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AMMONIA REMOVAL FROM WATER USING A GAS MEMBRANE

Abstract. The transport of ammonia from a weak aqueous solution through a gas membrane immobilized within the pores of a flat hydrophobic polymer filter was studied. Mass transfer characteristics of several microporous membrane materials were determined. A high ammonia removal with simultaneous producing of ammonium sulphate solution was achieved.

Introduction

Gas membranes consist of a gas, usually an air layer immobilized within the pores of a hydrophobic microporous filter separating two liquids, among them aqueous solutions. It has been demonstrated that volatile solutes, such as hydrogen sulphide, sulphur dioxide, ammonia, and free halogens can pass across these membranes, but nonvolatile solutes like electrolytes are completely retained [1-3]. Both stripping and absorption of the volatile component can be conducted simultaneously in a single apparatus. The process observed is similar to membrane distillation or pervaporation if both feed and permeate absorbing liquid are immediately contacted with a porous membrane [4]. The porous membrane must be liquid-repulsing enough to prevent the mixing of two solutions, unless the pressure difference across the membrane is more than the expel pressure. For aqueous solutions the hydrophobic polytetrafluoroethylene (PTFE) and polypropylene membranes have been applied.

However, it is necessary to examine several microporous polymers for selecting the most suitable ones for industrial use. As the purpose of this work is not only the removing of ammonia from waste water, but also its further utilization, the use of sulphuric acid as the stripping agent is motivated.

The present study aims at:
(1) determining mass transfer characteristics of the gas membrane in case of different microporous materials, and
(2) establishing the possibility of ammonia removal from a weak water solution (industrial waste water) and simultaneous absorption by the sulphuric acid solution.

Experimental

The apparatus (pertractor) consisted of two 130 cm³ glass vessels for feed and strip solutions; the vessels were clamped together by two flanges facing each other, giving a cross-sectional area of 16.6 cm³ where the membrane was positioned. Each vessel was provided with sampling and stirrer ports. The vessels were stirred with glass paddle stirrers driven by electric motors at a constant rate of 375 RPM. In some experiments, the stirring speed was changed between 100 and 400 RPM.

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All the experiments were carried out at room temperature ($16 \pm 1.0\,^\circ$C). A scheme of the apparatus used was presented in our previous report [5]. The characteristics of polymer membranes used will be described later. The concentration of sulphuric acid in the stripping solution varies from 2 to 12 wt%. Keeping in view the industrial application of the process, experiments with recurrent use of the stripping phase and addition of ammonium sulphate to the stripping solution were carried out. The initial ammonia concentration in the feed solution varies from 0.1 to 0.5 wt%. The samples for analysis were taken from the feed and stripping solutions at fixed time intervals. The total ammonium concentration (the sum of free ammonia and ammonium ions) was determined colorimetrically with Nessler's reagent [6]. The concentration of sulphuric acid was determined by titration with sodium hydroxide solution. All reagents used were analytically pure according to the specifications of Sojuzreaktiv, USSR.

Results

At the strip side of the membrane the diffused ammonia reacts with sulphuric acid practically instantly. Therefore the diffusion resistance of the strip phase boundary layer is negligible and we can take the concentration of ammonia in the stripping solution as well as at the membrane—solution interface equal to zero. In this case the differential mass balance in a batch pertractor is given by

$$dJ = KAC\,dt = V_f dC, \tag{1}$$

where J is the total flux of ammonia through membrane, A is the membrane area, V_f is the feed volume, K is the overall mass transfer coefficient, and C is the total ammonia concentration in the bulk of feed solution, i.e. the sum of ammonia and ammonium ion concentrations

$$C = C_{NH_3} + C_{NH_4^+}. \tag{2}$$

For an unbuffered ammonia solution the overall mass transfer coefficient is given by

$$\frac{1}{K} = \left(\frac{1}{k_f} + \frac{1}{k_m} \right) \left[\frac{q_i}{(\sqrt{q_i + 1} - 1)^2} \right], \tag{3}$$

