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PROCESS WATER RECYCLING TECHNOLOGIES

MEMBRANE FILTRATION PROCESSES

In membrane filtration processes, the range of particle size which can be removed from a solvent is increased from the normal range of particulate and colloidal matter as in normal filtration to include dissolved constituents (typically 0.0001 to 1.0 microns in size). The role of the membrane is to serve as a selective barrier that will allow the passage of certain constituents and will retain other constituents found in the solvent.

Membrane filtration processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), dialysis and electrodialysis (ED). Each of these different membrane filtration processes operate in different manners and have different characteristics which are shown in the table below.

Membrane processes	Membrane driving force	Typical separation mechanism	Operating structure (pore size)	Typical operating range, μm	Permeate description	Typical constituents removed
Microfiltration	Hydrostatic pressure difference or vacuum in open vessels	Sieve	Macropores (>50 nm)	0.08 – 2	Water + dissolved solutes	TSS, turbidity, protozoan oocysts and cysts, some bacteria and viruses
Ultrafiltration	Hydrostatic pressure difference	Sieve	Mesopores (2-50 nm)	0.005 – 0.2	Water + small molecules	Macromolecules, colloids, most bacteria, some viruses, proteins
Nanofiltration	Hydrostatic pressure difference	Sieve + solution/ diffusion + exclusion	Micropores (<2 nm)	0.001 – 0.01	Water + very small molecules, ionic solutes	Small molecules, some hardness, viruses
Reverse osmosis	Hydrostatic pressure difference	Solution/ diffusion + exclusion	Dense (<2nm)	0.0001 – 0.001	Water, very small molecules, ionic solutes	Very small molecules, colour, hardness, sulphates, nitrate, sodium, other ions
Dialysis	Concentration difference	Diffusion	Mesopores (2-50 nm)	-	Water + small molecules	Macromolecules, colloids, most bacteria, some viruses, proteins
Electrodialysis	Electromotive force	Ion exchange with selective membranes	Micropores (<2 nm)	-	Water + ionic solutes	Ionised salt ions

Membranes that are used in water or waste water treatment typically consist of a thin skin having a thickness on about 0.2 to 0.25 μm supported by a more porous structure of about 100μm in thickness. Most commercial membranes are produced in flat sheets fine hollow fibres or in tubular form. Membranes can be made from a number of organic and inorganic materials but the membranes typically used in waste water treatment are organic. These include polypropylene, cellulose acetate, aromatic polyamides and thin film composite (TFC). The choice of membrane and system configuration is based on minimising membrane clogging and deterioration, typically using pilot plant studies.

Microfiltration methods separate particles primarily by straining as does ultrafiltration. In Nanofiltration and reverse osmosis small particles are rejected by the water layer adsorbed on to the surface of the membrane which is known as a dense membrane. Ionic species are transported across the membrane by diffusion through the pores of the macromolecule comprising the membrane. Typically nanofiltration can be used to reject constituents as small as 0.001μm where as reverse osmosis can reject particles as small as 0.0001μm. Straining is also an important aspect of nanofiltμration especially at the larger pore size openings.

It can be seen from the previous table that there is a considerable overlap in the size of particles that can be removed by each of the membrane filtration processes.

The principle type of membrane modules used in the treatment of waste water are tubular modules, hollow fibre modules and spiral wound modules. Plate and frame modules are also available but are used more commonly in industrial applications.

In tubular modules the membrane is cast on the inside of a support tube and these tubes, either singly or in bundles are then placed in an appropriate pressure vessel. The feed water is pumped through the feed tube and the product water is collected on the outside of the tubes while the concentrate continues to flow through the feed tube. These units are generally used for water with high suspended solids or plugging potential since these tubular units are the easiest to clean which is accomplished by circulating chemicals and pumping a “foamball” or “spongeball” through to mechanically wipe the membrane.

Hollow-fibre modules consist of a bundle of hundreds to thousands of hollow fibres. The entire assembly is then inserted in to a pressure vessel. The feed can be applied to either the inside or the outside of the hollow fibre.

In spiral wound membrane units a flexible permeate spacer is placed between two flat membrane sheets and rolled up in to a tight circular configuration. The membranes are sealed on three sides and the open side is attached to a perforated pipe the feed is passed in between the two membrane sheets and the permeate flows through the membranes to the perforated pipe at the centre of the roll and the concentrate continues through the roll in between the membrane sheets.

