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Biofouling in Membrane Bioreactor

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Abstract: A membrane bioreactor (MBR) combines membrane separation and biological treatment, normally involving the activated sludge process, in municipal wastewater treatment. Despite excellent performance over years of full-scale operation, the interactions between microbes and the membrane in the MBR process, which determine its design and operational criteria, remain unclear. This report reviewed research regarding how numerous process parameters impact biofouling rates and, in particular, the possible contribution of microbial products to biofouling. This study also characterized different fractions of microbial products and assessed their potential affect on membrane fouling.

Keywords: MBR, fouling, mechanisms, extracellular polymeric substances

INTRODUCTION

The activated sludge process is used to treat municipal and industrial wastewaters. Micro-organisms in aerated mixed liquor degrade organic pollutants such as organic carbon and nitrogen compounds. However, the activated sludge process requires large tanks for aeration and sedimentation, produces a vast excess of sludge that must be disposed of, and experiences frequent technical difficulties, such as bulking and foaming. Furthermore, the potential of the activated sludge process to degrade organic matter is limited. The hygienic qualities of the treated water have attracted increasing concern, because of the strong correlation between the use of the surface water and the prevalence of infections of the body.

Smith et al. (1) first reported on the combined use of membranes in biological wastewater treatment. Their idea was to directly filter the mixed liquor in a biological reactor, to produce quality effluent by totally rejecting the impurities, using a membrane. In a submerged module, the membrane is directly merged in the aerated bioreactor, with aerated bubbles sweeping over the surface of the membrane to enhance permeate flux and reduce fouling. The submerged MBR could be easily retrofit using an activated sludge process with minor modifications. Presently, hundreds of full-scale MBRs are installed annually (2).

The main advantage of using MBR technology over using other conventional biological processes is to produce quality water from municipal wastewater for reuse, meeting the need for saving water, particularly in regions of water shortage. Other advantages include the need for less space, lower energy consumption, and the smaller excess of sludge to be handled. All shortcomings of membrane systems persist in MBR applications, such as high installation costs, low permeate flux, and occurrence of membrane degrading and fouling (3, 4). Despite performing excellently over years of full-scale operation, the interactions between microbes and the membrane in the MBR process, which determine its design and operational criteria, remain unclear. Just recently some mathematical modeling works were available for MBR applications (5, 6).

This report reviewed briefly how numerous process parameters influence biofouling rates and, in particular, the possible contribution of microbial products to biofouling.

MBR PRACTICE

Microfiltration (MF) and ultratfiltration (UF) membranes are frequently employed in membrane bioreactor (MBR) applications. Microfiltration membranes, which typically have pores 0.1–10 μm in size, can be utilized to separate particles. The most widely used materials in microfiltration membranes are polytetrafluoroethylene (PTFE), polypropylene (PP), poly (vinylidine fluoride) (PVDF), polyethylene, cellulose esters, polycarbonate, polyamide, and polyetherketone. UF membranes have pores (5–100 nm) and can remove macromolecules. Polyacrylonitrile, cellulose acetate, aliphatic polyamide, poly (vinylidine fluoride), poly imide/poly (ether imide) are typically used for UF membranes. For example, Zenon, Canada, had over 150 full-scale units installed by 2000 and utilized submerged hollow fiber polyethersulfone UF membranes. Other commonly employed membranes are ceramic or metallic membranes from Kubota (Japan), organic membranes made of polyvinilydene fluoride, and polysulfone. At a vacuum pressure as high as 0.7 bar, submerged UF or MF membranes typically have a constant permeate flux of 0.1–1 $\mathrm{m\,d^{-1}}$. Field experience has demonstrated that side-stream type MBR require cleaning after 2 months of use and submerged hollow fiber membrane type MBR must be cleaned after 6–8 months' of use, utilizing a chemical solution.

The two most critical process parameters in activated sludge processes are sludge retention time (SRT), which determines microorganism growth rate, and the hydraulic retention time (HRT), which governs pollutant removal rate. Both nutrient supply and available contact time affect bacterial growth rate; these two parameters are inter-related. In MBR, HRT, and SRT are entirely separated, enabling sludge age to be manipulated. The SRT for the MBR process is by definition infinitely long and rejects solids. The energy supplied is either fully utilized by microbes for maintenance, or is transferred to higher life forms like metazoa. Consequently, the biomass concentration in the MBR process can be sustained at 10,000–60,000 $\mathrm{mg\,l^{-1}}$, substantially higher than that in a traditional activated sludge process (3,000–4,000 $\mathrm{mg\,l^{-1}}$). This high biomass concentration effects organic degradation (7), generating an effluent chemical oxygen demand (COD) of $<5\,\mathrm{mg\,l^{-1}}$, $>80\%$ nitrogen removal (8), and $<0.5\,\mathrm{mg\,l^{-1}}$ total phosphate. The membrane rejects most filtrate particles. Total suspended solids (TSS) in effluent produced by the MBR process can easily be less than 1 $\mathrm{mg\,l^{-1}}$, and the total coliform count can be reduced from up to 10^7 to 100–300 CPU $\mathrm{l^{-1}}$. Madaeni et al. (9) determined that membranes can completely removing viruses via UF or substantially remove viruses via MF membranes.

