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PHENOL REMOVAL FROM WATER USING A GAS MEMBRANE

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Abstract. The possibility of using a gas membrane for phenol removal from a weak aqueous solution and simultaneous absorption by a sodium hydroxide solution is evaluated. The process is accelerated by using a temperature difference between the feed and stripping solutions. Equations describing concurrent phenol and water transport through membrane are presented.

Key words: membrane desorption-absorption, membrane distillation, gas membrane, phenol removal.

INTRODUCTION

Phenol and phenolic derivatives occur in waste waters coming from several works of chemical, petrochemical, and oil-shale industries. They must be removed before the biopurification of waste water. The common industrial methods of phenol recovery are solvent extraction, adsorption, and steam stripping. The liquid membrane technique seems to be an attractive alternative to solvent extraction as it combines the processes of extraction and stripping into a single step using a minimum amount of the organic phase. Both the emulsion [1] and supported [2, 3] liquid membranes have been applied for phenol recovery.

Gas membranes supported by microporous hydrophobic polymer filters have also been used for the separation of several volatile organic contaminants from water [4]. In a gas membrane, analogously to a liquid membrane, the desorption of phenol from water and its absorption by a sodium hydroxide solution can be carried out in the same apparatus (a pertractor) simultaneously.

Under isothermal conditions, without any temperature difference between the feed and stripping solutions, the driving force as well the rate of the mass transfer remain very low. In case there is a temperature difference the removal of phenol is accompanied by simultaneous distillation of water, so the process will become similar to membrane distillation, although one of the compounds is absorbed chemically.

Several authors have examined the pervaporation of organic compounds through a membrane. The pervaporative enrichment of phenol through an elastomeric polymer membrane has been studied by Böddeker et al. [5]. A filling-polymerized membrane for pervaporation of several organic mixtures has been designed by Yamaguchi et al. [6].

The main objectives of the present study were:

(1) to evaluate the possibility of using a gas membrane for the removal of phenol from a weak aqueous solution and simultaneous absorption by a sodium hydroxide solution; and

(2) to investigate simultaneous phenol and water transport through a gas membrane in the presence of a temperature difference between the feed and stripping solutions.

EXPERIMENTAL

The experiments for investigating the concurrent phenol and water transport through a gas membrane in the presence of a temperature difference between the feed and stripping solutions were carried out in a stirred-vessels pertractor. A scheme of the apparatus used is presented in Fig. 1. The pertractor consists of two 140 cm³ glass vessels (*1*, *2*) separated from each other by a membrane (*3*) and stirred with paddle stirrers (*4*). The feed vessel (*1*) was equipped with an electrical heating cell (*5*), a cooling spiral (*6*) was placed into the stripping vessel. Both the vessels were equipped with a thermometer (7). The current efficiencies of electricity and the cooling agent as well as the temperature of the cooling agent remained constant during each experiment. By choosing suitable initial temperatures of the solutions the full thermal steady-state regime can be achieved in less than 15 min.

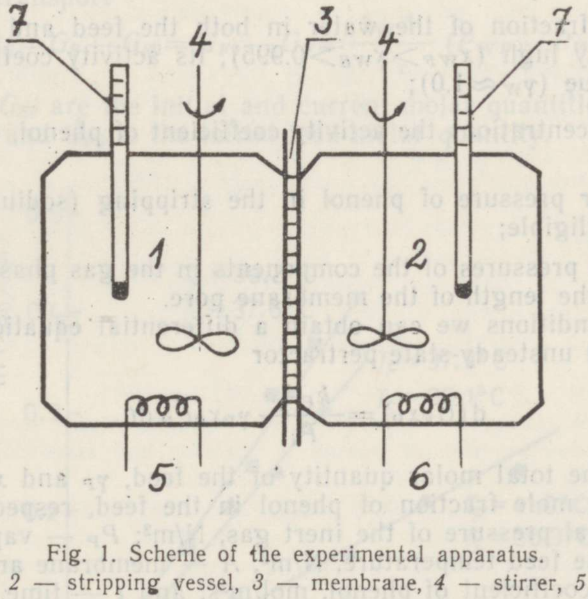

Fig. 1. Scheme of the experimental apparatus.
1 — feed vessel, *2* — stripping vessel, *3* — membrane, *4* — stirrer, *5* — heating, *6* — cooling, *7* — thermometer.

