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Application of Membrane Filtration Processes to Industrial Wastewater Treatment

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1. Introduction

The composition and concentration of industrial wastewater have wide variety from industry to industry. It is important to characterize the wastewater from the specific industry considered. Wastewater may have biodegradable component and/or hardly biodegradable and hazardous components. The former is major components in food manufacturing, e.g. caning, dairy, meat and poultry industries, pulp and paper manufacturing, textile and so on. The latter must be major ones in electrolating, inorganic chemical manufacturing and so on. It requires treatment other than biological one. Membrane process as a physical separation device might be successfully applied to these wastewater. Wastewater may contain solids and/or dissolved matters. Phase separation, i. e. physical separation of phases, such as solid-liquid, liquid-liquid, gas-iquid and so on, is one of effective treatment techniques. Substantial degree of purification is accomplished simply by solid-liquid separation in many industrial wastewaters. Oil separation is an example of liquid-liquid separation. Membrane process might be one of the alternatives for phase separation. Selection of treatment processes, anyhow, definitely depends on wastewater characteristics.

dustrial wastewaters have also wide spectrum in quantity as well as quality. Reduction of wastewater quantity has primary importance in getting effective treatment. In other words, so called Cleaner Technology Approach, which includes the effective use of water in processing, the recycle and reuse of water and therecovery of marketable or usable materials, must be considered to achieve waste minimization. In this connection, membrane process might give a powerful method for wastewater reclamation and recovery of valuable materials.

2. Summary of Membrane Application to Industrial Wastewater

The membrane processes that are practically used the treatment of industrial wastewater and recovery of valuable materials from the wastewater are reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), dialysis and electrodialysis (ED). RO, UF and MF utilize a difference in transmembrane pressure as driving force by the electrochemistry difference, while selective solute transport through membrane takes place in ED. There is also nanofiltration(NF) or low-pressure reverse osmosis, which is positioned midway between conventional reverse osmosis and ultrafiltration. Reverse osmosis membranes reject dissolved ions and typically used for desalination purpose, while ultrafiltration can be used to retain relatively large molecules, such as protein, polysaccharides and so on. Microfiltration is capable of eliminating parti-

Table 1. Applications of Membrane Processes in Industrial Wastewater Treatment, Reclamation, and Material Recovery

Industry of process	Membrane type	Application example
Food processing	RO	Recovery of protein and separation and concentration of amino acids from fish processing wastewater, Treatment of soy bean whey wastewater, Recovery of lactase from cheese whey
	UF	Recovery of protein from fish and meat processing, Wastewaters and starch factory wastewater
Biochemical industry	UF	Wastewater treatment from fermentation process
Chemical industry	RO	Treatment and recovery of glycerol from petrochemical wastewater, Recovery of lignin and xylose from pulp industry wastewater
	UF	Recovery of latex particles, recovery of PVA and chromium, Recovery from tanning wastewater, treatment of bleached kraft pulp alkaline wastewater and energy recovery by concentration of lignin, lipid refinery wastewater treatment
Textile and dyeing	RO	Removal of dye wastewater reclamation from dye processing wastewater, Recovery and reuse of processing oil agent
	UF	Recovery and reuse of processing oil agent, Recovery of lanolin from wool washing wastewater
Steel and machine industry	RO, UF	Cutting oil wastewater treatment, Oil separation of compressor drain
Metal finishing process	UF	Treatment and recovery of paints from electrodeposition and paints emulsion wastewaters, Removal of hydroxides heavy metal from electro planting wastewater, silicon-glinding wastewater treatment, lens-polishing wastewater treatment
Acid recovery	Dialysis	Acid recovery from various process, recovery from acid wastes from etching, pickling and others, Acid and alkali recovery from electro-plating wastewater
Nuclear power plant	RO, UF	Removal of radioactive substances from drain wastewaters
Water purification	RO, UF	Ultra-pure water production, removal of colloidal and suspended matters as pretreatment process
Desalination	RO, ED	Desalination as treatment and metal recovery of electro-plating wastewater, pulp wastewater, radio active wastewater and so on
Wastewater treatment	UF, MF	Solid-liquid separation in biological wastewater treatment

cles at submicron level, which is usually used to remove bacteria and fine particles for process water production.