Particle rejection by a membrane is primarily a product of pore size (10) and the dynamic membrane situated above the pores. Wakeman (11) noted that the impact of fouling in MF and UF is associated with a matrix of feed stream, membrane and operational parameters. Among all parameters the most important are particle size distribution of the feed and membrane pore size. Cho et al. (12) indicated that rejection of natural organic matter (NOM), based on dissolved organic carbon (DOC), is controlled by the particle size excluded, electrostatic repulsion and aromaticity/hydrophobicity interaction between the membrane surface and pores. Bacteriophage at 25–65 nm was effectively rejected by the UF membrane as demonstrated by Oe et al. (13), Bottino et al. (15) investigated the retention capacities of particles, microorganisms, algal, and disinfection-by products (DBPs) by MF ceramic membranes. Their experimental results showed that suspended solids and microorganisms are completely removed, whereas algal removal (99%) is near complete and TOC and chloroform retention was 64% and 56%, respectively.

Some constraints must be assessed prior to steady-state MBR operations with total sludge rejection. Zero net biomass production is required to prevent sludge accumulation in the bioreactor. Additionally, counterbalance of opposing factors controlling membrane fouling is essential guarantee a stable permeate flux over long-term operation. The microbial community must degrade organic matter mainly through the cell maintenance pathways; or an ecosystem must be generated in the bioreactor to achieve population equilibrium. Witzig et al. (15) assessed changes to the microbiological community utilizing MBR for complete biomass rejection. The number of filamentous bacteria increases from test start to a dramatically high value during steady-state operations. Thus, the microbial community in MBR evolves to an adaptive state, fully utilizing the limited energy supply for survival. Luxmy et al. (16) noted a metazoa population, primarily composed of rotifiers and oligochaete worms, increases in density as the loading rate increases. These microbes are concentrated on the membrane surface and, thus, can help removing the formed cake from the surface of the membrane.

Although the detailed mechanisms and interaction among numerous process parameters were not comprehensively explored (17), new developments in MBR applications are ongoing. For example, a nanofiltration membrane used in MBR applications is attracting increasing interest, partly due to frequent outbreaks of water-borne diseases in Japan and the United States, where treated municipal wastewater has been utilized as raw water. The nanofiltration membrane can filter out most viruses from treated water. However, since pore size of NF is substantially smaller than MF/UF membranes, fouling mechanisms change away from pore blocking to gel layer formation. The gel layer is not easily removed via backwashing as is the cake layer formed by biological cells. Moreover, modifying existing processes, such as utilizing an anoxic/aerobic membrane bioreactor, can effectively remove nitrogen and carbon simultaneously from wastewater

(18). The membrane bioreactor coupling with a photocatalyst process attains sufficient pollutant removal (19). New functional membranes, such as the ion-exchange membrane (20) or enzyme-immobilized bilayer membranes (21), have been effectively employed in MBR.

A significant obstacle preventing widespread application of membrane filtration in wastewater treatment is the flux decline over time (22–24). Regardless of the complexity of an MBR system, no appropriate processes can be applied without sufficient fouling control. The following sections discuss how various process parameters, particularly the characteristics and amount of microbial products, impact biofouling on membranes in MBR applications.

MEMBRANE FOULING

Membrane fouling is used to describe pore plugging and external pore blocking caused by deposition of particles and colloids on a membrane surface and precipitation of fine/dissolved materials in membrane pores and on a membrane surface (25–28). Typically, membrane fouling results in flux decline and fouling increases pressure drop across the membrane. Recent examinations of membrane fouling are available in Baker and Dudley (29), Judd (30, 31), Marrot et al. (32), and Liao et al. (33).

Factors controlling membrane fouling are as follows (34):

1. membrane and module (35, 36);
2. operating conditions (37–41); and,
3. biomass (35, 42–44), including suspended solids (45) and extracellular polymeric substances (EPSs) (46).

The extracellular polymeric substances are a principal foulant in MBR (42, 44, 47–50). Leslie et al. (51) and Hodgson et al. (52) implicated EPS fouling as the cause of flux decline of MF membrane systems. Wisniewski and Grasmick (53) argued that solutes are a significant pollutant of MBR membranes. Defrance et al. (54) noted that suspended solids are a primary foulant of MBR membranes. Bouhabila et al. (55) concluded that the colloids are the principal membrane foulant. Apparently no conclusive comments could be made based on these literature works.

Fouling-Membrane and Module

Several studies demonstrated that the flux decline is lower for hydrophilic membranes than hydrophobic membranes. Nakatsuka et al. (56) demonstrated that flux for hydrophilic membranes is quickly recovered by back washing, indicating that the substances in raw water are only minimally adsorbed by the hydrophilic membranes. Fan et al. (57) pointed out that the flux decline for a hydrophobic PVDF membrane is considerably quicker than that for its hydrophilic counterpart, suggesting that particle deposition significantly impacts membrane fouling. Carroll et al. (58) modified the surface of an MF membrane to minimize the declining flux problem. Hacck et al. (59) modified the hydrophobic membrane surface by grafting on a hydrophilic layer. These authors suggested that a PP membrane modified by polyacrylic acid has a lower rate of flux decline than an unmodified membrane. Other studies also utilized surface modification to reduce potential of membrane fouling (60, 61). Mueller and Davis (62) noted that when filtering a bovine serum albumin (BSA) suspension, rapid formation of a proteinous dynamic layer on a membrane surface moderates filtration flux, hence masking the effects of membrane substrate characteristics.

