (a) gel/cake formation (b) pore plugging and (c) pore narrowing (Bourgeous *et al.*, 2001).

Factors that can affect membrane fouling can be categorized and summarized into three different groups including the membrane, MLSS constituents (and their concentrations) and operating conditions. Figure 2-5 shows the connection between each of these factors and membrane fouling and their interrelations.

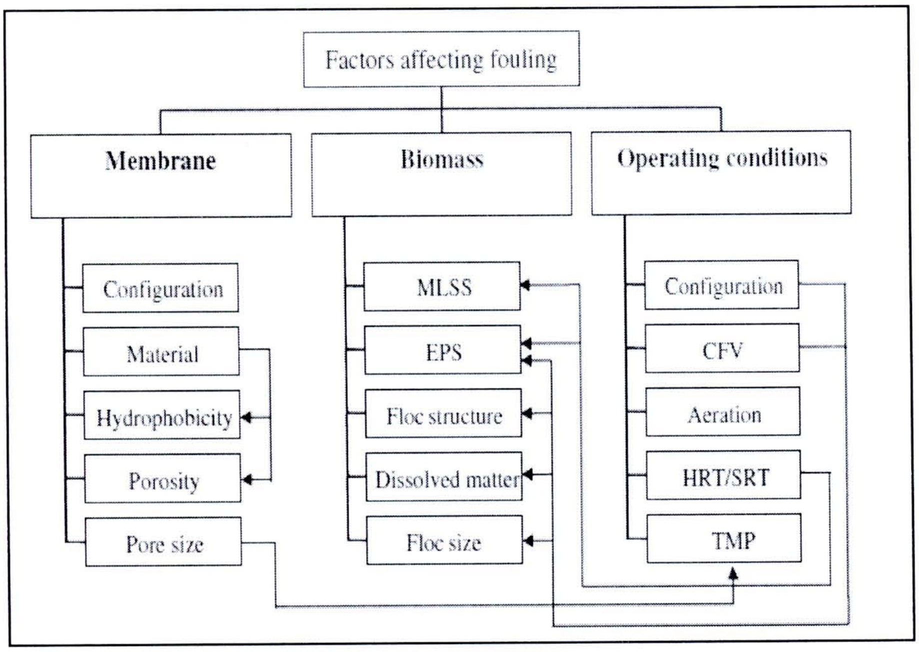

Figure 2.5 Factors influencing fouling of the membrane fouling in MBRs (Chang *et al.*, 2002).

2.6.2 Foulants

The composition of the MLSS with respect to constituents and concentrations is known to have a significant effect on membrane fouling propensity and is correlated with design of MBR and operational conditions. All MLSS constituents contribute to membrane fouling in different forms, however, the extent of their effect depends on their presence in the MLSS (Tak and Bae, 2005). Membrane fouling by inorganic constituents has not so far been adequately investigated; however, they may cause severe fouling especially for industrial wastewater treatment. Inorganic fouling is usually due to substances such as calcium carbonate that can cause scaling (Judd, 2006). Other constituents of MLSS include suspended solids and dissolved organic matter (DOC). From largest to smallest, the DOC of MLSS mainly includes biopolymers such as EPS which are bacterial products mainly made of protein and polysaccharides, humic substances, low-molecular weight acids and low molecular weight neutrals. MLSS also includes residual DOC from the feed water (Haberkamp *et al.*, 2007). During batch filtration under constant pressure, rate of flux decrease declines due to changes in contribution of each MLSS fraction to fouling. Fouling mechanisms change during the filtration period mostly due to the changes in permeation drag forces and back transport forces. Permeation drag forces cause deposition and attachment of MLSS fractions on the membrane by moving them toward the membrane surface which depends on membrane pore size since it can change the membrane permeability and flux. These fractions are detached by back transport forces which includes Brownian diffusion, inertial lift, shear induced migration/ diffusion, and electrostatic repulsion (Yoon *et al.*, 2005). Figure 2.6 shows a schematic of flux decline versus filtration time under constant TMP. Tak and Bae

(2005) defined three different zones/phases based on the fouling mechanism and fouling rate in each zone.

