

Full Length Research Paper

Comparison of membrane bioreactor technology and conventional activated sludge system for treating bleached kraft mill effluent

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The purpose of this paper was to review the use of membrane bioreactor technology as an alternative for treating the discharged effluent from a bleached kraft mill by comparing and contrasting membrane bioreactors with conventional activated sludge systems for wastewater treatment. There are many water shortage problems currently in the world, some of which are more serious than others. Public concern over health and the environment, combined with increased requirements for municipalities to reuse wastewater, have created a need for new technologies that can treat wastewater to generate high quality reusable water at low cost. In several of these technologies, membrane technology could make a great contribution since membranes have the ability to produce water of exceptional purity that can be recycled for reuse in a variety of places. This reuse of wastewater is already widely practiced in many countries, which reduces net demand on water supply systems. In industry, in particular the pulp and paper industry, large volumes of water are used with a significant amount of wastewater generated. This effluent needs to be treated prior to final disposal or reuse. The commonly used biological treatment methods of aerated lagoons and activated sludge of bleached kraft mill effluent have been found to be inadequate in achieving the desired level of toxicity removal. There is, therefore, the growing demand for greener/sustainable technologies for reuse/recycling of wastewater and the membrane bioreactors treatment of these effluents has shown some greater potential as it is much cleaner and meet stringent discharge requirements than with other techniques.

Key words: Membrane bioreactor, activated sludge, bleached kraft mill effluent, pulp and paper.

INTRODUCTION

Bleaching effluents from chemical pulp mills are said to be one of the pollution problems of the pulp and paper industry due to the large amounts of chlorinated organics discharged into the environment. Many of these chlorinated organic compounds are toxic, mutagenic, persistent, bioaccumulating and show considerable resistance to

biological and chemical degradation (Kringstad and Lindström, 1984). These compounds are produced primarily as a result of complex reactions occurring between the chlorine-containing bleaching agent and the residual lignin (5 to 10%) remains in the wood pulp after the preceding chemical pulping process (O'Connor and Voss,

1992). Pulp and paper industry is a major source of these chlorinated organics worldwide, since pulp bleaching usually involves the use of elemental chlorine or chlorine dioxide for oxidation of the wood pulp (Fulthorpe et al., 1993). According to O'Connor and Voss (1992), about 10% of the chlorine supplied to the pulp in the first stage of bleaching appears in the effluent discharge as organically bound chlorine which has been estimated at 250,000 tonnes/year by Kringstad and Lindström in 1984, while the remaining 90% ends up as chloride ions. The organically bound chlorine is measured as total adsorbable organic halogen (AOX) and kraft mill effluents show that a sizeable fraction of carbon compounds in these effluents is chlorinated (Fulthorpe et al., 1993). It should be noted that AOX discharge has decreased by ~60% since 1984 as Cl_2 has been replaced by ClO_2 , ozone, and peroxide in almost all large-scale mills. The AOX is said to be the main source of effluent toxicity of bleached kraft mill effluents. The other environmental impact of the bleached kraft mill effluents is due to suspended solids, organic matter and color.

The systems most commonly employed by the pulp and paper industry in treating their wastewater are biological using stabilization ponds, aerated lagoons and activated sludge processes. These treatments have been successful in lowering the chemical and biological oxygen demands (chemical oxygen demand (COD) and biochemical oxygen demand (BOD), respectively), but their applicability is limited by a great number of problems. These biologically treated effluents still contain significant amounts of colored compounds, microorganisms, recalcitrant organics and a minor amount of biodegradable organics, as well as suspended solids. If water of high organic matter content or biochemical oxygen demand (BOD) value flows into a river, the bacteria in the river will oxidize the organic matter consuming oxygen from the water faster than it dissolves back in the air which has an adverse effect on aquatic life (Attiogbe et al., 2007). Biological treatment does not significantly reduce the inorganic content in the effluent and desalting is sometimes needed before reuse of the effluents in the manufacturing processes (Assalin et al., 2009). Also, these methods are much less efficient in toxicity reduction of the effluent. Given the limitations of the current biological wastewater treatment, there is an increasing interest to develop a more effective treatment approach to reduce the impacts of pulp mill effluents on the environment.

The rapid increase of population and the increased demand for industrial establishments to meet human needs have created problems such as over exploitation of available resources, leading to pollution of the environment. There is a long list of water-related problems worldwide on existing water resources due to increases in hu-

man population and activity. Reuse and conservation of water resources has therefore taken a very high priority position. The Global Environment Outlook (GEO) 2000 report of the United Nations indicated that many countries will be experiencing severe water shortages by the year 2025, and this will be especially critical in areas where water from the same inadequate source is required by more than one country. Quantity demands may only be met by re-use and quality demands by advanced treatment in both cases indicating a potential role for membrane technologies. The membrane bioreactor technology has the potential to help industries and municipalities manage their water resources better. It is an innovative wastewater treatment (WWT) technology, based on proven processes of activated sludge biological treatment and membrane separation (Wang and Menon, 2009). The system has been implemented in several full-scale industrial and municipal applications in Europe, North America and Asia. The integration of biological treatment with membrane filtration in MBR produces an excellent effluent quality which is capable of meeting stringent discharge requirements. The possibility of the membrane retaining all bacteria and viruses results in a sterile effluent, eliminating disinfection before discharge or reuse. This provides the opportunity for facilities to recycle/reuse part or all the treated effluent, thereby reducing costs for fresh water and water treatment on one hand and reducing sewer surcharge (for pretreatment facilities) on the other hand (Wang and Menon, 2009).

In this paper, a review comparing and contrasting use of membrane bioreactors and conventional activated sludge system for the treatment of bleached kraft mill effluent (BKME) was done.

CONVENTIONAL ACTIVATED SLUDGE SYSTEM (CAS)

The activated sludge process was developed in England in 1914 by Arden and Lockett and was so named because it involved the production of an activated mass of microorganisms capable of stabilizing a waste aerobically. There are many version of the original process but fundamentally they are all similar (Metcalf and Eddy Inc., 1995).

The activated sludge process is a biological method of wastewater treatment technique in which a mixture of wastewater and biological sludge (microorganisms) is agitated and aerated. The biological solids are subsequently separated from the treated wastewater and returned to the aeration process as needed (Davis and Cornwell, 1991). The biological wastewater treatment with the activated sludge process is achieved using a

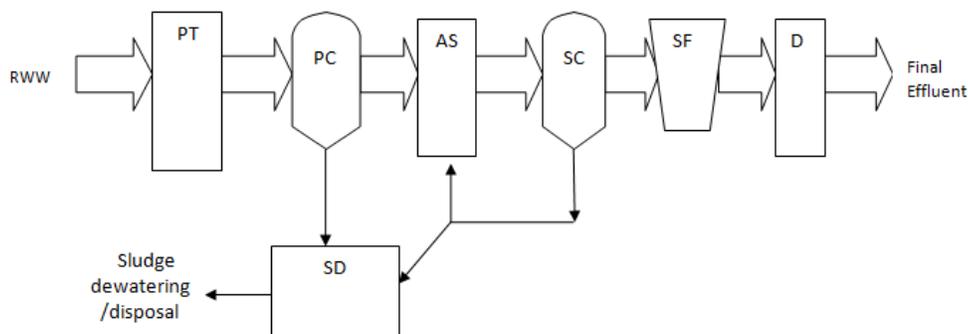
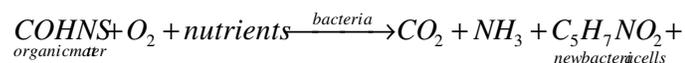


Figure 1. Conventional activated sludge treatment flow diagram. RWW- Raw wastewater; PT- primary treatment; PC- primary clarifier; AS- activated sludge; SC- secondary clarifier; SF- sand filter; D- disinfection; SD- sludge digestion.

flow diagram as shown in Figure 1.