in which

$$q_i = \frac{4C}{K_b} \left(\frac{k_m}{k_f} + 1 \right). \tag{4}$$

In Eqs. (3) and (4) k_f and k_m are the mass transfer coefficients in the feed boundary layer and across the membrane, respectively. The dissociation constant of ammonia, K_b, equals

$$K_b = \frac{C_{NH_4^+} C_{OH^-}}{C_{NH_3}}, \tag{5}$$

where C_{OH^-} is the concentration of hydroxyl ions. In an unbuffered solution

$$C_{NH_4^+} = C_{OH^-}. \tag{6}$$

The diffusion constant of ammonia in an aqueous solution at 15 °C $K_b = 1.65 \times 10^{-5}$, so from Eq. (5) it can be concluded that in the observed concentration interval the undissociated part of the ammonia remains in all cases higher than 0.98, so we can take

$$C \approx C_{NH_3}. \tag{7}$$

In the case of weak ionization and small K_b, q_i is large and Eq. (3) becomes

$$\frac{1}{K} = \frac{1}{k_f} + \frac{1}{k_m}.\qquad(8)$$

The diffusion resistance of aqueous boundary layer $1/k_f$ is strongly dependent on the stirring speed of the feed solution, at the same time $1/k_m$ remains constant. The dependence of K on the stirring rate for membranes with very high permeability (MFFK-4) and medium permeability (MFFK-1) are shown in Fig. 1. The experimental data indicate that above 250 RPM K becomes independent of the stirring rate and the diffusional resistance of the aqueous boundary layer reaches its minimum value. Then it can be considered that

$$\frac{1}{k_f} \ll \frac{1}{k_m}\qquad(9)$$

and

$$\frac{1}{K} \approx \frac{1}{k_m}.\qquad(10)$$

Eq. (1) with the initial condition

$$t = 0, \quad C = C_0\qquad(11)$$

and Eq. (10) can be integrated to

$$\ln \frac{C_0}{C} = k_m \frac{A}{V_f} t.\qquad(12)$$

Here k_m is given by the fluid phase concentration. If we go over to gas phase concentration we will have to divide k_m with Henry's constant H. In the observed case k_m equals the permeability coefficient P_D, used for the comparison of mass transfer characteristics of the membranes. So we get

$$P_D = k_m = \frac{D_m H \varepsilon}{\delta \chi} = \frac{D_e H}{\delta},\qquad(13)$$

where δ is membrane thickness, D_m is diffusion constant of ammonia in membrane pores, D_e is effective diffusion constant, ε and χ are void fraction and tortuosity of the membrane, respectively.
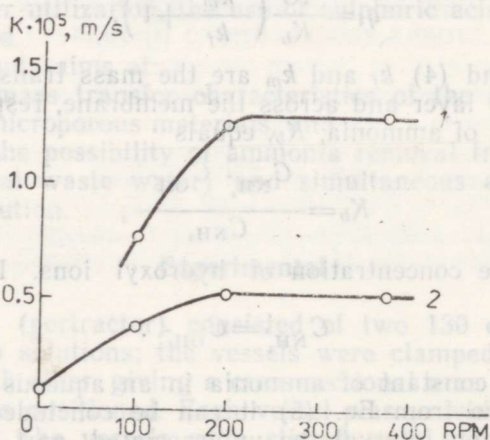