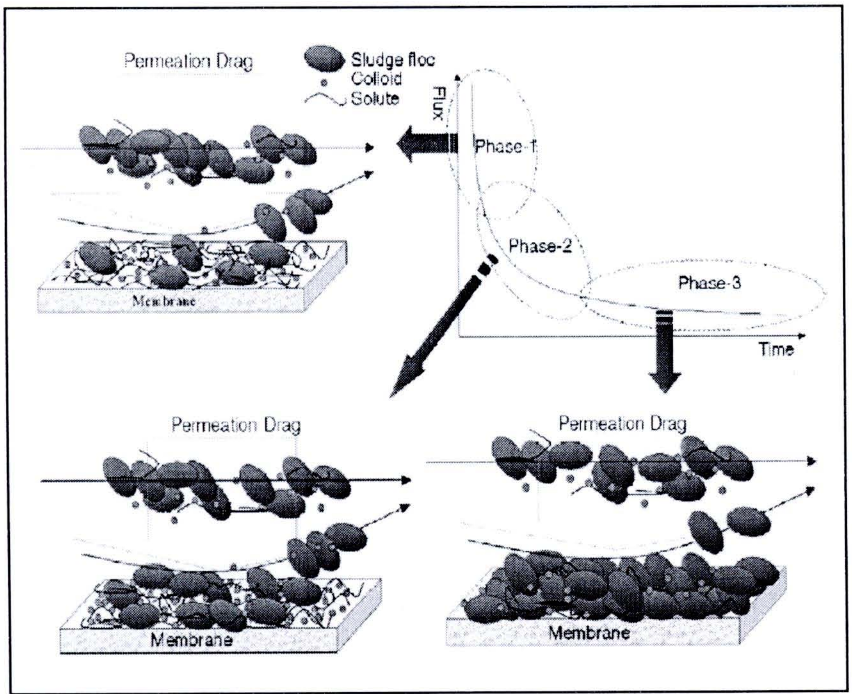

Figure 2.6 Fouling phases and flux diagram for operation under constant pressure (Tak and Bae, 2005).

At the beginning of the filtration, all MLSS components deposit on the membrane, however, larger flocs can be removed by cross flow forces. Soluble matter contributes the most to membrane fouling and deposits onto the membrane surface and into the pores to cause irreversible fouling. Colloidal matter contributes the least to membrane fouling at this point due to their lower fraction/concentration in MLSS as compared to the suspended solids and also because some of the deposited colloids are removed by cross flow. At this stage membrane flux decreases rapidly since all the MLSS components contribute to membrane fouling (Juang *et al.,* 2007).

During the second phase, the flux decreases at a lower rate as compared to phase one since the fouling in the first phase has decreased the flux and hence the drag permeation forces. The irreversible resistance due to soluble matter reaches steady state at the beginning of this stage since back transport and permeation drag of this fraction become equal. The fouling rate by colloidal matter decreases at this stage until its resistance also reaches steady state at the end of this stage. However, solids continue to deposit on the membrane surface and as a result, the fouling formed at this stage is mainly reversible (Juang *et al.,* 2007).

During the third stage, the flux decline rate decreases further until a sustainable flux is obtained. Fouling is caused by two mechanisms: deposition of larger particles which occurs in the beginning of this stage until permeation forces and back transport forces reach equilibrium; the second fouling mechanism is the compaction of the cake layer due to the transmembrane pressure which increases the resistance of the cake layer. This mechanism becomes more significant at this stage since the cake layer has a greater particle concentration as compared to the previous phases (Tak and Bae, 2005). Juang *et al.* (2007) reported that in the first 10 minutes of filtration in UF membranes the dominant fouling mechanism is pore blockage by the colloidal matter which is slightly different from Tak and Bae (2005) who stated that in the first stage all fractions contribute to membrane fouling with the soluble fraction having the highest contribution. However, both of these studies found that during the final stage suspended solids are the main contributor to membrane fouling.