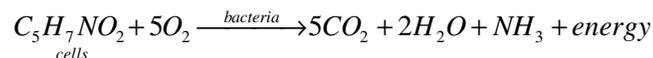
The pretreated wastewater is introduced into a reactor/aeration tank (AS) where an aerobic bacterial culture is maintained in suspension. The wastewater and the microorganisms are thoroughly mixed under conditions that stimulate their growth through the use of the organics as food. The reactor contents are referred to as the mixed liquor. In the reactor, the bacterial culture carries out the conversion in accordance with the stoichiometry shown (Metcalf and Eddy Inc., 1995):

Oxidation and synthesis:



other end products

Endogenous respiration:



In these equations, COHNS represents the organic matter in wastewater. The endogenous respiration reactions results in relatively simple end products and energy, stable organic end products are also formed (Metcalf and Eddy Inc., 1995).

The aerobic environment in the reactor is achieved by the use of diffused or mechanical aeration, which also serves to maintain the mixed liquor in a completely mixed regime. As the microorganisms are mixed, they collide with other microorganisms and stick together to form larger particles called floc. The large flocs that are formed settle more readily than individual cells. These flocs also collide with suspended and colloidal materials (insoluble organic materials), which stick to the flocs and cause the

flocs to grow even larger. The microorganisms digest these adsorbed materials, thereby re-opening sites for more materials to stick.

After a specified period of time, the mixture of new cells and old cells is passed into a settling tank/secondary clarifier (SC), where the cells (activated sludge) are separated from the treated wastewater. A portion of the settled cells/sludge is returned/recycle to the aeration tank (AS) to maintain a high population of microbes to permit rapid breakdown of the organics. The volume of sludge returned to the aeration tank is typically 20 to 30% of the wastewater flow. Usually, more activated sludge is produced than is desirable in the process, portion of the return sludge is therefore diverted or wasted to the sludge handling system (SD) for treatment and disposal. The clarified wastewater flows (SC) forward to further treatment or discharge. For further treatment, the effluent is sand filtered (SF) since it could still be high in biological solids and the resultant effluent is disinfected (D) to kill pathogens before final disposal.

In conventional activated sludge systems, the wastewater is typically aerated for six to eight hours in long rectangular basins; about 8 m³ of air is provided for each m³ of wastewater treated (Davis and Cornwell, 1991).

Three basic types of organisms important to the operation of an activated sludge system are bacteria, plants and animals. Plants include algae and fungi. The bacteria are the most important and constitute the majority of microorganisms present in activated sludge. Bacteria that require organic compounds for the supply of carbon and energy (heterotrophic bacteria) predominate; whereas bacteria that use inorganic compounds for cell growth (autotrophic bacteria) occur in proportion to concentrations of carbon and nitrogen. In general, bacteria in the activated sludge process include members of

Table 1. Plant efficiencies for activated sludge plants treating papermill wastewater (Thompson et al., 2001).

Activated sludge efficiency (%)		Country	Source
BOD	COD		
73.5-99.2	50.0-92.2	Finland	Saunamäki (1997)
-	90.6	Shotton Papermill, UK	Horan and Chen (1998)
97.9-98.5	72.5-92.4	UK	-

the genera *Pseudomonas*, *Zoogloea*, *Achromobacter*, *Flavobacterium*, *Nocardia*, *Bdellovibrio*, *Mycobacterium*, and the two most common nitrifying bacteria, *Nitrosomonas* and *Nitrobacter*. Additionally, various filamentous forms of bacteria and fungi, such as *Sphaerotilus*, *Beggiatoa*, *Thiothrix*, *Lecicothrix* and *Geotrichum*, may also be present (Metcalf and Eddy Inc., 1995). Bacteria are primarily responsible for the removal of organic substances from wastewater (Junkins et al., 1983). The algae and fungi in the system play a lesser role than bacteria. Animals include larger microorganisms such as protozoa, crustaceans and rotifers. The animals feed on dispersed bacteria that do not settle well and therefore help polish the quality of the treatment plant effluent (Junkins et al., 1983). Both aerobic and anaerobic bacteria may exist in the activated sludge process.

Activated sludge processes are designed based on the mixed liquor suspended solids (MLSS) and the organic loading of the wastewater, as represented by the BOD or COD. The MLSS represents the quantity of microorganisms involved in the treatment of the organic materials in the aeration basin, while the organic loading determines the requirements for the design of the aeration system. Table 1 (Thompson et al., 2001) shows plant efficiencies for activated sludge plants treating papermill wastewater. These show that very high removal efficiency can be obtained both for BOD and COD removal.

The success of the activated-sludge process is dependent upon establishing a mixed community of microorganisms that will remove and consume organic waste material, that will aggregate and adhere in a process known as bioflocculation, and that will settle in such a manner as to produce a concentrated sludge for recycling. The CAS is efficient in producing clear sparkling treated effluent which is free of odor. The purity of the effluent can be varied as desired depending on the length of time the aeration is carried out. However, the treated effluent from CAS will not be suitable for recycle and reuse, unless tertiary treatment process units are added for further purification.

The operation of CAS requires skilled supervision and constant check on the returned sludge. The process does

not work for some industrial wastes and large volume of sludge produced increases difficulties in disposal (Kamala and Kanth Rao, 1988) which are some of the drawbacks of this technology.

MEMBRANE BIOREACTORS (MBR)

The history of membranes applied to treatment of wastewater is relatively new, dating back to the late 1960s (Drioli and Giorno, 2009). The membrane bioreactors can be broadly defined as systems integrating biological degradation of waste products with membrane filtration (Cicek, 2003; Marrot et al., 2004; Wang and Menon, 2009; Drioli and Giorno, 2009). Combining membrane technology with biological reactors for the treatment of wastewaters has led to the development of three generic membrane bioreactors (MBRs): for separation and retention of solids; for bubble-less aeration within the bioreactor, and for extraction of priority organic pollutants from industrial wastewaters (Stephenson et al., 2000). Coupling membranes to biological processes are often used as a replacement of the sedimentation stage, that is, for biomass separation. According to Cicek (2003) the membrane bioreactors (MBRs) have proven quite effective in removing both organic and inorganic contaminants as well as biological entities from wastewater. The bioreactor and membrane module each have a specific function: (i) biological degradation of organic pollution is carried out in the bioreactor by adapted microorganisms; (ii) separation of microorganisms from the treated wastewater is performed by the membrane modules. The membranes constitute a physical barrier for all suspended solids and therefore causes not only recycling of the activated sludge to the bioreactor but also production of permeate free of suspended matter, bacteria and viruses. The use of membranes to separate solids and treated wastewater is the main difference between MBRs and conventional activated sludge systems for which the efficiency of the final clarification step depends mainly on the activated sludge settling properties (Marrot et al., 2004).