Membrane charge affects a membrane's selectivity for charged particles and ions and its resistance to fouling (63). Jarusutthirak and Amy (64) noted that the membrane surface charge was correlated with fouling mechanisms. Membrane zeta potential has been shown to be effective in detecting minimal reductions in membrane flux (65–67). Knoell et al. (68) and Campbell et al. (69) employed quantitative structure-activity relationship (QSAR) analysis to determine the correlation between a membrane's fouling potential and its features.

Sridang et al. (70) analyzed the fouling potential of a membrane utilizing different module configurations and hydrodynamic environments. Module configuration affects membrane fouling potential markedly (71, 72). Adding turbulence to membrane systems promotes effluent flux levels (73–77). Packing density of hollow fiber modules influences flux decline and fouling rates (78, 79). Yeo and Fane (80) pointed out that the hydrodynamic environment for individual fibers can differ significantly depending on their position in the bundle. Scridang et al. (70) compared the fouling rates from immersed membrane systems with different bundle configurations.

Fouling-operating Conditions

Hydrodynamic, chemical, and biological factors moderate membrane fouling. Reversible membrane clogging is preferable to operational sake as standard cleaning can easily wash the clogging layer away. Membrane fouling resulting from the dynamic layer on a membrane's surface decreases permeate flux after the operation starts. However, with adequate aeration, this flux decline does not normally proceed following a particular period of operation, since the fouled layer attains a dynamic balance between deposited and suspended particles (81). Chang and Judd (77) compared the fouling potentials of membranes sparged with different modes.

The critical flux concept presented by Field et al. (82) proposed that negligible cake deposition on membrane surface exists below filtrate flux. Critical flux increases as crossflow velocity and suspended particle size increases (83, 84). Wicaksana et al. (85) demonstrated that bubbling-induced vibration of hollow fibers increases critical flux. Moreover, Chang et al. (86) indicated that fouling always occurs, even at sub-critical flow conditions. Such type of biofouling is noted inevitable in MBR applications (87).

Jiang et al. (88) determined that the fouling rate would be higher at low temperatures (13–14°C) than at high temperatures (17–18°C), probably owing to the change in effluent viscosity.

Fouling-Biomass

Magara and Ito (89) and Nanem and Sanderson (90) noted that a high suspended solid concentration increases membrane fouling; whereas Lee et al. (91) noted that a high amount of suspended solids on the contrary reduces membrane fouling. Lee et al. (44) argued that the EPSs should be considered as part of the suspended solid concentration when evaluating membrane fouling. Rosenberget et al. (92) noted, based on literature findings, that with an increasing mixed liquor suspended solids (MLSS) the fouling potential would be reduced when MLSS $< 6{,}000\,\mathrm{mg\ l^{-1}}$, and increased when MLSS $> 15{,}000\,\mathrm{mg\ l^{-1}}$, and remained unchanged with an intermediate MLSS. Other parameters addressing the solid fraction on MBR fouling are effect of particle size, (40) floc surface hydrophobicity, (93) and sludge viscosity (49, 94).

Brinck et al. (95) showed that the undissocated fatty acid, predominantly presented in reduced pH, fouled the membrane more seriously than the dissociated species presented under alkaline conditions. Seo et al. (96) determined that the hydrophobic fraction of organic compounds fouled the membrane more than did hydrophilic fraction. Jarusutthirak et al. (97) indicate that polysaccharide colloids accounted for most fouling of UF and NF membranes. Cho et al. (98) argued that polysaccharides and related substances are the principal foulants of UF and NF membranes. Rosenberger et al. (92) indicated the impact of soluble or colloidal fractions in organic substances, particularly polysaccharides, on membrane fouling, and thereby arguing for characterizing liquid-phase compositions when monitoring membrane process performance.

Williams and Wakeman (99) indicated that BSA fouling of MF membranes starts with protein aggregates depositing on the membrane surface, thereby blocking some pores. They indicated that protein fouling comprises of two steps:

protein adsorption and desorption on pore walls and mouths; and,

accumulation of cake on the membrane surface resulting from aggregate deposition and growth.

In a pilot-scale MBR, Kimura et al. (41) demonstrated that the food-microorganism (F/M) ratio and membrane filtration flux markedly affected fouling rates. Protein at high F/M ratio and carbohydrates at low F/M ratio are the principal foulants.

You et al. (100), who investigated the anaerobic membrane process, determined that both membrane fouling and scaling are most important processes hindering factors (101–103).

Based on these process parameters that effect biofouling, the following techniques have been applied to reduce fouling potential:

1. intermittent suction (104);
2. backwashing;
3. improving module configurations (85, 105); and,
4. aeration improvement (106).