In the stream of process wastewater reclamation with recovery of valuable materials, UF, RO, dialysis and ED are utilized as a concentration or separation unit process. There is a variety of application in accordance with a variety of wastewaters. Table 1 summarizes some possible applications of membrane processes.

3. Examples of Reclamation and Recovery Processes

3.1. Metal Finishing Process (Nickel)

Fig. 1 shows a treatment and reclamation example of nickel-contained wastewater from metal

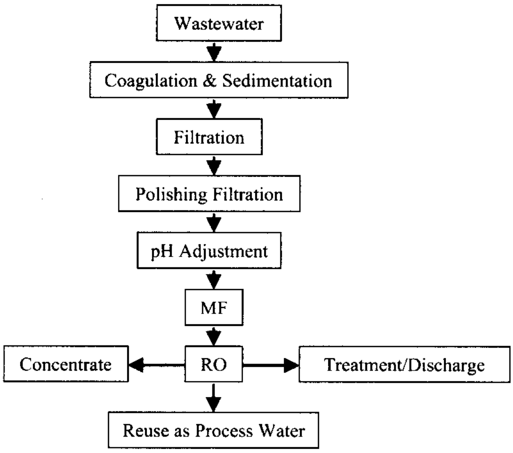

Fig. 1. Schematic flow diagram of the treatment and reclamation process of nikel-contained wastewater from metal finishing process.

Table 2. TYpical Influent and Effluent Water Quality of Nickel-Contained Wastewater Treatment

	Unit	Influent	Effluent
Flow	m^3/d	380	300
pH	-	5	-
Electric conductivity	μS/cm	14,400	<200
TDS	mg/l	3,100	<100
Ni	mg/l	230	<0.1
Fe	mg/l	20	<0.1
Cl	mg/l	1,580	<40
SS	mg/l	40	<0.1

finishing process, in which MF and RO are used in series. Table 2 shows typical influent and effluent water quality [1]. In the case of operation in a factory in Mie prefecture, Japan, operational cost was reported 2,600 won/m^3 in total (chemical agents 90, electricity 110, membrane replacement 600 won per cubic meter of treated water).

3.2. Recovery of Nitric Fluoric Acid by Dialysis from Effluent of Stainless-steel Acid-Cleaning

Fig. 2 shows an example of material balance in the recovery process of nitric and fluoric acid from

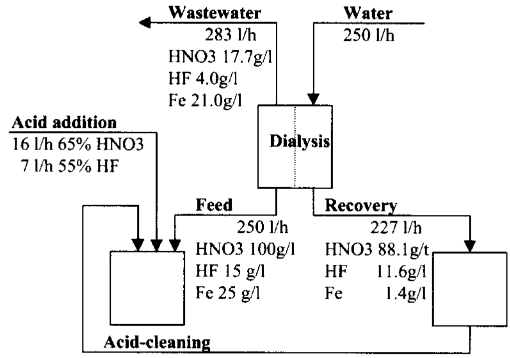

Fig. 2. Material balance in the recovery process of nitric and fluoric acid from effluent of stainless-steel acid-cleaning.

effluent of stainless-steel acid-cleaning. Dialysis using ion selective membrane(anion exchange membrane) was applied. Nitric and fluoric acids were highly recovered, while dissolved iron was almost rejected. In this example, the total treatment cost was estimated to be 8000 won/m^3, while the merit from acids recovery and reduction in cost of subsequent wastewater treatment and sludge disposal accounted 35,200 won/m^3 that clearly showed the recovery process was economical [2].

3.3. Membrane Processes in Combination with Biological Treatment

Wastewaters usually include dissolved organic matters, a large part of which is biodegradable. As biological treatment is the best available technology for the organic wastewaters in many cases, the membrane separation in combination with biological treatment is suitable for them. The activated sludge process that is the most typical suspended-growth biological wastewater treatment process normally achieves solid-liquid separation through gravity sedimentation. Membrane separation activated sludge (MSAS) is the name given to processes in which this role is fulfilled by membrane separation. Since the main purpose of using membrane separation is to separate biologically treated water from suspended solids, the use of reverse osmosis would inhibit microbial activities of the sludges. For this reason, membrane separation is carried out by means of ultrafiltration or microfiltration, which do not cause the accumulation of salts or organic substances that have been converted into low molecular weight ones as the final metabolic products of microorganisms.

The following part summarizes the characteristics of MSAS process first, as it is the main membrane process applied to biological treatment. Then, the latest trend of new membrane applications, i. e., immersed-type MSAS is also introduced.