The evolution and possible application of membranes

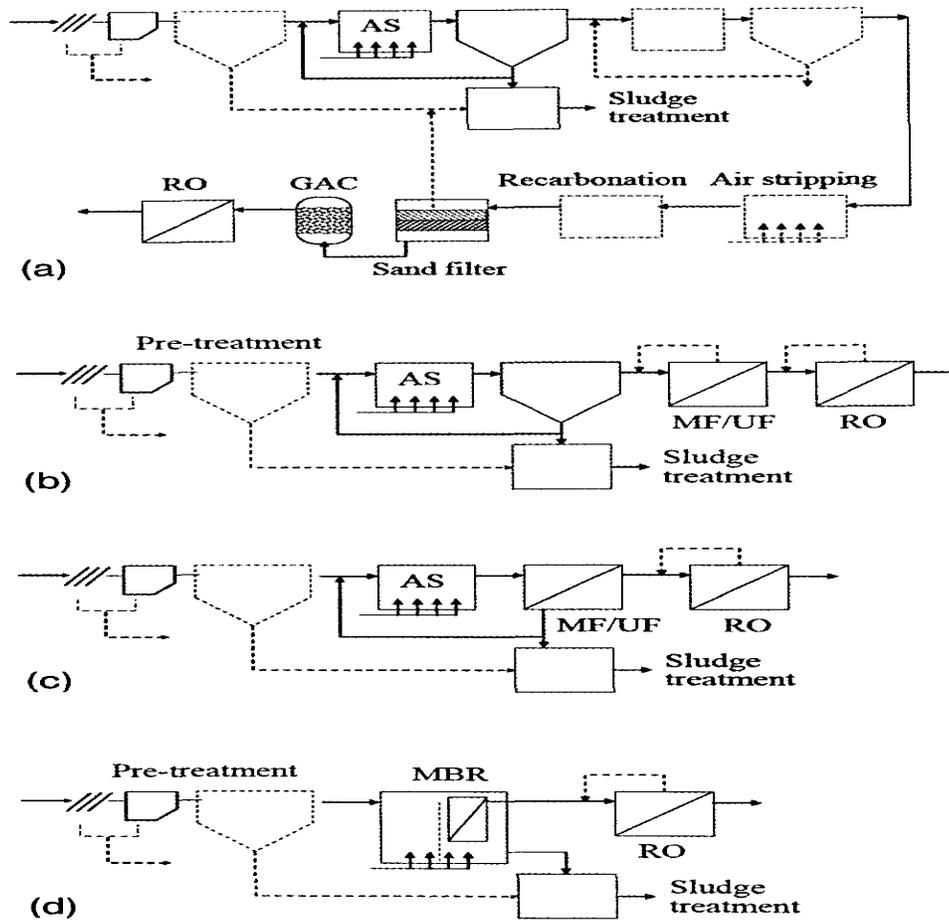


Figure 2. Illustration of evolution and use of membranes in wastewater treatment (Drioli et al., 2009).

in wastewater treatment is illustrated in Figure 2. Treatment of wastewater by membrane technology is an established alternative, particularly in sensitive areas, water scarce regions, and in cases where wastewaters reuse and recycling is required (Drioli and Giorno, 2009). Industries where the membrane bioreactor technology can be implemented include chemical, petrochemical, pharmaceutical, fine chemicals, cosmetics, dairy, automotive, pulp and paper, landfill leachate, food, textiles, etc. (Wang and Menon, 2009).

The membrane bioreactor has been demonstrated to achieve higher reductions of bacteriophages as compared to the activated sludge process in the treatment of municipal wastewater (De Luca et al., 2013; Francy et al., 2012; Marti et al., 2011). Bacteriophages were proposed as models of enteric viruses and are considered particularly suitable as viral indicators. In recent years, information on the effectiveness of virus removal by sewage treatment processes has become of major

concern, due to the epidemiological significance of viruses as waterborne pathogens (De Luca et al., 2013).

The efficiency of conventional activated sludge process (CASP) in removing pathogenic microorganisms has been investigated in several studies, which have concluded that these treatments may not be sufficient to achieve microbiologically safe effluent to be discharged into natural waters or to be reused. In order to reduce the potential microbiological risk, the secondary effluent is generally subjected to a further tertiary treatment by sand filtration, ultraviolet and ionizing radiation, or, more frequently, by chemical disinfection with chlorine, ozone and peracetic acid. The generation of harmful disinfection by-products such as trihalomethane (THM) and the persistence of disinfection residues are considered adverse environmental effects of chemical disinfection processes. However, the membrane bioreactor is considered an effective, non-hazardous advanced treatment alternative (De Luca et al., 2013).

Membrane materials and classifications

There is a large selection of commercial membranes that can potentially be used in MBR applications. Most polymers can be used to manufacture membranes in principle and there is a wide variety of commercially available polymeric membranes. In water and wastewater applications, most systems are based on a limited set of polymeric materials. The most common membrane materials are: polyvinyl difluoride (PVDF), polyethyl-sulfone (PES), polyethylene (PE) and polypropylene (PP).

Membranes are generally formed as a flat sheets or tubular/hollow-fiber geometry. Recent developments of manufacturing techniques have led to alternative products such as multibore or multitube in the market. Membranes are commonly given the following classifications:

1. Flat sheet (FS);
2. Hollow fiber (HF);
3. Capillary tubular (CT);
4. multibore or multibular (MT).

The flat-sheet membranes are commonly constructed in a plate-and-frame configuration or as spiral-wound (SW) modules. HF/CT/MT membrane typ; are commonly manufactured into bundles that are installed in housing units or designed to be unconfined in the fluid, that is, immersed units. The plate-and-frame FS and HT/CT membrane modules are the preferred option for MBR applications. The SW membrane modules are not used as the channels within the spiral which are prone to clogging when the feed water has high suspended-solids concentrations. The tubular membrane systems are not common either as they tend to become very expensive due to the low area to volume ratio. Commercial MBR systems today are normally based on immersed FS configurations or HF/CT configurations (Drioli and Giorno, 2009). The pore size of membranes used ranged from 0.01 to 0.4 μm (Cicek, 2003).

There are five main subcategories of membrane processes use for water and wastewater treatment. These are: (i) microfiltration (MF); (ii) ultrafiltration (UF); (iii) nanofiltration (NF); (iv) reverse osmosis (RO) and (v) electrodialysis (ED). Of these, only MF and UF are related to membrane bioreactors.

Microfiltration is a pressure process for the separation of suspended solids in the particle size-range of about 0.08 to 10 μm . The primary function affecting solids separation from water is the size of the suspended solids (SS). The hydraulic pressure (transmembrane pressure) applied in MF is about 1 to 2 bars, or 15 to 20 psig, primarily for overcoming resistance of the filter cake.

