

Original Paper

Recovery of Tetra-Methyl Ammonium Hydroxide from Waste Solution by Ion Exchange Resin

Junji SHIBATA¹, Norihiro MURAYAMA¹ and Shigeno MATSUMOTO²

¹Department of Chemical Engineering, Kansai University, Osaka 564-8680, Japan

²Department of Precision Science & Technology and Applied Physics, Graduate School of Engineering, Osaka University, Osaka 565-0871, Japan

Abstract

Tetra-methyl ammonium hydroxide is used in various electric and electronic parts production processes such as semiconductor, liquid crystal display and printed circuit board. The discharged amount of this chemical reaches about 2,500 ton/year from one factory in Japan. The waste liquor discharged from the liquid crystal display production contains 0.53wt% tetra-methyl ammonium hydroxide, 60 mg/dm³ phenol and ppb level of metal ions.

In the cation exchange reaction, tetra-methyl ammonium ion is captured on the cation exchange resin. Other non-ionic organic matter like phenol goes through the resin without being captured on it, the separation being attained in this step. In the elution step, tetra-methyl ammonium ion captured on the resin is released as tetra-methyl ammonium chloride into aqueous solution by the action of dilute hydrochloric acid. Tetra-methyl ammonium chloride is converted to tetra-methyl ammonium hydroxide by the reaction between tetra-methyl ammonium chloride and OH⁻ type anion exchange resin. The process is composed of three steps: cation exchange, elution and conversion. The experiments were carried out using ion exchange resin column of 20 mmφ and 735 mm height, in order to clarify the recovery and purity of tetra-methyl ammonium hydroxide at each step.

Key words: Tetra-methyl Ammonium Hydroxide, Ion Exchange, Recycle

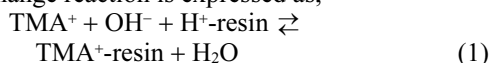
Introduction

Tetra-methyl ammonium hydroxide (TMAH) is used in various electric and electronic parts production processes such as semiconductor, liquid crystal display and printed circuit board. The discharged amount of this chemical reaches about 2,500 ton/year from one factory in Japan. The waste liquor contains a lot of organic matters, which means high BOD and COD⁽¹⁾. The TMAH waste liquor is mainly treated by an evaporation concentration method, or an incineration method. However, these methods cause some engineering problems such as high cost, high environmental load and so on. The development of new method to recover pure TMAH from the waste TMAH solution is strongly desired from the viewpoints of resources recycling and global environmental protection²⁻⁴⁾.

In this study, the separation and recovery of TMAH were investigated by an ion exchange resin method from a TMAH solution and an artificial TMAH waste solution containing phenol, which is a model material of dissolved photoresist.

TMAM Recovery Process Using an Ion Exchange Resin Method

The regeneration treatment process of TMAH waste solution and the separation principle of TMAH are shown in Fig. 1 and 2. The separation between TMA⁺ and phenol in the waste TMAH solution can be achieved by the cation exchange reaction between TMA⁺ in the aqueous solution and H⁺ type cation exchange resin. The cation exchange reaction is expressed as,



Washing step of the cation exchange resin column with water is needed to remove the TMAH waste

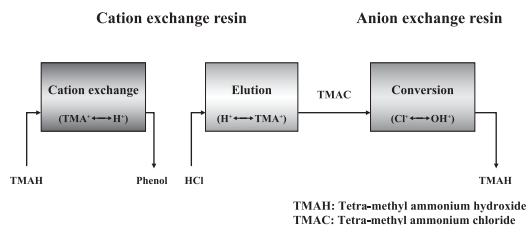


Fig. 1 Recovery process of TMAH.

