MEMBRANE PROCESSES IN HAZARDOUS WASTE TREATMENT

By

S. VIGNESWARAN
SCHOOL OF CIVIL ENGINEERING, UNIVERSITY OF TECHNOLOGY,
BROADWAY, NSW 2122, AUSTRALIA

C. VISVANATHAN
ASIAN INSTITUTE OF TECHNOLOGY,
P.O. BOX 2754, BANGKOK 10501, THAILAND

Summary Membrane processes find numerous applications in handling hazardous wastes. The recovery of valuable materials found in hazardous wastewater makes this process attractive. A short review of applications of membrane processes in metal finishing, electroplating and painting industries is presented. A laboratory-scale experimental study was conducted, and based on these results, a possible application of cross-flow electro-microfiltration in treating chromium wastewater is highlighted.

1. INTRODUCTION

In recent years an increasing attention has been given to the presence of heavy metals (Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Pb and Zn) in the aquatic environment, mainly due to their toxicity to the ecological system. Some of these metals are known to be highly toxic to man, while the others are more lethal to the aquatic micro-organisms, fish and plants. However the lethal effect of heavy metals to the aquatic organisms and human, predominantly depends on the type of the metal present in the waste stream and its concentration. The industrial effluents lead to detrimental effects on the ecological systems. Most of the developed and developing countries have established stringent standards on industrial effluent discharge. In order to meet these effluent standards, industries have to adopt an effective effluent treatment system.

Hazardous wastes are not necessarily from metallic contamination of industries only. Contamination due to pesticides in the stores, agricultural and other sources, contamination due to pathogenic micro-organisms disposed from hospital etc. are also classed into the hazardous wastes.

At present, several processes such as chemical precipitation, flocculation, flotation, ion exchange, solvent extraction, cementation, complexation, electro-chemical operation, biological treatment, evaporation and membrane filtration are employed in the removal of heavy metals from hazardous waste streams. In membrane separation, processes such as reverse osmosis (RO), ultrafiltration, (UF), cross-flow microfiltration (CFMF), cross-flow electro-microfiltration (CFEMF) and electrodialysis (ED) are used to separate hazardous materials from liquids.

The membrane process (mainly UF) is currently being used on a commercial scale to handle the hazardous wastes. The applications are aimed to,

- treat paint wastes and reuse of wastewater
- treat oily wastes from metal finishing, can forming, aluminum and steel coil cleaning, metal machining and rolling rinse waters, and to reuse water
- treat rinse waters from alkaline metal cleaning baths
- treat industrial laundry waste waters
- concentrate solvent/ink wastes generated during printing operations
- treat electroplating and metal finishing wastewater
- treat hazardous leachates

Some of the applications of membrane processes in hazardous waste treatment is highlighted in this paper. A laboratory-scale CFEMF studies is also presented to show the advantage of CFEMF over CFMF in treating chromium wastewater.

2. CFMF AND UF IN METAL FINISHING AND ELECTROPLATING INDUSTRY

The wastewater from metal industry can be classified into two categories based on the nature of contaminants: inorganics (common metals, valuable metals, metal complexes, hexavalent chromium, cyanide) and organics (grease and organic solvents).

The treatment methods used to recycle the water from the metal based industries are given in Table I.

TABLE I

PRINCIPAL TREATMENT ALTERNATIVES USED FOR RECOVERY OF PRODUCTS AND RECYCLE OF WATER

Application	Reverse osmosis	Evaporation	Ion exchange	Electrodialysis	Ultrafiltration recovery	Microfiltration	Advanced rinsing techniques
Acid metal plating recovery	x	x	x	x	-	-	x
Cyanide metal plating recovery	-	x	-	x	-	-	x
Precious metal plating recovery	-	x	x	x	-	-	x
Phosphating recovery	-	-	x	-	x	-	-
Mixed plating waste treatment	x	x	x	-	-	x	-
Electrocoating	-	-	-	-	x	-	-
Etching recovery	x	x	-	x	-	-	-
Chromating recovery	-	x	x	-	-	-	-

From laboratory studies and pilot plant applications, it has been observed that RO is an effective method to separate toxic matters (both organic and inorganic) from the waste streams. In the treatment of metal finishing wastewater and electroplating rinse water, application of RO takes a major role (Kiang and Metry, 1982; Werschulz, 1986). The most common metallic components in these streams are Ni, Cu, Zn, Brass, Hexavalent Chromium and other Cyanide fractions.