Ultrafiltration process is a pressure filtration process for the separation of macromolecular solids in the particle size range of about 0.01 to 0.1 μm . The primary factor affecting solids separation from water relies on the size of macromolecular solids. The hydraulic pressure required by UF for overcoming hydraulic resistance of the polarized macromolecular layer on the membrane surface is about 1 to 7 bars (Wang and Menon, 2009).

Nanofiltration membranes are multiple-layer thin-film composites of polymer consisting of negatively charged chemical groups, and are used for retaining molecular solids such as sugar and certain multivalent salts such as magnesium sulfate, but passing substantial amounts of most monovalent salts such as sodium chloride, at an operating pressure of about 14 bars or 200 psig. Both molecular diffusivity and ionic charge play important roles in the separation process. The sizes of molecular solids and multivalent salts to be rejected by NF are normally in the range of 0.0005 to 0.007 μm .

Reverse osmosis membranes are mainly made of cellulose acetate with the pore sizes of about 5 to 20 Å, and are for rejecting salts as high as 98% and organics as high as 100%, at an operating pressure of about 20 to 50 bars or 300 to 750 psig.

The hydraulic pressure through a pump is used to provide the driving force for permeation, or for overcoming the chemical potential difference between the concentrate and the permeate, expressed in terms of the osmotic pressure. The sizes of molecular solids and salts (multivalent as well as mono-valent) to be rejected by RO are normally in the range of 0.00025 to 0.003 μm (Wang and Menon, 2009).

Electrodialysis uses voltage or current as the driving force to separate ionic solutes. The sizes of ionic solutes to be rejected or separated by ED are normally in the range of 0.00025 to 0.08 μm , depending on the pore size of the ED membranes. Figure 3 illustrates the relationships among the five subcategories of membrane processes:

MBR process configurations

The process configurations of MBR plant depend partly on the type of membrane used (FS or HF/CT) and on the design of the biological treatment. Figure 4 depicts the typical configurations found in MBR treatment schemes. For immersed/submerged membrane designs, the membrane modules are either inserted directly into the biological reactor or placed in a separate reactor constructed to hold the membrane modules only (Figure 4, schemes A and B). In side-stream configuration, the membrane modules are placed outside the biological reactor and can be operated in deadend mode or in cross-

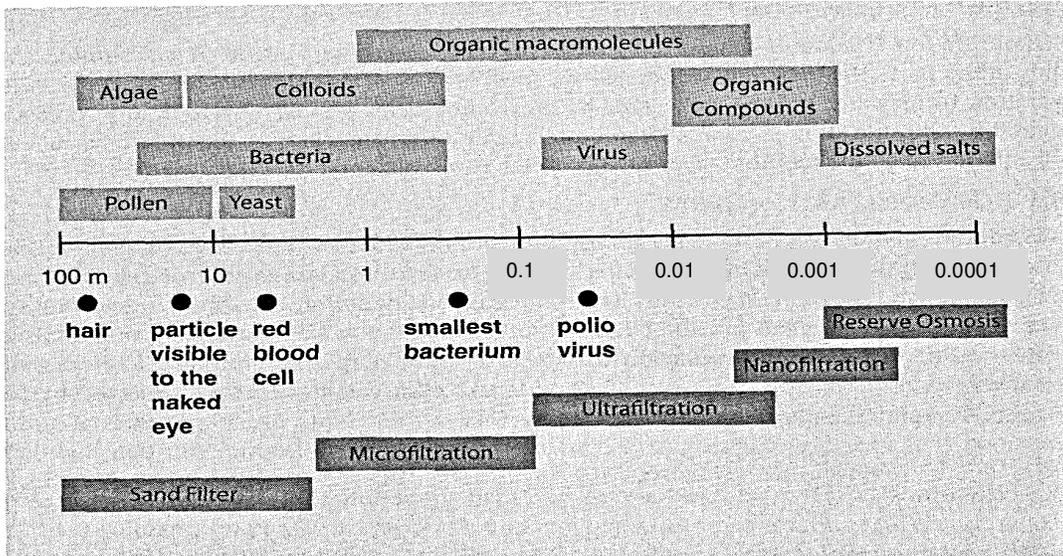


Figure 3. Particle size and separation processes (Wang et al., 2009).