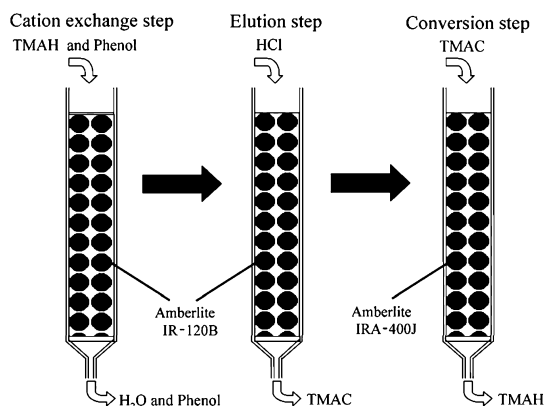
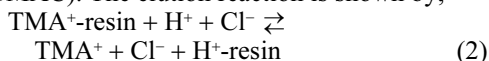


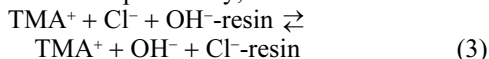
Fig. 2 Recovery and conversion methods.

solution remaining in the resin bed. It is necessary to wash the cation exchange resin adequately in order to keep the purity of TMAH high.

The TMAH captured in the cation exchange resin is detached in the elution step. When HCl solution is used as an eluent, TMA^+ is eluted as a form of tetra-methyl ammonium chloride (TMAC). The elution reaction is shown by,



In the next step, the TMAC solution obtained in the previous elution step is introduced into the column of OH^- type anion exchange resin, in order to convert and regenerate TMAH from TMAC by the anion exchange reaction between Cl^- in aqueous solution and OH^- in the resin. The anion exchange reaction is expressed by,



The regeneration of TMAH is carried out through the cation exchange, washing, elution and anion exchange steps.

Experimental

The ion exchange resin, Amberlite IR-120B and Amberlite IRA-400J, were used after conditioning to H^+ type and OH^- type resins, respectively. The

Table 1 Experimental condition.

	Cation exchange	Elution	Conversion
Space Velocity [h^{-1}]	10	10	10
Bed volume [cm^3]	48	48	70
Bed height [cm]	15.5	16.3	21.5

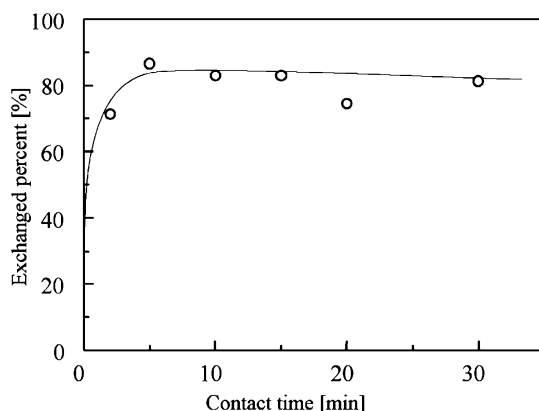


Fig. 3 Batch test for cation exchange velocity of TMA^+ with Amberlite IR-120B.

conditioning was carried out by contacting Amberlite IR-120B with 1.0 mol/dm^3 HCl solution and Amberlite IRA-400J with 1.0 mol/dm^3 NaOH solution. The ion exchange column was made by glass with 739 mm height and 20 mm diameter. The artificial waste solution was prepared by dissolving TMAH and phenol at a suitable concentration. The solution was passed through the resin column as a downward stream and the effluent was collected by a fraction collector. The concentrations of TMA^+ and Cl^- were determined by an ion chromatograph (DX-500, Nihon Dionex Co., Ltd.).

Table 1 shows the experimental conditions such as space velocity, bed volume and bed height in cation exchange, elution and conversion steps.

Results and Discussion

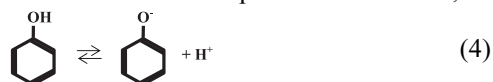
Cation exchange velocity of TMA^+ with H^+ type cation exchange resin (Amberlite IR-120B) in a batch exchange test is shown in Fig. 3. The cation exchange velocity of TMA^+ reaches an equilibrium value within 5 min, and the velocity is considerably fast. The velocity obtained in the batch test is important to determine the effluent velocity in a column method. In case of a column method,

space velocity (SV) is used as an effluent velocity. From the result shown in Fig. 3, the effluent velocity is determined to be SV 10. The SV 10 of effluent velocity is corresponding to residence time of 6 min⁵).

