Advanced technologies in water and wastewater treatment

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Abstract: The use of conventional water and wastewater treatment processes becomes increasingly challenged with the identification of more and more contaminants, rapid growth of population and industrial activities, and diminishing availability of water resources. Three emerging treatment technologies, including membrane filtration, advanced oxidation processes (AOPs), and UV irradiation, hold great promise to provide alternatives for better protection of public health and the environment and thus are reviewed in this paper. The emphasis was placed on their basic principles, main applications, and new developments. Advantages and disadvantages of these technologies are compared to highlight their current limitations and future research needs. It can be concluded that, along with the growing knowledge and the advances in manufacturing industry, the applications of these technologies will be increased at an unprecedented scale.

Key words: water treatment, wastewater treatment, membrane filtration, ozonation, advanced oxidation processes, UV irradiation.

Résumé : L'utilisation de procédés conventionnels de traitement de l'eau et des eaux usées sont de plus en plus mis au défi avec l'identification de plus en plus de contaminants, la croissance rapide de la population et des activités industrielles, et la disponibilité décroissante des ressources en eaux. Trois technologies de traitement en voie de développement, incluant la filtration par membrane, les procédés d'oxydation avancés (POA) et l'irradiation par ultra violet, tiennent la grande promesse de fournir des alternatives pour une meilleure protection de la santé publique et de l'environnement, et pour cela, elle ont été revues dans cet article. L'emphase a été placée sur leurs principes de base, les applications principales et les nouveaux développements. Les avantages et inconvénients de ces technologies ont été comparés pour mettre en lumière leur présentes limitations et les futurs besoins en recherche. Il peut être conclu que, conjointement avec les connaissances accrues et les avancées dans l'industrie manufacturière, les applications de ces technologies vont s'accroître à une échelle sans précédent.

Mots clés : traitement de l'eau, traitement des eaux usées, filtration par membrane, ozonation, procédés d'oxydation avancés, irradiation par ultra violet.

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Introduction

Conventional water and wastewater treatment processes have been long established in removing many chemical and microbial contaminants of concern to public health and the environment. However, the effectiveness of these processes has become limited over the last two decades because of three new challenges (Langlais et al. 1991; Mallevialle et al. 1996). First, increased knowledge about the consequences from water pollution and the public desire for better quality water have promoted the implementation of much stricter regulations by expanding the scope of regulated contaminants and lowering their maximum contaminant levels (MCLs). In water treatment, among the most important developments are the establishment of the possible link between halogenerated disinfection by-products (DBPs) and cancers, and the recent outbreaks caused by *Giardia* cysts and *Cryptosporidium* oocysts. These have promoted the United States Environmental Protection Agency (USEPA) to propose the Interim Enhanced Surface Water Treatment Rule for the mandatory destruction of these microbial contaminants and the Disinfection–Disinfection By-Product Rule for lowering the MCLs for total trihalomethanes (THMs) and setting new MCLs for haloacetic acids (HAAs). Similarly, the stricter regulations have been set over a much broader range of contaminants for wastewater discharge. Among them, the most significant are perhaps the new requirements to remove nutrients (nitrogen and phosphorus) and synthetic organic compounds (SOCs) because of their significant impacts on public health and the environment.

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The second factor is the diminishing water resources and rapid population growth and industrial development. The reuse of municipal and industrial wastewaters and the recovery of potential pollutants used in industrial processes become more critical. This is especially true in arid or semiarid areas where the potable water and irrigation water must be imported at great expense. The reclamation may be further justified in view of growing concern over the contamination of water resources by the release of more toxic compounds. Advanced treatment technologies have been demonstrated to remove various potentially harmful compounds that could not be effectively removed by conventional treatment processes.

In addition, advances in the manufacturing industry and the growing market associated with advanced treatment processes have resulted in substantial improvements to the versatility and costs of these processes at the industrial scale. Using life-cycle analysis, for example, Wiesner et al. (1994) concluded that the costs of new pressure-driven membrane filtration plants are expected to be comparable with or even less than those using conventional treatment processes for capacities up to 20 000 m^3/day.

To resolve these new challenges and better use economical resources, various advanced treatment technologies have been proposed, tested, and applied to meet both current and anticipated treatment requirements. Among them, membrane filtration, advanced oxidation processes (AOPs), and UV irradiation have been proven to successfully remove a wide range of challenging contaminants and hold great promise in water and wastewater treatment. As a result, this paper focuses on examining these three groups of advanced treatment technologies with emphasis on their process fundamentals, main applications, and advantages and disadvantages. The current limitations and future research needs associated with these technologies are also discussed.

Membrane filtration technologies

Membrane filtration can be broadly defined as a separation process that uses semipermeable membrane to divide the feed stream into two portions: a permeate that contains the material passing through the membranes, and a retentate consisting of the species being left behind (Mallevialle et al. 1996). More specifically, membrane filtration can be further classified in terms of the size range of permeating species, the mechanisms of rejection, the driving forces employed, the chemical structure and composition of membranes, and the geometry of construction. The most important types of membrane filtration are pressure-driven processes including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).

Membrane filtration system selection and design

The successful use of membrane processes depends on a proper selection of membrane material. Ideally, a membrane should have a high permeate flux, high contaminant rejection, great durability, good chemical resistance, and low cost. The permeate flux is usually defined as the rate at which permeate passes through a unit area of membrane. Extensive research has been conducted to develop new membrane materials (Wiesner and Chellam 1999). Inorganic membranes, although having very high chemical and temperature resistance, are now still of little commercial use due to brittleness and expense. Organic polymers remain the most widely used commercial membrane materials. They are usually constructed by coating a thin active polymeric layer onto a microporous support to provide desirable mechanic strength while having higher water permeability and chemical resistance. The polymers typically used for the active layer include cellulose acetates, polyamides, polypropylene, and polysulfones. More information about the properties of the membranes has been reviewed by Mallevialle et al. (1996) and the American Water Works Association (AWWA) Membrane Technology Research Committee (1998).

From a practical application point of view, one of the most important membrane properties in the selection of a membrane process is the pore size or molecular weight cutoff (MWC), which specifies the maximum molecular weight of a solute to be rejected. Table 1 summarizes the main characteristics of common membrane filtration processes. MF is permeable to species up to 0. 5 μm in diameter and is capable of a relatively high flux under a small pressure difference across the membrane. Thus, it is often used for separating micrometre particles and microorganisms from water. By comparison, RO has the smallest pore size and can virtually retain all the ions while operating under a very high pressure difference and at a relatively low permeate flux. It is commonly used for desalting brackish water and seawater. UF and NF have characteristics between those of MF and RO. Recently, these two types of membrane processes have gained considerable interest because they are very effective in removing natural organic matter (NOM) and trace SOCs while still maintaining a high permeate flux. Membrane processes are suitable for removing a wide range of contaminants in water and wastewater treatment because of the wide range of pore sizes available.

The performance of membrane processes also depends on the use of proper module configurations. A comparison among different model configurations is presented in Table 2. NF and RO are typically of the spiral wound configuration to promote turbulence, thereby reducing concentration polarization fouling and particle cake deposition. However, this type of membrane configuration is vulnerable to the occurrence of biofouling. The weakness of seals and glue lines also prevents the use of vigorous backwashing and may cause the loss of module integrity. In contrast, MF and UF usually use hollow fibre geometry to facilitate backwash and yield a high surface area to volume ratio. A major drawback is the high energy consumption necessary to maintain high cross-flow velocity. Recently, many new design concepts have been introduced by modifying module configurations to minimize membrane fouling and reduce operating costs. Winzeler and Belfort (1993) and Mallubhotla and Belfort (1997) studied the fluid dynamics in membrane modules and proposed a special curved wall configuration that

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Table 1. Main characteristics of common membrane filtration processes.

Membrane	Separation size (μm)	Main mechanisms	Typical transmembrane pressure, ΔP (MPa)	Permeate flux
Reverse osmosis (RO)	<0.001	Diffusion + exclusion	5–8	Low
Nanofiltration (NF)	0.001–0.008	Diffusion + exclusion	0.5–1.5	Medium
Ultrafiltration (UF)	0.003–0.1	Sieving	0.05–0.5	High
Microfiltration (MF)	>0.05	Sieving	0.03–0.3	High

Table 2. Comparison of different membrane configurations.