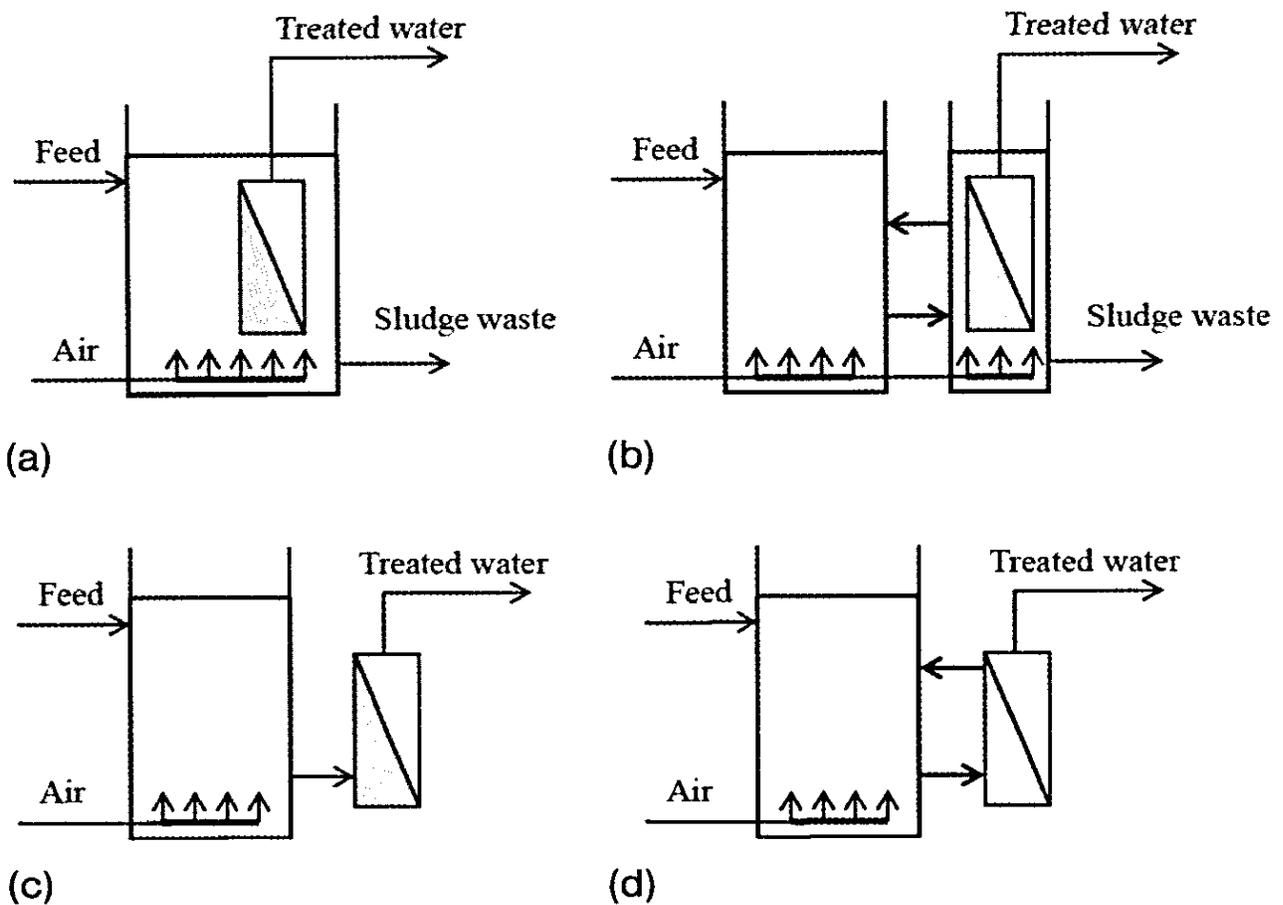


Figure 4. Typical configurations of MBR schemes, immersed vs. side-stream (Drioli et al., 2009).

-flow mode with recycling of the concentrate stream back to the biological reactor (Figure 4, schemes C and D). The treated water (permeate) from the submerged/immersed configuration is extracted from the membrane by vacuum (low pressure) while the permeate from the side-stream configuration is generally produced under pressure. The submerged configuration appears to be more economical based on energy consumption (Marrot et al., 2004) for two main reasons: no recycle pump is needed since aeration generates a tangential liquid flow in the vicinity of the membranes, and the operating conditions are much milder than in an external MBR system because of the lower values of transmembrane pressure (TMP) and tangential velocities. Generally, hollow fiber membranes are used in submerged MBR and tubular membranes are used in external MBR systems.

MBR systems classification

Membrane bioreactor systems are classified into two major groups according to their configuration. The first group is the submerged/immersed MBR, which has a membrane present in the bioreactor itself. The driving force across the membrane is achieved by creating negative pressure on the permeate side of the membrane (Baek and Pagilla, 2006). The submerged MBR has been developed to simplify the system and reduce the power consumption. However, this system operates at a lower transmembrane pressure, and, therefore, a lower permeation flux is achieved. The second group is the sidestream MBR, which recirculates the mixed liquor through a membrane module that exists outside the bioreactor. The driving force for this system is the pressure created by high-cross-flow velocity through the membrane unit. Although the pumping cost of the recirculation of mixed liquors is high, higher effluent fluxes, easier maintenance of the membrane, and less complicated scale-up makes this configuration attractive. The MBR systems could also be classified into these two groups: aerobic MBRs and anaerobic MBRs. The aerobic MBR is a combination of a membrane filtration unit and aerobic bioreactor. Most of the aerobic MBRs for municipal-wastewater treatment have been the submerged systems. For industrial wastewater treatment by aerobic MBRs, sidestreamed systems have generally been used. However, the operating costs for the aerobic MBRs are high because of the cost of aeration. Approximately 20 to 50% of the total-process-power requirements are used for aeration in sidestreamed MBRs, and 80 to 100% of the total-process-power consumption is required for aeration in submerged MBRs (Baek and Pagilla, 2006). The aerobic MBR process has been re-

ported to have been used successfully to treat effluents from a range of industrial wastewaters, including cosmetics, pharmaceuticals, metal fabrication, textiles, abattoir, dairy, food, beverage, pulp and paper, rendering and chemical manufacture (Stephenson et al., 2000). It has also been used for the treatment of landfill leachate. The anaerobic MBR is a combination of an anaerobic reactor coupled with the membrane unit. The anaerobic MBR has the advantages of aeration-energy savings, possible biogas recovery, and lower sludge production, resulting in competitive capital and operating costs. However, negligible or no ammonia, total nitrogen, or phosphorus removal can be expected from an anaerobic MBR process. Anaerobic MBRs could have potential application in municipal wastewater treatment to remove organic carbon or biochemical oxygen demand (BOD) from the wastewater. Use of an anaerobic process was previously not feasible for BOD removal in municipal wastewater because of the poor settleability of anaerobic sludge in gravity settlers and the potential for odors. In the case of the anaerobic MBR, the bioreactor is a closed unit like an anaerobic digester, and the solid-liquid separation is also a closed unit in the form of membrane filtration unit. Thus, the two drawbacks, which precluded the use of the anaerobic-sludge process for BOD removal from municipal wastewater, could be circumvented by using the anaerobic MBR (Baek and Pagilla, 2006).

Membrane characteristics on MBR performance

Membrane characteristics such as pore size, porosity, surface charge, roughness and hydrophilicity/hydrophobicity, etc., have been said to impact on MBR performance, especially on membrane fouling. Pore size distribution is likely to be one of the parameters affecting membrane performance. A narrow pore size distribution is preferred to control membrane fouling both in MBR process and in conventional membrane separation process.

The membrane materials always show different fouling propensity due to their different pore size, morphology and hydrophobicity. Polyvinylidene fluoride (PVDF) membrane is superior to polyethylene (PE) membrane in terms of prevention of irremovable fouling in MBRs used for the treatment of municipal wastewater (Meng et al., 2009). Regarding MBR processes, the fouling behavior of the membrane used is determined by the affinity between foulants (example, extracellular polymeric substances (EPS)/soluble microbial products (SMP)) and membrane.

Inorganic membranes, such as aluminum, zirconium and titanium oxide, show superior hydraulic, thermal and chemical resistance. A stainless steel membrane was used for MBR, and the result showed that the stainless

steel membrane could obtain a higher permeate flux (Meng et al., 2009), and it is a potential alternative for the treatment of high temperature wastewater. According to Meng et al. (2009) in the stainless steel membrane bioreactor, thermophilic bacteria could be cultivated when the MBR was operated at higher temperature. But, these inorganic membranes are not the preferred option for large-scale MBR plants because of their high costs. In addition, inorganic membranes can induce severe inorganic fouling (struvite formation). So, the inorganic membranes might be used only in some special applications such as high temperature wastewater treatment (Meng et al., 2009).

In general, membrane fouling occurs more readily on hydrophobic membranes than on hydrophilic ones because of the hydrophobic interaction between foulants and membranes.