Membrane Cleaning

Physical, chemical, and biological schemes are utilized to regenerate fouled membranes. The cleaning method and cleaning frequency depend on foulant type and a membrane's resistance to chemical cleaning agents. Choice of membrane materials, however, depends on feed composition and precipitated layers on a membrane surface and, in most cases, membranes are chosen through trial and error.

During physical cleaning, backflushing is frequently applied to a membrane's permeate side, forcing the solution through the membrane feed side. This technique is more effective for ceramic membrane filtration than for polymeric membranes, since ceramic membranes can withstand the high pressure associated with back flushing. Visvanathan et al. (107) and Chang and Judd (77) utilized air backflushing to decrease cake compression and pore clogging in MBRs. Zips et al. (108) utilized both ozone and ultrasound to clean a modified polysulfone membrane fouled by *Pseudomonas diminuta*. Lim and Bai (109) determined that sonication cleaning effectively removes loosened material still attached to a membrane surface or trapped in membrane pores.

Many chemical cleaning agents have been employed, such as nitric acid, hydrochloric acid, phosphoric acid, alkaline, carbonates, phosphates, EDTA, sodium hypochlorite, etc. Increasing temperature typically enhances cleaning efficiency; however, high temperatures cannot be used when cleaning most organic membranes. According to Bartlett et al. (110), particular cleaning agent concentration and temperature exists for optimal cleaning. In an investigation of cleaning BSA-fouled polysulfone and HEKLA membranes, sodium hydroxide achieved sufficient results at high temperatures (111). Based on the study by Mohammadi et al. (112) a combination of cleaning agents, such as sodium hydroxide and sodium hypochlorite, and sodium hydroxide and sodium dodecyl sulphate, clean more efficiently than single-agent methods. The presence of chloride ions can significantly decrease cleaning efficiency, whereas nitrate and sulphate ions improve cleaning efficiency.

Mild and environmentally friendly cleaning agents, such as purified enzymes and surfactants, have been employed to extract biologically derived foulants from polymer membranes. Enzymes are model cleaning agents as they are specific for the reactions they catalyze and the substrates with which they interact. Maartens et al. (113) investigated the capability of each cleaning agent to eliminate adsorbed proteins and lipids, as well as the ability of a cleaning agent to restore the water-contact angle and pure water flux of the fouled membrane. Munoz-Aguado et al. (114) achieved adequate cleaning effectiveness with an enzymatic cleaning agent. Arguello et al. (115) obtained very high (90%) cleaning efficiencies over short period (20 min) utilizing enzymatic cleaning for inorganic UF membranes fouled by whey proteins. A similar finding obtained by Arguello et al. (116) achieved 100% cleaning efficiency for protein from inorganic membranes. Allie et al. (117) demonstrated the feasibility of using of both proteases and lipages to clean their UF membranes fouled by abattoir effluent.

FOULING WITH MICROBIAL PRODUCTS

Microbial Products in Activated Sludge

Sludge liquor consists of living cells and microbial products, including EPSs, inert biomasses, and soluble microbial products (SMPs) (118). The EPSs are microbial products located on or outside cell surfaces that aggregate cells into flocs or granules, provide resistance to surrounding toxins, accumulate enzymes for cell use, and facilitate cell-cell communication (119). Early studies identified polysaccharide as the most abundant component found in EPSs (120). In examining biofilm systems, Nielsen et al. (121) noted that protein is the most abundant component of EPSs. In EPS-activated sludge, Dignac et al. (122) determined that protein is the predominant constituent. Protein has a high proportion of negatively charged amino acids and, hence, is more involved than sugars in generating electrostatic bonds with multivalent cations, a principal factor in stabilizing aggregate structures. Additionally, protein is the predominant component in enzyme-based biochemical reactions.

Choi et al. (98) proposed that EPSs bind with sludge flocs contributed significantly to permeate flux decline, resulting from the altered cake characteristics produced by the presence of EPSs. The same authors demonstrated that organic substances in supernatant do not contribute substantially to membrane fouling, a finding consistent with the conclusion obtained by Lee et al. (45) and Defrance et al. (55) The fraction of non-settled organic substances increases membrane fouling (123–125) via adsorption of macromolecular substances on a membrane and progressive pore clogging (45, 126).

The EPSs were further differentiated into extractable EPSs, the EPS fraction bound tightly with solid surfaces, and soluble EPSs (also called slime polymers), the fraction able to move freely between sludge flocs and surrounding liquor (8). Other classification paradigms have separated EPSs into "loosely bound" and "tightly bound" fractions (127). Leung (128) determined that most extraction approaches described in literature effectively extract both loosely and tightly bound EPSs. However, Li et al. (129) identified a correlation between loosely bound EPSs and the flocculation and sedimentation features of activated sludge.

The SMPs are soluble cellular components secreted by cells during synthesis or excreted for uncertain purposes (130–133). These SMPs can be further classified into two groups: substrate utilization-association products (UAPs), formed via substrate metabolism, and biomass-associated products (BAP), generated partly through biomass decay. Drewes and Croue (134) indicated that natural organic matter (NOM) in river water was significantly similar to SMPs produced by wastewater treatment plants. However the aromatic moieties of the SMPs and NOM are of different origins. By adding glucose or glutamic acid solution to an activated sludge system, the aromaticity of SMPs contained in the effluent increases (135).