Criteria	Spiral wound	Hollow fibre	Tubular	Plate and frame	Rotating disc
Packing density (m^2/m^3)	++	+++	–	+	–
Wall shear rate	++	+	+++	+	+++
Permeate flux ($L/(m^2 \cdot h)$)	++	++	+++	+	+++
Holdup volume	+	++	–	+	–
Cost per area	+++	+++	–	–	–
Replacement cost	++	++	–	+++	–
Energy consumption	+	++	–	+	++
Fouling tendency	+	++	+++	++	+++
Ease of cleaning	–	+	++	+	+
Pretreatment requirement	–	+	+++	+	+++

Note: The configurations are ranked from clear disadvantage (–) to clear advantage (+++).

promotes Taylor or Dean vortexes at the membrane surface as a means of minimizing membrane fouling. Reed et al. (1997) developed a rotating disc membrane filter which consists of hollow, membrane-covered disks stacked along a hollow rotating shaft inside a pressurized container to generate high shear at the membrane surface. Another noted development is the use of submerged hollow fibre bundles which can be mounted directly in process tanks. Permeate is drawn into the hollow fibres under a slight vacuum, thus eliminating the energy required to recirculate the flow to maintain sufficient cross-flow velocity. Air can also be introduced at the bottom of the membrane modules to create turbulence, which scours and cleans the outside of the membrane fibres, thereby reducing the membrane fouling caused by particle deposition and microorganism attachment. It appears that these submerged membrane configurations could offer greater tolerance to high turbidity and solids loading.

Because of complex transport phenomena and interactions between membrane and contaminants underlying membrane filtration, the design practices of membrane filtration remain largely empirical. Consequently, site-specific bench and pilot testing are often necessary to assess treatment feasibility and provide process parameters for plant scale-up. Common considerations and experimental protocols in conducting these tests have been summarized by Mallevialle et al. (1996).

Mass transport and fouling control

Particle separation and water permeation involve various mass transport steps in membrane filtration processes. Many efforts have been directed to identify and characterize basic mechanisms underlying mass transport. For colloids and fine particles, main transport mechanisms include convection, Brownian diffusion, shear-induced diffusion, inertial lift, gravitational settling, and lateral migration. Their relative importance depends strongly on shear rate, particle size, and, to a lesser extent, the bulk concentration of particles in the feed solution (Belfort et al. 1994). Recent research has shown that the mass transport is also affected by the short-range interactions between particles such as adsorption, van der Waals attraction, and electrostatic double layer repulsion. These forces become particularly significant near the membrane wall where the presence of concentration polarization and the formation of surface cake dramatically reduce the distances between particles. Consequently, any factors that could change the hydrodynamic characteristics of membrane modules and the chemical characteristics of feed solutions would affect the overall membrane performance.

Mass transport can lead to the attachment, accumulation, or adsorption of materials onto membrane surfaces and (or) within membrane pores, causing permeate flux decline over time, a phenomenon called membrane fouling. It has been observed that less soluble salts, dissolved organic compounds, colloids, fine particles, and biological growth can all cause membrane fouling (Braghetta et al. 1997*a*; Cho et al. 1999; Fu et al. 1994; Jacangelo et al. 1995*a*; Wiesner et al. 1989; Zhu and Elimelech 1995). Consequently, five principal fouling mechanisms have been identified: (*i*) concentration polarization, (*ii*) cake formation, (*iii*) inorganic precipitation, (*iv*) organic adsorption, and (*v*) biological fouling. Each of these fouling mechanisms has different effects on flux recovery from backwash. Fouling inside membrane pores by salt precipitates and small colloids is often considered as an irreversible process and is responsible for long-term declines in the flux rate unless they are dissolved by cleaning agents in backwash water. In contrast, flux decline due to the development of a surface cake is largely reversible.

Efforts to predict permeate flux decline are complicated by the simultaneous occurrence of these fouling mechanisms. For example, biofouling is usually accompanied first by adsorption

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of macromolecules to condition the membrane surface for the adhesion of microorganisms, and then by microbial multiplication (Baker et al. 1995; Ridgway et al. 1985). The relative significance of these mechanisms in membrane fouling is affected by raw water quality, membrane material properties, membrane module configuration, and operating conditions. For instance, salt precipitation and dissolved organic compounds may be important causes of fouling after lime softening in water treatment, whereas their roles in wastewater treatment may be less significant. In contrast, in municipal and high-strength industrial wastewater treatment, colloidal and biological fouling will play a dominant role because of the much higher colloidal concentration and biological growth potential.

As the permeate flux is a critical measure of membrane filtration performance and plays an important role in determining overall treatment costs, many studies have been conducted in an attempt to develop mathematical models to describe the permeate flux decline under different operating conditions (Braghetta et al. 1998; Chellam and Wiesner 1992). Belfort et al. (1994) provided an excellent review of these models by analyzing the hydrodynamic behaviour of suspension flow, particle transport, and fouling layer formation.

The oldest mathematical model is the resistance model based on the cake filtration theory. In this model, the particles that are too large to enter membrane pores are assumed to form a cake layer on the membrane surface, thus providing additional resistance to filtration. Considering that the cake and membrane act as two resistances in series, the permeate flux can be described by adapting Darcy's law:

$$[1] \qquad J = \frac{\Delta P - \sigma_k \Pi}{\mu(R_m + R_c)}$$

where J is the permeate flux, ΔP is the transmembrane pressure, σ_k is the correction factor, Π is the osmotic pressure, μ is the permeate viscosity, R_m is the intrinsic membrane resistance, and R_c is the cake resistance. The equation shows the effects of temperature on permeate flux by changing permeate viscosity μ. In general, as the temperature increases, the permeate flux increases.

The filtration theory has been successful in describing flux decline during dead-end membrane filtration or initial cake buildup in cross-flow filtration. However, it becomes inappropriate when the cake growth is arrested with the action of tangential flow. Furthermore, the model does not include the diffusion of macromolecules and colloidal particles. To resolve these shortcomings, concentration polarization models have been proposed from the adaptation of film theory, assuming that the rejection of particles will form a thin fouling layer, overlaid by a concentration polarization layer due to particle back-transport. At steady-state condition, the convective transport of particles towards the membrane surface will be balanced by the particle diffusion away from the membrane. Thus, a pseudo-steady-state convection–diffusion equation can be written as

$$[2] \qquad u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} = D_y\frac{\partial^2 C}{\partial y^2}$$

where u is the axial velocity, v is the transverse velocity, C is the particle concentration, and D_y is the diffusion coefficient in the transverse direction. The calculated transverse velocity is then considered equal to the permeate flux. In the earlier concentration polarization model, only Brownian diffusion was considered responsible for particle back-transport. The predicted permeate flux was found at least an order of magnitude less than that measured during the filtration of colloidal and fine particles. Consequently, several modifications were made by invoking other transport mechanisms such as initial lift and shear-induced diffusion to explain the enhanced back-transport and hence the "flux paradox." Models based on Brownian diffusion predict a decline in permeate flux with increasing particle size, whereas those based on the initial lift and shear-induced diffusion predict monotonic increases in permeate flux with increasing particle size. When these mechanisms are considered together, the predictions show a minimum in permeate flux with a particle size of around 0.1 μm, which has been confirmed experimentally (Chellam and Wiesner 1992). At present, this type of model has become the cornerstone to predict the flux decline and investigate new membrane system design. Recently, Lee and Clark (1998) have extended the convection–diffusion model to predict the transient permeate flux decline as a function of filtration time. However, note that the solution of the convection–diffusion equation requires two important parameters, namely the mass transfer coefficient and the particle concentration near the membrane wall. These parameters must be determined experimentally, thus rendering it semiempirical in application. In addition, the convection–diffusion equation implies that the permeate flux is independent of transmembrane pressure, which is only valid under mass transfer limited conditions.

Another category of mathematical models assumes that the particles are brought to the membrane due to permeation flow and then roll or slide along the membrane surface due to tangential convection. Thus, these surface transport models describe the simultaneous deposition of particles into the cake layer and the flow of this layer towards the filter exit. The flow equations are then solved to determine the velocity profiles in the bulk suspension and in the cake layer, and thereby the thickness and permeate flux at a steady-state condition are obtained. Alternatively, force and torque balances were written for particles under dynamic equilibrium condition by applying Newton's second law directly. Coupling with a particle adhesion probability function and a standard cake filtration theory (e.g., eq. [1]), a system of equations can be obtained which are numerically solved for the cake growth and permeate flux decline with time. The main drawback is that Brownian diffusion mechanisms are excluded, thus they are only applicable for larger particles. In addition, these models are only valid when a rather thick cake layer is formed.