A number of studies have fractionated the MLSS into three different fractions including suspended solids, colloidal matter, and soluble matter (Defrance *et al.*, 2000). In these studies, the fractions were separated and filtered individually to quantify the contribution of each fraction to membrane fouling. The results indicated which fraction contributed the most to membrane fouling, and consequently the dominant fouling mechanism was determined.

Tak and Bae (2005) found that suspended solids contributed the most to membrane fouling (72-83%) due to their high fraction in MLSS. Cake formation represented 90% of total fouling and was identified as the dominate mechanism. It is worth noting that these results were obtained from a bench scale dead-end cell operated at a relatively low cross flow velocity (1.2 m/s) and high TMP (100 kPa). Therefore, the permeation drag forces were higher and back transport velocity was lower than in what would be found in commercial membrane configurations and therefore, the contribution of each MLSS fraction to membrane fouling and correspondingly their fouling mechanisms may differ from full scale installations. Tak and Bae (2005) performed another dead-end filtration trial with a lower TMP (20 kPa) and higher cross flow velocity obtained using a high mixing speed (600 rpm) to assess the effect of TMP and cross flow velocity on the fouling mechanisms. The cake layer formation and its resistance decreased allowing for higher solute deposition on the membrane. As a result solutes became the main contributors to membrane fouling and contributed 67% of the total fouling resistance while suspended solids and colloidal matter contributed only 24% and 6% of total resistances, respectively. These results show the effect of different operating conditions and the importance of hydrodynamics of the filtration on the fouling mechanism.

Defrance *et al.* (2000) found that suspended solids had the highest contribution to membrane fouling. Suspended solids, colloids and solutes contributed 65%, 30% and 5% of the total membrane fouling resistance, respectively. They also observed that the sum of resistances found from filtration of each MLSS fraction was higher than the total resistance due to the filtration of MLSS compliment. Filtration of colloidal and suspended solids separately caused individual cake layer resistances whereas in MLSS these fractions were mixed and the cake layer was made of their combination which decreased their individual contribution to cake resistance. Defrance *et al.* (2000) concluded the ratios obtained by this method were not perfectly representative of each the components contribution to fouling. A more general explanation is that the effect of each of these components on membrane fouling are interrelated and correlated, illustrating a drawback to these experiments. A summary of the results of these studies is presented in Table 2.4. Table 2.4 provides a summary of the results of the four studies that evaluated the contribution of each of the MLSS components to fouling. From Table 2.4 it can be observed that the contribution of each MLSS fraction to fouling differed between the studies. The variation in their results was likely due to differences in several factors including fractionation methods employed, nature of the MBR influent (synthetic, municipal and industrial), system hydrodynamics, filtration time (back transport and permeation drag forces), system configurations and operating conditions (aeration and back washing or cross flow), the physiological properties of the biomass, membrane material and pore size and the concentration of DOC fractions (such as polysaccharide, phospholipid, protein) (Bouhabila *et al.,* 2001). These factors can change the biomass characteristics and composition and particle size distribution in the MLSS. The effects of these parameters on fouling should be considered when analyzing the results of membrane filtration.

Table 2.4 Contribution of MLSS fractions to total fouling

Fractions	Tak and Bae (2005)		Defrance *et al.* (2000)	Wisniewski *et al.*(1998)	Bouhabila *et al.* (2001)
	High flux & low cross flow	Low flux & high cross flow			
Suspended solids (%)	72 – 83	67	65	24	24
Colloids (%)	4 – 14	9	30	24	50
Solutes (%)	13 – 14	24	5	52	26

Table 2.4 also shows that all of MLSS fractions contributed to membrane fouling (to different degrees). However, it is unclear whether decreases in the concentration of each of these components would result in a decrease in membrane fouling. In the literature conflicting results regarding the relationship of membrane fouling and MLSS fractions exists. For example, Defrance *et al.* (2000) reported that membrane fouling increased insignificantly when the MLSS concentration was increased from 2 to 6 g/l while other studies have reported a linear relationship between MLSS and membrane resistance (Judd, 2004).