The membrane area was 16.6×10^{-4} m². In our experiments a polytetrafluoroethylene membrane (Vladipor MFF-3, NPO Polimersintez, Vladimir, Russia) with an average pore diameter 0.45×10^{-6} m, void fraction 0.66, and thickness 180×10^{-6} m was used.

The initial volumes of the feed and stripping solutions were 140 and 120 cm^3, respectively. The initial concentration of phenol in the feed solution was 1.1×10^{-3} *M*, that of sodium hydroxide in the stripping solution was 0.25 *M*. The samples for analysis were taken from the feed and stripping solutions at fixed time intervals. The phenol concentration was determined photometrically with 4-amino-2,3-dimethyl-1-phenyl-5-pyrazolone [7]. The concentration of sodium hydroxide was determined by titration with a sulphuric acid solution. The quantity of distilled water was determined by weight.

RESULTS

In the case of a temperature difference between the feed and stripping solutions the desorption of phenol from aqueous solution, its transport through the membrane, and absorption by sodium hydroxide solution are accompanied by simultaneous distillation of water.

For a mathematical description of the process the following simplifying assumptions can be made:

(1) at fixed temperatures of the feed and stripping solutions the rate of the mass transfer process is practically not affected by a simultaneous heat transfer;

(2) as the phenol concentration is low ($x_P < 2 \times 10^{-5}$), the phenol transfer does not influence the quantities of the feed and stripping solutions and the molar concentration of the water. On the contrary, the water transport affects strongly the quantities of the phases and hence, the concentration of phenol. So we can regard water transfer as an independent process, but phenol transfer as connected with that of water;

(3) the mole fraction of the water in both the feed and the stripping solution is very high ($x_{WF} > x_{WS} > 0.995$), its activity coefficient having a constant value ($\gamma_W \approx 1.0$);

(4) at low concentrations the activity coefficient of phenol, γ_P, is practically constant;

(5) the vapour pressure of phenol in the stripping (sodium hydroxide) solution is negligible;

(6) the partial pressures of the components in the gas phase are linearly dependent on the length of the membrane pore.

In these conditions we can obtain a differential equation for phenol transport in an unsteady-state pertractor

$$d(G_F x_P) = -\frac{k_P A}{P_i} \gamma_P x_P P_P \, dt, \qquad (1)$$

where G_F is the total molar quantity of the feed, γ_P and x_P — activity coefficient and mole fraction of phenol in the feed, respectively; P_i — the mean partial pressure of the inert gas, N/m^2; P_P — vapour pressure of phenol at the feed temperature, N/m^2; A — membrane area, m^2; k_P — mass transfer coefficient of phenol, mol/m^{2}s; and t — time, s.

In our conditions, basing on the data presented by Hwang et al. [8], we can take the value of the activity coefficient of phenol $\gamma_P = 43.9$ and the dependence of the phenol partial pressure on temperature

$$\log P_P = 3.423 - 1749.6/T_F. \qquad (2)$$

Here T_F is the feed temperature, K. The value of the activity coefficient used is also in full agreement with the data obtained by Mölder and Tamvelius [9].

The mean partial pressure of the inert gas (air), P_i, may be approximately expressed as

$$P_i = P - \frac{P_{WF} + P_{WS} + \gamma_P x_{P0} P_P}{2}, \qquad (3)$$

where P is total pressure, N/m²; P_{WF} and P_{WS} — partial pressure of water in the feed and stripping solutions, respectively; x_{P0} — initial mole fraction of phenol in the feed.