Despite these advances, a priori predictions of permeate flux based on the solution and membrane properties still remain elusive, particularly in the more realistic case of polydisperse particles. A fundamental understanding of physicochemical interac-

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Table 3. Common strategies for controlling membrane fouling.

Method	References
Direct methods	
Periodic hydraulic or chemical cleaning	Porter 1990
Impulse feed	Boonthanon et al. 1991
Turbulence promotor	Shen and Probstein 1979
Dean vortex	Mallubhotla and Belfort 1997
Rotating–vibrating membrane	Reed et al. 1997
Outside aeration	Silva et al. 2000
Inside gas sparging	Cabassud et al. 1997
Indirect methods	
Pretreatment by coagulation–filtration	Chellam et al. 1997
Pretreatment by air flotation	Braghetta et al. 1997*b*
PAC addition	
PAC addition	Adham et al. 1991
Membrane surface modification	Wiesner and Chellam 1999
Selecting optimum operating conditions	Belfort et al. 1994
Changing operating modes	Cote et al. 1998

tions between diverse particles, colloids, and macromolecules is needed. In addition, biofilm growth may also play a significant role in the long-term performance of membrane filtration and remains to be integrated into the models. A more detailed list of these research needs has been summarized by the AWWA Membrane Technology Research Committee (1998).

Owing to the fact that the key membrane fouling mechanisms are site specific, various membrane fouling control strategies have been proposed to lower the concentration gradient between the membrane surface and the bulk fluid, to re-entrain solids–biofilm deposited onto the membrane surface, or both. Table 3 lists common fouling control strategies currently used in practice. They include chemical modification of the membrane surface, physical improvement of the module geometric configuration by promoting hydrodynamic shear such as Dean vortex and using rotational discs, adjustment of operating conditions, the use of proper cleaning techniques, the pretreatment of influents, and the addition of powdered activated carbon to form a more porous surface cake. The effectiveness of these control strategies appears to be very site specific. In some applications, integrated approaches by coupling adequate pretreatment with selection of the proper membrane module and operating conditions are essential to mitigate fouling problems efficiently and economically.

Membrane filtration applications

As commercial membranes are available over a wide range of pore sizes, membrane filtration technologies can effectively remove various contaminants. Table 4 lists some applications reported in the literature for water and wastewater treatment. From a contaminant-based perspective, these applications can be grouped into three main areas: solid–liquid separation, organic removal, and inorganic removal. It should be noted that this distinction becomes rather blurred because the use of one membrane filtration process may remove several contaminants simultaneously.

Solid–liquid separation

The successes of membrane processes for solid–liquid separation have been demonstrated consistently over a wide range of water sources for both laboratory and full-scale applications. This is particularly important for MF and UF because they can be operated at very low pressure differentials. In water treatment, an increasing number of utilities use membrane processes to improve turbidity removal and eliminate chlorine-resistant pathogens. Both laboratory research and full-scale installations have consistently shown that these membrane filtration processes can provide an almost complete barrier to separate *Giardia* spp. and *Cryptosporidium* spp. from water, with a typical removal efficiency above 6 log-units (Ventresque et al. 1997; Yoo et al. 1995), provided that the membrane integrity is maintained. UF achieved an average removal of 6.8 log-units for the MS2 virus, but MF only removed the MS2 virus from 0.3–0.9 log-units as observed by Jacangelo et al. (1995*b*). Similar studies by Wiesner et al. (1989) showed that the pretreatment with coagulation would further improve the removal of suspended and microbial particles. However, caution should be taken because an excessive amount of coagulant polymers might lead to serious membrane fouling. Thus, a good practice would be to remove as much of the newly formed flocs as possible prior to membrane filtration. In addition, a secondary disinfectant is still needed to provide disinfectant residual so that the potential microbial regrowth in water distribution systems would be prevented after membrane filtration.

For the microbial removal applications, a critical issue is membrane integrity to ensure consistent performance. Adham et al. (1995) demonstrated that an artificially defective membrane with a needle hole would increase the particle counts dramatically, although its impact on the turbidity was less obvious. Other reported techniques include sonic sensor, air pressure testing, bubble point testing, and seeded microbial monitoring. A comparison of their advantages and disadvantages is given by Mallevialle et al. (1996).

In wastewater treatment, membrane filtration processes have been proposed to replace the clarification for the separation of suspended solids and to further polish the secondary effluents. Kilega et al. (1991) examined the MF process for treating primary sewage effluent and showed that the suspended solids and turbidity could be reduced to less than 1 mg/L and 1 NTU, respectively. In addition, biological oxygen demand (BOD), oils, and grease were removed considerably. One of the main advantages was that membrane filtration could often produce superior quality effluents suitable for water reuse.

Organic removal

Because of the difference in pore size, different membrane processes showed great disparity in removing organic compounds. In general, MF and UF by themselves are not effec-

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Table 4. Applications of membrane filtration in water and wastewater treatment.

Membrane	Configuration	Water source	Resulting effects	References
Water treatment				
RO			Desalination	
NF	Spiral wound	Surface water	NOM >90% and atrazine >92% removal at a flow recovery rate of 90%	Ventresque et al. 1997
NF	Spiral wound	Groundwater	Colour ≈97%, TOC ≈95%, THMFPs >92% removal for a very high colour groundwater at a flux rate of 34 L/(m^2·h) and a flow recovery of 90%	Fu et al. 1994
NF	Flat sheet test cell	Surface water; groundwater	TOC and DBP were removed from 71–94% and Br^- <10%; the permeate quality deteriorates as the water recovery increases	Chellam 2000
NF	Hollow fibre	Synthetic water	Both solute removal and flux rate decrease at low pH and high ionic strength	Braghetta et al. 1997*a*
RO, NF	Plate and frame	Synthetic water and surface water*	>92% removal for both As ions; >95% salt rejection by RO; the removal efficiency increased with $CaCl_2$, but was not affected by SO_4^{2-} and PO_4^{3-}	Waypa et al. 1997
MF	Hollow fibre	Surface water	>6 log-units removal of *Giardia* and *Cryptosporidium*, and <0.2 NTU in effluent	Yoo et al. 1995
MF	Submerged hollow fibre	Surface water	Very effective in removing turbidity and indicator bacteria; stable flux was obtained with air scrubbing with frequent backwashing	Suda et al. 1998
MF–NF	MF, hollow fibre; NF, spiral wound	Surface water	MF was effective in removing turbidity, *Giardia*, and *Cryptosporidium*, but only NF was able to remove organic matter	Lozier et al. 1997
Wastewater treatment				
UF	Tubular	Municipal wastewater		
MF, UF, NF	Compact tubular, vibratory, high shear rotary	Paper machine white water	All three shear-enhanced units produced a permeate flux up to 200 L/(m^2·h) and water quality suitable for internal recycle; pretreatments by adjusting pH and adding fixative increased the flux by 20%	Nuortila-Jokinen et al. 1998
NF	Flat sheet test cell	Paper mill effluent	Can achieve >98% rejection efficiency for both TOC and colour; however, the flux declined by 50% at a water recovery rate of 89%	Ahn et al. 1989
UF, RO	Tubular	Pulp mill effluents	55–60, 65–75, and 50% removal for COD, AOX, and toxicity, respectively; >98.9% for COD, AOX, and Cl^- with UF–RO combination	
UF	Dead-end flat sheet; high shear rotary	Oil and grease wastes	>97% removal for both oil and grease and SS	Reed et al. 1997
NF	Tubular	Textile wastewater	>99% removal for both colour and copper, 85% for salt at a water recovery rate of 85%	Wu et al. 1998
UF–bioreactor	Hollow fibre	Brewery wastewater	82% COD removal efficiency at a rate of 27 kg COD/(m^3·d)	Brindle et al. 1999

*Synthetic water prepared by dissolving polyethylene glycol, and surface water by dissolving Suwannee River organic matter.