Optimizing MBR operations

When first commercialized, MBR processes were considered to be very expensive systems and only suitable for small-scale plants and for very specific applications. The capital costs are said to have decreased significantly with the advent of several commercially available systems and treatment scheme that are competitive even for large treatment plants. For example, in 1996, ZENON Environmental Inc. was installing municipal ZeeWeed MBR systems with average capacities of 0.2 million gallons per day (MGD). In 2003, just eight years later, MBR plants with capacities >10 MGD were constructed by ZENON (Schneider, 2003). In the infancy of the technology, a major cost was the anticipated membrane-replacement costs, now this item has dropped significantly due to better production of membrane modules as well as an increase in life expectancy gained from operating experiences (Drioli and Giorno, 2009). The energy demands is said to be the largest cost so far today, in particular the need for aeration of the biological process and of the membrane process as depicted in Figure 5

COMPARISON OF MEMBRANE BIOREACTORS WITH CONVENTIONAL ACTIVATED SLUDGE SYSTEM

Throughout the world, there are hundreds of MBR systems in operation with many more in the design/construction phase. These range from small to large systems, treating both municipal and industrial wastewater. Small MBR systems are often used for water reuse within commercial developments, such as office complexes or shopping malls, whereas municipalities and

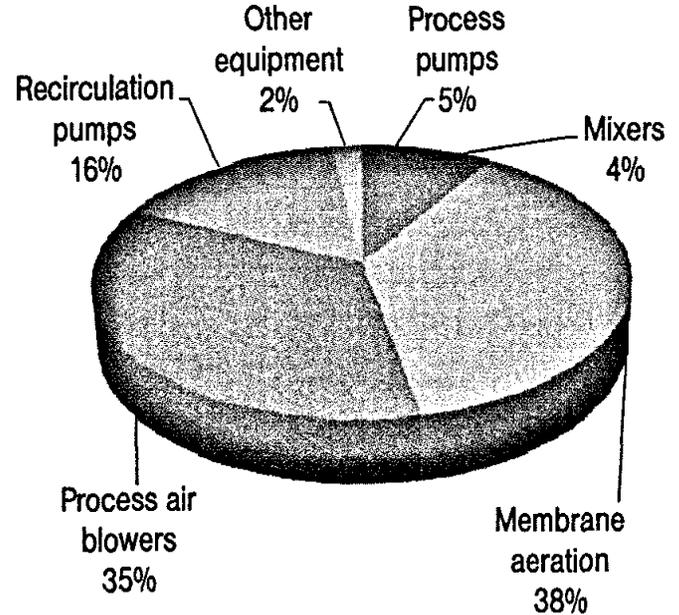


Figure 5. Typical energy demands in operation of a MBR process (Drioli et al., 2009).

industries operate the larger plants.

A major advantage of the MBR system as stated by Drioli and Giorno (2009) is that it can operate at a much higher solids concentration in the bioreactor than that of a CAS-mixed liquor suspended solids (MLSS) concentrations typically in the range 8 to 12 kg/l as compared to CAS that can only work at about 2 to 3 kg/l, because of limitations on settling. This higher sludge concentration is said to permit effective removal, not only of dissolved organic materials but also residual particulate solids. A comparison and assessment of MBR technology verses the conventional activated sludge process generally highlights the following issues:

Improve water quality

1. Meets stringent effluent requirements;
2. Filters out nearly all solids.

Allows wastewater reuse

1. As part of treatment scheme, provides water for potable reuse;
2. Reduces wastewater discharge fees and freshwater costs;
3. Provides water for nonpotable applications where fresh

water is in short supply.

Lowens capital cost

1. Clarifier is not needed;
2. Biological step can be scaled down in volume since bacteria concentration is higher.

Reduces plant space requirements

1. Footprint is up to 50% smaller than conventional plant;
2. Allows for expanded capacity within existing buildings.

Fewer operational problems

Bulking and floating sludge problems are avoided.

In spite of these benefits of the MBR process as compared to CAS, the technology is not without disadvantages. The early years of development of the process was considered to be expensive and this was attributed to high membrane costs, uncertainties of membrane lifetime and anticipated membrane replacement costs. However, as the MBR plants have been in operation for a while and experience has been gained, membrane lifetime appears to be longer than initially thought and replacement costs stipulated in the early 1990s to be 80 to 90% of operation and maintenance (O and M) costs is now estimated to be around 10 to 15% (Drioli and Giorno, 2009). The reduction is due to gain confidence in the technology, better and cheaper production of membrane modules and product development in general. Membrane fouling, an inherent phenomenon in all membrane processes has been mentioned as the main disadvantage of the MBR systems. Strategies and techniques to alleviate fouling coupled with the frequency of membrane cleaning are one main constraints of the process. The high energy demands for aeration, both for the biological process and membrane operation, is currently recognized as another major challenge and drawback of the technology (Drioli and Giorno, 2009).

MBR technology is said to be probably the membrane process that had most success and has the best prospects for the future in wastewater treatment. Trends and developments indicate that this technology is becoming accepted and is rapidly becoming the best available technology (BAT) for many wastewater treatment applications. The cost of an MBR plant for secondary treatment is still higher than that for a CAS plant, but as the numbers of MBR plants increase, and as membrane costs fall, the life cycle cost differential will

Table 2. Comparison of MBR and CAS systems (Wang et al., 2009).

Diary application	CAS	MBR
WW flow (m ³ /day)	600	600
Influent COD (mg/L)	5,000	5,000
Influent BOD ₅ (kg/day)	3,000	3,000
Recycle of treated effluent (m ³ /day)	0	400
Aeration volume (m ³)	4,500	600
Total floor space requirement (m ²)	1,300	260
Effluent COD (mg/L)	90	30
Effluent BOD ₅ (mg/L)	30	5
Effluent TSS (mg/L)	30	0

soon disappear, and the process advantages should lead to rapid installation of the MBR system by the wastewater treatment industry (Drioli and Giorno, 2009).

Process comparison

The similarities and dissimilarities of the CAS process system and the MBR process system are shown in Table 2. The data in the table is based on a 5-month study at a dairy site in Central France which needs a modern wastewater treatment system to treat its combined wastewater (Wang and Menon, 2009).

From the viewpoint of biochemical engineering, the CAS and MBR process system are similar. The basic process of either CAS or MBR includes the unit processes of: influent feed, biological oxidation, final clarification, treated effluent discharge, return activated sludge (RAS) and excess discharge. Both processes require air supply or oxygen to sustain the biological oxidation and can be operated for the purpose of carbonaceous oxidation, nitrification and denitrification. When compared with conventional activated sludge systems, the MBR offers many attractive advantages:

- (i) The traditional secondary clarifier is replaced by a membrane module. This module is more compact and the quality of rejected water is independent on the variations of sludge settling velocity.
- (ii) The MBR allows the biomass concentrations to be higher than for traditional treatment plants. Whereas MBR investigations have been reported with biomass concentration of 20 g/l (Marrot et al., 2004; Jefferson et al., 1999) and even as high as 30 g/l (Yamamoto et al., 1989), conventional processes utilize biomass concentrations less than 5 g/l in order to avoid problems inherent to settling of concentrated flocs.

With poor settling flocs avoided, biological degradation is said to be more complete and treatment efficiency is

higher. Also a report attributed to Lübbecke et al. (1995) indicates that, increasing the biomass concentration involves a reduction in the oxygen mass transfer rate depending on the type of wastewater and reactor used. Other advantages of this system are as follows:

- (i) The volume of the aeration tank can be reduced since a higher concentration of biomass can be stored in the bioreactor.
- (ii) The production of sludge, the disposal of which is often difficult, is decreased by a factor of 2 to 3, resulting in a reduction of the overall operating costs (Marrot et al., 2004).
- (iii) The membrane bioreactor is perfectly integrated in the industrial process because the wastewater can directly be treated *in situ*, allowing water reuse and concomitant reduction of the manufacturing costs linked to water consumption.