2.1 Electroplating Wastewater Treatment

A typical electroplating operation with a membrane system is shown in Fig. 1. Following immersion in the plating bath, metal parts are passed through a series of rinse tanks where the excess plating chemicals are rinsed off. During this process, plating chemicals are "dragged out" into the rinse tanks, which are typically operated in series with the flow of rinse water being countercurrent to the direction of metal parts movement. In the absence of recovery of metals by RO, the rinse water from the first tank would typically be routed to disposal. When RO is used, the most concentrated rinse water is fed to a RO unit. The concentrate from the module is returned to the plating bath, and the permeate is reused in the final rinse tank.

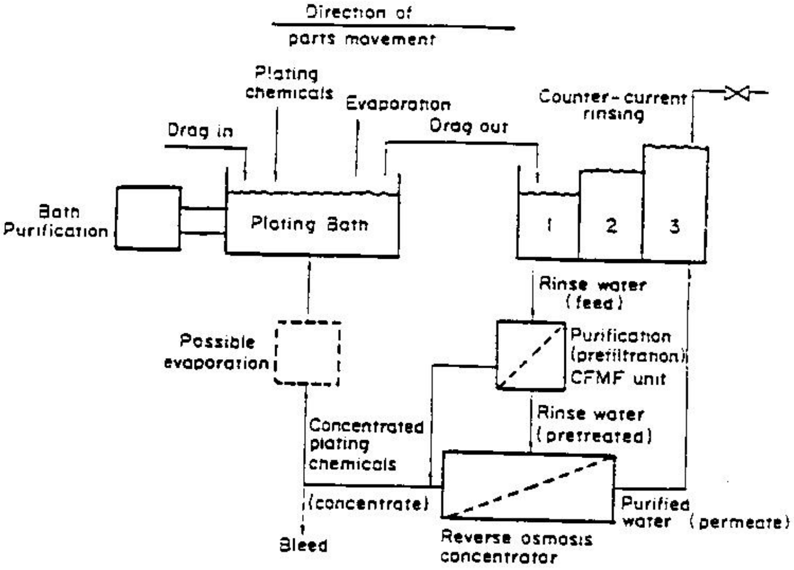

Fig. 1 Basic flow diagram for a reverse osmosis system treating electroplating rinse water

All electroplating and/or metal finishing wastes cannot be treated by a single membrane (Werschulz, 1985). Most of the RO installations use hollow fiber or spiral wound modules with proper pretreatment methods (Cartwright, 1984). For pretreatment, CFMF process is utilized.

UF is another proven technology in the electroplating industry (Werschulz, 1984). An example of a chemical treatment/UF system used to pretreat metal finishing wastewater prior to discharge to the municipal sewer was described by Roush (1984). Combined UF/MF modules are also used for this treatment.

Continuous flow treatment process used for this industrial wastewater includes few steps as stated below (McNeil, 1988).

a) reduction of hexavalent chromium to trivalent state with sodium metabisulphate
b) addition of NaOH to precipitate metal hydroxides
c) addition of 5% dithiocarbonate solution to precipitate soluble complex metals
d) filtration process using tubular UF modules or UF/MF combined modules

UF process showed a removal of 99.1% chromium and 99.6% copper in the trial tests. Membrane fouling due to the precipitation of gelatinous metal hydroxides causes a drop in permeate flow rate. MF units and sodium hypochlorite chemical cleaning led to an increase in flow rate.

2.2 Metal Painting Wastewater Treatment

The UF is used in the car painting industry especially where electrophoretic method of painting is adopted. 25% to 45% of paint consumed goes into the wastewater stream. This can be completely recovered if a UF system is incorporated in the process. This will also help in reusing the permeate in the process by which a water economy can be adopted (Short, 1982; Hayward, 1982).

Fig. 2 (a) shows a schematic diagram of conventional system to separate paint form rinsing water. Fig. 2 (b) illustrates the modification using a UF unit. Both paint and purified water are reused here. Typically tubular modules with CA membranes are used in these applications. The membrane life is also considerably high about 2 years (Strathmann, 1984).