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tive in removing dissolved organic compounds in surface water treatment, with typical removal efficiency of less than 15%, although the removal efficiency can be improved to an extent by using coagulation as a pretreatment. The maximum removal has been observed at a coagulation pH ranging from 5 to 7, corresponding to the maximum adsorption of NOM on the coagulation flocs. In contrast, NF and RO were very effective at removing many compounds including NOM, pesticides, and DBPs. It has been suggested that NF might be preferable to granular activated carbon adsorption for total organic carbon (TOC) and DBP precursor removal from water sources with TOC concentrations greater than 8 mg/L.

Membrane filtration processes are also used to remove various dissolved organic compounds from municipal and industrial wastewaters (Mallevialle et al. 1996; Brindle and Stephenson 1996). Reported applications include the separation of organic dyestuffs from textile processing effluents, decolorization of pulp and paper mill effluents, concentration of oils from oilfield brines and petroleum processing plants, removal of pesticides in contaminated groundwater, product recovery from food processing wastewaters, and landfill leachate treatment. For economical reasons, such applications are still limited to the cases where contaminants and (or) water can be recovered for recycle or reuse.

Inorganic contaminants

The removal of inorganic contaminants by NF and RO remains the largest application in water treatment. A survey showed that there were more than 4000 land-based RO plants worldwide in 1989 with a combined desalting capacity of approximately 3.8×10^6 m^3/d (AWWA Membrane Technology Research Committee 1992). This only includes plants with capacities larger than 95 m^3/d. In addition, RO and NF have been recently investigated to remove hardness, nitrate, and heavy metals (Rautenbach and Groschl 1990; Waypa et al. 1997). USEPA is currently considering RO as a best available technology to meet anticipated regulations for small surface-water plants without existing facilities and groundwater treatment plants.

Hybrid membrane processes

UF and MF are very effective in solid–liquid separation and can operate at very low pressure. Several recent developments have been reported to combine these membrane processes with other conventional treatment processes so that various dissolved species can also be removed. Among them, membrane filtration – powdered activated carbon (PAC) and membrane bioreactor have shown great promise in water and wastewater treatment and will be discussed below.

Membrane bioreactors use biomass to degrade contaminants and membrane filtration to separate biomass from water (Scott and Ollis 1995). As a result, the settling characteristics of biomass are no longer important in determining effluent quality, making it possible to operate at a higher biomass concentration in the aeration tank. At present, this hybrid process has been mainly used for (*i*) high-strength wastewaters (Boman et al. 1991; Brindle et al. 1999), (*ii*) strict disinfection requirements for treated water, and (*iii*) trace xenobiotic contaminant and nitrate removal (McCleaf and Schroeder 1995). More information can be found in the reviews by Brindle and Stephenson (1996) and the AWWA Membrane Technology Research Committee (1998). However, wider application of this technology has been hindered by the high biofouling tendency and energy requirement to recirculate wastewater through membrane modules. The problem can be partially overcome by immersing the hollow fibre membranes directly into the aeration tank as originally proposed by Yamanoto et al. (1989). The filtration is vacuum driven by sucking the permeate from the hollow fibre outside to inside. This outside-in operating mode eliminates the use of a large recirculation flow necessary to maintain sufficient tangential velocity and shear rate on the membrane surface in the traditional inside-out operating mode. It also greatly increases the effective membrane area because the outside surface of the membrane fibres is used for solid–liquid separation. Because the membrane filtration is operated at a much lower transmembrane pressure, a low fouling tendency has been reported. A further improvement to reduce membrane fouling has been suggested using air scrubbing outside the membrane surface. From an engineering perspective, this technology can be easily implemented without the installation of separate containers containing the membrane modules and thus can be used in plant retrofitting to increase water production and improve water effluent quality. A Canadian company, specializing in this technology, has successfully installed a number of such full-scale treatment plants (P. Cote, personal communication, 1999). It is expected that this technology will gain even wider applications in water and wastewater treatment in the future.

In PAC–membrane processes, PAC is added to the recirculation loop of the membrane systems (Adham et al. 1991; Jack and Clark 1998). Dissolved organic matter such as SOC and natural DBP precursors are adsorbed on activated carbon particles, which are then separated from water by either UF or MF. Several studies have reported that the use of PAC can also reduce membrane fouling, conceivably due to the shear scouring effects induced by the larger size of the PAC particles. Similar effects have been demonstrated recently by Chang and Benjamin (1996) using iron oxide. At present, PAC–membrane processes are mainly used for removing microbial contaminants, turbidity, and dissolved organic matter altogether in water treatment.

The use of membrane processes alone or combined with conventional treatment processes demonstrates that membrane processes may offer a number of advantages over conventional treatment processes, including (*i*) high-quality effluent over a wide range of raw water sources, (*ii*) no chemical addition except when organic removal is practiced, (*iii*) a small amount of solids requiring disposal, (*iv*) very compact installations, (*v*) simpler automation and control, and (*vi*) reduced operation and maintenance requirements. Moreover, Chellam et al. (1998) and Wiesner et al. (1994) prepared detailed cost analyses based on membrane fouling rates, backwash intervals and frequencies,

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Table 5. Redox potential for commonly used oxidants in water.

Oxidative species	Redox potential (V)
Hydroxyl radical	2.80
Ozone	2.07
Hydrogen peroxide	1.78
Permanganate	1.69
Chlorine dioxide	1.56
Chlorine	1.36
Oxygen	1.23

permeate fluxes, and feed water recoveries; they concluded that membrane filtration processes can have a comparable or even lower total cost per unit volume treated than that of conventional solid–liquid separation processes in water treatment for small communities with a capacity less than 20 000 m^3/d. This was confirmed by a survey of many recent installations for the removal of particles, dissolved organic matter, and biological contaminants such as *Giardia*, coliforms, HPC, and viruses (AWWA Membrane Technology Research Committee 1998).

Advanced oxidation technologies

Advanced oxidation processes (AOPs) have been broadly defined as near ambient temperature treatment processes based on highly reactive radicals, especially the hydroxyl radical (·OH), as the primary oxidant (Glaze 1987). Table 5 lists the redox potential of several oxidative species commonly used in water and wastewater treatment. Clearly, the ·OH radical is among the strongest oxidizing species used in water and wastewater treatment and offers the potential to greatly accelerate the rates of contaminant oxidation.

The generation of ·OH radicals is commonly accelerated by combining ozone (O_3), hydrogen peroxide (H_2O_2), titanium dioxide (TiO_2), heterogeneous photocatalysis, UV radiation, ultrasound, and (or) high electron beam irradiation. Of these, O_3–H_2O_2, O_3–UV, H_2O_2–UV, and heterogeneous photocatalytic processes hold the greatest promise to detoxify water and wastewater. Ozone at elevated pH will be decomposed into hydroxyl radicals. Thus, ozonation itself can be considered as one of the AOPs. In addition, the knowledge about many AOPs is based on the initiation of ozone decomposition in water. In view of its importance in understanding other AOPs and wide application, ozonation will also be reviewed. Table 6 lists representative applications of these processes in water and wastewater treatment.

Ozonation

Reaction mechanisms

Ozone has a low solubility and is a very reactive gas. It is usually generated on-site from dry air or pure oxygen through high-voltage corona discharge. Once dissolved into water, it undergoes very complex self-decomposition and oxidation reactions. The two most widely accepted mechanisms are the Staehelin, Bühler, and Hoignè (SBH) model (Staehelin and Hoignè 1982) and the Tomiyasu, Fukutomi, and Gordon (TFG) model (Tomiyasu et al. 1985). A more detailed comparison of these two models can be found in Langlais et al. (1991).

In general, both mechanisms postulated that ozone decomposition in water is a radical chain process in which decomposition intermediates will further catalyze depletion of molecular ozone. In addition, ozone molecules can directly react with organic compounds which have high electronic density sites. Such direct reactions are usually very selective. In contrast, hydroxyl radical reactions are nonselective and will virtually react with almost all the organic compounds by either H-atom abstraction, direct electron transfer, or insertion.