Most research treated EPSs and SMPs independently, as if no relationship existed. For example, Costerton et al., (136, 149) Nielsen et al. (121), Sutherland (137), Hsieh et al. (138), and Wingender et al. (119) analyzed EPSs and active biomass, whereas Furumui et al. (139), Namkung and Rittmann, (140) and Speitel et al. (141) examined the interactions between SMPs, biomass, and inert biomass. Laspidou and Rittmann (118) observed that soluble EPSs are SMPs in sludge liquor. Hence, based on current research, soluble EPSs = loosely bound EPSs = SMPs (mixed liquor) $\doteqdot$ NOM (river water).

Microbial Product Fouling

The EPSs are a complex mixture of proteins, carbohydrates, acid polysaccharides, lipids, DNA, and humic acid substances that surround cells and create a matrix of microbial flocs and films (142). These EPSs have been identified as the primary foulants in MBR processes (41, 48, 49, 51, 143). As noted by Rojas et al. (144), the speed of growth of microorganisms in MBR was negatively correlated with the amount of EPSs produced. The specific resistance of the membrane examined by Rojas et al. increased 10-fold when protein concentrations increased from 30 to 100 mg l^{-1}.

Kim et al. (145) utilized powdered activated carbon (PAC) to adsorb soluble EPSs and, hence, increased the effluent flow rate from the membrane. Park et al. (146) enhanced the filtrate flux by adding PAC to an anaerobic MBR.

On the other hand, the SMPs had also been identified as the principal membrane foulant in MBR systems (147, 148). Cicek et al. (149) determined that the SRT can be adjusted to minimize the SMP level in mixed liquor. The role of SMPs in membrane fouling remains controversial. Lee et al. (44) indicated that supernatant, at most, contributed 37% of total resistance in membrane filtration. However, Bouhabila et al. (55) found that total resistance of filtration by the supernatant was 76%. Wisniewski and Grasmick (53) attributed roughly 50% of total resistance in filtration to supernatant SMPs. Lee et al. (91) observed that attached cells and the SMPs produced a dynamic membrane. The cells attached to the membrane spread, accompanied by production of EPSs, thus forming a biofilm. Cells accumulated on the surface are relatively easily eliminated by washing. Consequently, controlling cell metabolism by altering membrane characteristics is essential to limiting membrane fouling.

Effects of NOM on membrane fouling has been thoroughly investigated (150–157). Natural organic matter has been differentiated into different fractions according to molecular weight (158), hydrophobicity (155, 159, 160), and GC-pyrolysis-MS (161, 162). Among numerous NOMs the polysaccharides are an important foulant on membranes (161, 162). Kwon and Lawler (163) determined different fouling rates for membranes with individual organic compounds, such as dextran, alginic acid, polygalacturonic acid, and tannic acid. Yuan and Zydney (164, 165) investigated MF and UF membrane fouling by humic substances. Pretreatment utilizing coagulation, ozonation, activated carbon adsorption were applied to eliminate NOM prior to membrane filtration (166–169). Jiang et al. (170) demonstrated that utilizing pre-coagulation significantly improves filtration of raw river water via the UF membrane since high-molecular weight humic substances and suspended particles were effectively removed.

EPS Fouling

Based on these findings, membrane biofouling via microbial products plays a critical role in determining the feasibility of utilizing MBR. As demonstrated by Li et al. (129), only loosely bound EPSs, and not total EPSs, correlated with performance of flocculation and sedimentation processes. This subsection characterizes and compares the differences and similarities between tightly and loosely bound EPSs extracted from a wastewater sludge sample and compares, and reveals their individual filterability for further comparison.

A test sample was collected from the return sludge stream at the wastewater treatment plant for the Neili Bread Plant, Presidential Enterprise Co., Taoyuan, Taiwan. The chemical oxygen demand (COD) and suspended solids (SS) data of the supernatant drawn from the sludge, measured via EPA Standard Methods, were 22.6 and 14.3 mg l^{-1}, respectively. The percentage weight of dried solids in the sludge sample was 0.83% w/w, determined by weighing and drying at 102°C.

The sludge sample was first dewatered by centrifugation at 6000 g for 10 min. The dewatered cake was then re-suspended in a 0.85% w/w NaCl solution with several glass beans, and then sonicated at 20 kHz and 330 W l^{-1} for 2 min, shaken horizontally at 120 rpm for 10 min, and sonicated again for an additional 2 min. The liquor was centrifugated at 8000 g for 10 min to separate solids and liquor. The supernatant was added with 2 volumes of acetone and maintained at 4°C for 24 h to precipitate soluble substances. The collected precipitate was called the loosely bound EPSs for the sludge sample.

The solids collected were resuspended in a 0.85% w/w NaCl solution, sonicated for 2 min and then heated at 80°C for 15 mins. The remaining liquor was centrifugated at 12000 g for 30 mins for supernatant collection. The obtained supernatant was added with 2 volumes of acetone and maintained at 4°C for 24 h. The precipitate was collected and named the tightly bound EPSs in the sample.