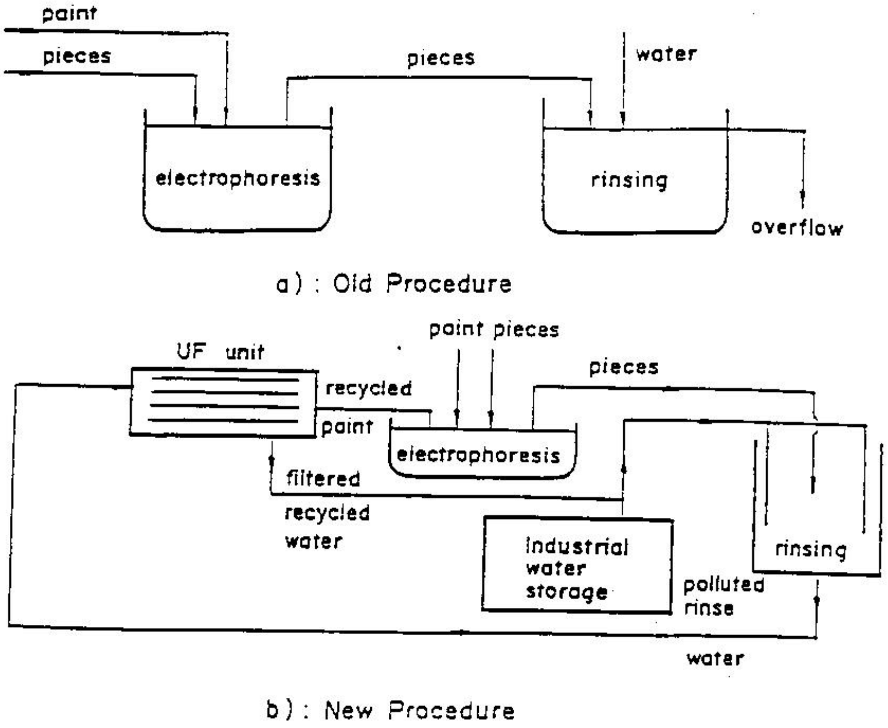

Fig. 2. Schematic diagram of separation of paint from rinsing water

Solvent/paint waste streams from automated paint spraying operations may also be treated using UF. These types of wastes are typically generated when the paint color is changed and the lines are cleaned with paint solvent to flush out the old paint. An automobile manufacturing plant, which installed a UF system to recycle paint cleaning solvent, reported a payback period of only 5.3 months due to savings in waste disposal and fresh solvent costs (Isooka et al., 1984). However, low fluxes were encountered because paint solutions typically contain high levels of dissolved polymers which form a gummy, gel-like layer on the membrane surface. This layer is difficult to remove hydrodynamically and also has a low permeability.

In a particular industry in France where they adopt cathodic painting, 70 cars are painted in an hour (250,000 cars/year). The total surface painted is 4500 m^2/h (65 m^2/car). A good rinsing requires 1 L water/m^2 of surface. 95% of this rinse water can be recycled if UF is used in the process line (Roulet, 1984).

In this industry, 135 m^2 area of membrane (3 modules of 45 m^2) was used. The cost estimation made (Table II) indicated that the capital cost of UF can be recovered within 4 months of operation. In this industry according to the calculations made, an economy of 4.9 million French Francs/year can be achieved by using UF process. The UF membranes fabricated by ROMICON, ABCOR, RHONE POULENC companies are generally used. These UF membranes can be replaced by properly chosen MF membrane with required pore size. Only MF membranes or combination of UF/MF also can be used for this purpose. This would considerably increase the profit, and shorten the payback period.

TABLE II

COST ESTIMATE OF A CAR PAINTING INDUSTRY (ROULET, 1984)

	Details Cost (In French F)
Capital cost 1,500,000 F	Modules + pumps + control units etc.
Operational cost 90,700 F/year	Energy cost (3 pumps at 18 kW/h; 8000 h operation/year, electricity cost 0.21 F/kW)
Maintenance cost 80,000 F/year	Changing of membranes once in 3 years + regular maintenance
Recovery 490,000 F/year	Paint recovery (9 g/m^2 x 4500 m^2/h x 3500 h/year x 0.035 F/g)
	Demineralized water recovery 450,000 F/year

If the amortisization period is 5 years, then:

* amortisization/year	+ 300,000 F
* O and M cost	+ 171,000 F
* annual saving by recovery of paints and deminerized water	- 5,3500,000 F
Economy	4,879,000 F/year

3. CFMF AND CFEMF IN HAZARDOUS WASTE TREATMENT

The toxic industrial wastes with heavy metals can also be treated using cross-flow microfiltration (CFMF). Similar to the other applications of CFMF, this treatment process also faces some limitations. Even though the flow rate is high in CFMF, the main problem observed here is the deposition on the membranes.