Further studies showed that the relative significance of different reaction mechanisms is affected by the presence of NOM. Staehelin and Hoignè (1985) proposed a reaction scheme to describe the interactions of solutes with radical chain reactions. The main features of this scheme include the following: (*i*) the radical pathway of ozone decomposition consists of initiation, propagation, and termination steps; (*ii*) the presence of inorganic and organic matter could initiate, promote, and prohibit the radical chain reactions; (*iii*) O_2^- radical is highly selective, thereby would predominately catalyze the decomposition of ozone molecules; and (*iv*) all the ·OH radicals react with a solute before they react with another radical. Based on this scheme, an overall kinetic equation was formulated to qualitatively describe the effects of pH, alkalinity, and NOM acting as radical initiators, promoters, and scavengers on radical generation. The important initiators include OH^-, H_2O_2, UV radiation, some metal ions, NOM, and heterogeneous photocatalysts, and the main scavengers are carbonate and bicarbonate ions. It is this initiation of ozone decomposition that provides a theoretical basis for the development of various AOPs.

In practice, however, it is very difficult to identify and characterize the concentration and reactivity of each compound in water. Consequently, Yurteri and Gurol (1988) simplified the above scheme to relate the dissolved ozone consumption in natural waters to raw water pH, TOC, and alkalinity. Recent experimental evidence has repeatedly shown that the specific ozone utilization rate w is not constant as the oxidation progresses (Hermanowicz et al. 1999; Oke et al. 1998; Zhou and Smith 1994*b*). A more general kinetic equation was proposed to account for the effects of raw water quality and the degree of ozonation. Further work is needed to verify the applicability of this kinetic equation for different natural water sources so that the performance of ozonation can be predicted more accurately.

Ozone dissolution

From an engineering perspective, it is critical to dissolve ozone into water efficiently. Because of its low solubility, ozone diffusion within a gas film is usually considered much faster than within a liquid film. Thus, liquid phase mass transfer becomes a rate-controlling step, and the overall mass transfer coefficient could be approximated reasonably well by the local liquid mass transfer coefficient. Numerous empirical relationships have been developed to correlate the overall mass trans-

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Table 6. Sample applications of ozonation and advanced oxidation processes in water and wastewater treatment.

Processes	Applications	Resulting effects	References
O_3	Coagulation aid	Change in primary coagulant demand and floc stability; increase in Al and Fe residual in finished water	Grasso and Weber 1988
	Fe and Mn removal	Increase with ratio of O_3 to DOC; Fe^{2+} oxidation followed by Mn^{2+}; MnO_4^- ions may be formed with excessive O_3	Paillard et al. 1989
	Colour removal	70% colour reduction for pulp mill effluents in practice	Zhou and Smith 1997
	Taste and odour control	Effective reduction in taste and odour	Ferguson et al. 1990
	Algae removal	Enhancement of filtration for algae removal	Bernhardt and Lusse 1989
	SOC oxidation	Atrazine oxidation is a first-order reaction rate which is affected by pH, temperature, alkalinity, and NOM	Adams and Randtke 1992
	Disinfection	Increase with ozone residual; general effectiveness follows bacteria > virus > *Giardia* > *Cryptosporidium*	Foster et al. 1980; Gyürék et al. 1999
	DBP control	THMFP reduction with the ratio of O_3 to DOC	Reckhow and Singer 1984
	Bromate formation	Bromate formation via both molecular and radical mechanisms	von Gunten and Hoigne 1994
	AOC formation	Produce various aldehydes; increase BDOC and AOC	Paode et al. 1997
O_3–H_2O_2	SOC oxidation	Decrease 447 μg/L TCE and 163 μg/L PCE to below 5 μg/L in groundwater	Karimi et al. 1997
	Taste and odour reduction, DBP control, and disinfection	90% removal of MIB and geosmin at an ozone dose of 2 mg/L for O_3–H_2O_2 compared with 4 mg/L for O_3 alone; low DBP formation, and comparable inactivation	Ferguson et al. 1990
O_3, O_3–UV	Micropollutant destruction	TCE, NOM precursors, PCBs, trihalomethanes, chloroform, and bromodichloromethane were effectively oxidized	Peyton et al. 1982*a*, 1982*b*
H_2O_2–UV photolysis	SOC oxidation	99% removal of atrizane from both types of oxidation; the oxidation rate was faster with H_2O_2–UV	Beltran et al. 1993
UV–TiO_2, etc.	Hazardous compounds oxidation	Effective mineralization of TCE, toluence, MEK, and 2,4-DCP, as evidenced by substantial TOC reduction	Suri et al. 1993

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fer coefficient ($k_L a$) with operating conditions (Roustan et al. 1993; Zhou and Smith 1994*b*, 1997). However, the predictions from these relationships differ considerably, perhaps because of different testing conditions, analytical methods, and data-reduction approaches. A further complication is that ozone mass transfer could be enhanced in the presence of chemical reactions. These reactions will not only increase the mass transfer driving force by lowering the concentration of dissolved ozone, but also enhance the apparent $k_L a$ value if reaction rates are fast enough to deplete dissolved ozone completely within the liquid film. By calculating the Hatta number, it was concluded that ozonation is most likely to fall within slow reaction absorption regimes in water treatment, whereas for those wastewaters characterized by high ozone demand, it could be shifted to fast or instantaneous absorption regimes (Zhou et al. 1994; Zhou and Smith 2000).

At present, various types of ozone contacting systems are used in practice (Langlais et al. 1991). The most widely used is the conventional fine bubble contactor. It offers several advantages, including (*i*) demonstrated performance, (*ii*) high ozone transfer efficiency (commonly 90%), and (*iii*) less maintenance due to a lack of moving parts. The main disadvantages include the need to construct the deep basin for effective mass transfer, potential pore clogging, and vertical bubble channeling at low gas flow rates. Thus, recent efforts have been directed to the development of new ozone contacting systems which will be compatible with more energy-efficient, high-concentration ozone generators. Most incorporate venturi-type injectors or static mixers in an attempt to achieve the uniform dispersion of gas flow into liquid flow. To further optimize the process performance, more research is needed to develop integrated models that can predict the interactions between the contactor hydrodynamics, ozone absorption, and ozone reaction kinetics.

Application

Currently, there are over 4000 ozonation plants operating worldwide and more are to be installed in the future. Based on the purposes of these applications, ozone applications can mainly be generalized into two categories, namely a powerful disinfectant and a strong oxidant. As a disinfectant, ozone has been long recognized to effectively inactivate coliform indicators and other bacteria from municipal waters and recently the more resistant pathogenic microorganisms such as *Giardia* spp. and *Cryptosporidum* spp. in water treatment. Although its effectiveness compared to other common disinfectants has been well documented (Sobsey 1989), reaction mechanisms are not yet firmly established. It is generally accepted that the inactivation is achieved mostly by the attack of molecular ozone instead of free radicals (National Research Council 1980). Based on this hypothesis, the acceleration of free radical generation from ozone decomposition by increasing pH or using other AOP technologies will be of limited benefit for the purpose of disinfection.

To oxidize chemical contaminants, ozone will become more powerful after decomposition into highly reactive radicals. As an oxidant, the process has been used to treat drinking water by (*i*) oxidizing iron and manganese, (*ii*) removing colour and odour, (*iii*) eliminating trace toxic synthetic organic compounds, and (*iv*) assisting in coagulation via the reactions with aquatic humic substances (Langlais et al. 1991). Fewer applications have been reported for municipal and industrial wastewater treatment because of higher ozone demand (Masten and Davies 1994). For example, Zhou and Smith (1997) showed that at a ozone dose over 40 mg/L, the ozonation of biologically pretreated pulp mill effluents resulted in up to 80% reduction in colour and 60% reduction in adsorbable organic halogens (AOX). An improvement of biodegradability was also observed, as the ratio of BOD_5 to chemical oxygen demand (COD) increased with an increase in the amount of consumed ozone. After storing for 2 days, up to 15% of colour rebound in the treated effluents was observed.

One major concern associated with ozone application is that bromide ions in water can be oxidized into bromate ions and other harmful bromated organic by-products (Ozekin et al. 1997; Singer 1990; Siddiqui et al. 1995; Song et al. 1997; von Gunten et al. 1996; Westerhoff et al. 1998). Bromate ions have been classified as potentially carcinogenic by the International Agency for the Research on Cancer (IARC). Both the United States and the European Community have set a maximum bromate concentration of 10 μg/L in drinking water. Another concern is the potential increase in biological regrowth in water distribution systems by transforming high-molecular-weight organic compounds into low-molecular-weight organic compounds such as aldehydes, ketones, and carboxylic acids. For this reason, it has been suggested that ozonation should be combined with filtration or granular activated carbon to reduce the amount of biodegradable by-products (Langlais et al. 1991; Shukairy et al. 1995).