Fig. 4 shows the breakthrough curve for TMA⁺ in cation exchange column and the pH of effluent, in using the cation exchange resin, IR-120B. When the TMAH initial concentration is 29.3 mmol/dm³, the breakthrough point of TMA⁺ appears at 3,200 cm³ of effluent volume, and the pH of eluent changes remarkably at this breakthrough point. The rapid change in pH indicates that H⁺ is not released from the cation exchange resin any more, because the H⁺ type cation exchange resin is already saturated with TMA⁺. In the region up to the breakthrough point, the total amount of exchanged TMA⁺ is 93.6 mmol/48 cm³ resin. The effluent volume of 3,200 cm³, where the breakthrough point appears, is about 67 times of bed volume (wet resin volume), and the value shows the performance of this cation exchange op-

eration.

A distribution diagram of phenol species in aqueous solution, which is one of impurity components, was calculated as a function of pH by using the dissociation constant (pK_a = 9.82⁶⁾). The dissociation reaction of phenol is as follows,



Phenol in aqueous solution exists as a form of neutral molecule or anionic species. The calculation revealed that the anionic species of phenol is predominant in the pH region higher than 10. The pH of typical TMAH waste solution is 12.4 and at this pH phenol exists as an anionic species. Therefore, phenol species are not captured by the cation exchange resin, and these components pass through the cation exchange resin column.

Fig. 5 shows the breakthrough curve for the artificial waste THAM solution containing 30.3 mmol/dm³ of TMAH and 200 ppm of phenol. Phenol is not captured by the cation exchange resin, and it runs out from this column. The breakthrough point of TMA⁺ appears at the 3,200 cm³ of effluent volume, and the exchange amount of TMA⁺ is about 95 mmol/48 cm³-resin until breakthrough point. The breakthrough points in Fig. 4 and 5 are almost same regardless of the existence of phenol.

The results of washing of the cation exchange column with water are shown in Fig. 6. The objective of washing step is to remove the TMAH waste solution remaining in the resin column, and the washing step is necessary to keep the purity of recovered TMAH high. The washing with water completes already at 286 cm³ of effluent volume, this effluent amount being equivalent to 6 times of

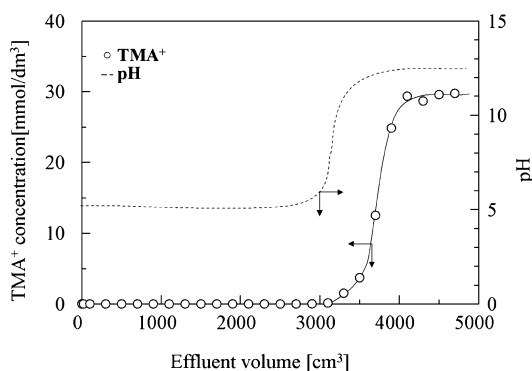


Fig. 4 Breakthrough curve of TMA⁺ with Amberlite IR-120B (Initial TMA⁺ concentration: 29.3 mmol/dm³).

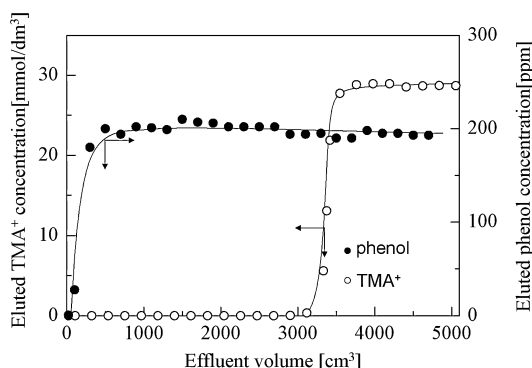


Fig. 5 Breakthrough curve of TMA⁺ and phenol with Amberlite IR-120B for binary solution.