The compositions of the loosely bound and tightly bound EPSs were compared utilizing a Fourier-transform infrared (FTIR) spectrophotometer (Perkin Elmer 1760, England; sample/KBr = 1/100, 4000–400 cm^{-1} at 4 cm^{-1} resolution for 100 cycles), Auger/X-ray induced photoelectron spectroscopy (VG Microtech MT-500, England; magnesium Kα X-ray source with electron food gun at 4 eV), and matrix-assisted laser desorption/ionization time of flight mass spectrometry (Bruker Daltonics AutoFlexÒ MALDI-TOF USA; using 2,5 dihydroxybenzoic acid as matrix, spectra acquired at positive ion linear reflectance mode); and in surface charge and floc size using a zetasizer (Zetasizer 3000 HS type A, Malverin, England).

Figure 1 presents the zeta potentials of suspensions containing loosely or tightly bound EPSs as a function of pH. The zeta potentials of both EPSs were roughly -14 mV at neutral pH. The isoelectric points (IEP) were located at around pH 2.5 for tightly bound EPSs and 2.0 for loosely bound EPSs.

Figure 2 presents the size distributions of both EPSs. These EPSs have bidispersed distributions: 300–500 nm and 2600–4800 nm for tightly bound; and, 200–400 nm and 800–1200 nm for loosely bound EPSs. The size of the tightly bound EPSs was larger than that of the loosely bound EPSs.

Figures 3a and 3b present the IR spectra of loosely bound and tightly bound EPSs, respectively. For the loosely bound fraction, the characteristic peaks demonstrated the presence of polysaccharides, proteins, and lipids. Conversely, the tightly bound EPSs lacked peaks at 1656 (amide 1, C=O) and 1542 (amide II, C-N + N-H) cm^{-1}, indicating an absence of proteins.

Figure 4 presents the XPS data for both EPSs. The binding energy distributions of C_{1s} and O_{1s} demonstrated that the EPSs were primarily composed of carbohydrates. Small amounts of lipids were detected in both EPSs, peaking at 284.5 eV [C- (C-H)]. The C_{1s} peaks at 286.72 and 286.27 eV in loosely bound and tightly bound EPSs suggest the presence of functional groups of

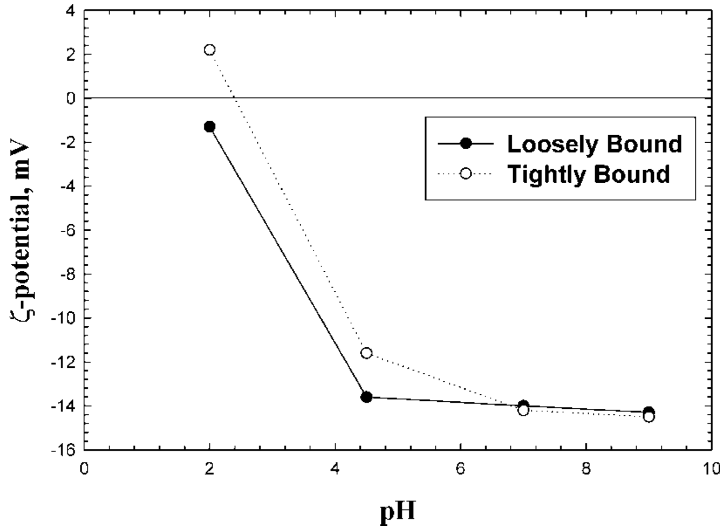

Figure 1. Zeta potentials of extracellular polymeric substances extracted from sludge samples.

C-O and C-N, respectively. The O_{1s} peaks in both EPSs were located at 531.7 eV, demonstrating the existence of C-OH and C-O-C. Small amounts of nitrogen were also detected in XPS spectra, giving a C:N ratio of 26 and 24 for loosely bound and tightly bound EPSs, respectively.

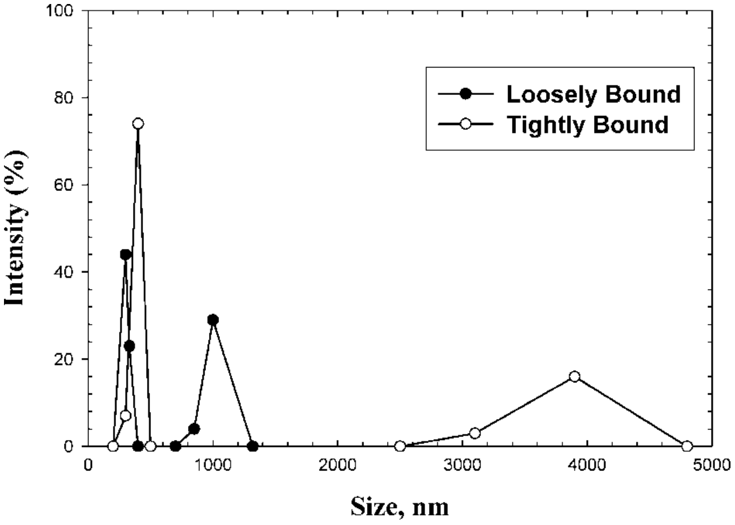

Figure 2. Size distributions of extracellular polymeric substances extracted from sludge samples.