Ozone – hydrogen peroxide (peroxone)

Mechanisms

Although H_2O_2 reacts very slowly with the ozone molecule in water, its conjugate base (HO_2^-) can rapidly react with molecular ozone, thereby initiating the formation of hydroxyl radicals in two steps (Glaze 1987):

$$[3] \qquad H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+$$

$$[4] \qquad HO_2^- + O_3 \rightarrow \cdot OH + O_2^- + O_2$$

The rate constant between HO_2^- and O_3 was measured to be 5.5×10^6 $M^{-1}\cdot s^{-1}$, as compared with 7.0×10^1 $M^{-1}\cdot s^{-1}$ between the OH^- ion and O_3. The result is that even at a very low concentration, the HO_2^- ion will be very effective in initiating ozone decomposition and facilitating the formation of hydroxyl radicals. The HO_2^- ions consumed by ozone are then regenerated by shifting the chemical equilibrium to the left according to eq. [3]. The higher the pH, the more H_2O_2 that will be dissociated into HO_2^- ions. As a result, the ozone decomposition rate will increase with increasing pH. After the hydroxyl radicals are formed, the propagation of radical chain reactions

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and the oxidation of contaminants follow the same mechanisms as those occurring in ozonation at the elevated pH condition.

Applications

The O_3–H_2O_2 process, often called the PEROXONE process, has been used most widely in practice among the AOPs except for ozonation because of simplicity and low radical-generation costs. In water treatment, the O_3–H_2O_2 process has been mainly used for the oxidation of micropollutants, the removal of pesticides, and the control of taste- and odour-causing materials (Ferguson et al. 1990; Karimi et al. 1997; Paillard et al. 1989). The optimum H_2O_2 to O_3 ratio usually ranges from 0.3 to 0.6. It was also tested for contaminated groundwater and wastewater treatment. Murphy et al. (1993) studied the removal of colour from three effluent streams from a pulp and paper mill. They reported that the O_3–H_2O_2 process could achieve colour removal up to 85% for the caustic extract stream, up to 90% for the acidic stream, and up to 50% in the final effluent.

Ozone – Ultraviolet radiation

Reaction mechanisms

The O_3–UV process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals (Peyton and Glaze 1982*a*, 1982*b*, 1988). Because the maximum absorption of ozone molecules is at 253.7 nm, the light source commonly used is a medium-pressure mercury lamp wrapped in a quartz sleeve. It can generate the UV light at a wavelength of 200–280 nm.

The reaction mechanism starts with activating the ozone molecule by UV to form oxygen radicals, which then combine with water to form ·OH radicals:

$$[5a] \quad O_3 + h\nu \rightarrow O_2 + O(^1D)$$

$$[5b] \quad O(^1D) + H_2O \rightarrow 2 \cdot OH$$

Later, Peyton and Glaze (1988) observed that the UV photolysis of ozone would also yield H_2O_2:

$$[6] \quad O(^1D) + H_2O \rightarrow H_2O_2$$

The formed H_2O_2 could be further photolyzed to form two ·OH radicals. Alternatively, it could be first dissociated into HO_2^- and then participate in a series of chain reactions along with ozone to produce hydroxyl radicals as occurs in the O_3–H_2O_2 process. As the photolysis of H_2O_2 molecules is very slow, the second pathway is most likely to be predominant at neutral pH range for ozone decomposition. Thus, the O_3–UV process resembles the O_3–H_2O_2 process in terms of reaction mechanisms, and the increased rate of organic destruction can be explained by H_2O_2 catalyzed decomposition of ozone. An important consideration is that because the generation of H_2O_2 in this way is much less efficient than the electrochemical method used in industry, the O_3–UV process would be expected to be more expensive than the O_3–H_2O_2 process.

It should be noted that other reaction mechanisms could also contribute to the increased rate of organic compound oxidation by the O_3–UV process. UV radiation can lead to the direct excitation of some organic compounds (Peyton and Glaze 1982*a*). The excited compounds then react with ozone molecules to form various degradable products. Thus, the efficiency of this mechanism would be enhanced by the high concentration of ozone. In normal cases, ozone itself will absorb UV light, competing with organic compounds for UV energy.

Applications

The O_3–UV process was initially developed by Prengle et al. (1980) and patented by Garrison et al. (1975) for the destruction of wastewaters containing cyanide. Since then, it has been tested to oxidize aliphatic and aromatic chlorinated organic contaminants (Glaze 1987), NOM (Peyton and Glaze 1982*b*), and pesticides (Beltrán et al. 1994*a*, 1994*b*). The results often showed that the O_3–UV process was more effective than ozone alone in terms of reaction rate and removal efficiency. Its use for the treatment of clear groundwater containing trichloroethylene (TCE) and perchloroethylene (PCE) had been commercialized by the early 1980s. However, the O_3–UV process is now considered less economical compared with the O_3–H_2O_2 and H_2O_2–UV processes in most cases.

Hydrogen peroxide – Ultraviolet

Mechanism

Under UV irradiation, H_2O_2 will be photolyzed to form two hydroxyl radicals. The formed hydroxyl radicals then react with organic contaminants or undergo an H_2O_2 decomposition–formation cycle (Crittenden et al. 1999):

$$[7] \quad H_2O_2 + h\nu \rightarrow 2 \cdot OH$$

$$[8] \quad H_2O_2 + \cdot OH \rightarrow H_2O + HO_2$$

$$[9] \quad HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

This decomposition–formation cycle of H_2O_2 was used to explain a nearly constant concentration of H_2O_2 during treatment as observed by Benitez et al. (1996). It is interesting to note that the H_2O_2 will also act as a scavenger for hydroxyl radicals as shown earlier, in which case an excessive H_2O_2 dose might hinder the radical degradation. On the other hand, sufficient H_2O_2 is necessary so that it can absorb UV to accelerate the generation of hydroxyl radicals. A trade-off between them will result in an optimum H_2O_2 dose, which still needs to be verified experimentally.

Unlike ozone, H_2O_2 has an exceptionally low molar absorptivity within the wavelength range of 200–300 nm. Thus, it is particularly susceptible to the competing absorption of UV by organic compounds and suspended solids in water. If organic compounds after activation could more rapidly react with H_2O_2, such direct photooxidation would be expected to have a major contribution to the overall degradation in the H_2O_2–UV system.

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Applications

Like the O_3–UV process, the H_2O_2–UV process is mainly used for the oxidation of refractory contaminants. For example, Beltrán et al. (1993) studied the H_2O_2–UV oxidation of atrazine in water. Results showed that, depending on the initial atrazine concentration, more than 99% of the atrazine can degraded in less than 15 min. By varying test water quality, it was also confirmed that carbonate–bicarbonate ions and humic substances had a significant influence on the oxidation rate.

Heterogeneous photocatalytic processes

Mechanisms

Heterogeneous photocatalytic processes use certain metal oxides that can readily generate hydroxyl radicals on the surface of particles when absorbing UV light. The anatase form of TiO_2 has low band-gap energy (approximately 3.2 eV), which is almost equivalent to 400 nm wavelength of light. Hence, the most important heterogeneous photocatalytic processes include TiO_2–UV and TiO_2–H_2O_2–UV. The principal reaction mechanisms include (Wang and Hong 1999)

[13] $$Ti_2O_2 + h\nu \rightarrow h_{TiO_2}{}^{+} + e_{TiO_2}{}^{-}$$

[14] $$h_{TiO_2}{}^{+} + H_2O \rightarrow \cdot OH_{TiO_2}{}^{+} + H^{+}$$

[15] $$e_{TiO_2}{}^{-} + O_2 \rightarrow O_{2,\,TiO_2}{}^{-}$$

[16] $$O_{2,\,TiO_2}{}^{-} + e_{TiO_2}{}^{-} \rightarrow O_2{}^{2-}$$

[17] $$O_2{}^{2-} + H^{+} \rightarrow HO_2$$

As shown, UV irradiation of TiO_2 particles generates valence-band holes ($h_{TiO_2}{}^{+}$) and conduction-band electrons ($e_{TiO_2}{}^{-}$). The $h_{TiO_2}{}^{+}$ is very reactive and can directly react with organic contaminants absorbed on the surface or indirectly via the formation of $\cdot OH_{TiO_2}{}^{+}$ radicals. The moderately reductive $e_{TiO_2}{}^{-}$ is most likely to react with organic compounds via the formation radicals such as $O_{2,TiO_2}{}^{-}$, $O_2{}^{2-}$, and HO_2. In addition, H_2O_2 can be formed in TiO_2 photocatalytic process by combining two HO_2. The formed H_2O_2 can then either participate in the radical chain reactions as a promotor or capture hydroxyl radicals as a scavenger. Among the above mechanisms, hydroxyl radicals are usually the most important for oxidation reaction. Unfortunately, the quantum yield for eq. [13] reaction is only about 0.04–0.05, perhaps due to rapid recombination of $h_{TiO_2}{}^{+}$ and $e_{TiO_2}{}^{-}$.

