

TREATMENT OF WASTE WATER FOR REMOVING HEAVY METALS BY MEMBRANE DISTILLATION

P.P. Zolotarev, V.V. Ugrozov I.B. Volkina and V.N. Nikulin
Laboratory of Membrane Process, L.Ya. Karpov Physico-Chemical
Research Institute, ul. Obukha 10, Moscow 103064, Russia

ABSTRACT

In this paper the model of membrane distillation was suggested for describing of MD-process through hydrophobic microporous membrane. The expressions for vapour flux of solvent through membrane was determined and influence of different membrane characteristics (the membrane thickness, the average value of the membrane pore size, etc.) and experimental conditions on the vapour flux has been analyzed. The possibility of waste water treatment for separation of heavy metals by membrane distillation have been studied on the model nickel-containing solutions within concentration range of NiSO_4 0.1-3.0 N. The selectivity coefficient of this process $\varphi = 0.997$.

INTRODUCTION

Membrane distillation could be used to solve various waste water problems, to separate and recover chemicals, and also to concentrate aqueous solutions of substances sensitive to high temperatures. Membrane distillation is a method which increases ecological characteristics of solution separation and concentration and excludes application of supplementary chemical substances.

The possibility of using solar and geothermal energy or existing low temperature gradients typically available in industrial processing plants, is particularly attractive. The

pure distillate could be ultrapure water produced on a large scale and at low cost. The viability of membrane distillation depends on the efficient use of available energy. A preliminary economic analysis has shown that membrane distillation (under some conditions) is competitive with RO for production of distilled or potable water for industrial or arid-zone use.

It is shown that it is possible to use membrane distillation for solution concentration and to remove heavy metals from waste water.

PRINCIPLE OF MEMBRANE DISTILLATION

A hydrophobic membrane separates two aqueous liquids of different temperature. For instance, we have a salt solution at an elevated temperature on one side of the membrane and pure water on the other. Both media do not penetrate the microporous membrane made of material with hydrophobic properties. This temperature difference results in a vapour pressure difference, so that on the warm side water will evaporate. The vapour diffuses from the warm to the cold side where it condenses. Fig. 1 illustrates the principle of membrane distillation and three variants of its practical realization.

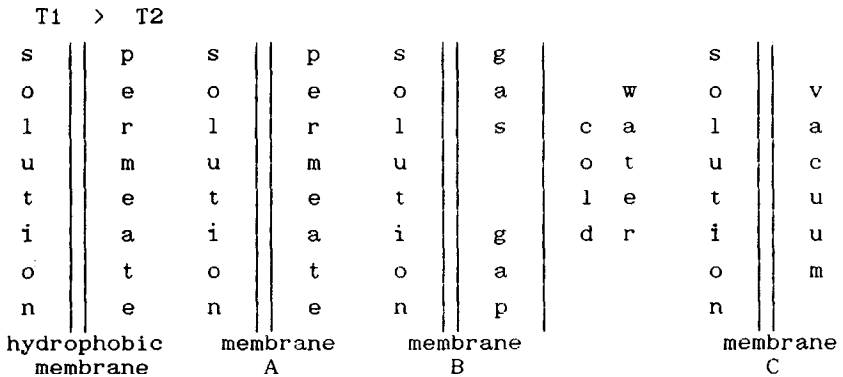


Figure 1. Principle of the membrane distillation and variants of its practical realization

In schematic representation A, the membrane is directly exposed to the warm solution and the cold permeate flow. This variant was called direct contact membrane distillation (CMD). Variant B involves an addition gas-gap (GMD). In variant C instead of a gas-gap vacuum is used and this variant was called vacuum membrane distillation (VMD).

THE THEORY OF CMD FOR MEMBRANE MODULE

The model describing the direct contact of membrane distillation (CMD) has been suggested for a inorganic salt solution in the membrane module. This model enables to calculate the mass of solvent vapour in the CMD process at arbitrary values of the Knudsen number (Kn) in comparison with the further previously suggested models of this process. Analytical expressions for the vapour flux through a membrane have been derived which may be written as:

$$J_i = C_i [p_1(T_1) - p_2(T_2)] \quad , \quad \text{where} \quad (1)$$

$$C_0 = D(T_m) M / [RT_m \delta (1+Kn)] \quad ,$$

$$C_1 = D(T_m) M / [RT_m \delta \ln(b/a)(1+Kn)]$$

$i = 0$, flat membrane; $i = 1$, fibre membrane; C_i vapour conduction coefficient; δ membrane thickness; M molecular weight of vapour, $D(T_m)$ effective molecular diffusion coefficient of solvent vapour/air in the membrane; $Kn = D/D_k$ Knudsen number; D_k the effective Knudsen diffusion coefficient of solvent vapour; $T_m = (T_1 + T_2)/2$; T_1 and T_2 the temperatures of warm side and cold side of the membrane; $p_1(T_1)$ and $p_2(T_2)$ the vapour pressures on warm side and cold side of the membrane; b and a outer and inner radius of the fibre membrane; R gas constant.

From the analysis of heat transfer into the membrane module (Fig. 2) analytical expressions describing the productivity of this module (P) have been derived. For flat membrane, it may be

written when $Q_1 = Q_2$ and $h_1 = h_2$ as:

$$P = C_o (dp/dT)_{\bar{T}} \Delta T S / [1 + 2(\tilde{\lambda}/\delta) + LC_o (dp/dT)_{\bar{T}} (1/h_1 + S/2c_p \rho Q_j)], \quad (2)$$

where $T = (T_s + T_d)/2$, $\tilde{\lambda}$ effective thermal conductivity of the membrane, $\tilde{\lambda} = (1-\epsilon)\lambda_p + \epsilon\lambda_v$, λ_p and λ_v thermal conductivity of the polymer and vapour, L latent heat of vaporization, c_p heat capacity of solution, ρ density of solution, Q_j volumetric flow rate of solution in the channel j , S area of the membrane, h_1 and h_2 heat transfer coefficients in the boundary layers between solution-membrane and membrane-permeate, T_s and T_d inlet temperatures of solution and permeate, $\Delta T = T_s - T_d$, j - index of channel $j = 1, 2$, ϵ porosity of the membrane.