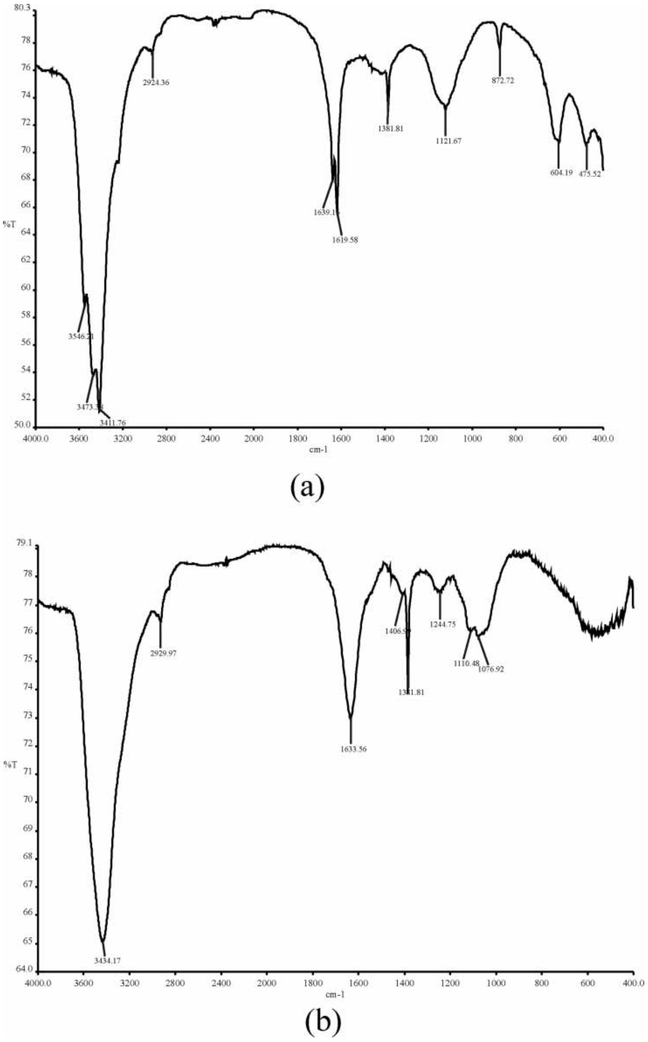

Figure 3. IR Spectra of extracellular polymeric substances extracted from sludge samples. (a) Loosely bound, (b) tightly bound.

The MALDI-TOF-MS spectra (Fig. 5) showed that EPSs were present as molecules <1000 Da in size. The major peaks detected for both samples were at similar locations, indicating that both had similar molecular weights of molecules.

In summary, the insoluble constituents of EPSs presented as fine particles of bidispersed size distributions (Fig. 1) and of negative surface charge (Fig. 2). The EPSs were aggregates composed of molecules with molecular weights <1000 Da (Fig. 5), and shared similar chemical compositions

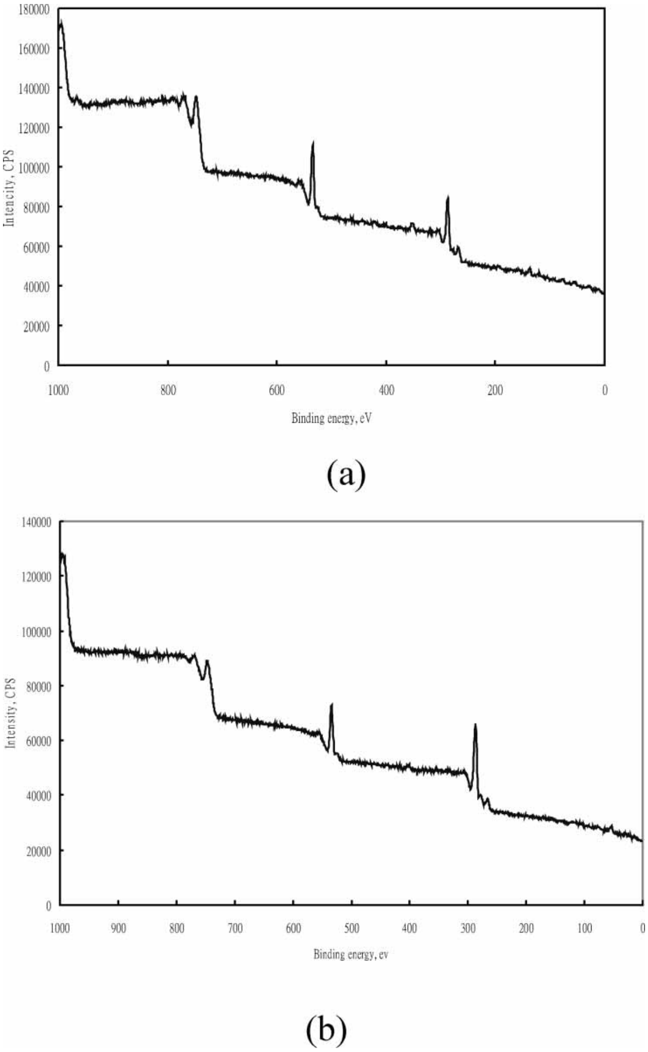

Figure 4. XPS Spectra of extracellular polymeric substances extracted from sludge samples. (a) Loosely bound, (b) tightly bound.