Applications

Heterogeneous photocatalytic processes are an emerging technology. Their applications in oxidizing refractory organic contaminants still remain mostly at the laboratory scale. Wang and Hong (1999) demonstrated that the TiO_2-based process is very effective in removing polychlorinated biphenyls (PCBs).

A key point in using this technology is to select the proper heterogeneous catalyst. Suri et al. (1993) showed that the maximum destruction of TCE, toluene, and MEK was obtained using platinum Aldrich TiO_2, whereas platinum MTU TiO_2 was the best catalyst for destruction of salicylic acid and 2,4-DCP. Future efforts should be directed to develop more active photocatalysts to increase UV quantum efficiency and develop innovative technologies to prevent the potential loss of photocatalysts.

Table 7. Theoretical molar ratio of oxidants consumed to ·OH radicals generated.

Process	O_3	H_2O_2	UV
O_3–OH^-	1.5	—	—
O_3–UV	1.5	(0.5)*	0.52†
O_3–H_2O_2	1	0.5	—
H_2O_2–UV	—	0.5	0.5

*Hydrogen peroxide formed in situ.

†Moles of photon required for each mole of ·OH radicals.

Comparison of the advanced oxidation processes

Various AOPs depend on the generation of hydroxyl radicals to facilitate the oxidation of organic compounds. Thus, their applications in water and wastewater treatment should be very similar, i.e., to detoxify refractory organic and inorganic compounds. From laboratory testing and very limited industrial applications, it is believed that AOPs offer several distinct advantages over conventional treatment processes because (*i*) they are very effective at removing resistant organic compounds, (*ii*) they are capable of complete mineralization of organic contaminant into carbon dioxide if desired, (*iii*) they are less susceptible to the presence of toxic chemicals, and (*iv*) they produce less harmful by-products.

Because hydroxyl radicals are very unstable in water, the use of AOPs can lower the effective disinfectant concentration. Thus, AOPs should offer few benefits for microbial disinfection. In addition, there is little evidence that the complete mineralization of organic compounds is either necessary or economically practical. Nevertheless, they could still be very useful by integrating with other treatment processes. Along with biological oxidation, for example, AOPs can be used as a pretreatment process for the partial oxidation of organic compounds that are either too toxic or refractory to biodegradation.

Despite these similarities, different AOPs require different radical initiators to generate hydroxyl radicals. Table 7 compares the theoretical quantities of these initiators to generate 1 mole of hydroxyl radicals. Because of this difference, the cost to generate hydroxyl radicals varies greatly for different AOPs.

The O_3–H_2O_2 process has gained the widest applications among the AOPs discussed in this paper because of the effectiveness and low cost. The H_2O_2–UV process has a distinct advantage because of its simplicity. The only chemical required is H_2O_2, which can be purchased at 30% solution, easily stored, and precisely fed according to the process demand with a metering pump. Because it is a liquid, completely miscible in water, no mass transfer problems will occur. Thus, the H_2O_2–UV process is well suited to small systems that require minimum maintenance, intermittent operation, or both. In cases where

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materials in the water can strongly absorb UV, however, the H_2O_2–UV process may not be effective due to the lack of radical reaction initiation. The use of ozone at elevated pH is of limited use, as a large quantity of neutralizing chemicals would be required. The O_3–UV process is considered less favorable than the O_3–H_2O_2 and H_2O_2–UV processes. However, it can be used for low flow rates, especially when the contaminants to be oxidized have strong UV absorbance. Perhaps least used are the heterogeneous photocatalytic processes. However, they offer the following potential advantages: (*i*) additional radical initiators such as H_2O_2 are not required, (*ii*) the photocatalysts may be reused, and (*iii*) natural radiation may be used as a light source to activate catalysts. At present, these processes suffer very low quantum yield for radical initiation. Various inorganic oxidants such as ClO_2^-, ClO_3^-, IO_4^-, $S_2O_8^{2-}$, and H_2O_2 have been suggested to provide the better electron acceptor, thereby reducing the recombination of $h_{TiO_2}^+$ and $e_{TiO_2}^-$. The results are still promising but more research is needed to verify these results and examine the effects of these chemicals for different water sources and operating conditions.

Ultraviolet irradiation

In addition to its use in various AOPs, UV irradiation has been widely used as a microorganism-reduction step since the mid-1970s. The process usually involves the use of low-pressure (the gas pressure inside the lamp <10 torr (1 torr = 133.322 kPa)) UV lamps with a principal wavelength of 254 nm. Recent studies have shown that both low- and medium-pressure (the gas pressure inside the lamp ≈1000 torr) UV lamps with a wavelength ranging from 200 to 300 nm could be equally effective in inactivating *Cryptosporidium* oocysts (Bukhari et al. 1999). In water and wastewater treatment, UV dose ($W{\cdot}s/cm^2$) is commonly used to represent the total exposure of a given microorganism to UV irradiation. It can be defined as the rate of total incident radiation per unit area from all the directions and at all wavelengths times the exposure time. To measure total incident radiation, various methods have been proposed which convert the light into either heat or an electric current. The signals generated are then detected by either a thermal or photonic sensor. Some of the measurement methods include radiometers, UV sensors, and actimometry as summarized by Bolton (1999).

Inactivation mechanisms

Ultraviolet irradiation can be absorbed by proteins, RNA, and DNA of microorganisms. At a high UV dose, the absorption by proteins may lead to the disruption of cell membrane and eventually death of the cells. At a much lower UV dose, however, inactivation is more likely due to the absorption of UV light by RNA and (or) DNA. DNA is a nucleic acid polymer in a double-stranded helix linked by hydrogen bonds in an orderly sequence from four constituent bases. Of these four bases, thymine could be linked together to form thymine dimer after UV exposure when they are located adjacent to each other. This disrupts the "basic pair" structure. If enough thymine dimers are formed, the DNA cannot replicate in cell mitosis, resulting in disruption of the multiplication systems of the microorganisms (Braunstein et al. 1996*a*, 1996*b*).

Some microorganisms possess repair systems that can reconstitute the altered DNA. Two repair mechanisms have been proposed. One is the dark repair of nucleic acids that involves a multienzymatic process in which one strand of the DNA, if not altered, can serve as a copy for the complementary-strain synthesis, thus producing an original DNA. Another is photoreactivation, which is triggered by the absorption of UV light to reactivate a particular enzyme to dissociate the thymine dimers formed from UV exposure. The repair mechanisms become a major concern because the UV treatment does not provide a disinfectant residual. Thus, a number of studies were directed to determine the relationship between the repair and UV dose (Baron 1997; Lindenauer and Darby 1994; Tosa and Hirata 1999). It is now usually accepted that these repair mechanisms can be inhibited, but at a higher UV dose.

Microbial reduction kinetics and process modelling

Unlike the chemicals used to reduce the number of microorganisms, UV irradiation uses a physical process to inactivate microorganisms. Thus, the microbial reduction kinetics is usually evaluated against UV dose, which is defined by the product of UV intensity and exposure time. Various microbial reduction kinetic models have been proposed to describe the different patterns of inactivation behaviour (Gyürék et al. 1999; Severin et al. 1983; Zhou and Smith 1994*a*, 1995). A review of these models and their applications in wastewater treatment is provided in USEPA (1992).