Fig. 1. Dependence of mass transfer resistance, K, on stirring speed, RPM. *1* — MFFK-4, *2* — MFFK-1.
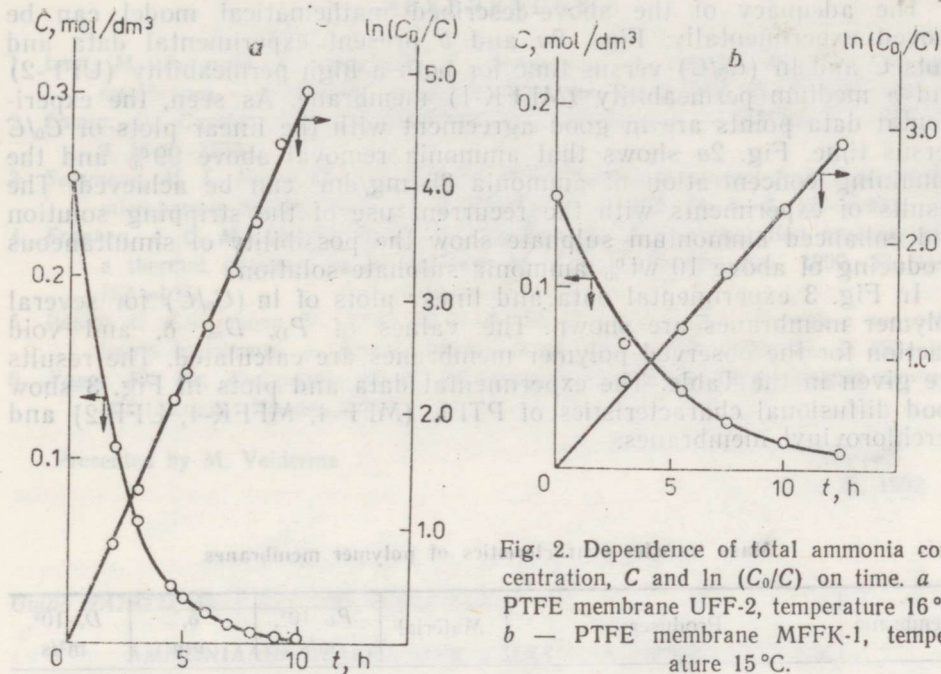
Fig. 2. Dependence of total ammonia concentration, C and ln (C_0/C) on time. a — PTFE membrane UFF-2, temperature 16 °C; b — PTFE membrane MFFK-1, temperature 15 °C.
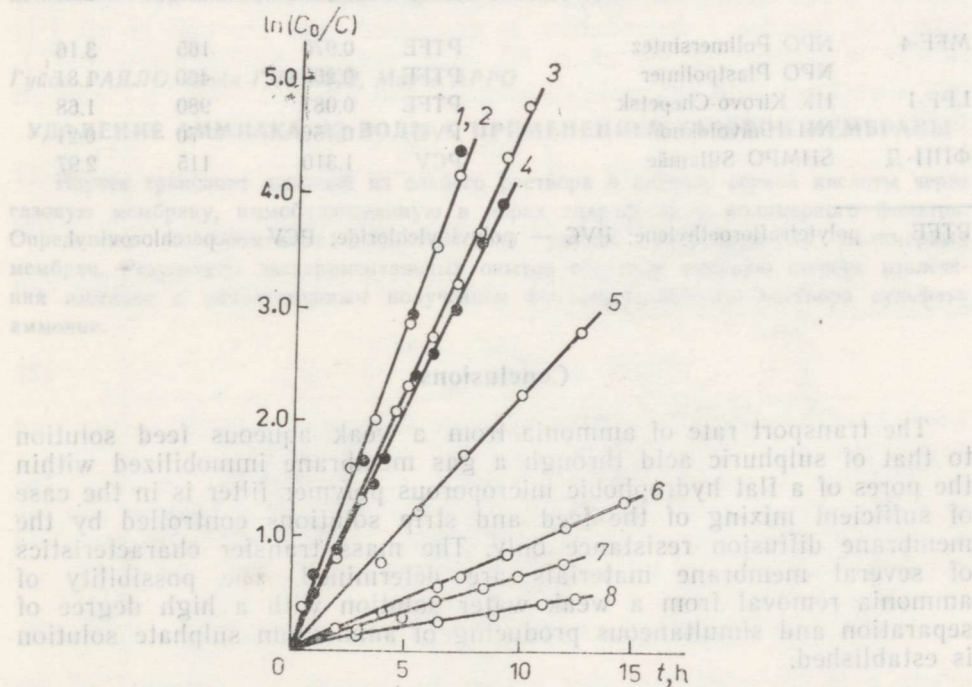

Fig. 3. Dependence of ln(C_0/C) on time. Temperature 16 ± 1 °C. *1* — MFFK-4, *2* — PCV (SHMPO Sillamäe), *3* — UFF-2, *4* — MFF-4, *5* — MFFK-1, *6* — PTFE (NPO Plastpolimer), *7* — PVC (NII Himvolokno), *8* — LPF-1.