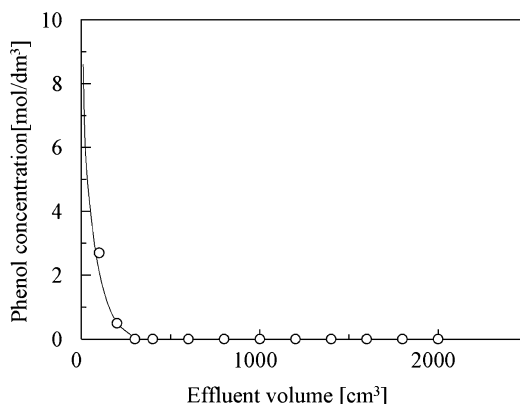


Fig. 6 Washing of feed solution from resin column with water.

the wet resin volume.

Elution curves of TMAC with HCl solutions of various concentrations are shown in Fig. 7. It is clear from the batch experiments of elution of TMA^+ in the resin that the elution velocity is fast and it depends on the concentration of HCl. For example, the elution reaches an equilibrium state within 3 min. The elution velocity corresponds to the space velocity of 5 hr^{-1} . Then, $\text{SV} = 10$ was applied to the elution test. TMA^+ is released as TMAC from the cation exchange resin by the cation exchange reaction between TMA^+ in the resin and H^+ in the solution. When the aqueous solution containing high HCl concentration is used, the elution curves becomes sharp and TMAC of high concentration can be obtained with a small amount of HCl solution. A decrease in HCl concentration causes low concentration of obtained TMAC as well as large volume of obtained TMAC solution.

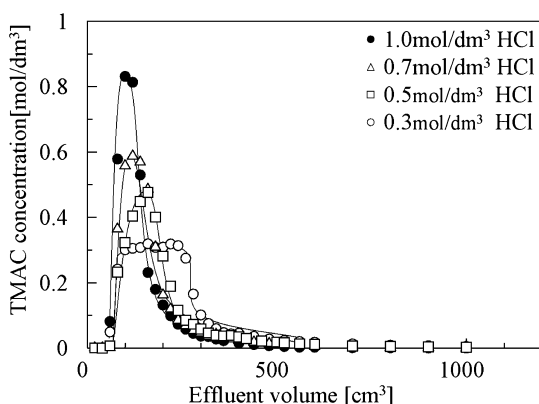


Fig. 7 Elution curves of TMAC (tetra-methyl ammonium chloride) with HCl solution from Amberlite IR-120B.

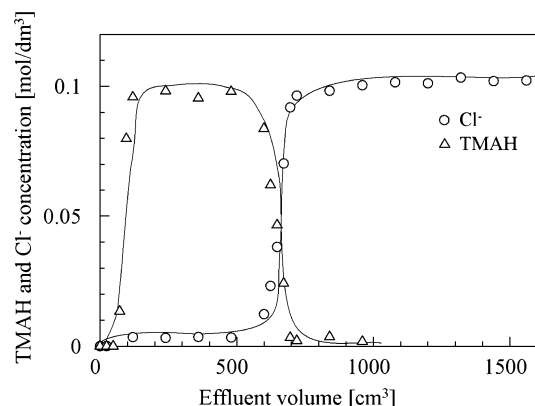
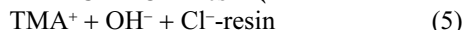
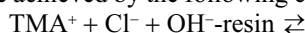


Fig. 8 Conversion of TMAC to TMAH using OH^- type anion exchange resin (Amberlite IRA-400J).

For example, the elution of TMA^+ completes at 410 cm^3 of effluent volume and the amount of recovered TMAC is $83.6 \text{ mmol}/48 \text{ cm}^3\text{-resin}$ in case of $1.0 \text{ mol}/\text{dm}^3$ HCl. The results show that it is not suitable to pass a large amount of eluent, HCl, through this elution column because this leads to contamination of TMAC with HCl in the eluent.