Colloidal particles: Colloidal matter can be defined as small non-settleable particles with sizes from 1 nm to 1 μm. Colloids include organic macromolecules such as polysaccharides, peptidoglycans, proteins, humic aggregates, and cellular debris (Huang *et al.,* 2009). Colloidal matter in MLSS may include residual non-biodegraded polymers such as residual defoamers from influent wastewater, or those that are generated from bacterial metabolism to produce EPS and SMP and bacterial lysis (Bouhabila *et al.,* 2001). Colloids contribute to membrane fouling by various mechanisms including pore blocking, pore constriction or cake formation and depend on their size relative to the membrane pore size (Huang *et al.,* 2009). Colloid deposition on membrane surfaces can improve the membrane removal efficiency by narrowing the pores and by the repulsive forces of colloids, as a result, lower molecular weight substances such as viruses may be removed (Huang *et al.,* 2009). The results of a study by Bouhabila *et al.* (2001) showed that residual colloidal matter increased membrane fouling more than colloidal matter formed in the bioreactor and improved biodegradation of influent colloidal matter decreased membrane fouling. Colloids generated in the MBR did not have a significant effect on membrane fouling in their study as they observed that with increasing SRT their concentration increased, however, membrane fouling decreased due to increased biodegradation of influent colloids (from the feed water and from defoamer agents that were employed).

EPS and SMP have been found to represent two of the major biopolymer membrane foulants (Judd, 2004). However, conflicting reports on the effect of increasing the concentrations of EPS and SMP on fouling exists in the literature which appears to be due mainly to different fouling mechanisms. A higher concentration of EPS may increase the membrane fouling due to its higher attachment to the membrane surface. However, the EPS composition may be more important than its concentration with regards to fouling as the protein to carbohydrate ratio affects the degree of sludge hydrophobicity and flocculation. SMP has two major components (carbohydrate and proteins) with the former having a higher contribution to membrane fouling by pore blocking (Yoon *et al.,* 2005).

Leiknes *et al.* (2006) observed that with municipal wastewater when the colloidal concentration decreased in the membrane reactor (due to operation of an MBR at higher HRTs), membrane fouling decreased correspondingly. Their results indicate a correlation between the concentration of the colloidal fraction and membrane fouling suggesting that decreasing the colloidal fraction may decrease membrane fouling.

2.7 Controlling of Membrane Fouling

From the study of factors influencing the membrane fouling in MBR, there are several ways to solve the problem respectively. Generally, there are three ways, process improvement, chemical method and operation condition control. Bubbling wash, backwash and intermediate operation are the most widely used technique to improve the MBRs process. Bubbling wash for submerged mode and control cross-flow velocity for side stream mode already became necessary for the MBR process. Backwash is a another widely used technique for membrane clean especially for hollow fibers, which is pumping the effluent or air through the filtration pipeline opposite (Cardew, 1998). Backwash is demonstrated that it can recover some of the membrane permeation in MBR by getting rid of the pore blockage and loosing the cake layer. Intermittent operation is to turn on and off the effluent suction pump intermediately upon different systems, which could keep the system continuously running for a longer time than constantly turning on the pump. This technique allows long-term sustainability even when operating above the critical flux. Because when the TMP is during the suspension of permeation, the force that holds the particles is negated, the particles deposited on the membrane will be removed by the cross-flow (Howell *et al.,* 2004). Sometimes, intermittent operation can combined with backwash. The operation conditions of MBR, like HRT, SRT, MLSS and F/M influence bunch of factors related to membrane fouling. Lots of studies are carried out, but there are still only few consistent conclusions on how to optimize the operation condition and get a less fouling system operation due to the complexity of the system.