3.3.1. Characteristics of MSAS Process

From the viewpoint of biological treatment, a number of advantages can be gained through combination with membrane separation. First, since suspended solids are totally eliminated through membrane separation, the settleability of the sludge has absolutely no effect on the quality of the treated water. Second, a long enough sludge retention time(SRT) can be provided, facilitating the proliferation of microorganisms with low growth rate, such as nitrifying bacteria. Third, the overall activity level can be raised, since it is possible to maintain high microbial concentrations in bioreactors while keeping the microorganisms dispersed as much as possible. Fourth, high concentrations of the sludges create a favorable environment for endogenous denitrification, thereby ensuring the efficient removal of nitrogen. Fifth, treatment efficiency is also improved in the sense that it is possible to prevent leakage of undecomposed polymer substances. Sixth, the method itself gives high enough removal of bacteria and viruses, although ultrafiltration membranes are not complete barrier for virus rejection [3].

From the perspective of membrane separation, the possible advantages of combination with biological treatment include the followings. First, dissolved organic substances with low molecular weights, which cannot be eliminated by membrane separation alone, can be taken up, broken down and gasified by microorganisms or converted into polymers as constituents of bacterial cells, thereby raising the microorganisms and improving the quality of treated water. Second, polymer substances retained by means of membranes can be broken down if they are biodegradable, which means that there will be no endless accumulation of the substances within the treatment process. This, however, requires the balance between the production and degradation rates. A high organic loading might give a higher production rate of intermediate polymer metabolites than that of the degradation, resulting their accumulation. The accumulation of intermediate metabolites may decrease the microbial activities [4].

As mentioned above, MSAS leads naturally to operation with high concentration of activated sludges, which can easily absorb shock loadings and give very stable treatability. The performance of MSAS may be affected by irreversible change in the membranes themselves, or by the fouling of membrane interiors or surfaces. In the membrane separation of highly concentrated activated sludges, there is a particularly conspicuous tendency for permeability to decline or separation characteristics to change due to the formation of cake and gel-like layers. The actual rejection performance of ultrafiltration membranes and microfiltration membranes is often similar [5], since separation characteristics are determined by the nature of the cake and gel-like layers formed.

There is also a correlation between sludge concentration and permeation flux. When sludge concentration exceeds a certain limit, the permeation flux rapidly decline due to a dramatic rise in viscosity of the sludge mixture. The limit for the filtration of the activated sludge concentration is typically 30,000 to 40,000 mg/l [6,7]. The correlation between sludge concentration and the permeation flux will not always be negative below this threshold concentration. There is no uniform tendency and there may be either no relationship or even a positive correlation. It appears that this situation largely attributable to the influence of colloidal or soluble substances, which cannot be measured in terms of sludge concentration within the sludge mixture.

Unlike the filtration of pure water, there is no guarantee that there will be linear relationship between operating pressure and permeation flux. An increase in pressure sometimes cause a decline in the permeation flux, and it is possible that the compaction of the cake layer is a key factor here [8].

Control of the cake layer plays an important role in the reduction of fouling, since the filtration is dominated by the cake layer on the surface or the membrane. One well-known approach is to improve the scouring effect by increasing the tangential flow velocity, but this method has the drawback of increasing energy consumption. It is also important to reduce compaction of the cake layer. Low-pressure filtration and intermittent filtration appear to offer an effective means of achieving this through the manipulation of system operation [7].

A new generation of MSAS is the immersed-type one where membrane modules are directly immersed in an aeration tank. This aims to tremendously reduce the energy consumption by eliminating such big circulation pumps as the conventional MSAS processes require for operation under crossflow condition that gives high energy consumption about 3-5 kWh/m^3 of the filtrate. These values are more than ten times larger than those for conventional sewage treatment plant operation.

A proto-type using hollow fibers has been developed in laboratory scale experiments, which showed the feasible operation of applying suction and intermittent filtration. The potential of the process as on-site small-scale advanced domestic wastewater treatment has been shown by the author and his coworkers [7,9-11]. Several full scale applications using hollow fiber modules [12-14], ceramic tubular membrane modules [15] and plate and flame type organic membrane modules [16] have demonstrated the processes are really feasible and promising.