Visvanathan et al. (1989) presented laboratory-scale results of the treatment of chromium wastewater using cross-flow electro-microfiltration (CFEMF). In most of the industrial effluents, chromium is present in the soluble form either as hexavalent chromium (Cr (VI)) or as trivalent chromium (Cr (III)).

The discharge of hexavalent chromium into the aquatic environment comes mainly from industries such as metal finishing, paint manufacture, dyeing etc. It is highly toxic to the aquatic organisms compared to the Cr (III), which is considered to be relatively less toxic, and industries such as textile, ceramic, tanneries, photographic etc., are the primary sources of this pollutant.

The separation of Cr (VI) consists of two steps namely; first the Cr (VI) has to be reduced using a reducing agent at an acidic pH range and then it has to be precipitated. Then these precipitates are allowed to settle down in a settling tank for a period of 6-8 hours. The effluent usually contains 5-20 mg/l of suspended solids, mostly in the form of precipitates of Cr (III). In order to accomplish total elimination of chromium and attain the required effluent standards, the settling tank effluent usually has to be filtered using a sand bed filter (Fig. 3). Meanwhile, the sludge produced at the settling tank is dewatered using a filter press or a vacuum filter.

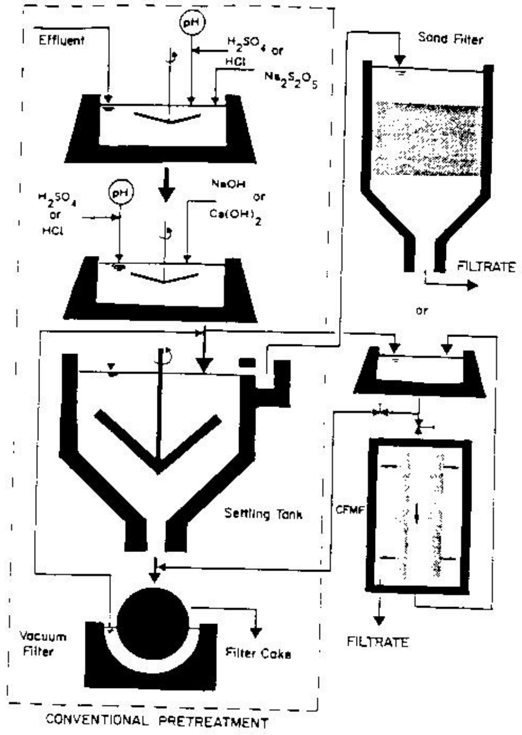

Fig. 3 Separation of hexavalent chromium in the form of Cr $(OH)_3$ precipitates

The application of CFMF has been intensively studied as an alternative separation process for precipitates of Cr (III). In the conventional chromium separation process, CFMF can be used in two possible modes: a) direct filtration of precipitates without the settling tank, b) filtration of settling tank effluent. In CFMF system, when the recirculating slurry attains a concentration of 10-15 percent solids, it is usually sent to the sludge dewatering system.

In spite of advantages like better quality of treated effluent and possibility of installing in most of the conventional treatment systems, at present, CFMF process has been confined to very few industrial applications. The effectiveness of a CFMF system is primarily limited by membrane fouling problems.

Cross-flow electro-microfiltration (CFEMF) is hybrid physical operation which combines both CFMF and electrophoretic separation techniques. By applying a DC electric field of sufficient strength and proper polarity, the charges ionic particles can be migrated from the membrane surface. CFEMF eventually leads to higher filtration flux with lower deposition and fouling. The efficiency can be further increased by changing the polarity of electrodes. Fig. 4 shows the experimental set-up of a CFEMF unit used in the study. Measurements of surface charge of precipitate of chromium hydroxide and observations of deposit signaled that the small surface charge of precipitate led to a notable reduction of the particle-particle repulsion and consequently permitted to the formation of particle clusters (Visvanathan, et al., 1989; Bhattacharya et al., 1971).