Application of flocculants was accepted as an efficient way for solid-liquid separation in wastewater treatment processing due to economic and environmental considerations (Singh *et al.,* 2000). Adding flocculants into the clarifier is an efficient way to improve the sludge settleability and effluent quantities in conventional activated sludge processes. Flocculants could help the small particles and colloidal in liquid to coagulation or flocculation into large particles, which can get rid of the free particles in supernatant and make the sludge have a faster settle speed. Since the particle size and organic solute are the significant reasons leading the membrane fouling, more and more researchers are interested in studying the effect of flocculation on MBR performance (Abdessemed *et al.*, 1999).

2.7.1 Flocculants in MBR System

It is well known that the cake layer formatted on the surface of the membrane during the MF process mostly limits the permeate flux. At the beginning, the membrane retains the particles, but later the cake layer retains the particles. This bond layer provides additional resistance to the permeate flow (Ripperger *et al.,* 2002). Thus, the porosity of the cake layer is critical to the membrane fouling. Flocculated particles can form a highly porous filtration cake. In crossflow filtration the flocculation somehow prevent the deposition of particles on the membrane, which would enable a higher permeate flux (Nguyen *et al.,* 2002). Some researchers also find out that effect of flocculants on the filtration process can be positive or negative, and a critical dosage does exist for certain system (Bes *et al.,* 2002). The adding flocculant may also adsorb on the surface of the membrane and wall of membrane pores as well as flocculate the fine particles. The previous activity can lead to an increase in hydraulic resistance (Nguyen *et al.,* 2002). Various attempts have been done to achieve better membrane permeability by addition of different kind of flocculant or coagulant into MBR for both industrial and municipal wastewater treatment.

2.7.2 General Aspects of Flocculants

Flocculation is termed as an aggregation process of colloidal particles involving in a solid-liquid separation (Barkert, 1988). Both inorganic and organic flocculant are used in various kinds of flocculation phenomena (Bratby, 1980). Inorganic flocculants are usually used in large quantities, formation of large amount of sludge and are very sensitive to pH changes (Barkert, 1988). Otherwise, polymeric flocculants are used in a very small dosage, form large cohesive floc, lower sludge volume to handle and comparatively inert to pH changes (Singh *et al.*, 2003).

Inorganic Flocculants

The salt of multivalent metals, such as aluminum, iron and calcium, are mostly used inorganic flocculants, like alum, iron salts or lime (Singh *et al.*, 2003). The metal flocculant is normally based on precipitation of phosphates as well as coagulation of colloids, which is the reason that leads to excessive sludge production (Odegaard, 1998). It also remains high total dissolved solids in the effluent with little potential for reutilization (Savant *et al.*, 2000). The inorganic polymers, such as polyaluminium chloride (PAC), polymerized ferrous sulfate (PFS) and copolymers of Al and Fe, are used as coagulant for their high flocculation effect and small dosage (Aguilar *et al.*, 2002). Powdered activated carbon is another inorganic flocculant used in wastewater treatment process. Several authors reported that powdered activated carbon addition improves the organic removal efficiency by adsorption and coprecipitating the smaller and less-biodegradable organic compounds. The sludge floc formed by addition of powdered activated carbon releases less amounts of fine colloids and EPS than conventional activated sludge does when they are under the pattern of floc breakage by similar pumping shear. The powdered activated carbon in the biological sludge floc also adsorbs and entraps some microfloc components into the floc and enhanced the membrane permeability (Kim *et al.*, 2003).