3.3.2. Immersed-type MSAS Applied to Industrial Wastewater Treatment

The following is the example of full-scale application of the immersed-type hollow fiber MSAS to industrial wastewaters [12]. New design of hollow fiber modules have been developed (Fig. 3)

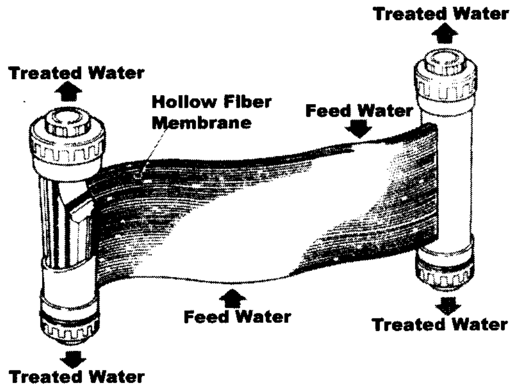

Fig. 3. A newly designed immersed-type hollow fiber module (Mistubish Rayon, Japan).

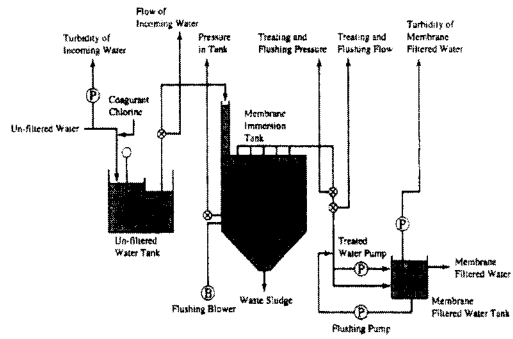

Fig. 4. Membrane arrangement in an aeration tank (Mistubish Rayon, Japan).

and some parallel sets of the modules are vertically positioned in a aeration tank, as shown in Fig. 4. Aeration is applied beneath the module sets, giving air bubbling to the membrane surface for washing as well as oxygen supply to microbial cells. The hollow fibers are made of polyethylene with inner and outer diameters of 270 and 410 μm, respectively. The nominal pore size of the membrane is 0.1 μm and the membrane surface has been treated to get hydrophilic nature.

Futamura showed that his immersed-type MSAS processes only require energy consumption as low as 0.006 kWh/m^3 and that it is recommended to operate the system as pressures below 30 kPa and at air to flux ratios of more than 1,800, which is defined as the volumetric amount of air supply rate per unit surface of membrane divided by permea-

Table 3. Treatability of Immersed-type Hollow Fiber MSAS to Wastewater from Food Industries

Industry	Cooked vegetables			Sweets			Bean paste		
Reactor volume, m^3	50			40			7		
MLSS, mg/l	8,530			9,540			10,000		
	Influent	Effluent	Removal	Influent	Effluent	Removal	Influent	Effluent	Removal
pH	5.4	7.4	-	5.5	7.6	-	4.4	7.6	-
BOD, mg/l	2,150	5	99.8%	1,590	1	100%	3,630	5.0	99.9%
COD_{Mn}, mg/l	852	19.4	97.7%	650	7	99.0%	2,20	12.6	99.5%
SS, mg/l	603	N.D.	100%	380	N.D.	100%	1,660	N.D.	100%
T-N, mg/l	89	5.6	93.7%	87.4	2.8	97.0%	209	8.6	95.9%
Transparency, cm	-	>100	-	-	>100	-	-	>100	-

tion flux [12]. Performance of the process in treating wastewaters from food industries is summarized in Table 3.

New membrane processes such as immersed-type MSAS give a direction in minimizing the energy required to operate systems. It is obviously necessary to achieve further reduction of membrane costs for wider applications of membrane process to wastewater treatment. We do not have to use the membranes with sophisticated quality control such as grade for medical use. It would be wasteful to use them in wastewater applications. Consideration should therefore be given to the development of membrane modules with quality standards and grades that are appropriate to the requirement of wastewater treatment. In this sense, there must be considerable scope for the reduction of membrane costs. It is also clear that existing membrane modules offer little scope for merits of scale. Before the MSAS processes can be expanded for large-scale application, it will be necessary to develop large-scale modules that offer merits of scale. On the other hand, it is also anticipated that the predominant direction of development will be toward downsizing in step with advances in remote monitoring and control technology. If this is indeed the case, it is possible that membrane separation technology, with offer reverse merit of scale, will become the dominant technology in the field of wastewater treatment.

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