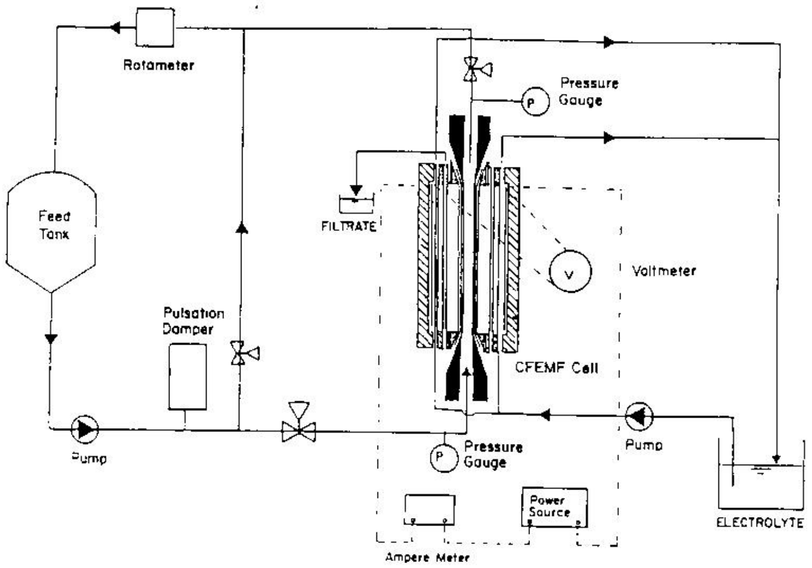

Fig. 4 Schematic representation of the CFEMF experimental set-up

The CFEMF system can be used to remove other metallic ions (which cause toxicity) in the wastewater systems and to recycle the ions and water. This is an attractive technique in electroplating industry, because the compounds in wastewater are mainly in ionic form.

4. CONCLUSION

The newly invented membranes (particularly inorganic membranes) and advanced membrane declogging techniques will lead to extensive membrane applications in the field of hazardous wastewater treatment. Use of membrane processes will enable the recovery of valuable materials from the wastes while the treated water may be recycled in the manufacturing process.

The laboratory-scale CFEMF study clearly shows the advantage of this system in treating Cr wastewater.

5. REFERENCES

BHATTACHARYA, D.; CARLTON, J.A. and GREIVES, R.B. (1971). Precipitate flotation of chromium. AIChE, 17(2):419-424.

CARTWRIGHT, P. (1984). An update on reverse osmosis for metal finishing. Plating Surf. Finish., 71(62):pp. 48.

HAYWARD, M.F. (1982). Ultrafiltration and reverse osmosis: A survey of industrial applications. 3rd World Filtration Congress, Croydon, England, September 13-17, 1982, pp. 572.

ISOOKA, Y.; IMAMURA, Y. and SAKAMOTO, Y. (1984). Recovery and reuse of organic solvent solutions. Met. Finish., 82, 113.

KIANG, Y.H. and METRY, A.A. (1982). Hazardous waste processing technology. Ann Arbor Science Publishers, Ann Arbor, Mich., pp. 409.

McNEIL, J.C. (1988). Membrane separation technologies for treatment of hazardous wastes. Critical Review in Environmental Control, 18(2):91-132.

ROGERS, A.N. (1984). Economics of the application of membrane processes. In: Synthetic Membrane Processes: Fundamentals and Water Applications. Belfort, G. (ed.), Academic Press, Orlando, Fla., Chap. 13.

ROULET, M. (1984). Les applications industrielles de l'ultrafiltration. Techniques Separatives sur Membranes, Cycle ICPI, Lyon, October 22-26, 1984.

ROUSH, P.H. (1984). Ultrafiltration treatment of a combined electroplating and metal finishing wastewater. Presented at the 1st Annual Hazardous Materials Management Conf./Southwest, Houston, October 31 - November 2.

SHORT, J.L. (1982). Selection, applications and optimization of hollow fibre UF membranes. Filtration and Separation, 5, 410.

STRATHMANN, H. (1984). Water and Wastewater treatment experience in Europe and Japan using ultrafiltration. In: Synthetic Membrane Processes - Fundamentals and Water Applications. Belfort, G. (ed). Academic Press, Orlando, Fla., Chap. 9.

SWEENEY, M.J. (1985). Recovery of metals from electroplating rinsewaters with electrodialysis. Presented at the Summer Natl. AIChE Meeting, Seattle, August 26, 1985.

The Liquid Filtration Manual, Vol. I, Chapter IX, The McIlvaine Company, U.S.A.

VISVANATHAN, C.; BEN AIM, R. and VIGNESWARAN, S. (1989). Application of cross-flow electro-microfiltration in chromium wastewater treatment, desalination.

WERSCHULZ, P. (1985). New membrane technology in the metal finishing industry. In: Toxic and Hazardous Wastes Proceedings of Seventeenth Mid-Atlantic Industrial Waste Conference. Kugelman, I.J. (ed). Technomic Publishing, Lancaster, Penn., pp. 445.