(Figs. 3 and 4). However, the tightly bound EPSs were large in size (Fig. 1) and were deficient in protein, as indicated by the IR spectrum (Fig. 3b).

Figure 6 presents the filtration tests for total sludge, and for the two EPS suspensions using a 0.4 μm MF membrane subjected to 35 mmHg vacuum. The flux declined with time, reaching steady-state flux at after 40–50 min filtration. Filtration of tightly bound EPSs had lower resistance than that of loosely bound EPSs. This finding may result from the larger particle size

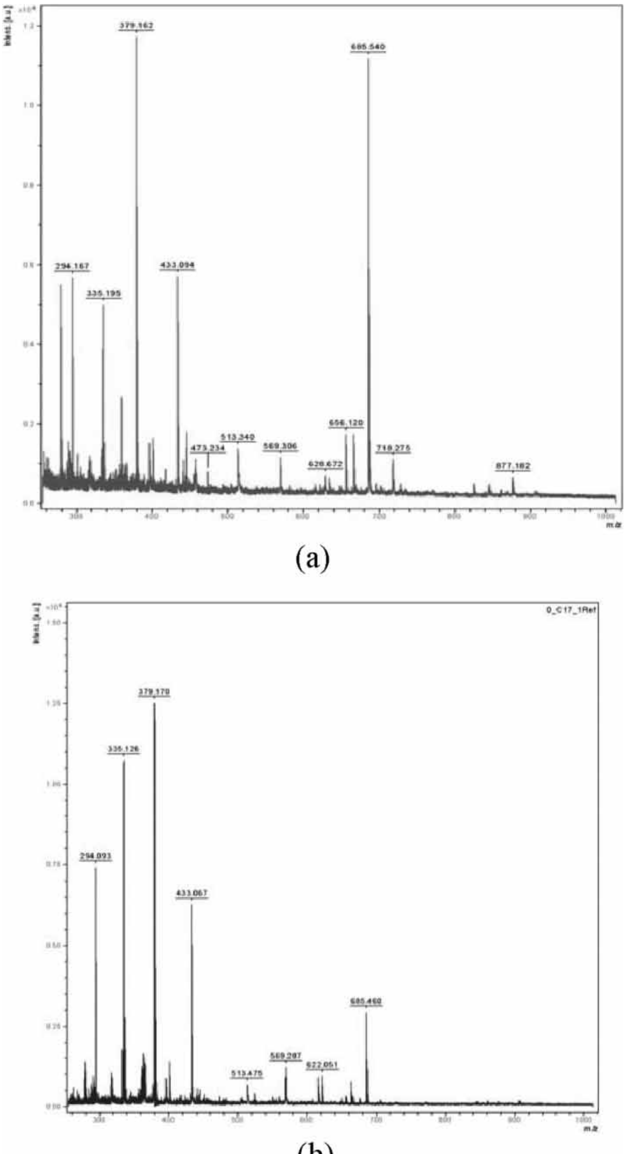

Figure 5. MALDI-TOF-MS spectra of extracellular polymeric substances extracted from sludge samples. (a) Loosely bound, (b) tightly bound.

noted for the tightly bound EPS. When the total sludge sample was filtered, the initial flux was higher than that for the loosely bound EPS test, and declined rapidly over time, merging with the loosely bound EPSs after 10 min of filtration. Hence, filtration resistance was primarily produced by the loosely

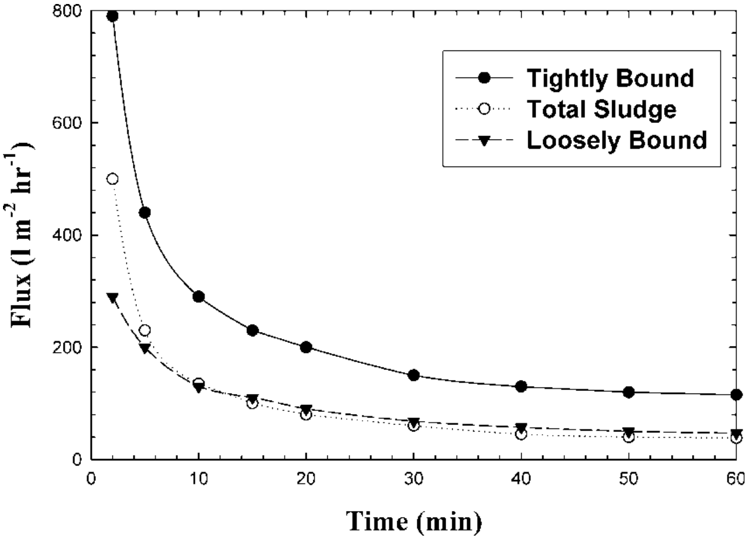

Figure 6. Dead-end filtration flux versus time plot of total sludge and of extracellular polymeric substances suspensions.

bound EPSs, but not by the tightly bound EPS. Experimental results indicate the significant role of loosely bound EPSs on membrane fouling, and the need to remove it to minimize potential membrane fouling in full-scale applications.

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