The UV process performance is not only determined by the microbial reduction kinetics, but also by the spatial distribution of microorganisms and the UV intensity in the reactor (Loge et al. 1996, 1999). To account for these effects, various process models have been proposed. Most of these models were developed based on the assumption of uniform UV transmittance in water, ignoring the effects of particles and fouling. Thus, UV intensity at any point is determined only by the optical characteristics of the system and the configuration of the UV sources, while independent of the flow field. The flow field is then characterized by various fluid hydrodynamic models. The simplest approach is to consider the UV microbial reduction process as a black box. The flow field is then characterized by the lumped parameters as exemplified by completely stirred tank reactor (CSTR) and plug flow models. Obviously, this approach does not take into consideration the effect of flow spatial variations in any detail. One-dimensional models attempt to incorporate the flow longitudinal variation more realistically by using mean dispersion parameters. The most widely used models of this type include the well-known axial dispersion models and CSTR-in-series. With the rapid advance in computer technology, numerical models based on the principles of computation fluid dynamics (CFD) can be easily used (Iranpour et al. 1999; Janex et al. 1998; Lyn et al. 1999).

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Table 8. Applications of UV disinfection in wastewater treatment.

Feed water	Turbidity (NTU)	TSS (mg/L)	UV transmittance (%)	UV dose (mJ/cm^2)	Inactivation	Reference
Secondary effluent	3.3	7.1	57	200–1100	>4 log-units (coliform)	Chesler and Jacangelo 1993
	3.7	7.1	57	200–1100	1–4 log-units (MS phage)	Chesler and Jacangelo 1993
Tertiary effluent	na	13	75.6	480	4.4 log-units (coliform)	Snider et al. 1991
Tertiary effluent	1.8	2.0	72.6	600–2000	4.2 log-units (coliform)	Chen et al. 1992
	1.8	2.0	72.6	900–2000	3.6–5.2 log-units (MS phage)	Chen et al. 1992
Tertiary effluent	na	4.0	74.4	500	4 log-units (coliform)	Oppenheimer et al. 1993
	na	4.0	74.4	730	4 log-units (male-specific)	Oppenheimer et al. 1993

Note: na, not available.

Applications

Table 8 summarizes representative applications of UV treatment in water and wastewater treatment under both laboratory and field applications. Three points of interest are apparent. First, the effectiveness of UV inactivation varies widely with the species of microorganisms (Karanis et al. 1992). Second, the reported data are usually associated with large variation. Third, the UV doses required for a specified inactivation are usually higher under field conditions than those obtained from the laboratory studies. These uncertainties warrant that caution should be exercised when the reported information is used for the design of full-scale UV facilities. Because most studies have been performed under laboratory conditions, only limited data are available regarding the UV inactivation of specific pathogens in actual operating systems. More studies are needed to generate the dose–response data, particularly for the concerned pathogenic microorganisms with scare data available, so that the effectiveness of UV disinfection can be better defined.

Most of the uncertainties may be related to three principal process parameters that determine the UV performance: UV intensity, exposure time, and characteristics of the water to be disinfected. The UV intensity can be affected by the characteristics of UV lamps, fouling characteristics of the materials in water, and reactor geometry. Improper reactor geometry can also cause the short-circuit of flow, thus affecting the effective exposure time. The performance of a UV system is strongly dependent on the characteristics of the water to be treated. Numerous papers have shown that the many constituents in water can absorb UV light, hence decreasing the average UV intensity within the reactor. Perhaps more important is the presence of suspended solids which not only absorb the UV light, but also provide a shield to protect microorganisms from UV exposure (Emerick et al. 1999; Parker and Darby 1995). Nevertheless, little success has been achieved in developing quantitative correlations that consistently relate the UV performance to specific water characteristics. White (1986), based on the operation records from municipal secondary treatment plants in the United States and Canada, recommended that suspended solids (SS) should be 20 mg/L or lower.

One of the very interesting results is that the advanced UV technologies developed recently have been shown to be very effective at inactivating *Cryptosporidium* oocysts in water treatment (Bukhari et al. 1999; Mofidi et al. 1999). Due to the scarcity of data, these technologies need to be tested further to verify the earlier findings and provide a better understanding of the effects of various water qualities on process effectiveness. If the earlier finding is true, the UV applications would be even more attractive, considering that the removal of *Cryptosporidium* oocysts is among the most challenging problems in drinking water treatment.

Kuo et al. (1997) reported the UV treatment of filtered secondary effluent at a high-purity oxygen-activated sludge plant. The pilot test results showed the strong dependence of UV dose on influent UV transmittance. For the wastewater with an average of 53% UV transmittance, a UV dose of 300 mJ/cm^2 would be required to reduce the total coliform concentrations to less than 2.2 MPN per 100 mL. The cost of this treatment was estimated to be US\$0.18/m^3 of water treated. Kuo et al. concluded that the cost of UV microbial reduction in wastewater treatment is comparable to that of conventional chlorination if the wastewater has a UV transmittance of no less than 53%. Dyksen et al. (1998) compared the costs of various common microbial reduction practices including UV, ozone, chlorine dioxide, chlorine, monochloramine, and their combinations.

As an alternative to chlorination, UV is used for microorganism reduction in more than 500 wastewater treatment plants in the United States (USEPA 1992). The main advantages of UV treatment in water and wastewater treatment are as follows: simplicity, no chemical addition, minimal space requirement, short contact time, and fewer harmful by-products. Recent studies have also demonstrated the high efficiency of advanced UV technology in reducing resistant *Cryptosporidium* (Dyksen et al. 1998). In treating drinking water, the advanced UV treatment technology may be more cost-effective when high log-inactivation rates are required.

One of the major shortcomings is the lack of disinfectant residual after UV treatment. To prevent the potential regrowth of microorganisms in water distribution systems, additional secondary microbial reduction chemicals such as chloramines and chlorine must be added to the water before it leaves the treatment plant. However, the problem is less of a concern in wastewater treatment, as the treated effluent usually has a short storage time

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prior to discharge into a receiving water body or prior to being reused internally.

Summary and recommendations

Three groups of advanced processes of water and wastewater treatment have been reviewed. Both laboratory research and practical applications have demonstrated that these processes can reduce a broad spectrum of chemical and biological contaminants which are otherwise difficult to remove with conventional treatment processes. In some cases, these processes become very cost-competitive, largely owing to the stricter regulatory requirements and the advances in equipment manufacturing.

Membrane filtration processes have been shown to be very effective in solid–liquid separation and the removal of organic and inorganic materials. Although desalination by reverse osmosis (RO) remains the most important application in water treatment in the near future, microfiltration (MF) and ultrafiltration (UF) will play increasingly important roles in response to the need for disinfection of resistant microorganisms such as *Giardia* spp. and *Cryptosporidium* spp. while removing disinfection by-products (DBPs) precursors. To further improve the membrane processes, the major issues include the better understanding of membrane fouling mechanisms, more effective fouling control strategies, better membrane materials and module designs, and membrane integrity management.

Ozone has been widely used as an alternative disinfectant to remove chlorine-resistant microbial contaminants. In addition, ozone has been used for colour reduction, taste and odour control, oxidation of trace synthetic organic compounds, and destabilization of particles. By properly combining ozone, hydrogen peroxide, UV, and heterogeneous photocatalysts, many advanced oxidation processes (AOPs) have been developed. Most of these processes are still in the development stage but hold great promise because they are more effective in oxidizing refractory organic contaminants. More research is needed to better understand and control ozonation by-products, such as bromate and bromated organic compounds, and improve the efficiency of AOPs for the oxidation of organic contaminants.

Ultraviolet irradiation is now mainly used in wastewater microorganism reduction of bacteria-indicator organisms. However, recent studies have shown that UV irradiation may also be very effective in killing *Cryptosporidium*. If this is true, it is likely that its application in water treatment will expand rapidly.

To further use these advanced treatment processes, a number of hybrid processes have been suggested which are formed by combining the advanced treatment processes with other conventional treatment processes. The samples of these hybrid processes include membrane–PAC, membrane bioreactor, and AOPs–biodegradation. These processes may hold the greatest promise in the future because, if properly used, they can provide the most effective and economical approach to dealing with challenging environmental problems. However, research is needed to better understand both synergistic and adverse effects.

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