In case of a temperature difference between the feed and stripping solutions, i.e. for simultaneous phenol and water transfer, analogously to the thermally forced membrane desorption-absorption process of ammonia [10], by integration of Eq. (1) the following mass transfer equations can be derived:

for phenol transport

$$\ln\frac{x_{P0}}{x_P} = \left(\frac{k_P \gamma_P P_P}{k_W (P_{WF} - P_{WS})} - 1\right) \ln \frac{G_{F0}}{G_{F0} - \frac{k_W A}{P_i}(P_{WF} - P_{WS})\, t} \qquad (4)$$

or

$$\frac{x_{P0}}{x_P} = \left(\frac{G_{F0}}{G_F}\right)^{\frac{k_P \gamma_P P_P}{k_W (P_{WF} - P_{WS})} - 1}, \qquad (5)$$

where k_W is the mass transfer coefficient of water, mol/m²s, and $P_{WF} - P_{WS} \neq 0$;

for water transport

$$\Delta G_S = G_S - G_{S0} = G_{F0} - G_F = \frac{k_W A}{P_i}(P_{WF} - P_{WS})\, t. \qquad (6)$$

Here G_S and G_{S0} are the initial and current molar quantities of the stripping solution and G_{F0} is the initial feed molar quantity.

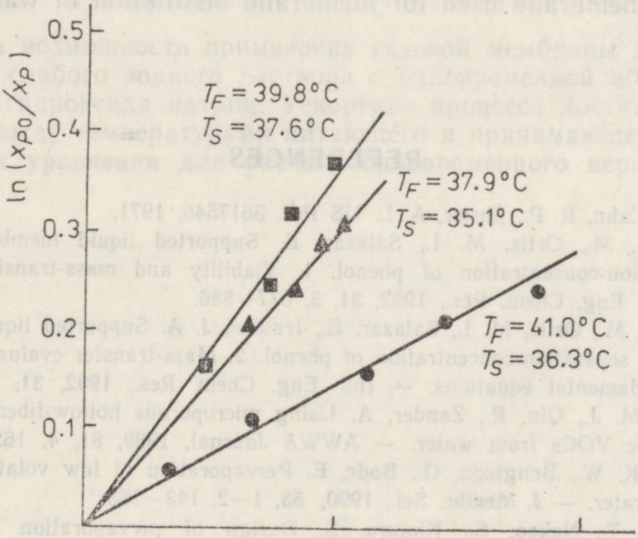

Fig. 2. Dependence of the phenol concentration ratio on the feed mole ratio.

Generally, the overall resistance to phenol mass transfer, $1/k_P$, equals the sum of partial resistances in the feed and stripping solutions and in the membrane, $1/k_{PF}$, $1/k_{PS}$, and $1/k_{PM}$, so

$$\frac{1}{k_P}=\frac{1}{k_{PF}}+\frac{1}{k_{PS}}+\frac{1}{k_{PM}}. \qquad (7)$$

The mass transfer in the stripping solution is strongly accelerated by a fast chemical reaction between sodium hydroxide and phenol, the stripping agent being in excess, so we can take $1/k_{PS}=0$. It has been shown [11] that at the stirring rate used the diffusion resistance of the laminar boundary layer in the feed remains negligible, i.e. $1/k_{PF}=0$. So we can take $k_P=k_{PM}$.

Fig. 2 presents experimental data and linear plots of $\ln(x_{P0}/x_P)$ vs. $\ln(G_{P0}/G_F)$ in the case of several temperatures of the feed and stripping solutions. The dispersion of experimental data is mainly due to the exactness of analytical determination of phenol concentration in weak solutions. The mean values of the mass transfer coefficients calculated from the results of our experiments and the slopes of linear plots in Fig. 2 were $k_W=1.23$ mol/m²s for water and $k_P=0.27$ mol/m²s for phenol.