Membrane filtrate unit operation

The operation of a membrane unit is quite simple. A pump is used to pressurize the feed solution and to circulate it through the membrane module. A valve is used to maintain the pressure of the retentate and the permeate is withdrawn usually at atmospheric pressure. As constituents from the feed water accumulate on the membranes (called membrane fouling) the pressure builds up on the feed side of the membrane. The membrane flux (flow through the membrane) starts to decrease and the percent rejection also starts to decrease. When the performance of the membrane has reached a certain level the membrane modules have to be taken out of service and backwashed and/or cleaned chemically

Microfiltration & Ultrafiltration

Three different process configurations are used with microfiltration and ultrafiltration. The first is known as cross flow where the feed water is pumped with cross flow tangential to the membrane. Water that does not pass through the membrane is recirculated through the membrane after blending with additional feed water. The second configuration is also known as cross flow and is very similar to the first with the exception that water that does not pass through the membrane but flows to a storage chest where it is blended with additional feed water before again being fed to the membrane. The third configuration is known as direct feed in that there is no cross flow. All of the water applied to the membrane passes through the membrane. Raw feed water is used periodically to flush the accumulated material from the membrane surface.

Reverse osmosis

When two solutions are separated by a semi-permeable membrane, a difference in chemical potential will exist across the membrane. Water will tend to diffuse through the membrane from the lower concentration side to the higher concentration side. In a finite volume system this flow will continue until the pressure difference balances the chemical potential difference. The balancing pressure difference is known as the osmotic pressure and is a function of the solute characteristics, concentration and temperature. If a pressure gradient opposite in direction and greater than the osmotic pressure is imposed across the membrane, flow from the more concentrated side to the less concentrated side will occur and this is called reverse osmosis.

Membrane fouling

The term fouling is used to describe the potential deposition and accumulation of constituents in the feed stream on the membrane. Membrane fouling is an important consideration in the design and operation of a membrane system as it affects pre-treatment requirements, cleaning needs, operating conditions, cost and performance. Fouling can occur in three general forms these are pore narrowing, pore plugging and gel/cake formation.

Pore narrowing occurs when particles that are smaller than the molecular weight cut off for the particular membrane attach themselves to the interior surface of the pores which results in the narrowing of the pores.

Pore plugging occurs when particles the same size as the pores become stuck in the pores of the membrane. Gel/cake formation, caused by concentration polarization, occurs when the majority of the solid matter in the feed is larger than the pore sizes or the molecular weight cut off of the membrane.

Concentration polarization can be described as the build up of matter close to or on the membrane surface that causes an increase in resistance to solvent transport across the membrane. Some degree of concentration polarisation will occur in the operation of any membrane but the formation of a gel/cake layer is an extreme case of concentration polarisation where a large amount of matter has actually accumulated on the membrane surface forming a gel or cake layer.

Typically there are three approaches to control membrane fouling. These are pre treatment of the feed water, membrane back-flushing and chemical cleaning of the membrane.

Pre-treatment of the feed water is used to reduce the TSS and bacterial content of the water and often the feed water will be treated chemically to limit chemical precipitation within the membrane unit.

The most commonly used method of eliminating the accumulated material from the membrane surface is back-flushing with water and/or air. Chemical treatment is used to remove constituents that are not removed during conventional backwashing.

Pre-treatment for nanofitration and reverse osmosis is usually required since a very high quality feed is required for efficient operation of these membrane units. To assess the need for pre-treatment for nanofiltration and reverse osmosis membrane units fouling factors can be calculated from simple membrane tests. The water sample must be passed through a 45µm Millipore filter with a 47 mm internal diameter at 30 psi gauge to determine the SDI (silt density index)

Each of the different membrane processes removes different constituents from waste water. It can be seen from the table below that a membrane system would need to be tailor made for the specific waste water regarding which constituents were in the waste water and which constituents it is necessary to remove from the waste water.

					Comments
Constituent	MF	UF	NF	RO	
Biodegradable organics		X	X	X	
Hardness			X	X	
Heavy metals			X	X	
Nitrate			X	X	
Priority organic pollutants		X	X	X	
Synthetic organic compounds			X	X	
TDS			X	X	
TSS	X	X			TSS removed during pre-treatment for NF and RO
Bacteria	X	X	X	X	Used for membrane disinfection. Removed as pretreatment for NF and RO with MF and UF
Protozoan cysts and oocysts and helminth ova	X	X	X	X	
Viruses			X	X	Used for membrane disinfection

Application of membranes

Microfiltration has been used most commonly as a replacement for depth filtration to reduce turbidity, remove residual suspended solids and reduce bacteria to condition the water for effective disinfection and as a pre-treatment step for reverse osmosis. A relatively recent development is the use of membranes for biological treatment of waste water. Membranes have been used for both aerobic and anaerobic treatment of wastewaters. In typical membrane bioreactors (MBRs) the membrane separation unit is internal and immersed in the bioreactor with the treated effluent withdrawn from the bioreactor via the application of a vacuum. Typical performance data for am membrane bioreactor used to treat waste water is shown below.