Conclusions

The transport rate of ammonia from a weak aqueous feed solution to that of sulphuric acid through a flat membrane immobilized within the pores of a flat hydrophobic microporous polymer filter is in the case of sufficient mixing of the feed and slip solution controlled by the membrane diffusion resistance only. The transport rate characteristics of several membrane materials differentiated by the possibility of ammonia removal from a weak feed solution with a high degree of separation and simultaneous producing of ammonium sulphate solution is established.

The adequacy of the above-described mathematical model can be proved experimentally. Figs. 2a and b present experimental data and plots C and ln (C_0/C) versus time for both a high permeability (UFF-2) and a medium permeability (MFFK-1) membrane. As seen, the experimental data points are in good agreement with the linear plots of C_0/C versus time. Fig. 2a shows that ammonia removal above 99% and the remaining concentration of ammonia 35 mg/dm³ can be achieved. The results of experiments with the recurrent use of the stripping solution and enhanced ammonium sulphate show the possibility of simultaneous producing of above 10 wt% ammonia sulphate solution.

In Fig. 3 experimental data and linear plots of ln (C_0/C) for several polymer membranes are shown. The values of P_D, D_m, δ, and void fraction for the observed polymer membranes are calculated. The results are given in the Table. The experimental data and plots in Fig. 3 show good diffusional characteristics of PTFE (MFF-4, MFFK-4, UFF-2) and perchlorovinyl membranes.

Mass transfer characteristics of polymer membranes

Membrane	Producer	Material	$P_D \cdot 10^5$, m/s	δ, μm	$D_e \cdot 10^6$, m²/s
MFFK-1	NPO Polimersintez	PTFE	0.51	140	1.41
MFFK-4	NPO Polimersintez	PTFE	1.300	80	2.05
UFF-2	NPO Polimersintez	PTFE	1.040	125	2.56
MFF-4	NPO Polimersintez	PTFE	0.970	165	3.16
	NPO Plastpolimer	PTFE	0.200	460	1.81
LPF-1	HK Kirovo-Chepetsk	PTFE	0.087	980	1.68
	NII Himvolokno	PVC	0.150	70	0.21
ФПП·Д	SHMPO Sillamäe	PCV	1.310	115	2.97

PTFE — polytetrafloroethylene; PVC — polyvinylchloride; PCV — perchlorovinyl.

Conclusions

The transport rate of ammonia from a weak aqueous feed solution to that of sulphuric acid through a gas membrane immobilized within the pores of a flat hydrophobic microporous polymer filter is in the case of sufficient mixing of the feed and strip solutions controlled by the membrane diffusion resistance only. The mass transfer characteristics of several membrane materials are determined. The possibility of ammonia removal from a weak water solution with a high degree of separation and simultaneous producing of ammonium sulphate solution is established.

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AMMONIAAGI ERALDAMINE VEEST GAASMEMBRAANI ABIL

On uuritud ammoniaagi ülekannet lahjast vesilahusest läbi hüdrofoobse polümeer-filtri poorides paikneva gaasmembraani väävelhappe lahusesse ja määratud mitme-suguste mikropoorsete polümeerkandjate massivahetusomadused. Laboratoorsete katsete tulemused kinnitavad kõrge ammoniaagi eraldusastme saavutamise ning samaaegse kontsentreeritud ammooniumsulfaadi lahuse saamise võimalust.

Гуйдо РАЯЛО, Майя ГЛУШКО, Марье АРРО

УДАЛЕНИЕ АММИАКА ИЗ ВОДЫ С ПРИМЕНЕНИЕМ ГАЗОВОЙ МЕМБРАНЫ

Изучен транспорт аммиака из слабого раствора в раствор серной кислоты через газовую мембрану, иммобилизованную в порах гидрофобного полимерного фильтра. Определены массообменные характеристики разных микропористых полимерных мембран. Результаты экспериментальных опытов показали высокую степень извлечения аммиака с одновременным получением концентрированного раствора сульфата аммония.