Organic Flocculants

The organic flocculants are most electrolytes and essentially polymeric nature (Singh et al., 2003). Both natural and synthetic water soluble polymers are used as flocculants (Glass, 1986). They can act as an agent for floc growth through binding already formed small flocs into larger ones and a establishing agent via a charge neutralization/precipitation mechanism (coagulation) as well (Bolto et al., 1996). The synthetic polymers are highly effective at very small dosages and have high tailorability, but poor shear stability (Singh *et al.*, 2003). The synthetic flocculants are available in all three ionic forms, i.e. cationic, anionic and nonionic. Some of the widely used synthetic polymers are polyacrylamide (PAM), polyacrylic acid, polystyrene sulphonic acid, polydiallyldimethyl ammonium chloride (DADMAC) etc (Singh *et al.*, 2003). Due to the tailorability, synthetic flocculant can be designed for versatile conditions by controlling the molecular weight, molecular weight distribution, chemical structure of polymer, and nature and ratio of functional groups on the polymeric backbone (Singh *et al.*, 2003). However, they are not biodegradable and shear resistant (Singh *et al.*, 2003). Nature polymers are biodegradable and are effective at comparatively large dosages but they are very shearing stable. Among the natural polymers, starch, guar gum alginates and products based on chitin, like chitosan, glue and gelatin are used as flocculants and retention aids. Polysaccharides are one of the mainly nature polymeric flocculants, which are moderately efficient due to their low molecular weights, shear stable, cheap and easily available from nature resources (Singh *et al.,* 2000).

2.8 Polymeric Flocculants: Polyacrylamide (PAM)

PAM is a water-soluble synthetic polymer. There are three types of PAM, each having different charge characteristics. A unique chemical reaction is used to produce each type of PAM. The three types of PAM are cationic, nonionic and anionic. All of the PAM types are used in water treatment, but due to unique properties they each have slightly different applications. The degree of negative (or positive) charge that PAM has is called the charge density. In anionic PAM, charge density is defined by the degree of hydrolysis; i.e., the percentage of OH^- groups substituted for NH_2 groups on the polymer during polymerization (Green *et al.,* 2000). In cationic PAM, the charge density is the percent of positively charged units in the polymer.

Cationic PAM is used mainly as a flocculant for sewage sludge and various industrial wastes (Barvenik, 1994). Nonionic PAM is used as a flocculant in solid-liquid separations, usually as an aid to primary coagulants such as aluminum and iron salts. Nonionic PAM is also used in erosion control, although in limited applications (Barvenik, 1994). Nonionic PAM is actually slightly anionic (1-2% charge density) due to the hydrolysis of acrylamide units during the manufacturing process (Barvenik, 1994).

The majority of anionic PAM is used in water treatment and industrial wastewater treatment (Barvenik, 1994). Since the 1970s there has been increased use of anionic PAM as a soil amendment for erosion control (Orts *et al.,* 1999). However, erosion control (agriculture) applications only account for 2% of all PAM produced. High molecular weight (MW) anionic PAM (12-18 $Mg.mol^{-1}$), with a charge density ranging from 7 to 50 is typically used in erosion control (Orts *et al.,* 1999. Anionic PAM is commonly produced by copolymerization of acrylamide and acrylic acid (or a salt of acrylic acid) (Barvenik, 1994).

PAM is typically purchased as a dry powder. Dry PAM has active polymer concentrations of 75 to 90%, the remainder being water, processing aids, and buffers (Sojka *et al.,* 1997). PAM is most efficient and effective if dissolved in water before application to soil (Sojka *et al.,* 1997). When mixing PAM solutions, PAM should always be added to water that is stirred or agitated (water should never be added to PAM) (Sojka *et al.,* 1997). The polymer solution must be rapidly agitated for at least 30-60 minutes for dry granular PAM to be thoroughly dissolved (Barvenik, 1994). Higher molecular weight PAMs require more time to dissolve and the solutions are more viscous (Levy *et al.,* 1995). Anionic PAM with a molecular weight between 15-20 $Mg.mole^{-1}$ forms extremely viscous solutions above 1-2% PAM concentrations (Barvenik, 1994). PAM is soluble in cold water, and heating does not increase the rate of dissolution (Montgomery, 1968). Pumping liquid PAM solutions may shear PAM molecules, reducing its viscosity and reducing its effectiveness to bridge particles in suspension (Orts *et al.*, 1999).