CONCLUSIONS

A gas membrane can be used for phenol removal from a weak aqueous solution, although the process rate is rather modest. The rate of phenol transfer can be significantly increased using a temperature difference between the feed and stripping solutions, but simultaneously distillation of water occurs. Equations describe the process adequately enough by taking into account the simultaneous mass transfer of both phenol and water. The process rate is to some degree lower than that obtained by Böddeker et al. [5] in the case of phenol—water pervaporation through an elastomeric polymer membrane at a higher feed temperature (50 °C). The mass transfer coefficient for water is somewhat lower than that obtained by Zinevich et al. [12] for a similar type but thinner membrane used for membrane distillation of water.

REFERENCES

1. Li, N. N., Cahn, R. P., Shrier, A. L. US Pat. 3617546, 1971.
2. Urtiaga, A. M., Ortiz, M. I., Salazar, E. Supported liquid membranes for the separation-concentration of phenol. 1. Viability and mass-transfer evaluation. — Ind. Eng. Chem. Res., 1992, **31**, 3, 877—886.
3. Urtiaga, A. M., Ortiz, M. I., Salazar, E., Irabien, J. A. Supported liquid membranes for the separation-concentration of phenol. 2. Mass-transfer evaluation according to fundamental equations. — Ind. Eng. Chem. Res., 1992, **31**, 7, 1745—1753.
4. Semmens, M. J., Qin, R., Zander, A. Using microporous hollow-fiber membrane to separate VOCs from water. — AWWA Journal, 1989, **81**, 4, 162—167.
5. Böddeker, K. W., Bengtson, G., Bode, E. Pervaporation of low volatility aromatics from water. — J. Membr. Sci., 1990, **53**, 1—2, 143—158.
6. Yamaguchi, T., Nakao, S., Kimura, S. Design of pervaporation membrane for organic—liquid separation based on solubility control by plasma-graft filling polymerization technique. — Ind. Eng. Chem. Res., 1993, **32**, 5, 848—853.
7. Лурье Ю. Ю. Аналитическая химия промышленных сточных вод. Химия, Москва, 1984, 374—376.

8. Hwang, Y.-L., Olson, J. D., Keller, G. E., II. Steam stripping for removal of organic pollutants from water. 2. Vapor—liquid equilibrium data. — Ind. Eng. Chem. Res., 1992, **31**, 7, 1759—1768.
9. Мэлдер Л., Тамвелиус Х. Использование теории регулярных растворов для описания распределения фенолов и ароматических аминов между фазами воды и органического растворителя. — Изв. АН ЭССР. Хим. Геол., 1972, **21**, 3, 204—212.
10. Rajalo, G., Tereping, O., Petrovskaya, T. Thermally-forced membrane desorption-absorption of ammonia. — J. Membr. Sci. In press.
11. Rajalo, G., Glushko, M., Arro, M. Ammonia removal from water using a gas membrane. — Proc. Estonian Acad. Sci. Chem., 1992, **41**, 4, 200—205.
12. Зиневич С. Ю., Угрозов В. В., Золотарев П. П. Исследование процесса контактной мембранной дистилляции на гидрофобных микропористых мембранах. — Теор. основы хим. техн., 1992, **26**, 6, 793—799.

FENOOLI ERALDAMINE VESILAHUSEST GAASMEMBRAANI ABIL

Maia GLUŠKO, Guido RAJALO

On uuritud gaasmembraani kasutusvõimalust fenooli eraldamiseks lahjast vesilahusest ja selle samaaegseks absorbeerimiseks naatriumhüdroksiidi lahusesse. Protsessi kiirendati lähte- ja vastuvõtulahuse vahelise temperatuuridiferentsiga. On tuletatud võrrandid fenooli ja vee üheaegse massiülekande arvutamiseks.

ИЗВЛЕЧЕНИЕ ФЕНОЛА ИЗ ВОДЫ С ПРИМЕНЕНИЕМ ГАЗОВОЙ МЕМБРАНЫ

Майя ГЛУШКО, Гуйдо РАЯЛО

Изучена возможность применения газовой мембраны для удаления фенола из слабого водного раствора с одновременной абсорбцией его раствором гидроксида натрия. Ускорение процесса достигнуто за счет разницы между температурами питающего и принимающего растворов. Составлены уравнения для расчета одновременного переноса фенола и воды.