Unlike the conventional activated sludge system, the membrane bioreactor is characterized by a complete retention of the biomass inside the bioreactor because of the use of membrane separation, which controls and increases the sludge retention time (SRT) independently from the hydraulic retention time (HRT). High SRTs enable one to increase the sludge concentration and the applied organic load, thereby increasing the pollutant degradation. The specific sludge activity during organic matter decomposition and nitrification depends on the SRT. The SRT is a significant operational factor for the biological process (Marrot et al., 2004). Huang et al. (2000) investigated the organic removal performance from a synthetic wastewater treated with a submerged membrane bioreactor, as well as the behavior of soluble microbial products during long-term operation indicating that a satisfactory chemical oxygen demand (COD), total organic carbon (TOC) and biological oxygen demand (BOD) removal efficiencies were achieved, averaging over 90, 94 and 95%, respectively.

The results of a study by Dufresne et al. (1998) was said to be the first ever comparison made of performances between membrane bioreactor (MBR) and conventional activated sludge system treatment of a chemi-thermomechanical pulping (CTMP) effluent indicating that the performances of the MBR were superior for the removals of COD, suspended solids and toxicity. The amount of lignin onto the biosludge in the MBR was also found to be higher as compared to that inside the CAS.

Gao et al. (2004) did a comparison between a submerged membrane bioreactor (SMBR) and a conventional activated sludge system on treating ammonia-bearing inorganic wastewater. The SMBR and the CAS were compared in parallel over a period of 210

days on treating synthetic ammonia-bearing inorganic wastewater under similar conditions. Their result indicated that, the SMBR which contained larger numbers of nitrifiers was more effective and stable than the CAS in treating the synthetic ammonia-bearing inorganic wastewater. Differences were also said to be observed in the microbial community in the two systems. SMPs were reported to tend to accumulate, and then biodegrade in SMBR and the sludge particle size in SMBR were reported to be smaller than that in CAS.

Cicek et al. (1999) studied a system in which the wastewater used contained casein and starch (high molecular weight compounds) and fed to the MBR and CAS at identical conditions except different SRT (20 days for CAS and 30 days for MBR) which showed that approximately 99.0% of COD and 96.9% dissolved organic carbon (DOC) were removed in the MBR as compared to 94.5 and 92.7% in the CAS. The sludge in the MBR system was found to be made up of small flocs of regular size composed of zooglycal bacteria and of a small number of filamentous bacteria. The sludge in CAS system was made up of large flocs and higher amounts of filamentous organisms. Better settleability was observed in the CAS system than the MBR.

Weiss and Reemtsma (2008) carried out a comparative study of the performances of a lab-scale membrane bioreactor system and conventional activated sludge system for polar pollutants removal from municipal wastewater. Their results indicated that for half of the studied compounds, single step MBR treatment was clearly superior to CAS treatment with aerobic and anaerobic stages and provided significantly lower effluent concentrations (22 to 56% lower). They also found that, all the compounds for which no improvement was noted were either well removed by CAS treatment or were hardly degradable in the municipal wastewater. Considering operational conditions on trace pollutant removal by MBR studied by them, no significant effects were found for variation of hydraulic retention time (7 to 14 h) and sludge retention time (26 to 102 days), suggesting that increasing these parameters did not improve removal significantly. They however, observed an improved removal with SRT increasing from 26 to 37 days which was considered as not significant. Results from their work also indicated that MBR is neither superior to well degradable compounds that are already extensively degraded in CAS treatment nor for recalcitrant compounds that are not amenable to biodegradation. For most compounds of intermediate removal in CAS treatment (15 to 80%), among them are personal care products, pharmaceuticals and industrial chemicals, the results from their work showed the MBR being superior and reduced the effluent concentration by 20 to 50%.

Mignani et al. (1999) evaluated the economics of using

the membrane processes to treat textile effluents of a factory located in the Northern part of Italy. The effluent after undergoing the conventional biological treatment was found not to meet the quality for discharge into the environment and have to be sent for additional external treatment in order to comply with the discharge standards. In order to avoid the costs of this added process, which represented 59% of the total costs, they installed an ultrafiltration module (standard Flamec-24 assembled modules) following the biological system. This unit was followed, in turn, by a reverse osmosis stage. This new process enabled them to reduce the total treatment costs of 122,000 €/year partly by the reuse of 50,000 m³/year of water (Marrot et al., 2004). The treated wastewater is recycled and used as cooling water for dyeing machines and/or as water for washing and rinsing. The return on investment of the membrane process (270 000 €) is 2.2 and 2.5 years. This study shows that the equipment cost of a membrane process is not a barrier to its use.

Ciardelli et al. (2000) studied the treatment of effluent of factories that use dyes. The treatment processes studied were activated sludge, sand filtration and ultrafiltration (UF) and reverse osmosis (RO). The study contains a technical and economic analysis of the application of membrane separation technique for the purification of wastewaters targeted at their reuse. The water quality after the membrane processes is much better than that obtained using conventional processes; this treated effluent can be reused at all steps of production, including the most demanding ones concerning water quality. Finally, preliminary analysis of investment and operating costs indicates economic feasibility of the approach by their study.

BLEACHED KRAFT MILL EFFLUENT (BKME) CHARACTERISTICS

BKME is the combined aqueous waste of a major chemical pulp-making process. A mill typically generates waste water from many of its sections, including pulping, chemical recovery, evaporation and condensation, and multistage bleaching operations. Thus, waste waters from acid, alkaline, chlorine oxidant and other chemically diverse processes are sewered together to form the whole-mill discharge. The mixing and ensuing reactions of these streams lead to a final effluent that is highly complex. It consists of simple inorganic salts as well as over 250 identified organic and inorganic compounds of low molecular weight (or mass) with probably many more yet to be identified. The effluent from the production of bleached kraft pulp contains sugars, polysaccharides, organic acids, resin acids, and lignin transformation products and a variety of chlorinated derivatives, 200 of

Table 3. Characteristics of mill effluent (Fulthorpe et al., 1992).

Prior to treatment	
Biological oxygen demand ^a	204 mg/L
pH ^a	6.6
Temperature	32°C
Organically bound chlorine	
During softwood pulp production	38.5 mg/L
During hardwood pulp production	13.9 mg/L
Chlorinated organics^b	
Total acids	5.0 (mg/L max)
Total phenolics	1.0 (mg/L max)
Total aldehydes, ketones, lactones	1.0 mg/L
High molecular weight lignin derivatives	40.0 (mg/L max)
After Treatment^c	
Biological oxygen demand	34.3 mg/L
pH	7.2
Total phosphorus	2.0mg/L
Total Kjeldahl nitrogen	1.9 mg/L
Ammonia-ammonium	0.9 mg/L
Chlorinated organics	
Adsorbable organic chloride	25.4 mg/L
Chlorodehydroabiatic acid	80 µg/L
Dichlorodehydroabiatic acid	100 µg/L
2,4- Dichlorophenol	3.8 µg/L
2,4,5-Trichlorophenol	7.5 µg/L
1,2,3-Trichlorobenzene	0.8 µg/L
Metals	
Aluminum	1.2 µg/L
Copper	4.2 µg/L
Zinc	107.8 µg/L

^aTwelve-month averages; Liss, unpublished data. ^bCalculated from data in Kringstad and Lindstrom (1984) and the estimate that the mill produces 1000 tonnes of pulp per 100,000 m³ of water discharged. ^cAverage concentrations detected in final effluent in the period January 1 to June 30, 1990; from Ontario Ministry of Environment, 1991.

which have been identified (Table 3). In addition, an unusual property of BKME is that many of the organic constituents are of high molecular mass (>1kDa). This material is thought to consist largely of the polar breakdown product(s) of lignin, with lesser amounts of lignin at various degradation stages as well as polysaccharides (Higashi et al., 1992). The high molecular weight constituent of the effluent tended to be resistant to biode-

Table 4. Characteristics of BKME with ECF bleaching sequence (Xavier et al., 2005).