The anion exchange reaction between Cl^- in TMAC solution and OH^- in the anion exchange resin, Amberlite IRA-400J, was conducted by passing the TMAC solution to the anion exchange resin column, which is obtained in the previous elution step. The performance of the anion exchange operation is shown in Fig. 8. The conversion or regeneration from TMAC into TMAH can be achieved by the following conversion reaction.



When the TMAC solution of $0.1 \text{ mol}/\text{dm}^3$ is passed to the anion exchange column, the breakthrough point of Cl^- appears at 670 cm^3 of effluent volume. The contamination of TMAC with HCl in the elution step causes the decline of TMAH purity in the final product.

The recovery amount and conversion of TMAH at 670 cm^3 of effluent volume are $66.8 \text{ mmol}/70 \text{ cm}^3\text{-resin}$ and 79.9% , respectively. The pH of effluent in the anion exchange step (namely, conversion step) quickly changes from pH 13 to 10 at the breakthrough point, which indicates that the conversion or regeneration already completes. Fig. 9 shows the recovered amount, recovery percent in each step and the overall yield of TMAH through a series of treatment steps.

The total recovery of TMAH in cation exchange and elution steps is 89.4% ($83.6/93.6 \times 100\% = 89.4\%$), and the conversion of TMAH is 79.9% ($66.8/83.6 \times 100\% = 79.7\%$). The overall yield of TMAH through a series of treatment steps is 71.4% . From these results mentioned above, it is

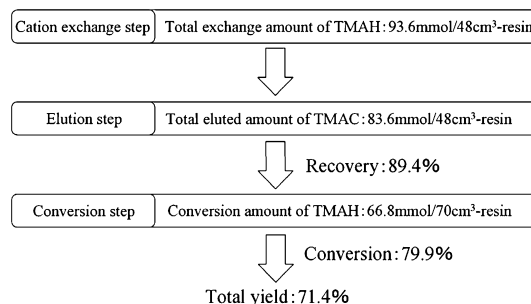


Fig. 9 Results of recovery process of TMAH using cation exchange resin and anion exchange resin.

found that TMAH can be recovered and regenerated from the TMAH waste solution by using two kinds of ion exchange resins.

Conclusions

The separation and recovery of TMAH from the waste TMAH solution containing phenol were investigated by an ion exchange resin method. The process is composed of three steps; cation exchange, elution and conversion. In the cation exchange step, TMAH waste solution can be treated by 67 times bed volume. Washing of cation exchange resin after TMA⁺ adsorption is adequately attained with water of 6 times bed volume. In the elution step, the concentration of obtained TMAC increases with increasing HCl concentration, but an increase in HCl concentration leads to the load of next conversion step at the same time. The conversion of TMAH at a breakthrough point is 79.9%. The total recovery of TMAH in the cation exchange and elution steps, the conversion of TMAH and the overall yield of TMAH through a series of the treatment steps are 89.4%, 79.9% and 71.4%, respectively. The TMAH can be recovered

and regenerated from the TMAH waste solution using two kinds of ion exchange resins.

Acknowledgment

This work was supported by the MEXT, Grant-in-Aid for Scientific Research (A)(1), (17206091) and Grant-in-Aid for Scientific Research (C)(1), (16636027).

References

1. Nihon Kagakukai: *Kagaku Binran —Ouyou-kagakuhen—*, pp. 993–1093 (1986)
2. T. Hisano, K. Yamayori: KEC Information, **164**, pp. 23–27 (1998)
3. S. Kiryuu: Denshizairyou, **4**, pp. 72–76 (1998)
4. M. Kawabata, H. Sugawara: Kogyozairyou, **9**, pp. 59–63 (2002)
5. M. Honda, H. Kakihana, Y. Yoshino: *Ion-koukanjushi Kihonsousa to Ouyou* (1955)
6. Nihon Kagakukai: *Kagaku Binran —Kiso-hen II—*, p. 341 (1984)