For laminar flow:

$$h_1 d_h / \lambda_s = 1.62 (\text{Re Pr } d_h / l)^{0.3} \quad (3)$$

For turbulent flow:

$$h_1 d_h / \lambda_s = 0.023 \text{Re}^{0.8} \text{Pr}^{0.25} \quad (4)$$

where $\text{Re} = \rho v d_h / \mu_s$ Reynolds number, $\text{Pr} = \mu_s c_p / \lambda_s$ Prandtl number, d hydraulic diameter of the channel, μ_s liquid viscosity, l length of membrane.

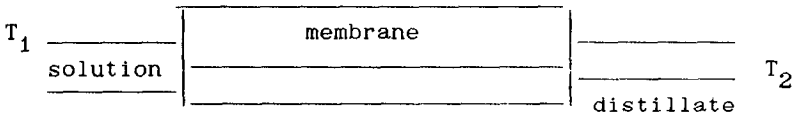


Figure 2. Membrane module for CMD

The influence of different membrane characteristics and experimental conditions on the P of membrane module may be analyzed by equations (2)-(4). For instance, it follows that J increases with increasing T_s and decreases with the

concentration of salts. This conclusions are in good agreement with the experimental results.

EXPERIMENTAL, RESULTS AND DISCUSSION

Experimental research was performed using an apparatus for direct contact of membrane distillation (CMD) shown in Fig. 1. The hydrophobic microporous "Vladipor" membrane was used, its nominal pore size was $0.25 \mu\text{m}$, the thickness was $120 \mu\text{m}$ and its porosity was about 70 %.

The influence of solution temperature containing nickel on transmembrane flux has been studied in the case of the direct contact of membrane distillation. Experiments were conducted with NiSO_4 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions of concentration 0.1 N. The cooling water temperature was 15°C for all experiments and the feed flow rate was 26 l/h. The feed temperature for all experiments were $T = 40, 50$ and 60°C .

Typical transmembrane flux versus T_s behaviour is presented for Ni containing solutions in Fig. 3. The transmembrane fluxes for all solutions increase monotonously albeit non-linearly, with increasing T_s . The coefficient selectivity was $\rho = 0.998$.

The influence of the concentration of NiSO_4 solutions on the transmembrane flux has been studied in the case of membrane distillation with gas-gap. The concentration process was investigated for solutions of NiSO_4 over a wide range of concentrations (from 0.5 N to 3.0 N). The feed flow rate was 30 l/h and feed temperature was 60°C . The cooling water temperature was maintained at 20°C for all experiments.

The effect of NiSO_4 concentration on transmembrane flux is shown in Fig. 4. Transmembrane flux decreases with increasing concentration of NiSO_4 , however, it is still enough large even for 3 N NiSO_4 . The selectivity coefficient was $\rho = 0.997$. It can be stated that model nickel-containing solutions can be concentrated to very high concentrations using the membrane distillation process.

$J * 10^3$, (kg/m² s)

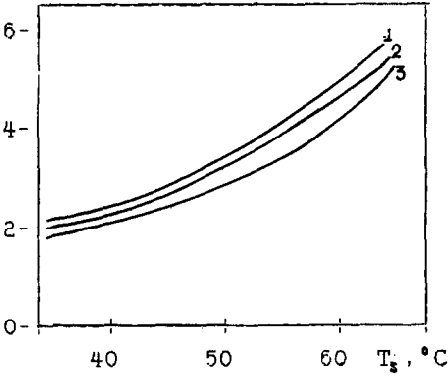


Figure 3. Transmembrane fluxes vs. feed temperature for Ni containing solutions:

- 1 - 0.1 N $Ni(NO_3)_2 \cdot 6H_2O$,
- 2 - 0.1 N $NiSO_4$,
- 3 - 0.1 N $NiCl_2 \cdot 6H_2O$

$J * 10^3$, (kg/m² s)

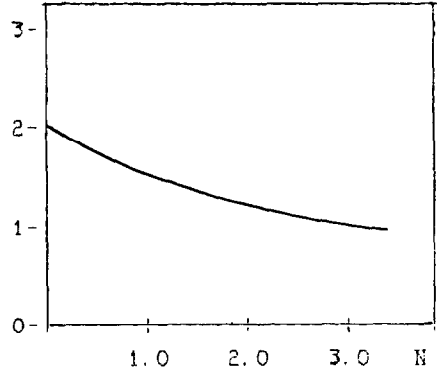


Figure 4. The relationships between transmembrane flux and concentration of $NiSO_4$ solutions.

$$T_s - T_d = 60 - 20^\circ C$$

CONCLUSION

The analysis of experimental results has shown that membrane distillation allows to concentrate salt solutions of heavy metals. It enables to extract from this solutions valuable components and to return the clear water for repeated using. Applications of this membrane method have a good prospect for treatment of industrial waste water and greatly improves the ecological situation.

REFERENCES

1. Ugrozov V.V., Zolotarev P.P., Timashev S.F.: About the processes of contact membrane distillation. Theoretical Fundam. of Chemical Technology (in Russian), 1991, V. 25, p. 17.