Parameter	**Unit**	**Typical**
Effluent BOD	mg/l	<5
Effluent COD	mg/l	<30
Effluent NH3	mg/l	<1
Effluent TN	mg/l	<10
Effluent turbidity	NTU	<1

It can be seen from the above table that the effluent is ideal for a number of reuse applications or for further processing by nanofiltration or reverse osmosis.

Ultrafiltraton membranes are used for many of the same applications for microfiltration. Some ultrafiltration units with small pore sizes have also been used to remove dissolved solid compounds with high molecular weight, such as colloids, proteins and carbohydrates. The membranes do not remove sugars or salt. Ultrafiltration is used typically in industrial applications for the production of high purity process rinse water.

Nanofiltration can reject particles as small as 0.001µm. Nanofiltration is used for the removal of selected dissolved constituents from waste water such as the multivaelent metallic ions responsible for hardness. The advantages of nanofiltration over lime softening include the production of a product water that meets the most stringent reuse water quality requirements. Because both inorganic and organic constituents and bacteria and viruses are removed, disinfection requirements are minimised. Although most NF facilities use polyamide TFC membranes in a spiral wound configuration, more than ten different types of membranes are available.

Reverse osmosis is used primarily for desalination. In waste water treatment reverse osmosis is used for the removal of dissolved constituents from waste water remaining after advanced treatment with depth filtration or microfiltration. The membrane excludes ions, but require high pressures to produce de-ionised water.

ADVANCED OXIDATION PROCESSES

Advanced oxidation processes are used to oxidise complex organic constituents found in waste water that are difficult to degrade biologically in to simpler end products. When chemical oxidation is used it may be necessary to oxidise completely a given compound or group of compounds. In many cases partial oxidation is sufficient to render specific compounds more amenable to subsequent biological treatment or to reduce their toxicity. The oxidation of specific compounds may be characterized by the extent of degradation of the final oxidation product as follows.

1. Primary degradation: A structural change in the parent compound
2. Acceptable degradation (defusing): A structural change in the parent compound to the extent that toxicity is reduced.
3. Ultimate degradation (mineralisation): Conversion of organic carbon to inorganic CO_2.
4. Unacceptable degradation (fusing): A structural change in the parent compound resulting in increased toxicity.

Advanced oxidation processes typically involve the generation and use of the hydroxyl free radical (HO•) as a strong oxidant to destroy compounds that cannot be oxidised by conventional oxidants such as oxygen, ozone and chlorine. The hydroxyl radical is one of the most active oxidants known. The hydroxyl radical reacts with the dissolved constituents initiating a series of oxidation reactions until the constituents are completely mineralized. Non-selective in their mode of attack and able to operate at normal temperatures and pressures, hydroxyl radicals are capable of oxidizing almost all reduced materials present without restriction to specific classes or groups of compounds, as compared to other oxidants.

Advanced oxidation processes differ from other treatment processes because waste water compounds are degraded rather than concentrated or transferred in to a different phase. Because secondary waste materials are not generated then there is no need to dispose of or regenerate materials.

At present there is a variety of technologies available to produce the hydroxyl radical but there are only 4 of them being used on a commercial scale. These are Ozone / UV, Ozone / Hydrogen Peroxide, Ozone / UV / Hydrogen Peroxide and Hydrogen Peroxide / UV.

Ozone/UV

The photolysis of ozone with UV light in wet air results in the formation of hydroxyl radicals, in water the photolysis of ozone with uv radiation results in the formation of hydrogen peroxide, which is subsequently photolyzed to form hydroxyl radicals. Therefore the use of ozone in this application is not cost effective.

Ozone/Hydrogen peroxide

For the destruction of compounds that do not adsorb UV, advanced oxidisation processes involving Ozone/H_2O_2 may be more effective. Compounds in water such as trichloroethylene and perchloroethylene have been significantly reduced with advanced oxidisation processes using hydrogen peroxide and ozone to generate the hydroxyl radicals.

Hydrogen peroxide/UV

Hydroxyl radicals are also formed when water containing hydrogen peroxide is exposed to UV radiation. In some cases the use of the hydrogen peroxide/UV process has not been feasible because H_2O_2 has a small molar extinction coefficient requiring high concentrations of H_2O_2 and not using the UV energy efficiently.

Most recently the hydrogen peroxide/UV process has been applied to the oxidation of trace constituents in treated water.

Based on numerous studies it has been found that combined advanced oxidisation processes are more effective than any of the individual agents (e.g., Ozone, UV, Hydrogen peroxide). Advanced oxidisation processes are usually applied to low COD waste waters because of the cost of ozone and/or hydrogen peroxide required to generate the hydroxyl radicals. Material that was previously resistant to degradation may be transformed in to compounds that will require further biological treatment.

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