Parameter	Value
pH	3.4±0.17
COD (mg/L)	881.5±24.3
BOD ₅ (mg/L)	300.5±9.5
Total phenolic compounds (mg/L)	271.9±14.2
Phytosterols (mg/L)	0.17±0.01
Color (VIS ₄₄₀) (1×1 cm)	0.41±0.01

gradation and has been shown to be the principal source of adsorbable organic halide (AOX), color and chemical oxygen demand present in the effluents discharged (Bullock et al., 1996). The high molecular mass (HMM) material in an untreated effluent was reported to comprise 80% of the AOX but only 20% of the soluble COD. The HMM constituent also were found to be polar, devoid of aromatic structure and had characteristics indicative of lignin breakdown products (Higashi et al., 1992). The majority of effluent toxicity were also attributed to the HMM, chlorinated phenolics and chlorinated lignin derivatives of pulp and paper mill effluents (Afonso et al., 1992). According to them, low-molecular weight chlorinated neutral compounds are major contributors to mutagenicity and bioaccumulation due to their hydrophobicity and ability to penetrate cell membranes.

The pulp and paper industry is reported to be a major source of chlorinated organics worldwide, since pulp bleaching usually involves the oxidation of wood pulp with elemental chlorine or chlorine dioxide (Fulthorpe et al., 1992). However, with the replacement of bleaching sequences using elemental chlorine (Cl₂) by chlorine dioxide (ClO₂), the industry has reduced considerably the formation and discharge of chlorinated organic material into the aquatic environment. The release of chlorinated organic compounds to the environment has an adverse effect because many of these compounds are persistent, bioaccumulable and toxic. The annual estimate of organically bound chlorine discharge from the industry was put at 250,000 tonnes in the mid 1980s (Kringstad and Lindstrom, 1984). That figure has decreased to the 100, 000 tonnes/annum range presently. The organically bound chlorine measured as adsorbable organic halogen (AOX) in kraft mill effluents treated in an aerated stabilization basin show that a sizeable fraction of the carbon compounds in these effluents is chlorinated (Table 3) (Fulthorpe et al., 1992). Chlorinated phenolics are said to account for less than 2% of the organically bound chloride in bleaching effluents but they are greater contributors to effluent toxicity (Afonso et al., 1992).

Table 4 shows the characteristics of bleached kraft mill effluent with elemental chlorine-free (ECF) bleaching sequence.

Treatment methods used for BKME

The activated sludge process and the aerated stabilization basin (aerated lagoons) are the most commonly used methods for the biological treatment of pulp and paper mill effluents (Mueller and Walden, 1976; Ataberk and Gökçay, 1997). Many pulp and paper mills are reported to be relying on the same technologies to reduce toxicity of the effluent to aquatic organisms and the overall levels of chlorinated organics. However, studies have shown that only 10 to 50% of organically bound chlorine is removed in these treatment systems (Fulthorpe et al., 1992).

Aerated lagoons are relatively shallow basins in which wastewater is treated either on a flow-through basis or with solids recycle. Oxygen is supplied by means of surface aerators or by diffused aeration units. The action of the aerators also maintains the solids of the lagoon in suspension. Most of these solids must be removed by settling prior to discharge.

Depending on the degree of mixing, lagoons may be operated as either aerobic or as aerobic-anaerobic systems. In aerobic lagoons, all biological solids are in continual suspension and stabilization of the organics occurs under aerobic conditions. In the case of the aerobic-anaerobic lagoon, a large portion of the solids settle at the bottom of the lagoon. As the solids build up, a portion will undergo anaerobic decomposition. Therefore, stabilization in this case occurs partly under aerobic conditions and partly under anaerobic conditions. The retention time is a function of the percent removal of BOD and depending on the detention/retention time, the effluent from an aerated lagoon contains about one-third to one-half the value of the incoming BOD in the form of cell tissue (Metcalf and Eddy Inc., 1995).

The biological treatment is generally effective in reducing the levels of suspended solids and BOD of the effluent prior to discharge but not in eliminating the toxicity and mutagenicity. The chlorinated organic compounds, which are difficult to decompose, remain in the effluent (Afonso et al. 1992).

The AOX removal efficiencies for these plants (CAS and aerated lagoons) are typically around 20 to 60% (Collins and Allen, 1991; Yu and Welander, 1993; Ataberk and Gökçay, 1997; Schnell et al., 2000).

The popularity of the aerated lagoons in the treatment of wastewater is due to its relatively lower cost of installation and also, technically it is one of the simplest

forms of engineered biological treatment systems. It is said to be effective in reducing the more readily degradable materials measured as BOD from wastewater as much as 80 to 95% after five to 10 days treatment (Lindström and Mohamed, 1988).

CONCLUSION

A major concern of the pulp and paper industry lies in the fact that even after more than 30 years of consistent efforts, a satisfactory treatment of BKME still remains elusive. This is primarily due to two reasons:

The processes employed in pulping as well as pulp processing (including pulp bleaching) are so diverse that the composition of the resulting wastewaters (in terms of critical components) are very different and no single process or combination of processes that is economical can apply to all;

2. The wastewaters invariably contain considerable quantities of materials that are toxic either to the wastewater treating organisms or to the aquatic species present in the recipient waters or both (Ali and Sreekrishnan, 2001).

MBR for wastewater treatment and reuse are proven systems and are rapidly being accepted by industries. The technology has proven its reliability and efficiency for a variety of industrial plants in North America, Europe and Asia. Its applicability for the treatment of pulp and paper effluent has been acknowledged in a few research papers. Membrane bioreactors are effective in treating wastewaters. They offer advantages of compactness over conventional technology, as well as producing a very high quality disinfected effluent. In comparison with the conventional activated sludge system, the MBR systems have better removal efficiency and a potential for water reuse in manufacturing. Membrane bioreactors application is expected to continue to increase in wastewater treatment, with the drivers being the need for compact plant; quality of effluent and value of recycling. The effluent quality for discharge is becoming an issue in many countries now with stringent legislation being put in place or about to be implemented, requiring removal of most of the toxic compounds. These stringent conditions appear to be more achievable with emerging MBR technologies.

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